Processing, Structure and Properties of Poly (ethylene terephthalate)/Carbon Micro- and Nano-composites

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# Table of Contents

List of Tables .......................................................................................................................... 7  
List of Figures .......................................................................................................................... 9  
List of Symbols ....................................................................................................................... 18  
List of Abbreviation ............................................................................................................... 20  
Abstract .................................................................................................................................. 22  
Declaration ............................................................................................................................... 24  
Acknowledgements .................................................................................................................. 26  
Chapter 1 Introduction ............................................................................................................. 27  
  1.1 Introduction .................................................................................................................... 27  
  1.2 Research Background ...................................................................................................... 27  
  1.3 Research Scope ............................................................................................................... 29  
  1.4 Aim and Objectives ........................................................................................................ 30  
  1.5 Structure of Thesis .......................................................................................................... 30  
  1.6 References ...................................................................................................................... 31  
Chapter 2 Literature Review .................................................................................................... 33  
  2.1 Introduction .................................................................................................................... 33  
  2.2 PET Matrix .................................................................................................................... 34  
  2.3 Carbon Fillers .................................................................................................................. 35  
    2.3.1 Introduction ............................................................................................................. 35  
    2.3.2 Graphite .................................................................................................................. 36  
    2.3.3 GNP ........................................................................................................................ 37  
    2.3.4 Carbon Nanotubes (CNT) ...................................................................................... 39  
      2.3.4.1 Introduction ...................................................................................................... 39  
      2.3.4.2 Preparation of CNT ......................................................................................... 39
Chapter 3 Experimental .......................................................... 102

3.1 Introduction ........................................................................ 102

3.2 Raw materials ................................................................... 102

3.2.1 PET (matrix) .............................................................. 102

3.2.2 Carbon Fillers ......................................................... 103

3.2.2.1 Graphite ........................................................... 103

3.2.2.2 GNP .............................................................. 103

3.2.2.3 MWCNT ......................................................... 103

3.3 Preparation of PET/Carbon Composites ......................... 103

3.4 Modification of A-MWCNT ........................................... 107

3.5 Characterization Techniques .......................................... 108

3.5.1 Electrical Impedance ................................................. 108

3.5.2 Morphology Characterization .................................... 109

3.5.2.1 Scanning Electron Microscopy (SEM) ................... 109

3.5.2.2 Transmission Electron Microscopy (TEM) ............ 110

3.5.3 Fourier-Transform Infrared Spectroscopy (FTIR) ....... 112

3.5.4 Thermal Analysis .................................................... 114

3.5.4.1 Differential Scanning Calorimetry (DSC) .............. 114

3.5.4.2 Thermo-Gravimetric Analysis (TGA) .................... 116

3.5.5 Mechanical Analysis ................................................. 118

3.5.5.1 Dynamic Mechanical Thermal Analysis (DMTA) .... 118

3.5.5.2 Tensile test ...................................................... 120

3.6 References ....................................................................... 120

4.1 Electrical Properties of PET/Carbon Composites .......... 122

4.1.1 Introduction ............................................................ 122
4.1.2 Electrical conductivity of the PET/graphite microcomposites .......... 123
4.1.3 Electrical conductivity of the PET/GNP nanocomposites .................. 125
4.1.4 Electrical conductivity of PET/A-MWCNT nanocomposites .......... 127
4.1.5 Electrical conductivity of PET/T-MWCNT nanocomposites .......... 129
4.1.6 Insulator – conductor transition analysis of PET/carbon composites .... 131
4.1.7 Effect of processing conditions on electrical conductivity of composites .... 138
4.1.8 Influence of moulding techniques on the electrical conductivity of composites .. 142
4.1.9 Summary ......................................................................................... 144
4.1.10 References ..................................................................................... 145

4.2 Morphologies of PET/Carbon Composites ........................................... 151
4.2.1 Introduction ...................................................................................... 151
4.2.2 Morphologies of Carbon Fillers ........................................................ 151
4.2.3 FTIR ................................................................................................. 153
4.2.4 Cryogenically Fractured Surface Morphologies ............................... 154
4.2.5 Tensile Fracture Surfaces ................................................................. 160
4.2.6 Summary ......................................................................................... 165
4.2.7 References ...................................................................................... 165

4.3 Thermal Behaviour of PET/Carbon Composites .................................... 169
4.3.1 Introduction ...................................................................................... 169
4.3.2 Crystallization Behaviour of PET ....................................................... 170
4.3.2.1 Effect of Cooling Rates ................................................................. 170
4.3.2.2 Effect of Graphite ......................................................................... 174
4.3.2.3 Effect of GNP ............................................................................. 177
4.3.2.4 Effect of A-MWCNT ................................................................. 180
4.3.2.5 Effect of T-MWCNT ................................................................. 184
4.3.3 Thermal stability .................................................................................. 189
  4.3.3.1 Thermal stability of fillers .............................................................. 190
  4.3.3.2 Thermal stability of PET/carbon composites ............................... 192
    4.3.3.2.1 Effect of Graphite ................................................................. 193
    4.3.3.2.2 Effect of GNP .................................................................... 195
    4.3.3.2.3 Effect of A-MWCNT and T-MWCNT ................................. 198
  4.3.4 Summary ......................................................................................... 202
  4.3.5 References ....................................................................................... 203

4.4 Mechanical Properties of PET/Carbon Composites .............................. 211
  4.4.1 Introduction ....................................................................................... 211
  4.4.2 DMTA of the PET matrix ................................................................. 211
  4.4.3 DMTA of PET/graphite microcomposites ....................................... 214
  4.4.4 DMTA of PET/GNP nanocomposites ............................................. 219
  4.4.5 DMTA of PET/A-MWCNT nanocomposites .................................. 225
  4.4.6 DMTA of PET/T-MWCNT nanocomposites .................................. 231
  4.4.7 Tensile Properties ........................................................................... 236
    4.4.7.1 Tensile properties of PET/graphite microcomposites ............... 236
    4.4.7.2 Tensile properties of PET/GNP nanocomposites ..................... 242
    4.4.7.3 Tensile properties of PET/A-MWCNT nanocomposites ........... 246
    4.4.7.4 Tensile properties of PET/T-MWCNT nanocomposites .......... 249
  4.4.8 Halpin-Tsai model .......................................................................... 253
    4.4.8.1 Introduction ............................................................................. 253
    4.4.8.2 Variation of Filler Modulus and Aspect Ratios ......................... 256
    4.4.8.3 Predication of Tensile Modulus for PET/A-MWCNT nanocomposites .... 260
    4.4.8.4 Predication of Tensile Modulus for PET/ GNP nanocomposites .... 263
**List of Tables**

Table 2.1 Measured and theoretical properties of carbon fillers .................................................. 35

Table 2.2 functionalization methods; their advantages and disadvantages................................. 70

Table 3.1 General physical properties of PET................................................................................. 103

Table 4.1.1 Percolation threshold values ($\Phi_c$), network dimensionality ($t$) and error fitting ($R^2$) values for PET/carbon composites................................................................. 135

Table 4.1.2 Electrical conductivity of PET with graphite loading of 14 wt. % and 15 wt. % measured at different processing condition................................................................. 139

Table 4.1.3 Electrical conductivity of PET with GNP loading of 5 wt. % and 6 wt. % measured at different processing condition................................................................. 139

Table 4.1.4 Electrical conductivity of PET with A-MWCNT loading of 0.25 wt. % and 0.35 wt. % measured at different processing condition................................................... 139

Table 4.3.1 DSC results of the first heating and cooling runs for PET samples ......................... 172

Table 4.3.2 DSC-derived data from second heating run for PET samples ......................... 173

Table 4.3.3 DSC data for PET/graphite microcomposites.................................................. 177

Table 4.3.4 DSC data for PET/GNP nanocomposites .................................................. 180

Table 4.3.5 DSC results of PET/A-MWCNT nanocomposites ........................................... 184

Table 4.3.6 DSC results of PET/ T-MWCNT nanocomposites........................................... 187

Table 4.3.7 Thermal degradation temperatures ($T_{5\%}$) for PET/graphite microcomposites under nitrogen and air atmospheres................................................................. 193

Table 4.3.8 Thermal degradation temperatures ($T_{5\%}$) for PET/GNP nanocomposites under nitrogen and air atmospheres................................................................. 195

Table 4.3.9 Thermal degradation temperatures ($T_{5\%}$) for PET/ A-MWCNT nanocomposites under nitrogen and air atmospheres................................................................. 200
Table 4.3.10 Thermal degradation temperatures (T_{5\%}) for PET/T-MWCNT nanocomposites under nitrogen and air atmospheres. ................................................................. 200

Table 4.4.1 Selected DMTA data for E’, T_g and tanδ of PET/graphite microcomposites. 215
Table 4.4.2 Selected DMTA data for E’, T_g and tanδ of PET/GNP nanocomposites. ......... 221
Table 4.4.3 Selected DMTA data for E’, T_g and tanδ of PET/A-MWCNT nanocomposites. 226
Table 4.4.4 Selected DMTA data for E’, T_g and tanδ of PET/T-MWCNT nanocomposites. 233
Table 4.4.5 Tensile properties of the PET/graphite microcomposites. ............................. 238
Table 4.4.6 Tensile properties of the PET/GNP nanocomposites. .................................. 244
Table 4.4.7 Tensile properties of the PET/A-MWCNT nanocomposites. ......................... 247
Table 4.4.8 Tensile properties of the PET/T-MWCNT nanocomposites.......................... 251
Table 4.4.9 Tensile modulus obtained experimentally and compared using different Halpin-Tsai models. ................................................................. 261
List of Figures
Chapter 2

Figure 2.1 Chemical structure of PET [6]. ................................................................. 34

Figure 2.2 Graphite structure depicting $sp^2$ hybridization of carbon atoms bonded in hexagonal fashion [7]. ................................................................. 36

Figure 2.3 Schematics diagram of GNP preparation [14]. ........................................ 38

Figure 2.4 A schematics of the arc discharge method used for CNT production[17]. ....... 40

Figure 2.5 A typical schematics of oven laser vaporisation setup for producing CNT [19]. .... 40

Figure 2.6 The typical CVD process schematics for CNT production. ......................... 41

Figure 2.7 The two common types of CNT: SWCNT (left) and MWCNT [22] (right). ....... 42

Figure 2.8 Schematic exhibiting how a hexagonal sheet of graphene is rolled to develop a CNT with various chirality, as A represents the armchair, B depicts the zigzag and C shows the chiral [24] ................................................................. 42

Figure 2.9 Pre-treatment of MWCNT using mixture of HNO$_3$ and H$_2$SO$_4$ acids [29] .......... 44

Figure 2.10 SEM micrographs showing of MWCNT before and after treatments, (a) no treatment(as received), (b) treated with acidic mixture and (c) ultrasonically treated [27]. .... 45

Figure 2.11 Possible states of distribution and dispersion of filler into the matrix, number 1 represents poor distribution and dispersion, 2 shows good distribution but poor dispersion, 3 is the poor distribution and good dispersion and 4 shows both good dispersion and distribution. (redrawn from Gulrez et al [33]) ................................................................. 47

Figure 2.12 Shows the TEM images at 5 wt. % MWCNT into PS/MWCNT nanocomposites; (a) injection moulded and (b) compression moulded. The arrow shows the flow direction [45]. ................................................................. 50

Figure 2.13 A typical electrical conductivity curve of a composite showing three states; A, B, and C. These correspond to insulating, conductive at critical loading and conductivity of the filler network, respectively, (redrawn from ref. [24]). ................................................................. 51
Figure 2.14 Comparative analysis of electrical percolation threshold of composites made using varying concentrations of CNT in different polymer matrices [52] ......................... 53
Figure 2.15 Structural features of spherulites [56]. ............................................................... 54
Figure 2.16 Transmission electron microscopy (TEM) image of CB [62]. ......................... 56
Figure 2.17 Electrical conductivities of graphite reinforced HDPE and LDPE composites [70]. ......................................................................................................................... 58
Figure 2.18 Comparative filler contents of both graphene and graphite incorporated in a PET matrix [120]. ......................................................................................................................... 71
Figure 2.19 Electrical conductivities before (a), and (b) after annealing treatments and %crystallinity (c) using different carbon fillers [121]. .................................................. 72
Figure 2.20 Schematics of the interaction through hydrogen bonding between MWCNT and the PET matrix [142]. ......................................................................................................................... 78
Figure 2.21 Conductivities of PP/carbon composites (a) [33] and the conductivities required to develop electronic devices (b) [24]. ......................................................................................................................... 80

Chapter 3
Figure 3.1 Thermo-Hakke Minilab microcompounder. The magnified image shows the chamber and the screws[1]. ........................................................................................................ 104
Figure 3.2 Haake Minijet II injection moulding machine with different moulds [1]. ........ 105
Figure 3.3 Process flowcharts of PET/ carbon composites for specimen preparations. .... 106
Figure 3.4 Schematic representation of the acid treatment of A-MWCNT. ....................... 107
Figure 3.5 Schematics of beam-specimen interaction exhibiting backscattered electrons (BSE), secondary electrons (SE) and X-rays (redrawn from ref. [8]). ......................... 110
Figure 3.6 Signals generated when a high-energy beam of electrons interacts with a thin specimen. Most of these signals can be detected in different types of TEM [9]. ............. 111
Figure 3.7 The infrared spectrum of 2-methylbutyric acid [10] ........................................ 113
Figure 3.8 Block diagram of an FTIR spectrometer (redrawn from ref. [11]) ................... 113
Figure 3.9 DSC curve of a quenched PET sample [12] .................................................. 114
Figure 3.10 Block diagram of a DSC: (a) heat flux DSC; and (b) power compensation DSC. A: furnace; B: separate heater; and C: sample and reference holders[13] .................. 115
Figure 3.11 TGA typical curve for a material that exhibits decomposition starting and finish temperatures [13] ............................................................................................................. 116
Figure 3.12 Block diagram of a TGA apparatus[13] ......................................................... 117
Figure 3.13 The DMTA sinusoidal stress-strain response for ideal elastic, viscous and viscoelastic materials[14] .......................................................................................... 118
Figure 3.14 Single cantilever beam geometry in the DMA Q-800 .................................... 119

Chapter 4

Figure 4.1.1 Log-log plot of electrical conductivity vs. frequency for the PET/graphite microcomposites tested at room temperature ............................................................. 124
Figure 4.1.2 Semi log plot of electrical conductivity at 10 Hz vs. fillers loading for the PET/graphite microcomposites tested at room temperature ......................................... 125
Figure 4.1.3 Log-log plot of electrical conductivity vs. frequency for the PET/GNP nanocomposites tested at room temperature ......................................................... 126
Figure 4.1.4 Semi log plot of electrical conductivity at 10 Hz vs. filler loading for the PET/GNP nanocomposites tested at room temperature ......................................... 126
Figure 4.1.5 Log-log plot of electrical conductivity vs. frequency for the PET/A-MWCNT nanocomposites tested at room temperature ............................................... 128
Figure 4.1.6 Semi log plot of electrical conductivity at 10 Hz vs. filler loading for the PET/A-MWCNT nanocomposites tested at room temperature ............................................... 128
Figure 4.1.7 Log-log plot of electrical conductivity vs. frequency for the PET/T-MWCNT nanocomposites tested at room temperature

Figure 4.1.8 Semi log plot of electrical conductivity at 10 Hz vs. filler loading for the PET/T-MWCNT nanocomposites tested at room temperature

Figure 4.1.9 Percolation threshold, $\Phi_c$ determination plot. Electrical conductivity of PET/graphite microcomposites as a function of graphite content. The inset plot is $\log \sigma$ versus $\log (\Phi-\Phi_c)$. 

Figure 4.1.10 Percolation thresholds, $\Phi_c$ determination plot. Electrical conductivity of PET/GNP nanocomposites as a function of GNP content. The inset plot is $\log \sigma$ versus $\log (\Phi-\Phi_c)$.

Figure 4.1.11 Percolation threshold, $\Phi_c$ determination plot. Electrical conductivity of PET/A-MWCNT nanocomposites as a function of MWCNT content. The inset plot is $\log \sigma$ versus $\log (\Phi-\Phi_c)$.

Figure 4.1.12 Electrical conductivity of PET with graphite loading of 14 wt. % and 15 wt. % measured at different processing conditions in the Minilab twin-screw extruder tested at room temperature.

Figure 4.1.13 Electrical conductivity of PET with GNP loading of 5 wt. % and 6 wt. % measured at different processing conditions in the Minilab twin-extruder tested at room temperature.

Figure 4.1.14 Electrical conductivity of PET with A-MWCNT loading of 0.25 wt. % and 0.35 wt. % measured at different processing conditions in the Minilab twin-extruder tested at room temperature.

Figure 4.1.15 Semi log plot of electrical conductivity vs. MWCNT loading for the compression and injection moulded (flow direction) samples tested at room temperature.
Figure 4.2.1 SEM images of as-received fillers; (a) graphite, (b) GNP, (c) A-MWCNT and (d) T-MWCNT.

Figure 4.2.2 TEM images of (a) A-MWCNT and (b) T-MWCNT.

Figure 4.2.3 FTIR spectra of A-MWCNT and T-MWCNT.

Figure 4.2.4 SEM images of cryo-fracture surfaces of PET/graphite microcomposites at low and high magnifications; (a) 10 wt. %, (b) 15 wt. % and (c) 20 wt. %. The arrows in the magnified images indicate the graphite.

Figure 4.2.5 SEM images of cryo-fracture surfaces of PET/GNP nanocomposites at low and high magnifications; (a) 2wt. %, (b) 6 wt. % and (c) 8 wt. %. The arrows in magnified images indicate the GNP.

Figure 4.2.6 TEM images of as-received GNP (left) and a PET/GNP nanocomposite containing 6 wt.% of GNP (right). The arrows show the rolled up sheets of GNP.

Figure 4.2.7 SEM images of cryo-fracture surfaces of PET/A-MWCNT and T-MWCNT nanocomposites at 0.1, 0.2 and 1 wt. % CNT loadings, shown as a, b and c, respectively.

Figure 4.2.8 TEM images of PET/A-MWCNT and PET/T-MWCNT nanocomposites at 0.2 wt. %. The inset images show magnified CNT in the PET matrix.

Figure 4.2.9 Tensile fracture surface of the pure PET matrix.

Figure 4.2.10 Tensile fracture surfaces of PET/graphite microcomposites at low and high magnifications; (a) 2 wt. % graphite and (b) 15 wt. % graphite.

Figure 4.2.11 Tensile fracture surfaces of PET/GNP nanocomposites at low and high magnifications; (a) 2 wt. % GNP and (b) 10 wt. % GNP.

Figure 4.2.12 Tensile fracture surfaces of PET/A-MWCNT nanocomposites at low and high magnifications; (a) 0.1 wt. % A-MWCNT and (b) 1 wt. % A-MWCNT.

Figure 4.2.13 Tensile fracture surfaces of PET/T-MWCNT nanocomposites at low and high magnifications; (a) 0.1 wt. % T-MWCNT and (b) 1 wt. % T-MWCNT.
Figure 4.3.1 DSC curves of PET samples subjected to heat-cool-heat cycle; (a) first heating run (b) cooling run, both heating and cooling rate of 10 °C/min. ................................................................. 171

Figure 4.3.2 Second heating DSC curves of PET samples at a heating rate of 10 °C/min. The curves show the double peak or shoulder but the T_m taken from DSC machine is a single value of ~ 245 °C. ........................................................................................................... 173

Figure 4.3.3 DSC curves (heating/cooling rate 10 °C/min) for PET/graphite micro composites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan. ............... 175

Figure 4.3.4 DSC curves (heating/cooling rate 10 °C/min) for PET/GNP nanocomposites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan. .................. 178

Figure 4.3.5 DSC curves (heating/cooling rate 10 °C/min) for PET/A-MWCNT nanocomposites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan. ............... 181

Figure 4.3.6 DSC curves (heating/cooling rate 10 °C/min) for PET/T-MWCNT nanocomposites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan. .................. 185

Figure 4.3.7 Crystallinity of PET/carbon composites at 2wt. % carbon fillers ............... 188

Figure 4.3.8 Melt-crystallization peaks for PET/carbon composites at 2 wt. % of carbon filler, at the cooling rate of 10°C/min. ........................................................................................................ 188

Figure 4.3.9 TGA curves of graphite, GNP, A-MWCNT and T-MWCNT in (a) N_2 and (b) air (both at a heating rate of 10 °C/min). ........................................................................................................ 191

Figure 4.3.10 TGA thermograms (heating rate of 10 °C/min) of PET/graphite microcomposites with various graphite contents examined under (a) nitrogen and (b) air atmospheres. ........................................................................................................ 194
Figure 4.3.11 TGA thermograms (heating rate of 10 °C/min) of PET/GNP nanocomposites with various GNP contents examined under (a) nitrogen and (b) air atmospheres. ................................. 196

Figure 4.3.12 TGA thermograms (heating rate of 10 °C/min) of PET/A-MWCNT nanocomposites with various A-MWCNT contents examined under (a) nitrogen and (b) air atmospheres. .......................................................................................................................... 199

Figure 4.3.13 TGA thermograms (heating rate of 10 °C/min) of PET/T-MWCNT nanocomposites with various T-MWCNT contents examined under (a) nitrogen and (b) air atmospheres. .......................................................................................................................... 201

Figure 4.4.1 DMTA curves of dynamic storage modulus (E') and tanδ as a function of temperature for the PET matrix. .......................................................................................................................... 212

Figure 4.4.2 Second DMTA curve of dynamic storage modulus as a function of temperature for the specimen of PET matrix shown in Figure 4.4.1. The insert shows a first heating run on DSC for the same (now crystallised) PET specimen. .......................................................................................................................... 213

Figure 4.4.3 DMTA dynamic storage modulus data of PET/graphite microcomposites. ................................. 215

Figure 4.4.4 Dynamic storage modulus values at 25 °C for PET/graphite microcomposites as a function of graphite concentration. .......................................................................................................................... 216

Figure 4.4.5 Comparison of E' data from reference [4] (PMMA matrix) and [5] (PVDF matrix) with the present experimental results. .......................................................................................................................... 217

Figure 4.4.6 DMTA tanδ versus temperature data for the PET/graphite microcomposites. 218

Figure 4.4.7 DMTA dynamic storage modulus data of PET/GNP nanocomposites. ............ 220

Figure 4.4.8 Dynamic storage modulus values at 25 °C for PET/GNP nanocomposites as a function of GNP concentration. .......................................................................................................................... 222

Figure 4.4.9 Comparison of E' data from reference [4] (PMMA matrix) and [13] (PET matrix) with the present experimental results. .......................................................................................................................... 223

Figure 4.4.10 DMTA tanδ versus temperature data for the PET/GNP nanocomposites. ..... 224
Figure 4.4.11 DMTA dynamic storage modulus data of PET/A-MWCNT nanocomposites. .................................................................................................................................................................................. 225

Figure 4.4.12 Dynamic storage modulus values at 25 °C for PET/A-MWCNT nanocomposites.............................................................................................................................................................................................................. 227

Figure 4.4.13 Comparison of storage moduli data from references [19] (PP matrix) and [18] (PE matrix) compared with the present experimental results.......................................................................................................................................................................................................................... 228

Figure 4.4.14 DMTA tanδ versus temperature data for the PET/A-MWCNT nanocomposites. ............................................................................................................................................................................................................................................ 230

Figure 4.4.15 DMTA dynamic storage modulus data of PET/T-MWCNT nanocomposites. 232

Figure 4.4.16 DMTA dynamic storage modulus data of PET/MWCNT nanocomposites. .. 234

Figure 4.4.17 Comparison of storage moduli from references [24] (PET matrix) and [25](PTT matrix) with the present experimental results.......................................................................................................................................................................................................................... 234

Figure 4.4.18 DMTA tanδ versus temperature data for the PET/T-MWCNT nanocomposites. ............................................................................................................................................................................................................................................ 236

Figure 4.4.19 Typical stress-strain curves of the PET/graphite microcomposites. ........... 237

Figure 4.4.20 Comparison of E data from reference [33] (HDPE matrix) and [34] (HDPE matrix) with the present experimental results.......................................................................................................................................................................................................................... 238

Figure 4.4.21 The dependence of σu on graphite content of both calculated (equation 4.4) and experimental results. ............................................................................................................................................................................................................................................ 241

Figure 4.4.22 Typical stress-strain curves of the PET/GNP nanocomposites............... 243

Figure 4.4.23 Comparison of E data from Yasmin et al [6] (Epoxy matrix) and Al-Jabareen et al [38]( PET matrix) with the present experimental results.......................................................................................................................................................................................................................... 244

Figure 4.4.24 Comparison of E data from Al-jabareen et al [38] (PET matrix) and King et al [39] (Epoxy matrix) with the present experimental results.......................................................................................................................................................................................................................... 245

Figure 4.4.25 Typical stress-strain curves of the PET /A-MWCNT nanocomposites.... 246
Figure 4.4.26 Comparison of $E$ data from Santoro et al [23] (PET matrix) and Aalaei et al [42] (LLDPE matrix) with the present experimental results. .................................................. 248

Figure 4.4.27 Typical stress-strain curves of the PET/T-MWCNT nanocomposites. ........ 250

Figure 4.4.28 Comparison of $E$ data from Zaman et al [44] (PET matrix) and Gupta et al [10] (PTT matrix) to the present study. ................................................................. 250

Figure 4.4.29 The dependence of tensile modulus on $E_f$ as predicted by the Halpin-Tsai model. ............................................................................................................. 256

Figure 4.4.30 Halpin-Tsai calculations showing the effect of MWCNT weight fractions and aspect ratio on the modulus of PET/MWCNT nanocomposites.................................. 257

Figure 4.4.31 The dependence of tensile modulus on $E_f$ as predicted by the Halpin-Tsai model compared to experimental data for the GNP composites. ........................................... 258

Figure 4.4.32 Halpin-Tsai calculations showing the effect of GNP weight fractions and aspect ratio on the modulus of PET/GNP nanocomposites. ................................................ 259

Figure 4.4.33 Tensile modulus of PET/A-MWCNTs, by using Halpin-Tsai equations at different wt. % loadings of MWCNT. .............................................................. 261

Figure 4.4.34 Tensile modulus of PET/MWCNT nanocomposites using Halpin-Tsai models, the experimental data obtained from ref. [23]. ..................................................... 262

Figure 4.4.35 Tensile modulus of PET/GNP, by using Halpin-Tsai equations at different wt. % loadings of GNP. ..................................................................................... 263
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
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<td>$T_{cc}$</td>
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<td>$nm$</td>
<td>Nanometre</td>
</tr>
<tr>
<td>$E$</td>
<td>Tensile Modulus (MPa)</td>
</tr>
<tr>
<td>$\sigma_u$</td>
<td>Tensile strength (MPa)</td>
</tr>
<tr>
<td>$\varepsilon_u$</td>
<td>Elongation at break (%)</td>
</tr>
<tr>
<td>$\sigma_m$</td>
<td>Matrix strength (MPa)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
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<tr>
<td>$E_m$</td>
<td>Matrix modulus (MPa)</td>
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<tr>
<td>$E_f$</td>
<td>Filler Modulus (MPa)</td>
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<tr>
<td>$\eta$</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>wt.%</td>
<td>Percentage by weight</td>
</tr>
<tr>
<td>vol.%</td>
<td>Percentage by volume</td>
</tr>
<tr>
<td>$A$</td>
<td>Sectional Area ($m^2$)</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter (m)</td>
</tr>
<tr>
<td>$L$</td>
<td>Length (m)</td>
</tr>
<tr>
<td>$T$</td>
<td>Thickness (m)</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance ($\Omega$)</td>
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<tr>
<td>OH</td>
<td>Hydroxyl group</td>
</tr>
<tr>
<td>COOH</td>
<td>Carboxyl group</td>
</tr>
<tr>
<td>$HNO_3$</td>
<td>Nitric acid</td>
</tr>
<tr>
<td>$H_2SO_4$</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>C=O</td>
<td>Carbonyl group</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Error fitting</td>
</tr>
<tr>
<td>$E_c$</td>
<td>Predicted tensile modulus (MPa)</td>
</tr>
<tr>
<td>$\phi_f$</td>
<td>Volume fraction of filler</td>
</tr>
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## List of Abbreviation

<table>
<thead>
<tr>
<th>Short Form</th>
<th>Description</th>
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<tbody>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>GNP</td>
<td>Graphite Nanoplatlets</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multiwall Carbon Nanotubes</td>
</tr>
<tr>
<td>A-MWCNT</td>
<td>As-received Multiwall Carbon Nanotubes</td>
</tr>
<tr>
<td>T-MWCNT</td>
<td>Acid Treated Multiwall Carbon Nanotubes</td>
</tr>
<tr>
<td>PMCs</td>
<td>Polymer Microcomposites</td>
</tr>
<tr>
<td>PNCs</td>
<td>Polymer Nanocomposites</td>
</tr>
<tr>
<td>CPNCs</td>
<td>Conductive Polymeric Nanocomposites</td>
</tr>
<tr>
<td>EG</td>
<td>Exfoliated graphite</td>
</tr>
<tr>
<td>GO</td>
<td>Graphite oxide</td>
</tr>
<tr>
<td>1D</td>
<td>One Dimension</td>
</tr>
<tr>
<td>2D</td>
<td>Two Dimension</td>
</tr>
<tr>
<td>3D</td>
<td>Three Dimension</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electrons</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electrons</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>MC</td>
<td>Melt Compounding</td>
</tr>
<tr>
<td>iSP</td>
<td>In-situ Polymerization</td>
</tr>
<tr>
<td>SM</td>
<td>Solution Method</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethanes</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
</tr>
<tr>
<td>PVOH</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>PTT</td>
<td>Poly(trimethylene terephthalate)</td>
</tr>
<tr>
<td>PA6</td>
<td>Polyamide 6</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultrahigh molecular weight polyethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic Mechanical Thermal Analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo Gravimetric Analysis</td>
</tr>
</tbody>
</table>
Abstract
Processing, structure and properties of poly (ethylene terephthalate)/carbon micro- and nano-composites
The University of Manchester
Basheer A. Alshammari
Doctor of Philosophy
18, September, 2014

Incorporation of conductive carbon fillers into polymer matrices can improve electrical, thermal and mechanical properties of the resulting composites. In this work, three different conductive carbon fillers were used; i.e. graphite, graphite nanoplatelets (GNP) and as-received multiwall carbon nanotubes (A-MWCNT). In addition, A-MWCNT were modified using mixed acids and named as T-MWCNT. These four fillers were incorporated into poly (ethylene terephthalate) (PET) to prepare four types of PET/carbon micro- and nano-composites. These composites were prepared by melt compounding using a Haake Minilab extruder equipped with a co-rotating twin screws. The extruded samples were compression moulded to films of 1 mm thickness and were subsequently quenched to obtain low crystallinity samples. The extruded samples were also injection moulded to obtain dumbbell shaped specimens. The electrical, morphological, thermal and mechanical properties of these composites were studied and characterized as a function of carbon filler types and contents using a wide range of analytical and testing techniques: namely; impedance spectroscopy, DSC, TGA, SEM, TEM, FTIR, DMTA and tensile testing. The results demonstrated that the addition of graphite, GNP and A-MWCNT produced electrically conductive composites and that the conductivities were found to be dependent on several factors; including filler type, filler content and processing conditions. The PET/A-MWCNT nanocomposites showed an excellent electrical conductivity (~ 0.2 S/m at 2 wt. % A-MWCNT) with a low percolation threshold ($\Phi_c \sim 0.33$ wt. %). In contrast, PET/T-MWCNT nanocomposites displayed similar electrical conductivity to that of pure PET and no percolation threshold was observed in this case (until 2 wt. % of CNT), this was attributed to the acid treatment which disrupted the inherent electrical conductivity of the CNT and also reduced their aspect ratio. However, T-MWCNT showed better dispersion and distribution into the PET matrix as well as reduced CNT-CNT interactions and therefore do not as readily form network structures. This resulted in better mechanical properties in comparison to the PET/A-MWCNT nanocomposites. In terms of processing, increasing screw speed during mixing was found to enhance the electrical conductivities of PET/carbon nanocomposites (GNP and A-MWCNT), but only above the percolation thresholds values, by $\sim 2 – 3$ orders of magnitude. However, no significant change was observed in the electrical conductivities of PET/graphite microcomposites. All the carbon fillers, with different dimensions, were found to act as nucleating agents for the PET matrix and hence accelerated crystallization and increased the degree of crystallinity. CNT were found to accelerate the crystallization at lower loadings compared to GNP and graphite. In addition, it was found that quenched PET and composite samples were not fully crystallized after processing and therefore (cold) crystallized during the first heating cycle in both DSC and DMTA, as indicated by crystallisation peaks during the DSC first-heat and a rise in storage moduli above $T_g$ during the DMTA first heat. In general, TGA showed that carbon fillers improved the resistance to thermal and thermo-oxidative degradation under both air and nitrogen atmospheres. However, a reduction in thermal stability was observed for the composites containing T-MWCNT in air. The carbon fillers increased the storage and tensile moduli of the composites compared to pure PET. However; tensile strength and elongation at break were reduced except for composite containing T-MWCNT which showed no significant change at lower loadings. The tensile
moduli of nanocomposites were predicted using Halpin-Tsai models, which showed good agreement at low loadings of A-MWCNT (≤ 0.2 wt. %) and GNP (≤ 2 wt. %). However, poor agreement was observed at higher loadings of fillers where the composites displayed reduced reinforcement efficiency. This correlates with results from SEM, which showed agglomeration, poorer distribution, debonding and rolling up of fillers in the PET matrix at higher loadings.
Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Basheer AlShammari

18, September, 2014
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Chapter 1 Introduction

1.1 Introduction

This chapter is intended to present a brief research background of micro and nanocomposites based on polymer matrices including their applications. This will be followed by discussion of the scope and objectives of the work and thesis structure.

1.2 Research Background

A composite is a material composed of two or more components or phase [1]. In fact, a composite material is envisioned to offer properties in excess of both the matrix and reinforcement phases which are not possible in conventional isotropic materials (polymers, metals, ceramics etc.). Composites are being made using numerous matrices; such as metals, ceramics, carbon, glasses and polymers, with polymers being the most common. This is due to the fact that polymers offer properties such as low density, good wettability of reinforcements and good toughness and are easy to mould to a desired shape, but have lower strength and modulus in comparison to ceramics and metals [2]. Strength properties are greatly improved by the addition of reinforcing fillers into polymer matrices. Amongst the most exciting reinforcements are the conductive fillers that have the potential of improving the electrical, thermal and mechanical properties of polymer matrices.

Much research focussed on preparing conductive polymers composites (CPCs) for high performance applications, particularly using carbon and its allotropes which includes both micro- and nano-size fillers such as carbon black (CB), graphite, carbon fibres, graphite nanoplatlets (GNP), graphene and carbon nanotubes (CNT). Traditionally polymers are filled with microfillers to improve electrical and mechanical properties. However; high loading are required which can negatively influence mechanical properties and processing [2, 3].
contrast, previous studies have demonstrated that even low addition levels of nanofillers can
give significant improvements in the electrical, mechanical and thermal properties [4-6] of
polymers. However, poor interfacial adhesion between the reinforcement and the matrix,
inadequate dispersion and non-uniform distribution are parameters of major concern that
need to be addressed before reaping the full potentials of particulate conductive nanofillers.
In order to resolve these issues, much effort has been also applied to the chemical
modification of nanofillers [7].

Micromechanics [2] show that the properties of polymer composites are a function of the
behaviour of the individual constituents, their shapes and arrangements, volume fractions and
the interfaces between matrices and reinforcements. For the micro-scale fillers, the properties
are largely independent of their sizes. However, when reinforcements are of nano-scale, their
size plays a vital role due to their high surface areas and aspect ratios, as in the case of CNT,
graphene and GNP. This notion is at the epicentre of current research to develop advanced
carbon-particulate nanocomposites from these fillers in order to benefit from their excellent
electrical, thermal and mechanical properties. The most common applications of conductive
polymer/carbon composites are as antistatic and electromagnetic shielding materials.
However, these composites could also be used as heaters, separators or electrodes [8-10].
Despite these wide applications, there is a lack of understanding of the processing-structure-
property correlations for these composites. In particular, comparative studies dealing with
various types of carbon fillers incorporated into polymers [11]. Therefore, the present work
is to prepare conductive micro and nanocomposites using poly (ethylene terephthalate) (PET)
matrix and carbon fillers which includes; graphite, graphite nanoplatlets (GNP), as-received
multiwall carbon nanotubes (A-MWCNT) and acid treated multiwall carbon nanotubes (T-
MWCNT) to investigate their processing, structure and properties relationships.
PET is a thermoplastic semi-crystalline polymer used widely in applications such as fibres, films and packaging. This because of its good strength, chemical resistance and dimensional stability [12, 13]. Despite the aforementioned properties of PET, improvement of its electrical, thermal and mechanical properties is required for high performance applications and these are the objectives of the present project. Improved electrical conductivity of PET is needed for making electrostatic devices [14]. Another exciting application of conductive PET/carbon nanocomposites is the replacement of indium tin oxide (ITO) electrodes because of its poor mechanical and higher sheet resistance when compared with CNT [15, 16].

It is often difficult to produce satisfactory polymer nanocomposites as several studied have noted. There is no single unanimously agreed production method, as each type of polymer may need special processing procedures resulting in wide variations in properties [2, 17]. The environmentally friendly mass production route known as melt compounding was employed in this research. This is a common method of preparing polymer-particulate composites [11] and therefore it is natural to investigate this method for producing polymer/carbon nanocomposites.

1.3 Research Scope

This research deals with the preparation and characterization of PET/carbon composites: namely; PET/graphite, PET/GNP, PET/A-MWCNT and PET/T-MWCNT composites. Melt compounding was used to prepare the composites; followed by compression or injection moulding to produce film or dumbbell test specimens, respectively. The prepared composites were characterized using a wide range of analytical testing techniques: namely; Electrical Impedance Spectroscopy, DSC, TGA, DMTA, SEM, TEM, FTIR and mechanical response via tensile testing. In the first stage of the study percolation thresholds are determined for the composites, based on percolation theory calculations on electrical conductivity curves. This
is followed by morphological studies of cryogenic and tensile fracture surfaces and measurement of the thermal and mechanical properties at selective loadings of all the fillers. Finally, the Halpin-Tsai equations were utilized to model the tensile modulus of PET/carbon nanocomposites.

1.4 Aim and Objectives

The present study is designed to fabricate micro and nanocomposites using PET as the matrix and graphite, GNP, A-MWCNT and T-MWCNT as the conductive carbon fillers, with an aim to investigate their processing parameters and structure - properties correlations.

The above aim will be achieved via the following objectives;

1. To investigate the processing-structure-property relationships of polymer composites prepared by incorporating microfiller (Graphite) and nanofillers (GNP and MWCNT) into a PET matrix.

2. To examine the electrical conductivity and percolation thresholds of PET/carbon composites with varying weight fractions of the conductive carbon fillers.

3. Examine the morphology of PET/carbon composites at different loadings of fillers i.e. below, around and above the percolation thresholds.

4. To study the effect of fabrication methods (compression and injection moulding) and processing parameters, such as screw speed and time, on the electrical conductivity of PET/carbon composites.

5. To compare the physical and mechanical properties of PET/carbon composites over a range of weight fractions of carbon.

1.5 Structure of Thesis

This thesis is structured into five chapters. Chapter 1 outlines the research problems and objectives of the present study. Chapter 2 surveys the literature published in the field of polymer-based carbon micro- and nano-composites. In particular, PET-based micro- and
nano-composites were discussed in details. Chapter 3 describes the experimental methodologies; including the materials, sample preparations, treatments and characterisation techniques used. Chapter 4 presents and discusses the results obtained from impedance spectroscopy, DSC, TGA, SEM, TEM, FTIR, DMTA and tensile testing machine and discussion is presented. Finally, chapter 5 presents the conclusions and suggestions for future work.

1.6 References


Chapter 2 Literature Review

This chapter reviews previous studies on carbon-particulate reinforced polymer composites with matrices such as thermoplastics, thermosetting polymers and elastomers. More specifically, previous published studies on the processing, structure, and properties of PET-based micro- and nano-composites will be discussed in light of the latest developments in this subject, which are directly related to this study. Finally, on the basis of previous studies and our best understanding, conclusions will be presented.

2.1 Introduction

The most commonly used and extensively researched particulate carbon fillers and reinforcements include carbon black (CB), graphite, graphite nanoplatelets (GNP), carbon nanofibre (CNF) and carbon nanotubes (CNT) that are used to make polymer matrix composites (PMCs) for a wide variety of electronic applications. Moreover, different types of polymer can be used as matrices to produce PMCs including thermoplastics, thermosetting polymers and elastomers.

Traditionally, micron sized inclusions are used as fillers to modify and improve the properties of polymer composites, and the resulting composites are termed polymer microcomposites (PMCs). However, over the last few years, nanofillers, which have at least one dimension in the nanometre scale, have been used instead of microfillers as due to their small size they offer marked enhancement to the properties of polymer matrices when used to form polymer nanocomposites (PNCs). PNCs have a huge interfacial area between the polymer matrix and filler due to the small size of the filler particles. This huge interfacial area creates a significant volume fraction of polymer in close proximity to the interface (often called the interphase) with properties which differ from the bulk properties of the matrix polymer even at low concentration of nanoscale filler. Previous studies demonstrated that even low
The contents of nanoscale filler could bring tremendous changes in electrical, mechanical and thermal properties of polymers [1-4]. The most significant advantages of PNCs over PMCs are the possibility of multifunctional properties and the reduction of the amount of filler needed to achieve high performance properties. However, the final properties of the composites rely on several factors such as the individual properties of the components, the interaction between them and the preparation method used for fabrication.

2.2 PET Matrix

Poly (ethylene terephthalate), commonly abbreviated to PET, is an aromatic polyester which is a condensation product of a diacid (e.g. terephthalic acid) and a dialcohol (e.g. ethane 1,2-diol, which is known as ethylene glycol) [5]. It is made in two steps; the first step involves the reaction of the acid and alcohol to form ester molecules followed by polymerization. To form PET, the chemical structure of which is shown in Figure 2.1. The term PET denotes a large family of compounds having a wide variety of applications. PET is a common thermoplastic polymer used in applications such as packaging etc. [5], due to its excellent properties such as clarity, wear-resistance, hardness, chemical resistance, thermal and dimensional stability etc. Moreover, PET has a high glass transition temperature (T_g) of around 85 °C and melting point of about 255 °C.

![Figure 2.1 Chemical structure of PET](image)

Figure 2.1 Chemical structure of PET [6].
2.3 Carbon Fillers

2.3.1 Introduction

Carbon fillers are one of the most important filler groups used in composites. Carbon has an extraordinary ability to join with it and various other elements. It is available in abundant quantity in nature as coal and natural graphite and more rarely as diamond (allotrope of carbon). The discovery of a new allotrope family, the fullerenes in 1985, was an exciting addition to the family of carbons that prompted extensive research that lead to the discovery of carbon nanomaterial such as CNT in 1991 and graphene in 2004 [7]. For example; Table 2.1 shows properties of graphite, GNP, CNT and Graphene.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Graphite</th>
<th>GNP**</th>
<th>CNT*</th>
<th>Graphene***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g cm⁻³</td>
<td>~ 2.26</td>
<td>~1.8 ~ 2.2</td>
<td>0.8 SWCNT</td>
<td>~ 0.5</td>
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<tr>
<td>Elastic Modulus</td>
<td>TPa</td>
<td>~ 1(in-plane)</td>
<td>~1 (in-plane)</td>
<td>~1 SWCNT</td>
<td>~ 1</td>
</tr>
<tr>
<td>Modulus</td>
<td></td>
<td></td>
<td></td>
<td>0.3-1 MWCNT</td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>GPa</td>
<td>~ 130</td>
<td>~100 - 400</td>
<td>50-500 SWCNT</td>
<td>~ 130</td>
</tr>
<tr>
<td>Resistivity</td>
<td>µΩcm</td>
<td>~ 50 (in-plane)</td>
<td>~50 (in-plane)</td>
<td>10-60 MWCNT</td>
<td>~ 1</td>
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<tr>
<td>Thermal Conductivity</td>
<td>Wm⁻¹ K⁻¹</td>
<td>3000(in-plane)</td>
<td>~5300 (in-plane)</td>
<td>3000 (theoretical)</td>
<td>~ 5500</td>
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<td>Thermal Stability</td>
<td>°C</td>
<td>~450-650</td>
<td>~450 - 650</td>
<td>&gt;700 (in air)</td>
<td>~ 500</td>
</tr>
<tr>
<td>Stability</td>
<td></td>
<td>(in air)</td>
<td>(in air)</td>
<td>2800 (in vacuum)</td>
<td>(in air)</td>
</tr>
</tbody>
</table>

*From ref. [7], ** from ref. [8] and *** from references [147-151].
Several types of carbon such as carbon black, carbon fibre, graphite, CNT, graphite nanoplatelets (GNP) and graphene have been used as fillers, to produce composites with excellent electrical, thermal and mechanical properties. All such forms of carbon are possible because of the element's unique hybridization ability. In the following section a brief review of forms of carbon that used in this study and utilized for making PET based conductive micro- and nano-composites will be presented.

2.3.2 Graphite

Graphite exists naturally and can be synthetically prepared. The elemental carbon is at its lowest energy level in graphite at room temperature [7, 9]. The structure of graphite consists of parallel layers of graphene sheets with \( sp^2 \) hybridized carbon that is bonded hexagonally (figure 2.2).

![Graphite structure](image)

**Figure 2.2** Graphite structure depicting \( sp^2 \) hybridization of carbon atoms bonded in hexagonal fashion [7].

Carbon atoms are connected to each other through strong covalent bonds within the graphene sheets, whereas the parallel sheets in graphite are held together by weak van der Waals forces of attraction. Thus, graphite is an anisotropic material; the elastic modulus is significant
higher in parallel (1 TPa) but its lower in the perpendicular direction (36.4 GPa) [10]. Graphite has high elastic modulus, thermal conductivity, thermal stability and good electrical resistivity (~ 50 μΩcm at room temperature) [7, 11-13] as shown in Table 2.1. It should be noted that the π orbitals spread into entire graphene layers of graphite allowing electrical and thermal conductivities [7]. The layered structure of graphite shows a 3D order which is shown in Figure 2.2.

2.3.3 GNP

Graphite nanoplatelets (GNP) are also known as graphene nanoplatelets, graphite nanosheets, graphite nanoflakes, exfoliated graphite or expanded graphite (EG). GNP are usually prepared by modification of graphite [7] which allow certain atoms, molecules and ions to be inserted between its graphene sheets. GNP can be also synthesized by CVD and arc discharge method but the two fabrication approaches that are usually used are mechanical milling and graphite intercalation. The mechanical milling approach breaks up graphite resulting larger sized GNP that is followed by intercalation method. In this method, the large sizes GNP are exposed to acid for separation of graphene layers. Usually natural graphite is immersed in a concentrated sulphuric acid solution with other oxidizers such as O₃, HNO₃, H₂O₂, KMnO₄. The resulting products are known as graphite intercalation compounds (GIC) and also as expandable graphite. The most commonly used GIC are graphite bisulfate and graphite oxide (GO, also known as graphitic acid). This GIC is heated to a temperature of about 1000 °C for 15 – 30 seconds which generates large amounts of gases such as SO₂ and H₂O resulting in further expansion of graphite; which is known as exfoliated or expanded graphite (EG). Further exfoliation of EG can produce thin layers of graphite to obtain the GNP. This process is performed under nitrogen or in air. Nitrogen is preferred because it reduces the GO formation during intercalation. GIC, GO and EG are common modified
graphite forms and have all been used for preparing polymer/graphite nanocomposites [7, 14]. Figure 2.3 shows a schematic of entire process.

As discussed earlier, graphite has high elastic modulus, thermal conductivity and good electrical conductivity. However, when its layers are separated down to the nanometre scale thickness, they would have high aspect ratio (200 - 1500) and excellent elastic modulus. Therefore dispersion plays a key role in the enhancement of both mechanical and physical properties of polymer matrices, as well as its electrical properties (theoretically, a single layer of GNP has an excellent electrical conductivity). This excellent conductivity, if realised, would make it possible for GNP nanocomposites to be used as electrode materials.

![Figure 2.3 Schematics diagram of GNP preparation [14].](image)
2.3.4 Carbon Nanotubes (CNT)

2.3.4.1 Introduction

CNT are a form of carbon discovered in 1991, which opened up new research horizons in both engineering and life sciences. Extensive research has been performed on polymer/CNT nanocomposites systems to try to develop their potential as reinforcement is due to their remarkable properties. CNT exist in either a single rolled-sheet of graphene known as single wall carbon nanotubes (SWCNT) or as multiple concentric layers known as multiwall carbon nanotubes (MWCNT). The distance between two wall layers is ~0.34 nm [15, 16]. It should be noted that, similar to graphite, the layers are bonded by weak van der Waals forces of attractions due to which they arrange themselves into bundles. The bonding between carbon atoms within the tube walls is covalent bonding and that imparts a great strength to weight ratio.

2.3.4.2 Preparation of CNT

Interestingly, the preparation methods of CNT are simple but it can be quite tricky to acquire the desired geometry of CNT. In general, three methods are commonly employed; laser ablation, chemical vapour deposition (CVD) and arc discharge. The arc discharge technique utilizes an electric potential across two electrodes made up of graphite in an inert atmosphere [15]. Bringing electrodes together allows vaporisation by arc discharge depositing CNT onto one of its terminals as shown in the process diagram in Figure 2.4. The structure of deposited carbon can be controlled by varying the potential difference between the electrodes used. Use of metal powder (Pt, Fe, Ni, Co or bi-mixtures) in the anode by drilling a hole facilities thickness control of CNT [17].
In laser ablations, shown in Figure 2.5, material is removed in a solid state using the beam from a high powered laser. The starting material is graphite that is heated to high temperatures in an inert atmosphere, which at the same time is targeted by a high intensity laser beam. An optimum heating temperature reported is 1200 °C for preparation of nanotubes of ~ 300 nm in length having thickness ranging in 4 – 24 layers [18]. In order to facilitate easy collection of CNT, the Argon gas is introduced in the way of the laser beam.
In comparison, the common way for producing high performance CNT is the CVD technique. In this method, a volatile compound or material is produced first and then the substrate is exposed to it thereby depositing CNT [20]. The catalyst materials are heated in CVD reactor in the temperature range of 500 – 1200°C and either carbon monoxide (CO) or hydrocarbon gas is passed through it. The reaction time controls the length of the CNT. In order to ensure effective deposition in CVD processes the catalysts are believed to be mandatory part of this technique [21], as hydrocarbons dissociate at the surface of the catalyst, hence generating carbon and hydrogen. The diffusion of carbon atoms through the catalyst forms CNT. Figure 2.6 shows a schematic for the CVD process.

![Figure 2.6 The typical CVD process schematics for CNT production.](image)

### 2.3.4.3 Types of CNT

As discussed earlier the two common types of carbon nanotubes are SWCNT and MWCNT; the latter are used extensively as filler materials in PNCs. From Figure 2.7 it is not difficult to realize that rolling of graphene sheet yields seamless SWCNT cylinders while coaxial arrangement of these cylinders forms MWCNT. The production of MWCNT straightforward, whilst SWCNT production id somehow is more difficult, This is relatively reflected in the price; for SWCNT is ~ $170/gram while MWCNT are $8/gram [7].
MWCNT can reach diameters of up to 100 nm and several micrometres in length. SWCNT is the simplest geometry and usually the diameters range from 0.34 to 3.00 nm and have excellent mechanical and electrical properties [16, 22].

### 2.3.4.4 Structure and Properties of CNT

CNT have excellent properties such as conductivity and strength. It is worth discussing the structural features responsible for such properties.

Figure 2.8 Schematic exhibiting how a hexagonal sheet of graphene is rolled to develop a CNT with various chirality, as A represents the armchair, B depicts the zigzag and C shows the chiral [24].
The hexagonal carbon ring is responsible for the type of structure when oriented differently [23]. CNT form three structures, armchair, and zig-zag and chiral, those depend on the rolling angle of graphene. Such chirality is explained by the chiral vector, \( C_h = n a_1 + m a_2 \) as shown in figure 2.8. The integers ‘n’ and ‘m’ are the steps to unit vectors \( a_1 \) and \( a_2 \) of hexagonal lattice. Such a naming scheme allows three types of orientation of the carbon atoms around tube circumference. When \( n = m \) the CNT are called armchair, in the case where \( m = 0 \) is called zigzag or otherwise known as chiral. The chirality of CNT has important effect on their electrical properties. In the case when \( 2n + m \) is a multiple of 3 then CNT have conductivity equivalent to the metals.

2.4.4.5 Modification of MWCNT

Several issues related to forming composites with MWCNT need to be addressed including interaction between polymer and filler, compatibility and dispersion quality. In addition, the considerable lengths of MWCNT causes entangling and the large surface area to volume ratio connected with van der Waals forces between the tubes which leads to agglomeration in the polymer matrix. The production methods used lead to impurities and defects, such as residual catalyst and amorphous carbon; on CNT surface therefore pre-treatments are often required. In order to make them more reactive, functional groups can be attached, but this is inhibited by their seamless nature. CNT are therefore most reactive at their ends and the attack of reagents such as acids is selective towards defect regions [16, 24-26]. Moreover, it has been reported in the literature that ultrasonic treatment causes shortening of CNT [27].

Two common methods of pre-treatments are employed, namely chemical (or covalent) and physical (or non-covalent) functionalization. The chemical functionalization of CNT has proven especially useful for making composites. Both covalent and non-covalent pre-treatments are useful, in particular in helping to connect functional groups to CNT.
Non-covalent (physically absorbed) treatment is achieved by van der Waals interaction between the treatment molecules CNT. Most importantly, the structure of CNT remains unaffected after this sort of treatment, hence their electrical properties are preserved [16, 26]. The covalent functionalization may result in loss of such properties due to change in hybridisation from $sp^2$ to $sp^3$ and loss of the delocalized $\pi$ electrons. Nitric acid (HNO$_3$) and sulphuric acid (H$_2$SO$_4$) or mixtures of both are often used in covalent functionalization and this method was used in the present study. Figure 2.9 shows the corresponding schematic diagram. Successful application of such treatments requires optimizing of the concentration and volume of acids, as well as the duration of exposure of the CNT to the acid and the temperature. Carefully selected modification treatments would avoid any unnecessary damage to the CNT and will assist in attaching the desired amounts of functional groups. Numerous studies have been dedicated to functionalization treatments using different experimental techniques to minimise the damage of CNT [28].

![Figure 2.9 Pre-treatment of MWCNT using mixture of HNO$_3$ and H$_2$SO$_4$ [29].](image)

Furthermore, it is worth investigating the impact of such treatments on the morphology and electrical properties of MWCNT. A study of pre-treatment of MWCNT by a mixture of
HNO₃/H₂SO₄ acids and ultrasonic treatment for making polymer nanocomposites was conducted by Park et al. [27]. The authors reported that both of these treatments greatly affected the electrical conductivities and size distribution of MWNCTs relative to as-received untreated samples. However, less damage was observed by sonication. Figure 2.10 demonstrates that acid treatment of MWCNT causes appreciable damage when compared to sonication.

![Figure 2.10 SEM micrographs showing of MWCNT before and after treatments, (a) no treatment(as received), (b) treated with acidic mixture and (c) ultrasonically treated](image)

2.4 Polymer/Carbon Composite Processing

The most common methods of fabricating polymer/carbon composites were detailed by Harris et al, [16]. Moreover, recent reviews by Sengupta et al, [7] and Pang et al, [4] showed that a large number of micro- and nano-composites are produced by using following methods: in situ polymerisation (iSP), solution processing (SP) and melt compounding (MC).

2.4.1 In-situ Polymerisation (iSP)

The in situ polymerization method is an effective technique to enhance the dispersion of carbon fillers into polymeric matrices. In this process, the monomers are polymerized in the presence of the fillers, thus allowing stronger interactions to form between the matrix and the
filler. Therefore, the composites made by this method tend to exhibit improved mechanical properties and lower percolation thresholds than those obtained by either the SP or MC processes; this is due to improved dispersion of filler. However, there are disadvantages; such process needs high electrical energy to disperse the fillers in the polymer during manufacturing. Therefore, in situ polymerisation may not be the right choice for the mass production of polymer based nanocomposites [4, 7, 26].

2.4.2 Solution Processing (SP)

In this process, the polymer matrix is dissolved in a suitable solvent and filler is dispersed into the solution. Once mixing is complete, the solvent is removed to produce the composite. Electrical conductivity of the composite is achieved at a low percolation threshold by this method due to good dispersion of the filler. The use of solvent, with the associated cost and potential for environmental contamination on removal of such solvents, has limited the industrial acceptance for mass production [4, 7, 26].

2.4.3 Melt Compounding (MC)

The MC method is the industrial choice for mass production of polymer based composites. This is a more economic and environmentally friendly technique compared with iSP and SPs, as no solvents are used during manufacturing. It utilizes traditional melt mixing machines such as internal mixers and extruders which are the most common techniques to fabricate conductive polymer composites. It was reported that composites made by MC have higher percolation thresholds compared with iSP and SP and that composites with higher percolation threshold typically suffer from poor mechanical properties [4]. However, MC is one of the most commonly used methods for producing polymer micro- or nano-composites [4, 7, 26].
2.4.4 Effect of Fillers on Polymer Structure

It is worthwhile and important to discuss the effect of the filler addition on the structural development of the polymer matrix. Some research studies reported changes in morphology and crystallization behaviour of the matrix upon addition of a filler, such as CNT [16]. For example, increased crystallinity content has been reported in poly(vinyl alcohol) (PVOH) based composites [30] and composites based on other semi-crystalline polymers matrices [31, 32], such changes are significant for improvement in the properties of these composites. Therefore, it is well established that matrix morphology is strongly influenced by the addition of fillers.

Figure 2.11 Possible states of distribution and dispersion of filler into the matrix, number 1 represents poor distribution and dispersion, 2 shows good distribution but poor dispersion, 3 shows poor distribution and good dispersion and 4 shows both good dispersion and distribution. (redrawn from Gulrez et al, [33])

47
The influence of filler depends on how effectively it is dispersed into the matrix. Poor dispersion or distribution will develop localized effects, hence leading to non-uniform behaviour. For example, Figure 2.11 shows schematics of the possible distribution and dispersion states of filler in a matrix. In the figure: number 1 shows poor distribution and dispersion; number 2 good distribution but poor dispersion; number 3 poor distribution and good dispersion and 4 shows both good dispersion and distribution. The relatively poor distribution of well dispersed fillers exhibited in case of sketch 3 in figure 2.11 is the preferred state for the formation of a conductive network [33].

2.4.5 Alignment of Fillers in Nanocomposites

Alignment of fillers such as CNT, either during processing or after processing, is necessary for creating the desired properties. Because of their sizes and aspect ratio, it is necessary to control the alignment of the CNT in order to impart the optimum properties to the composite. Several studies have been conducted on the influence of geometry and alignment of fillers into the polymer matrix [34-37]. Several approaches were adopted to enhance the required properties of polymer/CNT composites; including mechanical stretching [34], electrospinning [35] and by applying a magnetic field [36]. The work of Haggenmueller et al, [37] used a combination of solvent casting and melt mixing to disperse SWCNT into PMMA matrix. Their results showed that these methods could successfully disperse and align the CNT in the matrix, resulting in improvement in the mechanical properties (elastic modulus and yield strength) of the composites. Improved mechanical properties were also reported by Camponeschi et al, [36] after applying magnetic field that resulted in good orientation of CNT.

The orientation of CNT into polymer matrices has also been achieved using shear. The study of Abu Bakar et al, [38] reported that the addition of only 1 wt. % of as-received MWCNT
into polyethylene (PE) enhances Young’s modulus by 75 %, in addition to tensile strength and elongation at break compared to the unfilled matrix. These mechanical properties improved with increasing shear rate due to an increase in the degree of alignment of the MWCNT [38]. A moderate shear force and short time of mixing are recommended for forming conducting networks of MWCNT and good dispersion of filler into the matrix [39]. The good dispersion and high alignment level of MWCNT into polypropylene (PP) has been achieved at low levels of MWCNT (< 0.5 wt. %), but as the concentration of MWCNT was increased the dispersion was seen to deteriorate [40].

Processing techniques and their parameters can affect properties. For example, in injection moulding the injection velocity, mould temperature, processing temperature and holding pressure, screw speed and time of mixing are important in determining the final properties [41]. Eric et al, [42] achieved highly aligned nanocomposites films using melt extrusion through a slit-die; the tensile strength and modulus of PS/MWCNT nanocomposites containing 5 wt. % CNT was enhanced by 137 % and 49 % respectively compared to unfilled PS films. These improvements were found to be five times higher than the effect of randomly oriented CNT. Similarly twin screw extrusion melt blending process parameters were proposed to affect the properties of the resultant composites by Willmow et al [43] who studied poly(lactic acid) (PLA)/MWCNT nanocomposites. The authors found high screw speed (500 rpm) capable enough to disperse and distribute MWCNT into PLA. However, an increasing temperature profile showed slightly better nanotube dispersions. In addition, percolation threshold was found at 0.5 wt. % MWCNT.

In another example, injection moulding was shown to give an enhancement of the preferential alignment of GNP along the flow direction, the results also showed a higher percolation threshold for the composites made by injection moulding in comparison to compression moulding (which generates a more planar-random orientation) [44]. Similar work was carried
out by Arjmand et al. [45] who compared the electrical properties of injection and compression moulded PS/MWCNT nanocomposites and reported similar conclusions to [44]. This is due to lower chances of contacts between MWCNT because of their alignment (see Figure 2.12a) in comparison to a more random distribution (see Figure 2.12b).

Figure 2.12 Shows the TEM images at 5 wt. % MWCNT into PS/MWCNT nanocomposites; (a) injection moulded and (b) compression moulded. The arrow shows the flow direction [45].

2.5 Percolation Theory

Percolation theory is of great importance in understanding how a non-conductive polymer matrix becomes conductive by using conductive fillers. It has been reported [46] that electrical conductivity depends on the volume fraction of conductive filler as the concept of the percolation theory was derived on the basis of the volume fraction of the fillers. However; weight fraction is also used to determine the percolation threshold value [47, 48]. There are three distinct regions in a typical electrical conductivity versus filler wt. % curve as shown in Figure 2.13. At low filler loading (region A), the conductivity of the polymer composite is still close to that of the pure matrix used, typically electrically insulating. As the loading of the conductive filler increases, the conductive particles are more likely to come
into contact with each other, hence forming a network which allows the movement of electrons. However; the tunnelling mechanism by which the electrical conductivity of composites can increase when the filler particles are close enough to each other (approximately 10 nm) [49], but not necessary in direct contact, should not be excluded here. At some critical loading the electrical conductivity increases by several orders of magnitude with very little increase in the filler content (Figure 2.13, region B).

![Figure 2.13 A typical electrical conductivity curve of a composite showing three states; A, B, and C. These correspond to insulating, conductive at critical loading and conductivity of the filler network, respectively, (redrawn from ref. [24]).](image)

In this region, the amount of filler is sufficient to begin the formation of a continuous conductive network throughout the polymer matrix and composites exhibits insulator-conductor transition. This critical loading is defined as the percolation threshold value ($\Phi_c$).
After region B, the electrical conductivity levels off and only moderate increases in conductivity are observed with further addition of the conductive filler (Figure 2.13, region C).

Percolation theory has been adopted to work out the critical level of filler, i.e. the level where a large increase in the conductive of the composites occurs. The following equation 2.1 is usually used to describe the relationship between electrical conductivity and filler contents and to determine the value of the percolation threshold [4, 50, 51].

\[
\sigma = \sigma_0 (\Phi - \Phi_c)^t \quad \text{for } \Phi > \Phi_c \quad \text{--------- (2.1)}
\]

Here \(\sigma\) is the specific conductivity (S/m), \(\sigma_0\) the proportionality constant (S/m), \(\Phi\) is filler content (vol. %), and \(\Phi_c\) is the critical filler content or percolation threshold (vol. %). The \(t\) superscript, the power constant, is related to the dimensionality of the conductive network of composite. It is predicted [51] that \(t = 1.33\) for a two dimensional conductive network whereas a value of 2.2 is indicative of the formation of a three dimensional conductive network within the composite material. However, the experimental values of \(t\) usually differ from the predicted values [4].

A recent comprehensive comparative analysis was carried out by Delphine et al [52] who compared the properties of nanocomposites made by CNT addition into different matrices (including PET) to compare the percolation thresholds (see Figure 2.14). It was concluded that the filler response varies and also that the percolation threshold is dependent on the matrix used and the method employed to prepare the composite material. Ideally, the conductivity at steady state (C in Figure 2.13) is similar to the filler conductivity. Typical conductivities of polymer matrices are between \(10^{-14}\) to \(10^{-17}\) S/cm, while carbon fillers ranges from \(10^2\) to \(10^5\) S/cm and metal fillers \(10^5\) S/cm [46].
2.6 Crystallization Behaviour

It is important for composites with semi-crystalline matrices polymers to investigate how fillers affect crystallization behaviour as many of properties of semi-crystalline polymers are strongly influenced by the overall crystalline content and morphology [54, 55]. In most processing methods for thermoplastic polymers (melt processing techniques) they are heated to high temperatures at which the viscosity becomes low enough for the material to be formed into a desirable shape. If the polymer is crystallisable, then crystallization in the melt spreads through the polymer during the cooling stage of processing.

Crystallization comprises of nucleation followed by crystallite growth. Nucleation is essential in determining the morphology of crystalline polymer. Generally, nucleation represents the initial step of crystallization which can be explained as the development of
region of short-range order in the polymer, which act as growth centres for crystallization. It is worth mentioning the phenomenon called cold crystallization, which has been observed experimentally after quenching the polymer from above its melting point to below its $T_g$ to form a randomly oriented glass as crystallization is inhibited below $T_g$. Upon reheating, as soon as lining up of chain segments becomes possible, crystalline structure are formed via self-assembly of adjacent chains in the amorphous state [53]. For example the crystallization of PET involves the formation of nuclei and followed by growth, either by heating amorphous PET from its glassy state (cold crystallization) or cooling from the molten state (melt crystallization). The lamellae develop from the nucleus by chain folding in the direction of growth as shown in Figure 2.15. There are numerous factors that influence the overall crystallization rate and degree of crystallinity; for instance, cooling rate and filler addition into polymer matrices [54, 55].

![Figure 2.15 Structural features of spherulites (redrawn from ref. [56]).](image)

It is well-known that semi-crystalline polymers, such as PET, have crystalline and amorphous phases. However; three phases have been reported for several semi-crystalline polymers, including PET [57-59]. The third phase lies between the crystalline and amorphous phases and is the called rigid amorphous fraction (RAF) or the complex constrained region. The
RAF increases with increasing degree of crystallinity while the amount of mobile amorphous region reduces. RAF strongly influences the physical properties of the polymer nanocomposites such as $T_g$ and $X_c$. These effects can be usually ignored in the case of composites containing micron sized fillers but can be significant polymers composites containing nanoscale fillers, this is because the interfacial interaction controls the dispersion state and significantly affects the bulk properties of polymer nanocomposites [59].

### 2.7 Polymer/Carbon Microcomposites

The use of conductive fillers i.e. various members of the carbon family, prompted a vast amount of research to make conductive polymer composites owing to their wide range of potential applications. A large number of carbon based fillers are used for making conductive polymer composites (CPCs) such as carbon black (CB), graphite, GNP, CNT and graphene.

CB is carbon micron-scale filler and is available in abundant quantity at low price and is used extensively for a large number of applications including pigments, fillers, additives, etc. It is an amorphous form of carbon, produced by partial combustion and thermal degradation of hydrolis (e.g. crude oil, coal tar, natural gas etc.) at high temperatures [60]. Specialised grades are used extensively for making low cost conductive polymer composites [61]. These microcomposites are produced by several well establish manufacturing methods e.g. melt compounding (predominantly), solution blending and in situ polymerization. The type of process, matrices, and fillers influence the properties of polymer composites. In addition to good distribution, strong interaction between carbon black and the matrix is of key importance in determining the properties of the resultant microcomposites. For example CB agglomerates could form (Figure 2.16).
For example, a study using a PP matrix showed significant interaction of the PP with CB and leading to a significant increase in viscosity as CB content was increased, which in turn had a significant influence on morphology and crystallinity [63]. At higher CB concentration, a lower the degree of crystallinity of the PP composites was observed, that influenced mechanical properties including tensile strength and elongation at break. The electrical percolation threshold was found in the region of 5 to 10 % by volume (vol. %) of CB.

Graphite is another micron-scale carbon filler which is commonly used in the fabrication of polymer composites. Polyurethane (PU), silicone rubber and epoxy matrices filled with graphite for electrodes applications were prepared by Calixto et al, [64] as an alternative to mercury (Hg), because the Hg electrodes are not environmental friendly due to toxicity. The study concluded that all composites examined were electrically conductive, but that at least 50 wt. % of graphite was needed to achieve sufficient conductivity for electrical applications. Krupa et al [65] found that the level of electrical conductivity achievable was found to depend on the particle size of the graphite and the type of polymer matrix used. The latter, PS and high density polyethylene (HDPE) as matrices were investigated with two different grades of graphite filler of differing particle size. It was concluded that the percolation
concentration for PS/graphite microcomposites was independent of the particle size, whilst in HDPE/graphite microcomposites a particle size dependency was found. Moreover, the percolation concentration was lower in the HDPE/graphite microcomposites than in the PS/graphite composites. In a similar study carried out by Sun et al, [66] HDPE/graphite microcomposites were prepared using four graphite grades of different particle sizes. The study revealed that the change in the physical properties of the polymer/graphite composites was closely related to the particle diameter of the graphite used. Moreover, it has been reported [12] that reduced filler particle size can affect the volume fraction of interfacial region in polymer/graphite systems and improve the mechanical, thermal and electrical of the polymer matrix.

Graphite/HDPE composites prepared by Wang et al, [67] indicated that incorporation of graphite into a HDPE matrix enhanced the Young’s modulus but reduced elongation at break, whereas yield strength was found to improve at graphite loadings up to 55 % wt. % and thereafter decreases. The crystallization temperature and thermal stability also showed an improvement as graphite content was increased. Pre-treatment of graphite with coupling agents such as silanes was suggested to give a good dispersion in the HDPE matrix.

Wakabayashi et al, [68] fabricated PP/graphite microcomposites using a solid-state shear pulverization method. This method was found to result in a good dispersion of the graphite into the PP matrix. The authors found that incorporation of only 2.7 wt. % graphite increased the Young’s modulus and tensile strength by 100 % and 60 %, respectively, with only a ~30% reduction in elongation at break (from 810 % to 560 %). This was attributed to graphite exfoliation during the preparation of PP/graphite composites.

Akinic et al, [69] studied the mechanical and structural properties of polypropylene (PP)/graphite composites. In this study it was noted that the elastic modulus increased with increasing the content of graphite in the PP while elongation at break and tensile strength
values reduced. According to Krupa et al, [70] a decrease of elongation at break with the increase in the amount filler is a usual occurrence. The same authors [70] studied the electrical and thermal properties of low density polyethylene (LDPE) and HDPE filled with graphite filler. The results showed a reduction in elongation at break. On the other hand, electrical conductivity increased for both HDPE and LDPE with increasing graphite loading. The percolation threshold was reported at 11 vol. % of graphite for both composites as shown in Figure 2.17. The incorporation of graphite showed no effect on the crystallinity of both polyethylene, whereas graphite was reported to act as a nucleating agent for PP [71] and PVDF [72] matrices and also to increase their crystalline content. Moreover, Yasmin et al, [73] suggested that 2.5 wt. % of graphite platelets exhibited the best balance of storage modulus, strength, and thermal stability for an graphite/epoxy composite. This was attributed to uniform dispersion of the graphite.

![Figure 2.17 Electrical conductivities of graphite reinforced HDPE and LDPE composites [70].](image-url)
2.8 Polymer/Carbon Nanocomposites

2.8.1 Polymer/GNP

In the last three decades, a vast variety of conductive polymer nanocomposites (CPNCs) were produced by using nanoscale fillers (nanofillers) [74]. Because of the uniqueness of nanofillers, associated with high interfacial area when properly dispersed it is argued that could bring tremendous improvements when combined with polymer matrices to form CPNCs. It is worth mentioning that the surface area and aspect ratio of nanoscale fillers are key to achieving their exciting electrical, thermal and mechanical properties at low addition levels compared to micron-scale fillers such as CB and graphite, for which much higher addition levels are required, that could be detrimental to the mechanical integrity of the composites. However, efficient processing strategies are required to disperse the nanofillers into polymer matrices as effective integration of these fillers in matrices is essential for transferring their superior properties to the polymers. Several factors are reported to affect the properties of CPNCs such as: matrix type, filler properties, filler size, structure and addition levels and processing techniques. Of such nanofillers, graphite nanoplatelets (GNP) have attracted significant attention as nanofillers for preparation of CPNCs due to their excellent electrical, thermal and mechanical properties [7, 75].

Different methods have been used for the preparation of CPNCs in order to enhance dispersion of the filler, optimum interaction between filler and matrix, to improve the properties of final products and achieve lower particle percolation thresholds in the polymer nanocomposites prepared. A large number of studies have been targeted of understanding the improvement of filler-matrix interaction that is responsible for the resultant properties of the composites [76, 77].

Achievement of uniform dispersion of GNP is still a difficult task, whereas dispersion of graphene oxide (GO) nanosheets in polymer matrix is relatively easy to achieve. This is
because of oxygen containing functional groups on the surface of GO work as compatibilizing agents [78]. Kalaitzidou et al [79] investigated the nucleating effects of GNP in a PP matrix. Composites were prepared by melt mixing followed by injection moulding. The results demonstrated that even at 0.01 vol. % the GNP served as nucleating agents for PP. However, no increase in the degree of crystallinity was found. Also, the authors investigated the effect of cooling rates on crystallinity and percolation thresholds of composites. It was found that a fast cooling rate increases the percolation threshold. The author argued that during fast cooling smaller and thinner polymer crystal structures were formed thus increasing the volume of the amorphous phase in which the platelets reside. A great number of smaller crystals therefore disturb the formation of a conductive network which increases the percolation threshold. Kuvardina et al [80] found that larger diameter GNP resulted in a higher percolation threshold value in PP/GNP nanocomposites. PP/GNP nanocomposites prepared by Ferriera et al, [81] showed an increase in the storage modulus although no significant interaction between filler and matrix was noted.

Kim et al, [82] reinforced linear low density polyethylene (LLDPE) with GNP using solution mixing and melt mixing with different twin-screw extruders (co-rotating and counter-rotating screws). The study revealed that counter-rotating screws system gave better GNP dispersion and electrical and mechanical properties than the co-rotating screw system. The percolation threshold was found to range between 12 – 15 wt. % GNP when composites were prepared with either type of extruder. A similar study by Liu et al, [83] reported the effect of processing on the properties of polyamide/GNP nanocomposites, and similar observations were made by these authors.

Chen et al, [84] aimed to achieve good dispersion of expanded graphite (EG) in a PS matrix by in situ polymerization. The monomer/EG mixture was sonicated in order to facilitate of the styrene into the EG, the system was intercalation then polymerized in situ. These
composites had a lower percolation threshold with much higher conductivities relative to equivalent graphite based composites. Ramanathan et al. [12] reported that EG has pores which are capable of adsorbing polymer molecules and therefore facilitate filler-matrix interaction. The authors prepared PMMA composites with different fillers, namely: as-received graphite, expanded graphite (EG) and GNP. The GNP was found to have the highest aspect ratio, higher surface area as well as good dispersion in the polymer matrix. This resulted in there being a large interfacial area in the PMMA/GNP nanocomposites. This was in contrast to the results of the PMMA/graphite microcomposites and PMMA/EG nanocomposites that both exhibited reduced interfacial area. This was thought to be due to the larger particle thickness in both the graphite and when EG compared with GNP.

Similarly, a study on a poly (phenylene sulfide) (PPS) nanocomposites based on EG and ultrasonicated EG prepared by melt blending [85]. Indicated that PPS/ultrasonicated EG nanocomposites showed higher mechanical strength, electrical conductivity, percolation threshold, crystallinity and thermal stability than non-sonicated PPS/EG nanocomposites. It was suggested that this was due to the small particle sizes of EG attained by ultrasonication process. Zheng et al. [86] prepared PMMA composites with EG, graphite and CB using the solution method. The authors reported that electrical percolation thresholds values were 0.6 vol. %, 2 vol. % and 4.5 vol. % for PMMA/EG, PMMA/graphite and PMMA/CB composites, respectively. Similar behaviour was reported by Goyal et al. [87] for the electrical properties of PPS composites containing EG and natural graphite flakes as conductive fillers. Only 1 wt. % of EG was found impart electrical conductivity, while 5 wt. % of natural graphite flakes was required to reach the percolation threshold. Moreover, SEM showed a conductive network of EG in the PPS/EG nanocomposites which constitute a pathway to the flow of the current through the nanocomposites. Miloaga et al. [88] prepared polymer/GNP nanocomposites using poly(3-hydroxybutyrate) (PHB). The study was aimed
at determining the nucleating effects of GNP. The authors demonstrated that GNP effectively nucleated the crystallization of PHB. Li et al, [89] prepared and characterized poly(trimethylene terephthalate) (PTT) based composites using GNP. The results showed good dispersion even at 7 wt. % GNP, resulting in improved thermal stability, electrical and mechanical properties. The percolation threshold was found between 3 – 5 wt. % filler. A similar study by the same authors studied poly(butylene terephthalate) (PBT)/GNP nanocomposites, [90], and they reported improved dynamic storage modulus, thermal stability and electrical conductivity at the same percolation threshold as in their previous study. They attributed such improvement to uniform distribution and good interfacial adhesion between the filler and the matrix.

2.8.2 Polymer/As-received CNT

CNT possess an excellent combination of thermal, electrical and mechanical properties which make them one of the most promising fillers to produce nanocomposites having excellent properties with low percolation thresholds for wide applications. The improvement of these properties is governed by many parameters including dispersion of the filler, interfacial interaction between the filler and the polymer, filler concentration as well as the type of polymer used [24, 74]. During the last two decades, there has been an intense focus on the development of polymer/CNT nanocomposites, due to the fact that CNT have superior properties over other carbon forms such as carbon fibres and graphite. Polymer/CNT nanocomposites can be prepared by solution processing, in situ polymerisation or melt processing [91]. The latter method is recommended especially for making thermoplastic matrices based nanocomposites [24].

Despite the Prolific published work in this field, Min et.al, [92] argues that there are relatively few published studies on developing nanocomposites having good electrical
properties. For example, preparing a composite have the same filler and matrix may produce composites with different electrical conductivities or percolation thresholds because of the variable variation in CNT structure/morphology i.e. different sizes, aspect ratios etc. Recently, graphene has emerged as an excellent material for the enhancement of electrical and mechanical properties of composites; but production complexities, costs and scalability of production are issues of concern. Therefore, CNT are the candidate materials for making polymer nanocomposites due to their similar properties and structure to graphene. Despite this similarity, they are different in terms of matrix-filler interactions and dispersion [1]. Many problems are hindering CNT applications, such as inefficient preparation techniques. In addition, there are two more basic overriding problems that need to be addressed e.g. interfacial interactions between the CNT and polymer matrices and achieving homogenous dispersion of fillers into matrices.

Poor dispersion of CNT within a polymer matrix is caused by the significant agglomeration, which is aided by the intrinsic van der Waals attractive forces between the tubes, coupled with their high surface area and high aspect ratio. Realization of the expected advantage of these CNT requires resolution of these problems. It well established that efficient dispersion of the CNT in the polymer matrix is mandatory for acquiring the beneficial properties of CNT in a polymer matrix, in addition to a large aspect ratio of the filler and interfacial load transfer from the polymer to the CNT [91]. Dispersion and distribution of fillers into polymer matrices [93] are known to influence the resultant properties of the composite. One of the common issues with CNT is entangling. One approach that has been proposed to overcome entangling of CNT, and achieve good dispersion into LLDPE matrix, is by multiple post extrusion (5 x). By doing so, very good dispersion and reduced entanglement were achieved that enhanced the electrical properties. But this approach seems to be not an economical option and could pose a great risk for the degradation and recyclability of
thermoplastics polymer [94]. Another strategy for addressing the problems of entanglement and dispersion of CNT is the modification of their surfaces. Thus covalent or non-covalent functionalization might be solutions to the challenging problems of interfacial interactions and dispersion in polymers. The non-covalent method is preferred, as it enhances the processability and dispensability of CNT without changing the properties of carbon nanotubes. However, a wide variety of functional groups for the intended application can be attached by using the covalent method.

The first use of CNT as fillers for enhancement of the mechanical and electrical properties of an epoxy matrix was reported in 1994 by Ajayan et al, [91, 95], however no mechanical properties measurements were reported in their study. The first mechanical study was reported by Schadler et al [91] in 1998. The authors studied tensile properties of epoxy/MWCNT nanocomposites. The tensile modulus increased by ~ 24%, but tensile strength did not change. Moreover, In 1990s, the Toyota Central Research Laboratories conducted a study on polyamide 6 (PA6)/MWCNT nanocomposites and they reported that a very small amount of CNT resulted in a significant improvement in both mechanical and thermal properties [74].

Vega et al, [96] prepared HDPE/MWCNT nanocomposites by melt mixing the matrix with an in situ polymerized nanocomposites, and achieved a 100% increase in the elastic modulus of HDPE with only a small amount of MWCNT (0.52 wt. %) without affecting the matrix ductility. Moreover, it suggested that MWCNT act as a strong nucleating agent. A similar study conducted by Qian et al [97] achieved a homogenous us distribution of MWCNT into PS, reporting that the Young’s modulus increased by 36 – 42% and that tensile strength increased by 25% at 1 wt. % of MWCNT.

Yeh et al, [98] reported that the Young’s modulus and tensile strength of MWCNT reinforced epoxy nanocomposites increased by 51.8 % and 17.5 % at 5 and 3 wt. % of MWCNT,
respectively, due to effective interaction between the MWCNT and the epoxy matrix. However, a reduction in tensile strength and small increase in modulus were seen beyond CNT level of 3 wt. %. This behaviour was attributed to the random orientation and poor dispersion of CNT at loadings above 3 wt. % loading. In a similar study, a 20 % improvement in Young’s modulus at only 0.1 wt. % MWCNT was observed for epoxy/MWCNT nanocomposites by Xu et al, [99].

McNally et al, [100] fabricated PE/MWCNT nanocomposites using melt compounding methods. A reduction in tensile strength and elongation at break was observed at initial loading used in this study (0.1 wt. % MWCNT) due to agglomeration of the CNT. In comparison, the composites showed lower ductility compared to the unfilled PE matrix. Electrical conductivity of the composites reached 16 times higher than that of the pure matrix and the percolation threshold was 7.5 wt. % of MWCNT.

Lisunova et al, [101] studied ultra-high molecular weight polyethylene (UHMWPE)/MWCNT nanocomposites and reported their percolation behaviour. The authors concluded that the percolation threshold occurred at low values ~ 0.0004 – 0.0007 vol. % due to the high aspect ratio and poor distribution of MWCNT into the matrix. Sandler et al, [48] also achieved a very low percolation threshold (0.0025 wt. %) for epoxy nanocomposites by using aligned-CVD grown MWCNT. The same authors studied electrical conductivity of an epoxy/MWCNT nanocomposites system [102]; they concluded that CNT improved the conductivity of the epoxy and $10^{-2}$ S/m was reported at 0.1 vol. % of MWCNT with a percolation threshold value of 0.04 wt. %.

Wang et al, [103] prepared thermotropic liquid crystalline polymer (TLCP)/MWCNT nanocomposites by in situ polymerization. The authors observed that lower concentrations of filler led to strong interfacial interactions (using Raman spectroscopy and polarization microscope) between the CNT and the polymer matrix and better dispersion than obtainable
at higher concentration of MWCNT. Thermal stability was found to increase because MWCNT acted as a stabilizer for the polymer nanocomposites at high temperatures. Aalaie et al [104] prepared LLDPE/ MWCNT composites by melt compounding. The authors investigated the morphological, rheological, electrical and mechanical properties of the LLDPE/MWCNT nanocomposites. They demonstrated using SEM that there were agglomerates of MWCNT and individual CNT in the LLDPE. Electrical percolation was found to occur at 5 wt. % loadings of MWCNT. Examination of the mechanical properties showed the Young’s modulus increased slightly at expense of ductility. In addition, the degree of crystallinity of LLDPE was observed to increase in this study 22.1 % for neat polymer matrix to 30.3 % for a 5 wt. % MWCNT nanocomposites.

A study by Wang et al, [105] investigated the thermal stability, rheology and crystallization behaviour of MWCNT-reinforced poly(butylene succinate) (PBS) nanocomposites prepared by melt compounding. The results demonstrated good dispersion of MWCNT into PBS and storage and loss moduli were also seen to improve. In addition, the crystallization temperature and thermal stability of nanocomposites was higher than that of pure PBS by 10 °C and 5 °C at 3 wt. % of MWCNT respectively.

Logakis and co-workers, [106] produced PA6/MWCNT nanocomposites using melt mixing. The results indicated that the MWCNT facilitated the formation of the crystalline phase of the PA6 matrix. Such structural changes caused an increase in the storage modulus of the composites. A similar study by the same authors revealed similar results using isotactic polypropylene (iPP) [107], i.e. enhancement of storage modulus, a significant change in the crystallization behaviour and degree of crystallinity. The percolation threshold for these nanocomposites was reported at 0.6 – 0.7 vol. % of MWCNT.

A review carried out by Bauhofer et al, [51] considered 147 studies; the type of polymer matrix and dispersion state were proposed to have more influence on the properties than the
type of CNT or the route by which the CNT are prepared. Moreover, a review on the thermal conductivity of CNT and polymer/CNT composites was published by Han Z. et al,[108]. It was argued that, thermal conductivity of CNT depends on their morphology, chirality, level of defect, size and amount of impurities etc.

2.8.3 Polymer/Modified CNT

The surface of a MWCNT does not contain functional groups, which limits their interfacial interactions with polymers. Once again, effective CNT integration into a polymer matrix is mandatory for transferring their unique properties to composites. Functionalization of the CNT’ surfaces would allow them to interact more easily with a matrix via polar-polar, hydrogen bonding, and covalent bonding. However, using covalent functionalization to disrupt CNT agglomeration, can lead to changes in CNT morphology and changes in some unique characteristic [109, 110]. Bose et al, [110] reviewed various treatment methods for CNT and their influence on the properties of polymer nanocomposites thereby emphasising the importance of treatments on resultant properties of composites.

Several review papers have been published in which the different methods of functionalization are discussed in detail [24, 91, 109]. However, it must be emphasized that there is no fixed procedure to be followed that is suitable for achieving efficient dispersion for all the various polymers used to produce CNT-based nanocomposites. Many parameters including polymer type used and its state (i.e. solid or liquid), CNT type and their loading, composite processing methods, collectively affect the properties of the composites produced. There is no doubt that achieving good dispersion of CNT into a polymer matrix is a big challenge.

The study of Kim J et al, [111] investigated the influence of acid-treated MWCTNs on the physical properties of TLCP polymer nanocomposites prepared using melt compounding.
The results demonstrated that even a small amount of CNT (0.5 wt. %) resulted in improvements in the mechanical and thermal properties due to good dispersion and interfacial adhesion between the filler and the matrix. In addition, the interfacial adhesion between TLCP and MWCTNs was more effective at low CNT content than at higher content. Gupta et al, [112] examined the thermal and mechanical properties of PTT reinforced by acid-treated MWCNT. The results showed an improvement in mechanical properties but thermal properties remain unaffected. Similar study has been conducted by Kanagaraj et al [113] who fabricated HDPE nanocomposites containing acid treated MWCNT. The composites showed improved load transfer and good interfacial adhesion between the filler and matrix after acid treatment. The authors reported significant improvements in mechanical properties of the composites. The Young’s modulus increased from 1.1 GPa for pure HDPE to 1.3 GPa for HDPE/MWCNT composites when the concentration of MWCNT was 0.44 wt. % and elongation at break increased by 24% at this loading. As the MWCNT content increased, the Young’s modulus of HDPE/MWCNT composites increased and was found to have doubled at 2 wt. % MWCNT.

Amr et al, [114] investigated the effect of acid-treatment of MWCNT on the mechanical, rheological and thermal properties of PS nanocomposites. The authors observed no appreciable influence of acid treatment on the \( T_g \) of the composites. However, tensile modulus improved by 22 % at 0.5 wt. % of MWCNT, but elongation at break and tensile strength were reduced. This reduction indicates that the high stiffness of the resultant nanocomposites caused by addition of the filler. Moreover, the viscosity remained unaffected by the addition of treated CNT.

In the study by Liu et al, [115] Young’s modulus was found to increase by 78 % on incorporation of only 0.8 wt. % of functionalized SWCNT within PVOH. Noncovalent surface modifications of CNT using end-functionalized polymers was studied by Sun Lee and
et al, [116]. The study demonstrated that good dispersion and interfacial bonding between the polymer and CNT is possible by using non-covalent treatment method of filler to prepare PS/MWCNT nanocomposites. The electrical and mechanical properties of PS/MWCNT nanocomposites were markedly increased compared to the unfilled PS matrix. In similar study [117], MWCNT were modified using surfactants and then incorporated into PP to examine the effect of surface modification of CNT on matrix properties. The results showed that surface treatment of MWCNT improved interfacial adhesion. This was attributed to the reduction in interfacial energy between matrix and filler.

In a comparative study conducted by He et al, [118] it was concluded that functionalized MWCNT improved dispersion and resulted in improvement of the mechanical properties of the nanocomposites. Also, they found that increasing the sonication process time (> 2 hour) resulted in a reduction in composites mechanical properties. In another comparative study carried out by same authors, covalent and noncovalent methods of binding MWCNT to an epoxy matrix by using polyethylenimine (PEI) which acted as both covalently and noncovalently. both methods were found to improve the dispersion of MWCNT into the epoxy matrix [119]. Epoxy composites containing covalently modified MWCNT exhibited greater storage modulus and reduced electrical conductivity compared with MWCNT modified using monovalent methods. In the latter were composites had similar conductivity when as received nanotubes were used. Chemical treatment of the MWCNT surface proved to be essential for providing good interfacial interaction and dispersion, both of which are needed for achieving better composites mechanical properties of the polymer. Table 2.1 shows the possible merits and demerits of the both of functionalization treatments (adopted from ref. [24]).
Table 2.2 functionalization methods; their advantages and disadvantages.

<table>
<thead>
<tr>
<th>Method</th>
<th>Principle</th>
<th>Possible CNT damages</th>
<th>Easy to use</th>
<th>Polymer matrix interaction</th>
<th>CNT Re-agglomeration in matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>Side walls</td>
<td>✓</td>
<td>x</td>
<td>Strong</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>SP² to SP³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hybridization of C atoms</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Defect</td>
<td>✓</td>
<td>✓</td>
<td>Strong</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Defect transformation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noncovalent</td>
<td>Polymer wrapping Van der waals</td>
<td>x</td>
<td>✓</td>
<td>Variable</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>π-π stacking</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surfactant</td>
<td>Physical wrapping</td>
<td>x</td>
<td>✓</td>
<td>Weak</td>
<td>x</td>
</tr>
</tbody>
</table>

From these studies, it has been established that both physical and chemical functionalization of CNT is thought to bring about significant improvements in properties of the nanocomposites. Although much has been said about the effect on properties and morphology of the filler, it must be emphasised that nature of the matrix is also very important as properties of the resultant composites for identical fillers vary from matrix to matrix.

### 2.9 PET/Carbon Composites

In this section, selected published studies on conductive composites based on a PET matrix with graphite, GNP and CNT as filler materials will be discussed.

#### 2.9.1 PET/Carbon Microcomposites

In order to develop better understanding for the electrical percolation response, a study by Zhang et al, [120] presented comparative analysis of different fillers. In this study, graphene nanosheets were made by oxidation of graphite, followed by exfoliation and reduction
sequences. Melt compounding was utilized for preparing PET/graphene nanocomposites. The results demonstrated uniform dispersion of graphene nanosheets in PET polymer. The addition of graphene to PET was found to significantly enhance the electrical conductivity, a rapid transition at the percolation threshold of 0.47 vol. % of graphene from insulator to semiconductor was observed. The authors attributed such a change to a uniform distribution of filler in the matrix, its high aspect ratio and large specific surface area. Figure 2.18 shows the comparative electrical conductivity of graphene and graphite, where the difference is clearly observed.

![Graph showing electrical conductivity](image)

**Figure 2.18** Comparative filler contents of both graphene and graphite incorporated in a PET matrix. The insert graph is $\log(\sigma)$ versus $\log (\Phi-\Phi_c)$ [120].

Another comparative study on PET, using CB, graphite and CNT, was conducted by Xin et al, [121]. The study focussed on conductivity and crystallinity of PET. Carbon fillers were incorporated individually and in combination whilst keeping the same matrix. The results showed that all these carbon fillers produced electrically conductive composites. CNT were the most effective fillers for imparting high electrical conductivity. Several factors were
found to affect the conductivities including; type of fillers and level, dispersion state, melt annealing and combination of two fillers type together.

An increase of seventeen orders of magnitude in the electrical conductivity compared to pure PET was observed (Figure 2.19a). Melt annealing was found to significantly enhance electrical conductivity of PET/carbon composites (see Figure 2.19b), which was attributed to filler movements in the molten matrix, resulting in agglomeration and the formation of a conductive network. Moreover, these fillers were found to behave as nucleating agents, although a reduction in crystallinity of the composite was witnessed when filler contents were increased (see Figure 2.19c) [121].

Figure 2.19 Electrical conductivities before (a), and (b) after annealing treatments and % crystallinity (c) using different carbon fillers [121]
2.9.2 PET/GNP Nanocomposites

Over the past three decades a great amount of research work was carried out on conductive composites and the subject is still being extensively researched because of important applications in the material for electromagnetic shielding, antistatic materials, conductive film and coating sectors [122-124]. Also conductive polymers are used for making conductive electrodes for numerous applications discussed in the previous section.

A study by Paszkiewicz et al, [125] on the electrical conductivity of PET/EG nanocomposites prepared by iSP, demonstrated that nanocomposites exhibited good dispersion of GNP in the matrix. The sharp transition from insulator to conductor or semiconductor system was found at levels as low as 0.05 wt. % EG in PET. Addition of 0.4 wt. % of EG resulted in an electrical conductivity of $10^{-3}$ S/cm. Such low a percolation threshold and high conductivity compared to pure PET, were related to the large surface area, high aspect ratio, and uniform dispersion of the EG. Zhang et al, [126] prepared PET/EG conductive nanocomposites using melt blending. A homogenous dispersion of EG in the PET matrix was noted in this study after some shearing has been used to improve interaction between PET and EG.

Recent work by Li et al, [127] who fabricated PET based nanocomposites with different concentrations of EG using melt mixing, reported well dispersed EG within the PET matrix, leading to improvements in the mechanical, electrical and thermal properties of PET/EG nanocomposites compared with the pure PET. The electrical percolation threshold was found to be ~ 5 wt. %.

The thermal behaviour of PET/EG nanocomposites has been investigated by Sandra et al, [128] using iSP method at filler loading ranging from 0.025 – 0.4 wt. %. The authors observed improved thermal stability but degree of PET crystallinity remained unaffected.
Ahmad et al, [129] added GNP into PET by melt mixing to enhance its oxygen barrier properties. The authors observed a uniform distribution and dispersion of GNP into PET. The results indicated an increase in crystallinity, thermal stability and Young’s modulus of the resultant composite compared to pure PET matrix. However, tensile strength and elongation at break showed reductions of 56 % and 40 %, respectively.

2.9.3 PET/CNT Nanocomposites

The following literature will explore both as-received (or untreated) MWCNT and chemically treated (or functionalized) MWCNT.

2.9.3.1 PET/ As received MWCNT

This section deals with recent relevant published papers on MWCNT incorporated into a PET matrix for making nanocomposites with enhanced thermal, mechanical and electrical properties.

Tzavalas et al, [130] prepared PET/MWCNT nanocomposites by melt mixing and investigated the crystallization behaviour. The results showed significant increasing in crystallinity at low loadings of MWCNT (less than 0.5 wt. %) but at 1 wt. %, the nanocomposites suffered a sharp decline in crystallinity. This coincided with the formation of MWCNT agglomerates leading to a substantial reduction in the interfacial interactions between filler and the matrix. Further addition of MWCNT caused a gradual restoration of crystallinity due to higher filler concentration.

Kim et al, [131] reported similar properties for PET/MWCNT nanocomposites prepared by melt mixing. The study concluded that the addition of MWCNT in the PET matrix improved the mechanical properties and enhanced the crystallization of PET/MWCNT nanocomposites.
with addition of small amount of CNT (< 0.5 wt. %), further incorporation of CNT did not affect these properties.

A study of PET/MWCNT along with PET containing other fillers was reported by Hu and co-workers [132]. Interestingly, the comparison between MWCNT and other traditional nucleating agents (sodium benzoate, carbon fibre and glass fibre) was explored. It was confirmed that MWCNT are suitable nucleating agents for crystallization in PET particularly when dispersed homogenously. Dispersion is a key to the mechanical, and many other properties, of polymer nanocomposites.

Shiua et al, [133] incorporated 0.25 – 1.5 wt. % MWCNT into PET to examine the effects on electrical and thermal properties. The powders of both PET and MWCNT were thoroughly premixed followed by hot pressing to make the film composite samples. Good homogeneity and the formation of conductive network were observed in the resultant composite films. The results indicated enhancement of electrical conductivity up to a loading of 0.75 wt. % of MWCNT thereafter only a slight increase was observed. Moreover, the influence of temperature on composite conductivity was investigated. It showed that it is not controlled by CNT alone but by polymer between neighbouring MWCNT. This means that MWCNT showed a kind of metallic behaviour as increasing temperature increases their resistance.

To achieve good dispersion, several approaches have been investigated in this regard. Incorporation of MWCNT into PET has been reported by Santoro et al, [134]. The PET and MWCNT powders were mixed firstly using cryogenic milling of as-received CNT with PET matrix and then both were used to prepare the composites by the MC method. The mechanical properties were greatly enhanced at large due to a good dispersion of MWCNT in the PET matrix. The tensile strength was increased by 25 % at 0.25 wt. % of MWCNT. Hu et al, [135] used a coagulation method to prepare PET/MWCNT nanocomposites, aiming at determining the electrical and rheological properties. The percolation threshold for
rheological and electrical properties was found at 0.6 wt. % and 0.9 wt. % respectively. They argued that a thicker conductive network is required for electrical conduction, so the percolation threshold is higher compared to that obtained for rheological properties.

Low electrical percolation thresholds in PET/MWCNT system were observed by Logakis et al, [136] using iSP and MC methods to fabricate the nanocomposites. The results demonstrated the highest percolation threshold (0.1 wt. % MWCNT) for the composites made by MC, while only 0.06 wt. % was required for the nanocomposites prepared by iSP. In another similar study by Hu et al, [135] who prepared PET/MWCNT nanocomposites using solution method and reported percolation threshold of 0.9 wt. % MWCNT for PET/MWCNT system. In addition, at 1 wt. % of CNT loading, the electrical conductivity was found to exceed the antistatic criterion.

2.9.3.2 PET/ Acid-treated MWCNT

Another important aspect is the interfacial compatibility between CNT and matrices, which is one of the concerns for achieving good dispersion and adhesion when making polymer nanocomposites. A poor dispersion results in a weak interfaces in the agglomerates act as stress concentrators, leading to premature failure of the composite. Such issues can be addressed to a great extent by pre-treatment of CNT (discussed previously) before incorporation into polymer matrices.

Wang et al, [137] fabricated PET/MWCNT nanocomposites by an iSP method using a mixture of H$_2$SO$_4$ and HNO$_3$ for treatment of the MWCNT. The work involved investigating the effect of low loading of acid treated MWCNT (0.01 – 0.2 wt. %) on the morphology, crystallization and mechanical properties of PET/MWCNT nanocomposites. The results revealed good dispersion and a 6.4 °C increase in crystallization temperature at 0.01 wt. % MWCNT were added to the polymer. Increasing the loading of MWCNT resulted in
agglomeration of CNT. The storage modulus of the composite was found to be lower in comparison to pure PET at 0.2 wt. % of MWCNT. A similar study was conducted by Zhu et al, [138] who achieved good dispersion in PET/MWCNT nanocomposites containing less than 0.4 wt. % of MWCNT, using an iSP method. Incorporation of MWCNT (0.2 and 0.4 wt. %) was found to accelerate the crystallization process, as well as improving the mechanical properties due to uniform dispersion, as observed by SEM. In contrast, agglomerates were observed at > 0.6 wt. % MWCNT. Young’s modulus and tensile strength were reported to increase by 25 % and 15 % respectively at 0.4 wt. % of MWCNT.

Two different acid treatments were used by May Pat et al, [139] to modify MWCNT; namely mixtures of conc. H$_2$SO$_4$ and HNO$_3$ compared to HNO$_3$ and H$_2$O$_2$. Higher amounts of oxygen-containing functional groups were observed in the case of the first mixture. However, tensile properties were found to be enhanced as a result of the second treatment compared to pure PET whilst in the case of first treatment, composite toughness reduced. A similar study by Yoo et al, [140] studied the effect of interaction between PET and MWCNT on the properties of nanocomposites prepared by MC. The MWCNT used were as-received, acid treated (HNO$_3$ and H$_2$SO$_4$) and also modified by benzyl isocyanate and phenyl isocyanate. The authors found that MWCNT modified with benzyl isocyanate and phenyl isocyanate had a better dispersion in the PET matrix than the others. However, an increase in the melt crystallization temperature by ~ 13 – 16 $^\circ$C was observed with all fillers, meaning that they act as nucleating agents. Gao et al, [141] prepared PET/MWCNT nanocomposites by MC using MWCNT treated by maleic anhydride after acid treatment. Results showed that the functionalization of MWCNT surface led to a good dispersion in the PET matrix and strong interfacial interaction between filler and matrix. The presence of MWCNT was found to accelerate the crystallization process in the nanocomposites.
Kim et al., [142] modified MWCNT using a mixture of HNO$_3$ and H$_2$SO$_4$ then prepared PET/MWCNT nanocomposites by MC. The effect of acid treatment of MWCNT on the physical properties and crystallization behaviour of PET/CNT nanocomposites were investigated. The authors concluded that incorporation of a small amount of MWCNT into PET significantly enhanced the interfacial adhesion between the nanotubes and the PET matrix and resulted in nucleation of PET crystallization. These result in improved mechanical properties and crystallization behaviour of the PET/MWCNT nanocomposites.

![Figure 2.20 Schematics of the interaction through hydrogen bonding between MWCNT and the PET matrix [142].](image)

This was attributed to the functionalization of MWCNT which improves interaction between the filler and matrix through hydrogen bonding and aids dispersion into the PET matrix, as shown in Figure 2.20. In addition, reduced entangling of CNT after acid treatment was observed. The enhancements in the mechanical properties of these nanocomposites resulted from the improved interfacial interaction between PET and modified CNT in addition to a good dispersion of modified CNT in the PET matrix.
Good dispersion and interaction between PET and HNO$_3$/H$_2$SO$_4$ treated MWCNT were also observed by Jin et al., [143] who prepared PET/MWCNT nanocomposites films by iSP. The study demonstrated that PET/MWCNT nanocomposites exhibited better dispersion and interfacial adhesion after such treatments, despite some damage of the MWCNT due to acid treatments. In another study by the same authors similar behaviour was reported [144] when studying the effect of functionalization of MWCNT on the properties of PET/MWCNT nanocomposites.

Yesil et al., [145] prepared PET/CNT nanocomposites and also studied the effect of MWCNT purification on the surface properties and morphology of the CNT, the mechanical and electrical properties of PET/MWCNT nanocomposites prepared by MC were assessed. The PET was compounded with as-received MWCNT and acid-treated MWCNT to study the effect of the acid treatment. The PET/acid treated MWCNT exhibited better mechanical properties compared to the as-received PET/MWCNT nanocomposites. The authors argued that the improved mechanical properties (tensile strength and modulus) were due to strong interaction between PET and the purified MWCNT. However, the electrical conductivity was to be found to be much higher for composites containing the as-received fillers. This behaviour was attributed to the acid treated MWCNT having a modified surface: the crystalline structure of the CNT was damaged by formation of oxygen containing functional group. The latter was assessed by X-ray diffraction analyses. However, the damage became more pronounced with increasing treatment time and acid ratio. Moreover, lower electrical conductivity values of PET nanocomposites containing acid-treated MWCNT compared to composites made using as-received MWCNT was reported elsewhere [136, 146].
2.10 Applications of Carbon Composites

The excellent range of properties offered by the carbon family of fillers, particularly GNP and CNT, has opened up new pathways for research and development to which enable the tailoring of the properties of polymer composites to a wide variety of high value applications. The most promising applications of nanocomposites are for electronic devices. This includes making conductive electrodes, antistatic materials, semi-conductors and damping materials.

A review of electrically conductive PP and PE composites by Gulrez et al, [33] summarized the comparative properties of carbon family fillers based conductive polymers, as in Figure 2.21(a) which summarizes the conductivities of PP/carbon composites reported in the literature. Whereas Figure 2.21(b) presents the range of electrical conductivities required for developing electronic devices [23].

![Figure 2.21 Conductivities of PP/carbon composites (a) [33] and the conductivities required to develop electronic devices (b) [24].](image-url)
2.11 Conclusions

The study of carbon based conductive polymer composites has opened up new era of research and development. In particular, it is envisioned in conductive polymer composite research to impart the excellent electrical properties of the fillers into polymer matrices. Meeting the desired goals, involves understanding and controlling a complex interplay between the matrix and the fillers. This is due to numerous factors affecting the resultant composites that include the type of polymer matrices, filler types and sizes, preparation methods, filler treatments, and processing parameters, filler-matrix adhesion etc. All these parameters are important for acquiring the desired properties and to understand the processing, structure and properties relationships of the polymer composites. The common concern in conductive polymer composite research is inefficient dispersion, poor orientation and entangling of the fillers, this particularly applies to CNT (SWCNT/MWCNT) in order to transfer their excellent properties to the matrix used. However, it is widely agreed upon that filler pre-treatments (via electrical, chemical, physical, alignment etc.) could be beneficial strategies for attainment of uniform dispersion, and efficient stress transfer to the matrix. However, treatment of CNT affects filler properties such as electrical and thermal conductivity. In spite of the excellent electrical, thermal and mechanical properties reported in composites studies over the last three decades, some gaps in knowledge in the field of polymer/carbon composites remain, for example a lack of comparative studies using exactly the same processing conditions and the same polymer matrix and carbon fillers.

Another important aspect that needs attention is the processing methods and conditions. For example it has been reported that in situ polymerisation/solution blending results in a high quality composite with improved mechanical properties but suffers from low scalability and the handling of solvents which poses environmental problems. In contrast, melt
compounding is an environmentally friendly method that yields composites with good electrical, mechanical and thermal properties, especially after functionalization of the fillers. Finally, the notable applications of conductive polymer composites includes; antistatic, electrodes, semiconductors, EMI shielding material and numerous other uses in electronic devices. In addition, the use of nanofillers reduces the weight of composites tremendously which could bring the breakthrough in the aerospace materials because of the need for lightweight materials.

2.12 References


[105] G. Wang, B. Guo, J. Xu, and R. Li, "Rheology, crystallization behaviors, and thermal stabilities of poly(butylene succinate)/pristine multiwalled carbon nanotube


Chapter 3 Experimental

The materials and experimental procedures used during this research are covered in this chapter.

3.1 Introduction

Section 3.2 gives brief descriptions of the raw materials which were used. PET was used as a matrix and three different conductive carbon fillers were used. These conductive carbon fillers are: graphite, which was used as microfiller; GNP and A-MWCNT were used as nanofillers. All materials used, and in particular the PET matrix, were dried prior to compounding and/or before performing any characterization. This was necessary to avoid hydrolytic degradation of PET during melt processing. Melt compounding was used to prepare the PET and its composites; followed by compression, injection moulding and quenching processes. These, together with other sample preparation methods, are described in Section 3.3. Key factors to utilise the advantages of MWCNT in composites are good dispersion and a homogeneous distribution in the PET matrix. Chemical functionalization of the surface of A-MWCNT using acid treatment may allow them to bond better with the PET matrix. Therefore, Section 3.4 summarizes the procedure followed for the acid treatment of the MWCNT. Section 3.5 includes a description of the equipment and characterization techniques used to analyse the raw materials; PET, fillers and PET/carbon composites.

3.2 Raw materials

3.2.1 PET (matrix)

PET grade LIGHTER™ C93 was supplied by Equipolymers. Table 3.1 shows the general physical properties of the PET provided by the supplier.
Table 3.1 General physical properties of PET.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Values</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Viscosity (IV)</td>
<td>0.80</td>
<td>dl/g</td>
</tr>
<tr>
<td>Glass Transition Temperature (T_g)</td>
<td>78</td>
<td>°C</td>
</tr>
<tr>
<td>Melting Point Temperature (T_m)</td>
<td>247</td>
<td>°C</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>0.88</td>
<td>g/cm³</td>
</tr>
</tbody>
</table>

3.2.2 Carbon Fillers

3.2.2.1 Graphite

As-received flakes of synthetic graphite was purchased from Sigma-Aldrich Company in the form of powder of particle size < 20 µm and density of 1.9 g/cm³.

3.2.2.2 GNP

The GNP (grade xGnPs-15) used in this study was purchased from XG Sciences (Lansing, MI, USA). Its average diameter and thickness are ~ 15 µm and 6 – 8 nm, respectively and is composed of short stacks of graphene sheets as per standard specifications by supplier.

3.2.2.3 MWCNT

As-received MWCNT (grade NC-7000) were purchased from Nanocyl. As per supplier specifications, MWCNT were manufactured via catalytic carbon vapour deposition (CVD) process with purity > 90 %, average length 1.5 µm and average diameter =10 nm.

3.3 Preparation of PET/Carbon Composites.

Melt compounding was used for the preparation of PET composites. The PET and carbon fillers were dried in a vacuum oven at 120 °C for 24 hour prior to melt compounding. The PET/carbon composites were mixed by melt compounding using a laboratory scale (7 cm³)
Thermo-Haake Minilab co-rotating twin-screw compounding as shown in Figure 3.1. The operational conditions include; 5 minute as mixing time at 270 °C at a screw speed of 45 rpm.

Figure 3.1 Thermo-Haake Minilab microcompounder. The magnified image shows the chamber and the screws[1].

The extruded samples were cooled by passing through an ice-water bath, chopped into pellets using pelletiser and then dried before any further processing by compression moulding or injection moulding. Extruded PET and the composites samples were compression moulded to obtain films of about 1 mm thick (frame mould). The compression moulding procedure involved preheating at 280 °C for 10 min, followed by compression for an additional 10 min at a pressure of 18 MPa at the same temperature followed by quenching in an ice-water bath and drying in the vacuum oven at 40 °C for 24 hour. The quenched films were stored for further characterization and analytical tests.

Extruded PET and the composites samples were also injection moulded using Haake Minijet II injection moulding machine (Thermo Electron Corp., Hamburg, Germany) under a pressure of 400 MPa. Before injection, the injection cylinder and the mould were preheated to 280 and 60 °C, respectively. The moulded samples obtained for tensile test were dumbbell shaped with length gage ~ 30 mm, thickness ~1.5 and width ~ 4.5 mm. Figure 3.2 shows the type of mini injection machine used in this study and Figure 3.3 shows the process flow chart for composite sample preparations as discussed earlier.
The degree of crystallinity of the PET matrix can be controlled by the cooling rate of the melt. Therefore, the effect of cooling rate on the crystallinity of PET was investigated. In addition, mixing time and screw speed were changed during compounding studies in order to study their influence on the electrical conductivity of PET/carbon composites. These two studies are discussed in more detail in results and discussion chapter.
Figure 3.3 Process flowcharts of PET/carbon composites for specimen preparations.
3.4 Modification of A-MWCNT

Poor dispersion of MWCNT throughout a polymer matrix as well as weak interfacial adhesion with the matrix can have an adverse effect on the mechanical and other properties of composites. Chemical modification of fillers has been suggested in several studies to be a route for purification and addition of functional groups, which result in improved dispersion and interfacial bonding with the polymer matrices [2-4]. For this reason, acid treatment was employed on A-MWCNT. The A-MWCNT were mixed into a concentrated H$_2$SO$_4$/HNO$_3$ mixture (3:1 respectively) and the mixture was refluxed at 120 °C for 30 minutes. Upon cooling, the mixture washed with distilled water until neutral pH was obtained and filtered through a polypropylene membrane-filter of 0.2 µm pore size in order to recover the T-MWCNT from the mixture.

In a typical acid modification procedure [5], 1 g of the nanotubes was added to 40 mL of the acid mixture in a round-bottomed flask and refluxed under the conditions mentioned earlier. Sulphuric and nitric acids were purchased from Sigma-Aldrich with concentrations of 98% and 70%, respectively. A schematic diagram of chemical functionalization of the A-MWCNT by oxidation with acids is shown in Figure 3.4.

Figure 3.4 Schematic representation of the acid treatment of A-MWCNT.
3.5 Characterization Techniques

3.5.1 Electrical Impedance

The electrical conductivities of the PET/carbon composites were measured at room temperature using a phase sensitive multimeter (NumetriQ PSM1735). The NumetriQ PSM1735 is a powerful tool for detecting the formation of a conductive network and measuring the electrical conductivity of samples of various resistances. Conductive composite samples would exhibit a low resistance response as a result of applying a current to the sample. Since pure PET is an insulator, any conductivity in its composites is due to the incorporation of the conductive carbon filler. Square plates ~ (10 mm x10 mm x1 mm) were cut from compression and injection moulded samples, polished and then coated with silver paint (Agar, UK-G3691) to minimise the contact resistance between the PET/carbon composite specimen and the copper wires. Silver epoxy adhesive (Agar, UK-G3349) was used to attach the copper wires to the specimen. The NumetriQ PSM1735 was connected to an impedance analysis interface (IAI) to provide a wide range of shunts (1 mΩ - 500 MΩ) that enabled the measurement of samples of various resistances. The alternating current (AC) resistances (R) of PET/carbon composites were measured in a frequency range of 1 - 1x10^6 Hz at an amplitude voltage of 1.0 V for all experiments. From impedance spectroscopy the real and imaginary parts of the complex impedance are obtained as a function of frequency. Values for the conductivities were determined from the real part of the complex impedance using the following (Equation [6, 7]) :

\[
\sigma = \frac{L}{RA} \quad (3.1)
\]

Where \(\sigma\) is the electrical conductivity (S/m), \(L\) is the distance between the electrodes (m), \(A\) is the cross sectional area of the sample (m^2) and \(R\) is the measured electrical resistance (Ω). The copper wires were clipped on each side of the silver paint to allow current to pass through the composite specimen as the frequency was varied. Each measurement was
conducted five times and the average value. Before an impedance measurement, the NumetriQ PSM1735 was turned on for at least thirty minutes to warm up, and then a resistor of known resistance value was tested to verify that the machine was working normally.

3.5.2 Morphology Characterization

3.5.2.1 Scanning Electron Microscopy (SEM)

SEM is one of the most commonly used techniques in studies of the morphology of polymer composites. An SEM instrument produces images by scanning the composite surface using a beam of electrons, which interact with the surface of the sample. Three different interactions may occur which can be summarized as follows [8]:

A) Some beam electrons are backscattered (BSE) as result of the electrostatic attraction between the negatively charged free electron and the positively charged nucleus within the samples.

B) Some beam electrons interact with electrons within the atoms in the specimen, knocking some free as secondary electrons (SE).

C) After secondary electrons have been removed from an inner shell, an electron from an outer shell falls into the inner shell with the emission of X-rays.

The above are the most common interactions and most widely used in SEM imaging modes. Figure 3.5 shows schematic beam-specimen interactions.

Different detectors are arranged in the sample chamber for measuring the response of the sample. BSE are useful in resolution of elemental composition contrast, whereas X-rays are used for both elemental analysis and chemical characterization of a sample, while SE is useful in getting surface topographic contrast. Therefore, SE mode was used in this study to examine the morphology of raw materials and PET/carbon composites.
In present study, the Philips SEM XL30 and Zeiss EVO60 SEM were used to characterize the filler and carbon composite samples at an accelerating voltage of 10 – 20 kV. The specimens were taken from the compression moulded films which were frozen in liquid nitrogen for 5 min before being fractured. Also, tensile fracture samples were prepared for SEM observations. The specimens were mounted on 0.5 inch pin stubs (Agar Scientific) using carbon adhesive tape (Agar Scientific). The fracture surfaces of samples were coated with a thin layer of gold before SEM test using an Edwards S150B sputter coater, to prevent charging of the specimen surface. The risk of charges was further reduced using a silver paint to form a conductive path between the specimens and the pin stub to avoid electron accumulation on the specimens.

3.5.2.2 Transmission Electron Microscopy (TEM)

TEM is a useful technique for observation of the morphologies of wide variety of samples with resolution down to the atomic scale. In the TEM, an electron beam passes through a condenser lens to focus the beam onto the specimen. Some of the electrons pass through, but
some hit atoms in the specimen and are scattered. Figure 3.6 shows the signals generated when a high-energy beam of electrons interacts with a thin specimen. The direct beam electrons (electrons transmitted through the sample), pass through an objective lens then pass through a projector lens and onto a fluorescent screen where the final image is obtained. TEM can provide detailed structural information and much higher magnification and resolution than SEM [9]. TEM was used in this study to investigate the morphologies of the PET nanocomposites and to image the structure of MWCNT before and after acid-treatment.

Figure 3.6 Signals generated when a high-energy beam of electrons interacts with a thin specimen. Most of these signals can be detected in different types of TEM (redrawn from ref. [9]).

A Philips CM200 TEM was used in this work at a 200 kV accelerating voltage. The specimens for TEM should be very thin in order to allow transmission of electrons. A diamond blade was used to cut slices of approximately 50 nm thickness from the core of the
samples. The PET/MWCNT samples were first embedded into epoxy resin and cured at room temperature for 24 hours. After that thin slices were cut using an ultra-microtome (Leica EM UC6). For the MWCNT, the nanoparticles were mixed with ethanol (Fisher Scientific, UK) and then sonicated in an ultrasonic bath at room temperature for about 30 minutes to separate the agglomerated MWCNT. A few drops of this suspension were dropped onto a copper grid (Agar Scientific) using a micropipette. The grid was then left to dry in a fume cupboard for 10 minutes to evaporate the ethanol.

3.5.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is the study of the interactions that occur between infrared light and matter. The most common technique is Fourier transform infrared spectroscopy (FTIR) [10]. In transmission FTIR, a beam of infrared (IR) radiation is passed through a sample. Part of the IR is absorbed by the sample (causing the chemical bond in the sample to vibrate) and the rest of it is transmitted (passed through the sample). The resulting spectrum represents the molecular absorption and transmission, creating a fingerprint of the sample. An infrared spectrum, which is a plot of measured infrared intensity versus wavenumber or wavelength, with absorption peaks corresponding to the frequencies of vibrations of the bonds between the atoms making up the material. These absorptions peaks are taken as fingerprints for the presence of certain functional groups in the sample under investigation. For example, a peak for the carbonyl group (C=O) appears at about 1709 cm\(^{-1}\) as shown in Figure 3.7 [10]. Therefore, FTIR was used in this study to identify the functional groups attached to the A-MWCNT following modification by acid treatment (described in Section 3.4 of this Chapter). Figure 3.8 shows a block diagram of an FTIR spectrometer. FTIR spectroscopic measurements were performed using a Nicolet 5700 FTIR (Thermo Electron Corporation). The samples were prepared by mixing dried carbon filler with dried potassium bromide.
(KBr) (Fisons Scientific). Samples were dried at 120 °C overnight, followed by mixing and grinding the sample with KBr (1 mg of the sample with 220 mg of KBr) for several minutes until the sample was reduced to a very fine powder. A very low concentration of MWCNT is required due to their black colour to reduce strong absorption. FTIR spectra were taken from 400 – 4000 cm⁻¹ wave number.

![Figure 3.7 The infrared spectrum of 2-methylbutyric acid [10].](image)

![Figure 3.8 Block diagram of an FTIR spectrometer (redrawn from ref. [11]).](image)
3.5.4 Thermal Analysis

3.5.4.1 Differential Scanning Calorimetry (DSC)

DSC is a thermal analytical technique used for investigating the thermal properties of materials. It is the most widely used thermal analysis technique for polymeric materials as it allows the study of all major transitions of interest such as crystal melting and the glass transition[8].

DSC is commonly used for characterizing the crystalline melting temperature ($T_m$), crystallization temperature ($T_c$), glass transition temperature ($T_g$) and heat of fusion ($\Delta H$) of the materials. The degree of crystallinity can also be calculated from DSC. A typical curve from DSC is a plot of heat flux rate versus temperature at a constant temperature ramp rate. Figure 3.9 shows typical DSC curve for a sample of PET during the first heating cycle. There are two common types of DSC systems[13]; heat flux DSC and power-compensation DSC (Figure 3.10). In a heat flux DSC system, the temperature difference between a sample and a reference placed in the same heating chamber is recorded directly and then converted to a heat flow difference (enthalpy changes).

![DSC curve of a quenched PET sample](image)

Figure 3.9 DSC curve of a quenched PET sample [12].
In power-compensation DSC technique, the temperatures of a sample and a reference are controlled independently in separate heating chambers. To maintain the temperature in these chambers, the electrical power input is varied. The energy required to do this compensation is a measure of the enthalpy changes of the sample during a thermal event. The heat flux DSC technique was used in this work.

![Block diagram of a DSC](image)

Figure 3.10 Block diagram of a DSC: (a) heat flux DSC; and (b) power compensation DSC. A: furnace; B: separate heater; and C: sample and reference holders[13].

In this work, a TA Instrument DSC Q100 was used to investigate the effect of the conductive carbon fillers on $T_m$, $T_c$, $T_g$ and degree of the crystallinity ($X_c$) of the PET matrix. The PET and the PET composites samples (7 - 10 mg) were hermetically sealed in aluminium pans, and an empty pan was sealed and used as a reference. The sealed pans were scanned from 23 °C to 270 °C in a nitrogen atmosphere using a heat-cool-heat run, at heating and cooling rates
of 10 °C/min. To erase their thermal history, samples were kept at 270 °C for 5 minutes and then cooled down to 23 °C. Data obtained from all runs were used for analysis. To confirm the results, three samples from each material were measured.

3.5.4.2 Thermo-Gravimetric Analysis (TGA)

TGA or thermogravimetry (TG) is a thermal analysis technique employed to study the decomposition and thermal stability of materials by measuring changes in mass during heating as a function of temperature or time, under a controlled atmosphere. The sample is placed in a furnace and its weight changes are monitored using a thermo balance [14]. TGA can be run in a reactive or non-reactive atmosphere; air and nitrogen are commonly used as such atmospheres [8].

![TGA Typical Curve](image)

**Figure 3.11** TGA typical curve for a material that exhibits decomposition starting and finish temperatures [13].
Figure 3.12 Block diagram of a TGA apparatus[13].

The typical curve of a TGA is a plot of mass change expressed in wt. % versus temperature at a constant heating rate. Figure 3.11 shows a typical thermogravimetric curve that exhibits decomposition temperature. Figure 3.12 is a block diagram of a TGA apparatus.

TGA was carried out on a TGA Q-500 (TA Instruments) in nitrogen and air atmospheres (60 ml/min). All samples (∼5 mg) were scanned from 23 °C to 1000 °C at a heating rate of 10°C/min, and weight-temperature curves were recorded. TGA was used to study the effect of graphite, GNP, A-MWCNT and T-MWCNT fillers on the thermal stability of the PET matrix. Thermal and thermo-oxidative degradation temperatures were measured for the PET and the composites under nitrogen and air, respectively, from ambient temperature to 700 °C at a ramp rate of 10 °C/min.
3.5.5 Mechanical Analysis

3.5.5.1 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA also known as dynamic mechanical analysis (DMA) is a technique used to study the viscoelastic property characterization of materials, in particular polymers because they are viscoelastic materials. The viscoelastic properties of polymeric materials are typically characterized by applying a controlled cyclic strain to a sample and the resulting stress response is measured [14]. Figure 3.13 shows the sinusoidal stress-strain response for ideal elastic, viscous and viscoelastic materials during DMTA. If the applied strain is in-phase with the resultant stress (0 degree), the sample is purely elastic. On the other hand, if the applied strain is in out of phase with the resultant stress by 90 degrees, the sample is purely viscous.

Figure 3.13 The DMTA sinusoidal stress-strain response for ideal elastic, viscous and viscoelastic materials[14]
However, viscoelastic materials like polymers show neither pure viscous nor pure elastic behaviour, but a combination of both. Therefore, the phase lag ($\delta$) between the strain and the stress is between 0 and 90 degree. This $\delta$ which is taken as a measure of the viscoelastic property of the polymer can be related to the stress relaxation of polymeric materials when a sinusoidal strain is applied.

DMTA data are usually reported as the ratio of stress to strain which is known as the complex modulus ($E^*$). The complex modulus is given by $E^* = E' + iE''$; where $E'$ is the storage modulus given by $E' = E\cos(\delta)$, and $E''$ is the loss modulus which is given by $E'' = E\sin(\delta)$.

In addition, the ratio of the loss modulus to the storage modulus is typically reported in DMTA data as the loss factor, loss tangent or $\tan\delta$ and represents the ratio of the energy dissipated to energy stored in a sample during one cycle of deformation.

![Figure 3.14 Single cantilever beam geometry in the DMA Q-800.](image)
In this study, DMTA was conducted using a DMA Q-800, (TA Instruments), in single cantilever mode (Figure 3.14). The specimen of dimensions 40x10x1 mm$^3$ were heated from 23 to 220 °C at the heating rate 3 °C/min. The sample was deformed at constant amplitude of 10 µm and a frequency of 1 Hz. The curves of $E'$, $E''$, and tan δ were obtained as a function of temperature via Universal Analysis software that is installed in the DMTA system.

3.5.5.2 Tensile test
Specimens for tensile testing were prepared using injection moulding machine. The tensile testing was performed using Instron instrument of model 4301 at crosshead speed of 5 mm/min by following ASTM D638 standard. The average of five test results was reported as a final value of tensile properties. All the tensile tests were carried out at room temperature.

3.6 References


Chapter 4 Results and Discussions

4.1 Electrical Properties of PET/Carbon Composites

4.1.1 Introduction

While most polymers are electrically insulating certain industrial applications, including fuel cell electrodes, antistatic materials and electromagnetic shielding, require polymers to be electrically conductive. Hence, a wide range of conductive fillers have been incorporated into various polymer matrices to produce electrically-conductive polymer composites [1-5]. A polymer is classified as conductive if it has the ability to protect against electrostatic discharge [6]. To understand the principles of electrical conductivity in polymer composites, it is important to know the percolation threshold theory (see Section 2.5, Chapter2). Percolation threshold is defined as the critical loading of conductive filler at which the electrical conductivity of polymer composite increases by several orders of magnitude, as it changes from insulating to the semi-conductive or conductive (when the resistivity of polymer < $10^6 \ \Omega.cm$) [7]. This is due to the establishment of continuous electrically-conductive paths in the polymer matrix, through which electrons are transported.

PET is a common polymer matrix used to form conductive composites; for example, as electrostatic dissipation materials etc. [8]. The electrical conductivity of PET can be increased by the addition of conductive carbon fillers [4, 9]. Hence, three conductive carbon fillers namely, graphite, GNP and A-MWCNT (described in the Experimental Chapter, Section 3.2) were added to a PET matrix at varying concentrations to fabricate three types of PET/carbon composites. The effect of these carbon fillers on the electrical conductivity of the PET matrix was investigated using electrical conductivity measurements, (as described in Section 3.5) and the results of these tests are discussed in Sections 4.1.2, 4.1.3 and 4.1.4, respectively. Moreover, A-MWCNT were modified using acid treatment (see Section 3.4) to study the effect of this treatment on the electrical properties of PET/A-MWCNT.
nanocomposites, which is discussed in Section 4.1.5. Insulator – conductor transition analysis of the PET/carbon composites was used to determine the percolation threshold values ($\phi_c$), which is discussed in detail in Section 4.1.6. The influence of extrusion processing conditions on the electrical conductivity of PET/carbon composites is presented in Section 4.1.7. For electrical conductivity measurements, PET/carbon composite samples (~1 mm film thickness) were cut from compression moulded samples. In addition, compression moulded nanocomposites specimens were compared with equivalent injection moulded test pieces. MWCNT have high aspect ratios that make them susceptible to orientation during processing. For instance, the injection moulding processes leads to alignment of MWCNT in the direction of flow [9-12]. Therefore, the effect of injection moulding on the electrical conductivity of PET/A-MWCNT has been investigated in this study and is discussed in Section 4.1.8. Section 4.1.9 presents the conclusions reached during this study.

### 4.1.2 Electrical conductivity of the PET/graphite microcomposites

The variation of electrical conductivity ($\sigma$) of the PET/graphite microcomposites as a function of frequency is shown in Figure 4.1.1. For each concentration, three different samples were fabricated under the same conditions and tested. For the PET matrix, and for composites with graphite contents below 14.75 wt. %, $\sigma$ is dependent on the frequency. However, for graphite concentrations above 14.75 wt. %, $\sigma$ is independent of the frequency. This behaviour indicates the transition of the composites from electrically insulating to semi-conductive or conductive when the resistivity ($\Omega$.cm) falls below the $10^6$ value [7]. For loadings ranging from 5 wt. % to 14 wt. %, $\sigma$ remains constant from $10^0$ Hz up to $10^2$ Hz but beyond this frequency conductivity increases. This increase is similar to that of the PET matrix, which is typical for an insulating material [13]. With further increases in graphite
loading, $\sigma$ becomes independent of frequency over the entire frequency range investigated, indicating that the PET/graphite microcomposites become conductive.

![Graph showing electrical conductivity vs. frequency](image)

**Figure 4.1.1 Log-log plot of electrical conductivity vs. frequency for the PET/graphite microcomposites tested at room temperature.**

Figure 4.1.2 shows the variation of $\sigma$ as a function of wt. % concentration of the graphite at room temperature and 10 Hz. It is clear that a large increase in $\sigma$ occurs between 14 wt. % and 14.75 wt. %. Therefore, the percolation threshold value $\phi_c$, defined as the minimum loading of the filler associated with the change in the electrical behaviour of the composite from insulative to conductive, occurs between 14 wt. % and 14.75% for the PET/graphite microcomposites. The theoretical electrical conductivity curve for composites (see Figure 2.13 in Chapter 2) indicates that the PET/graphite composites exhibit a typical percolation transition. In general, $\sigma$ increases as the graphite loading increases up to a certain loading, after which only moderate increases in $\sigma$ is observed with further addition of graphite. Addition of about 14.75 wt. % of graphite increases $\sigma$ by ~ 2 orders of magnitude at 10 Hz compared to the PET matrix. The value of $\sigma$ is about $10^{-6}$ S/m, which is considered to be the
minimum value for avoidance of electrostatic charge build-up in an insulating matrix [14].

The maximum value of $\sigma$ of the PET/graphite composites is (0.0016 S/m) at 25 wt. % which is within the range for semiconducting materials [7].

![Semi log plot of electrical conductivity at 10 Hz vs. fillers loading for the PET/graphite microcomposites tested at room temperature.](image)

Figure 4.1.2 Semi log plot of electrical conductivity at 10 Hz vs. fillers loading for the PET/graphite microcomposites tested at room temperature.

Moreover, the PET matrix is an excellent insulating polymer with $\sigma$ of about $10^{-15}$ S/m [15, 16]. The lower limit of $\sigma$ that could be measured with the equipment used in this research was about $10^{-9}$ - $10^{-8}$ S/m. These limitations however, do not have an effect on defining the percolation threshold.

### 4.1.3 Electrical conductivity of the PET/GNP nanocomposites

The measured $\sigma$ as a function of frequency for different GNP loadings is shown in Figure 4.1.3. The behaviour observed is similar to that for the PET/graphite microcomposites, except that changes in behaviour occur at lower addition levels.
Figure 4.1.3 Log-log plot of electrical conductivity vs. frequency for the PET/GNP nanocomposites tested at room temperature.

Figure 4.1.4 Semi log plot of electrical conductivity at 10 Hz vs. filler loading for the PET/GNP nanocomposites tested at room temperature.
The $\sigma$ data for samples containing up to 5 wt. % GNP show no variation in the frequency range $10^0$ Hz - $10^2$ Hz, followed by an increase as the frequency increases, indicating that the composites are insulating. The $\sigma$ data of samples within the range 6 - 6.5 wt. % stay constant over the frequency range $10^0$ Hz – $10^4$ Hz, after which $\sigma$ starts to increase slightly with increasing frequency. However, PET/GNP nanocomposites with GNP loading greater than 6.5 wt. % exhibit that $\sigma$ is independent over entire range of frequency used. This behaviour indicates the transition of PET from insulating to conducting.

Furthermore, the values of $\sigma$ plotted as a function of GNP loadings in PET (at 10 kHz and room temperature) are shown in Figure 4.1.4. From the latter, it is clear that the $\sigma$ is nearly constant when GNP levels are in the range of 0.25 – 5 wt. %. On the other hand, a large increase in $\sigma$ occurs between 5 and 6.5 wt. % GNP, this is followed by the moderate improvement in electrical conductivity. Thus, the percolation threshold of nanocomposites is expected to lie between 5 and 6.5 wt. % GNP and the plot (Figure 4.1.4) indicates the typical percolation transition from insulating to conductive. In general, the values of $\sigma$ increase as the GNP loading increases up to a certain loading after which only moderate increase in the conductivity is observed with further addition of GNP.

### 4.1.4 Electrical conductivity of PET/A-MWCNT nanocomposites.

Figure 4.1.5 shows the results obtained from impedance spectroscopy. Similar behaviour to that observed for both graphite and GNP is seen with A-MWCNT, in that the $\sigma$ data are independent of frequency above a certain loading ($\phi_c$). However, in PET/A-MWCNT nanocomposites changes in electrical behaviour occur at low weight fraction and for levels above 0.35 wt. %, the conductivity is independent of the frequency over all the frequency range investigated which typical for conductive materials. This behaviour indicates the transition from the insulating composites to semi-conductive.
Figure 4.1.5 Log-log plot of electrical conductivity vs. frequency for the PET/A-MWCNT nanocomposites tested at room temperature.

Figure 4.1.6 Semi log plot of electrical conductivity at 10 Hz vs. filler loading for the PET/A-MWCNT nanocomposites tested at room temperature.
Figure 4.1.6 shows the variation of $\sigma$ as a function of wt. % A-MWCNT. PET/A-MWCNT composites exhibit a sharp transition from insulator behaviour to conductive, in which $\sigma$ increased from about $\sim 5.5 \times 10^{-9}$ S/m to 0.2 S/m as the concentration increased from 0.25 wt. % to 2 wt. %. Therefore, $\phi_c$ occurs between 0.25 wt. % and 0.35 % for the PET/A-MWCNT composites investigated here. There is a significant increase in $\sigma$ above 0.25 wt. %, where the addition of only an extra 0.1 wt. % (to 0.35 wt. %) of A-MWCNT increases the electrical conductivity by 2 orders of magnitude. The curve also indicates that the PET/A-MWCNT nanocomposites exhibit a typical percolation transition, similar to the graphite and GNP composites. Detailed investigations of this transition region for all PET/carbon composites will be presented in Section 4.1.6.

**4.1.5 Electrical conductivity of PET/T-MWCNT nanocomposites**

Figure 4.1.7 shows $\sigma$ as a function of frequency for the PET/T-MWCNT nanocomposites. All the composites had similar conductivity curves to that of the unfilled PET. Therefore, percolation behaviour was not observed within the filler loading used in this study (up to 2 wt. %). Further investigation into the electrical behaviour of these nanocomposites above 2 wt. % filler is recommended.

Excessive acid treatment can damage and fragment MWCNT into smaller pieces and create oxygen containing functional groups and defects on the surface of MWCNT. These treatments can adversely affect the aspect ratio of the CNT, thus resulting in poor electrical conductivity of polymer nanocomposites containing T-MWCNT [17-24]. The $\sigma$ of PET/A-MWCNT nanocomposites increased with loading level of as-received MWCNT as was shown in Fig 4.1.6. However, $\sigma$ values were much lower after acid treatment of the as-received MWCNT, and figure 4.1.8 shows them to be essentially unchanged compared to the PET matrix.
This could be attributed to shortening of the tube lengths of MWCNT after acid treatment and improved compatibility to PET, resulting in good dispersion and distribution which hinders the formation of conductive network. In addition, the attachment of functional groups on MWCNT walls reduces electrical conductivity of nanocomposites. Observation of low composites conductivities as a result of acid conditioning, were also reported by Yesil et al [23] and Yesil et al [24] and Royan et al [21]. They attributed this behaviour to the formation of functional groups and defects sites on the surface of the A-MWCNT after acid treatments. However, the authors reported an improvement in mechanical properties after acid treatment of CNT. Moreover, according to the review studies by Ma et al [20] who concluded that the electrical conductivity of composites incorporated with functionalized CNT strongly depends on the acid treatment conditions.
For example excessive treatment induces several heterogeneous atoms onto the surface of CNT, resulting in the perturbation of π electrons and therefore affecting the intrinsic electrical properties of CNT.

4.1.6 Insulator – conductor transition analysis of PET/carbon composites

This Section discusses percolation theory and the percolation threshold values, where the insulator-conductor transitions occur, in detail for the PET/carbon composites. In this section the addition of conductive filler, i.e. conductive carbon fillers of different size and morphology, was shown to increase the σ of an insulating polymer (PET) by many orders of magnitude. The variation in the conductivity of a polymer composite as a function of the conductive filler content typically exhibits usually an S-shaped curve (see Figure 2.13, Chapter 2) and can be described by a power-law relationship as according to percolation
Percolation theory is often used to characterize the insulator-conductor transitions of the polymer composites containing conductive fillers in order to determine the percolation threshold value and the dimensionality of the conductive path network in the polymer matrices. According to percolation theory, the $\sigma$ of the polymer/carbon composites is given by Equation 4.1

$$\sigma = \sigma_0 (\Phi - \Phi_c)^t, \quad \text{for } \Phi > \Phi_c \quad \ldots \ldots \ldots \ldots (4.1)$$

Where: $\sigma$ is the conductivity of composite (S/m), $\sigma_0$ is the proportionality constant, $\Phi_c$ is the critical loading, (percolation threshold in vol. %), and $\Phi$ is the filler content (vol.%). $t$ describes the dimensionality of the system and depends on the geometry of the network, although its physical meaning is controversial [26]. In theory, $t$ values of 1.33 and 2.2 represent two dimensional and three dimensional systems, respectively [1]. Usually, experimental results are fitted by plotting log $\sigma$ vs. log ($\Phi - \Phi_c$) and incrementally varying $\Phi_c$ until the best linear fit is obtained. Although the concept of the percolation theory was derived on the basis of the volume fraction of the filler, however weight fraction has been used for the determination of the percolation threshold values in several studies [27, 28]. This is due to the fact that the density of the nanofillers, i.e. CNT is often an estimate, rather than an exact value. Therefore, the determination and evaluation of $\Phi_c$ in this study will be in terms of weight fractions. In this work, the values of $\sigma$ at 10 Hz have been taken for comparative purpose for all the PET/carbon composites. This low frequency value was chosen because of the transition from the insulating to the conductive regime can only be observed of low frequency [29]. According to percolation theory, certain steps need to be followed to determine $\Phi_c$. These steps are illustrated in the following paragraph. At first, the values of $\Phi_c$ are approximated initially from a critical filler loadings where $\sigma$ values begin to deviate significantly.
Figure 4.1.9 Percolation threshold, $\Phi_c$ determination plot. Electrical conductivity of PET/graphite microcomposites as a function of graphite content. The inset plot is $\log \sigma$ versus $\log (\Phi-\Phi_c)$.

Secondly, such $\sigma$ values are plotted versus values of $(\Phi-\Phi_c)$ on a log-log scale and incrementally changing $\Phi_c$ until the best fit is obtained using the power law. The data of $R^2$ are recorded to examine the fitting errors. Next, the process is repeated by changing $\Phi_c$ to reduce the fitting errors. Finally, $\Phi_c$ is obtained using the $R^2$ values closest to unity. The fitting of the percolation equation to the experimental data is represented in Figures 4.1.9 – 4.1.11 for the PET/graphite microcomposites, PET/GNP and PET/A-MWCNT nanocomposites, respectively. Table 4.1.1 shows the percolation thresholds, $t$ exponents and the fitting errors for PET/carbon composites were determined following the percolation theory. Correlation values factor $R^2$ were close to unity demonstrating a good fit of the experimental data to the power-law model.
Figure 4.1.10 Percolation thresholds, \( \Phi_c \) determination plot. Electrical conductivity of PET/GNP nanocomposites as a function of GNP content. The inset plot is \( \log \sigma \) versus \( \log (\Phi - \Phi_c) \).

Figure 4.1.11 Percolation threshold, \( \Phi_c \) determination plot. Electrical conductivity of PET/A-MWCNT nanocomposites as a function of MWCNT content. The inset plot is \( \log \sigma \) versus \( \log (\Phi - \Phi_c) \).
A best fit data (Figures 4.1.9 to 4.1.11) was achieved at the values of \( \Phi_e \) of 14.7, 5.7 and 0.33 wt. % for the composites containing graphite, GNP and A-MWCNT, respectively. In contrast, the percolation threshold was not observed for T-MWCNT at the loadings used presently.

**Table 4.1.1 Percolation threshold values (\( \Phi_e \)), network dimensionality (t) and error fitting (R\(^2\)) values for PET/carbon composites.**

<table>
<thead>
<tr>
<th>Composites</th>
<th>( \Phi_e ) (wt.%)</th>
<th>t</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/Graphite</td>
<td>14.7</td>
<td>1.29</td>
<td>0.957</td>
</tr>
<tr>
<td>PET/GNP</td>
<td>5.7</td>
<td>4.72</td>
<td>0.981</td>
</tr>
<tr>
<td>PET/A-MWCNT</td>
<td>0.33</td>
<td>2.89</td>
<td>0.998</td>
</tr>
<tr>
<td>PET/T-MWCNT</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

PET/A-MWCNT nanocomposites exhibit a sharp transition from insulator to conductor behaviour as shown in figure 4.1.11 with lower percolation threshold compared to other PET/carbon composites. The \( \sigma \) increased from \( \sim 5.5 \times 10^{-9} \) S/m to 0.2 S/m at 0.25 and 2 wt. % A-MWCNT, respectively. Moreover, the conductivity of \( \sim 10^{-4} \) S/m was obtained at 0.5 wt. % of A-MWCNT, which is higher than the value \( (10^{-6} \) S/m) considered to be necessary to avoid an electrostatic charging of an insulating matrix [14]. Whereas, such value was obtained at higher loadings in the case of graphite and GNP reinforced composites. It is known that aspect ratio is an important factor in determining the \( \sigma \) and the \( \Phi_e \). The high aspect ratio found to aid the formation of a conductive network at lower values of \( \Phi_e \). Based on the average dimensions given for both A-MWCNT and GNP fillers in their suppliers’ data sheets, the calculated aspect ratio for these fillers is approximately \( \sim 158 \) and \( \sim 1875 \), respectively. Hence based on these values one would have expected to observe lower \( \Phi_e \) for the PET nanocomposites using GNP filler than those using A-MWCNT. As can be seen our
results show the opposite. One reason for this could be that some of the GNP filler has not been fully reduced in the commercial nanoplatelets used and the presence of some functional groups on its surface. In addition, there is a possibility of rolling up of GNP during the composites compounding process; this could reduce their aspect ratio. These results seem to agree with the results obtained by Chatterjee et al [30] and Du et al [31] who compared MWCNT with GNP as reinforcements in polyamide 12 and HDPE matrix, respectively. The authors found lower $\Phi_c$ values and higher electrical conductivity in composites containing MWCNT rather than GNP. The authors attributed this behaviour to both the presence of unreduced graphite oxide in the GNP as well as GNP usually wrinkles and even roll up into a tube-like structure, resulting in lower aspect ratios.

According to the literature, the lowest $\Phi_c$ reported is 0.06 wt. % for PET/MWCNT nanocomposites by Logikis et al [32] who used an in-situ polymerization method to fabricate their composites, while same authors reported $\Phi_c$ at 0.2 wt. % for same nanocomposite when prepared by melt compounding. These authors have also investigated the effect of functionalized MWCNT on the electrical conductivity. They reported much lower $\sigma$ for composites containing functionalized CNT. On the other hand, the highest value of $\Phi_c$ is found to be 0.9 wt. % MWCNT reported by Hu et al [15] who used solution method in their study.

Furthermore, for PET/GNP nanocomposites, Zhang et al [33] obtained a percolation threshold for nanocomposites at 3.4 vol. % ($\sim$ 6 wt. %) using melt compounding method. Moreover, Li et al [8] who used same method and reported that, the electrical conduction path of GNP in the PET matrix is formed at about 5 wt. % of GNP. These studies are in good agreement with the results obtained in present study.

In contrast, the PET/graphite microcomposites showed lower values of conductivity and much higher percolation threshold value (14.75 wt. %). Krupa et al [34] examined the
electrical properties of PE/graphite composites and reported even higher $\Phi_c$ value of $\sim 11$ vol. % ($\sim 24$ wt. %). In another study, She et al [35] reported also higher $\Phi_c$ values i.e. $\sim 22.2$ wt. % for PE/graphite microcomposites. These values are higher in comparison to that obtained in present study. The difference in percolation threshold values could be attributed to the difference in filler sizes and preparation method used. These results show the advantage of using conductive nanofillers (GNP and A-MWCNT) over conductive microscale fillers i.e. graphite.

The theoretical value of the conductivity exponent ($t$) is in the range 1.33 to 2 (for progression from 2D to 3D networks). However; experimental values outside this range are also reported [27]. In this study, the $t$ value for the graphite composites (1.29) which is close to theoretical value of 2D system. However, for the A-MWCNT composites, it is higher ($t = 2.9$) than the theoretical. A similar $t$ value was reported for a PET/A-MWCNT system by Logakis et al [32] and Hu et al [15] reported 2.9 and 2.2 respectively. The authors argued that the deviation in the value of $t$ from the theoretical could be due to the absence of physical contacts between the CNT nanoparticles. Thus, a tunnelling mechanism of conductivity may be in operation in the composites.

Moreover, the $t$ value for the GNP nanocomposites ($t = 4.72$) in this study was much higher than the theoretical values. Similar values ($t = 4.25$) have been obtained in previous study by Zhang et al [33] for PET/GNP nanocomposites. These authors suggested that three factors should be responsible for this deviation; the microstructures of the composites, tunnelling conduction and anisotropic behaviour of fillers in the PET matrices.

According to a review by Bauhofer et al [27] who collected data from 147 studies of electrical percolation of polymer/CNT nanocomposites. These authors reported values of $t$ ranging from 1.3 to 4. They also concluded that the dimensionality of a percolated CNT network cannot be determined directly by evaluating the ($t$) value. It further suggests that the
evaluation of network dimensionality using classical percolation theory for a CNT networks may not be simple. Furthermore, classical percolation theory has been derived for an ideal system that consists of homogenous dispersion of identical particle sizes.

4.1.7 Effect of processing conditions on electrical conductivity of composites

In twin-screw extrusion, the screw speed and residence time in the extruder are expected to influence the values of $\sigma$ of Polymer/carbon composites [36, 37]. Therefore, the effects of these two variables on the $\sigma$ values of PET/carbon composites were investigated. Figures 4.1.12 to 4.1.14 show $\sigma$ data for PET/carbon composites processed in the twin screw extruder at two different screw speeds and residence times and Tables 4.1.2 to 4.1.1 illustrate $\sigma$ data for these composites with standard deviation values. Samples were chosen with values of wt. % falling just before and just after the $\phi_c$ values in Figures 4.1.9, 4.1.10 and 4.1.11.

![Graph of Electrical conductivity](image)

**Figure 4.1. 12 Electrical conductivity of PET with graphite loading of 14 wt. % and 15 wt. % measured at different processing conditions in the Minilab twin-screw extruder tested at room temperature.**
Table 4.1.2 Electrical conductivity of PET with graphite loading of 14 wt. % and 15 wt. % measured at different processing condition.

<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>σ (S/m) 14 wt.% Graphite</th>
<th>σ (S/m) 15 wt.% Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 rpm / 5 min</td>
<td>9.8x10^{-9} ± 2.6x10^{-9}</td>
<td>1.9x10^{-5} ± 3.4x10^{-6}</td>
</tr>
<tr>
<td>45 rpm / 10 min</td>
<td>5.1x10^{-9} ± 1.6x10^{-9}</td>
<td>1.3x10^{-5} ± 1.3x10^{-9}</td>
</tr>
<tr>
<td>90 rpm / 5 min</td>
<td>2.6x10^{-8} ± 1.0x10^{-9}</td>
<td>3.8x10^{-5} ± 2.3x10^{-6}</td>
</tr>
<tr>
<td>90 rpm / 10 min</td>
<td>5.9x10^{-9} ± 1.1x10^{-9}</td>
<td>4.1x10^{-5} ± 2.0x10^{-5}</td>
</tr>
</tbody>
</table>

Table 4.1.3 Electrical conductivity of PET with GNP loading of 5 wt. % and 6 wt. % measured at different processing condition.

<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>σ (S/m) 5 wt.% GNP</th>
<th>σ (S/m) 6 wt.% GNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 rpm / 5 min</td>
<td>7.7x10^{-9} ± 1.3x10^{-9}</td>
<td>3.4x10^{-7} ± 5.2x10^{-8}</td>
</tr>
<tr>
<td>45 rpm / 10 min</td>
<td>7.4x10^{-9} ± 2.1x10^{-9}</td>
<td>3.2x10^{-7} ± 1.7x10^{-7}</td>
</tr>
<tr>
<td>90 rpm / 5 min</td>
<td>6.8x10^{-9} ± 3.0x10^{-9}</td>
<td>3.1x10^{-5} ± 1.9x10^{-5}</td>
</tr>
<tr>
<td>90 rpm / 10 min</td>
<td>7.4x10^{-9} ± 1.8x10^{-9}</td>
<td>4.7x10^{-5} ± 1.7x10^{-5}</td>
</tr>
</tbody>
</table>

Table 4.1.4 Electrical conductivity of PET with A-MWCNT loading of 0.25 wt. % and 0.35 wt. % measured at different processing condition.

<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>σ (S/m) 0.25 wt.% CNT</th>
<th>σ (S/m) 0.35 wt.% CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 rpm / 5 min</td>
<td>5.6x10^{-9} ± 4.1x10^{-10}</td>
<td>4.8x10^{-7} ± 2.3x10^{-8}</td>
</tr>
<tr>
<td>45 rpm / 10 min</td>
<td>3.9x10^{-9} ± 1.3x10^{-9}</td>
<td>3.2x10^{-7} ± 2.1x10^{-7}</td>
</tr>
<tr>
<td>90 rpm / 5 min</td>
<td>5.8x10^{-9} ± 1.5x10^{-9}</td>
<td>4.1x10^{-4} ± 9.8x10^{-5}</td>
</tr>
<tr>
<td>90 rpm / 10 min</td>
<td>4.3x10^{-9} ± 2.0x10^{-10}</td>
<td>3.4x10^{-4} ± 8.5x10^{-5}</td>
</tr>
</tbody>
</table>

Figure 4.1.12 shows that for the two samples of PET/graphite microcomposites investigated, with graphite loading of 14 wt. % and 15 wt. %, no significant changes in the electrical conductivity occur by changing the processing conditions. However, for PET composites
containing GNP or MWCNT the screw speed was found to have a significant effect on $\sigma$ for the samples having a filler loading above that of the percolation threshold. This is evident in Figures 4.1.13 and 4.1.14, where the respective value of $\sigma$ increased by 2 to 3 orders of magnitude for the GNP and MWCNT nanocomposites processed at 90 rpm.

![Graph showing electrical conductivity of PET with GNP loading of 5 wt. % and 6 wt. % measured at different processing conditions in the Minilab twin-extruder tested at room temperature.](image)

**Figure 4.1.13** Electrical conductivity of PET with GNP loading of 5 wt. % and 6 wt. % measured at different processing conditions in the Minilab twin-extruder tested at room temperature.

Whereas increasing the residence time at either screw speed appears to have little effect. In contrast, there is no discernible effect of processing conditions on the electrical conductivity of PET/GNP and PET/MWCNT nanocomposites with a filler loading below that of the percolation threshold values. It is suggested that this is due to the amount of GNP or MWCNT added being insufficient to form an electrically conductive path whatever the state of filler dispersion in the composite.
Figure 4.1.14 Electrical conductivity of PET with A-MWCNT loading of 0.25 wt. % and 0.35 wt. % measured at different processing conditions in the Minilab twin-extruder tested at room temperature.

Increasing the screw speed at a fixed residence time of mixing is seen to increase $\sigma$ for the two samples containing nanoscale fillers above the percolation limit. For example, the $\sigma$ of PET/GNP at 6 wt. % jumped from $3.37 \times 10^{-7}$ S/m to $3.13 \times 10^{-5}$ S/m when screw speed was increased to from 45 to 90 rpm. Similarly, for the composite containing 0.35 wt. % MWCNT $\sigma$ jumped from $4.84 \times 10^{-7}$ S/m to $4.14 \times 10^{-4}$ S/m when the screw speed increased to 90 rpm. This could be due to improved dispersion of these fillers into the PET matrix. Similar behaviour has been observed by Guehenec et al [36], who studied the variation of $\sigma$ in poly(ether ketone) (PEEK)/CNT nanocomposites upon varying the screw speed of a twin-screw extruder (100, 200, 300 and 400 rpm). They found that $\sigma$ increased from 0.02 to 0.05 S/cm with increasing screw speed up to 200 rpm. However, they observed a decrease in $\sigma$ values (to 0.025 S/cm) when screw speed was increased above 200 rpm. This was attributed to the degradation of the CNT at high screw speeds. The best dispersion was reported at 200
rpm in their study. Another study conducted by Liu et al [38] also concluded that the highest σ for composites of 12 wt.% PA6/GNP nanocomposites was achieved as a result of the best dispersion.

There are two crucial factors that influence the σ of polymer composites which are the dispersion and distribution of the filler within the polymer matrix. These aspects are discussed in Chapter 2 Section 2.4.4 and Figure 2.11; it is clear that optimum combination of these parameters can result in the formation of a conductive network within the matrix. According to these latter figures and the present results, the dominant effect of screw speed indicates that changes in dispersion quality rather than fillers distribution are occurring.

4.1.8 Influence of moulding techniques on the electrical conductivity of composites

In general, the σ of polymer/CNT nanocomposites depends strongly on the arrangement of the CNT in the polymer matrix [39] which, in turn, depends on the processing methods used for the fabrication of the final product. Two processing methods; namely, injection moulding (using the Haake Minjet described in Chapter 3) and compression moulding (used for all the other composites studied in this Section), were used for the fabrication of the final specimens of PET/A-MWCNT nanocomposites. Impedance spectroscopy was conducted on these samples with the aim of determining any effect of the processing method on the electrical properties of the nanocomposites prepared. The results obtained for all the samples investigated presently are shown in Figure 4.1.15. It shows that the σ values for injection moulded samples are lower than that of compression molded samples which contain more randomly distributed MWCNT. This is due to the fact, that injection moulding causes the MWCNT to become oriented and partially aligned in the direction of flow, thus interrupting tube-to-tube contacts and hence, reducing σ.
Figure 4.1.15 Semi log plot of electrical conductivity vs. MWCNT loading for the compression and injection moulded (flow direction) samples tested at room temperature.

Figure 4.1.15 also shows the injection moulded samples exhibit a higher $\phi_c$ value compared to the compression moulded samples. TEM imaging in a study by Villmow et al [12] and Parmar et al [11] revealed that CNT become partially aligned in the flow direction in injection moulded PC based composites. When the mould is full, the PC composite melt is static; the final orientations of the CNT become frozen as the injection moulding vitrifies upon cooling. Due to the high aspect ratio of CNT, these orientations lead to reduction in the electrical behaviour, and thus to an increase in the $\phi_c$ of the PC/MWCNT nanocomposites. The study by Arjmand et al [40] which compared the electrical properties of injection and compression moulded PS/MWCNT nanocomposites, also found similar conclusions. It was concluded from TEM that the CNT are partially aligned in the flow direction (see Figure 2.12, Chapter 2). According to Arjmand et al, the $\sigma$ curves of the parallel and transverse to
the flow direction exhibited nearly same trends, but in parallel direction, the values were one order of magnitude higher than transverse.

The orientation effects were also found for polymer/GNP nanocomposites by Kalaitzidou et al [10]. The authors concluded that the fabrication method used for the preparation of PP/GNP nanocomposites had an impact on the electrical conductivity of the nanocomposites. The authors used the same GNP that has been used in this work. In their study, they reported higher σ values in compression mouldings relative to those made by injection mouldings. Also, they proposed that GNP nanoparticles could be aligned parallel to each other along the flow direction during the injection moulding process.

4.1.9 Summary

The following observations can be summarized from the studies of the electrical properties and percolation behaviours of PET/carbon composites.

The electrical conductivity was independent of the frequency for the composites above Φ_c values while dependent on frequency to below Φ_c. The σ of the samples at frequency of 10 Hz was plotted as a function of the loading (wt. %). An increase in the σ values is observed at Φ_c for all PET/carbon composites which mark the insulator – conductor transition. The values of Φ_c obtained were determined from fitting a power-law equation derived from percolation theory. The PET/A-MWCNT nanocomposites exhibit an excellent σ with a low percolation threshold compared to the PET/graphite micro composites and PET/GNP nanocomposites.

Acid modification of the surface of A-MWCNT was carried out in this work. The effect of acid treatment on the σ of PET/A-MWCNT nanocomposites was investigated. It was found that T-MWCNT did not form a conductive network; this is more likely that such treatment has shortened the tubes. Thus the percolation threshold was not observed in this case.
However, the presence of functional groups was also confirmed on CNT surfaces, resulting in lower electrical conductivity of composites.

The effect of extrusion processing conditions on the $\sigma$ of PET/carbon composites was investigated. It can be concluded that the screw speed had a significant effect on $\sigma$, particularly for the PET nanocomposites systems. In contrast, increasing the residence time of the composites in the extruder had no significant effect on $\sigma$.

PET/A-MWCNT nanocomposites were prepared by injection moulding to compare this method with compression moulding. Composites prepared by injection method showed lower conductivity values for the same level of conductive filler used, as well as a higher percolation threshold value. This is due to the partial alignment of MWCNT in the flow direction, which leads to interruption of tube-to-tube contacts.

4.1.10 References


[33] M. Zhang, D. J. Li, D. F. Wu, C. H. Yan, P. Lu, and G. M. Qiu, "Poly (ethylene terephthalate)/expanded graphite conductive composites: structure, properties, and


4.2 Morphologies of PET/Carbon Composites

4.2.1 Introduction

The morphologies of the pure fillers, the PET matrix and the PET/carbon composites are presented in this section. Three samples of each composite were chosen to examine their morphologies containing filler levels below, close and above the percolation threshold value of each PET/carbon composite system. Specimens of the PET matrix and its composites were prepared by cryogenic fracturing using liquid nitrogen. Moreover, tensile fracture surfaces were also investigated by selecting two samples of each composite with different filler loading based on the observation of the tensile properties.

4.2.2 Morphologies of Carbon Fillers

The fillers were examined using SEM and TEM to study their morphology before incorporation into the PET matrix. Figure 4.2.1(a – d) shows SEM images of graphite, GNP, A-MWCNT and T-MWCNT, respectively. The graphite exhibits large platelets of the scale of ~ 10 -100 µm. GNP shows the separated nanoplatetes appearing in the image resulting from break down of expanded graphite structures during the exfoliation process [1] having dimensions as per the supplier specifications, the length is 15µm and thickness is 6 – 8 nm. The GNP normally appears as the unique nanoparticles comprising of short stacks of graphene sheets having a platelet shape (Figure 4.2.1b). Similar morphologies were obtained in several previous studies [1-3]. An entangled network arrangement typical of MWCNT [4] is clearly visible in the SEM image for the A-MWCNT (Figure 4.2.1c). In contrast, acid treatment of the MWCNT (Figure 4.2.1d) caused them to be shorter and less entangled. Treatment of A-MWCNT with acids usually shortens their length and reduces their diameter.
TEM was also used to characterize the morphology of CNT as shown in Figure 4.2.2. The typical entangled nature of A-MWCNT is quite visible from the image. On the other hand, it is clear that acid treatment of the MWCNT has made them less entangled with some defects sites. Furthermore, at some locations catalyst particles can be seen on the surface of the A-MWCNT (black dots) as shown in Figure 4.2.2(a). Similar morphology has been reported previously [4]. However these particles were found to disappear after acid treatments of CNT as shown in Figure 4.2.2(b). In this figure, it is also clear that there are some defects, pointed out by the black arrows, resulting from the acid treatment process.

Figure 4.2.1 SEM images of as-received fillers; (a) graphite, (b) GNP, (c) A-MWCNT and (d) T-MWCNT
In addition to removing contaminants (e.g. catalyst particles, amorphous carbon), the acid treatment shortens the length of the CNT. This results in less entanglement of CNT which may improve their dispersion and distribution into the PET matrix in comparison to the A-MWCNT. In addition, the acid treatment attaches some hydroxyl and carboxyl functional groups to the walls of CNT [5-7]. The number of these groups on the A-MWCNT depends on the acid treatment conditions including time, temperature and oxidizing agents [8]. It is expected that these functional groups may improve interaction with the PET matrix. In order to confirm the presence of such functional groups FTIR was conducted.

4.2.3 FTIR

Figure 4.2.3 shows the FTIR spectra of both the T-MWCNT and A-MWCNT. In comparison to the nearly featureless spectrum of the A-MWCNT, the spectrum of the T-MWCNT shows two strong peaks in the ranges of 1600 - 1750 and 3200 - 3600 cm\(^{-1}\) that are characteristic of carboxyl (-COOH) and hydroxyl (-OH) functional groups, respectively [5, 7], indicating the successful modification (by HNO\(_3\) and H\(_2\)SO\(_4\)) obtained in this study. According to the literature, the peak in the range ~ 1710 -1730 cm\(^{-1}\) is due to the stretching vibration of the C=O groups in -COOH [5, 9]. Whilst in another study, the stretching vibration mode of the C=O group in acid often appears in the range of 1690 - 1660 cm\(^{-1}\) in FTIR spectra.
However, it was reported that wavenumber at which this peak appears, depends on the acid treatment time. Zhang et al, [9] found that such a peak around 1735 cm\(^{-1}\) was shifted from 1737 cm\(^{-1}\) to 1720 cm\(^{-1}\) as the time of acid treatment increased. Yesil et al, [10] reported that the C=O vibration peak appeared at ~ 1637 cm\(^{-1}\) whereas Verdejo et al, [7] observed a strong signal at 1725 cm\(^{-1}\) for the carbonyl group in COOH. The present FTIR results agree well Yesil et al, [10]. It was suggested [11] that the attachment of -COOH groups onto the walls of CNT is of a great importance when compared with other functional groups, as it is active and a range of chemical reactions can occur with this functional group.

4.2.4 Cryogenically Fractured Surface Morphologies

The morphologies of cryo-fracture surfaces of the PET/carbon composites were determined using SEM. Figure 4.2.4 shows the SEM micrograph of the PET/graphite microcomposites.
Figure 4.2.4 SEM images of cryo-fracture surfaces of PET/graphite microcomposites at low and high magnifications; (a) 10 wt. %, (b) 15 wt. % and (c) 20 wt. %. The arrows in the magnified images indicate the graphite.
The graphite flakes appear white in the images and the PET matrix grey. At the loading of graphite below the percolation threshold value ($\Phi_c = 14.7$) (see Section 4.1.6), the particles of graphite are relatively far from each other (Figure 4.2.4 (a)). As a result the electrons will not be able to move effectively, so the resistance of the microcomposites remains high. However, when the graphite loading reaches $\Phi_c$ (Figure 4.2.4 (b)), a sufficient number of graphite particles come into contact with each other to form a conductive network. This transforms the insulating PET to become conductive. When the graphite loading is increased above the percolation threshold, agglomeration is observed and some graphite layers are sufficiently large to be pulled out of PET matrix during fracture (Figure 4.2.4 (c)). Moreover, the PET/graphite microcomposites consist of both large and small particles. The small particles could have been formed during melt mixing which causes fragmentation of the large particles.

Figure 4.2.5 shows the PET/GNP nanocomposites at 2 to 8 wt. % of GNP. Compared to the graphite specimens, the images show a much smoother surface typical of a more brittle fracture. The nanocomposites containing 2 wt. % of GNP exhibits uniform dispersion, distribution and no indication of aggregations (Figure 4.2.5 (a)). However, at higher loadings, the aggregation and rolling up of GNP is observed. The addition of 6 wt. % of GNP into PET (Figure 4.2.5 (b)) is slightly above the percolation threshold value of $\Phi_c = 5.7$ wt. % indicating that a conductive network has formed. Whereas more agglomeration could be seen in Figure 4.2.5 (c) as the filler content is increased.
Figure 4.2.5 SEM images of cryo-fracture surfaces of PET/GNP nanocomposites at low and high magnifications; (a) 2 wt. %, (b) 6 wt. % and (c) 8 wt. %. The arrows in magnified images indicate the GNP.

Figure 4.2.6 shows the TEM images of both pure GNP and PET/GNP nanocomposites. The folding and rolling up of nanoplatelets in the composite is clearly observed. Similar
observations have been reported by Kalaitzidou et al. [12] for same grade of GNP in a PP matrix. Zhang et al. [13] studied the relationship between the morphology of fracture surfaces and the electrical conductivity of PET/expanded graphite nanocomposites. In their SEM images of composites, the addition of graphite nanoplatelets at the percolation threshold was found to develop a conductive network. Below the threshold value, the particles were seen far away from each other, hence giving no path for the electric current to flow. Moreover, Li et al [14] who studied effect of expanded graphite on the properties of PBT observed that although electrical percolation occurred between 3 – 5 wt. % there was no obvious agglomeration until the addition of 7 wt. % of filler. The authors attributed the electrical conduction behaviour to the electron tunnelling mechanism.

![Figure 4.2.6 TEM images of as received GNP (left) and a PET/GNP nanocomposite containing 6 wt. % of GNP (right). The arrows show the rolled up sheets of GNP.](image)

The cryo-fracture surfaces of both the PET/A-MWCNT and PET/T-MWCNT nanocomposites are shown in Figure 4.2.7. The bright spots in microstructure appear to be CNT which increase in number upon increasing filler levels while the dark background is the PET matrix. The A-MWCNT shows many of the bright spots to be exposed on the surface of the polymer matrix (Figure 4.2.7 left column), while in the case of T-MWCNT these are more embedded into the matrix, indicating better matrix-CNT adhesion (see Figure 4.2.7)
right column). Figure 4.2.8 shows TEM images of PET/A-MWCNT and PET/T-MWCNT nanocomposites at 0.35 wt. % loading. The agglomeration and poor distribution is quite clearly noticed for PET/A-MWCNT compared to PET/T-MWCNT.

Figure 4.2.7 SEM images of cryo-fracture surfaces of PET/A-MWCNT and T-MWCNT nanocomposites at 0.1, 0.35 and 1 wt. % CNT loadings, shown as a, b and c, respectively.
Similar SEM observations were made for PET/MWCNT nanocomposites by Santoro et al, [15] who concluded that a good dispersion has been achieved at ~ 0.25 wt.% , followed by agglomeration of CNT. Similar observations were made by Zaman et al, [16] who reported improved dispersion, filler-matrix adhesion and distribution of acid treated MWCNT in PET matrix.

![Figure 4.2.8 TEM images of PET/A-MWCNT and PET/T-MWCNT nanocomposites at 0.35 wt. %](image)

**Figure 4.2.8 TEM images of PET/A-MWCNT and PET/T-MWCNT nanocomposites at 0.35 wt. %. The inset images show magnified CNT in the PET matrix.**

### 4.2.5 Tensile Fracture Surfaces

Fractographic examinations provide information about the failure behaviour and the interfacial bonding of composites. Figure 4.2.9 – 13 show the tensile fracture surfaces of the pure PET and PET-based micro- and nano-composites which reveal different fractographic features. In general, a rough fracture surface indicates more ductile behaviour with deformation of the matrix during tensile loading. On the other hand, a smooth surface indicates more brittle fracture and lower fracture toughness.

The pure PET fracture surface appears smooth and rough which is a typical of brittle and ductile fractured as shown in Figure 4.2.9. Moreover, it is clear from this figure that the pure PET is free of air voids.
Figure 4.2.9 Tensile fracture surface of the pure PET matrix.

Figure 4.2.10 Tensile fracture surfaces of PET/graphite microcomposites at low and high magnifications; (a) 2 wt. % graphite and (b) 15 wt. % graphite.

SEM micrographs of the PET/graphite microcomposites at 2 and 15 wt. % loading of graphite are shown in Figure 4.2.10(a – b), respectively. It is clear that as the graphite
content is increased, the agglomeration level increased. The debonding of graphite from the PET matrix was clearly observed at higher filler loading that possibly generated cracks resulting in composite failure (see figure 4.2.10b). Similar observations have been reported by Akinci et al.[17] for PP/graphite microcomposites.

Similarly, the fracture surfaces of PET/GNP nanocomposites are shown in Figure 4.2.11(a – b) for 2 and 10 wt. % of GNP, respectively. GNP agglomeration is absent at 2 wt. % of GNP but some rolling and folding up of sheets is obvious. On the other hand, as the GNP level is increased from 2 wt. % to 10 wt. %, agglomeration and poor distribution were observed as shown in Figure 4.2.11(b).

![Figure 4.2.11 Tensile fracture surfaces of PET/GNP nanocomposites at low and high magnifications; (a) 2 wt. % GNP and (b) 10 wt. % GNP.](image-url)
GNP agglomerates formed at higher loadings act as stress concentrators in the PET matrix and generate cracks. These cracks may join together and cause the composite fractures/failures. These images confirm that poor dispersion of GNP reduces the available interfacial area between the GNP platelets and PET matrix. Karevan et al, [18] observed a similar agglomeration effect at 12 wt. % of GNP in a PA6 matrix.

Figure 4.2.12(a – b) shows the tensile fracture surfaces of PET/A-MWCNT nanocomposites. At 0.1 wt. % A-MWCNT (Figure 4.2.12(a)), a reasonable dispersion and distribution of CNT was found on the fracture surfaces.

Figure 4.2.12 Tensile fracture surfaces of PET/A-MWCNT nanocomposites at low and high magnifications; (a) 0.1 wt. % A-MWCNT and (b) 1 wt. % A-MWCNT.
On the other hand, at 1 wt. % A-MWCNT (Figure 4.2.12(b)) there is poorer dispersion and distribution. In addition, CNT those are exposed or pulled out onto the surface are also evident in this figure, indicating weak interfacial interaction/bonding between PET and the CNT.

In contrast PET/T-MWCNT nanocomposites showed better distribution and dispersion in comparison to PET/A-MWCNT due to their acid treatment. CNT were observed to be more embedded into the surface of the PET specimens as shown in Figures 4.2.13(a – b), indicating better matrix-CNT adhesion. Pat et al [19] reported similar SEM observations for PET nanocomposites containing 0.5 wt. % MWCNT before and after acid treatment.

![Figure 4.2.13](image)

Figure 4.2.13 Tensile fracture surfaces of PET/T-MWCNT nanocomposites at low and high magnifications; (a) 0.1 wt. % T-MWCNT and (b) 1 wt. % T-MWCNT.
4.2.6 Summary

The morphologies of the carbon fillers and PET/carbon composites were investigated in this section using SEM and TEM. Both cryogenic and tensile fractures surfaces were investigated at different loading of carbon fillers. The graphite morphologies consisted of large platelets whereas GNP appeared to be more fine platelets. The A-MWCNT found to be highly entangled, however; acid treatment shortened the tubes and reduced entanglement and removed residual catalyst particles. In general, the morphologies of PET/carbon composites determined from cryogenically-fractured specimens showed a higher agglomeration and poorer distribution of conductive fillers into the PET around their percolation thresholds values, resulting in the formation of electrically-conductive networks. Similarly, the tensile fracture surfaces showed agglomeration, debonding, rolling up of GNP platelets, and pulling out of fillers at higher loadings, which may compromise the tensile strength of these composites. Moreover, all composite samples exhibited more brittle fracture surfaces in comparison to the PET matrix. Furthermore, in the case of the acid-treated CNT, better dispersion and distribution were achieved compared to the as-received CNT. This is because of the reduction in entanglement and the attachment of functional groups caused by such treatments.

4.2.7 References


4.3 Thermal Behaviour of PET/Carbon Composites

4.3.1 Introduction

Studying thermal behaviour of polymer/carbon composites is essential to understanding their thermal stability and the capability of carbon fillers to act as nucleating agents. In spite of the fact that the crystallization behaviour of polymers strongly depends on their molecular weight, there are some external factors that could also affect the crystallization and degree of crystallinity including; cooling rate and the addition of fillers into polymer matrices [1]. The aim of this section is to show the effect of cooling rate on crystallization of compression moulded PET. It includes slow cooling and rapid quenching into ice water. In addition, the effect of incorporating conductive carbon fillers as describe earlier into PET is explored. Furthermore, the effect of those fillers on the thermal stability of the PET matrix and the composites will be investigated.

DSC and TGA are thermal analysis techniques, widely utilized to study crystallization behaviour and thermal stability of polymers and composites. In order to reduce the effect of oxidative degradation, DSC scans were conducted under nitrogen atmosphere, however both nitrogen and air atmospheres were used in TGA analysis to examine thermal and thermo-oxidative degradations of pure PET and PET/carbon composites, (experimental procedures were described in Section 3.5.4, Chapter 3). Section 4.3.2.1 presents the effect of cooling rate on the crystallization behaviour of PET, while Sections 4.3.2.2 to 4.3.2.5 will cover the respective influence of graphite, GNP, A-MWCNT and T-MWCNT on crystallization behaviour of PET. Section 4.3.3 covers the thermal stability of pure PET, carbon fillers and PET/carbon composites. Finally, Section 4.3.4 presents a summary of this part of the study.
4.3.2 Crystallization Behaviour of PET

4.3.2.1 Effect of Cooling Rates

Figure 4.3.1(a) shows the first heating DSC data curves for quenched and slow-cooled PET samples obtained at a heating rate of 10 °C/min, in which the main thermal events (cold crystallization, melting and melt-crystallization) can be observed. Peak temperatures for cold crystallization, melting and melt crystallization were recorded as cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), and melt-crystallization temperature ($T_{mc}$), respectively. The glass transition temperature ($T_g$) was determined as mid-point from the endothermic baseline shift by extrapolation of baselines. A summary of all data obtained during the heating and the cooling runs is presented in Table 4.3.1.

Amorphous PET is capable of crystallization when heated above its $T_g$. This is commonly known as cold crystallization behaviour. The initial morphological state of a PET sample is a controlling parameter of crystallization behaviour. The quenching process significantly inhibits crystallisation (and can produce essentially low crystallinity or amorphous PET samples) since too little time is allowed for crystallization to occur. The PET molecular chains therefore remain arranged in a disordered manner. Quenched PET samples absorb energy when reheated and exhibit a cold crystallization peak (see Figure 4.3.1(a)). However, when the molten PET sample is cooled slowly, enough time is permitted for its molecular chain segments to arrange themselves in ordered regions resulting in a crystalline phase. The slow-cooled PET sample therefore exhibits only melting endotherms during reheating. In addition, no glass transition baseline shift can be observed in the slow-cooled PET sample. This is due to the reduction in volume fraction of amorphous phase and to the fact that DSC is not a sensitive technique for the detection of the glass transition [2]. The quenched PET sample was chosen for further analysis because it is ductile compared to slow-cooled sample which is brittle, especially when fillers are added to it.
Figure 4.3.1(b) shows the exothermic melt crystallization peaks of both PET samples (quenched and slow-cooled). As can be seen from this figure, $T_{mc}$ for the quenched PET sample is lower than of the slow-cooled sample, indicating that the rate of cooling impacts on the melt crystallization behaviour of PET.

![DSC curves of PET samples subjected to heat-cool-heat cycle; (a) first heating run (b) cooling run, both heating and cooling rate of 10 °C /min.](image)

The rapid cooling rate retains the molecular chains as randomly orientated so that such chains require a high degree of super-cooling ($\Delta T$) to crystallize during the melt-crystallization process. $\Delta T$ is defined as $\Delta T = T_m - T_{mc}$ at a given cooling rate. $\Delta T$ reflects the rate of crystallisation, usually lower $\Delta T$ values indicates a higher rate of crystallization [3, 4].

The % degree of crystallinity ($X_c$) of PET and its carbon composite was calculated from the first-heat data as these data reflect the thermal history of the PET/carbon composites. The initial $X_c$ (of the specimen placed in the DSC) can be calculated using the enthalpies of both crystallization and melting, according the following Equation [5, 6]:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{(1-w_f)\Delta H_o} \times 100 \quad \text{------------------------ (4.2)}$$

Where $\Delta H_m$ is the melting enthalpy (J/g) measured in the heating experiments, $\Delta H_{cc}$ is the cold crystallization enthalpy (J/g), $\Delta H_o$ is the theoretical enthalpy of 100 % crystalline PET ($\Delta H_o=140$ J/g) [7, 8] and $w_f$ is the weight fraction of carbon fillers.
From Table 4.3.1, it can be seen that the $X_c$ for the quenched PET sample is about 11.8%, which is in agreement with the value reported by Santoro et al. [9] for a quenched PET sample. Whilst for the slow-cooled sample ~31.0% crystallinity is calculated according to Equation 4.2. This difference in $X_c$ between the two PET samples is not surprising. This can be explained by the fact that the quenching of the PET greatly decreased the time available for its chains to crystallize; hence the amorphous state was frozen immediately from the molten state. In contrast, the slow cooling rate provided sufficient time for significant crystalline regions to form in the PET matrix, hence the higher $X_c$ value. Similar crystallization behaviour has been reported by Kalaitzidou et al. [10] who investigated the effect of cooling rate on the crystallization behaviour of PP nanocomposites.

**Table 4.3.1 DSC results of the first heating and cooling runs for PET samples**

<table>
<thead>
<tr>
<th>PET Samples</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_{mc}$ (°C)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly-cooled</td>
<td>76.8 ± 0.6</td>
<td>---</td>
<td>252.9 ± 1.2</td>
<td>213.3 ± 0.2</td>
<td>31.0 ± 0.6</td>
</tr>
<tr>
<td>Quenched</td>
<td>72.9 ± 1.2</td>
<td>133.6 ± 0.1</td>
<td>253.4 ± 0.4</td>
<td>209.2 ± 0.1</td>
<td>11.8 ± 1.8</td>
</tr>
</tbody>
</table>

Figure 4.3.2 displays the second heat DSC data for both quenched and slow-cooled PET samples. As can be seen from this figure, both PET samples now show similar DSC curves. No cold crystallization is visible and both samples show a double melting peak. This double peak behaviour is a well-known phenomenon for many semi-crystalline polymers [11-15] which have been subjected to similar treatments as in this study, i.e. recording of DSC curves after removing of its thermal history. This phenomenon, which is associated with a melting-recrystallization-melting effect, has been investigated extensively and attributed to the formation of crystals with different degrees of perfection. Previous studies proposed the formation of crystals with different lamellar thicknesses that form during the crystallization from the melt. For instance, thin and thick lamellar have different melting points. The most
Important factor that controls thickness of lamellar is the crystallization temperature, and lamellar thickness increases with increasing of $T_{mc}$ [16].

Furthermore, $T_m$ values recorded from the second heating runs are lower than those values recorded from the first heating cycles for both PET samples as can be seen in Figures 4.3.1, 4.3.2 and Tables 4.3.1 and 4.3.2. This is because, in a second heating run, the sample was cooled slowly ($10 \, ^\circ\text{C/min}$) allowing more time for crystals to rearrange significantly; on the other hand, $X_c$ increased for both samples (Table 4.3.2) which indicates that PET crystallized during heating treatment in the DSC.

![Second heating DSC curves of PET samples at a heating rate of 10 °C/min.](image)

The curves show the double peak or shoulder but the $T_m$ taken from DSC machine is a single value of $\sim 245 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>PET Samples</th>
<th>$T_m$ (°C)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly cooled</td>
<td>$245.7 \pm 0.4$</td>
<td>$49.0 \pm 2.9$</td>
</tr>
<tr>
<td>Quenched</td>
<td>$246.0 \pm 0.9$</td>
<td>$31.1 \pm 1.7$</td>
</tr>
</tbody>
</table>
4.3.2.2 Effect of Graphite

Pure PET and its microcomposites with varying concentration of synthetic graphite (2, 5, 10, 15 and 20 wt. %) were subjected to a heat-cool-heat cycle at 10 °C/min in the DSC. The DSC curves in Figure 4.3.3(a) – (d) show a range of peaks; cold crystallization peaks ($T_{cc}$), melting peaks from the first heating scans ($T_m$), melt crystallization peaks during cooling ($T_{mc}$) and the melting peaks from second heating scans of the PET/graphite microcomposites. The data derived from these curves are summarized in Table 4.3.2.

The incorporation of graphite into the PET matrix is seen to significantly affect crystallization behaviour. As can be seen from Figures 4.3.3(a), 4.3.3(c) and Table 4.3.3, the $T_{cc}$ values decrease with the addition of graphite in PET microcomposites; decreasing by $\approx 11$ °C at 2 wt. % graphite loading and by $\approx 22$ °C at 20 wt. %, indicating that cold crystallization of PET in the graphite composites is nucleated at a lower temperature than in the pure PET matrix. Moreover, $T_{mc}$ of the PET/graphite composites increased from $\approx 209$ °C to $\approx 223$ °C as graphite content increased from 0 to 20 wt. %. The degree of super-cooling ($\Delta T$) decreased with increasing of graphite concentration, from $\approx 44$°C for pure PET to $\approx 36$ °C for PET composites containing 2 wt. % of graphite content and to $\approx 30$ °C for those with 20 wt. %.

All observations here indicate clearly that graphite acts as a strong nucleating agent, ascribed to the fact that graphite is well known to interact with PET repeat units [17, 18], causing restrictions in their movement and ultimately resulting in heterogeneous nucleation. Incorporation of > 2wt.% graphite results only in a relatively small shift in the crystallization temperatures, indicating that in this study 2 wt. % loading of graphite is the optimum loading for graphite to act as a nucleating agent for the PET matrix.
Typically, an efficient nucleating agent reduces the energy required for nucleation and hence accelerates the crystallization process [19]. Furthermore, both the cold and melt crystallization peaks (Figure 4.3.3(a) and (c), respectively) show that the crystallization peaks of the PET/graphite microcomposites are getting broader with increasing graphite content. This could be due to a broadening of the crystal size distribution as a result of heterogeneous nucleation. Heterogeneous nucleation of PET with carbon fillers is well known, and has been
reported for the carbon fillers such as CNT, graphite, GNP and carbon black (CB) [5, 17, 19, 20]. For example, Xin et al. [17] reported an increase of 11 °C in the T_{nc} of pure PET with a loading of 5 wt. % graphite.

The nucleation process is also reflected in the X_{c} values obtained after quenching (Table 4.3.3). Values of X_{c} were calculated from the first heating cycles using Equation 4.2 as these values reflect the thermal history of the PET/graphite microcomposites. X_{c} was found to increase upon adding graphite; from \approx 12 to \approx 16\% at addition levels up to 10 wt. \%, rising to \approx 20\% upon addition of 15 - 20 wt. \% of graphite. Similar enhancement in X_{c} values have been reported for poly(vinylidene fluoride) (PVDF)/graphite composites [21], PP/graphite composites [22] and PET/graphite composites [17]. However, Xin [17] found that the X_{c} of PET decreased when the loading of graphite exceeded 10 wt. \%. They attributed this decrease to the barrier effect of graphite, via which graphite obstructs crystal growth.

Incorporating graphite into the PET matrix seems to have no appreciable effect on T_{m} values, which stay essentially constant at 254 ±1 °C (Figure 4.3.3(b) and (d), Table 4.3.3). Similar results have been reported for PET/carbon composites; such as PET/GNP nanocomposites [5], PET/MWCNT nanocomposites [9, 23-25] and PET/SWCNT nanocomposites [26, 27].

In addition, the melting-recrystallization-melting effect (leading to twin melting peaks) was found to disappear upon adding graphite into the PET matrix (Figure 4.3.3(d)), indicating more uniform sized crystals formation caused the filler. Values of T_{g} were found to be unaffected by incorporation graphite up to 10 wt. \% loading. However, at 15 wt. \% which is above the percolation threshold value of 14.7 wt. \% (see Section 4.1.6), T_{g} values drop by nearly 8 °C, to \approx 65 °C. The T_{g} of polymers was found to be dependent on the free volume that is available for the movement of polymer chains [1, 16]. The free volume has a critical value which defines the T_{g}, because this facilitates the chains segmental motion. Thus, high graphite content may have influence on free volume which is indicative of reduction in T_{g} of
composites. However, the interactions between carbon fillers and a PET matrix have been reported to give a decrease [25, 28], increase [29] or no change [5, 9] in the T_g of the composites [5, 9, 25]. The reduction in the T_g values of the PET/graphite composites could also be attributed to a poor affinity of graphite for the PET matrix, as its loading is increased [18].

Table 4.3.3 DSC data for PET/graphite microcomposites

<table>
<thead>
<tr>
<th>Graphite (wt. %)</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>T_m (°C) *</th>
<th>T_m (°C) **</th>
<th>T_mc (°C)</th>
<th>X_c (%) ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>72.9 ±1.2</td>
<td>133.6 ±0.1</td>
<td>253.4 ±0.4</td>
<td>245.9 ±0.9</td>
<td>209.2 ±0.1</td>
<td>11.8 ±1.8</td>
</tr>
<tr>
<td>2</td>
<td>73.9 ±0.1</td>
<td>122.6 ±0.5</td>
<td>254.4 ±0.9</td>
<td>249.1 ±0.1</td>
<td>218.1 ±0.8</td>
<td>15.9 ±2.0</td>
</tr>
<tr>
<td>5</td>
<td>74.2 ±0.1</td>
<td>120.5 ±1.5</td>
<td>254.9 ±1.0</td>
<td>249.2 ±0.4</td>
<td>220.5 ±0.5</td>
<td>15.6 ±1.6</td>
</tr>
<tr>
<td>10</td>
<td>73.8 ±0.1</td>
<td>119.1 ±0.5</td>
<td>253.5 ±1.7</td>
<td>249.8 ±0.2</td>
<td>220.1 ±0.4</td>
<td>15.8 ±2.0</td>
</tr>
<tr>
<td>15</td>
<td>65.0 ±0.5</td>
<td>116.5 ±0.1</td>
<td>253.7 ±1.0</td>
<td>249.9 ±0.4</td>
<td>221.2 ±0.2</td>
<td>19.8 ±1.1</td>
</tr>
<tr>
<td>20</td>
<td>64.1 ±0.1</td>
<td>111.6 ±0.7</td>
<td>253.0 ±0.9</td>
<td>250.5 ±0.2</td>
<td>223.4 ±0.1</td>
<td>21.3 ±2.8</td>
</tr>
</tbody>
</table>

* Melting temperatures obtained from the first heating scans
** Melting temperatures obtained from the second heating scans
*** Crystallinity after quenching (X_c=X_m-X_cc), where X_m is degree of crystallinity associated with melting processes and X_cc is degree of crystallinity associated with cold crystallization process.

Graphite agglomerates were observed in the PET matrix at higher loadings using SEM (Section 4.2). A reduction in T_g upon addition of 10 wt.% of expanded graphite into a phenylethyny-terminated polyimide matrix (PETI-5) was reported, that was attributed to a poor dispersion (partially agglomerated) in these PETI-5/graphite microcomposites [30].

4.3.2.3 Effect of GNP

DSC was also used to investigate the effect on the PET matrix of the addition of various loadings (2, 4, 6, 8 and 10 wt. %) of graphite nanoplatelets (GNP) on the crystallization
behaviour of PET, with the aim of comparing their effect on the thermal properties of the PET matrix as compared to the micro-sized filler, graphite. The DSC curves of the PET/GNP nanocomposites in figure 4.3.4 (a) – (d) show the same range of peaks as in figure 4.3.3, and the data obtained from these curves are shown in Table 4.3.4.

**PET/GNP Nanocomposites**

![DSC curves](image)

Figure 4.3.4 DSC curves (heating/cooling rate 10 °C/min) for PET/GNP nanocomposites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan.

The addition of 2 wt. % GNP into PET causes a reduction in $T_{cc}$ from $\approx 134$ °C to $\approx 120$ °C, followed by gradual decrease with further loadings. As $T_{cc}$ of $\approx 114.7$ °C were recorded at
8 wt. % and 10 wt. % loadings (Figure 4.4.3(a)), indicating the acceleration of the cold crystallization of PET matrix. Furthermore, during the cooling scan (Figure 4.3.4(c)), the PET/GNP nanocomposites exhibited approximately 10 °C higher crystallization temperatures than pure PET (Table 4.3.2) and $\Delta T$ decreased with increasing of GNP concentration, from $\approx 44^\circ C$ for pure PET to 34 °C for PET nanocomposites containing 2 wt. % of GNP content and $\approx 31 ^\circ C$ for those with 10 wt.% . It should be noted that a small change was observed for $T_{cc}$, $T_{mc}$ and $\Delta T$ at loadings higher than 2 wt. % of GNP. This suggests that both the cold and melt crystallization processes of PET were improved significantly, due to the nucleating effect of GNP, such an effect is in agreement with previous work [10, 31]. Moreover, GNP addition is found to affect the $X_c$ of PET as shown in Table 4.3.4, with an improvement of around 7.5 % in the degree of crystallinity upon addition of 2 wt. % of GNP. However, further addition of GNP does not seem to exhibit any appreciable change in $X_c$ values. Similar behaviour was observed by Al-jabareen [5], who studied PET/GNP nanocomposites, and reported an improvement of 4 % in $X_c$ at 1.5 wt. % GNP loading. In contrast, in other study it was reported that GNP did not affect the $X_c$ of a PP matrix, although the rate of crystallization and the number of nucleation sites grew with increasing GNP loading [10].

The addition of GNP into the PET matrix seems to have no appreciable effect on $T_m$ values within the loading range used (Table 4.3.4). On the other hand, a slight reduction of $T_g$ was observed for PET/GNP nanocomposites at all loadings used compared to pure PET. A reduction of $T_g$ has been reported for graphitic nanofillers into PMMA by Ramanathan et al [32]. Other authors observed an enhancement in $T_g$ values at 2 wt. % and 5 wt. % for EG and GNP respectively, but upon further addition observed reduction in the $T_g$ values. This has been attributed to poor interactions between PMMA and the GNP. Comparative values of $T_m$ from two heating cycles are shown in Figures 4.3.4(b) and (d).
Table 4.3.4 DSC data for PET/GNP nanocomposites

<table>
<thead>
<tr>
<th>GNP (wt. %)</th>
<th>T_g (°C)</th>
<th>T_cc (°C)</th>
<th>T_m (°C)*</th>
<th>T_m (°C)**</th>
<th>T_mc (°C)</th>
<th>X_c (%)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>72.9 ± 1.2</td>
<td>133.6 ± 0.2</td>
<td>253.4 ± 0.4</td>
<td>245.9 ± 0.9</td>
<td>209.2 ± 0.1</td>
<td>11.8 ± 1.8</td>
</tr>
<tr>
<td>2</td>
<td>68.1 ± 0.9</td>
<td>120.1 ± 0.3</td>
<td>253.8 ± 0.5</td>
<td>247.1 ± 1.0</td>
<td>220.0 ± 0.2</td>
<td>19.3 ± 0.3</td>
</tr>
<tr>
<td>4</td>
<td>68.3 ± 0.4</td>
<td>118.8 ± 0.7</td>
<td>251.5 ± 0.4</td>
<td>248.3 ± 1.7</td>
<td>219.9 ± 0.2</td>
<td>19.6 ± 2.4</td>
</tr>
<tr>
<td>6</td>
<td>67.2 ± 0.1</td>
<td>116.6 ± 0.2</td>
<td>251.2 ± 1.0</td>
<td>248.8 ± 0.5</td>
<td>220.7 ± 0.4</td>
<td>21.1 ± 1.3</td>
</tr>
<tr>
<td>8</td>
<td>67.3 ± 0.4</td>
<td>114.7 ± 0.3</td>
<td>251.9 ± 1.4</td>
<td>249.2 ± 0.3</td>
<td>220.9 ± 0.7</td>
<td>22.0 ± 1.8</td>
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<tr>
<td>10</td>
<td>67.8 ± 0.5</td>
<td>114.7 ± 1.2</td>
<td>251.5 ± 0.4</td>
<td>249.3 ± 0.5</td>
<td>220.7 ± 0.6</td>
<td>22.4 ± 0.6</td>
</tr>
</tbody>
</table>

* Melting temperatures obtained from the first heating scans

** Melting temperatures obtained from the second heating scans

*** Crystallinity after quenching (X_c = X_m - X_cc), where X_m is degree of crystallinity associated with melting processes and X_cc is degree of crystallinity associated with cold crystallization process.

It can be noted that the values of T_m obtained from the second heating scans are lower than the first heating run for all PET/carbon composites. In addition, incorporation of GNP makes the smaller crystals sizes with homogeneity as indicated by narrowing of melting peaks (see Figure 4.3.5(d)). Moreover, the double melting peak disappeared; this indicates uniformly sized crystal formation caused by the filler loadings. Similar observations were reported by Kalaitzidou et al, [10] who studied the nucleation effects and crystallization behaviour of PP/GNP nanocomposites. They observed that GNP altered the melting behaviour of PP. The authors attributed this behaviour to the increased overall homogeneity and thinning of crystal size.

4.3.2.4 Effect of A-MWCNT

PET/A-MWCNT nanocomposites with different loadings (0.1, 0.2, 0.4, 1 and 2 wt. %) of MWCNT were investigated using DSC. The DSC curves in Figure 4.3.5(a) – (d) show a
range of peaks; cold crystallization peaks, melting peaks from the first heating scans, melt crystallization peaks during cooling and the melting peaks from the second heating scans of the PET/PET/A-MWCNT nanocomposites.

**Figure 4.3.5** DSC curves (heating/cooling rate 10 °C/min) for PET/A-MWCNT nanocomposites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan.

The corresponding data for thermal properties is presented in Table 4.3.5. It is clear that the cold crystallization peaks shift to lower values upon the addition of A-MWCNT; i.e. $T_{cc}$ decreased from 133.6 °C for pure PET to 122.2 °C for nanocomposites at 0.1 wt. % A-
MWCNT as shown in Figure 4.3.5(a) and Table 4.3.5. However, further addition of the nanofiller does not bring a significant change in the values of $T_{cc}$. Similarly, the melt crystallization peaks (Figure 4.3.5(c)) shifted by $\approx 10 \, ^\circ C$ higher than pure PET at similar loading of 0.1 wt. % of A-MWCNT, while further CNT addition does not affect $T_{mc}$ values. The $\Delta T$ values decreased from $\approx 44 \, ^\circ C$ for pure PET to $\approx 34 \, ^\circ C$ for PET composites containing 0.1 wt. % of A-MWCNT content followed by no significant change; this indicates that A-MWCNT promote heterogeneous nucleation during the process of crystallisation at very low concentrations. These observations are in agreement with the previous work of Tzavalas et al, [13] who reported about a 12 $^\circ C$ increment in $T_{mc}$ of pure PET at same loadings of MWCNT (0.1wt.%). Another similar study was conducted on poly (ethylene 2,6-naphthalate)/MWCNT nanocomposites by Kim [33], who also observed a 7 $^\circ C$ reduction in $T_{cc}$ and a 22$^\circ C$ increase in $T_{mc}$ after addition of 0.1 wt. % MWCNT.

It is interesting to note that when the content of A-MWCNT increased to around the percolation threshold value ($\Phi_c = 0.33$ wt. %, see Section 4.1.6); CNT do not affect the $T_{mc}$ of the PET nanocomposites. This is due to aggregation and poor distribution of A-MWCNT in the PET matrix. Moreover, the data also indicate that 0.1 wt. % loading of A-MWCNT shows a strong heterogeneous nucleation effect. Similar effect have also been widely reported in the literature that CNT are efficient polymer crystals nucleating agents [33]. Similar results have been reported by Zhu [25], who observed an increase in $T_{mc}$ values up to 0.4 wt. % of MWCNT, after which little change in $T_{mc}$ was observed. They attributed this behaviour to the presence of aggregates of entangled CNT within the PET matrix.

Furthermore, it can be observed that crystallization peaks become broader upon further addition of A-MWCNT (Figure 4.3.5 (a) and 4.3.5(c)). This behaviour could be due to a broadening of the lamellar thickness distribution as a result of heterogeneous nucleation. This behaviour is in agreement with the study of Tzavalas et al, [13] who observed an
increase in the broadening of crystallization peaks with increasing concentration of MWCNT into PET. The authors attributed this increment to a wider distribution lamellar thickness. The incorporation of A-MWCNT into the PET matrix has had little effect on the $T_g$ and $T_m$ of the PET/A-MWCNT nanocomposites (see Table 4.3.5 and Figure 4.3.5). These observations agree with previous published studies that reported similar behaviour for PET/MWCNT [4, 9], PET/SWCNT [26] and pol(ethylene 2.6-naphalate)/MWCNT nanocomposites [33].

The influence of A-MWCNT on $X_c$ was investigated as shown in Table 4.3.5. $X_c$ was found to increase upon adding A-MWCNT; from $\approx 12$ to $\approx 17\%$ at addition levels up to 0.1 wt. %, rising to $\approx 19.5\%$ upon addition of 0.2 wt. % of A-MWCNT, thereafter further addition gave only slight enhancement. Similar observations were made by Santoro et al. [9] who reported an improvement of $X_c$ by $\approx 10\%$ at 1 wt. % of MWCNT. In another study on PP/MWCNT composites, Pollatos et al. [34] observed slight increases in $X_c$ values (from 19.4 % for PP to 21.3 for nanocomposites at 5 wt. % MWCNT) with increasing CNT content. However, another study conducted by Xin et al. [17] reported a reduction of $X_c$ for PET/MWCNT nanocomposites. The authors argued that the carbon particles act as barriers, hence retarding crystals growth although the filler particles could act as heterogeneous nuclei.

Thus, crystallization behaviour of the PET based composites is more strongly influenced by the incorporation of small concentrations of MWCNT than of graphite and GNP. In addition, the melting peaks appeared narrower compared with PET and the double melting peak disappeared; this indicates uniformly sized crystal formation caused by the filler loadings and crystal refinement by serving as nucleating agent. Therefore, it is suggested that MWCNT promote the formation of better quality crystals for polymer nanocomposites [34] that is noticed by the appearance of only one melting peak in the PET/MWCNT nanocomposites.
Table 4.3.5 DSC results of PET/A-MWCNT nanocomposites

<table>
<thead>
<tr>
<th>A-MWCNT (wt. %)</th>
<th>T&lt;sub&gt;e&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;cc&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;* (°C)</th>
<th>T&lt;sub&gt;mc&lt;/sub&gt; (°C)</th>
<th>X&lt;sub&gt;c&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>72.9 ± 1.2</td>
<td>133.6 ± 0.2</td>
<td>253.4 ± 0.4</td>
<td>245.9 ± 0.9</td>
<td>209.2 ± 0.1</td>
<td>11.8 ± 1.8</td>
</tr>
<tr>
<td>0.1</td>
<td>73.8 ± 0.4</td>
<td>122.2 ± 0.9</td>
<td>253.6 ± 0.3</td>
<td>249.5 ± 0.3</td>
<td>219.3 ± 0.6</td>
<td>16.9 ± 0.5</td>
</tr>
<tr>
<td>0.2</td>
<td>73.8 ± 0.8</td>
<td>119.8 ± 0.1</td>
<td>254.3 ± 0.7</td>
<td>250.3 ± 0.6</td>
<td>221.0 ± 0.2</td>
<td>19.5 ± 1.4</td>
</tr>
<tr>
<td>0.4</td>
<td>72.9 ± 0.5</td>
<td>118.8 ± 0.4</td>
<td>252.2 ± 0.8</td>
<td>249.6 ± 0.4</td>
<td>221.5 ± 0.5</td>
<td>20.4 ± 1.5</td>
</tr>
<tr>
<td>1.0</td>
<td>73.3 ± 0.5</td>
<td>116.6 ± 0.7</td>
<td>254.5 ± 2.0</td>
<td>251.3 ± 0.4</td>
<td>220.7 ± 0.5</td>
<td>23.4 ± 0.7</td>
</tr>
<tr>
<td>2.0</td>
<td>73.1 ± 0.2</td>
<td>118.3 ± 2.0</td>
<td>253.1 ± 0.2</td>
<td>250.4 ± 0.5</td>
<td>219.6 ± 0.3</td>
<td>22.5 ± 1.8</td>
</tr>
</tbody>
</table>

* Melting temperatures obtained from the first heating scans

** Melting temperatures obtained from the second heating scans

*** Crystallinity after quenching (X<sub>c</sub>=X<sub>m</sub>-X<sub>cc</sub>), where X<sub>m</sub> is degree of crystallinity associated with melting processes and X<sub>cc</sub> is degree of crystallinity associated with cold crystallization process.

4.3.2.5 Effect of T-MWCNT

The influence of the incorporation of T-MWCNT into the PET matrix on the crystallization and melting process were investigated in this section. For comparative analysis, identical loadings of both A-MWCNT (Section 4.3.2.4) and T-MWCNT into PET are presented. Figure 4.3.6 (a)-(d) shows cold crystallization and melting peaks of the first heating scan, melt crystallization during cooling and melting peaks of the second heating scan of the nanocomposites, respectively. The heating and cooling rate of 10 °C/min was set for DSC observations of PET/T-MWCNT nanocomposites and corresponding data is presented in Table 4.3.6. Incorporating T-MWCNT into the PET matrix seems to have no significant effect on values of T<sub>m</sub>, but T<sub>e</sub> values decreased very slightly (~ 2.5 °C) in comparison to the pure PET matrix (Table 4.3.6). Similar results have been observed for poly(trimethylene terephthalate) (PTT) and polyethylene naphthalate (PEN) nanocomposites containing acid-treated MWCNT [33, 35].
Figure 4.3.6 DSC curves (heating/cooling rate 10 °C/min) for PET/T-MWCNT nanocomposites; showing cold crystallization peaks (a), melting peaks from the first scan (b), subsequent cooling curves (c) and melting peaks from the second heating scan.

This could be due to in fact that the degree of crystallization decreased. Yesil et al. [6] reported a similar decrease in values of $T_g$ (~ 2 %) for PET nanocomposites containing 0.5 wt. % acid treated-MWCNT and attributed this reduction to the plasticizing effect of the surface modification of the MWCNT. However; These results are in contrast to observations of Kim and co-workers [29] who observed an improvement of $T_g$ values from 84.4 °C to 90.4 °C for a PET matrix and nanocomposites containing 0.1 wt. % T-MWCNT, respectively.
This was followed by a gradual increase to 92.0 °C for nanocomposites at 2 wt. % loading of MWCNT. The authors attributed such improvement to the hindrance of the segmental motion of PET chain. The cold crystallization temperature, $T_{cc}$, of the matrix reduced from 133.6 °C to 126.1 °C at a loading of 0.1 wt. % T-MWCNT and remained more or less unchanged upon further addition (Figure 4.3.6 (a) and Table 4.3.6). Furthermore, the melt crystallisation behaviour was found to be accelerated ~ 8 °C by addition a small quantity of the filler as shown in Figure 4.3.6(c) and Table 4.3.6. Also, $T_{mc}$ exhibited forward trend upon further addition, suggested that a small amount of T-MWCNT as nucleating agent. These results agree with previous works on PET/T-MWCNT and PTT/T-MWCNT nanocomposites [28, 29, 35]. The PET/T-MWCNT nanocomposites also have lower $\Delta T$ values, which decreased from $\approx 44^\circ$C for pure PET to $\approx 37^\circ$C for all PET nanocomposites. Similar $\Delta T$ results were observed by Kim et al, [29] who reported that $\Delta T$ decreased from $\approx 61^\circ$C to $\approx36^\circ$C for all nanocomposites. These results indicate that T-MWCNT can effectively serve as a nucleating agent similar to other carbon fillers. However, T-MWCNT are not more effective for enhancing crystallization rate and crystallinity of the PET matrix than A-MWCNT; as the $\Delta T$ values of PET/A-MWCNT nanocomposites are lower than the T-MWCNT nanocomposites at identical loadings. Moreover, all PET/T-MWCNT nanocomposites showed slight improvement of about 5 % in $X_c$, while $X_c$ rose with increasing A-MWCNT content. Such behaviours are due to the acid treatment that reduces the length and aspect ratio of the A-MWCNT. In addition, strong attraction can occur between the ester groups (-C=O) of PET matrix and functional groups such as carboxylic acids (-COOH) on the surface of MWCNT attached by acid treatment. These strong attractions hinder the motion of PET chains and retard the crystallization process, resulting in lower $X_c$ values compared with to the A-MWCNT nanocomposites. Similar crystallization behaviour has been reported for PET/acid treated MWCNT nanocomposites [24, 29] as well as for PA6/acid treated MWCNT
nanocomposites [36]. In these studies, the authors attributed this behaviour to strong interactions between the fillers and matrices. Hence it emerges here that CNT hinder the motion of polymer chains, restricting the crystal growth, and consequently retarding crystallization.

**Table 4.3.6 DSC results of PET/ T-MWCNT nanocomposites.**

<table>
<thead>
<tr>
<th>T-MWCNT (Wt. %)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_{cc}$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)$^*$</th>
<th>$T_m$ ($^\circ$C)$^{**}$</th>
<th>$T_{mc}$ ($^\circ$C)</th>
<th>$X_c$ (%)$^{***}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>72.9 ± 1.2</td>
<td>133.6 ± 0.2</td>
<td>253.4 ± 0.4</td>
<td>245.9 ± 0.9</td>
<td>209.2 ± 0.1</td>
<td>11.8 ± 1.8</td>
</tr>
<tr>
<td>0.1</td>
<td>70.6 ± 1.2</td>
<td>126.1 ± 0.1</td>
<td>254.2 ± 1.3</td>
<td>247.1 ± 0.3</td>
<td>217.4 ± 0.7</td>
<td>15.8 ± 0.4</td>
</tr>
<tr>
<td>0.2</td>
<td>70.2 ± 0.2</td>
<td>125.4 ± 0.6</td>
<td>253.3 ± 1.1</td>
<td>247.5 ± 0.2</td>
<td>217.8 ± 0.5</td>
<td>15.1 ± 0.5</td>
</tr>
<tr>
<td>0.4</td>
<td>69.8 ± 0.3</td>
<td>123.2 ± 0.2</td>
<td>255.7 ± 0.1</td>
<td>247.3 ± 0.5</td>
<td>218.7 ± 0.4</td>
<td>16.6 ± 0.4</td>
</tr>
<tr>
<td>1.0</td>
<td>70.2 ± 0.2</td>
<td>123.3 ± 0.6</td>
<td>253.8 ± 1.6</td>
<td>247.1 ± 0.4</td>
<td>218.6 ± 0.1</td>
<td>16.3 ± 0.6</td>
</tr>
<tr>
<td>2.0</td>
<td>71.4 ± 0.2</td>
<td>121.5 ± 0.1</td>
<td>255.2 ± 0.3</td>
<td>246.9 ± 0.1</td>
<td>219.0 ± 0.1</td>
<td>16.5 ± 1.0</td>
</tr>
</tbody>
</table>

* Melting temperatures obtained from the first heating scans
** Melting temperatures obtained from the second heating scans

*** Crystallinity after quenching ($X_c = X_m - X_{cc}$), where $X_m$ is degree of crystallinity associated with melting processes and $X_{cc}$ is degree of crystallinity associated with cold crystallization process.

For comparison, the $X_c$ values of all PET/carbon composites at 2 wt. % filler loading were calculated using Equation (4.2) as shown in Figure 4.3.7. In general, $X_c$ values of all composites are higher than the pure PET matrix. In particular, the PET/A-MWCNT nanocomposites showed the highest $X_c$ amongst all the fillers. Additionally, A-MWCNT initiated melt-crystallization earlier than the other fillers used (Figure 4.3.8), due to its high aspect ratio. However, the calculated aspect ratio of the GNP is higher than that of A-MWCNT as discussed earlier, so PET/GNP nanocomposites may be expected to show better $X_c$ values than the PET/MWCNT nanocomposites.
Figure 4.3.7 Crystallinity of PET/carbon composites at 2 wt. % carbon fillers

Figure 4.3.8 Melt-crystallization peaks for PET/carbon composites at 2 wt. % of carbon filler, at the cooling rate of 10°C/min.
One reason is that, during melt mixing the GNP can roll up or fold (see Section 4.2), reducing their aspect ratio [37, 38]. Also, because GNP contains some oxygen-containing functional groups (attained during fabrication) as observed in TGA (Section 4.3.3.1) as well as per supplier specification. In contrast, PET nanocomposites containing T-MWCNT showed lower an $X_c$ value (~ 16.5 %) than A-MWCNT (~ 22.5 %). In this case it is likely that acid treatment has shortened the tubes and reduced their aspect ratios, resulting in lower $X_c$ values. In other cases, it has been reported that $X_c$ of the polymers could be reduced if the fillers act as barrier that hinder crystallization, resulting in lower $X_c$ of the nanocomposites [39].

Generally, low-dimensional fillers such as CNT and GNP provide a stronger nucleating ability for semi-crystalline polymers compared with traditional fillers such as graphite and carbon black [31]. Usually, the crystalline regions provide better mechanical properties than the amorphous. Consequently, for PET/A-MWCNT nanocomposites the higher $X_c$ values imply better mechanical properties than for the PET/T-MWCNT nanocomposites. However; other factors could affect the properties of the final nanocomposites, including dispersion, distribution and polymer-filler interactions resulting in efficient load transfer between the matrix and the filler, giving improved mechanical properties, as reported in the case of PET/T-MWCNT nanocomposites.

**4.3.3 Thermal stability**

The thermal stability of a polymer composite is an important parameter in deciding its application. This section reports the thermal stability of the fillers used and resulting composites. Thermal stability is commonly evaluated by determining the onset of thermal decomposition temperature (IDT) and the temperature at 0.05 (5%) weight loss ($T_{5\%}$). The IDT may be difficult to measure accurately and depends on the sensitivity of balance used for weighing. Thermal stability is also reported as the temperature of thermal decomposition at
which maximum mass loss rate ($T_{\text{max}}$) takes place. $T_{\text{max}}$ can be determined by plotting a derivative graph usually called a derivative thermogravimetry (DTG) curve; that is the rate of mass loss against temperature (%/°C) vs. the experimental temperature (°C). This curve is also useful for materials that exhibit multistep decomposition behaviour [4, 40].

4.3.3.1 Thermal stability of fillers

Figure 4.3.9 (a)-(b) shows TGA curves of graphite, GNP, A-MWCNT and T-MWCNT in nitrogen and air atmospheres, respectively. It can be seen that the thermal behaviour of these carbon fillers is different from each other. Thus, these fillers exhibit higher thermal stability in a nitrogen atmosphere compared to air. In nitrogen, graphite, GNP, A-MWCNT and T-MWCNT showed a total weight loss at 1000 °C of about 5, 20, 20 and 40 wt. % of their initial weight, respectively. Whilst, when they heated in air to the same temperature, they lost about 90 wt. % each as shown in Figure 4.3.9(b). Similar results have been reported for graphite [41], GNP [42], A-MWCNT and T-MWCNT [43] fillers. In particular, graphite is the most stable of all carbon fillers investigated here in air and nitrogen. Figure 4.3.9(b) shows that in air weight loss of graphite becomes evident at 700 °C, followed by a very sharp weight loss. This behaviour is attributed to the formation of carbon dioxide gas [44]. In contrast, the thermal decomposition of GNP in air exhibited three separate mass-loss events. The first one starts at ~ 100 °C, extending to about 350 °C at associated weight loss of nearly 5 wt. % that is due to the loss of moisture and other volatiles. The second event commences at ~ 350 °C and finishes at about 550 °C, with the mass loss of around 25 wt. %. The third event is characterized by higher rates of thermal degradation, as indicated by the slope of TGA curve that is associated by loss of ~ 70 wt. % of GNP. The first and third events are attributed to the degradation of oxygen containing functional groups in GNP that are believed to form during its preparation accompanied by generation of carbon dioxide. Similar groups
have been reported at identical oxidation temperatures for same GNP (grade xGnP-15) [42] same grade that have been used in present study.

From Figure 4.3.9 (b), it is observed that A-MWCNT started to oxidize at ~ 500 °C and lose about ~ 1 wt. % of its initial weight due to the dehydration. This indicates that there is no amorphous carbon in A-MWCNT. After that, a sharp decline was observed accompanied by loss of about 40 wt. %, followed by two overlapping thermal degradation events that are extending from 630 °C to 1000 °C, leaving a residual mass of about 5 wt. %. A similar study conducted by Mahajan et al [45,47] found that the walls of MWCNT started to deteriorate at 500 °C, that was assessed by TEM.

TGA examination of T-MWCNT shows various overlapping weight loss events and it is difficult to assign a starting temperature to each. The T-MWCNT started to decompose at a lower temperature (~200 °C). The lower decomposition temperature is probably related to the removal of functional groups such as hydroxyls and carboxylic acids that formed due to the acid treatment accompanied by generation of carbon dioxide.

Figure 4.3.9 TGA curves of graphite, GNP, A-MWCNT and T-MWCNT in (a) N₂ and (b) air (both at a heating rate of 10 °C/min).
The residual weight is lower than A-MWCNT; which could be due to removal of metal catalysts during acid cutting treatment. Similar behaviour has been reported for acid treated-MWCNT by May et al. [43] and Yudianti et al. [46] who attributed the weight loss from 150 to 350 °C to degradation of functional groups present on the surface of MWCNT due to their acid treatment.

### 4.3.3.2 Thermal stability of PET/carbon composites

Figures 4.3.10 to 4.3.13 show the TGA results collected for all the PET/carbon composites under nitrogen and air atmospheres compared to the neat PET matrix. The results demonstrate no significant weight loss up to ~ 350 °C for all PET composites. As the temperature is increased (> 350°C), the weight loss increased significantly over a narrow temperature range, as seen by the steep slopes (Figure 4.3.10 – 13). However; the onset temperature at which weight loss begins is different as shown by the inset figures. T\textsubscript{5%} for each of the PET/carbon composites is reported in Tables 4.3.7, 4.3.8, 4.3.9, and 4.3.10 for the PET/graphite, PET/GNP, PET/A-MWCNT and PET/T-MWCNT composites, respectively. The mass of residue for each composite is also shown in all figures.

It has been reported that PET generates a large amount of carbonaceous residue in a nitrogen atmosphere [47]. It is noted that the weight of residue for all the composites that were heated under oxidative-degradation conditions is lower than under a nitrogen atmosphere. This could be attributed to high temperature (460 °C – 580 °C) where oxygen reacts with carbon causing further weight loss of composites. Moreover, all the PET/carbon composites under nitrogen exhibit one decomposition step at ~ 380 °C whereas in air they show two decomposition steps. The first step is due to the degradation of PET chains and the second one is associated with thermal degradation of char products that were formed during the first
decomposition step. Similar behaviours have been reported for PET/EG nanocomposites [48] and PET/clay nanocomposites systems [49].

### 4.3.3.2.1 Effect of Graphite

Figure 4.3.10(a) and (b) and Table 4.3.7 show the TGA data for the PET/graphite microcomposites with varying loading of graphite under nitrogen and air atmospheres. The $T_{5\%}$ of pure PET are \(~ 382.3 \, ^\circ\text{C} \text{ and } 370.1 \, ^\circ\text{C}\), in nitrogen and air respectively, and increase to \(~ 392 \, ^\circ\text{C} \text{ and } 384 \, ^\circ\text{C}\) upon 15 wt. % addition of graphite. Moreover, the residual weight of PET is \(~ 9.5 \, \text{wt. } % \) at about 580 \, ^\circ\text{C} in nitrogen, while no residual weight was observed in air. Also, the amount of residue increases with increasing graphite content (see Figures 4.3.10(a)-(b). In general, it has been established that the thermal stability of PET/graphite microcomposites is increased (4 – 9 \, ^\circ\text{C}) in nitrogen and (8 – 18 \, ^\circ\text{C}) in air atmospheres, compared to pure PET. The $T_{5\%}$ value of 368 \, ^\circ\text{C} was recorded at 5 wt. % graphite that differs from rest of loadings, for the time being we have to record this as an anomaly. Graphite has been used in previous studies for the enhancement of thermal stabilities of several polymer matrices.

<table>
<thead>
<tr>
<th>Graphite (wt. %)</th>
<th>N\textsubscript{2}</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{5%}$ (^\circ\text{C})</td>
<td>$T_{5%}$ (^\circ\text{C})</td>
</tr>
<tr>
<td>0</td>
<td>382.3 ±1.4</td>
<td>370.1 ±1.0</td>
</tr>
<tr>
<td>2</td>
<td>389.8 ±0.8</td>
<td>373.1 ± 6.0</td>
</tr>
<tr>
<td>5</td>
<td>387.7 ±0.4</td>
<td>368.0 ±4.3</td>
</tr>
<tr>
<td>10</td>
<td>386.7 ±3.0</td>
<td>372.7 ±2.6</td>
</tr>
<tr>
<td>15</td>
<td>391.7 ±0.5</td>
<td>383.7 ±1.9</td>
</tr>
</tbody>
</table>

Table 4.3.7 Thermal degradation temperatures ($T_{5\%}$) for PET/graphite microcomposites under nitrogen and air atmospheres.
Figure 4.3.10 TGA thermograms (heating rate of 10 °C/min) of PET/graphite microcomposites with various graphite contents examined under (a) nitrogen and (b) air atmospheres.
For example, Otieno et al. [50] studied the thermal behaviour of PU/graphite composites, and reported enhancement of thermal stability by about 20 °C at 50 wt. % loading of graphite. The thermal stability of a HDPE/graphite composite was reported by Wang et al. [51] who found an improvement of only 3 °C with increasing graphite contents up to 50 wt.%. Moreover, the addition of 5 wt. % of graphite was shown to give an enhancement of the $T_{5\%}$ of an epoxy resin [52] by 25 °C under nitrogen.

**4.3.3.2.2 Effect of GNP**

Graphite derivatives such as graphite oxide (GO) and GNP has been used to retard the degradation of polymer matrices. The addition of 10 wt. % of GNP into PET was found to delay the onset of degradation by 11 °C, indicating enhancement of thermal stability of the PET/GNP nanocomposites [5]. The authors attributed this improvement in thermal stability to the two-dimensional planer structure of GNP that acts as barrier.

A similar argument was given by Li et al. [48] who also investigated the thermal stability of PET/GNP nanocomposites in both nitrogen and oxygen atmospheres.

**Table 4.3.8 Thermal degradation temperatures ($T_{5\%}$) for PET/GNP nanocomposites under nitrogen and air atmospheres.**

<table>
<thead>
<tr>
<th>GNP (wt. %)</th>
<th>$N_2$</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{5%}$ (°C)</td>
<td>$T_{5%}$ (°C)</td>
</tr>
<tr>
<td>0</td>
<td>382.3 ±1.4</td>
<td>370.1 ±1.0</td>
</tr>
<tr>
<td>2</td>
<td>391.9 ±1.3</td>
<td>378.2 ±0.5</td>
</tr>
<tr>
<td>6</td>
<td>393.2 ±1.3</td>
<td>384.9 ±3.0</td>
</tr>
<tr>
<td>8</td>
<td>392.3 ±1.1</td>
<td>386.9 ±0.7</td>
</tr>
<tr>
<td>10</td>
<td>393.1 ±0.9</td>
<td>388.5 ±0.1</td>
</tr>
</tbody>
</table>
Figure 4.3.11 TGA thermograms (heating rate of 10 °C/min) of PET/GNP nanocomposites with various GNP contents examined under (a) nitrogen and (b) air atmospheres.
In other studies, thermal stability improvements have been reported for polycarbonate/GNP nanocomposites [42], using the same GNP grade as utilized in this study; and when using PMMA as a matrix [32]. The results of the current study agree with these authors, as in the present work, GNP enhanced thermal stability of PET in nitrogen and air as shown in Figure 4.3.11 (a)-(b). The $T_{5\%}$ values taken from curves for the PET/GNP nanocomposites are also presented in Table 4.3.8, and are higher than the pure PET in both atmospheres, indicating that GNP improved the thermal stability of the PET matrix. The $T_{5\%}$ values for neat PET are $\approx 282.3\,^\circ C$ and $\approx 370.1\,^\circ C$ in nitrogen and air respectively. These values go up to $\approx 392\,^\circ C$ and $\approx 378\,^\circ C$ for the nanocomposites containing 2 wt.% GNP in nitrogen and air, respectively. Further addition of GNP improves the thermal stability of PET composite slightly.

Figure 4.3.11(b) shows thermo-oxidative decomposition curves for the PET/GNP nanocomposites obtained in air. As was noted earlier, that $T_{5\%}$ values of both pure PET and the nanocomposites are lower in air than nitrogen. However; it was also observed that the improvement of $T_{5\%}$ under air in comparison to neat PET is higher than in nitrogen. For the nanocomposites with 10 wt. % GNP, the $T_{5\%}$ values are $388.5\,^\circ C$ and $393.1\,^\circ C$, which are higher than pure PET by $\sim 18\,^\circ C$ and $11\,^\circ C$ in air and nitrogen atmospheres, respectively. The improved thermal stability maybe explained by a barrier effect associated with GNP which hinders the diffusion of oxygen into the PET nanocomposites and diffusion of flammable volatiles out of the nanocomposites. Similar results have been reported for PET/GNP nanocomposites by Li et al, [48] who observed an increase of about $42\,^\circ C$ in $T_{5\%}$ of pure PET at 7 wt.% loading of GNP in oxygen atmospheres and $\sim 3\,^\circ C$ under nitrogen.
4.3.3.2.3 Effect of A-MWCNT and T-MWCNT

Figures 4.3.12 and 4.3.13 show the TGA data for PET nanocomposites containing A-MWCNT and T-MWCNT and their T$_{5\%}$ values are presented in Tables 4.3.9 and 4.3.10, respectively. It can be observed that addition of A-MWCNT caused an improvement in the thermal and thermo-oxidative stabilities of PET matrix based nanocomposites in both environments. However, PET/T-MWCNT nanocomposites showed an enhancement of thermal stability only in nitrogen that is higher than for the PET/A-MWCNT nanocomposites. For example, at 0.1 wt. % loadings in nitrogen, the T$_{5\%}$ of PET/A-MWCNT and PET/T-MWCNT is higher than pristine PET by 5°C and 11°C, respectively. This could be due to the stronger interfacial attraction between the carboxylic acid groups (-COOH) of the T-MWCNT and the ester groups (-C=O) on the PET matrix due to hydrogen bonding. In addition, the presence of the T-MWCNT can lead to stabilisation of PET matrix and may restrict the thermal motion of molecules. These result are in agreement with other studies [29, 53], where an improvement in the thermal stability PET nanocomposites containing acid treated-MWCNT under nitrogen atmosphere was observed. In contrast, other researchers [20, 35] reported that the acid treatment has no effect on the thermal stability of PET/MWCNT and PTT/MWCNT nanocomposites. Moreover, it has been reported that MWCNT can increase thermal stability of polymers because of the high thermal stability of CNT themselves and their ability to readily form aggregates, resulting in a retardation of diffusion of degradation products through the nanocomposites [54]. However, functional groups such as hydroxyl on the surface of MWCNT could accelerate the thermal degradation of the polymer nanocomposites [53, 55].
Figure 4.3.12 TGA thermograms (heating rate of 10 °C/min) of PET/A-MWCNT nanocomposites with various A-MWCNT contents examined under (a) nitrogen and (b) air atmospheres.
Table 4.3.9 Thermal degradation temperatures ($T_{5\%}$) for PET/ A-MWCNT nanocomposites under nitrogen and air atmospheres.

<table>
<thead>
<tr>
<th>A-MWCNT (wt. %)</th>
<th>N₂</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{5%}$ (°C)</td>
<td>$T_{5%}$ (°C)</td>
</tr>
<tr>
<td>0</td>
<td>382.3 ±1.4</td>
<td>370.1 ±1.0</td>
</tr>
<tr>
<td>0.1</td>
<td>387.3 ±2.2</td>
<td>376.9 ±0.8</td>
</tr>
<tr>
<td>0.2</td>
<td>388.8 ±2.3</td>
<td>372.0 ±0.9</td>
</tr>
<tr>
<td>1</td>
<td>389.8 ±2.7</td>
<td>392.5 ±2.2</td>
</tr>
<tr>
<td>2</td>
<td>392.8 ±1.5</td>
<td>390.0 ±1.5</td>
</tr>
</tbody>
</table>

Table 4.3.10 Thermal degradation temperatures ($T_{5\%}$) for PET/T-MWCNT nanocomposites under nitrogen and air atmospheres.

<table>
<thead>
<tr>
<th>T-MWCNT (wt. %)</th>
<th>N₂</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{5%}$ (°C)</td>
<td>$T_{5%}$ (°C)</td>
</tr>
<tr>
<td>0</td>
<td>382.3 ±1.4</td>
<td>370.1 ±1.0</td>
</tr>
<tr>
<td>0.1</td>
<td>392.8 ±0.2</td>
<td>346.5 ±0.8</td>
</tr>
<tr>
<td>0.2</td>
<td>392.7 ±2.3</td>
<td>360.9 ±1.3</td>
</tr>
<tr>
<td>1</td>
<td>390.7 ±0.9</td>
<td>356.5 ±6.4</td>
</tr>
<tr>
<td>2</td>
<td>391.3 ±0.9</td>
<td>351.3 ±2.0</td>
</tr>
</tbody>
</table>

Moreover, comparatively PET/T-MWCNT nanocomposites exhibit lower thermal stability than pure PET when heated in air. Bikiaris et al. [56] reported thermal stability studies of isotactic polypropylene nanocomposites containing acid treated-MWCNT in air and nitrogen atmospheres using different times of acid treatment. The authors concluded that as the time of acid treatment increases, the onset temperature of thermo-oxidative decreases, i.e. producing less thermally stable composites.
Figure 4.3.13 TGA thermograms (heating rate of 10 °C/min) of PET/ T-MWCNT nanocomposites with various T-MWCNT contents examined under (a) nitrogen and (b) air atmospheres.
Therefore, further study on the effect of acid treatments time is recommended to establish the reasons for observed decline in the thermal stability of the PET/T-MWCNT nanocomposites as found in this study.

4.3.4 Summary

The influence of cooling rate and carbon fillers on the thermal behaviour of PET was investigated using DSC and TGA. Cooling rate was found to affect the crystallization behaviour of PET, in which a higher cooling rate results in a reduction of crystallisation. In addition, it was found that quenched PET samples were not fully crystallized after processing and therefore, crystallized during the first heating cycle in DSC, as indicated by presence of a cold crystallization peak.

All the carbon fillers, with different size and morphology, were found to act as nucleating agents for the PET matrix and hence accelerate crystallization. The essentially one dimensional (MWCNT) was found to affect the crystallization at very low loading (0.1 wt. %) compared to the two dimensional (GNP) and three dimensional micro-size filler (graphite) that exhibit similar crystallization behaviour at 2 wt. % loadings.

Acid treatment of MWCNT showed reduction in $X_c$ of PET/T-MWCNT nanocomposites compared to one produced using A-MWCNT. This reduction is attributed to an improvement in the dispersion and adhesion between the PET and the T-MWCNT that retards crystallization hence lowering $X_c$.

In general, the addition of carbon fillers into the PET matrix improved the resistance to thermal and thermo-oxidative degradation in both air and nitrogen atmospheres. However, no clear relationship between such improvement and the amount of fillers used was observed. However, acid-treatment of MWCNT was found to have a negative influence on the thermal stability of the PET nanocomposites in air.
4.3.5 References


4.4 Mechanical Properties of PET/Carbon Composites

4.4.1 Introduction

In this study the mechanical properties of the PET matrix and the PET/carbon composites were studied using DMTA and tensile testing. Specimens for DMTA were cut from compression moulded sheets whereas the dumbbell specimens for tensile testing were injection moulded.

DMTA in single cantilever beam mode was used to study the effect of carbon fillers on the viscoelastic properties of the PET matrix (Sections 4.4.2 - 4.4.6), in particular the storage modulus, tanδ and glass transition temperature (T_g) under controlled cyclic strain (amplitude 10 µm, frequency 1 Hz) and temperature ramp (3 °C /min) conditions. Storage modulus (E′) is the measure of the elastic response of the polymer and the composites, whereas tanδ (damping factor or loss tangent), is the ratio of the loss modulus to the storage modulus that can reflect the extent of the polymer-fillers interactions in composites and commonly is also used to determine T_g. Loss modulus (E″) is related to the energy lost in the form of heat and measures the viscous response for the polymer and the composites. Tensile testing was used to study the effect of carbon fillers on mechanical properties (Section 4.4.7) including tensile modulus (E), tensile strength (σ_u) and elongation at break (ε_u). Finally, the Halpin-Tsai model was utilized to model the tensile moduli of the PET/carbon nanocomposites (Section 4.4.8).

4.4.2 DMTA of the PET matrix

Figure 4.4.1 shows the E′ and tanδ (E″/E′) data as a function of temperature for the quenched PET sample. The figure shows that in the glassy state, the E′ values gradually decrease with temperature up to the T_g, (T_g ≈ 80 °C); but as the temperature increased above T_g the E′
decreases sharply from ~ 1330 MPa at 25 °C to reach a minimum value of 10 MPa at 100 °C, which is indicative of a glass-to-rubber transition of an essentially amorphous polymer. Above 100 °C, however, cold crystallization occurs during the DMTA heating scan and the crystallites formed as a result increase the value of $E'$. The most unusual feature in the $E'$ curve of quenched PET samples is this influence of cold crystallization at temperatures above the $T_g$. However this behaviour is in agreement with the DSC results presented in Section 4.3.2., and similar behaviour has been reported previously for quenched PET [1, 2]. This behaviour of quenched PET during DMTA was also observed for all the PET/carbon composites examined in this study. Parvinzadeh et al, [3] reported similar behaviour for PET/clay nanocomposites.

![Figure 4.4.1 DMTA curves of dynamic storage modulus ($E'$) and tanδ as a function of temperature for the PET matrix.](image)

In order to confirm that the increase in $E'$ in the rubbery state is due to cold crystallization, a second DMTA run was conducted for the same (now crystallised) PET specimen, as shown
in Figure 4.4.2. The insert graph shows a first heating run on DSC for the same (now crystallised) PET specimen. It can be seen from the figure that the cold crystallization peak has disappeared. Moreover, the $E'$ value for the crystallized sample at 100 °C (i.e. above $T_g$) in the second DMTA run is about 530 MPa which is much higher than the value of $E'$ at 100 °C during the first run (~10 MPa).

![Second DMTA curve of dynamic storage modulus as a function of temperature](image)

**Figure 4.4.2 Second DMTA curve of dynamic storage modulus as a function of temperature for the specimen of PET matrix shown in Figure 4.4.1. The insert shows a first heating run on DSC for the same (now crystallised) PET specimen.**

Using Equation 4.2, the $X_c$ of the specimen after the first run of DMTA was calculated to be ~ 35 % compared to ~ 11.8 % obtained before the DMTA run (see Section 4.3). These observations indicate that the quenched PET samples crystallized during the heating cycle of DMTA. The $E'$ corresponding to PET with crystallinities of 11.8 % and 35 % were extrapolated, using a linear function, in order to estimate the values of $E'$ for the amorphous
and totally crystalline phases of PET. The results gave $E'$ values of ~1200 MPa and 2200 MPa for the amorphous and crystalline phases, respectively.

Moreover, a small endothermic peak appears before the melting peaks in the PET sample that was tested in the DSC after DMTA; the position of which is dependent on the final temperature attained during the first DMTA test. For example, the insert graph in Figure 4.4.2 shows the peak at 220 °C, which the PET sample heated and maintained for 5 min at this temperature, followed by gradual cooling to room temperature. This small peak also appeared in all the PET/carbon composites studied.

### 4.4.3 DMTA of PET/graphite microcomposites

The $E'$ versus temperature curves for the PET matrix and microcomposites with different loadings of graphite (2, 5, 10 and 15 wt. %) are shown in Figure 4.4.3, and Table 4.4.1 shows comparative $E'$ values at approximately room temperature (25 °C) and above $T_g$ (100 °C). Figure 4.4.3 shows that the $E'$ curves for all the samples are essentially of the same shape; i.e. values of $E'$ (although different for each material, see Table 4.4.1) all show relatively little reduction in the glassy region below $T_g$ (~80 °C) and then decrease dramatically following the glass transition region reaching minimum values at ~100 °C (Table 4.4.1).

Furthermore, upon increasing the temperature above 100 °C an increase in the values of $E'$ for all microcomposites samples is observed in the rubbery region as shown in the insert Figure 4.4.3. This is due once again to cold recrystallization of the amorphous regions formed during the quenching process. It is also clear that cold crystallisation of the microcomposites begins at lower temperatures than for the pure PET, which is in agreement DSC data (Section 4.3.3), indicating that graphite nucleates the cold crystallization of the PET matrix.
Table 4.4.1 Selected DMTA data for $E'$, $T_g$ and $\tan \delta$ of PET/graphite microcomposites.

<table>
<thead>
<tr>
<th>Graphite (wt. %)</th>
<th>$E'$ at 25 °C (MPa)</th>
<th>$E'$ at 100 °C (MPa)</th>
<th>$T_g$ (°C)</th>
<th>$\tan \delta$ at $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1330 ±92</td>
<td>10.0 ±2.5</td>
<td>80.5 ±1.3</td>
<td>1.15 ±0.1</td>
</tr>
<tr>
<td>2</td>
<td>1417 ±130</td>
<td>10.0 ±4.0</td>
<td>80.7 ±0.3</td>
<td>1.08 ±0.1</td>
</tr>
<tr>
<td>5</td>
<td>1536 ±177</td>
<td>13.0 ±6.0</td>
<td>80.8 ±0.6</td>
<td>1.00 ±0.1</td>
</tr>
<tr>
<td>10</td>
<td>1893 ±119</td>
<td>11.0 ±3.0</td>
<td>82.4 ±1.2</td>
<td>1.02 ±0.2</td>
</tr>
<tr>
<td>15</td>
<td>1928 ±142</td>
<td>13.5 ±0.8</td>
<td>82.7 ±1.5</td>
<td>0.88 ±0.1</td>
</tr>
</tbody>
</table>

Similar crystallization behaviour during DMTA has been observed for PET nanocomposites containing clay by Parvinzadeh et al, [3], with the authors reporting an increase in modulus above $T_g$ due to cold crystallization.

![Figure 4.4.3 DMTA dynamic storage modulus data of PET/graphite microcomposites.](image)

Another observation from Figure 4.4.3 is that the $E'$ values of PET/graphite microcomposites below $T_g$ increase with increasing amount of graphite. Figure 4.4.4 and Table 4.4.1 show the
values of $E'$ at room temperature for 2, 5, 10 and 15 wt. % graphite loadings increased by ~ 7, 16, 42 and 45 % respectively compared to the neat PET matrix.

These results show that graphite increases the modulus of PET because of its higher modulus compared to the matrix. However, graphite also increases the $X_c$ (obtained during DSC) from 11.8 % for pure PET to ~ 19.8 % for microcomposites containing 15 wt. % graphite (Table 4.3.3, Section 4.3). In order to understand the improvements in $E'$ caused by $X_c$ and filler reinforcement, the modulus of the matrix was estimated using the modulus values obtained from the extrapolation procedure outlined in the previous section.

![Graph showing dynamic storage modulus values at 25 °C for PET/graphite microcomposites as a function of graphite concentration.](image)

The results from extrapolation showed the value of $E'$ at $X_c$ of ~ 19.8% is ~ 1400 MPa for pure PET. Thus, the improvement in $E'$ values due to increased crystallinity is ~ 5%, whilst the remaining 40 % of the improvement is attributed to filler reinforcement effect. Extrapolation of the data in Figure 4.4.4 (up to 10 wt. %) gave a value of ~ 8 GPa as an estimate of the effective modulus of the graphite in these composites.
Improvement of $E'$ at 25 °C in DMTA has also been observed for PMMA/graphite microcomposites by Ramanthan et al. [4] and in PVDF/graphite microcomposites by He et al. [5]. Figure 4.4.5 shows $E'$ as a function of graphite content for polymer/graphite microcomposites obtained from references [4] and [5] compared to the present experimental data. In general, it is clear that as graphite content is increased the $E'$ increases. However, the improvement in present study is much lower compared to the two previous studies. This could be due to different composite preparation methods (e.g. solvent vs melt in the case of [4]) affecting the dispersion states of fillers in the matrices.

![Graph showing the comparison of $E'$ data from references [4] (PMMA matrix) and [5] (PVDF matrix) with the present experimental results.](image)

**Figure 4.4.5** Comparison of $E'$ data from reference [4] (PMMA matrix) and [5] (PVDF matrix) with the present experimental results.

The data in the literature is very scattered; for example at 5 wt.% graphite an ~ 18 % increase of $E'$ at 30 °C of epoxy/graphite composites was reported by Yasmin and co-workers [6] and of 25 % for HDPE/graphite composites by Zheng [7], both much closer to the values
observed in the present study. Whereas, Zheng et al, [8] found that incorporation of 5 wt. % graphite had no significant effect on the $E'$ of a PMMA matrix.

The tan$\delta$ versus temperature plots for the PET/graphite microcomposites are shown in figure 4.4.6 and data extracted from this Figure are summarized in Table 4.4.1. The $T_g$ values indicate that no appreciable change occurs upon the addition of graphite; and similar results were observed by Yasmin et al, [6] for epoxy/graphite composites. However, these results are in contrast with Ramanathan et al, [4] who observed an increase in $T_g$ of 30 $^\circ$C for PMMA/graphite microcomposites containing 5 wt. % of graphite. Generally, an increase of $T_g$ is attributed to segmental constraint due to interaction between the polymer matrix and the graphite particles.

![Figure 4.4.6 DMTA tan$\delta$ versus temperature data for the PET/graphite microcomposites.](image)

The values of $T_g$ obtained from DMTA are higher than those obtained from DSC data, this is due to the different principle behind the techniques and the frequency effect in the DMTA test [9]. DMTA is more sensitive to molecular motion, as mentioned earlier when discussing
the thermal behaviour of PET/carbon composites (Section 4.3). This difference in \( T_g \) values recorded when using the two techniques is observed for all the PET/carbon composites samples investigated in this study.

One of the important properties of polymer composites is the damping response, i.e. how efficiently the composite loses energy by molecular rearrangements, which in this case is indicated by the values of tan\( \delta \) [10, 11]. The tan\( \delta \) values at \( T_g \) are inversely related to the volume of confined polymer within filler aggregates or interacting strongly with the surface of the filler, as such constraint hinders the mobility of chain segments [12]. Figure 4.4.6 shows the intensities of the tan\( \delta \) peaks decrease slightly and become broader as graphite content is increased in the composites. The tan\( \delta \) value of the microcomposites containing 15 wt. % graphite is about 0.88 which is \( \approx \) 24\% lower than that of pure PET (1.15); which could be due to both an increase in the degree of crystallinity from 11.8\% to 19.8\% (see Table 4.3.3, Section 4.3) as well as to chain segment constrain at the interface between the polymer and the filler (interfacial region) [12]. Other peaks shown in the tan\( \delta \) curves at higher temperatures ~ 110 -140 \( ^\circ \)C reflect the cold crystallization effect. As graphite content increases, the maximum temperature of this peak decreases, although for 10 and 15 wt. % loadings, it becomes difficult to define their maximum temperature. This is in an agreement with the DSC results discussed earlier in Section 4.3.

**4.4.4 DMTA of PET/GNP nanocomposites**

The \( E' \) versus temperature curves for the PET matrix and nanocomposites with different loadings of GNP (2, 6, 8, 10 wt. %) are presented in Figure 4.4.7, and Table 4.4.2 shows comparative \( E' \) values at approximately room temperature (25 \( ^\circ \)C) and above \( T_g \) (100 \( ^\circ \)C). Figure 4.4.7 shows curves of similar characteristic to those obtained for the PET/graphite composites (Figure 4.4.3), the \( E' \) curves for all the samples are essentially the same shape; i.e.
values of $E'$ (although different for each material, see Table 4.4.2) all show relatively little reduction in the glassy region below $T_g$ ($\sim 80 \, ^\circ C$) and then decrease dramatically following the glass transition region reaching minimum values at $\sim 100 \, ^\circ C$ (Table 4.4.2). However, in contrast to the graphite microcomposites the values of $E'$ are generally somewhat higher, indicating a greater degree of reinforcement and/or inducement of a greater degree of crystallinity.

![Figure 4.4.7 DMTA dynamic storage modulus data of PET/GNP nanocomposites.](image)

Furthermore, upon increasing the temperature above $100 \, ^\circ C$ an increase in the values of $E'$ for all nanocomposites samples is observed as shown in the insert of Figure 4.4.7. This is due, once again, to cold recrystallization of the amorphous regions developed during the quenching process. It is also obvious that the cold crystallisation of the GNP nanocomposites begins at lower temperatures than for the pure PET, and for the graphite microcomposites (Figure 4.4.3) which is in agreement with the results obtained by DSC (Section 4.3.4).
<table>
<thead>
<tr>
<th>GNP (wt. %)</th>
<th>$E'$ at 25 °C (MPa)</th>
<th>$E'$ at 100 °C (MPa)</th>
<th>$T_g$ (°C)</th>
<th>tanδ at $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1330 ±92</td>
<td>10.0 ±2.5</td>
<td>80.5 ±1.3</td>
<td>1.15 ±0.10</td>
</tr>
<tr>
<td>2</td>
<td>1447 ±88</td>
<td>22.9 ±2.2</td>
<td>80.0 ±0.9</td>
<td>1.02 ±0.30</td>
</tr>
<tr>
<td>6</td>
<td>2308 ±62</td>
<td>44.6 ±5.2</td>
<td>82.7 ±0.5</td>
<td>0.93 ±0.02</td>
</tr>
<tr>
<td>8</td>
<td>2095 ±84</td>
<td>129.4 ±14</td>
<td>83.5 ±0.7</td>
<td>0.69 ±0.04</td>
</tr>
<tr>
<td>10</td>
<td>1782 ±33</td>
<td>120.0 ±44</td>
<td>82.1 ±0.9</td>
<td>0.69 ±0.10</td>
</tr>
</tbody>
</table>

In addition, the increase in moduli following cold crystallisation is much greater in Figure 4.4.7 and Table 4.4.2. This behaviour indicates that GNP nucleates the cold crystallization of the PET matrix more efficiently than graphite, which may be due to their greater surface area. Figure 4.4.8 and Table 4.4.2 show the maximum increase in $E'$ of 72 % at 6 wt. % GNP. This improvement is due to both the reinforcing effect of the stiff GNP particles and an increase in the degree of crystallinity from 11.8% to 21.1% at 6 wt. % GNP (Table 4.3.4, Section 4.3). According to the extrapolation $E'$ results, the $E'$ values improved by ~ 6% due to the increase in $X_c$ and by 66 % due to reinforcement by GNP. Extrapolation of the data (up to 6 wt. %) in Figure 4.4.8 gave a value of 22.5 GPa as an estimate of the effective modulus of the GNP in these composites. Incorporation of GNP beyond 6 wt. % into PET decreases the $E'$ values (Figure 4.4.8), but they remain higher than pure PET. The observed reduction could be due to agglomeration, resulting in poorer dispersion and distribution of higher levels of GNP into the PET matrix. In addition, there is the possibility of GNP to rolling up during melt blending as mentioned in earlier, which reduces both their aspect ratio and interfacial area. This has been reported in the morphology Section (4.2). In fact, the
value of $E'$ at 10 wt. % in figure 4.4.8 is very close to the value for graphite at the same wt. % in figure 4.4.4, indicating that the effective modulus of GNP has reduced to that of graphite.

Figure 4.4.8 Dynamic storage modulus values at 25 °C for PET/GNP nanocomposites as a function of GNP concentration.

Figure 4.4.9 shows comparative storage moduli as a function of GNP content of polymer/GNP nanocomposites obtained from the literature [4] and [13] compared with the present experimental data. The highest $E'$ values can be clearly seen in this figure for the data taken from Ramanathan et al; which could be due to the solution preparation method that was used to produce the GNP nanocomposites in their study. Melt compounding was utilized in by Le et al [13] which report results much closer to the present study. The same authors also studied the effect of GNP on the dynamic mechanical properties of PTT and PBT matrices; reporting enhancement in $E'$ (at ~ 25°C) of 112 % and 66 % for PTT [14] and PBT [15] nanocomposites respectively at 7 wt. % GNP. Such improvement was attributed to efficient load transfer from matrix to filler, resulting from uniform distribution and good interfacial adhesion between GNP and the thermoplastic matrices. Some authors [4, 7, 8]
have compared the effect of graphite and GNP on the $E'$ values and generally observed that the addition of GNP gave greater improvement in $E'$ values than graphite. This was attributed to the small size particles, high aspect ratio and large surface area GNP compared to graphite. These results seem to be in agreement with the results in this study.

Figure 4.4.9 Comparison of $E'$ data from reference [4] (PMMA matrix) and [13] (PET matrix) with the present experimental results.

Figure 4.4.10 shows $\tan\delta$ versus temperature for PET/GNP nanocomposites system, and Table 4.4.2 summarises values of $T_g$ and $\tan\delta$ obtained from this figure. It is clear that the intensity of the $\tan\delta$ peaks decline for the nanocomposites compared to pure PET. The $\tan\delta$ values reduced from ~ 1.15 to 0.69 for pure PET to PET/GNP nanocomposites containing 8 wt. % GNP. The reduction in $\tan\delta$ values could be attributed to both an increase in the degree of crystallinity from 11.8 % (pure PET) to 22 % for the PET nanocomposites. It has been reported that the area under the $\tan\delta$ peaks, usually decreases with increasing
GNP [16], which is attributed to the 2D structure of the graphene sheets which hinder the transition from the rigid glassy to the rubbery state. The reductions in tanδ values for the GNP (Table 4.4.2) are much greater than those observed for graphite (Table 4.4.1); for example the reduction at 10 wt. % is -0.46 (-40 %) for GNP compared to – 0.13 (-11 %) for graphite. This reflects the difference in specific surface area between the two carbon fillers.

![Figure 4.4.10 DMTA tanδ versus temperature data for the PET/GNP nanocomposites.](image)

The DMTA results of the present study agree with previous studies [16] in terms of enhancement of E’ and reduction of tanδ values upon incorporating GNP within polymer matrices. However; the T_g values of PET/GNP nanocomposites indicate no appreciable change (Table 4.4.2). Similar observations of T_g and tanδ have been reported for different matrices such as PET/GNP [13], PTT/GNP [14] and PBT/GNP [15] nanocomposites. Zhang et al [17] reported a slight increase in T_g values and attributed this behaviour to higher filler surface area and the possibility of the existence of functional groups which can promote the attraction of chain segments of PET onto the GNP surface thereby restricting their mobility.
4.4.5 DMTA of PET/A-MWCNT nanocomposites

The E′ curves of the PET matrix and nanocomposites with different loadings of A-MWCNT (0.1, 0.2, 1 and 2 wt.%) are shown in Figure 4.4.11 and Table 4.4.3 shows comparative E′ data at approximately room temperature (25 °C) and above Tg (100 °C). Figure 4.4.11 shows that the E′ curves of all the sample are actually the same basic shape; i.e. values of E′ (although different for each material, see Table 4.4.3) all show relatively little reduction in the glassy region below Tg (~80 °C) and then decrease dramatically following the glass transition region reaching minimum values at ~100 °C (Table 4.4.3).

![Figure 4.4.11 DMTA dynamic storage modulus data of PET/A-MWCNT nanocomposites.](image)

However, in contrast to the GNP nanocomposites (Figure 4.4.7) the values of E′ are generally much higher at additions of ≤ 2 wt. %, indicating a greater degree of reinforcement and/or inducement of a greater degree of crystallinity.
However, DSC studies have shown that $X_c$ is at most of approximately 3% greater for the nanocomposites containing A-MWCNT at loadings of ≤ 2 wt. %, indicating that the MWCNT provide superior reinforcement than GNP.

Above 100 °C an increase in the values of $E'$ for all nanocomposites samples is observed, as shown in the insert Figure 4.4.11, due to cold recrystallization. The cold crystallisation of the nanocomposites begins at lower temperatures than for the pure PET, which is in agreement with the results obtained by DSC (Section 4.3.5), indicating that A-MWCNT nucleates the cold crystallization of the PET matrix. The effect of 1 wt. % nanotubes appears to have a similar effect to the addition of 2 wt. % of GNP. However, the nanocomposites containing 2 wt. % nanotubes behaves very differently; showing a very high modulus at 100 °C of 169 ±43 MPa (compared to approximately 30 MPa for 2 wt. % GNP), which therefore increases relatively little upon cold crystallisation.

Table 4.4.3 Selected DMTA data for $E'$, $T_g$ and $\tan\delta$ of PET/A-MWCNT nanocomposites.

<table>
<thead>
<tr>
<th>A-MWCNT (wt. %)</th>
<th>$E'$ at 25 °C (MPa)</th>
<th>$E'$ at 100 °C (MPa)</th>
<th>$T_g$ (°C)</th>
<th>$\tan\delta$ at $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1330 ±92</td>
<td>10.0 ±2.5</td>
<td>80.5 ±1.3</td>
<td>1.15 ±0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>1668 ±111</td>
<td>20.0 ±1.4</td>
<td>82.0 ±2.0</td>
<td>0.98 ±0.2</td>
</tr>
<tr>
<td>0.2</td>
<td>1396 ±108</td>
<td>8.0 ±1.7</td>
<td>83.0 ±2.0</td>
<td>1.16 ±0.1</td>
</tr>
<tr>
<td>1</td>
<td>1627 ±123</td>
<td>46.0 ±1.3</td>
<td>81.0 ±1.0</td>
<td>0.55 ±0.02</td>
</tr>
<tr>
<td>2</td>
<td>1550 ±167</td>
<td>169 ±43</td>
<td>84.4 ±0.6</td>
<td>0.30 ±0.02</td>
</tr>
</tbody>
</table>

Figure 4.4.12 shows values of $E'$ at 25 °C. It is clear from this figure and Table 4.4.3 that all nanocomposites possess higher $E'$ values than that of pure PET. This clearly shows that an A-MWCNT loading of only 0.1 wt. % increases $E'$ by ~ 26%. This could be attributed to the high modulus of CNT (~ 1TPa) and its good dispersion and uniform distribution into the
matrix at this loading. In addition, the level of $X_c$ increased with A-MWCNT loading from 11.8% (for pure PET) to ~17% for the nanocomposites containing 0.1 wt. % A-MWCNT (Table 4.3.5, Section 4.3). Based on the extrapolation calculations for crystallinity, only 3% of this increase in $E'$ is due to the raised $X_c$ whereas 23% is due to the reinforcement effect of 0.1 wt. % A-MWCNT.

Further addition of 0.2 wt. % of A-MWCNT, decreased the value of $E'$ from 1668 MPa to 1397 MPa (-16%), however, most of this reduction was recovered upon increasing the loadings to 1 and 2 wt. %. The result for 0.2 wt. % may be anomalous, but the general reduction in reinforcement above 0.1 wt. % can be attributed to entanglement/agglomeration of MWCNT and their non-uniform distribution into the PET matrix [11] as was observed in SEM and TEM images (Section 4.2) which reduces their aspect ratio and the surface area of their interface with the matrix. Extrapolation of the data (up to 0.1 wt. %) in Figure 4.4.12 gave a value of 339 GPa as an estimate of the effective modulus of the A-MWCNT in these
composites. The value of $E'$ at 2 wt. % in Figure 4.4.12 is very close to the value for GNP and graphite at the same wt. % in Figures 4.4.4 and 4.4.8, respectively, indicating that the effective modulus of the CNT has reduced to that of graphite. The enhancement of $E'$ is actually more distinct in the rubbery state, especially at 2 wt. % additions, as shown in Figure 4.4.11 and Table 4.4.3. This may be due to the formation of a rigid percolating network within the PET matrix effect as the MWCNT content increases and CNT- CNT interactions become dominant. Figure 4.4.13 shows literature values of $E'$ for MWCNT based composites compared to those of the present study.

![Graph showing comparison of storage moduli data from references](image)

Figure 4.4.13 Comparison of storage moduli data from references [19] (PP matrix) and [18] (PE matrix) compared with the present experimental results.

McNally et al, [18] reported that $E'$ of PE/MWCNT improved by ~ 60 % upon incorporation of 0.5 wt. % MWCNT compared to pure PE but that $E'$ then fell to ~ 15 % at 7 wt.% MWCNT. This behaviour was attributed to poor interfacial interaction between the matrix and filler. Logakis et al, [19] reported a similar trend to the current study (Figure 4.4.13). Both show an abrupt improvement in $E'$ values at low levels of MWCNT addition, followed
by a sharp decline at higher loadings. The sharp reduction is attributed to agglomeration while the recovery could be due to the higher amount of CNT beginning to form a percolated network.

A comparison between CNT and carbon black in terms of dynamic mechanical properties for PP/CB composites was reported by Manchado et al., [20], who observed dramatic improvement in $E'$ for both fillers. However, they also noted a significant decrease in the modulus when CNT loading exceeded 0.75 wt. %. On the other hand, when carbon black was used, the modulus gradually increased and no reduction occurred despite the presence of some agglomerates in the PP matrix. This was attributed to the different interfacial areas and shapes of the fillers used in their study.

Variations in the values of $E'$ for several polymer/CNT systems have been reported which mainly depend on the dispersion state, interfacial adhesion, preparation methods and CNT contents [21]. For example, Anaad et al [22] reported the $E'$ of PET/SWCNT nanocomposites improved by 66 % as compared to pure PET at 3 wt. % CNT. Similarly, Logakis et al [19] reported the $E'$ of iPP/MWCNT nanocomposites increased by 77 % at 3 wt.% MWCNT. The $\tan\delta$ versus temperature data for PET/A-MWCNT nanocomposites are shown in Figure 4.4.13. The $T_g$ and $\tan\delta$ values at $T_g$ extracted from this figure are reported in Table 4.4.3.
There appears to be no appreciable change in $T_g$ values as A-MWCNT content is increased. Similar behaviour has been reported for PET/MWCNT by Santoro et al, [23] despite good dispersion being achieved in their system. Moreover, similar trends in $T_g$ values has been observed for PE/MWCNT nanocomposites by Logakis et al [19] who incorporated up to 5 wt. % of MWCNT and did not observe any change in the values of $T_g$.

Figure 4.4.14 shows the intensities of the tanδ peaks to decrease slightly and become broader as A-MWCNT content is increased in the nanocomposites except the nanocomposites containing 0.2 wt. % (tanδ ≈ 1.16) which already been identified as a possible anomaly that displays values similar to pure PET (tanδ ≈ 1.15). Whereas the tanδ value of the nanocomposites at 0.1 wt. % of A-MWCNT is about 0.98 which is ≈ 15 % lower than for pure PET. The materials with higher loadings showed sharp reduction in tanδ values i.e. 0.55 and 0.3 for PET nanocomposites containing 1 and 2 wt. % A-MWCNT, respectively, as shown in Table 4.4.3. The tanδ value of 0.3 at 2 wt. % is significantly lower than for the
equivalent GNP nanocomposites (1.02). This behaviour is often ascribed to an increase in the
degree of crystallinity and/or to greater chain segment constrain within the interfacial region
between the A-MWCNT surface and the PET matrix. As the degree of crystallinity in the 2
wt. % MWCNT nanocomposites is not significantly different to that of the 2 wt. % GNP
composite (≈ 3.5 % greater) crystallinity can be ruled out. Given that the degree of
reinforcement provided by both the MWCNT and GNP at 2 wt. % addition appears to be
similar (their values of E′ are within 4 %) significant differences in interfacial interactions
appear unlikely. A plausible cause of the large decrease in tanδ at 2 wt. % MWCNT is the
formation of a percolated network of nanotubes, which would impose a significant constraint
on molecular movement.

Other peaks shown in the tanδ curves at higher temperatures ~ 110 -140 ºC reflect the cold
crystallization process. As A-MWCNT content increases, the maximum temperature of this
peak decreases, although for 1 and 2 wt. % loadings, it becomes difficult to define their
maximum temperature. This is in agreement with the DSC results discussed earlier in
Section 4.3.

4.4.6 DMTA of PET/T-MWCNT nanocomposites

Figure 4.4.15 shows the E′ of PET/T-MWCNT nanocomposites as a function of temperature
at loadings of 0.1, 0.2, 1 and 2 wt. % T-MWCNT. The E′ values at 25ºC and 100 ºC
extracted from this figure are shown in Table 4.4.4. The curves in Figure 4.4.14 are the same
general shape as those in for the A-MWCNT composites in Figure 4.4.11, but closer
inspection shows that the values of E′ at 25 ºC are generally higher and that the values of E′
at 100 ºC are much lower. Upon increasing the temperature above 100 ºC an increase in the
values of E′ for all nanocomposites samples is observed, as shown in the insert to Figure
4.4.15, due to cold crystallization as discussed earlier.
Figure 4.4.15 DMTA dynamic storage modulus data of PET/T-MWCNT nanocomposites.

Figure 4.4.16 and Table 4.4.4 show the values of $E'$ of PET/T-MWCNT nanocomposites at 25 °C. As can be seen, $E'$ values increase significantly from ~ 1330 MPa (for pure PET) to 1847 MPa (+ 39 %) for nanocomposites containing only 0.1 wt. % T-MWCNT. This illustrates the significant reinforcing effect of incorporating this small amount of T-MWCNT into PET because of the high modulus of the filler compared to the matrix and possibly good filler-matrix adhesion due to relatively strong interactions between these acid-modified CNT and the matrix, particularly as the increase in degree of crystallinity contributes only by ~ 2 % to the 39 % increase (as calculated by extrapolation data). Further addition of T-MWCNT into PET matrix showed a similar trend to that observed with A-MWCNT. However, the values of $E'$ are higher in the case of the T-MWCNT nanocomposites samples as shown in Figure 4.4.16. This could be ascribed to better dispersion and more uniform distribution of T-MWCNT into the PET matrix compared with A-MWCNT and shown in the electron microscopy data of Section 4.2. In addition, good interfacial adhesion may result from
interaction between the –COOH groups at the surface of T-MWCNT and the C=O groups in the PET via hydrogen bonding (as illustrated in Figure 2.20, Chapter 2). It is typically found that acid treatment reduces the size of aggregation of MWCNT in the polymer nanocomposites.

**Table 4.4.4 Selected DMTA data for $E'$, $T_g$ and $\tan\delta$ of PET/T-MWCNT nanocomposites.**

<table>
<thead>
<tr>
<th>T-MWCNT (wt. %)</th>
<th>$E'$ at 25 °C (MPa)</th>
<th>$E'$ at 100 °C (MPa)</th>
<th>$T_g$ (°C)</th>
<th>$\tan\delta$ at $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1330 ±92</td>
<td>10 ±2.5</td>
<td>80.5 ±1.3</td>
<td>1.15 ±0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>1847 ±41</td>
<td>16 ±4.0</td>
<td>83.0 ±1.1</td>
<td>1.05 ±0.1</td>
</tr>
<tr>
<td>0.2</td>
<td>1458 ±67</td>
<td>6.6 ±1.9</td>
<td>78.7 ±0.5</td>
<td>0.98 ±0.2</td>
</tr>
<tr>
<td>1</td>
<td>1740 ±15</td>
<td>9.7 ±1.3</td>
<td>80.0 ±0.4</td>
<td>1.10 ±0.01</td>
</tr>
<tr>
<td>2</td>
<td>1594 ±44</td>
<td>4.3 ±0.2</td>
<td>79.7 ±0.6</td>
<td>1.12 ±0.1</td>
</tr>
</tbody>
</table>

Similar behaviour for PET nanocomposites containing T-MWCNT has been observed by Wang et al [24] who reported a 24 % increase in $E'$ for PET nanocomposites containing 0.05 wt.% MWCNT. This improvement was followed by a reduction in the value of $E'$ when MWCNT increased from 0.1 to 0.2 wt. % that is in agreement with the results of the current study. The authors attributed this decline to the poor dispersion of CNT into PET matrix above 0.1 wt. %. In contrast, Gupta et al [10] investigated the effect of T-MWCNT on the $E'$ values of PPT and observed ~ 14 and 24 % improvements at 0.5 and 2 wt. % of CNT, respectively, which they attributed to good interfacial interaction between the CNT and the PTT matrix. Figure 4.4.17 presents a comparison of T-MWCNT filled nanocomposites obtained from the literature and the results from the present work. It is clear from the figure that in general, low concentrations of MWCNT provide significant improvements in the $E'$ values followed by much less significant improvements (or even reductions) at higher
loadings. This could be due to poor dispersion and distribution of the fillers at the higher loadings despite pre-treatment.

Figure 4.4.16 DMTA dynamic storage modulus data of PET/MWCNT nanocomposites.

Figure 4.4.17 Comparison of storage moduli from references [24] (PET matrix) and [25](PTT matrix) with the present experimental results.
Bikiars et al. [26] studied the effect of acid treatment time on the properties of PP/MWCNT nanocomposites and reported that the maximum values of $E'$ occurred after 15 minutes treatment of acid treatment of the MWCNT, then reduced as the duration of treatment increased.

The tan$\delta$ curves are presented in Figure 4.4.18; and the data for $T_g$ and tan$\delta$ values at $T_g$ are summarized in Table 4.4.4. The examination of these curves reveals two transitions of different intensities, similar to the other PET/carbon composites systems discussed earlier. It may be expected that the $T_g$ of a polymer matrix would tend to increase with the addition of T-MWCNT, due to CNT-polymer interactions reducing polymer chain mobility. However, in this study, no appreciable effect of T-MWCNT was observed on $T_g$ values. This behaviour is in agreement with a study conducted by Bikiaris et al [26] who reported no influence of T-MWCNT on $T_g$ for PP/nanocomposites at 2.5 wt. % loading. However, variation in $T_g$ has been reported elsewhere for nanocomposites containing T-MWCNT. For example, an increase by $\sim 7 \, ^\circ C$ in $T_g$ was reported for PET nanocomposites with 0.5 wt. % T-MWCNT [27]. On other hand, a reduction of $\sim 6 \, ^\circ C$ was reported for PET nanocomposites with 0.4 wt. % T-MWCNT [28].

Further inspection of Figure 4.4.18 and Table 4.4.4 shows tan$\delta$ values of PET/T-MWCNT nanocomposites are lower than pure PET at all loadings used. However, these values were found to be much higher in comparison to the equivalent PET/A-MWCNT nanocomposites (except for the possibly anomalous 0.2 wt. % A-MWCNT composite which is the highest of all).

It has reported that enhanced CNT dispersion can improve the damping behaviour of nanocomposites [10] and [11]. Thus the higher tan$\delta$ values for the nanocomposites containing T-MWCNT, particularly at the higher loadings of 1 and 2 wt. %, coupled with their much lower values of $E'$ at 100 $^\circ C$ indicate that the acid-treated MWCNT show reduced
CNT-CNT interactions (due to their surface treatment and reduced length) and therefore do not as readily form network structures.

Figure 4.4.18 DMTA tanδ versus temperature data for the PET/T-MWCNT nanocomposites.

4.4.7 Tensile Properties

This section presents results for the tensile properties (modulus (E), tensile strength (σ_u) and elongation at break (ε_u)) of PET/carbon composites at various loadings of carbon.

4.4.7.1 Tensile properties of PET/graphite microcomposites

The stress-strain behaviour of the PET matrix and PET/graphite microcomposites at different loadings of graphite are shown in Figure 4.4.19. The values of E, σ_u and ε_u derived from the curves are summarized in Table 4.4.5. The variation of E with graphite content is shown in Figure 4.4.19 and Table 4.4.5. A significant increase in E occurs with increasing loading of graphite; rising by ~ 14 % and ~ 73 % for microcomposites containing 2 wt.% and 15 wt.% graphite, respectively, in comparison to neat PET.
Such increases in $E$ have been reported by several previous studies on polymer/graphite microcomposites because of the high modulus of graphite and increases in degree of crystallinity of a semi-crystalline matrix [6, 29-34]. For example, Figure 4.4.20 shows $E$ as a function of graphite content for polymer/HDPE microcomposites obtained from references [33] and [34] compared to the present experimental data. In general, it is clear that as graphite content is increased the value of $E$ increased in an essentially linear manner. The $E$ values obtained in the present study are higher than Wang et al, [33] although pre-treatments of graphite and smaller particle size were used in their study. However, $E$ values are identical up to 5 wt. % of graphite in comparison to the study of Sarikanat et al, [34] thereafter an abrupt increase in $E$ was observed in their study. The differences in $E$ in the referenced works are due to variation in filler particle sizes and preparation methods that are different from the present study.
Figure 4.4.20 Comparison of E data from reference [33] (HDPE matrix) and [34] (HDPE matrix) with the present experimental results.

Table 4.4.5 Tensile properties of the PET/graphite microcomposites.

<table>
<thead>
<tr>
<th>Graphite (wt. %)</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1073.3 ±15.7</td>
<td>45.8 ±2.3</td>
<td>6.3 ±1.9</td>
</tr>
<tr>
<td>2</td>
<td>1220.1 ±14.8</td>
<td>31.3 ±2.9</td>
<td>3.2 ±0.3</td>
</tr>
<tr>
<td>5</td>
<td>1375.5 ±36.2</td>
<td>28.5 ±1.6</td>
<td>2.4 ±0.1</td>
</tr>
<tr>
<td>10</td>
<td>1620.4 ±40.2</td>
<td>28.1 ±8.0</td>
<td>2.1 ±0.7</td>
</tr>
<tr>
<td>15</td>
<td>1858.1 ±83.5</td>
<td>23.0 ±5.5</td>
<td>1.4 ±0.4</td>
</tr>
</tbody>
</table>

The above results indicate that graphite increases the tensile modulus of PET because of its higher modulus compared to the matrix. However, graphite also increases the $X_c$ from 11.8 % for pure PET to ~ 19.8 % for microcomposites containing 15 wt. % graphite (Table 4.3.3, Section 4.3). In order to understand the improvements in tensile modulus caused by $X_c$ and
filler reinforcement; it is proposed that a similar percentage increase in tensile modulus occurs with increasing $X_c$ as occurred in storage modulus obtained by DMTA. The storage modulus at room temperature for totally amorphous and crystalline PET was estimated as ~1200 MPa and 2200 MPa, respectively, which were obtained from the extrapolation procedure outlined in the previous section. This shows an increase of ~83% in the modulus (0.83 % increase for every 1 % increase in $X_c$). Thus, using the results from extrapolation it is calculated that an approximately 785 MPa (73 %) improvement in $E$ for the microcomposites containing 15 wt. % graphite, ~71 MPa (9 % of the increase) is due to $X_c$ and while the remaining 91% of the improvement (approximately 714 MPa) is due to graphite reinforcement. The extrapolation of the modulus data from Table 4.4.5 (to 100 % graphite) gave a value of ~5900 MPa as an estimate of the effective modulus of the graphite in the microcomposites.

In contrast, Figure 4.4.19 and Table 4.4.5 show a sharp reduction in $\sigma_u$ and $\varepsilon_u$ with increasing graphite content. For example, $\sigma_u$ decreased from ~46 MPa for pure PET to 31 MPa (-33 %) for microcomposites containing 2 wt. % graphite loading, accompanied by a drop in $\varepsilon_u$ from ~6.3 to 3.2 % (-49 %). These large reductions are followed by more gradual drops in $\sigma_u$ and $\varepsilon_u$ with further graphite addition. These results indicate that increasing graphite content made the composites weaker and less ductile. Presumably this is due, firstly, to restriction of the movement of molecular chain segments, their rearrangements and orientation during tensile deformation in the presence of graphite and, secondly, to poor interaction between matrix and filler that result in weak interfaces and low homogeneity of microcomposites as agglomerates form (as was observed and discussed in Section 4.2). The stress concentration that occurs around agglomerates typically results in lower bulk stresses and strains at failure.

Numerous studies have been carried out for the prediction of the tensile strength of polymer composites. Several factors could affect such properties; including heterogeneity, stress
concentration, particle size, interfacial adhesion and filler concentrations [35, 36]. The simplest strength prediction model is based on the area reduction of the matrix in the presence of fillers. This model assumes that there is no adhesion between the matrix and filler [35].

\[ \sigma_u = \sigma_m \frac{A_m}{A_c} \]  \hspace{1cm} (4.3)

Where, \( \sigma_m, A_m \) and \( A_c \) are the matrix strength, matrix without filler area and matrix area with filler, respectively.

The ratio \( \frac{A_m}{A_c} \) can be expressed as a function of filler volume fraction (\( \phi_f \)) as;

\[ \frac{A_m}{A_c} = 1 - \beta \phi_f^{2/3} \]  \hspace{1cm} (4.4)

Where \( \beta \) is a parameter which depends on the type of filler distribution; for example it takes value of 1.11 for a hexagonal array [35]. Volume fractions for the PET/graphite composites were calculated based on densities of graphite (2 g/cm\(^3\) from supplier data sheet) and PET (1.33 g/cm\(^3\) calculated for \( \sim\)12% crystallinity on the basis of densities of amorphous and fully-crystalline PET [37]). Figure 4.4.21 shows the dependence of \( \sigma_u \) on the graphite content based on both calculated and experimental results. The sharp reduction of tensile strength can be seen from the figure at 0.01 volume fraction of graphite followed by gradual reduction upon further addition of filler. However, all these values are much lower than the predicted model; indicating that the strength of the PET has been reduced to a much greater extent than simply replacing matrix with a non-bonding filler that does not contribute to strength. This could be due to several factors, particularly heterogeneity which creates stress concentrations [35, 36]. Several studies have reported reductions in \( \sigma_u \) values [4, 5, and 6]. Unal et al, [4] reported \( \sim \)10 \% and 33 \% decline in \( \sigma_u \) and \( \varepsilon_u \) respectively at 15 wt. \% of graphite loading. The authors attributed this reduction to the restriction in the motion of polymer chains and to aggregation of graphite, inhibiting uniform deformation of the
composites. Similar results were observed by Krupa et al, [31] upon the incorporation of graphite into PE. The authors found elongation at break to decrease with increasing graphite content and attributed this reduction to the presence of irregular graphite particles creating stress concentrations. However, nonlinear behaviour was observed between $\sigma_u$ and graphite loading and the authors concluded that addition of the graphite into the PE matrix resulted in two effects; namely an easier initiation of cracks and a reduction in chain mobility due to polymer-filler interactions, resulting in lower deformability of the composites.

![Figure 4.4.21 The dependence of $\sigma_u$ on graphite content of both calculated (equation 4.4) and experimental results.](image)

In the contrast to these results, Otieno et al, [32] observed an improvement in the $\sigma_u$ of PU/graphite composites upon using polyethylene oxide as a dispersion agent. However, they observed a reduction in the $\varepsilon_u$ values and it was concluded that a reduction in $\varepsilon_u$ is a typical characteristic for particulate filled polymers. Wang et al, [33] used a coupling agent as a dispersion aid in HDPE/graphite microcomposites and found that $\varepsilon_u$ improved significantly after treating graphite with this agent. The authors attributed such improvement to improved
dispersion of graphite within the HDPE matrix and good interaction between the graphite and HDPE, as a result of pre-treatment of the graphite.

4.4.7.2 Tensile properties of PET/GNP nanocomposites

Figure 4.4.22 shows the stress-strain curve of PET/GNP nanocomposites with different GNP loadings and data obtained from these curves is shown in Table 4.4.6. The results show that E improves with increasing GNP loadings up to 8 wt. %. The E of pure PET is 1073.3 MPa which increases to ~ 1709 MPa at 8 wt. % GNP (+ 59 %). This is followed by reduction at 10 wt. % of GNP; However E values are still higher than pure PET and the microcomposites, indicating a greater degree of reinforcement and/or inducement of a higher degree of crystallinity in the case of nanocomposites. Furthermore, as per extrapolation results, the E values were improved by ~ 11 % due to the increase in Xc and by 48 % by reinforcement effect of GNP. Extrapolation of the modulus data (up to 2 wt. %) shown in Table 4.4.6 to 100 % GNP gave a value of ~ 18.9 GPa as an estimate of the effective modulus of the GNP in these nanocomposites which is much higher than that of graphite (~ 6 GPa) in the microcomposites, indicating a greater reinforcement effect of the nanofiller over the microfiller. Several studies have been reported an improvement in E values for polymer/GNP nanocomposites such as Yasmin et al, [6] and Al-jabareen et al, [38]. Figure 4.4.23 shows comparative tensile moduli as a function of GNP content of polymer/GNP nanocomposites obtained from these studies compared with the present experimental data. It can be clearly seen in figure that as GNP content is increased, the value of E is increased for all composites.
Figure 4.4.22 Typical stress-strain curves of the PET/GNP nanocomposites.

However, data from the present study is equivalent to or greater than data from the other studies up to 8 wt. % of GNP, followed by a reduction in E values. The data obtained from the present study and Al-jabareen et al (PET/GNP) are close to each other in comparison to Yasmin et al (Epoxy/GNP), reflecting the similarity in materials and methods for making of composites.

In contrast to the results for E, Figure 4.4.22 and Table 4.4.6 demonstrate that $\sigma_u$ and $\varepsilon_u$ reduce with increasing GNP content (in agreement with the results for the graphite microcomposites). For example; $\sigma_u$ reduced from ~ 46 MPa (neat PET) to ~ 39 MPa (~ 15 %) for the nanocomposites containing 2 wt. % GNP. This reduction is accompanied by a decline in $\varepsilon_u$ from ~ 6.3 (neat PET) to ~ 3.4 (~ 46 %) for the same nanocomposites. Such reductions are followed by gradual decrease in $\sigma_u$ and $\varepsilon_u$ upon further addition of GNP. These reductions indicate that increasing GNP loadings, results in brittleness in nanocomposites, as discussed for microcomposites in the previous section.
Figure 4.4.23 Comparison of E data from Yasmin et al [6] (Epoxy matrix) and Al-Jabarneen et al [38] (PET matrix) with the present experimental results.

Table 4.4.6 Tensile properties of the PET/GNP nanocomposites.

<table>
<thead>
<tr>
<th>GNP (wt. %)</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1073.3 ±15.7</td>
<td>45.8 ±2.3</td>
<td>6.3 ±1.9</td>
</tr>
<tr>
<td>2</td>
<td>1429.5 ±42.0</td>
<td>38.6 ±4.7</td>
<td>3.4 ±0.6</td>
</tr>
<tr>
<td>6</td>
<td>1611.3 ±53.0</td>
<td>24.4 ±3.4</td>
<td>1.6 ±0.1</td>
</tr>
<tr>
<td>8</td>
<td>1708.7 ±65.0</td>
<td>18.8 ±1.3</td>
<td>1.2 ±0.1</td>
</tr>
<tr>
<td>10</td>
<td>1443.2 ±71.9</td>
<td>16.8 ±2.5</td>
<td>1.2 ±0.3</td>
</tr>
</tbody>
</table>

Moreover, similar results have been reported for PET/GNP nanocomposites by Al-jabarrean et al [38] who observed that addition of 1.5 wt. % of GNP in the PET matrix results in a decline in $\sigma_u$ and $\varepsilon_u$ values by - 45 % and -60 %, respectively. Moreover, King et al, [39] studied the effect of GNP addition on the tensile properties of epoxy and reported an increase in the
tensile modulus but a reduction by – 54 % and – 81 % in the values of $\sigma_u$ and $\varepsilon_u$, respectively. Yasmin et al, [6] reported brittleness of composites containing more than 5 wt. % loading of graphite, which was accompanied by a decline in the $\sigma_u$ and $\varepsilon_u$. In addition, agglomeration of graphite was observed leading to a reduction of these properties for epoxy/graphite composites.

Figure 4.4.24 shows $\sigma_u$ as a function of GNP content for polymer/GNP nanocomposites obtained from references [38] and [39] compared to the present experimental data. It is clear that as GNP content is increased, $\sigma_u$ decreases. However, the reduction in the present study is much lower compared to the two previous studies up to 6 wt. % of GNP. This could be due to different composite preparation methods and filler geometries.

![Graph showing comparison of $\sigma_u$ with GNP content](image)

**Figure 4.4.24** Comparison of $E$ data from Al-jabareen et al [38] (PET matrix) and King et al [39] (Epoxy matrix) with the present experimental results.
4.4.7.3 Tensile properties of PET/A-MWCNT nanocomposites

The addition of A-MWCNT into the PET matrix was expected to enhance its mechanical properties significantly. However, PET/MWCNT usually suffers from poor tensile strength. Good dispersion of A-MWCNT into a PET matrix is vital for enhancing its mechanical properties as it has been established that good dispersion of MWCNT minimises the stress concentration of composites under service loading conditions [40, 41]. Figure 4.4.25 shows the tensile stress-strain curves for PET and PET/A-MWNTs nanocomposites. The $\sigma_u$, $\epsilon_u$ and $E$ of PET/A-MWCNT nanocomposites are shown in Table 4.4.7. These results demonstrate significant improvement of $E$ from 1073.3 MPa (for PET) to 1302.7 MPa at 2 wt. % A-MWCNT (21.4%). Such improvements could be due to the high aspect ratio, strength and modulus of MWCNT which is in agreement to studies reviewed by Spitalsky et al, [21]. In addition to that A-MWCNT nucleated the crystallization of the PET (as discussed in Section 4.3.2.4), and increased the degree of crystallinity of these nanocomposites, thus resulting in stiffer PET nanocomposites.

![Figure 4.4.25 Typical stress-strain curves of the PET/A-MWCNT nanocomposites.](image)
According to the extrapolation procedure used previously, the E values improved by ~ 4 % due to the increase in $X_c$ and by 17.4 % due to reinforcement by A-MWCNT. The modulus data (up to 0.2 wt. %) in Table 4.4.7 was extrapolated to 100 % CNT and gave a value of 59.4 GPa as an estimate of the effective modulus of the A-MWCNT in the nanocomposites.

In comparison to nanocomposites containing GNP, the effective modulus of CNT was found to be much higher than that of GNP (18.9 GPa). This could be due to greater retention of aspect ratios of CNT in nanocomposites compared to GNP, resulting in higher effective modulus. Figure 4.4.26 compares the E values obtained from previous studies to present data. The study of Santoro et al, [23] showed a sharp increase in E at 0.1 and 0.2 wt. % MWCNT, thereafter levelling off. A similar trend has been observed in the present study; however their E values are much higher than ones obtained in present study, despite similar melt compounding conditions. This could be due to pre-mixing of CNT and PET by cryogenic milling before melt compounding in their study, resulting in good dispersion. In contrast, Aalaei et al, [42] observed a slight reduction in E at low loadings followed thereafter by a gradual increment. Such a slight improvement was attributed to gradual increase in the degree of crystallinity of the nanocomposites.

<table>
<thead>
<tr>
<th>A-MWCNT (wt. %)</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1073.3 ±15.7</td>
<td>45.8 ±2.3</td>
<td>6.3 ±1.9</td>
</tr>
<tr>
<td>0.1</td>
<td>1124.0 ±24.7</td>
<td>44.8 ±5.0</td>
<td>4.9 ±0.9</td>
</tr>
<tr>
<td>0.2</td>
<td>1182.3 ±52.1</td>
<td>32.0 ±2.5</td>
<td>3.1 ±0.2</td>
</tr>
<tr>
<td>1</td>
<td>1252.6 ±31.3</td>
<td>30.0 ±3.8</td>
<td>2.6 ±0.3</td>
</tr>
<tr>
<td>2</td>
<td>1302.7 ±30.0</td>
<td>25.2 ±4.1</td>
<td>2.0 ±0.3</td>
</tr>
</tbody>
</table>
The values of $\sigma_u$ and $\varepsilon_u$ decrease with increasing A-MWCNT content in the PET/A-MWCNT nanocomposites. At 0.1 wt. % A-MWCNT no appreciable change was observed between pure PET and composite, but upon further addition to 2 wt. % a sharp reduction occurred. Values of $\sigma_u$ reduced from 46 MPa for pure PET to 25 MPa for composites containing up to 2 wt. %. The elongation at break showed a decrease from 6 % for pure PET to 2 % at 2 wt. % A-MWCNT. This reduction is believed to be due to the failure initiated at the A-MWCNT aggregates within the composites which results in lower bulk stresses and strains at failure. The decline of $\sigma_u$ is usually attributed to the agglomeration of CNT in the polymer matrix, as reported by Aalaei et al [42] who observed a 50 % reduction in $\sigma_u$ for their PP/MWCNT nanocomposites at 5 wt. % filler. These results seem to be in contrast with Santoro et al [23] who observed enhancement in both elastic modulus and tensile strength of PET/MWCNT nanocomposites by 25 % and 26 %, respectively at 0.25 wt. % of MWCNT. The authors also concluded that further loadings did not increase these properties. The improvement in the
mechanical properties in their study was suggested to be due to the good dispersion of A-MWCNT into the PET matrix.

Good dispersion of MWCNT into PET matrix also was achieved at < 0.4 wt. % by Zhu et al [28]. Addition of MWCNT, was found to improve Young’s modulus and \( \sigma_u \) by 25 % and 15%, respectively, at 0.4 wt. %. This was followed by a slight drop in \( \sigma_u \) at 0.6 and 0.8 wt. % of MWCNT loading. A similar study conducted by Kim et al [43] investigated the effect of A-MWCNT loading on the mechanical properties of a PET matrix. The authors reported a 10 % improvement for both \( \sigma_u \) and E at 0.5 wt. % MWCNT. No significant improvement was observed with further loading of A-MWCNT, which they attributed to the tendency of CNT to bundle up and aggregate together at higher loading, resulting in lowering the efficiency of load transfer between the PET and MWCNT.

### 4.4.7.4 Tensile properties of PET/T-MWCNT nanocomposites

Figure 4.4.27 shows stress–strain curves for neat PET and PET/T-MWCNT nanocomposites, and the results obtained from these curves are summarized in Table 4.4.8. It can be seen that the addition of T-MWCNT can improve the values of E of the PET nanocomposites as they are seen to increase from ~ 1073 MPa for the PET matrix to 1343 MPa for nanocomposites containing 2 wt. % (+25 %). According to the extrapolation, the E values enhanced by only ~ 3 % due to an increase in \( X_c \) and by ~ 22 % because of the reinforcement effect of the T-MWCNT. Extrapolation of the modulus data (up to 0.2 wt. %) from Table 4.4.8 showed an estimated value of 89.2 GPa for 100 % T-MWCNT as an effective modulus of T-MWCNT in nanocomposites. This is much higher (+ 50.2 %) than the 59.4 GPa for A-MWCNT, indicating better load transfer between the T-MWCNT and PET.
Figure 4.4.27 Typical stress-strain curves of the PET /T-MWCNT nanocomposites.

Figure 4.4.28 Comparison of E data from Zaman et al [44] (PET matrix) and Gupta et al [10] (PTT matrix) to the present study.
Improvements in E values have been reported for PET [44] and PTT [10] nanocomposites containing T-MWCNT as shown in Figure 4.4.28. Interestingly, the trend shown in the figure is similar in all studies. The E value at 0.1 wt. % in the present study is identical to Zaman et al and Gupta et al who obtained similar improvement in modulus but at higher loadings i.e. 0.3 and 0.5 wt. %, respectively. This indicates uniform dispersion at lower loadings of CNT. Upon further filler addition the sharp improvement in E values in all studies thereafter levelled off.

Table 4.4.8 and Figure 4.4.27 reveal that no appreciable change in $\sigma_u$ up to a loading of 0.2 wt. % of T-MWCNT. This can be attributed to a better dispersion state compared with A-MWCNT. However, significant reductions in $\sigma_u$ of ~ 44 % and 50 % were observed for the composites containing 1 wt. % and 2 wt. % T-MWCNT, respectively. This is probably due to poor dispersion and distribution, as agglomeration was noticeable at this loading as reported in Section 4.2. Similar behaviour has been reported for PS nanocomposites containing acid-treated MWCNT by Amr et al, [45].

<table>
<thead>
<tr>
<th>T-MWCNT (wt. %)</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1073.3 ±15.7</td>
<td>45.8 ±2.3</td>
<td>6.3 ±1.9</td>
</tr>
<tr>
<td>0.1</td>
<td>1141.9 ±17.3</td>
<td>46.3 ±2.9</td>
<td>4.7 ±0.5</td>
</tr>
<tr>
<td>0.2</td>
<td>1230.0 ±34.0</td>
<td>43.3 ±2.9</td>
<td>4.1 ±0.3</td>
</tr>
<tr>
<td>1</td>
<td>1222.5 ±105</td>
<td>25.6 ±6.0</td>
<td>2.7 ±0.8</td>
</tr>
<tr>
<td>2</td>
<td>1343.2 ±13.8</td>
<td>22.7 ±1.8</td>
<td>1.8 ±0.1</td>
</tr>
</tbody>
</table>

Such results seem to be in contrast with Gupta et al [10] who reported an increase in the values of $\sigma_u$ for PTT nanocomposites containing acid-treated MWCNT. This variation in results could be attributed to different preparation methods and acid-treatment conditions; for
example Gupta utilized sonication of fillers before acid treatment. On the other hand, Amr et al utilized only HNO$_3$ for pre-treatments of CNT.

The $\varepsilon_u$ values of the PET nanocomposites also decrease upon incorporation of T-MWCNT, indicating that PET composites became somewhat less ductile and more brittle compared to the neat PET due to the increased modulus of the PET composites. Gupta et al, [10] and Meng et al, [46] have reported similar reduction in values of $\varepsilon_u$ for PTT and PA6 nanocomposites containing T-MWCNT. Pat et al, [47] reported that the PET/T-MWCNT nanocomposites were also extremely brittle.

In contrast, Zaman et al, [44] reported improvement of both the $\sigma_u$ and $\varepsilon_u$ values of PET composites with increasing the loading of T-MWCNT (same grade as in present study) up to 0.5 wt. %, followed by a decline due to aggregation. It should be noted that they treated MWCNT in a mixture of concentrated nitric and sulphuric acids for 24 hours at room temperature, which resulted in enhancement of interfacial interactions between CNT and polymer matrix, hence effective load transfer. However, It was reported that [48] the mechanical properties of composites containing acid treated CNT depends on the treatment temperature, time and the composition of the acid mixture, indicating that severe surface modification lowers the mechanical properties of the final composites. Bikiaris et al, [26] concluded that a smaller size of agglomeration was obtained by increasing the time of acid treatment which can improve mechanical properties.

It is worthwhile to compare the tensile properties of both A-MWCNT and T-MWCNT based on PET matrix nanocomposites. Interestingly, the E values of PET/T-MWCNT were found to be higher than PET/A-MWCNT at all identical concentrations, while values of $\sigma_u$ at 0.1 and 0.2 wt. % T-MWCNT are higher than obtained at the same loading of A-MWCNT nanocomposites. Such enhancement of the tensile properties of PET/T-MWCNT can be
attributed to an improved level of interfacial interaction between the T-MWCNT and the PET matrix along with more uniform dispersion of filler.

A comparison between A-MWCNT and T-MWCNT has been conducted by Yoo et al [49] who produced PET nanocomposites containing 3 wt. % CNT. They found $\sigma_u$ and $\sigma$ values were lower than that of pure PET when A-MWCNT were incorporated into PET; whereas addition of T-MWCNT was found to improve the tensile properties of the composite which was attributed to good dispersion. Another comparison has been made by Yesil et al [41] who found that all of their PET/T-MWCNT nanocomposites had better mechanical properties than PET/A-MWCNT. The authors attributed this to improved interaction between PET and T-MWCNT, even with the expected damage to the MWCNT created by its acid treatment. A similar study was carried out by the same authors [40] using the same grade of CNT as in this study (Nanocyl-7000), which drew similar conclusions to that mentioned above. Similar behaviour was observed by Jin et al, [50] when studying the effect of a functionalization process of MWCNT on the properties of PET/MWCNT nanocomposites with different MWCNT contents (0.1, 1 and 2 wt. %). It was concluded that the good adhesion between T-MWCNT and PET resulted in an increase in the mechanical properties of PET/T-MWCNT nanocomposites compared to pristine CNT despite the damages caused by acid treatment such as shortening of CNT. Several other studies have concluded that treatment of MWCNT is required to improve the tensile properties of PET nanocomposites [27, 44].

4.4.8 Halpin-Tsai model

4.4.8.1 Introduction

The tensile modulus of nanofiller-reinforced composites can be predicted by using several models based on the geometry, orientation, the elastic properties of the fillers and matrices [12, 51-55]. One of the most common models is the Halpin-Tsai model, used for predicting
tensile moduli of polymer composites that contain fillers oriented in both longitudinal and transverse directions. The original Halpin-Tsai models Equations (4.5) and (4.6) have the following forms.

\[
\frac{E_c}{E_m} = \frac{1 + \zeta \mu f}{1 - \mu f} \quad \text{................................. (4.5)}
\]

\[
\mu = \frac{E_f - 1}{E_f + \zeta} \quad \text{................................. (4.6)}
\]

Where \(E_c\) and \(E_m\) are the composite and the matrix moduli, respectively, \(\phi_f\) is the volume fraction of filler, \(\zeta\) is a shape factor that depends on filler geometry and loading direction. In this study, the value of \(\zeta\) was taken as \(2(L/t)\), where \(l\) and \(t\) are the length and thickness of the GNP, respectively; whereas for MWCNT: \(\zeta = 2(L/d)\) where, \(L\) and \(d\) are the length and diameter. Thus, \((L/T)\) and \((L/d)\) are the aspect ratios of the GNP and MWCNT, respectively. Aspect ratio is an important factor in in the reinforcement of nanocomposites that drives an interest in achieving a high level of GNP exfoliation or MWCNT disaggregation. The parameter \(\zeta = 2\eta\) (\(\eta\) is the aspect ratio of the reinforcement) has shown good agreement for longitudinal modulus however transverse modulus was found to be insensitive to \(\eta\) [55]. It should be noted that as \(\zeta \to 0\), the Halpin-Tsai reduces to the series model of the rule of mixtures (lower bound) (given in Equation (4.7)) and conversely, as \(\zeta \to \infty\) Equation (4.8) reduces to the parallel model of the rule of mixture (upper bound).

\[
E^{\text{lower}} = \frac{\phi_f}{E_f} + \frac{(1-\phi_f)}{E_m} \quad \text{................................. (4.7)}
\]

\[
E^{\text{upper}} = E_f \phi_f + E_m (1 - \phi_f) \quad \text{................................. (4.8)}
\]

The rule of mixture model was modified by Cox and Krenchel [51] who took into account the influence of filler length and orientation. This modification includes; the factor of ordination [43, 51, 56] called \(\alpha\), to account for the orientation of the fillers. If the \(L\) is greater than the thickness of the specimen, the fillers are assumed to be in 2D (planar) random orientation and
\( \alpha = 1/3 \) is used to calculate the composite modulus \( (E_c) \). In contrast, \( \alpha = 1/6 \) if \( L \) is smaller than the thickness of the specimen and 3D random orientation is assumed.

There are a number of assumptions that are inherent in this model: i) the filler and matrix are linearly elastic, isotropic and perfectly bonded. ii) The fillers are homogeneously dispersed, aligned, asymmetric and identical in shape and size. iii) particle-particle interactions are not considered. iv) Fully exfoliated and perfectly oriented and aligned in the case of GNP and MWCNT, respectively. Clearly, these simplifying assumptions will result in disparities between the predictions of the Halpin-Tsai theory and the behaviour of real and more complex systems such as MWCNT and GNP.

In the present study, the average length of GNP and A-MWCNT are taken as 15 and 1.5\( \mu \)m, respectively, as per supplier specifications. Moreover, these both lengths are shorter than the thickness of the specimens (Mini Jet mouldings). Therefore, a 3D filler random distribution is assumed for PET/carbon nanocomposites samples. For nanocomposites containing randomly oriented and discontinuous nanofillers, \( E_c \) can be calculated from the modified Halpin-Tsai [43, 56, 57] using the Equations 4.9 – 4.11.

\[
E_c = \left( \frac{3}{8} \right) \left( \frac{1+2\zeta \eta_L \phi_f}{1-\eta_L \phi_f} \right) + \left( \frac{5}{8} \right) \left( \frac{1+2\eta_T \phi_f}{1-\eta_T \phi_f} \right) E_m \quad \text{............ (4.9)}
\]

Where,

\[
\eta_L = \frac{\left( \frac{E_f}{E_m} \right)^{-1}}{\left( \frac{E_f}{E_m} \right)^{+2\zeta}} \quad \text{................................. (4.10)}
\]

\[
\eta_T = \frac{\left( \frac{E_f}{E_m} \right)^{-1}}{\left( \frac{E_f}{E_m} \right)^{+2}} \quad \text{................................. (4.11)}
\]

Although the concept of Halpin-Tsai theory was derived on the basis of the volume fraction of the filler, the weight fraction \( (w_f) \) has often been employed for the determination of the elastic modulus of the composites [43,63,58,59].
This is due to the fact that precise density values of some nanofillers, such as CNT, are not accurately known, and estimated values are sometime used.

4.4.8.2 Variation of Filler Modulus and Aspect Ratios

Figure 4.4.29 reveals a clear difference between calculated and experimental modulus values of composites. Theoretically, the modulus of the PET nanocomposites increases with increasing $E_f$ values. It is clear that a good agreement (when $E_f = 270$ GPa) between the calculated and the experimental data for composite modulus at low filler levels ($\leq 0.2$ wt. %) of filler was observed which is lost upon further loadings.

![Figure 4.4.29 The dependence of tensile modulus on $E_f$ as predicted by the Halpin-Tsai model.](image)

As mentioned an $E_f$ of 270 GPa gave the best fit to the experimental data when $w_f < 0.2$ wt.%. Therefore, an $E_f$ of 270 GPa to generate further figures in this study. The most widely reported theoretical $E$ of MWCNT is 1 TPa which is similar to the value of monolayer graphene [60] and also GNP that exfoliates to form graphene monolayers [61]. However, it
has been reported that the effective values of $E_f$ for MWCNT range from 270 to 910 GPa [62] and the results from the current study are at the low end of this range. The effective moduli of fillers in the nanocomposites that were obtained by extrapolation of experimental tensile data to 100% filler were 19 and 59 GPa for GNP and A-MWCNT, respectively. These values are much lower than the obtained value from figure 4.4.29 and reflect the poor filler dispersion in the range of nanocomposites and error in the simple extrapolation approach.

Figure 4.4.30 Halpin-Tsai calculations showing the effect of MWCNT weight fractions and aspect ratio on the modulus of PET/MWCNT nanocomposites.

Moreover, the influence of $\eta$ on the values of $E_c$ has been investigated. The moduli of PET/A-MWCNT nanocomposites and pure PET are plotted as a function of MWCNT contents in Figure 4.4.30. The values of $E_m$ and $E_f$ used in this calculation are 1.1 GPa and 270 GPa for the PET matrix and MWCNT, respectively. The $E_m$ used was obtained by tensile testing. The lines marked as ‘S’ and ‘P’ indicate the upper and lower model calculated using the series and parallel Equations of the rule of mixtures models, Equations
The dashed lines are Halpin-Tsai calculations obtained by using Equation (4.9) for values of $\eta$ between 20 and 1000.

The experimental data is shown as half-filled circles. In this case MWCNT are considered to be completely oriented asymmetrically with identical shapes and sizes; the reduction in experimental modulus could therefore be due to some random orientation of filler. It is clear from the figure that fillers with large values of $\eta$ are more efficient in terms of improving modulus. The experimental data at $\leq 0.2$ wt. % appears to lie between the lines defining $\eta$ values of 100 and 200, dropping at higher wt. % to give of $\eta$ values of $\leq 20$ indicating that agglomeration and/or nanotube breakage has occurred.

![Graph showing the dependence of tensile modulus on $E_f$ as predicted by the Halpin-Tsai model compared to experimental data for the GNP composites.](image)

**Figure 4.4.31** The dependence of tensile modulus on $E_f$ as predicted by the Halpin-Tsai model compared to experimental data for the GNP composites.

Similarly variation in aspect ratios and moduli were studied for PET/GNP nanocomposites and compared with their theoretical and experimental values. Figure 4.4.31 shows the obvious difference between calculated and experimental moduli values of nanocomposites.

Theoretically, the modulus increases with increasing $E_f$ values of the PET nanocomposites.
A reasonable agreement was found between the experimental and calculated modulus data at low filler contents (≤ 2 wt. %) which is lost upon further loadings.

An $E_f$ of 50 GPa was therefore chosen to create further figures for modelling of PET/GNP nanocomposites. The effective modulus of GNP in the nanocomposites, determined by extrapolation of experimental tensile values to 100 % GNP, was 19 GPa. This is much lower than the value obtained from Figure 4.4.31 and once again and reflects poor platelets dispersion in the matrix and error in the simple extrapolation approach used.

**Figure 4.4.32** Halpin-Tsai calculations showing the effect of GNP weight fractions and aspect ratio on the modulus of PET/ GNP nanocomposites.

Furthermore, the influence of $\eta$ on the values of $E_c$ has been examined. The moduli of PET/GNP nanocomposites and pure PET were constructed as a function of GNP loadings in Figure 4.4.32. The values of $E_m$ and $E_f$ used in this calculation are 1.1 and 50 GPa for the PET matrix and GNP, respectively.
The lines marked as ‘S’ and ‘P’ show the upper and lower predictions model using the series and parallel rule of mixtures models, Equations (4.7) and (4.8), respectively. The dashed lines are Halpin-Tsai calculations obtained using Equation (4.9) for values of \( \eta \) between 20 and 1000. The experimental data is shown as half-filled circles. Here GNP is considered to be completely exfoliated with identical shapes and sizes and also it assumed uniform dispersion and distribution into PET. The deviation in experimental moduli could be due to poor dispersion, and/or rolling up or folding of the platelets etc.

Obviously those fillers that have high \( \eta \) are more effective of increasing modulus. The experimental data at \( \leq 2 \)wt. % appears to lie between the values of \( \eta = 200 \) and \( \eta = 500 \), and this reduction in \( E_c/E_m \) at higher filler loadings results in data points falling below \( \eta = 20 \) line at filler levels greater than 4.5 wt. %. This is clear evidence of particles agglomeration and/or rolling up and folding of the GNP platelets.

**4.4.8.3 Prediction of Tensile Modulus for PET/A-MWCNT nanocomposites**

Figure 4.4.33 and Table 4.4.9, show the \( E \) values obtained by both original and modified models (Equations 4.5 and 4.9, respectively). It is clear that the data fit the predict model given by modified Halpin-Tsai equation well up to 0.2 wt. % A-MWCNT, whereas the original Halpin-Tsai model significantly overestimates the modulus. This improved fit is due to orientation factor (3/8 for random filler orientation) which is not taken into account in the original model. However; both models exhibited significant deviation from the experimental data at higher filler loadings. This indicates that some other factors could have an influence on the reinforcement mechanism such as agglomeration etc.

It has been reported that the Halpin-Tsai equation is well known to fit some data very well at low volume fractions but overestimates the modulus at high volume fractions [56]. Similar behaviour has been observed for PPS/MWCNT nanocomposites by Jiang et al [63] who
concluded that modified Halpin-Tsai model could effectively be utilized to predict the tensile modulus of MWCNT reinforced thermoplastic polymers.

Table 4.4.9 Tensile modulus obtained experimentally and compared using different Halpin-Tsai models.

<table>
<thead>
<tr>
<th>A-MWCNT (wt. %)</th>
<th>E (MPa) (Experimental)</th>
<th>E (MPa) (Original Halpin-Tsai)</th>
<th>E (MPa) (Modified Halpin-Tsai)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1073.3 ±15.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>1124.0 ±24.7</td>
<td>1223.5</td>
<td>1131.6</td>
</tr>
<tr>
<td>0.2</td>
<td>1182.3 ±52.1</td>
<td>1373.9</td>
<td>1190.0</td>
</tr>
<tr>
<td>1</td>
<td>1252.6 ±31.3</td>
<td>2581.8</td>
<td>1659.1</td>
</tr>
<tr>
<td>2</td>
<td>1302.7 ±13.8</td>
<td>4103.7</td>
<td>2250.4</td>
</tr>
</tbody>
</table>

Figure 4.4.33 Tensile modulus of PET/A-MWCT, by using Halpin-Tsai equations at different wt. % loadings of MWCNT.
The modified model was further tested by applying it to a published experimental data that obtained for PET/MWCNT nanocomposites [23] fabricated by melt compounding and under similar conditions that were used in the this research. Figure 4.4.34 depicts the results of these models. It is clear that the E predicted by modified equation is close to the experimental values at the loading ranging from 0 to 0.3 wt. %, whereas the original model showed a deviation from the experimental data at same MWCNT loadings.

![Graph showing tensile modulus of PET/MWCNT nanocomposites using Halpin-Tsai models, the experimental data obtained from ref. [23].](image)

**Figure 4.4.34** Tensile modulus of PET/MWCNT nanocomposites using Halpin-Tsai models, the experimental data obtained from ref. [23].

In both studies, these models deviated from the experimental data at high content of CNT. Kim et al. [43] modelled the $E_c$ of the PET/MWCNT nanocomposites and they found the deviation between the experimental and theoretical moduli increased with increasing wt.% of A-MWCNT. The differences between theoretically predicted and experimentally obtained tensile moduli are believed to be reduced by homogeneous dispersion and a better interfacial interaction between the MWCNT and PET matrix.
4.4.8.4 Predication of Tensile Modulus for PET/GNP nanocomposites

Figure 4.4.34 shows the E values for PET/GNP nanocomposites plotted as a function of GNP content. E values were estimated using by both the original and modified Halpin-Tsai models (Equations 4.5 and 4.9, respectively). It should be mentioned that the assumptions made by the Halpin-Tsai models regarding the GNP filler are: (1) perfect adhesion between the GNP and PET, (2) perfect 2D planar structure of GNP sheet (formed by perfect exfoliation) and (3) uniform dispersion and distribution of GNP into the PET matrix. It can also be seen from Figure 4.4.35 that the moduli predicted by the modified Halpin-Tsai models show in a good agreement with the experimentally obtained values when filler level is less than 2 wt. %.

![Figure 4.4.35 Tensile modulus of PET/GNP, by using Halpin-Tsai equations at different wt. % loadings of GNP.](image)

Figure 4.4.35 Tensile modulus of PET/GNP, by using Halpin-Tsai equations at different wt. % loadings of GNP.
However, the results obtained are in agreement with several other studies on polymer/GNP nanocomposites [14, 52, 64]. Several studies have reported overestimation of $E$ between the theoretical and experimental data at different filler loadings for polymer/GNP nanocomposites; for example Li et al, [14] compared the Halpin-Tsai predictions with experimental data for PTT/GNP nanocomposites, they observed similar moduli at GNP levels less than 1 wt. %. The experimental modulus was much lower than that predicted by the Halpin-Tsai model when filler levels were greater than 1 wt. %. Such deviation was attributed to poor interfacial adhesion between the filler and matrix. In another study on PET/GNP [13] and PBT/GNP [15] nanocomposites by the same authors, similar conclusions were reported. Duguay et al, [64] studied PP/GNP nanocomposites and found a poor agreement between theoretical and experimental values of tensile modulus. According to the authors the model over-estimates the modulus, which is due to the theoretical $\eta$ value used in the model. In real situations, platelets distortion and agglomeration takes place during melt processing that could lead to smaller values of $\eta$ than the predicted values which are based on perfect exfoliation of GNP. Shokrieh et al [52] who measured the tensile modulus of epoxy/GNP nanocomposites, observed that the Halpin-Tsai predication deviated from the experimental values of GNP levels greater than 0.25 wt. %. This deviation was attributed to poor dispersion resulting from misalignment of GNP in the epoxy matrix. Such misalignment was not taken into consideration when using Halpin-Tsai model.
4.4.9 Summary

The influence of different carbon fillers on the mechanical properties of PET was investigated using DMTA and tensile techniques. In addition, DSC was used after the DMTA runs to confirm the occurrence of cold crystallization. Cold crystallization was observed in DMTA curves for the quenched PET specimens and the PET/carbon composite, resulting in increased storage moduli above $T_g$.

Both tensile and DMTA investigations showed that the addition of carbon fillers into PET can improve the modulus of the resultant composites. Such improvements were attributed to both an increase in the degree of crystallinity, a minor degree, as well as reinforcement by the filler which predominated. However, incorporation of these filler types resulted typically in decreased tensile strength of composites and elongation at break compared with pure PET; except for T-MWCNT at 0.1 and 0.2 wt. % loadings which showed no significant change.

The $T_g$ values of PET/carbon composites remain essentially unchanged upon incorporation of fillers. However, tanδ values at $T_g$ showed reduction, indicating (in addition to volume fraction reduction of the polymer) restricted polymer chain mobility due to polymer-filler interactions as well as increased crystallinity in the composites.

The experimentally determined tensile moduli were compared to predication model using the modified Halpin-Tsai model. The comparison showed a good agreement to the theoretical model at low loadings of A-MWCNT ($\leq 0.2$ wt. %) and GNP ($\leq 2$ wt. %). However, poor agreement was observed at higher loadings of fillers where the composites displayed reduced reinforcement efficiency. This is due to the fact that the model assumes perfect between fillers-matrix adhesion, their uniform particles dispersion and distribution and also complete exfoliation and total orientation in the direction in the direction of applied stress; which is typically not the case during in real nanocomposites.
4.4.10 References


Chapter 5 Conclusions and Recommendations for Future Work

5.1 Conclusions

5.1.1 Introduction

In this work, conductive carbon filled PET composites were prepared using graphite, GNP, A-MWCNT and T-MWCNT for intended use in applications such as antistatic discharge, electrodes materials etc. These composites were prepared by melt compounding using a co-rotating twin-screw extruder and moulded into films and tensile test pieces by compression and injection mouldings, respectively. The electrical, morphological, thermal and mechanical properties of these composites were characterized as a function of carbon filler types and their weight fraction of filler added. The characterization techniques used were electrical impedance spectroscopy, SEM, TEM, FTIR, DSC, TGA, DMTA and tensile testing. The following conclusions were derived from the experimental work reported in this thesis.

5.1.2 Electrical Properties

The electrical conductivities of PET/carbon composites were investigated over a wide range of filler concentrations, in order to determine the percolation thresholds. Values of percolation thresholds were determined by fitting a power-law equation, derived from percolation theory to the experimental data. The conductivity increased abruptly at percolation thresholds which indicate the insulator – conductor transitions for the PET based composites. The PET/A-MWCNT nanocomposites exhibited excellent electrical conductivity (maximum 0.2 S/m at 2 wt. % A-MWCNT) and the lowest percolation threshold (0.33 wt. %) of all the fillers investigated in this study. In contrast, PET/T-MWCNT nanocomposites showed very low conductivity which was similar to the unfilled matrix at the same loadings as for A-MWCNT and no percolation threshold was observed over the filler
level range investigated (0 to 2 wt. %). This is could be due to the acid treatment which disrupted the inherent electrical conductivity of CNT due to the presence of oxygen containing functional groups and defects on the surface of A-MWCNT. Acid treatment also led to reduction in CNT length resulting from the treatment.

The percolation thresholds of the composites were found to be 0.33 wt. %, 5.7 wt. % and 14.7 wt. % for graphite, GNP and A-MWCNT, respectively. The dimensionality constants (t) values were obtained were 1.29, 4.72 and 2.89 for graphite, GNP and A-MWCNT particles into PET, respectively. Such values deviated from theoretical, i.e. 1.33 and 2.2 which indicate the formation of 2D and 3D networks in the composites, respectively. The variation in value of t is usually described differently that includes the limitations of percolation theory and tunnelling effects.

The electrical conductivities of the PET/carbon composites were also investigated as a function of frequencies. These conductivities were found to be independent of the applied frequencies for the composites loaded above the percolation threshold values; this is typical behaviour for conductive materials. In contrast, at filler level below the percolation threshold, the electrical conductivities of the PET and composites were frequency dependent. The conductivities of PET/carbon composites at 10 Hz were then plotted as a function of filler loading. For example; the electrical conductivity of PET/A-MWCNT nanocomposites was found to be between $10^0$ and $10^1$ S/m at a loading of 2 wt. % A-MWCNT, while rest of the PET/carbon composites at the same filler loadings showed conductivities similar to that of the matrix. However, the conductivities values of PET/carbon composites when loaded just above the percolation thresholds were observed to be around $10^6$ S/m, which is the minimum value required for anti-static applications. Upon further addition of filler, the conductivities of the composites were increased sharply with increasing fillers contents, followed by slight increment or levelled off.
The effects of extrusion processing conditions i.e. screw speed and residence time, on the electrical conductivities of PET/carbon composites were investigated for samples with fillers loadings above and below the percolation thresholds. The screw speed had a significant effect on the conductivity particularly when filler level was above the percolation thresholds; this was especially true for the PET nanocomposites (GNP and MWCNT). When screw speed increased from 45 to 90 rpm, the conductivity increased by 2 to 3 orders of magnitudes for the nanocomposites. In contrast, increasing the residence time of the composites in the extruder from 5 to 10 minutes had no significant effect on their electrical conductivity.

PET/A-MWCNT nanocomposites were also prepared by injection moulding in order to compare the electrical conductivities to those obtained by compression moulding. Composites prepared by injection moulding showed lower electrical conductivity for the same level of filler than compression moulding, as well as higher percolation threshold values. This is due to the partial alignment of MWCNT in the flow direction, which leads to interruption of tube-to-tube contacts.

5.1.3 Morphology

The morphologies of the carbon fillers and PET/carbon composites were investigated using SEM and TEM. In general, the morphologies of PET/carbon composites obtained from cryogenically-fractured specimens showed higher agglomeration and poorer distribution of conductive fillers into the PET when filler loading was around their percolation threshold values, resulting in the formation of electrically-conductive networks. Similarly, the tensile fracture surfaces showed agglomeration, debonding, rolling up of GNP, and pulling out of fillers at higher loadings, which reduced the tensile strength of these composites. Also, the stress concentration around such agglomerates typically results in lower bulk stresses and strains at failure. In general, all composite samples exhibited more brittle fracture surfaces in
comparison to the PET matrix. Furthermore, in the case of T-MWCNT better adhesion and
distribution in the polymer matrix were achieved compared to the A-MWCNT. This is
because of the reduction in entanglement and the attachment of functional groups (-COOH
and -OH) caused by the acid-treatment that were confirmed by FTIR.

5.1.4 Thermal Behaviour
Thermal behaviour of the PET and composites was studied in order examine the influence of
these carbon fillers on crystallization, degree of crystallinity and thermal stability using DSC
and TGA techniques. In addition, the effect of cooling rate on crystallization behaviour of
PET was also studied. The crystallization behaviour of PET was found to be affected by
cooling rates, in which a higher cooling rate resulted in a significant reduction in the degree
of crystallinity. In addition, it was found that quenched PET samples were not fully
crystallized after processing and therefore, crystallized during the first heating cycle in DSC,
as indicated by the presence of a cold crystallization peak.

All the carbon fillers, with different dimensions, were found to act as nucleating agents for
the PET matrix, resulting in increased degree of crystallinity and accelerated crystallization
behaviour. At identical loadings of carbon fillers, the highest degree of crystallinity was
observed for PET/A-MWCNT nanocomposites. Moreover, the 1D fillers were found to
affect the crystallization at very low loadings (0.1 wt. %) in comparison to 2D and 3D fillers
that exhibited similar crystallization behaviour at higher loadings (2 wt. %). For example,
the crystallization temperature increased by ~ 10 °C and cold crystallization temperature
temperatures decreased by ~ 13 °C for both of these cases. However, the melting and glass
transition temperatures of composites remained approximately unaffected upon the addition
of fillers types or their contents.
The thermal stability of carbon composites was investigated in air and nitrogen. Generally, the addition of carbon fillers into the PET matrix improved the resistance to thermal and thermo-oxidative degradation in both air and nitrogen atmospheres. However, no clear relationship between such improvements and the amount of fillers used was observed. However, the acid treatment of CNT was found to have a negative influence on the thermal stability of the PET nanocomposites under an air atmosphere.

5.1.5 Mechanical Properties

The influence of carbon fillers on the mechanical properties of PET was investigated using DMTA and tensile testing. Both tensile and DMTA investigations showed that the addition of carbon fillers into PET can improve the modulus of the resultant composites. Such improvements were attributed to both an increase in the degree of crystallinity, to a minor degree, as well as reinforcement by the filler which predominated. However, incorporation of all these filler types resulted typically in decreased tensile strength and elongation at break of the composites compared with unfilled PET; except for T-MWCNT at 0.1 and 0.2 wt. % loadings which showed no significant change.

Cold crystallization was observed in DMTA curves for the quenched PET specimens and the PET/carbon composites, resulting in storage moduli increasing at temperatures above $T_g$. The $T_g$ values of PET/carbon composites remained essentially unchanged upon incorporation of fillers. However, tanδ values at these temperatures showed reduction, indicating (in addition to volume fraction reduction of the polymer) restricted polymer chain mobility due to polymer-filler interactions as well as increased crystallinity in the composites.

The experimental tensile moduli were compared to calculations using the modified Halpin-Tsai model. The comparison showed a good agreement at low loadings of A-MWCNT ($\leq 0.2$ wt. %) and GNP ($\leq 2$ wt. %). However, poor agreement was observed at higher loadings of
fillers where the composites displayed reduced reinforcement efficiency. This is due to the fact that the model assumes the perfect adhesion between fillers and matrix, their uniform dispersion and distribution and also perfect exfoliation/orientation; which is typically not the case during in real nanocomposites.

To summarise the results reported in this thesis; it is suggested that there are several factors that could affect the final properties of composites, this include filler type, filler content, filler dimensions, preparation methods and processing parameters, modification techniques, interfacial adhesion and dispersion. All such factors are important to acquire the desired properties and develop an understanding of the processing-structure-property relationships of polymer composites.

5.2 Recommendations for future work

Based on experimental studies and literature review, the following are recommendations for future work.

1. Incorporation of two different nanofillers into a polymer matrix for fabrication of composites such as mixing both modified and as-received CNT as a filler. This is proposed to optimise both mechanical and electrical properties of polymer composites. Since the best mechanical properties for both were obtained at 0.1 wt. % CNT loadings, combining 0.05 wt. % of each may bring about synergy mechanical and electrical properties. A similar search can be done at 0.33 wt. % CNT where the electrical conductivity percolation was attained for PET/A-MWCNT nanocomposites.

2. Combination of microfiller and nanofiller into a polymer matrix for fabrication of composites. This is proposed to reduce the cost and improve the properties of composites.
3. Optimise the acid treatment conditions for CNT such as time, temperature and acid ratios. Also, use such treatment for GNP and graphite, in addition to CNT. This will improve the interaction between fillers and matrices for enhanced interfacial adhesion.

4. Optimisation of processing parameters such as the screw speed, extrusion temperature and residence time for the extrusion process. This will affect the viscosity of the system therefore improved dispersion and distribution of the fillers is expected.

5. Higher loadings of T-MWCNT should be investigated in order to find out the percolation threshold loading for PET/T-MWCNT nanocomposites.

6. Further study on the effect of acid treatments is recommended to establish the reasons for observed decline in the thermal stability of the PET/T-MWCNT nanocomposites as found in this study. For example, changes in molecular weight of the nanocomposites can be investigated as possible reason for this reduction.

7. This work has investigated the electrical, morphological, thermal and mechanical properties of PET/MWCNT over a range of compositions. It is suggested that investigating similar properties can be extended to PET/SWCNT nanocomposites.

8. One of the future works may focus on the effect of the cooling rate variations on the structure and properties of PET and its carbon composites.