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Department of Materials

Development of High Performance Carbon Nanotube/Polymer composites

By
Dongyu Cai

A doctoral thesis submitted in partial fulfilment of the requirement for the award of Doctor of Philosophy of Loughborough University

Supervisor: Dr Mo Song

Department of Materials
Loughborough University

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## List of abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerisation</td>
</tr>
<tr>
<td>BA</td>
<td>n-Butyl acrylate</td>
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<tr>
<td>BDO</td>
<td>1,4-Butanediol</td>
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<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>CIPP</td>
<td>Chlorinated polypropylene</td>
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<tr>
<td>DBTL</td>
<td>Dibutyltin dilaurate</td>
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<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
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<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
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<tr>
<td>DMPA</td>
<td>A,A-dimethylol propionic acid</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>EG</td>
<td>Expandable graphite</td>
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<tr>
<td>FEGSEM</td>
<td>Field emission gun scanning electron microscopy</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectrometry</td>
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<tr>
<td>GA</td>
<td>Gum Arabic, polysaccharide</td>
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<tr>
<td>GO</td>
<td>Graphite oxide</td>
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<td>GONP</td>
<td>Graphite oxide nanoplatelet</td>
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<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
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<tr>
<td>MA</td>
<td>Maleic anhydride</td>
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<tr>
<td>MDI</td>
<td>4,4-Methylenebis (phenyl isocynate)</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated differential scanning calorimetry</td>
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<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
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<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
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<td>MWCNT-OH</td>
<td>Multi-walled carbon nanotube with hydroxyl group</td>
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<tr>
<td>NHSK</td>
<td>Nanohybrid shish-kebab</td>
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<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscopy</td>
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<tr>
<td>PA</td>
<td>Polyamide</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactone</td>
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<td>PE</td>
<td>Polyethylene</td>
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<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
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<tr>
<td>PmPV</td>
<td>Poly(m-phenylenevinylene-co-2,5-di-octyloxy-p-phenylenevinylene)</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl acrylate)</td>
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<tr>
<td>POM</td>
<td>Polarised optical microscopy</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>PPG</td>
<td>Polyether Polyol</td>
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<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PU</td>
<td>Polyurethane</td>
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<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
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<tr>
<td>PVAc</td>
<td>Polyvinylacetate</td>
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<tr>
<td>PVK</td>
<td>Polyvinylcarbazole</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
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<tr>
<td>TEA</td>
<td>Triethyl amine</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>UHMWPE</td>
<td>Ultra high molecular weight polyethylene</td>
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</table>
Abstract

This project mainly concerned the development of novel engineering approaches to optimise the physical properties of the polymer composites with a low loading of carbon nanotubes (CNTs). It was additionally discovered that graphite oxide nanoplatelets (GONPs) can be a strong and affordable substitute for the CNTs in the polymer composites.

Colloidal physics and coating methods were applied to fabricate semi-conductive CNT/polymer composites with low percolation threshold. Polyurethane (PU) latex and ultra high molecular weight polyethylene (UHWMPE) powder were used as hosting matrix in the colloidal physics method and coating method, respectively. In the colloidal physics method, the percolation threshold was found to be around 0.5wt% MWCNTs and the electrical conductivity of the composites was improved by more than four orders of magnitude with the addition of 1wt % multi-walled carbon nanotubes (MWCNTs). The study of rheological behaviour revealed that the addition of the MWCNTs led to the increase in the viscosity of the PU dispersion. In the coating method, the scanning electron microscopy (SEM) images confirmed the strong adhesion of the nanotubes on the surface of the powders. Sheet samples were prepared using compression moulding for electrical test. The percolation threshold for the powders with the size of 60μm was around 1wt% MWCNTs and the percolation threshold for the powders with the size of 100μm was around 0.5wt% MWCNTs.

A novel route was revealed to reduce the interfacial phonon scattering that is considered as the bottleneck for CNTs to highly improve the thermal conductivity of CNT/polymer composites. Semicrystalline PU dispersions were used as latex host to accommodate the MWCNTs following the colloidal physics method. The thermal conductivity increased from 0.15 Wm⁻¹K⁻¹ to 0.47 Wm⁻¹K⁻¹, by ~210%, as the addition of the MWCNTs increased to 3wt%. The morphology of the
composites suggested that the continuous nanotube-rich phase existing in the interstitial space among the latex particles and the crystallites nucleated at the nanotube-polymer interface were the main factors for the effective reduction of interfacial phonon scattering.

The optimisation of the crystalline layer around CNTs was studied based on the MWCNT/polycapro!actone (PCL) composites using differential scanning calorimetry (DSC). The study of the non-isothermal crystallisation showed that crystallisation temperature ($T_c$) increased with increasing incorporation of the nanotubes, and melting temperature ($T_m$) and heat of fusion ($\Delta H_m$) was almost unchanged. The incorporation of 2wt% nanotubes resulted in the biggest increase of the $T_c$ to be $\sim$11°C. The study of the isothermal crystallisation showed the temperature, 14°C higher than the $T_c$, was appropriate one to optimise the crystalline layer in the composite melts. It was revealed that the incorporation of 0.1wt% nanotubes significantly affected the rate of crystal growth and crystalline morphology. For more incorporation of the nanotubes, the rate of crystal growth and crystalline morphology was less affected. The improvement in the Young's modulus of the composite with the thermal treatment confirmed the contribution of the crystalline layer to the load transfer across the non-covalent interface between the nanotube and polymer matrix.

The preparation of the exfoliated GONPs in DMF was revealed. With this method in hand, two kinds of polymers including semi-crystalline PCL and amorphous PU were selected to be incorporated with the GONPs using the solution method. It was found that the GONPs showed strong nucleating ability in the PCL matrix. The thermal treatment under the “14°C” rule could create an optimised crystalline layer on the surface of the GONPs from the composite melts. The bigger increase in the Young’s modulus of the treated GONP/PCL composites confirmed that the crystalline layer nucleated on the surface of the GONPs could act as a non-covalent interface between the GONPs and PCL matrix. The significant
reinforcement of the PU using GONPs was also disclosed. Morphologic studies showed that, due to the formation of chemical bonding, strong interaction occurred between the GONPs and the hard segment of the PU, which allowed effective load transfer. The GONPs can prevent the formation of crystalline hard segments due to their two-dimensional structure. With the incorporation of 4.4wt% graphite oxide nanoplatelets, the Young's modulus and hardness of the PU were significantly increased by ~900% and ~327%, respectively. The resultant high anti-scratch property pointed to the promising application of these composite materials in surface coating.
Acknowledgement

I am really grateful to my supervisor, Dr Mo Song, who guided me to the world of polymer nanocomposites. His constant encouragement and support, in both professional and personal ways, and his invaluable scientific inputs, discussions and supervision helped me go through hard moment in the research and complete this final thesis.

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Table of Content

List of abbreviation ......................................................................................................... i
Abstract ........................................................................................................................ iii
Acknowledgement ........................................................................................................ iv
Table of Content ........................................................................................................... iv
List of Figures and Tables ............................................................................................. iv
Chapter 1 Background and aims of the project ............................................................. 4
  1.1 Background of the project ........................................................................... 4
  1.2 Aims of the project ........................................................................................... 4
Chapter 2 Literature review ........................................................................................... 4
  2.1 Introduction of CNTs .................................................................................... 4
  2.2 Synthesis of CNTs ........................................................................................... 4
  2.3 Fabrication of CNT/polymer nanocomposites ................................................. 4
      2.3.1 Pretreatment of CNTs .......................................................................... 4
      2.3.2 Solution method .................................................................................... 4
      2.3.3 Melt processing ..................................................................................... 4
      2.3.4 In situ polymerisation .......................................................................... 4
      2.3.5 New methods ......................................................................................... 4
  2.4 Electrical property of CNTs and CNT/polymer composites ............................ 4
      2.4.1 Electrical property of CNTs ................................................................ 4
      2.4.2 Electrical property of CNT/polymer composites ................................ 4
  2.5 Thermal conductivity of CNTs and CNT/polymer composites ....................... 4
      2.5.1 Thermal conductivity of CNTs ............................................................... 4
      2.5.2 Thermal conductivity of CNT/polymer composites .............................. 4
  2.6 Mechanical Properties of CNTs and CNT/polymer composites ..................... 4
      2.6.1 Mechanical properties of CNTs ............................................................. 4
      2.6.2 Mechanical properties of CNT/polymer composites .......................... 4
  2.7 Conclusions ....................................................................................................... 4
Chapter 3 Experimental ................................................................................................. 4
Table of Content

3.1 Materials .................................................................................................................. 4

3.2 Sample preparation ........................................................................................................ 4

3.2.1 Preparation of polyether-based PU dispersions ........................................ 4

3.2.2 Preparation of PCL-based PU dispersions .................................................. 4

3.2.3 Preparation of MWCNT/PU composites by a colloidal physics method ...... 4

3.2.4 Preparation of MWCNT-OH/PHMPE composites by a coating method. 4

3.2.5 Preparation of MWCNT-OH/PCL composites by a solution method .......... 4

3.2.6 Preparation of exfoliated graphite oxide nanoplatelets (GONPs) in DMF .... 4

3.2.7 Preparation of GONP/PCL composites ........................................................ 4

3.2.8 Preparation of GONP/PU composites ......................................................... 4

3.3 Characterisation ....................................................................................................... 4

3.3.1 Fourier transform infrared (FTIR) spectroscopy ............................................. 4

3.3.2 Raman spectroscopy ....................................................................................... 4

3.3.3 Scanning electron microscopy (SEM) ............................................................. 4

3.3.4 Transmission electron microscopy (TEM) ...................................................... 4

3.3.5 Differential scanning calorimetry (DSC) ...................................................... 4

3.3.6 Dynamic mechanical analysis (DMA) ........................................................... 4

3.3.7 Optical microscopy (OM) and polarised optical microscopy (POM) ........ 4

3.3.8 X-Ray photoelectron spectroscopy (XPS) ................................................... 4

3.3.9 Wide angle X-ray diffraction (WXRD) ........................................................ 4

3.3.10 Measurement of the viscosity of the MWCNT/PU dispersions .......... 4

3.3.11 Measurement of the electrical conductivity using a two-probe method ..... 4

3.3.12 Measurement of the thermal conductivity using a DSC method .......... 4

3.3.13 Tensile testing ............................................................................................... 4

3.3.14 Nanoindentation ............................................................................................ 4

Chapter 4 Preparation and characterisation of semi-conductive carbon nanotube/polymer composites with low percolation threshold ......................... 4

4.1 Introduction ............................................................................................................. 4

4.2 Results and discussion (Part A): MWCNT/PU composites ........................................ 4

4.2.1 FTIR characterisation of PPG and its derivated PU ....................................... 4
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.2 Dispersion of MWCNTs in water and PU composites</td>
<td>4</td>
</tr>
<tr>
<td>4.2.3 Film formation of MWCNT/PU dispersions</td>
<td>4</td>
</tr>
<tr>
<td>4.2.4 Rheological behaviour of MWCNT/PU dispersions</td>
<td>4</td>
</tr>
<tr>
<td>4.2.5 Electrical property of MWCNT/PU composites</td>
<td>4</td>
</tr>
<tr>
<td>4.3 Results and discussion (Part B): MWCNT-OH/UHMWPE composites</td>
<td>4</td>
</tr>
<tr>
<td>4.3.1 Characterisation of MWCNTs and MWCNTs-OH</td>
<td>4</td>
</tr>
<tr>
<td>4.3.2 Dispersion of MWCNTs-OH in DMF and UHMWPE particles</td>
<td>4</td>
</tr>
<tr>
<td>4.3.3 Electrical conductivity of MWCNT-OH/UHMWPE composites</td>
<td>4</td>
</tr>
<tr>
<td>4.4 Conclusions</td>
<td>4</td>
</tr>
<tr>
<td>Chapter 5 Latex technology as a simple route to improve the thermal conductivity of a carbon nanotube/polymer composite</td>
<td>4</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>4</td>
</tr>
<tr>
<td>5.2 Results and discussion</td>
<td>4</td>
</tr>
<tr>
<td>5.2.1 Basic theory of heat conduction</td>
<td>4</td>
</tr>
<tr>
<td>5.2.2 Thermal conductivity of MWCNT/PU composites</td>
<td>4</td>
</tr>
<tr>
<td>5.2.3 SEM imaging the morphology of MWCNT/PCL-based PU composites</td>
<td>4</td>
</tr>
<tr>
<td>5.2.4 Study of the crystalline morphology of MWCNT/PCL-based PU composites</td>
<td>4</td>
</tr>
<tr>
<td>5.3 Conclusions</td>
<td>4</td>
</tr>
<tr>
<td>Chapter 6 Study of thermal-induced crystalline interface for the load transfer in a carbon nanotube/polymer composite</td>
<td>4</td>
</tr>
<tr>
<td>6.1 Introduction</td>
<td>4</td>
</tr>
<tr>
<td>6.2 Results and discussion</td>
<td>4</td>
</tr>
<tr>
<td>6.2.1 Dispersion of MWCNTs-OH in PCL matrix</td>
<td>4</td>
</tr>
<tr>
<td>6.2.2 DSC study of the crystallisation behaviour of MWCNT-OH/PCL composites</td>
<td>4</td>
</tr>
<tr>
<td>6.2.3 Morphological study of the PCL crystals in MWCNT-OH/PCL composites</td>
<td>4</td>
</tr>
<tr>
<td>6.2.4 Understanding of the contribution of the crystalline layer surrounding CNTs to the Young's modulus of CNT/polymer composites</td>
<td>4</td>
</tr>
<tr>
<td>6.3 Conclusions</td>
<td>4</td>
</tr>
</tbody>
</table>
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers .................................................. 4

7.1 Introduction .............................................................................................................. 4

7.2 Results and discussion (Part A): characterisation of GONPs ......................... 4

7.3 Results and discussion (Part B): GONP/PCL composites .......................... 4

7.3.1 Uniform dispersion of GONPs in PCL matrix .............................................. 4

7.3.2 Non-isothermal crystallisation of GONP/PCL composites ....................... 4

7.3.3 Isothermal crystallisation of GONP/PCL composites ............................. 4

7.3.4 Morphological study of the PCL crystals in GONP/PCL composites ........ 4

7.3.5 Comparative study on the Young’s modulus of the GONP/PCL composites before and after the thermal treatments ............................................ 4

7.4 Results and discussion (Part C): GONP/PU composites .......................... 4

7.4.1 Morphology of the GONP/PU composites ................................................... 4

7.4.2 Mechanical properties of the GONP/PU composites ............................ 4

7.4 Conclusions .............................................................................................................. 4

Chapter 8 Conclusions and future work ................................................................. 4

8.1 Conclusions .............................................................................................................. 4

8.2 Future work .............................................................................................................. 4

References ...................................................................................................................... 4

List of publications ........................................................................................................ 4
List of Figures and Tables

Figure 2.1 Multi-walled carbon nanotubes discovered by Iijima in 1991

Figure 2.2 (a) Schematic honeycomb structure of a graphene sheet. Single-walled carbon nanotubes can be formed by folding the sheet along lattice vectors. The two basis vectors $a_1$ and $a_2$ are shown. Folding of the (8,8), (8,0), and (10,-2) vectors lead to armchair (b), zigzag (c), and chiral (d) tubes, respectively

Figure 2.3 Scheme of continuous production liquid-nitrogen reaction chamber for nanotube synthesis

Figure 2.4 Oven laser-vaporization apparatus

Figure 2.5 Scheme of the reaction between carboxylated CNTs and PVA activated by carbodiimide

Figure 2.6 Typical TEM image of a specimen from the cross-sectional microtomy of a PVA-MWCNT composite film

Figure 2.7 Schematic illustration of the grafting process of polyurethane on the multi-walled carbon nanotubes. The bar represents 50 nm in A1, 20 nm in A2, 50 nm in B2 and 20 nm in B2

Figure 2.8 Scheme of the reaction between pMS-Cp-Fe-MWCNTs and polystyrene

Figure 2.9 Schematic preparation process of modified CNT with PSt

Figure 2.10 Proposed formation mechanism of polymer-encapsulated carbon nanotubes through ultrasonically initiated in-situ emulsion polymerisation

Figure 2.11 Scheme of preparation of alkene-functionalised SWCNTs (f-SWCNTs) and SWCNT-g-PE via the copolymerisation technique

Figure 2.12 Scheme of the method for preparation of the CNTs bundle wires with PMMA shells

Figure 2.13 Mechanism of atom transfer radical polymerisation

Figure 2.14 Scheme of functionalising the CNTs using ATRP

Figure 2.15 Cryo-TEM micrographs of A) a 1:1 w/w SWCNT-SDS aqueous solution; B) 1:1 w/w SWCNT-GA in an aqueous, 5wt.-% dialyzed PS-latex solution. Note the strong SWCNT-latex repulsion; C) 1:1 w/w SWCNT-GA in an aqueous, 5wt.-%
PS-latex solution, to which 0.5wt.-% NaCl had been added to overcome the repulsion. Note the growth of individual or bundles of very few SWCNTs from the Ni-Y catalyst nanoparticles (arrows in part (B) and (C) and inset in part (B). Scale bar=100 nm

Figure 2.16 Grafting of PE-MA on MWCNTs

Figure 2.17 A spraying scheme: SWCNTs suspended solution was uniformly spurted onto the surface of HDPE powders from sprinkler

Figure 2.18 SEM image of the morphology of SWCNTs on the surface of HDPE powder by spraying method

Figure 2.19 Schematic route of in situ anionic polymerisation of MMA using debundled CNTs salts as anionic initiator

Figure 2.20 Chemical routes for preparation of PU–CNT composite

Figure 2.21 Schematic procedure for preparation of CNTs-MA/Epoxy nanocomposites

Figure 2.22 SEM images of the rapture region of the MWCNT freestanding film after stretching tests

Figure 2.23 SEM images of 980 nm polystyrene particles coated with one layer of MWCNTs

Figure 2.24 SEM images of polystyrene particles with hexagonal order before (a and d) and after (b,c,e,f) assembly of carbon nanotubes. All images correspond to the same sample but images (c) and f have been obtained with a tilting angle of 10°. Scale corresponds to (a)

Figure 2.25 Schematic illustration of the drying process of SWCNT-filled polymer emulsion. Initially, the nanotubes and polymer particles are uniformly suspended in water (left). Once most of the water has evaporated, the polymer particles assume a close-packed configuration with the nanotubes occupying interstitial space (center). Finally, the polymer particles will interdiffuse (i.e., coalescence) to form a coherent film, locking the SWCNTs within a segregated network (right)

Figure 2.26 Optical micrographs of the cross-sections of SWCNT/PS nanocomposites prepared by the coated particle process (CPP) with (a) faceted PS domains and (b) elongated PS domains due to higher pressures during compressionmolding. The lines
across the polymer domains are from the diamond saw. (c) SEM image of the fracture surface of NTPSpe1 with 0.5 wt% SWCNT showing evidence that PS spans across the SWCNT layer

**Figure 2.27** SEM micrographs of the fracture surface of the ultralightweight CNT/PU foam composite with a density of 0.05 g cm⁻³. a) Low magnification (with some cell walls and cell struts therein indicated by the arrows). b) High-magnification micrograph of the cross-section of the cell strut in **Figure 2.27a**

**Figure 2.28** Schematic diagram of the microstructural changes in the CNT/PU foam composites with the decrease of density. The thin black lines represent the CNTs and the wide lines represent the boundaries of the cells. The density decreases gradually from (a) to (d). The arrows in the cells show the growth directions of the air bubbles during foaming

**Figure 2.29** Schematic of the infiltration method

**Figure 2.30** (a) Optical and (b) SEM image of the SWCNT/epoxy composite fabricated by the infiltration method

**Figure 2.31** The model of an ideal structure for thermal interface material (TIM) application. All the CNTs are aligned in the matrix and protrude out of the surfaces to form an ideal thermal conducting path from one surface to the other

**Figure 2.32** SEM images of a CNT array and a CNT array composite. a) Side view of an aligned CNT array. The inset is a HRTEM image of a typical CNT showing eight graphite layers. b) Side view of the aligned CNT composite film, showing that the CNTs still remain in aligned in the composite. c) Tilted view (65°) of the aligned CNT composite film, showing most of the CNT tips protruding out of the surface. d) Top view of the aligned CNT array composite film after RIE treatments, showing almost all tips protruding out of the film surface

**Figure 2.33** A) SEM image showing an overall morphology of failure surface for PA-6 nanocomposite containing 0.5% MWCNTs. B) Enlarged morphology of selected region in (A). C) SEM image showing microcracks linked by stretched nanotubes and their bundles in PA-6 nanocomposites. D) Enlarged SEM image of the microcrack connected by MWCNTs sheathed with polymer in the nanocomposites. Some
MWCNTs are sheathed by several small polymer beads

**Figure 2.34** (A) Typical stress-strain curves and (B) Typical loading-unloading curves for neat PA6 and its nanocomposite containing 1 wt% MWCNTs

**Figure 2.35** TEM images of a MWCNT-containing PMMA thin film taken at different time: a) t=0, b) t=4, and c) t=10 min

**Figure 2.36** Stress-strain curves: a) PE/PE-g-MWCNTs composites; b) PE/MWCNTs composites

**Figure 2.37** Stress-strain profiles of nylon 6-SWCNT composite fibres at different SWCNT loadings. The curves are labeled with the percentage of SWCNTs in the polymer matrix

**Figure 2.38** Effect of the CNT content on the (a) tensile strength, (b) elongation-at-breaks, and (c) tensile moduli of the CNTs/epoxy nanocomposites

**Figure 2.39** TEM image of the MWCNTs pulled out from PVA

**Figure 2.40** DSC curves (on the left) for PVA-based composites as a function of nanotube volume fraction (Note the area under the melt peak(160-210°C) increase with nanotube content) and graph of crystallinity (on the right) as calculated from the DSC melt curves versus volume fraction for PVA-based composite simples

**Figure 2.41** Representative stress-strain curves for PVA-based composites (left) and Cl-PP composites (right) for a range of nanotube volume fractions

**Figure 3.1** Ringed poly-3-hydroxy butyrate spherulites (Micrographe NO. 601, Micrograph Library, DoITPoMS, Department of Materials Science and Metallurgy, University of Cambridge)

**Figure 3.2** Schematic diagram of the sample arrangement on the DSC sensor. h is the height of the sample cylinder; Φ is the heat flow that flows from the sensor into the sample; Tₘ is the temperature of the metal melt, Tₛ is sensor temperature under sample; Tᵣ is the temperature of the reference sample. The reference crucible is empty without a lid. A crucible containing the pure metal is placed on the top of the sample. The spaces between the crucible-sample and sample-sensor interfaces are filled with heat transfer oil (straight line).

**Figure 4.1** FTIR spectra of PPG (a) and its derivated polyurethane before
neutralization (b)

**Figure 4.2** TEM images of the MWCNTs individually dispersed in water

**Figure 4.3** Mechanism of nanotube isolation from the bundle obtained by ultrasonication and stabilization

**Figure 4.4** Schematic representations of the mechanism by which surfactants help to disperse SWCNT. (a) SWCNT encapsulated in a cylindrical surfactant micelle (both cross section and side view); (b) hemimicellar adsorption of surfactant molecules and a SWCNT; (c) random adsorption of surfactant molecules on a SWCNT

**Figure 4.5** SEM images of the MWCNT(3wt%)/PU composites (fracture surface)

**Figure 4.6** Photographs for the MWCNT/PU composites. The size of all samples is 3.5cm×3.5cm (a) 0 wt% of MWCNTs, (b) 2 wt%, (c) 0 wt% with 0.5 wt% NaCl, and (d) 2 wt% with 0.5 wt% NaCl

**Figure 4.7** Viscosity of the MWCNT/PU dispersions vs. shearing rate with different loadings of MWCNTs at 20°C

**Figure 4.8** Flow behaviour index (n) of MWCNT/PU dispersions at 20°C

**Figure 4.9** Electrical conductivity of the MWCNT/PU composites

**Figure 4.10** Fitting of the experimental data (the electrical conductivity) into the classical percolation power law (dotted line). The parameters of the classical percolation power law are revealed inside the graph.

**Figure 4.11** General illustration of the microstructure of a CNT/polymer composite. Thick straight line represents the CNTs and the thin random line represents the polymer chains. Highlighted places in the circles represent typical CNT-polymer-CNT junctions in the composite.

**Figure 4.12** Optical microscopy images of the MWCNT/PU dispersions. (a) is the transmitted image of the PU dispersion, and (c) and (e) are its reflected images, focusing on particle and non-particle zones, respectively. (b) is the transmitted image of the PU dispersion with 5wt% MWCNTs, and (d) and (f) are its reflected images focused on particle and non-particle zones, respectively.

**Figure 4.13** FTIR spectra of MWNTs and MWNTs-OH

**Figure 4.14** Raman spectra of MWNTs and MWNTs-OH
List of Figures and Tables

Figure 4.15 TEM images of exfoliated MWCNTs-OH in DMF

Figure 4.16 The Digital picture of the MWCNT/DMF dispersion (left), the MWCNT-OH/DMF dispersion (middle) and residual DMF after coating (right)

Figure 4.17 The Digital picture of pure UHMWPE powders (left), 0.1wt%MWCNT-OH/UHMWPE powders (middle) and 1wt%MWCNT-OH/UHMWPE powders (right).

Figure 4.18 SEM images of the UHMWPE powders (a and b) and MWCNT-OH(1wt%)/UHMWPE composite powders (c and d). The images (a and c) are taken under low voltage, and SEM images (b and d) are taken under high voltage.

Figure 4.19 Scheme of the UHMWPE powders fully coated with the nanotubes. The white circle represents the UHMWPE particle and the dark area represents the nanotubes coating on the surface of the particle. R is the radius of the particle and ΔR is the thickness of the nanotube coating.

Figure 5.1 Schematic process of heat transfer

Figure 5.2 Thermal conductivity of MWCNT/polyether-based PU composites as a function of MWCNT content

Figure 5.3 Thermal conductivity of the MWCNT/PCL-based PU composites as a function of MWCNT content. All the samples were consistently loaded with 1wt% SDS

Figure 5.4 Thermal conductivity of the MWCNT/PCL-based PU composites as a function of MWCNT content. All samples were prepared with consistent weight ratio (1:1) of SDS to MWCNTs

Figure 5.5 FESEM images of the MWCNT(3wt%)/PCL-based PU composite. a, b and c are the fractured surface images; d and e are the top surface images.

Figure 5.6 Polarised optical microscopy images of the MWCNT/PCL-based PU composites. a: the pure PU; b: the MWCNT(1wt%)/PU composite

Figure 5.7 PE/MWCNT NHSK structure produced by crystallisation of PE on MWCNTs at 103°C in p-xylene for 0.5h: a) SEM image shows that MWCNTs are decorated by dis-shaped PE single crystals and PE-functionalised MWCNTs MWCNTs can therefore be achieved. b) TEM image of enlarged PE/MWCNT NHSK
structures. a) and b) show that periodicity of the kebabs is ~50-70nm. c) Schematic representation of the PE/CNT NHSK structure

Figure 5.8 Typical DSC curves of the PCL-based PU and MWCNT/PCL-based PU composites; A: all samples with consistent loading of 1wt% SDS; B: all samples with consistent weight ratio (1:1) of SDS to MWCNTs

Figure 5.9 Derivated DSC curves of the PCL-based PU and MWCNT/PCL-based PU composites; A: all samples with consistent loading of 1wt% SDS; B: all samples with consistent weight ratio (1:1) of SDS to MWCNTs

Figure 6.1 SEM images of the (a) PCL, (b) MWCNT-OH(0.1wt%)/PCL composite, (c) MWCNT-OH(0.5wt%)/PCL composite, (d) MWCNT-OH(1wt%)/PCL composite and (e) MWCNT-OH(2wt%)/PCL composite

Figure 6.2 Non-isothermal DSC curves of the MWCNT-OH/PCL composites

Figure 6.3 DSC curves of heat flow vs temperature after completion of the isothermal crystallisation in the MWCNT(1wt%)/PCL composite at three temperatures

Figure 6.4 DCS curves of heat flow vs time for the 1wt%MWCNT-OH/PCL composite, which are tracking the whole process of the isothermal crystallisation

Figure 6.5 DSC curves of the MWCNT-OH/PCL composites after completion of isothermal crystallization. The isothermal crystallizations were performed based on the "14°C" rule for all samples.

Figure 6.6 Optical microscopy images of the (a) the PCL, (b) the MWCNT-OH(0.1wt%)/PCL composite, (c) the MWCNT-OH(0.5wt%)/PCL composite, (d) the MWCNT-OH(1wt%)/PCL composite and (e) the MWCNT-OH(2wt%)/PCL composite taken by built-in digital camera during the isothermal crystallisation that follows the "14°C" rule for all samples.

Figure 6.7 Relative crystallinity $\chi_c$ as a function of time for the MWCNT-OH/PCL composites

Figure 6.8 (a) Schematic representation of a single polymer strand coiling along the axis of a nanotube. (b) In the two-dimensional depiction, the unwrapped tube is represented by an infinitely long stripe of width $2\pi R$ and the coiling angle $\theta$ defines a unit cell of length $2\pi R/\tan \theta$. The black stripe of width $\omega$ symbolizes the polymer
strand.

**Figure 6.9** (a) Total energy as a function of the coiling angle $\theta$ for PA (solid line) and PmPV (dashed line) wrapped around a 1nm long nanotube of 1.3nm diameter. (b) Corresponding probability density. The parameter for PA and PmPV are $\sigma=378\text{meV/nm}^2$, $\omega=0.48\text{nm}$; $D=32.5\text{meVnm}$ and $\sigma=770\text{meV/nm}^2$, $\omega=2.1\text{nm}$; $D=250\text{meVnm}$, respectively.

**Figure 6.10** Relationship between the coefficient ($\phi$) and the Young's modulus of polymers ($Y_p$).

**Figure 6.11** Comparison of experimental data with the model prediction for and the CNT/polyester-based PU and the CNT/PVA composites with an optimised crystalline layer surrounding CNTs.

**Figure 6.12** Comparison of experimental data with the model prediction for the CNT/PVA composites without an optimised crystalline layer surrounding CNTs.

**Figure 6.13** Young's modulus of the MWNCT/PCL composites as a function of the nanotube volume fraction ($\bullet$: the thermally treated composites; $\circ$: the untreated composites)

**Figure 6.14** DSC curves (a) of heat flow vs temperature as a function of the nanotube weight fraction. The samples are prepared using the compression moulding following the "14°C" rule.

**Figure 6.15** SEM images of the (a) 0.1wt%MWCNT-OH/PCL composite, (b) 0.5wt%MWCNT-OH/PCL composite, (c) 1wt%MWCNT-OH/PCL composite and (d) 2wt%MWCNT-OH/PCL composite. All samples are prepared in the compression moulding following the "14°C" rule.

**Figure 7.1** Board scan XPS spectra of expandable graphite (A) and expandable graphite oxide (B)

**Figure 7.2** C 1s XPS spectra of expandable graphite (A) and expandable graphite oxide (B)

**Figure 7.3** Digital pictures of expandable graphite/DMF (left) and expandable graphite oxide/DMF dispersions (right).
Figure 7.4 TEM images of exfoliated graphite oxide nanoplatelets in DMF

Figure 7.5 X-ray diffraction patterns of expandable graphite powder, expandable graphite oxide powder and GONP/DMF dispersion

Figure 7.6 SEM images of the GONP(0.1wt%)/PCL composite (a), the GONP(0.5wt%)/PCL composite (b), the GONP(1wt%)/PCL composite (c) and the GONP(2wt%)/PCL composite (d)

Figure 7.7 Non-isothermal crystallisation of the GONP/PCL composites

Figure 7.8 Non-isothermal crystallisation kinetics of the GONP/PCL composites

Figure 7.9 DSC curves of heat flow vs temperature after completion of the isothermal crystallisation of the GONP(2wt%)/PCL composite at three temperatures

Figure 7.10 DSC curves of the GONP/PCL composites after completion of isothermal crystallization. The isothermal crystallizations were performed based on the “14°C” rule for all samples.

Figure 7.11 Relationship between the crystallinity (χc) and GONP concentration (wt%). Straight line is for eye guide.

Figure 7.12 Optical microscopy images of the PCL (a), the GONP(0.1wt%)/PCL composite (b), the GONP(0.5wt%)/PCL composite (c), the GONP(1wt%)/PCL composite (d) and the GONP(2wt%)/PCL composite (e) taken by built-in digital camera during the isothermal crystallisation that follows the “14°C” rule for all samples.

Figure 7.13 Relative crystallinity χc as a function of time for the GONP/PCL composites

Figure 7.14 Young’s modulus of the GONP/PCL composites as function of GONP weight fraction. ■ represents the samples without the thermal treatment; ○ represents the sample with thermal treatment following the “14°C” rule.

Figure 7.15 DSC curves (a) of heat flow vs temperature as a function of GONP weight fraction. The samples are prepared using compression moulding following the “14°C” rule.

Figure 7.16 (a) SEM image of the PU; (b) SEM image of the 4.4wt%GONP/PU composite; (c) SEM image of the 4.4wt%GONP/PU
Figure 7.17 MDSC curves of heat flow against temperature: (a) the PU; (b) the 4.4wt%GONP/PU composite

Figure 7.18 Storage modulus (A) and damping factor tan\(\delta\) (B) of the PU (a) and 4.4wt%GONP/PU composite (b) as a function of temperature

Figure 7.19 FTIR spectra of the PU (a) and 4.4wt%GONP/PU composite (b). R is hydrogen bonding index and DPS is the degree of phase separation.

Figure 7.20 Typical strain-stress curves of the PU and 4.4wt%GONP/PU composites

Figure 7.21 Mechanical properties of the PU and 4.4wt%GONP/PU composite

Figure 7.22 Nanoindentation results of the PU and 4.4wt%GONP/PU composites

Figure 7.23 Nano-scratch depth profiles for the PU and 4.4wt%GONP/PU composite at a scratch rates of 3\(\mu\)m/s(A) and 5\(\mu\)m/s(B), respectively.

Table 2.1 Electrical property of CNT/polymer nanocomposites

Table 4.1 Electrical conductivities of the MWCNT-OH/HMWPE composites

Table 6.1 Crystallisation parameters in the MWCNT-OH/PCL composites.

Table 6.2 Relationship between Avrami exponent and shape of crystals

Table 6.3 Values of parameters (n and K) in Avrami equation

Table 6.4 Values of the Young's modulus (\(Y_p\)) and the coefficient (\(\phi\)) for PVA, CIPP and polyester-based PU in published literatures

Table 7.1 Non-isothermal crystallisation parameters of the GONP/PCL composites

Table 7.2 Isothermal crystallisation parameters of the GONP/PCL composites

Table 7.3 Avrami parameters (n and K) of the GONP/PCL composites
Chapter 1 Background and aims of the project

1.1 Background of the project

Nanofillers have been widely applied to develop functional polymer composites for two decades [1]. Since the discovery of carbon nanotube (CNTs), they have generated a great deal of interests in the development of the functional composites due to their super mechanical [2], electrical [3] and thermal properties [4][5]. All these advantages make people have high expectation on the potential application of CNTs in polymer composites although the price of CNTs is extremely high in comparison with polymer matrix. The main aim of this project is to understand the relationship between the two-phase microstructure and physical properties of the composites, and develop practical engineering approaches to develop high performance CNT/polymer composites. The word of “performance” in this project refers to the mechanical properties, electrical and thermal conductivity.

Reducing the incorporation of CNTs in polymer matrix is the main target in development of conductive polymer composites in order to reduce the cost of the composites. A colloidal physics method [6][7] was developed to fabricate the conductive composites with lower percolation threshold in comparison with other conventional processing approaches. The core idea of the colloidal physical methods is to form the cellular structure of CNTs in the polymer matrix as CNTs are exclusively located in the limited boundary area between polymer particles during the film formation. The limited choice of the polymer latex restricts the application of this method. The first sub-task is to develop a coating technology for the extension of the “cellular structure” idea form polymer latex to polymer powders.

The strong phonon scattering at the CNT-polymer interface is the bottleneck for significantly improving the thermal conductivity of polymers as theoretically expected [8][9]. Reducing the area of the CNT-polymer interface is considered as the possible key to solve this problem. Based on this thought, several approaches have been
Chapter 1 Background and aims of the project

designed. The colloidal physics method has shown the advantage in reducing the area of the CNT-polymer interface as the latex particles are exclusive to CNTs. The second sub-task is to explore if the colloidal physics method is an effective tool to reduce the interfacial phonon scattering and improve the thermal conductivity of CNT/polymer composites.

CNTs are known to have an extremely high Young’s modulus of up to 1TPa and tensile strength approaching 60GPa [2][10], which have been considered to be ideal candidates for mechanical reinforcement of polymers. Two issues need to be considered in the development of highly strong CNT/polymer composites [11]: (1) uniform dispersion of CNTs in the polymer matrix; (2) a strong interface between CNTs and polymers. It seems the uniform dispersion of CNTs is not a big challenge any more in labs as chemically functionalised CNTs are widely used. How to achieve the effective load transfer between CNTs and polymers currently presents to be the biggest challenge in this field. The functional groups or macromolecules attached onto CNTs are capable of enhancing the compatibility between inorganic components (CNTs) and organic components (polymers) [12][13]. The covalent bonding between CNTs and polymers until now is commonly considered as the most effective interface for the load transfer. In poly(vinyl alcohol) (PVA) solution, it has been recently found that the PVA crystallites nucleated by CNTs, also called the crystalline layer surrounding CNTs, can act as a strong non-covalent interface in the load transfer [14]. However, it is not clear how to fabricate an optimised crystalline layer around CNTs from polymer melts, although the nucleating role of CNTs in crystalline polymers has been commonly recognised. As the third sub-tasks, we will take polycaprolactone (PCL) as polymer matrix to find out a specific thermal treatment to create a crystalline layer from PCL melts, and establish the empirical relationship between the mechanical reinforcement and the crystalline layer.

Very recently, the role of CNTs in polymer composites is strongly challenged by graphene sheets [15][16][17], which have similar properties to CNTs. It is very
difficult to strip graphene sheets from graphite due to the strong bonding between the sheets. Introduction, by means of strong oxidation, of oxygenated groups into graphite can reduce this mutual bonding, allowing the exfoliation of graphite oxide (GO) in water by assistance of ultrasonication. However, it was found that GO cannot be exfoliated in organic solvents. We will develop a method to fully exfoliate the GO in an organic solvent at first. With this method in hand, the preparation and characterisation of graphene/polymer composites can be carried out.

1.2 Aims of the project

The aims of this PhD project are summarised as follows:

(1) To understand the mechanism of the electrical conductance in the CNT/polymer composites semi-conductive CNT/polymer composites and develop a novel coating technology to fabricate the semi-conductive CNT/polymer composites with low percolation threshold

(2) To understand the mechanism of the thermal conductance in the CNT/polymer composites and develop a simple method to reduce the interfacial phonon scattering

(3) To understand the mechanism of the load transfer across the semi-crystalline interface between CNTs and polymers and develop a method of thermal treatment to optimise the semi-crystalline interface in polymer melts for effective load transfer.

(4) To develop a method to fabricate functionalised graphene sheets in an organic solvent and highlight two samples to confirm that functionalised graphene sheets can be a strong substitute for CNTs in the reinforcement of polymers.
2.1 Introduction of CNTs

Following the discovery of fullerenes [18] the first report of carbon nanotubes (CNTs) was published by Iijima [19] in 1991. As shown in Figure 2.1, CNTs can be generally considered as seamless cylinders rolled up by graphene sheets, which have a great length-to-diameter ratio. According to the diameter of the cylinders, the family of CNTs is divided into multi-walled carbon nanotubes (MWCNTs) [20] with a diameter range from 4 to 30 nm, double-walled carbon nanotubes (DWCNTs) [21] with a diameter in the range of 2-5 nm, and single-walled carbon nanotubes [22] with a diameter range from 0.4 to 2-3 nm. According to the ways of rolling up graphene sheets (the chiral angle between hexagons and the tube axis), CNTs can be categorised as “armchair” nanotubes (Figure 2.2(b)), “zig-zag” nanotubes (Figure 2.2(c)) and “chiral” nanotubes (Figure 2.2(d)). As shown in Figure 2.2(a), the ways of rolling up graphene can be defined by a lattice vector \( \mathbf{c}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \), where \( n, m \) are integers and \( \mathbf{a}_1, \mathbf{a}_2 \) are the unit vectors of graphite. For \( m=0 \), graphene sheet is rolled up to the zig-zag nanotube; for \( m=n \), graphene sheet is rolled up to the armchair nanotube. The nanotube diameter \( d \) is defined by \( d = |c_h| \).

![Figure 2.1 Multi-walled carbon nanotubes discovered by Iijima in 1991 [20]](image-url)
These unique structures have generated a great deal of interests from academia and engineers in developing novel CNT-based multi-functional materials. Thousands of papers are being published every year to report the application of CNTs, such as emission devices [23], sensor devices [24], electrochemical devices [25], CNT-based composites [26], and thermal management materials [27]. However, high production cost of high quality nanotubes is the biggest bottleneck for the commercial application of CNTs.

![Figure 2.2 (a) Schematic honeycomb structure of a graphene sheet. Single-walled carbon nanotubes can be formed by folding the sheet along lattice vectors. The two basis vectors $a_1$ and $a_2$ are shown. Folding of the (8,8), (8,0), and (10,-2) vectors lead to armchair (b), zigzag (c), and chiral (d) tubes, respectively [28].](image)

### 2.2 Synthesis of CNTs

Simple, inexpensive and large-scale production of CNTs with high yield and purity is the target in the synthesis of CNTs. This part briefly reviews the most popular techniques to synthesize CNTs, including arc-discharge, laser ablation and chemical vapour deposition [28].

1. **Arc-discharge**

   Arc-discharge refers to the growth of CNTs by arc-discharging graphite in insert
gas [29], hydrocarbon [30], or hydrogen atmospheres [30]. In 1992, Ebbesen and Ajayan [29] firstly used arc-discharge technique to prepare high quality MWCNTs at the gramme level. In the following year, Bethune and co-worker [31] reported a cobalt-catalysed growth of SWCNTs by using arc-discharge, in which electrodes were prepared by filling graphite rods with mixture of powdered metals (Fe, Ni or Co) and graphite. Ishigami et al [32] reported a modified arc-discharge method to continuous synthesise MWCNTs in liquid nitrogen. The schematic view of apparatus [32] is shown in Figure 2.3. In the growth of the MWCNTs, graphite anodes were dipped into an open container with a short non-consumable copper or graphite cathode. The container was filled with liquid nitrogen. After arc discharge struck as two electrodes contacted, the MWCNTs formed in the arc-plasma region dropped to the bottom of the container. This method was cheaper and simpler in comparison with conventional arc-discharge method, and showed industrial potential to produce MWCNTs in large scale. Sano et al [33] release another report in regard to synthesis of SWCNTs in liquid nitrogen by using composite electrodes consisting of graphite and Ni. Later, other liquid media such as deionised water [34][35] or aqueous solution of FeSO₄ [35] or NaCl [36] were used to replace

![Figure 2.3 Scheme of continuous production liquid-nitrogen reaction chamber for nanotube synthesis [32]](image-url)
liquid nitrogen due to the strong evaporation of liquid nitrogen that caused less cooling efficiency. Arc-discharge method is usually used to produce high quality and nearly perfect nanotube structure for scientific research.

(2) Laser ablation

Laser ablation as another useful technique to produce CNTs with high quality and high purity was firstly invented by Samlley and co-workers in 1995 [37]. This technique involved direct vaporisation of the mixture of graphite and transition metals by using a pulsed laser in a high temperature reactor with inert gas going through the chamber. Compared with the arc-discharge method, laser ablation showed greater control over growth, continuous operation, higher yield production and better quality. Later, Yudasaka et al [38] used double-target laser ablation to produce SWCNTs with higher purity than single-target one. The idea of "double targets" mainly concerned application of two independent targets containing carbon and metal-alloy, respectively. Afterward, much work has covered optimisation of the growing process of CNTs, such as composition of the target [39][40], type of gas [41], gas pressure and its flow rate [42][43][44], ambient temperature, and laser parameters [45][46][47].

![Oven laser-vaporisation apparatus](image)

Figure 2.4 Oven laser-vaporisation apparatus [37]

(3) Chemical vapour deposition

Chemical vapour deposition (CVD) is a classical method to produce carbon
materials such as carbon fibre, filament and nanotube materials [48][49]. The CVD method involves synthesizing CNTs from hydrocarbon or carbon-containing feedstock on catalysts at high temperature (500-1000°C) in a tube furnace [50]. The choice of feedstock covered methane [50], ethylene [51], carbon monoxide [52], benzene [53] etc. Transition-metallic nanoparticles formed on porous aluminum oxide with large surface areas are always used as catalysts [54]. The growth mechanism of CVD method is commonly interpreted as follows [28]: (1) the dissociation of hydrocarbon molecules catalyzed by transition-metallic nanoparticles; (2) the dissolution and saturation of carbon atoms in transition-metallic nanoparticles; (3) the formation of tubular carbon solid results from the precipitation of carbon from the saturated transition-metallic nanoparticles. Compared with above two methods, the CVD method has significantly attracted industry due to its advantage on large-scale production of CNTs from kilogramme to tonne level for commercial purposes.

2.3 Fabrication of CNT/polymer nanocomposites

The micrometre inorganic fillers have conventionally been applied to prepare polymer composites with desirable properties for a long time. Since the appearance of nanotechnology in early 1970s, a great deal of interest has been generated to fabricate functional polymer nanocomposites. In 1985, the first fabrication of clay/nylon-6 nanocomposites by Toyota Central R&D Lab (Japan) opened the door to the world of polymer nanocomposites. Since the discovery of CNTs in 1991, CNTs have been considered as ideal nanofillers for polymers in last decades due to their super mechanical, thermal and electrical properties. Since the first report of CNT/polymer nanocomposites released by Ajayan et al [26] in 1994, a large number of papers have been published, which covered a variety of high performance CNT/polymer nanocomposites. This review was kicked off from the fabrication of the nanocomposites, which determines the morphology and properties of the nanocomposites. Achieving a homogenous dispersion of CNTs on
in polymers is a key challenge in the fabrication of the nanocomposites. “A homogenous dispersion of CNTs in polymers” does not mean the individualisation of single tubes in polymers on a scale of billionths of a metre without any agglomerates or aggregates. It means CNTs in polymers are distributed into polymers with a scale of less than or equal to 100nm in one of the dimensions at least. According to several review articles, fabricating techniques generally can be categorised as melting processing, solution methods, in-situ polymerisation and some novel techniques. In all these techniques, the pre-treatment of CNTs using chemical modification or wrapping technology has been popularly regarded as useful assisting methods to achieve good dispersion of CNTs in polymers. In this part, the introduction of the pre-treatment was separated from the other fabricating techniques.

2.3.1 Pretreatment of CNTs

The active reactivity of sp²-rich carbon structure drives the chemical modification to be the most popular mean to tailor the surface of CNTs with attachment of functional groups and macromolecules.

Liu et al [55] firstly reported an oxidising method to purify and shorten SWCNTs by the assistance of sonication in a 3:1 (v/v) concentrated H₂SO₄/HNO₃ mixture. It was discovered that the oxidisation can generate many carboxylic groups on the open-ends of the SWCNTs. The use of other oxidants was successively reported to produce oxygenated groups on the ends and walls of CNTs, which included H₂SO₄/H₂O₂ [56] and KMnO₄ [57]. These oxygenated groups mainly contain carboxylic groups, hydroxyl groups and ether groups. Zhang et al [58] compared the chemical structure of the SWCNTs that had been treated by three kinds of oxidants including HNO₃ (2.6M), a 3:1 (v/v) concentrated H₂SO₄ (98%)/concentrated HNO₃ (16M) mixture and KMnO₄. It was discovered that the treatment of the SWCNTs by dilute HNO₃ only generates carboxylic groups at the
initial defects already existing in the SWCNTs and fails to increase amounts of carboxylic groups along with refluxing time. In contrast, sonication can create some new defects along the walls of the SWCNTs for attachment of carboxylic groups in H$_2$SO$_4$/HNO$_3$ mixture. Differently, KMnO$_4$ in alkali was found to be a mild oxidant producing hydroxyl groups, carboxylic groups and quinine groups on the surface of the SWCNTs. The authors finally made a description about the whole oxidising process. The oxidation started from the initial defects that are brought from the CVD growth of the SWCNTs. Then, the oxidising process was divided into two steps: (1) the defect-generating step where the oxidants attacked the graphene structure of the SWCNTs by electrophilic reactions, commonly generating hydroxyl groups; and (2) the defect-consuming step where the graphene structure broke down at the sites attacked by the oxidants and the tubes were cut off. In both steps, only strong oxidant generated carboxylic groups and quinine groups and made the defect-consuming step happen.

Fluorination is another feasible mean to chemically modify CNTs, which was firstly discovered by Hamwi et al [59]. They discovered that 100% fluorination of MWCNTs can be achieved at 500°C under fluorine atmosphere, which leads to the damage of tubular structure. At room temperature, fluorination was conducted under a gaseous atmosphere of F$_2$, HF, and IF$_5$, after which the tubular structure of the MWCNTs was preserved because of low fluorination level (the value of F/C was only 0.4). Afterward, Mickelson et al [60] investigated the fluorination of SWCNTs at different temperatures. FTIR results confirmed the formation of C-F bonds on the sidewalls of the SWCNTs as reacting temperature reached 250°C or higher. It was visually disclosed by TEM images that the tubular structure of the SWCNTs is destroyed at a reacting temperature of 500°C and interestingly converts to MWCNT-like structure. This work also mentioned that the restoration of the fluorinated SWCNTs could be fulfilled using anhydrous as a defluorinating agent. In addition to oxidation and fluorination, several other chemicals were also reported to functionalise CNTs, such as aryl diazonium [61][62], dichlorocarbene
[63], and azomethine ylides [64].

\[ \begin{align*}
\text{Carboxylated CNTs} & \quad \text{PVA activated by carbodiimide} \\
\text{Functionalisation of CNTs with macromolecules that hold structural similarity} & \quad \text{with the polymer matrix is considered as a more effective pre-treating approach to}
\text{prevent the aggregation of CNTs in polymers in comparison with the covalent} \\
\text{attachment of functional groups. "Grafting to" and "grafting from" are two main} \\
\text{strategies to functionalise CNTs with long macromolecular chains. So-called} \\
\text{"grafting to" takes place via the reactions between the reactive groups on CNTs} \\
\text{and end-functionalised macromolecules} \[66][67][68][69][70][71][72]. \text{Lin et al} \\
\text{[65] employed carbodiimide-activated esterification reaction to graft PVA to} \\
\text{carboxylated CNTs (CNTs-g-PVA) (Figure 2.5). The solubility of the CNT-g-PVA} \\
\text{was presented in highly polar solvents and water, which consequently resulted in} \\
\text{uniform dispersion of the CNTs-g-PVA in the PVA matrix (Figure 2.6).}
\end{align*} \]

**Figure 2.5** Scheme of the reaction between carboxylated CNTs and PVA activated by carbodiimide [65]

**Figure 2.6** Typical TEM image of a specimen from the cross-sectional microtomy of a PVA-MWCNT composite film [65]
Xia et al [73][74] grafted isocyanate-terminated PU to the CNTs with hydroxyl groups (CNTs-OH) using the reaction between hydroxyl groups and isocyanate groups (Figure 2.7). It was found that the CNTs grafted with PU showed better dispersion in DMF and polyether polyols in comparison with pristine CNTs and the CNTs-OH.

![Figure 2.7](image)

Figure 2.7 Schematic illustration of the grafting process of polyurethane on the multi-walled carbon nanotubes. The bar represents 50 nm in A1, 20 nm in A2, 50 nm in B1 and 20 nm in B2 [74].

Liu et al [75] presented an approach to anchor living macromolecules to the MWCNTs appended unsaturated double bonds (Figure 2.8). Ligand-exchange reaction of ferrocene (Cp-Fe-Cp) was employed to chemically modify the MWCNTs. The modified MWCNTs (Cp-Fe-MWCNTs) were then monolithiated by tert-butyllithium and terminated by p-chloromethylstyrene (pMS). Finally, the living polystyllumithium anions were grafted to pMS-terminated MWCNTs via anionic polymerisation.
Chapter 2 Literature Review

Figure 2.8 Scheme of the reaction between pMS-Cp-Fe-MWCNTs and polystyrene [75].

Wang et al [76] employed cycloaddition to graft azide-terminated polystyrene (PSt) to CNTs (Figure 2.9). The PSt was converted from halogen atom terminated PS that was prepared by means of atom transfer radical polymerisation. This method took advantage of the double bonds existing in the CNTs instead of the functional group.

The “grafting from”, as another approach to covalently anchor macromolecules to the surface of CNTs, refers to the polymerisation of monomers initiated by CNTs. How to create appropriate initiators on the surface of CNTs is a key issue for a variety of reported “grafting from” methods. In fact, “grafting from” partially overlaps with in-situ polymerisation. Opening the double bonds of CNTs by initiators facilitates the “grafting from” of vinyl monomers, such as methyl methacrylate and styrene, onto the surface of CNTs.

Figure 2.9 Schematic preparation process of modified CNT with PSt [76]
Hwang et al [77] grafted MWCNTs with PMMA using emulsion polymerisation. A typical experiment was described as followed: a 500ml, 0.11M cetyltrimethylammonium bromide was added with 25g purified MMA monomer in presence or absence of the MWCNTs. After sonication was applied to the solution for 5 min, 0.12g radical initiator, potassium persulfate (K$_2$S$_2$O$_8$), was added to the solution that had been purged with N$_2$. The reaction was initiated and kept for 5 h after the solution was heated to 70°C. Afterward, water was removed by purging with air. The resulted polymer slurry was washed several times with methanol to the surfactant, and then dried to powders in a vacuum oven. Then, the powders were dissolved in chloroform and filtered via a microfiltration cell (0.2µm, Nylon 66 membrane) to wash out physically absorbed free PMMA. The step was repeated for several times. Finally, the PMMA-grafted MWCNTs were thus obtained" Xia et al [78] reported a similar method to graft MWCNTs from BA and MMA (Figure 2.10). Emulsion polymerisation was initiated by ultrasonic irradiation, which was the novel issue in this method.

![Proposed formation mechanism of polymer-encapsulated carbon nanotubes through ultrasonically initiated in-situ emulsion polymerisation](image)

**Figure 2.10** Proposed formation mechanism of polymer-encapsulated carbon nanotubes through ultrasonically initiated in-situ emulsion polymerisation [78].
Li et al. [79] reported another route to make SWCNTs join in the copolymerisation reaction (the first leg of the scheme in Figure 2.11). Afterward, polyethylene chains were successfully grafted onto the sidewalls of the SWCNTs via copolymerisation of ethylene with functionalised SWCNTs catalyzed by rac-(en)(THInd)₂ZrCl₂/MAO (the second leg of the scheme in Figure 2.11).

Figure 2.11 Scheme of preparation of alkene-functionalised SWCNTs (f-SWCNTs) and SWCNT-g-PE via the copolymerisation technique [79,79].

Liu et al. [80] discovered that grafting efficiency and grafting ratio is very low and uncontrollable when the “grafting from” occurs as a result of copolymerizing vinyl monomers with the π-bonds in MWCNTs directly in the presence of free radical initiators. They even failed to observe any PS chains were grafted to the MWCNTs when the radical initiator (benzoyl peroxide or potassium persulfate) was used directly to initiate the grafting polymerisation of styrene. However, the grafting efficiency and grafting ratio could be optimised and controlled using the MWCNTs as macro-initiators. The detailed procedure (Figure 2.12) was introduced step by step as followed: (1) The MWCNTs were dispersed into the initiator solution composed of potassium persulfate and hydrogen peroxide and kept gently stirring for 2-5 hours in ice-water bath for the adsorption of initiator species. A small quantity of sodium dodecyl sulfate (SDS) was added to improve the dispersion of the MWCNTs. (2) The methyl methacrylate (MMA) monomers containing divinyl benzene used as crosslinking agent were emulsified in SDS aqueous solution under N₂ gas. (3) The CNT/initiator blends were centrifuged to
precipitate the CNTs that had done with absorption of initiators. Then, precipitated CNTs were immediately dispersed in MMA/SDS emulsion. (4) The reductive initiator (ferrous sulfate) was dissolved in water and added into the CNT/MMA/SDS/water system. (5) The polymerisation was first performed in ultrasonic bath at 60°C for 30 min and then carried out in water bath (80°C) for another 3 h under magnetic stirring.

Atom transfer radical polymerisation (ATRP) is a “living” polymerisation that derivates from radical polymerisation. In comparison with other “living” polymerisation methods such as anionic or ionic polymerisation, ATRP displays at least three advantages [81]: (1) a “living” polymer with functional groups can be synthesized, which is a precursor to form a blocked polymer with controlled structure; (2) the “living” sites in polymer remain constant and stable, which can resist moisture environment; (3) it presents flexible access to a wide range of functional groups on polymer chains.

![Figure 2.12](image-url) Scheme of the method for preparation of the CNTs bundle wires with PMMA shells [80]

\[
R \cdot \rightarrow \frac{k_d}{k_t} + M_t^n / \text{Ligand} \rightarrow \frac{k_d}{k_t} R^* + \frac{k_p}{k_t} M_t^{n+1} / \text{Ligand} \rightarrow R-R
\]

![Figure 2.13](image-url) Mechanism of atom transfer radical polymerisation
monomers. The schematic mechanism [81] of ATRP shown in Figure 2.13 informs that ATRP commonly uses simple alkyl halides as initiators and simple transition metals (iron, copper) that are complexed by one or more ligands as the catalysts.

Kong et al [82] reported an ATRP approach to graft macromolecules from CNTs. As shown in Figure 2.14, the polymerisation route included four steps: (1) the preparation of carbonyl chloride groups functionalised CNTs (CNT-COCl) via the reaction of thionyl chloride with carboxyl-contained CNTs (CNTs-COOH); (2) the introduction of hydroxyl groups onto the surface of the CNTs via the reaction of the CNTs-COCl with glycol; (3) the formation of CNTs-Br used as initiating sites by reacting the CNTs-OH with 2-bromo-2-methylpropionyl bromide; and (4) the grafting polymerisation of methyl methacrylate from the CNTs-Br by means of ATRP. The authors found that this novel approach was capable of controlling the thickness of the grafting layers in the end.

![Figure 2.14 Scheme of functionalising the CNTs using ATRP [82]](image)

2.3.2 Solution method

Solution method is considered as perhaps the most common method to prepare the CNT/polymer nanocomposites [11], which mainly involves two steps: (1) the dissolution of CNTs and polymers in solvents; and (2) the evaporation of solvents. Mechanical stirring, shear mixing, and ultrasonication are generally used to disperse CNTs in solvents. The advantage of this method is that the mechanical
agitation especially ultrasonication can effectively reduce the aggregation of CNTs. Qian et al [83] employed a typical solution method to fabricate MWCNT/PS nanocomposites. The PS was firstly dissolved in toluene with a mass ratio of 1:10. Then, the MWCNTs were dispersed in toluene by high-energy ultrasonication at 150 W for a period of time. The mixing of the PS solution and the MWCNT suspension subsequently underwent ultrasonication again in a bath for 30 minutes. Afterward, the mixture was cast into a culture dish, and dried completely to form uniform films. To date, solution method has been applied to incorporate CNTs into a variety of polymers including epoxy, PE, PP, PA, PC, PS, PET, PU and PVA. Chemical modification or surfactant wrapping of CNTs, in some case, is used to improve the dispersion of CNTs in solvents. Specifically, surfactant wrapping technology is quite useful to disperse CNTs in water-based polymers such as polymer latex. Colloidal physics method was interestingly developed to incorporate CNTs into polymer latex with the help of surfactant wrapping technology. Dufresne et al [84] firstly reported a typical route to incorporate CNTs into polymer latex, which included: (1) dispersing the CNTs in distilled water by the aid of sodium dodecyl sulfate (SDS) surfactant; (2) mixing the CNT suspension and poly(styrene-co-butyl acrylate) latex. The colloidal physics method displays several advantages: (1) surfactants used in this method facilitate the dispersion of CNTs in polymer matrix without damaging the properties of CNTs; (2) polymer hosts can be flexibly selected and the synthesizing process of polymer latexes is not affected by the incorporation of CNTs; (3) electrical conductivity can be highly improved with low CNT concentration (low percolation threshold); and (4) this method is environmentally friendly due to the use of water as medium instead of toxic solvents. Later, Regev et al [6] and Grunlan et al [7] both applied the colloidal physics method to incorporate CNTs into different polymer latex. Regev et al incorporated the SWCNTs wrapped by SDS or GA (Gum Arabic, polysaccharide) into PS latex, respectively (Figure 2.15). The homogenous SWCNT/PS nanocomposites were obtained following the treatments of free-
Figure 2.15 Cryo-TEM micrographs of A) a 1:1 w/w SWCNT-SDS aqueous solution; B) 1:1 w/w SWCNT-GA in an aqueous, 5wt.-% dialyzed PS-latex solution. Note the strong SWCNT-latex repulsion; C) 1:1 w/w SWCNT-GA in an aqueous, 5wt.-% PS-latex solution, to which 0.5wt.-% NaCl had been added to overcome the repulsion. Note the growth of individual or bundles of very few SWCNTs from the Ni-Y catalyst nanoparticles (arrows in part (B) and (C) and inset in part (B). Scale bar=100 nm [6]

drying and compression moulding. Interestingly, it was found the addition of salt (NaCl) to the SWCNT-latex solution could reduce electrostatic and steric repulsions between GA-stabilized SWCNTs and SDS-stabilized PS latex, which were both negatively charged. Grunlan et al [7] mixed GA-stabilized SWCNTs with PVAc homopolymer emulsion (55wt% solid content) to produce a colloidal mixture with 10wt% solid content. The solid nanocomposites with an opaque
black appearance were obtained after drying under ambient conditions.

Generally, the evaporation of solvents at a certain temperature for long time is necessary to obtain end products in solution method. Du et al [85] reported another method named hot coagulation, which avoided long-time drying to fabricate SWCNT/PMMA nanocomposites. After dissolving the SWCNTs and PMMA in DMF, the suspension was dripped into a large amount of distilled water ($V_{DMF}/V_{water} = 1:5$) during blending. The precipitation of the PMMA immediately occurred to have the final nanocomposite, which was due to insolubility of the PMMA in the DMF/water mixture. SWCNTs were entrapped and stopped to aggregate again during the coagulation.

2.3.3 Melt processing

By using high temperature and shear mixing, melting processing is particularly suitable for dispersing CNTs in thermoplastic polymers. In this method, CNTs are mechanically dispersed in melting polymers by some conventional processing methods such as extrusion, injection moulding and compression moulding. To date, various commercial polymers have been used to fabricate polymer nanocomposites by the melt processing such as PC [86][87], PMMA [88] and PE [89]. Simplicity and large scale production make the melt processing become a welcomed technique in industry. However, the melt processing shows the weakness in achieving homogenous dispersion of CNTs in polymer matrix. Numerous efforts are being made to overcome this challenge. Haggenmueller et al [88] applied the solution casting to enhance the dispersion of SWCNTs in PMMA before the melt processing of SWCNT/PMMA nanocomposites by compression moulding. Pötschke et al [87] used a commercialised masterbatch of the PC containing 15wt% MWCNTs, which was produced by Hyperion Catalysis Internationals (USA). The masterbatch was diluted by pure PC in DACA micro compounder at 260 °C to prepare MWCNT/PC nanocomposite. Microscopic studies confirmed that no significant agglomeration of the MWCNTs exists in the
PC matrix. Shear stress in connection with the shear rate of extruders is a key factor to break down the agglomeration of nanofillers in polymer melts. A Japanese company (Imoto, Co. Ltd) has recently developed a high-shear extruder (HSE3000mini) with a maximal screw rotation speed of 3000rpm. Li and Shimizu used this extruder to achieve the good dispersion of unmodified MWCNTs in poly(styrene-b-butadiene-co-butylene -b-styrene) [90]. The use of chemically modified CNTs is another effective method to enhance the dispersion of CNTs in polymer matrix and the interfacial interaction between CNTs and polymer matrix. Zhang et al [91] reported that the MWCNTs treated by nitric acid could be well dispersed in Nylon-6 by simple melt-compounding. Li et al [92] also reported a homogenous dispersion of amino-functionalised MWCNTs in Nylon-6. In both reports, the loose accumulation of functionalised MWCNTs was considered as another factor benefiting the dispersion of the nanotubes in Nylon-6 matrix. Yang et al [93] unveiled a novel route shown in Figure 2.16 to prepare PE grafted MWCNTs (MWCNTs-g-PE). PE chains chemically attached onto the MWCNTs effectively individualised the nanotubes in the PE matrix and enhanced the MWCNT-PE interfacial adhesion. Significantly, mechanical reinforcement was demonstrated that the Young's modulus and tensile strength of the PE increased by ~92% and ~23%, respectively, with the incorporation of 2wt% MWCNTs-g-PE, and the ductility and toughness increases by ~6% and ~61%, respectively, with the

![Figure 2.16 Grafting of PE-MA on MWCNTs](image-url)
incorporation of 1.5wt% MWCNTs-g-PE. Non-chemical modification of CNTs was used to improve the compatibility between CNTs and polymer matrix. Poly(n-butyl acrylate) [78] and styrene maleic anhydride copolymer [94] were selected to encapsulate CNTs before the melt processing of CNT/Nylon nanocomposites. However, the effect of non-chemical encapsulation on the dispersion could not compare to the chemical modification of CNTs.

Very recently, coating technology has been applied to pre-mix polymer powder with CNTs before the melt processing. Cooper et al [95] reported a dry powder method to coat CNTs over polymer particles. Ultrasonication was used to distribute the CNTs over the surface of PMMA spherical particles in ethanol. After ultrasonication, the mixture was spread out thinly on a foil surface, dried in a vacuum oven at 50°C for 1-2 hours, and mechanically mixed using a Molinex Attritor (Netzsch Feinmahl Technick, Germany) at 2000rpm for 30 min. Finally, the PMMA particles coated with the CNTs were kneaded to uniform viscous mass in a twin-screw compounder at 170°C for 10-30 minutes. High-shear stress provided by the compounder further could de-agglomerate remaining CNT bundles formed during the coating procedure. Shofner et al [96] applied a similar method to fabricate SWCNT/PE nanocomposites including dispersing the SWCNTs into alcohol solvents, coating SWCNTs on the surface of PE particles, high shear mixing and compression moulding. The results from SEM imaging and Raman spectroscopy confirmed that the fluorination of the SWCNTs effectively enhances both the dispersion and interfacial interaction between the nanotubes and PE matrix. In addition, the partial restoration of the SWCNTs resulting from the occurrence of defluorination during the melt processing was observed by Raman spectroscopy and TGA-FTIR. The authors considered that in-situ direct covalent bonding between the nanotubes and PE matrix formed as a result of defluorination makes the fluorinated SWCNTs show better mechanically reinforcing ability than pure SWCNTs. Zhang et al [97] reported a spraying method to coat the SWCNTs onto the surface of HDPE powder. The SWCNTs were dispersed in water with the
Chapter 2 Literature Review

aid of SDS and ultrasonication. Then, the SWCNT aqueous solution was sprayed onto a thin layer of the HDPE powder, as shown in Figure 2.17. During the spraying process, the tray with the HDPE powder was being shaken to ensure the uniform absorption of the SWCNT aqueous solution around the HDPE particles (Figure 2.18). After drying for 1 hour at 90°C, the HDPE powders coated with the SWCNTs was melt processed to uniform mass in DACA Micro Compounder

Figure 2.17 A spraying scheme: SWCNTs suspended solution was uniformly spurted onto the surface of HDPE powders from sprinkler [97]

Figure 2.18 SEM image of the morphology of SWCNTs on the surface of HDPE powder by spraying method [97]
(screw speed: 50rpm) at 160°C for about 20 minutes. Bakshi et al [98] used milling method to coat the MWCNTs onto the surface of ultra high molecular weight polyethylene (UHMWPE) powders. The UHMWPE powders coated with the MWCNTs were sprayed onto a teflon coated substrate using an electrostatic powder coating system. This electrostatic spraying technique ensured a uniform deposition of the MWCNT/UHMWPE powders with negligible overspray and loss of the MWCNTs. The consolidation of the powders to a film was performed in a heated oven at 180°C for 30-40 minutes. Kanagaraj et al [99] reported a heating method to coat chemically modified CNTs on HDPE pellets. First of all, the chemical modified CNTs were subjected to ultrasonication in deionised water for 1 hour to form a stable nanofluid. Then, the mixture of the nanofluid and HDPE pellets underwent continuous heating and stirring to achieve a uniform coating of the CNTs on the surface of the HDPE pellets. After the evaporation of water, these pellets were dried in an oven for another 24 hours at 110°C to remove residual water. Finally, these pellets were processed to tensile specimen using an injection moulding machine. Mu et al [100] very recently unveiled another approach to coat polystyrene (PS) pellets with CNTs by heating. The whole process was quite similar to Kanagaraj's method. The novel issue in the method is the heating temperature (130°C) was set to be higher than $T_g$ of the PS, which could soften the PS pellets. Enhanced adhesion between the CNTs and softened PS pellets could reduce the quantity of the tubes remaining in water and increase the coating efficiency.

### 2.3.4 In situ polymerisation

In situ polymerisation has attracted comprehensive attention since five years ago, which generally consists of two steps: (a) the dispersion of CNTs in monomers or monomer/solvent mixtures; (b) the polymerisation of monomers in presence of CNTs. Functionalised CNTs are commonly used to achieve better dispersion in the first step of in situ polymerisation. Jia et al [101] initially reported the fabrication
of CNT/PMMA nanocomposites via in situ radical polymerisation. The author considered that the initiator 2,2'-azobisisobutyronitrile (AIBN) could open the \( \pi \)-bonds of the CNTs and led the CNTs to participate the polymerisation of MMA. As a result, a covalent interface was formed between the CNTs and PMMA to favor an increase of tensile strength. Liang et al \cite{102} reported on the preparation of CNT/PMMA nanocomposites using in situ anionic polymerisation, in which debundled CNTs salts were used as anionic initiator. The schematic route is simply shown in Figure 2.19. Like the \( \pi \)-bonds in CNTs, functional groups also can make CNTs join in the polymerisation of monomers. The CNTs with oxygenated groups have shown their advantage in participating into the synthesis of PU, which mainly involves the reaction between hydroxyl groups and isocyanate groups. Xiong et al \cite{103} revealed a route to prepare CNT/PU nanocomposites using in-situ polymerisation (Figure 2.20), which contained (a) the preparation of the CNTs with carboxylic acid groups; (b) the synthesis of the CNT amide derivative; (c) the dispersion of the CNT amide derivate in polyoxytetramethylene (PTMO); and (d) the synthesis of the PU in the presence of the CNT amide derivate. Jung et al \cite{104} reported on the crosslinking role of the MWCNTs with carboxylic acid groups for PU. The whole crosslinking process was tracked by FT-IR spectroscopy. Testing results showed that the Young's modulus and tensile strength of the PU was improved by nearly 300% and 130%, respectively, as the incorporation of the chemical modified MWCNTs was up to 4wt%.

![Figure 2.19](image)

Figure 2.19 Schematic route of in situ anionic polymerisation of MMA using debundled CNTs salts as anionic initiator \cite{102}
The esterification reaction between carboxylic acid groups and epoxy is commonly applied to covalently integrate carboxylated CNTs into epoxy composites during curing process, which is another type of in situ polymerisation. Zhu et al [105] used open-end oxidation and sidewall fluorination to functionalise SWCNTs with carboxylic groups on their open end-tips and fluorine groups on their sidewalls. These functional groups were used to yield a good dispersion of the SWCNTs in an epoxy matrix, and form covalent bonds between the SWCNTs and epoxy during curing process. Beside esterification reaction, they also pointed out that the reaction between the fluorine groups and diamine curing agents at a high temperature may be another mean to covalently introduce the SWCNTs into epoxy. It was found that 1wt% functionalised SWCNTs resulted in 30% increase in modulus and 18% increase in tensile strength, respectively. Tseng et al [106] considered that the strong chemical modification by acid could result in damaging the structure of tube walls and shortening the length of tubes, which was not easy to control as well. They reported another route to fabricate CNT/epoxy nanocomposites (Figure 2.21), which could overcome the disadvantage of the
chemical modification. In Tseng et al’s work, a plasma treatment was used to generate a large number of radicals on the surface of the CNTs in a vacuum reactor. The initiation of maleic anhydride (MA) was subsequently performed on the surface of the CNTs by the radicals. The CNTs with amino groups were prepared via the reaction between the CNTs grafted with MA and diamine. Finally, the CNTs with amino groups co-cured epoxy with the diamine serving as a main curing agent, by which the CNTs were chemically incorporated into epoxy. A significant improvement in mechanical properties was observed, i.e. the tensile modulus increased by more than 100% and the tensile strength showed an average 50% higher than pure epoxy with the incorporation of 1 wt% CNTs-g-MA.

![Diagram of CNTs-MA nanocomposites](image)

**Figure 2.21** Schematic procedure for preparation of CNTs-MA/Epoxy nanocomposites [106]

### 2.3.5 New methods

In this part, some novel methods to prepare CNT/polymer nanocomposites are introduced. An alternating deposition technique called layer-by-layer assembly was invented to fabricate highly CNT-filled films with multilayer structure as seen in **Figure 2.22**, which mainly took advantage of electrostatic and van der Waals interaction between oppositely charged CNTs and polyelectrolytes. Olek et al [107] reported the preparation of MWCNT/polyethylenimine (PEI-b) nanocomposites
Figure 2.22 SEM images of the rapture region of the MWCNT freestanding film after stretching tests [107]

Figure 2.23 SEM images of 980 nm polystyrene particles coated with one layer of MWCNTs [108]

by manually committing cyclic immersion of solid substrates in oppositely charged PEI and MWCNT solutions. Correa-Duarte et al [108] reported on the assembly of MWCNTs on nanosized PS particles used as substrates, which was also driven by the electrostatic interaction between the oppositely charged MWCNTs and PS particles. The MWCNTs were treated by acid to be negatively charged. The PS particles were positively charged with the help of poly(diallyldimethylammonium chloride (PDDA). After mixing the oppositely charged components, the MWCNTs were self-assembled on the surface of the PS
particles, as shown in Figure 2.23 and Figure 2.24. Shim et al [109] reported on the preparation of SWCNT/poly(vinyl alcohol) (PVA) nanocomposites using layer-by-layer assembly. The SWCNTs positively charged by poly(sodium-4-styrene) (PSS) and PVA formed layer-by-layer assemblies on a clean silicon substrate.

Figure 2.24 SEM images of polystyrene particles with hexagonal order before (a and d) and after (b,c,e,f) assembly of carbon nanotubes. All images correspond to the same sample but images (c) and f have been obtained with a tilting angle of 10°. Scale corresponds to (a) [108]

2.4 Electrical property of CNTs and CNT/polymer composites

2.4.1 Electrical property of CNTs

One-dimensional CNTs have been regarded as giant molecular quantum wires in which electrons can propagate along their transverse direction freely. Due to the confinement of electron transport in the transverse direction, the conductance is quantised into a series of discrete values. This quantisation results in the validation of Ohm's law for calculating the electrical resistance of a quantum wire. It is believed that the boundary condition with relation to the diameter and the helicity of carbon atoms in nanotube shell determines the electrical property of CNTs [110]. As mentioned above, the diameter and helicity are specified by the vector $c_h = na_1 + ma_2$. If $n - m$ is a multiple of 3, then the nanotube is metallic, otherwise the
Chapter 2 Literature Review

nanotube is a semiconducting [3].

In the early stage, experimental measurement of the electrical transport in CNTs was conducted using two-probe [111] and four-probe tests [112][113]. Thess [113] et al used a four-probe method to obtain the resistivity of metallic SWCNT ropes, which was less than $10^{-4}$ ohm-centimetres at 300 Kelvin. However, it is very difficult to make ideal electrode-tube contacts with CNTs (An ideal electrode-tube contact will not backscatter any electron entering or leaving CNTs). Strong electron scattering at electrode-tube contacts results in lower experimental values than predicted. In 1998, Frank et al [114] experimentally measured the conductance of arc-produced MWCNTs using a scanning probe microscopy with a tip replaced by nanotube fibre. The tip of the fibre was lowered into a drop of liquid metal to establish gentle electrical contacts with a MWCNT. The electrical conductance of the MWCNTs is one unit of the conductance, $G_0=2e^2/h=(12.9\text{ kilohms})^1$, where $e$ is the charge on the electron and $h$ is the Planck constant. They also found that the MWCNTs appear to be ballistic conductors, despite the interaction expected between the different tube walls. Moreover, extremely high stable current density in excess of $10^7$ Amps per square centimetre was attained. Later, Sanvito et al [115] stated their explanation for Frank et al's discovery, which was the interwall interactions blocked the quantum conductance channels and redistributed the current nonuniformly over individual nanotubes across the structure.

2.4.2 Electrical property of CNT/polymer composites

Semi-conductive polymer composites have been widely applied in anti-static films, electromagnetic interference (EMI) shielding, chemical sensor, photoconductors, bipolar plates for fuel cells and impedance adapters for organic light emitting diodes (OLEDs). Conductive fillers including carbon black and graphite have been widely used to enhance the electrical conductivity of polymers [116] [117]. A percolation theory is created to explain the conductive mechanism of polymer
composites, which reveals that the conductive pathway in polymer matrix formed by certain amount of conductive fillers can convert non-conductive polymers to be conductive. The critical amount of the fillers is called percolation threshold. In order to comprise the electrical conductivity with the mechanical properties and cost of the composites, the percolation threshold is required to be as low as possible. It has been reported that the percolation threshold of carbon black was around 25wt% [124] and graphite exhibited a lower percolation threshold around 8wt% [125] due to their higher aspect ratio. CNTs are standing under spotlights due to their super electrical conductivity (>10^4 S/cm) and extremely high aspect ratio.

Table 2.1 Electrical property of CNT/polymer nanocomposites

<table>
<thead>
<tr>
<th>Types of polymer matrix</th>
<th>Types of CNTs</th>
<th>Types of processing</th>
<th>Percolation threshold (wt%)</th>
<th>Maximum conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE [89]</td>
<td>CVD-MWCNTs</td>
<td>Melt mixing</td>
<td>7-8</td>
<td>10^4</td>
</tr>
<tr>
<td>PC [118]</td>
<td>CVD-MWCNTs</td>
<td>Melt mixing</td>
<td>5-6</td>
<td>10^6</td>
</tr>
<tr>
<td>PP [119]</td>
<td>Acid-treated MWCNTs</td>
<td>Melt mixing</td>
<td>1-2</td>
<td>10^3</td>
</tr>
<tr>
<td>PP [120]</td>
<td>Acid-treated MWCNTs</td>
<td>Oxidised</td>
<td>1-2</td>
<td>10^3</td>
</tr>
<tr>
<td>PS [121]</td>
<td>Solution casting</td>
<td>0.4-0.5</td>
<td>10^7</td>
<td></td>
</tr>
<tr>
<td>PS [121]</td>
<td>PmPV-treated SWCNTs</td>
<td>Solution casting</td>
<td>0.17</td>
<td>10^7</td>
</tr>
<tr>
<td>Epoxy [122]</td>
<td>Solution casting</td>
<td>0.5</td>
<td>10^6</td>
<td></td>
</tr>
<tr>
<td>Epoxy [123]</td>
<td>Silane-treated MWCNTs</td>
<td>In-situ polymerisation</td>
<td>0.1</td>
<td>10^4</td>
</tr>
</tbody>
</table>
Chapter 2 Literature Review

ratio (>1000), which show much lower percolation threshold than carbon black and graphite in the polymer matrix. Percolation thresholds are summarised in Table 2.1 according to types of polymer matrix and processing methods. The highest percolation threshold (~7wt%) appears in the melt processing of thermoplastic polymers with raw MWCNTs. The use of acid-treated MWCNTs decreases the percolation threshold to 1-2wt%. Much lower percolation threshold (less than 0.5wt%) appears in the solution processing of CNT/PS composites, which could be attributed to good dispersion of chemically modified CNTs in polymer matrix. Macromolecules functionalised CNTs facilitated lower the percolation threshold than the CNTs with functional groups.

Recently, a novel cellular structure of CNTs in polymeric matrix has been created to achieve extremely low percolation threshold. The approaches to produce the cellular structure have been introduced in the section of "fabrication", including colloidal physics method and coating technology. Regarding the colloidal physics method, Regev et al [6] reported that the percolation threshold was 0.3wt% for PS latex (75nm) and PMMA latex (75nm). Grunlan et al [7] found that the percolation threshold based on PVAc latex (105nm) was lowered to 0.04wt%. Grunlan et al proposed a morphological model (Figure 2.25) to explain the formation of the cellular structure hosted by latex. During the film formation of polymer latex, the CNTs are pushed to the interstitial space between spherical particles to form the cellular structure. The dramatic reduction of the free volume available for the CNTs to form conductive networks results in achievement of extremely low percolation threshold. Coating technology concerns the coating of the CNTs on the surface of polymer powders or pellets before film formation by static compression moulding at high temperature. The film formation of the powders or pellets under static condition locks the CNTs in the powder-powder or pallet-pallet boundary, allowing the formation of the cellular structure (Figure 2.26). Mu et al [100] applied the coating technology to PS pellets and found that the percolation threshold approached 0.1wt% for the statically compressed films. The percolation
threshold whereas rose up to 1wt% for the composites prepared by the hot coagulation method. It has to be pointed that the cellular structure cannot be formed if the coated powders or pellets are processed by shear mixing. It was reported that melt processing of HDPE coated with the CNTs only achieved a percolation threshold around 4wt% [97]. Some researchers discovered the cellular structure of the CNTs formed in foam matrix [126][127]. Xu et al [127] fabricated PU foam by using water as blown agent in presence of the CNTs. SEM images in Figure 2.27 show that the CNTs are located in the cell walls. In this work, the percolation threshold was reflected by the density of the foam instead of filler concentration. The conductivity sharply increased with the increase of density from 0.03gcm$^{-3}$ to 0.05gcm$^{-3}$. The investigation of microstructure revealed that pore size increases and cell-wall thickness decreases with the decrease of density (Figure 2.28). The thinner cell-wall with less CNT content is the reason for the decrease of the conductivity.

![Schematic illustration of the drying process of SWCNT-filled polymer emulsion](image)

**Figure 2.25** Schematic illustration of the drying process of SWCNT-filled polymer emulsion. Initially, the nanotubes and polymer particles are uniformly suspended in water (left). Once most of the water has evaporated, the polymer particles assume a close-packed configuration with the nanotubes occupying interstitial space (center). Finally, the polymer particles will interdiffuse (i.e., coalescence) to form a coherent film, locking the SWCNTs within a segregated network (right) [7].

33
Figure 2.26 Optical micrographs of the cross-sections of SWCNT/PS nanocomposites prepared by the coated particle process (CPP) with (a) faceted PS domains and (b) elongated PS domains due to higher pressures during compression moulding. The lines across the polymer domains are from the diamond saw. (c) SEM image of the fracture surface of NTPSpel with 0.5 wt% SWCNT showing evidence that PS spans across the SWCNT layer [100]
Figure 2.27 SEM micrographs of the fracture surface of the ultralightweight CNT/PU foam composite with a density of 0.05 g cm$^{-3}$. a) Low magnification (with some cell walls and cell struts therein indicated by the arrows). b) High-magnification micrograph of the cross-section of the cell strut in Figure 2.27a [127].

Figure 2.28 Schematic diagram of the microstructural changes in the CNT/PU foam composites with the decrease of density. The thin black lines represent the CNTs and the wide lines represent the boundaries of the cells. The density decreases gradually from (a) to (d). The arrows in the cells show the growth directions of the air bubbles during foaming [127].
Chapter 2 Literature Review

2.5 Thermal conductivity of CNTs and CNT/polymer composites

2.5.1 Thermal conductivity of CNTs

The thermal properties of CNTs have been disclosed in many communications, which make CNTs become promising materials in thermal management. Mizel et al [128] measured the specific heat of MWCNTs and SWCNT ropes in a temperature range \(1 \leq T < 200\) K, respectively. The MWCNTs exhibit graphite-like specific heat due to their structural similarities. The SWCNT ropes show stronger temperature dependence and larger specific heat at low temperature than the MWCNTs and graphite. Yi et al [129] measured the specific heat and thermal conductivity of millimetre-long aligned MWCNTs. It was found that the specific heat of a MWCNT linearly depends on temperature in a range of 10-300K, and the thermal conductivity of CVD-grown MWCNTs was found to be a function of \(T^2\) in a range of 4-300K. It was also mentioned that substantial amounts of defects in as-grown MWCNTs results in low value of the thermal conductivity in comparison with what is generally expected [130]. Hone et al [131] measured the specific heat of SWCNT ropes at low temperature down to 2 K. The experimental data at a temperature above 4K are in agreement with theoretical curve of individual SWCNT, but differ remarkably from the curves of graphene and graphite. This indicates the tube-tube coupling is relative weak. Hone et al [132] also reported that the thermal conductivity of SWCNT ropes smoothly decreases as temperature decreases from 350K to 8K. The thermal conductivity was found to be linearly dependent on the temperature below 30K. An energy-independent phonon mean free path of 0.5\(\mu\)m-1.5\(\mu\)m was calculated based on this linear relationship. Kim et al [133] used a microfabricated suspended device to measure the thermal conductivity of individual MWCNT at room temperature. A value of more than 3000W/mK was obtained and almost one hundred times higher than that from previous work using macroscopic mat sample (~20W/mk [129], ~35W/mK [132]). Berber et al [4] used molecular dynamics simulations to determine the
thermal conductivity of CNT at room temperature, which gave a value of ~6600 W/mK for isolated (10,10) nanotube.

2.5.2 Thermal conductivity of CNT/polymer composites

As mentioned above, CNTs are super thermal conductors according to their nearly perfect crystalline lattice structure and free length of path for phonon and electron transport. Due to their outstanding thermal conductivity, CNTs have been considered as potential candidates to improve the thermal conductivity of polymers and develop thermal management materials. At an early stage, researchers believed that the percolated CNT network in polymer matrix should facilitate the phonon transport as well as the electron transport. A simple model was proposed by Nan et al to predict the thermal conductivity of CNT-based composites [134]:

\[
\frac{K_c}{K_m} = 1 + \frac{fK_{CNT}}{3K_m} \tag{1}
\]

where \(K_c\) is the thermal conductivity of composites; \(K_m\) is the thermal conductivity of polymer matrix; \(K_{CNT}\) is the intrinsic thermal conductivity of CNTs; \(f\) is the filler content. Theoretically, the thermal conductivity of CNT-based composites filled with 0.1 wt% MWCNTs can be six time higher than that of pure polymers. However, most published experimental results indicated poor performance of CNTs as the thermal conductors was not desirable in polymer matrix. Gojny et al [8] found that the thermal conductivity of MWCNT/epoxy composites is only slightly enhanced, and significantly lower than those estimated by the Nan et al's model. They even discovered that the epoxy composites with chemical treated SWCNTs or with low SWCNT content exhibit lower thermal conductivity than neat epoxy. Xia et al [135] found that, with the incorporation of 1 wt% SWCNTs and MWCNTs, the thermal conductivity of PU was improved by ~42% and ~21%, respectively. Xu et al [136] reported a slight enhancement in the thermal
conductivity of poly(vinylidene fluoride) with the incorporation of SWCNTs up to 50vol% SWCNTs. Yuen et al [137] reported that the thermal conductivity of poly(acrylate-co-vinyltriethoxysilane) was maximally improved by 87.5% with the incorporation of 0.99wt% MWCNTs.

Phonon scattering at CNT-polymer interfaces has been considered as the bottleneck limiting the thermal transport in CNT/polymer nanocomposites [8][9]. Some researchers have made breakthroughs in reducing the interfacial phonon scattering, although these experimental results still fail to match with theoretical prediction. Haggenmueller et al [138] considered that the formation of crystallites at CNT-polymer interfaces could be a practical way to reduce the interfacial phonon scattering. They found that the thermal conductivity of low density polyethylene (LDPE) (0.26Wm/k) and high density polyethylene (HDPE) (0.5Wm/k) was improved to 1.8Wm/k and 3.5Wm/k, respectively, with 20vol% SWCNTs. Du et al [139] invented an infiltration method for preparing SWCNT/epoxy composites with highly improved thermal conductivity, which included four steps (Figure 2.29): (1) 1wt%SWCNT/PMMA composite was prepared via hot coagulation method; (2) nitrogen gasification of 1wt% SWCNT/PMMA (disc) was conducted in radiant gasification apparatus (nitrogen gasification was a thermal degradation process to convert the PMMA matrix to MMA monomers leaving the composites in gas phase); (3) epoxy and curing agent were infiltrated into the residue of the SWCNT/PMMA composite (the residue left after nitrogen gasification was robust and freestanding nanotube framework with nanotube/nanotube junctions); and (4) Curing the epoxy in presence of the SWCNTs. The core of this method was the formation of the freestanding nanotube framework after nitrogen gasification. This freestanding nanotube framework formed a continuous nanotube-rich phase (Figure 2.30) in the epoxy matrix, which reduced nanotube/polymer/nanotube junctions and increase nanotube/nanotube junctions. It was considered that the nanotube/nanotube junctions could incur less phonon scattering than the nanotube/polymer/nanotube
junctions. A 220% improvement in the thermal conductivity of the epoxy was achieved with the incorporation of 2.3wt% SWCNTs.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{infiltration_method.png}
\caption{Schematic of the infiltration method [139]}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{composite_image.png}
\caption{(a) Optical and (b) SEM image of the SWCNT/epoxy composite fabricated by the infiltration method [139].}
\end{figure}
Figure 2.31 The model of an ideal structure for thermal interface material (TIM) application. All the CNTs are aligned in the matrix and protrude out of the surfaces to form an ideal thermal conducting path from one surface to the other [27]

Figure 2.32 SEM images of a CNT array and a CNT array composite. a) Side view of an aligned CNT array. The inset is a HRTEM image of a typical CNT showing eight graphite layers. b) Side view of the aligned CNT composite film, showing that the CNTs still remain in aligned in the composite. c) Tilted view (65°) of the aligned CNT composite film, showing most of the CNT tips protruding out of the surface. d) Top view of the aligned CNT array composite film after reactive-ion etching (RIE) treatments, showing almost all tips protruding out of the film surface [27]
Chapter 2 Literature Review

Huang et al [27] designed a novel composite structure (Figure 2.31) for effectively reducing interfacial phonon scattering by using in-situ injection of polymers into the CNT arrays. SEM images (Figure 2.32) reveal the true face of the novel composite structure: 1) all the CNTs are aligned in polymer matrix; 2) all the CNT tips are protruding out of the surface. To our best knowledge, this novel structure so far resulted in the highest improvement of thermal conductivity. It was found that an enhancement of 0.65 W/mK was obtained from the composites with an aligned CNT array (0.3 wt%). At 0.4 vol% aligned CNTs, an increase of about 120%, from 0.55 W/mK to 1.21 W/mK, was seen in thermal conductive elastomer S160. The thermal conductivity of the low-thermal-conductivity silicone elastomer was improved by about 280%, from 0.23 W/mK to 0.88 W/mK, with the incorporation of 0.4 vol% aligned CNTs.

2.6 Mechanical Properties of CNTs and CNT/polymer composites

2.6.1 Mechanical properties of CNTs

Since the discovery of CNT, it was predicted that CNTs have high stiffness and axial strength due to the covalent sp² bonding formed between individual carbon atoms. Much effort has been made to disclose the values of their mechanical properties. Treacy et al [2] valued the Young’s modulus of individual MWCNT in a range of 0.41-4.15 TPa by measuring the amplitude of their intrinsic thermal vibration in transmission electron microscope. The experimental measurement of Young’s modulus of isolated SWCNT gave an average value 1.25 TPa obtained by observing their freestanding room temperature vibrations in transmission electron microscopy [140]. Poncharal et al [141] also took advantage of electromechanical resonant vibrations to measure Young’s modulus of individual CNT in transmission electron microscope, by which the values were obtained in a range of 0.7-1.3 TPa. Wong et al [142] directly measured the mechanical properties of MWCNTs using atomic force microscopy (AFM). The average Young’s modulus and bending strength was valued as 1.28 TPa and 14 GPa, respectively [143].
2.6.2 Mechanical properties of CNT/polymer composites

CNTs have been considered to be an ideal candidate for the mechanical reinforcement of polymers due to their extremely high Young's modulus of up to 1TPa and tensile strength approaching 60GPa. In the development of ultra-strong CNT/polymer nanocomposites, two key issues need to be considered: (1) the uniform dispersion of CNTs in polymer matrix without aggregation and entanglement; and (2) the strong interfacial interaction between CNTs and polymer matrix. It is easy to make a conclusion from published literatures that tailoring the surface of CNTs by chemical modification is commonly considered to be effective way to meet these two requirements. Zhang et al [91] used nitric acid treated MWCNTs to reinforce polyamide 6 (PA6) by a simple melt-compounding. The defects such as carboxylic and hydroxyl groups existing on the nanotubes facilitated a homogenous dispersion of the nanotubes in the PA6 matrix (Figure 2.33(A and B)), and acted the role of anchoring sites forming the strong interfacial interaction with the PA6 matrix (Figure 2.33(C and D)). In Figure 2.34(A), typical stress-strain curves show that the incorporation of 1 wt% MWCNTs increases tensile modulus and tensile strength nearly 115% and 120%, respectively. Figure 2.34(B) shows typical loading-holding-unloading curves obtained from nanoindentation, and it indicates that the increase of modulus and hardness reaches 70% and 67%, respectively, with the incorporation of 1 wt% the MWCNT. Liu et al [144] reported on the significant reinforcement of PVA using functionalised SWCNTs. In this case, the hydroxyl groups on the SWCNTs were capable of de-aggregating the nanotubes in the PVA matrix, and enhancing the interfacial interaction with the nanotubes due to the formation of hydrogen bonding. At 0.62 vol% nanotubes, the tensile modulus and tensile yield strength of the PVA was improved by 79% (from 2.4 GPa to 4.3 GPa) and 47% (from 73 MPa to 107 MPa), respectively.
Figure 2.33 A) SEM image showing an overall morphology of failure surface for PA-6 nanocomposite containing 0.5% MWCNTs. B) Enlarged morphology of selected region in (A). C) SEM image showing microcracks linked by stretched nanotubes and their bundles in PA-6 nanocomposites. D) Enlarged SEM image of the microcrack connected by MWCNTs sheathed with polymer in the nanocomposites. Some MWCNTs are sheathed by several small polymer beads [91]

Figure 2.34 (A) Typical stress-strain curves and (B) Typical loading-unloading curves for neat PA6 and its nanocomposite containing 1wt% MWCNTs [91]
Hwang et al [77] discovered that the storage modulus of commercial PMMA is significantly enhanced by ~29GPa (or by ~1100%) at 20°C with the incorporation of 20wt% PMMA-grafted MWCNTs. The TEM images in Figure 2.35 show a strain failure of the MWCNTs takes place rather than an interfacial adhesion failure between the MWCNTs and PMMA matrix, which indicates that PMMA chains chemically attached to the MWCNTs strongly enhance the interfacial interaction between the MWCNTs and the PMMA matrix. Blond et al [145] placed their focus on reinforcement of PMMA by using small addition of PMMA-grafted CNTs. It revealed that the nanocomposites containing 0.1vol% nanotubes exhibited a biggest increase in the Young’s modulus, break strength, ultimate tensile strength and toughness of \( \times 1.9, \times 4.7, \times 4.6 \) and \( \times 13.7 \), respectively.

\[ \text{(a)} \]
\[ \text{(b)} \]
\[ \text{(c)} \]

167nm

**Figure 2.35** TEM images of a MWCNT-containing PMMA thin film taken at different time: a) t=0, b) t=4, and c) t=10 min [145].

Yang et al [93] reported on the strong reinforcement of polyethylene (PE) using PE grafted CNTs (PE-g-CNTs). As shown in Figure 2.36, it can be obviously seen that pristine CNTs cannot compete with PE-g-CNTs in reinforcing the PE. The yield stress, tensile stress and Young’s modulus of the PE is improved by 61%,
33% and 75%, respectively, with the incorporation of 1.5wt% PE-g-CNTs. The counterparts with pristine CNTs exhibit unsatisfied reinforcing performance. The yield stress and Young’s modulus both increase slightly, and the tensile strength even deteriorates (down by 17%). The more exciting thing is the improvement of ductility and toughness with the incorporation of the PE-g-CNTs, which is not common case in CNT/polymer nanocomposites.

![Figure 2.36 Stress-strain curves: a) PE/PE-g-MWCNTs composites; b) PE/MWCNTs composites [93]](image)

The formation of the chemical bonding is more effective approach to engineer a strong interface between CNTs and polymer matrix. As introduced in the section of “fabrication” above, two types of ways are feasible to form the chemical bonding, which include (1) the reaction of the functional groups existing in CNTs and polymers; and (2) the copolymerisation of CNTs and vinyl monomers via opening double bonds. Gao et al [12] fabricated strong melt-spun PA6 fibres with the chemical integration of SWCNTs via the condensation reaction between carboxylic acid groups on the SWCNTs and the amino end groups in the PA6. The stress-strain curves in Figure 2.37 shows that a 127% increase in tensile strength and a 170% increase in Young’s modulus take place with the incorporation of 1.5wt% SWCNTs into the PA6. Zhu et al [105] reported that the chemical integration of 1wt% CNTs with carboxylic and fluorine groups into epoxy matrix via ring-open reactions resulted in a 30% increase in modulus and a 18% increase
in tensile strength. Tseng et al [106] reported on much more significant reinforcement of epoxy using diamine curing agent (NH₂-R-NH₂) to chemically connect maleic anhydride (MA)-grafted CNTs (CNTs-MA) with epoxy matrix. As shown in Figure 2.38, the tensile strength, the elongation-at-break and tensile modulus of the epoxy increases about 50%, 350%, and 100%, respectively, with the incorporation of 1wt% the CNTs-MA. Untreated-CNTs (u-CNTs) show poor reinforcing performance in the epoxy nanocomposite due to the poor dispersion and interfacial interaction. Jung et al [104] reported on the crosslinking of isocyanate-terminated polyurethane using CNTs with carboxylic groups. Tensile strength and modulus is improved by about 300% and 130%, respectively, with the incorporation of 4wt% nanotubes into the polyurethane. The typical example for the second approach was the in situ polymerisation of MMA in presence of CNTs [101]. The incorporation of 5wt% CNTs improved the tensile strength and hardness by about 30% and 43%, respectively.

![Figure 2.37](image.png)

**Figure 2.37** Stress-strain profiles of nylon 6-SWCNT composite fibres at different SWCNT loadings. The curves are labeled with the percentage of SWCNTs in the polymer matrix [12].

Coleman and co-workers [14][146][147] made significant contribution to work out non-covalent interface between CNTs and crystalline polymers for efficient load transfer. They found that the crystallites nucleated by CNTs can act as a strong and
non-covalent interface for load transfer. Several articles have been published to disclose their viewpoints. Cadek [147] found that Young's modulus and hardness increased by factors of 1.8 and 1.6 at 1wt% MWCNTs in PVA and 2.8 and 2.0 at 8wt% MWCNTs in poly(9-vinyl carbazole) (PVK). DSC results revealed that the PVK nanocomposites were totally amorphous, and the crystallinity of the PVA increased sharply to 24% with very small addition of the MWCNTs before rising to 27% as the MWCNTs content increased to 1wt%. The TEM image in Figure 2.39 was taken from a torn PVA film by concentrated electron beam, which shows that this tube is coated with a thin layer of crystalline polymer. Therefore, they drew a conclusion that a shell of crystalline layer around the CNTs was the trigger for the efficient load transfer between the CNTs and the PVA matrix.

Figure 2.38 Effect of the CNT content on the (a) tensile strength, (b) elongation-at-breaks, and (c) tensile moduli of the CNTs/epoxy nanocomposites [106]
Figure 2.39 TEM image of the MWCNTs pulled out from PVA [147]

Figure 2.40 DSC curves (on the left) for PVA-based composites as a function of nanotube volume fraction (Note the area under the melt peak(160-210°C) increase with nanotube content) and graph of crystallinity (on the right) as calculated from the DSC melt curves versus volume fraction for PVA-based composite samples [14].

Later, Coleman et al [14] studied the same transfer mechanism based on other two types of polymer matrix: polyvinyl alcohol (PVA) and chlorinated polypropylene (Cl-PP). As seen in Figure 2.40(right), the crystallinity of PVA-based nanocomposites linearly increases with the volume fraction of the CNTs, indicating the existence of PVA crystalline layers around the CNTs. An equation was proposed to calculate the thickness of the crystalline layer based on the
assumption of a cylindrical geometry for the nanotube-nucleated layer:

\[ \chi = \frac{V_0 + N[\pi(R + b)^2l_{NT} - \pi R^2l_{NT}]}{V} \]  

(2)

where \( \chi \) is the crystallinity; \( N \) is the number of the nanotubes in the film; \( V_0 \) is the volume of crystalline regions not associated with the nanotubes; \( R \) is the average nanotube radius (7.5±2.5nm); \( b \) is the average thickness of the crystalline layer; \( l_{NT} \) is the nanotube length; and \( V \) is the film volume. By fitting the crystallinity data from Figure 2.40(left) into the equation, \( b \) was valued as 21±7nm, which was in agreement with the rough value directly obtained from the SEM images of the PVA nanocomposite. From the stress-strain curves in Figure 2.41(left), it can be seen that the Young's modulus, tensile strength and toughness of the PVA-based nanocomposite containing 0.6vol% nanotube presents to be 3.7, 1.3 and 1.7 times higher than the PVA, respectively. Regarding chlorinated polypropylene (Cl-PP) nanocomposites, a satisfied dispersion of the CNTs in the Cl-PP matrix was achieved with the help of the covalent attachment of Cl-PP chains to the surface to the CNTs. No increase in the crystallinity of the Cl-PP nanocomposites was found in comparison with the PVA nanocomposites. The coating layer around nanotubes (16±7nm) composed of Cl-PP chains played a similar role to the crystalline coating for load transfer. There was no mention that why crystalline Cl-PP failed to form the crystalline coating around the CNTs. A significant improvement of mechanical properties is presented in Figure 2.41(right). It has to point out that Coleman and co-workers only discovered the crystalline coating around CNTs available for effective load transfer in the case of semi-crystalline PVA.

Xia et al [73][135] reported on the mechanical reinforcement of polyurethane (PU) materials using CNTs. This is a case that could support Coleman el al’s discovery. Polyether-based PU (amorphous) and polycaprolactone-based PU (semi-crystalline) were both used as polymer matrix in their research work. The mechanical reinforcement of the amorphous PU was not impressive. e.g. the modulus at 50%
strain was only improved by ~38%, with the incorporation of 2wt% MWCNTs. In terms of the semi-crystalline PU, the Young’s modulus was improved by nearly 278% with the incorporation of 0.7wt% PU grafted SWCNTs. Similar to Coleman’s discovery, DSC results revealed that the crystallinity of the PU increased with the incorporation of the SWCNT. However, the role of crystallites around the SWCNTs in the load transfer was not highlighted by the authors. They considered that the effective load transfer was mainly attributed to PU chains covalently attached to the SWCNTs. To date, there are not many literatures covering the study of non-covalent interface. But the formation of the crystalline layer around CNTs could be a promising way to engineer non-covalent interface for effective load transfer between CNTs and polymers.

![Representative stress-strain curves for PVA-based composites (left) and Cl-PP composites (right) for a range of nanotube volume fractions [14]](image-url)
2.7 Conclusions

Since the first report of the CNT/polymer composites by Ajain [26] in 1994, a large amount of research work has gone for the understanding of their structure-property relationship. This part reviewed the recent advances in this field. Currently, the high cost of CNTs is commonly considered as the barrier for the commercial application of the CNT/polymer composites. Developing simple and practical engineering approaches to fabricate high performance CNT/polymer composites using small amount of CNT is a challenge faced by researchers to push lab technologies over to real world. This thesis will address our efforts and contribution for dealing with this challenge.
Chapter 3 Experimental

3.1 Materials

MWCNTs and MWCNTs-OH (3-5wt% hydroxyl groups) with a diameter between 8-15 nm and a length of ~50μm were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Expandable graphite (EG) was purchased from Chinese Qingdao Graphite Company. All materials used for the oxidation of EG, such as H₂SO₄, HNO₃, HCl, KMnO₄, 30% H₂O₂ solution and BaCl₂, were purchased from Fisher Ltd (UK). Polyether polyol-6000 (molecular weight: 6000; functionality: 3) and polyether polyol-4000 (molecular weight: 4000; functionality: 2), abbreviated as PPG-6000 and PPG-4000, respectively, were supplied by Elastogran UK, Ltd. Polycaprolactone (PCL, CAPA 2205) with a molecular weight of ~2000 and polycaprolactone (PCL, CAPA 6800) with a molecular weight of ~80000 were both Solvay products, which were kindly provided by Brian Jones & Associates Ltd, UK. 4,4-Methylenebis (phenyl isocyanate) (MDI) was kindly provided by Hyperlast Ltd. Sodium dodecyl sulphate (SDS, Aldrich), 1,4-butanediol (BDO, Aldrich), a,a-dimethylol propionic acid (DMPA, Aldrich), dibutyltin dilaurate (DBTL, Aldrich), triethyl amine (TEA, Aldrich), acetone, N-methyl-2-pyrrolidone (NMP, Aldrich) and N, N-dimethylformamide (DMF, Aldrich) were used without further purification. Two grades of ultra high molecular weight polyethylene (HMWPE) powders (60μm and 100μm) were synthesised by Sanjay Rastogi’s research group.

3.2 Sample preparation

3.2.1 Preparation of polyether-based PU dispersions

Polyether polyol was vacuumed at 100°C for about 3 hour to remove minimal
water before use. DMPA solution (in NMP 30%) was achieved before use. The PU dispersion was prepared using the “acetone method” [148]. The formulation details for the preparation of the PU dispersion was shown as followed: NCO/OH=0.96; Carboxylic group content (wt%) = 1.7%; Neutralisation degree=100%; Hard segment content = 30%. The synthesis was carried out in a 500-ml four-neck round-bottom flask equipped with mechanical stirrer, a thermometer and a nitrogen gas inlet. Reaction temperature was controlled by heating mantle connected with temperature controller. Polyether polyol was added into flask, and heated to 55-60°C. Afterward, MDI with certain amount was poured into the flask and mixed with polyether polyol for 5 minutes, and then the mixture was slowly heated to 80°C. After 1 hour, DMPA solution and 1.4-Butanediol was added into the mixture, followed by adding 0.5% DBT and 10% acetone (based on the total weight of all reaction monomers). The reaction was kept under 75°C for another 3 hours until the stretching band of NCO group (2270cm⁻¹) disappeared in FTIR spectra. After obtaining homogeneous PU solution, the reaction temperature was cooled down to 55°C. Neutralisation was performed at 50°C after addition of TEA and another 10% acetone for 30minutes, then water was added dropwise to the PU for 15 min at 50°C. The stirring was continued for further 30min. After removal of acetone, the PU dispersion with about 30% solid content was obtained.

3.2.2 Preparation of PCL-based PU dispersions

PCL was vacuumed at 100°C for about 3 hour to remove minimal water before use. DMPA solution (in NMP 30%) was achieved before use. The synthesis was carried out in a 500-ml four-neck round-bottom flask equipped with mechanical stirrer (half-moon type), a thermometer and a nitrogen gas inlet. Reaction temperature was controlled by heating mantle connected with temperature controller. 30g PCL was added into flask, and heated to 55-60°C. Afterward, 7.3g MDI with certain amount was poured into the flask and mixed with PCL for 5 minutes, and then the mixture was slowly heated to 80°C. After 1 hour, 6.7g
DMPA/NMP solution was added into the mixture, followed by adding 0.5% DBT and 10% acetone (based on the total weight of all reaction monomers). The reaction was kept under 75°C for another 3 hours until the stretching band of NCO group (2270cm⁻¹) disappeared in FTIR spectra. After obtaining homogeneous PU solution, the reaction temperature was cooled down to 55°C. Neutralisation was performed at 50°C after addition of TEA and another 10% acetone for 30 minutes, then water was added dropwise to the PU solution for 15 min at 50°C. The stirring was continued for further 30 min. After removal of acetone, the PCL-based PU dispersion with milky appearance and about 30% solid content was obtained.

3.2.3 Preparation of MWCNT/PU composites by a colloidal physics method

The mixture of 0.468g SDS and as-received 0.468g MWCNTs in 30 ml water firstly was treated by ultrasound with a power of 300 W for 30 minutes at room temperature. Then, the polyether-based PU dispersion was mixed with the MWCNT/SDS dispersion for one hour. After removing the bubble by vacuum, the MWCNT/PCL-based PU dispersion was cast on a polytetrafluoroethylene (PTEF) substrate and kept for 12 days at room temperature, and then vacuumed for another 5 days at room temperature. The MWCNT/PCL-based PU composites were also prepared following this method.

3.2.4 Preparation of MWCNT-OH/UHMWPE composites by a coating method

The MWCNTs-OH were firstly dispersed in DMF using ultrasonication, then were mixed with the amount of UHMWPE powders in DMF at a certain temperature for few minutes. Finally, the powdery CNT/UHMWPE composite was obtained after drying off the solvent. The powdery sample was processed to sheets using compression moulding with a pressure of 10 tons at a temperature of 150°C for 5 min, then cooled at a pressure of 5 tons for 3 min with the circulation of tap water.
3.2.5 Preparation of MWCNT-OH/PCL composites by a solution method

The mixture of 10mg MWCNT-OH and 4g DMF was subjected to strong ultrasonic treatment (Fisher Scientific Sonic Dismembrator Model 500, 300w) for 1 hour at room temperature. The MWCNT-OH/PCL composites were prepared by drying the mixture of PCL and MWCNT-OH in DMF at 80 °C for two weeks. The sheet samples were made using a compression moulding for tensile testing. The thermal treatment of the samples was also conducted in the compression moulding, which was described as followed: the bulk sample was melted at 80°C, then slowly cooled to a certain temperature by air for 3 hours in which the isothermal crystallisation was completed.

3.2.6 Preparation of exfoliated graphite oxide nanoplatelets (GONPs) in DMF

The oxidation of EG was conducted following the procedure mentioned in reference [149]. 2.5g EG was mixed with 57.5 ml concentrated H₂SO₄ in ice bath (0°C) for half an hour. 7.5g KMnO₄ was slowly added into the mixture in order to keep the temperature of the mixture not exceeding 20°C. The mixture was then heated to 35±3°C and kept stirring for 30min. Dropwise addition of 115ml distilled water caused the temperature increase to 98°C. The reaction was kept at this temperature for 15min. Finally, the oxidation reaction was terminated by the addition of 350ml distilled water and 25ml 30% H₂O₂ solution. Collection of the EGO by filtering and successive washing with 5% HCl aqueous solution was repeated by three times until there was no sulphate detected by BaCl₂ solution. The EGO was dried at 50°C under vacuum for one week. The exfoliation of 100mg EGO in 10g DMF was conducted using ultrasonication with a power of 300W for 1 hour at room temperature to obtain stable GONP/DMF dispersion.

3.2.7 Preparation of GONP/PCL composites

The GONP/PCL composites were prepared using solution method. Amount of
PCL pellets were melted and mixed with the GONP/DMF dispersion at 85°C for 2 hours by using mechanical stirring (500 rad/min). The proportion of the FGSs to PCL is designed to 0, 0.1 wt%, 0.5 wt%, 1 wt% and 2 wt%, respectively. The solid GONP/PCL composites were obtained after drying the GONP/PCL/DMF dispersion at 70°C for three days. The solid samples were vacuumed for another four days at 70°C to remove minimal DMF.

3.2.8 Preparation of GONP/PU composites

6g PPG-4000, 1.5g PPG-6000, 0.8g BDO, 3.89 MDI and 0.11g DBTL (catalyst) were stirred in DMF at 60°C for 24 hours in a four-necked flask protected by N₂, by which PU/DMF solution was finally obtained with 40 wt% solid content. Afterward, the calculated amount of the GONP/DMF dispersion was mixed with the PU/DMF solution at 80°C for another 1 hours. The two-week drying at 50°C was the last step for the preparation of the GONP/PU composites. The solid samples were vacuumed for another two days at 50°C to remove minimal DMF.

3.3 Characterisation

3.3.1 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is widely used to investigate the chemical structure of a material by measuring the frequencies of molecules in the material [150]. As infrared radiation goes through the material, some of the infrared radiation is absorbed by the material and some of it is transmitted through the material. It is due to the specific frequencies of molecules that rotate or vibrate corresponding to discrete energy levels (vibrational mode). These frequencies that are unique for different molecules can help identify the complex functional groups in the material.

FTIR spectra were recorded on Mattson 3000 FTIR spectrometer using
transmission mode with a 4 cm\(^{-1}\) resolution over 120 scans. Thin films of PPG and its derivative PU were prepared on the KBr pellets. MWCNT and MWCNT-OH powders are ground with KBr powders and pressed into thin films. For the GONP/PU composites, FTIR spectra were recorded on a SHIMADZU FTIR-8400s spectrophotometer using ATR mode with a 4 cm\(^{-1}\) resolution over 120 scans.

3.3.2 Raman spectroscopy

Raman spectroscopy is a technique to investigate the vibrational frequencies of molecules and provides spectroscopic fingerprints for uniquely identifying a material [151]. The principle of Raman spectroscopy is based on inelastic scattering of monochromatic light from a laser source after interacting with the material. Photons of the laser light are absorbed by the material and then reemitted. The vibrational frequencies of molecules can be determined by the change in the frequency of the reemitted photons in comparison with original monochromatic frequency. In FTIR spectroscopy, the vibrational frequencies of molecules are determined by the frequencies of infrared photons that are absorbed by a vibrating molecule. This is the difference between two spectroscopic techniques.

In chapter 4, Raman spectra of MWCNTs and MWCNTs-OH were recorded by scanning the 20-3000 cm\(^{-1}\) region with a total acquisition time of 3 min on a Jobin Yvon Horiba high-resolution LabRam 800 Raman microscope system equipped with an optical microscope adapted to a double grating spectrograph and a CCD array detect. The laser excitation was provided by a Spectra-Physics model 127 helium-neon laser operating at 35 mW of 633 nm output. The laser power at the sample was ~8 mW and was focused to ~10 \(\mu\)m. Calibration was carried out using the 520.5 cm\(^{-1}\) line of a silicon wafer. A spectra resolution of ~1 cm\(^{-1}\) was used. There was no specific requirement for sample preparation. Sample could be scanned at glass substrate directly.
3.3.3 Scanning electron microscopy (SEM)

As a type of electron microscopy, SEM is generally used to image a sample surface by scanning it with a high-energy electron beam emitted from an electron gun fitted with a filament cathode. The interaction between the electron beam and the atoms of the sample generates a variety of signals containing the information about the topography of the sample surface. The signals produced by SEM include secondary electrons, back-scattered electrons, characteristic X-rays, light, heat and transmitted electrons (beam electrons that pass through the sample). As the most common imaging mode, the low energy secondary electrons are generated within a few nanometres from the surface of the specimen by the inelastic scattering interactions between the specimen atoms and beam electrons. Secondary electrons are normally used to show morphology and topography of the specimen. Back-scattered electrons are high-energy electrons elastically scattered from the specimen after electron beams interact with specimen atoms. The back-scattered electrons are generally used to detect the contrast between the areas with different chemical compositions in a multiphase material due to stronger backscattering of electrons by heavy elements (high atomic number) than light elements (low atomic number) [152]. In this project, SEM images were taken on field emission gun scanning electron microscopy (FEGSEM) (LEO 1530VP instrument). The composites were fractured in liquid nitrogen. The samples with fracture surfaces on the top were placed on specimen holder using double-sided carbon conductive tape. No gold coating was used for fracture surfaces. The UHMWPE powders coated with the MWCNTs-OH were placed on the specimen holder for direct observation.

3.3.4 Transmission electron microscopy (TEM)

TEM is an electron-optical microscopy that produces an image of the sample as an electron beam is transmitted through an ultra thin specimen, which has a
significantly higher resolution than light microscopy due to the small de Broglie wavelength of electrons. Basically, TEM image contrast is generated from the absorption of electrons in materials with the difference in the thickness and composition [153]. In this project, TEM analysis was conducted using a JEOL 2100 FX instrument. The MWCNT/water, MWCNT-OH/DMF and GONP/DMF dispersions were dropped on copper grid for TEM imaging directly.

3.3.5 Differential scanning calorimetry (DSC)

DSC is a thermoanalytical technique that measures the energy compensating for substance to establish a nearly zero temperature difference between a substance and an inert reference, as the two specimens undergo identical thermal history (heating or cooling) [154]. The application of DSC was mainly placed on the detection of phase transitions in a sample during the change of thermal environment by observing the difference in heat flow between the sample and reference. For instance, as a solid sample melts to a liquid more heat flowing to the sample is needed to increase its temperature at the same rate as the reference (endothermic process). For crystallisation of a sample (exothermic process), releasing heat is needed to keep the zero difference between the sample and reference. A curve of heat flow versus temperature or time is the typical result of a DSC experiment. The information provided by the DSC cuvre such as heat of fusion, crystallisation and melting temperature, as well as glass transition temperatures can be used to investigate the physical or chemical properties of the sample. MDSC is also a thermoanalytical technique to provide the qualitative and quantitative information about physical and chemical changes within a material by measuring the difference in heat flow between a sample and a reference under controlled heating or cooling process.

In chapter 5, DSC analysis was conducted on a TA Instrument DSC 2920 calorimeter to characterise the MWCNT/PCL-based PU composites. The samples
were heated from -10°C to 70°C at a heating rate of 10°C/min. All samples were prepared at same time and kept at room temperature for one month, by which all samples underwent some thermal history. In chapter 6 and 7, non-isothermal crystallisation and isothermal crystallisation of MWCNT-OH/PCL and GONP/PCL composites were performed using a TA Instrument DSC 2920 calorimeter. For the non-isothermal crystallization, the samples were melted at 80°C for 5min to ensure the complete removal of pre-existing crystals. Afterward, the melted samples were cooled to -20°C at a rate of 10°C/min and heated to 80°C at a rate of 10°C/min again. For the isothermal crystallization, the samples were melted at 80°C for 5min and quenched to the certain temperature for a period of time when the isothermal crystallisation was completed. The non-variation of heat flow signal was used to judge the completion of the isothermal crystallization. In chapter 7, DSC analysis of the GONP/PU composites was conducted on a TA Instrument 2920 modulated differential scanning calorimeter with a heating rate of 4 °C/min. The amplitude and period of oscillation was 1°C and 60s, respectively.

3.3.6 Dynamic mechanical analysis (DMA)

DMA is a useful technique to characterise the viscoelastic property of polymers [155]. As an oscillating force is applied to a sample, the resulting displacement of the sample is measured. By measuring the deformation of the sample under the external force, the modulus of the sample (stiffness) can be determined. Besides, damping property of the sample can be measured according to the time lag in the displacement in comparison with the external force. The damping property reflects the viscous property (internal friction) of the solid sample. In chapter 7, DMA was performed on a TA Dynamic Mechanical Thermal Analyzer Q800. The GONP/PU composites were scanned from -100°C to 50°C at a heating rate of 3°C/min. The amplitude and frequency of dynamic oscillatory loading was 100µm and 10 Hz, respectively.
3.3.7 Optical microscopy (OM) and polarised optical microscopy (POM)

OM is a type of microscopy that magnifies the image of a sample using visible light and a system of lenses. POM is a type of optical microscope which can magnify the images of polymer crystallites using polarised light and a system of lenses. In POM, polarised light is created using a Polaroid filter that is capable of allowing one-plane vibration of an electromagnetic wave go to polymer crystallites. Spherulites are the basic morphology for most polymer crystallites formed from polymer melts or solutions. After the formation of nucleus, the growth of polymer crystallites prefers to occur in one direction conventionally called b-axis. The growth in other two axes (c- and a- axes) presents the same speed. The c- and a- axes can be free to rotate provided that they are orthogonal to the b-axis. According to this growth way, polymer crystallites grow in helical strands radiating from the nucleus, allowing the formation of the spherulites. Polymer crystallites are highly anisotropic in electron density because they have strong

![Image](image_url)

**Figure 3.1** Ringed poly-3-hydroxy butyrate spherulites (Micrographe NO. 601, Micrograph Library, DoITPoMS, Department of Materials Science and Metallurgy, University of Cambridge)
covalent bonds along the macromolecular chain axes, whereas laterally Van der Waals or hydrogen bonds drive the cohesion of the crystallites. This anisotropy leads to the birefringence of spherulites. This is why the POM image of spherulites presents a cross-like extinction classically named "Maltese Cross" as spherulites are observed between crossed polarisers. Figure 3.1 specifically reveals another type of spherulites with periodic extinction pattern (radial banding), which are called "ringed (or banded) spherulites". The periodic extinction of ringed spherulites is commonly considered to be resulted from lamellar twisting along the radial direction during crystal growth, which takes place when the direction of rotative optic axis (molecular chains) are parallel to the polarised axes.

In chapter 4, the PU and the MWCNT (5wt%)/PU dispersion was diluted to a concentration of 3wt% and dropped on the polished glass substrate, respectively. After drying at 30°C for one week, both of them were observed using a Leica DMLM OM equipped with a Leica DFC350FX digital camera. Images were taken in both transmitted and reflected modes. In chapter 5, POM observation of the spherulites was conducted in a Leica DMLM OM equipped with a Leica DFC350FX digital camera. The MWCNT/PCL-based PU dispersions were dropped on polished glass substrates and kept at room temperature for one month before observation. In chapter 6 and 7, POM observation of the crystals grown during the isothermal crystallisation was conducted by Leica DMLM OM equipped with a Leica DFC350FX digital camera and hot stage. The hot stage was used for the control of the thermal treatments.

3.3.8 X-Ray photoelectron spectroscopy (XPS)

XPS is a spectroscopic technique that can quantitatively measure the elemental composition of the surface within a depth of 1-10nm, empirical formula of a pure material, chemical and electronic state of the element in the surface. As a sample is irradiated with a beam of X-rays, the kinetic energy (E_K) and number of electrons
Experimental

Excaping from the top 1 to 10nm of the material will be experimentally measured. The binding energy of the electron \( E_B \) is specifically used to identify the electron, which is with relation to its parent element and atomic energy level. The \( E_B \) of the emitted electrons can be determined by the equation as follows [156]:

\[
E_B = E_{\text{photon}} - E_K - W
\]

where \( E_{\text{photon}} \) is the photon energy and \( W \) is the spectrometer work function.

In chapter 7, XPS analysis of EG and GO powders was performed on a VG ESCALAB 5 (VG Scientific Ltd., England) under \( 10^{-7} \) Torr vacuum with a AlK\( \alpha \) X-Ray source using power of 200 W.

3.3.9 Wide angle X-ray diffraction (WXRD)

X-rays are electromagnetic radiation with short wavelength in range of \( 10^{-6} \) to \( 10^{-10} \) cm. When X-ray photons interact with electrons in atoms, some photons from the radiation will be deflected away from their original track. If x-ray photons do not lose any energy, the process is called elastic scattering. If some energy of X-ray photons is transferred into the electrons, these scattered x-ray photons will have different wavelength from original photons. Interference can take place among deflected waves and result in the distribution of intensity. When electromagnetic radiation interacts with the atoms arranged in a periodic structure (crystals), diffraction will take place and result in sharp interference peaks in diffraction patterns. The crystal structures of materials can be determined by measuring the diffraction patterns. According to Bragg equation, the distance between crystal planes relates to the angles of incoming X-ray beams [157]. The diffraction can be observed at some specific angles in a XRD spectrum, which provides the information of the crystalline structure in the material.

In chapter 7, XRD analysis was performed using a Philip-X' Pert X-ray
3.3.10 Measurement of the viscosity of the MWCNT/PU dispersions

The viscosity of the MWCNT/PU dispersions was measured by a Haake VT500 rheometer equipped with a Haake K20 circulator at 20°C. The shear rate varied from 27.05 s⁻¹ to 2702 s⁻¹.

3.3.11 Measurement of the electrical conductivity using a two-probe method

The electrical conductivity was measured by a digital four-point probe multimeter at room temperature. The contact resistance between electrodes and samples was eliminated by silver coating on the surface of the samples.

3.3.12 Measurement of the thermal conductivity using a DSC method

Thermal conductivity was determined by a differential scanning calorimetry (DSC) method [158]. The measurement was conducted on a TA Instrument 2920 DSC calorimeter. Five samples were tested for each composite to obtain an average value. Figure 3.1 shows the typical setup of thermal conductivity measurement. The details of measurement are described as followed: pure gallium with melting temperature 29.8 °C was used. The cylindrical sample with a height of ~1mm was punched from the PU composites, and its circular end surfaces were coated with heat transfer oil. The cylindrical sample was placed in the middle of DSC sensor and an uncovered aluminum crucible containing gallium (about 80 mg). An empty aluminum crucible without a lid was used as the reference. The gallium was heated from -20°C to 35°C with the heating rate of 10 °C /min to obtain a melting curve. As mentioned in the mechanism of heat conduction, the relationship between the rate of heat flow (Φ) and thermal conductivity (λ) can be defined by the equation:
\[
\varphi = \lambda A \frac{\Delta T}{h} \quad (4)
\]

For a cylindrical sample with a diameter of D, the cross-sectional area, A, is equal to \(\pi D^2/4\), and h is the height of a material body. The thermal resistance, \(R_s\), relates to the material-dependent thermal conductivity and the geometry of the body:

\[
R_s = \frac{h}{\lambda} A \quad (5).
\]

Considering the thermal resistance \((R_T)\) at the sensor-sample and sample-crucible interface, the equation \((4)\) can be rewritten as

\[
\Phi = \frac{T_s - T_m}{R_s + R_r} \quad (6)
\]

**Figure 3.2** Schematic diagram of the sample arrangement on the DSC sensor. h is the height of the sample cylinder; \(\Phi\) is the heat flow that flows from the sensor into the sample; \(T_m\) is the temperature of the metal melt, \(T_s\) is sensor temperature under sample; \(T_r\) is the temperature of the reference sample. The reference crucible is empty without a lid. A crucible containing the pure metal is placed on the top of the sample. The spaces between the crucible-sample and sample-sensor interfaces are filled with heat transfer oil (straight line).
In this measurement, $R_T$ can be neglected because heat transfer oil is used to fill the interfacial spaces. Therefore, $\lambda$ can be determined by the single melting curve of the gallium according to the equation (4). $\Delta T$ is the difference between the temperature $T_s$ at a time $t$ and the onset temperature of melting $T_{onset}$. The corresponding heat flow $\Phi$ is the difference between the heat flow at the same time $t$ and the heat flow at $T_{onset}$. Referring $\frac{\Phi}{\Delta T} = \frac{\Phi_t - \Phi_{onset}}{T_t - T_{onset}}$ that is regarded as the slope of the linear side of the melting curve, the value of $\lambda$ is finally obtained.

3.3.13 Tensile testing

Tensile stress-strain testing is a typical method to determine the mechanical properties of solid polymeric materials [159]. As the sample is subjected to the deformation at a constant extension rate, the tensile force is measured as a function of deformation. The specimen was cut into a dumb-bell shape by a die punch cutter with following dimensions: overall length: 75mm, width of ends: 12.5mm, length of narrow portion: 25mm, width of narrow portion: 3.8mm.

In this project, tensile tests were carried out using a Hounsfield test machine. Five specimens were tested to obtain average values. The extension rate was 50 mm/min for the MWCNT-OH/PCL and GONP/PCL composites, and was 500 mm/min for the GONP/PU composites

3.3.14 Nanoindentation

Nanoindentation is a technique to measure the mechanical properties of materials at smaller length and load scales than other testing method. This testing method uses a rigid indenter, typically with diamond or diamond-coated tips, to apply external force to the materials [160]. The typical result of nanoindentation experiment is a curve reflecting the quantitative relationship of external force versus displacement, which can determine the elastic modulus and hardness of the materials [161].
Nanoindentation experiments were performed using a Nano Test™ (Micro Materials, UK) equipped with a Berkovich (three sided pyramidal) diamond indenter tip at room temperature. The maximum load and initial load placed on the indenter tip was 2.5mN and 0.15mN, respectively. The loading and unloading rate of indenting was 0.05mN/s. The holding time at maximum load was 180s. Nano-scratch test was conducted using a Nano Test™ (MicroMaterial, UK) equipped with Rockwell indenter tip at room temperature. The scratch load and length was 0.05mN/s and 100μm, respectively. Two scratch rates used were 3μm/s and 5μm/s. The square shaped samples with a thickness of ~1mm were used both for nanoindentation and nano-scratch tests.
Chapter 4 Preparation and characterisation of semi-conductive carbon nanotube/polymer composites with low percolation threshold

4.1 Introduction

Carbon nanotubes (CNTs) have been considered as an ideal nanofillers to fabricate the semi-conductive polymer composites due to their highly intrinsic electrical conductivity and high aspect ratio [162]. The electrical conductivity of polymer composites simply relies on the conductive pathway formed by a sufficient amount of conductive nanofillers in polymer matrix. Percolation threshold is usually used to mathematically describe the critical insulator-to-conductive transitions in the composites. The high incorporation of the nanofillers significantly affects the mechanical properties of polymers, specifically toughness and ductility, and also increases the cost of composite products. Therefore, how to achieve minimum percolation threshold is a core challenge in this research field. Recently, the cellular structure of CNTs in polymer matrix has been considered as an ideal microstructure to achieve the lowest percolation threshold. The core idea in designing so-called cellular structure is to limit the free space for the location of CNTs in polymer matrix. Polymer latex is considered as a natural host to form the cellular structure because the boundary area between the latex particles is the only place for the settlement of CNTs. A colloidal physics method is designed for polymer latex to accommodate CNTs [6][7]. However, the choice of polymer latex or emulsion is limited. Long-time drying is another weakness of this method. Very recently, the cellular structure of CNTs has been uniquely designed based on polymer pellets [100]. The core issue in this technology is how to coat CNTs onto the surface of the pellets. Under static compression moulding, CNTs are locked in the boundary area among the pellets to form the cellular structure of CNTs can be formed through the boundary area among the pellets.

PU dispersions are well-known latex products, which have been widely used in many industrial fields such as adhesives and coatings [148]. PU is a typical
Chapter 4 Preparation and characterisation of semi-conductive carbon nanotube/polymer composites with low percolation threshold

segmented polymer containing alternative soft segments (polyol) and hard segments (isocyanate). The hydrophilic segments chemically incorporated into PU chains allow the stabilization of PU latex in water [148]. The PU dispersions are very versatile latex products with demanding properties due to the flexible choice of soft and hard segments. In this chapter, we explored the application of the colloidal physics method in the PU dispersions and understood the effect of CNTs on the rheological behaviour, film formation and electrical conductivity. As another aspect of this chapter, we developed a novel technology to coat CNTs onto the surface of polymer powders. We believe, with this coating technology, the "cellular structure" idea can be extended from polymer latex and emulsions to most general polymers such as PP, PE, PVC, PA, and etc.

4.2 Results and discussion (Part A): MWCNT/PU composites

4.2.1 FTIR characterisation of PPG and it derivated PU

![Figure 4.1 FTIR spectra of PPG (a) and its derivated polyurethane before neutralization (b)](image)

Figure 4.1 FTIR spectra of PPG (a) and its derivated polyurethane before neutralization (b)
Figure 4.1 illustrates FTIR spectra of PPG (a) and its derivated PU (b) before neutralization. No peak shown around 2270 cm\(^{-1}\) proves that residual NCO reached the desired value before neutralisation (NCO/OH=0.96). Besides, several PU characteristic peaks can also be seen in FTIR spectra (a). Peaks located at 3310 cm\(^{-1}\) and 1600 cm\(^{-1}\) are attributed to stretching and bending vibration of \(-\text{NH}\) group, respectively. Peak of \(-\text{C}=\text{O}\) group was observed to be split distinctly into 1730 cm\(^{-1}\) for hydrogen bonded \(-\text{C}=\text{O}\) and 1703 cm\(^{-1}\) for free \(-\text{C}=\text{O}\). Stretching vibration of \(-\text{CH}\) group (2962-2853 cm\(^{-1}\)) and C-O-C group (1100 cm\(^{-1}\)) can be observed in FTIR spectra of PPG and the water-based PU.

### 4.2.2 Dispersion of MWCNTs in water and PU composites

CNTs tend to aggregate due to strong inter-tube Van de Waals interaction. In the colloidal physics method, the first step is to exfoliate the MWCNTs in water with the assistance of an anionic surfactant, sodium dodecyl sulphate (C\(_{12}\)H\(_{25}\)SO\(_4\)Na), and ultrasonication technique. This systematical study has been previously

Figure 4.2 TEM images of the MWCNTs individually dispersed in water
Figure 4.3 Mechanism of nanotube isolation from the bundle obtained by ultrasonication and stabilization [164]

performed to find out suitable conditions for the exfoliation such as sonication energy, sonication time, CNT concentration and the ratio of CNT to the surfactant. A mature procedure given in reference [6] was selected in our experiments. The TEM images shown in Figure 4.2 confirm the good dispersion of the MWCNTs in water. Strano et al [164] proposed an "unzipping" mechanism to explain the individualisation of CNTs from nanotube bundles with combined assistance of ultrasonication and surfactant adsorption. As shown in Figure 4.3, ultrasonication provides high local shear, particularly to the end of nanotube bundles, allowing the

Figure 4.4 Schematic representations of the mechanism by which surfactants help to disperse SWCNT. (a) SWCNT encapsulated in a cylindrical surfactant micelle (both cross section and side view); (b) hemimicellar adsorption of surfactant molecules and a SWCNT; (c) random adsorption of surfactant molecules on a SWCNT [165]
formation of gaps at the bundle ends. Then, surfactant adsorption results in the propagation of these gaps, and ultimately in the separation of individual CNTs from the bundles. In terms of mechanism of surfactant adsorption, three models have been proposed including [165]: (1) the formation of SDS cylindrical micells around a SWCNT (Figure 4.4a), (2) the formation of helices, double helices or hemimicells on the surface of a SWCNT (Figure 4.4b), and (3) the random adsorption of SDS molecules with no preferential arrangement on the surface of a SWCNT (Figure 4.4c). It is well-known that SDS contains a hydrophilic \( \text{SO}_4^\text{-Na}^+ \) head and a hydrophobic \( \text{C}_{12}\text{H}_{25}^- \) tail in its chemical structure. As the hydrophobic tail strongly interacts with CNTs, the hydrophilic head left in water generates strong electrostatic repulsion among CNTs. In combination with steric hindrance, the colloidal stability of aqueous CNT dispersion can be maintained for several months. After fully exfoliating the nanotubes in water, the incorporation of the nanotube into PU latex was performed by simply mixing the aqueous CNT dispersion and PU latex. SEM images in Figure 4.5 show the dispersion of the nanotubes in the solid MWCNT(3wt%)/PU composite. It is indicated that the colloidal physics method can yield good dispersion of the nanotubes in polymer matrix. In the high resolution SEM images (Figure 4.5(b and c)), some nanotube bundles can be obviously observed. Although the nanotubes could be fully exfoliated in water, it seems the bundles cannot be completely avoided after the solidification of the MWCNT/PU dispersions.

### 4.2.3 Film formation of MWCNT/PU dispersions

Film formation is the process that achieves a continuous and homogenous film from polymer latex under appropriate conditions, which is very important for commercial application of latex products. Generally, the film formation process of polymer latexes is divided into three stages: evaporation and particles ordering (stage 1), latex particle deformation (stage 2) and polymer chain diffusion across
Figure 4.5 SEM images of the MWCNT(3wt%)/PU composites (fracture surface)
latex boundaries (stage 3) [166]. It is believed that incorporation of CNTs would inhibit polymer chain diffusion across the particle boundaries. PU dispersions were reported to hold low minimum film formation temperature that is close to the glass transmission temperature (below 0°C) [167][168]. The selected film formation temperature (30°C) was enough for formation of a continuous and homogenous film observed visually. Interestingly, Regev et al [6] found that addition of 0.5wt % salt (NaCl) (based on total mass of solution) to SWCNTs-latex solution can reduce electrostatic repulsion between latex particles and CNTs, and led to well-dispersed SWCNTs-latex solution. After freeze-drying SWNTs-latex solution at -80°C over night, film formation was conducted by compression moulding at 170°C between poly(ethylene terephthalate) sheets. However, it has not been reported whether the addition of NaCl can influence the film formation of polymer latexes. Figure 4.6 shows digital images for the dried

Figure 4.6 Photographs for the MWCNT/PU composites. The size of all samples is 3.5cm×3.5cm (a) 0 wt% of MWCNTs, (b) 2 wt%, (c) 0 wt% with 0.5 wt% NaCl, and (d) 2 wt% with 0.5 wt% NaCl
films of the PU dispersion, MWCNT (2wt%)/PU, and MWCNT (2wt%)/PU with 0.5wt% NaCl (based on the total solution). It can be seen that the addition of NaCl caused cracking in the PU films with and without MWCNTs. NaCl can form solid crystals and precipitate from saturated salt solution. These solid crystals could interrupt the mutual diffusion of macromolecular chains of particles. Stress resulting from capillary force, polymer/air interfacial tension and polymer/water interfacial tension produced in the stage of the deformation of latex particles could be concentrated on the solid crystals, which could cause the damage of the film. It was found that some small cracks also existed in the films even though the loading of NaCl was lower than 0.15wt%. These results indicate that introducing NaCl cannot be considered as a practical method, at least, in anionic PU-SDS-MWCNT systems.

4.2.4 Rheological behaviour of MWCNT/PU dispersions

Rheological behaviour is thought to be correlated with practical applications of polymer latexes in coatings, inks and adhesives. Although CNT/polymer-latex composites have been reported, the effect of CNTs on the rheological behaviour of polymer latexes has been hardly studied. Here, a Haake VT500 viscometer was used to determine the effect of the addition of MWCNTs on the viscosity of the MWCNT/PU colloidal system. Figure 4.7 shows the viscosity of the MWCNT/PU dispersions with different MWCNT contents plotted against shear rate. The rheological curves show that the MWCNT/PU dispersions exhibit shear thinning behaviour. From Figure 4.7, it can be seen that, at low shear rates, the viscosity of the MWCNT/PU dispersions shows a noticeable enhancement with increased loading with MWCNTs. The rheological behaviour of the PU dispersions is slightly affected by the MWCNTs at high shear rates. In the MWCNT/PU dispersions, the interactions between MWCNTs wrapped by SDS and PU particles can result in the increase in viscosity of the PU dispersion. The orientation and mobility of the particles can be restricted by the MWCNTs. With increasing shear
stress, these interactions can be gradually broken and the movement of these particles becomes easy. Therefore MWCNT/water-based-PU dispersions displayed a gradual decrease in viscosity and exhibited shear thinning behaviour. All of the data in Figure 4.7 can be fitted to the Herschel-Bulkley equation [169]. The model equation is described in the equation:

\[
\eta = \lambda_0 / \gamma + K \gamma^{n-1}
\]  

(7)

where \( \gamma \) is the shear rate (s\(^{-1}\)), \( K \) and \( \lambda_0 \) are constants, and \( n \) is the flow behaviour index. It is known that the type of fluids, which is determined by \( n \), consist of Newtonian fluids (\( n = 1 \)), pseudoplastic (shear-thinning) fluids (\( n < 1 \)), shear-thickening fluids (\( n > 1 \)). The fitting results of the flow behaviour index are shown in Figure 4.8, and reveals that the \( n \) value decreases with increased loading of MWCNTs, indicating the shear thinning behaviour of MWCNT/PU dispersions
turns out to be stronger in comparison with the PU dispersion.

Figure 4.8 Flow behaviour index (n) of MWCNT/PU dispersions at 20°C

4.2.5 Electrical property of MWCNT/PU composites

Percolation theory has usually been used to explain the improvement in electrical conductivity of the CNT/polymer composites [7]. According to percolation theory, the conductive pathway formed by conductive fillers in the composites favours insulator-to-conductive transitions in the composites and the critical concentration of the fillers is called the percolation threshold. In the colloidal physics method, Grossiord et al [163] assumed a better dispersion of CNTs might be achieved with the help of a surfactant, which generally is regarded as the key factor to maximize the functionality of CNTs in composites. Furthermore, Grunlan et al [7] gave another explanation. When preparing CNT-filled polymers by a solution or melt blending method, CNTs will be locked individually and randomly in the polymer matrix. Since spherical particles are exclusive for CNTs in polymer latexes, it can
be thought that the CNTs have to be pushed into the interstitial spaces between particles during film formation, which leads to decrease in the percolation threshold. Figure 4.9 shows the electrical conductivity of the CNT/PU composites plotted against the MWCNT content. At 0.5 wt% loading of MWCNTs, the electrical conductivity is improved by 3 orders of magnitude in comparison with pure PU. It was also found that the electrical conductivity did not show a significant increase when the MWCNT content increased from 0.5 wt% to 7 wt%. The percolation threshold in this system is below 0.5wt%, which indicates that the colloidal physics method is very flexible and works very well with PU latex. However, it is clear that the maximum conductivity of the composites is 2 to 4 orders of magnitude lower than that of either conducting CNTs or semi-conducting CNTs. According to the classical percolation theory, the relationship between conductivity and volume fraction of filler is quantitatively described by the classical percolation power law [8]:

$$\sigma = \sigma_0 (p - p_c)^\delta$$  (8)
where $\sigma$ is the conductivity of composites, $\sigma_0$ is a scaling factor related to the intrinsic conductivity of the filler, $s$ is the power law exponent, $p$ is the concentration of filler in the polymer matrix and $p_c$ is the value of the percolation threshold. Origin software was used to fit our experimental data into the equation. The fitting results are shown in Figure 4.10. The fitting results show that $\sigma_0$ is around $1.1 \times 10^{-4}$ S/m, which is significantly lower than the intrinsic conductivity of single nanotubes. It seems that the electrical capacity of CNTs cannot be fully transferred in polymer composites. The conductance of polymer composites is given by the conductive pathway formed by CNTs in the polymer matrix. In fact, the electrical conductivity of the pathway cannot compare to the single nanotube. The pathway contains a number of CNT junctions. The structure of CNT junctions is illustrated in Figure 4.11, which should be CNT-polymer-CNT junctions as CNTs are coated with polymers. SEM image in Figure 4.5(c) shows that

![Figure 4.10](image-url)  

Figure 4.10 Fitting of the experimental data (the electrical conductivity) into the classical percolation power law (dotted line). The parameters of the classical percolation power law are revealed inside the graph.
Figure 4.11 General illustration of the microstructure of a CNT/polymer composite. Thick straight line represents the CNTs and the thin random line represents the polymer chains. Highlighted places in the circles represent typical CNT-polymer-CNT junctions in the composite.

The surface of the nanotubes is not smooth and has been wrapped with the PU. As the polymer exists in the intermediate space between two tubes, the transfer of electron through the CNT junctions is very complicated. We simply considered that the polymer in the intermediate space could prevent the transfer of electrons from one nanotube to another. So the conductance of the pathway totally depends on the conductance of the CNT-polymer-CNT (C-P-C) junctions. Theoretical study [170] revealed that the conductance of the C-P-C junctions was relative to the thickness of the polymer in the intermediate space. e.g. as the thickness of the polymer was less than 0.6nm, the effect of the polymers on the transfer of electron across the C-P-C junctions could be ignored. As the thickness of the polymer was around 8nm, the conductance of the C-P-C junctions dropped to 1% of the conductance of single nanotube. This phenomenon is called “tunnelling behaviour”, which means the transfer of electron depends on the void space between nanotubes. In polymer composites, “tunnelling behaviour” is impossible to eliminate. This is why it is common to see the maximum conductivity is almost 2-4 orders of magnitude lower than intrinsic conductivity of pure CNTs.
The visualisation of the conductive pathway is performed using microscopy. The conductive pathways of bundled MWCNTs formed in PU matrix can be observed using optical microscopy and the results are shown in Figure 4.12. Although it is

![Figure 4.12](image_url)

**Figure 4.12** Optical microscopy images of the MWCNT/PU dispersions. (a) is the transmitted image of the PU dispersion, and (c) and (e) are its reflected images, focusing on particle and non-particle zones, respectively. (b) is the transmitted image of the PU dispersion with 5wt% MWCNTs, and (d) and (f) are its reflected images focused on particle and non-particle zones, respectively. (40µm ——— )
hard to image a clear picture for a single MWCNT, optical microscopy (OM) has the advantage in observing a large area that can provide the true face of the conductive pathway of CNTs in polymer latexes. Compared to the images of PU particles (a, c and e in Figure 4.12), the images (b, d and f in Figure 4.12) show that the hair-like, dark lines should be the bundled MWCNTs that are located at the side and the top of PU particles, respectively. In this case, the conductive pathway of the MWCNTs could be formed in parallel and orthogonal directions after complete coalescence of the particles. The nanotubes are not uniformly located in each boundary between two single PU particles. In fact, it is very difficult for the nanotubes to enter into the boundary area between two single PU particles due to strong electrostatic repulsion between both negative charged PU particles and nanotubes. As PU particles get close each others with the gradual evaporation of water, the electrostatic repulsion will be stronger and stronger to drive the nanotube out of the boundary to be together. It can help us have better understanding how the free space is tightened for the settlement of CNTs in polymer latex, which subsequently results in low percolation threshold.

4.3 Results and discussion (Part B): MWCNT-OH/UHMWPE composites

4.3.1 Characterisation of MWCNTs and MWCNTs-OH

In this chapter, two types of CNTs including pristine MWCNTs and functionalised MWCNTs with 3-5wt% hydroxyl groups were used. As FTIR spectra of MWCNTs and MWCNTs-OH are shown in Figure 4.13, the typical peak of hydroxyl groups around 3400 cm\(^{-1}\) can be seen in line b, but it also can be unexpectedly seen in the line a, which is due to the existing trace of water in KBr that is hard to remove completely. This introduces a small problem to identify the hydroxyl groups on the MWCNTs. The peak of hydroxyl group calculated by Original software was normalized by -CH peak at 2853 cm\(^{-1}\) and 2953 cm\(^{-1}\). The calculated result revealed stronger -OH absorption occurred in the MWCNT-OH/KBr sample in comparison with MWCNTs/KBr sample. In other
words, OH group was proven to be introduced to MWCNTs after chemical modification. In order to further clarify this conclusion, Raman was used to characterise the MWCNTs and MWCNTs-OH. Raman spectroscopy is an effective tool to characterise structure of CNTs. Many reports have aimed at the characteristic peaks of CNTs in their Raman spectra. The disorder mode (D-band) peaking around 1325 cm$^{-1}$, resulted from sp$^3$-hybridised carbon in the framework of CNTs and amorphous carbon, is related to impurities and defect on CNTs. The tangential graphite mode (G-band) at 1574 cm$^{-1}$ is another feature of CNTs in Raman spectra, corresponding to the crystalline graphitic structure [171]. Figure 4.14 demonstrates the Raman spectra of MWCNTs (line a) and MWCNTs-OH (line b). Compared to MWCNTs, D band of MWCNT-OH is upshifted to 1323 cm$^{-1}$ and its G band of MWCNTs-OH is downshifted to 1566 cm$^{-1}$. Due to D-band and G-band reflects disorder-induced mode and in-plane graphite structure, ratio of D-band intensity to G-band intensity (D/G) is a common parameter to characterise the defecting degree of CNTs. The D/G of MWCNTs was 1.3 that was less than D/G of MWCNT-OH (1.6). MWCNTs-OH exhibited more defect in
Chapter 4 Preparation and characterisation of semi-conductive carbon nanotube/polymer composites with low percolation threshold

the side wall after chemical modification. In the range of high frequency, there is a peak around 2640 cm\(^{-1}\) which is assigned to G-band. Shift of G-band was another evidence to confirm some damage occurring in graphite structure of CNTs.

![Raman spectra of MWNTs and MWNTs-OH](image)

**Figure 4.14** Raman spectra of MWNTs and MWNTs-OH

### 4.3.2 Dispersion of MWCNTs-OH in DMF and UHMWPE particles

In this coating process, functionalised nanotubes (MWCNTs-OH) firstly were dispersed in a polarised organic solvent (DMF) with the assistance of ultrasonication. The TEM images in **Figure 4.15** show the exfoliated nanotubes in DMF. In comparison with the TEM image of pure MWCNTs, some defects (black dots) can be seen on the surface of the functionalised nanotubes, which could be attributed to the existence of the hydroxyl groups. The contribution of the hydroxyl groups to the stability of the MWCNT-OH/DMF dispersion is from two aspects: (1) the hydroxyl groups could sterically hinder the aggregation of the nanotubes in DMF after ultrasonication; and (2) the hydroxyl groups could reduce the surface energy of the nanotubes and enhance the compatibility between the nanotubes and DMF. This aspect can be explained according to thermodynamic
theory: \[ \Delta G = \Delta H - T \Delta S, \] where \( \Delta G \) is the change in Gibbs free energy, \( \Delta H \) is the change in enthalpy, \( T \) is the temperature in degrees Kelvin, and \( \Delta S \) is the change in entropy. If \( \Delta G \) is negative, the mixing of two components will take place spontaneously. \( \Delta S \) is always positive, since system tends to go from ordered to less ordered states. Therefore, \( \Delta H \) should be close to zero for the spontaneous occurrence of mixing two components. According to the literature [172], \( \Delta H_{\text{mix}} \) is approximately proportional to \( V_{\text{mix}} (\delta_{\text{C}} - \delta_{\text{sol}})^2 \varphi \), where \( \delta = \sqrt{E_{\text{SURF}}} \) is the square root of the component surface energy, \( V_{\text{mix}} \) is the volume of the mixture and \( \varphi \) is the nanotube volume fraction. The surface energy is defined as the energy per unit area required to overcome the van der Waals forces when exfoliating nanotube bundles. The surface energy of CNTs and DMF has been reported as \(-70-80\text{mJ/m}^2\) and \(40-50\text{mJ/m}^2\), respectively [172]. As the exfoliation of CNTs in DMF expects a minimal value of \( \Delta H_{\text{mix}} \), surface functionalisation is an effective approach to reduce the surface energy of CNTs to match that of CNTs.

Figure 4.15 TEM images of exfoliated MWCNTs-OH in DMF

Macroscopically, the digital picture in Figure 4.16 shows the dispersion of MWCNTs (left) and MWCNTs-OH (middle) in DMF. The picture was taken after
shaking the glass bottles. Some big black aggregates are observed on the inner wall of the glass bottle containing the MWCNT/DMF dispersion, indicating unsatisfied dispersion of MWCNTs in DMF. The wall of the glass bottle containing the MWCNT-OH/DMF dispersion is still transparent, indicating good

Figure 4.16 The Digital picture of the MWCNT/DMF dispersion (left), the MWCNT-OH/DMF dispersion (middle) and residual DMF after coating (right)

Figure 4.17 The Digital picture of pure UHMWPE powders (left), 0.1wt%MWCNT-OH/UHMWPE powders (middle) and 1wt%MWCNT-OH/UHMWPE powders (right).
Figure 4.18 SEM images of the UHMWPE powders (a and b) and MWCNT-OH (1 wt%)/UHMWPE composite powders (c and d). The images (a and c) are taken under low voltage, and SEM images (b and d) are taken under high voltage.

dispersion of MWCNTs-OH in DMF. After the good dispersion of the MWCNTs-OH in DMF is confirmed, the UHMWPE particles are added into the dispersion and stirred at a certain temperature to ensure the homogenous and strong coating of the MWCNTs-OH on the surface of the UHMWPE particles. The glass bottle (right) in Figure 4.16 contains residual DMF after the MWCNTs-OH are coated on the surface of UHMWPE particles. The appearance of residual DMF turns to be yellow, which indicates most of the MWCNTs-OH have been pulled out from DMF. Figure 4.17 shows the appearance of UHMWPE
powders before and after coating. Pure UHMWPE powders is white, the
UHMWPE powders coated with 0.1 wt% MWCNTs-OH is grey, and the
UHMWPE powders coated with 1 wt% MWCNTs-OH turns to dark finally.

SEM was further used to observe the surface of the UHMWPE powders before
and after coating. The SEM image in Figure 4.18(a) shows the size of the
UHMWPE powders is around 60 µm. The high resolution SEM image in Figure
4.18(b) shows their neat surface. In comparison with that of the UHMWPE
powders, the SEM image in Figure 4.18(c) shows the MWCNTs have been
adsorbed on the surface of the UHMWPE. The high resolution SEM image in
Figure 4.18(d) shows more clear observation of the nanotubes with strong
bonding with the surface of the UHMWPE powders.

4.3.3 Electrical conductivity of MWCNT-OH/UHMWPE composites

The powdery samples are processed to polymer films with a thickness of 1 mm
using hot compression for electrical testing. Like the colloidal physics method, the
nanotubes will be located in the boundary area among polymer particles after film
formation. In the both methods, the core idea of lowering the percolation threshold
is to reduce the free space for the settlement of the nanotubes in polymer matrix.
The different issue is the nanotubes are locked into the surface of polymer
particles before film formation in the coating method, but the nanotubes are
mobile in polymer latex and locked into the boundary area after film formation.
Table 4.1 shows the electrical conductivity of the MWCNT-OH/UHMWPE
composites. Two grades of UHMWPE powders with different sizes (60 µm and
100 µm) were used as the host. It can be seen that the percolation threshold for the
powders with the size of 60 µm is around 1 wt% and the percolation threshold for
the powders with the size of 100 µm is around 0.5 wt%. The smaller particle size
leads to higher percolation threshold. This relationship could be estimated by a
simple geometrical calculation. It is assumed that the polymer particle with a
radius of R is fully coated with a layer of the nanotubes and the thickness of the
Chapter 4 Preparation and characterisation of semi-conductive carbon nanotube/polymer composites with low percolation threshold

A nanotube layer is assumed to be $\Delta R$, as shown in Figure 4.19. Consider a polymer particle, percolation threshold $\approx \Delta V/V = 4\pi R^2 \Delta R / 4\pi R^3 = 3\Delta R / R$, where $\Delta V$ is the volume of coated nanotube layer and $V$ is the volume of a polymer particle. Therefore, as the $R$ is bigger, the percolation threshold is lower.

Table 4.1 Electrical conductivities of the MWCNT-OH/HMWPE composites

<table>
<thead>
<tr>
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<th>0wt%</th>
<th>0.1wt%</th>
<th>0.5wt%</th>
<th>1wt%</th>
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<tbody>
<tr>
<td>HMWPE-a</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$2.1\times10^{-3}$S/m</td>
</tr>
<tr>
<td>HMWPE-b</td>
<td>-</td>
<td>-</td>
<td>$1.3\times10^{-3}$S/m</td>
<td>$3.2\times10^{-3}$S/m</td>
</tr>
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</table>

Note: the particle size of HMWPE-a and HMWPE-b is 60μm and 100μm, respectively.

Figure 4.19 Scheme of the UHMWPE powders fully coated with the nanotubes. The white circle represents the UHMWPE particle and the dark area represents the nanotubes coating on the surface of the particle. $R$ is the radius of the particle and $\Delta R$ is the thickness of the nanotube coating.
4.4 Conclusions

In this chapter, the colloidal physics and coating method were applied to fabricate semi-conductive CNT/polymer composites with low percolation threshold. Polymer latex and powdery polymers were used as hosting matrix for the colloidal physic and coating method, respectively. The core idea of these two methods is to engineer a unique micro structure in which the settlement of CNTs in polymer matrix is limited to boundary area since particulate hosts are exclusive for CNTs. In this unique micro structure, very small amount of CNTs is needed to form the conductive pathway, which means a low percolation threshold.

In the first part of this chapter, we mainly investigated the MWCNT/PU composites prepared by the colloidal physics method. The MWCNTs were exfoliated in water with the assistance of surfactant and ultrasound. The solid composites were obtained via drying the colloidal mixture of the MWCNTs and PU latex at room temperature. The percolation threshold was found to be around 0.5wt% and the electrical conductivity of the composites was improved by more than 4 orders of magnitude with the addition of 1 wt % MWCNTs. The polymer existing in the intermediate space between two nanotubes (C-P-C junctions) could be the reason that the maximal electrical conductivity of the composites could not reach the electrical conductivity of pure CNT network. The addition of NaCl that was considered to reduce electrostatic repulsion existing in solution of anionic PU-SDS-MWCNTs resulted in the cracking of the PU films. The study of rheological behaviour revealed that the addition of CNTs led to the increase in the viscosity of the PU dispersion.

In the second part of this chapter, a novel coating technology to cover the UHMWPE powders with the MWCNTs-OH was invented. The functionalised MWCNTs could be fully exfoliated in DMF with the assistance of functional groups and ultrasound. The visual evidences from SEM images confirmed the nanotubes were adhered to the surface of the powders very well. After film
formation using the compression moulding, the nanotubes were locked into the boundary area to form the conductive pathway with a low percolation threshold. The electrical testing showed that percolation threshold for the powders with the size of 60\(\mu\)m was around 1wt\% and the percolation threshold for the powders with the size of 100\(\mu\)m was around 0.5wt\%. Overall, the smaller particle size led to higher percolation threshold. Different from the colloidal physics method in which the nanotubes are mobile in polymer latex and locked into the boundary area after film formation, the nanotubes are locked into the surface of polymer particles before film formation in the coating method. We believe both of them will be promising approaches to work out the semi-conductive polymer composites with low percolation threshold.
Chapter 5 Latex technology as a simple route to improve the thermal conductivity of a carbon nanotube/polymer composite

5.1 Introduction

The extremely high thermal conductivity of carbon nanotubes (CNTs) has been disclosed in several communications [4][5]. The thermal conductivity of single-walled carbon nanotubes (SWCNTs) has been theoretically demonstrated at $\sim 6000 \text{Wm}^{-1}\text{K}^{-1}$ at room temperature by molecular dynamics simulations [4]. The thermal conductivity of isolated multi-walled carbon nanotubes (MWCNTs) was experimentally measured at $\sim 3000 \text{Wm}^{-1}\text{K}^{-1}$ [5]. Due to their outstanding thermal conductivity, CNTs have been considered as potential candidates to improve the thermal conductivity of polymers. Strong interfacial phonon scattering has been commonly considered as the biggest bottleneck limiting the thermally transporting performance of CNTs in polymer composites [8][9]. Novel nanotechnologies are being explored to reduce the interfacial phonon scattering, allowing development of thermally conductive composites for thermal management [27][139][176]. It was revealed that randomly-dispersed nanotube bundles contributed to the enhancement of the thermal conductivity significantly less than the continuous nanotube-rich phase that strongly reduced the nanotube-polymer interfacial area in the composites. The colloidal physics method based on latex technology has been reported to prepare electrically conductive CNT/polymer composites with lower percolation threshold than other traditional methods [6][7][177]. This method simply concerned drying the mixture of CNT aqueous dispersion and polymer latex. Grunlan et al [7] proposed a model to describe a unique morphology created by this method, which indicated that CNTs could be self-aligned in the interstitial space between latex particles during film formation. We anticipated that the created continuous nanotube-rich phase going through the boundary area between latex particles was available for the electrical transport as well as the thermal transport. In chapter 4, it was discovered that the colloidal physics method was
available for the preparation of smei-conductive PU composites with the low incorporation of CNTs. In this chapter, we tried to dig out the advantages of the colloidal physics method in the reduction of the interfacial phonon scattering based on PU latex.

5.2 Results and discussion

5.2.1 Basic theory of heat conduction

Heat transfer refers to the movement of heat from a high-temperature object to a low-temperature object, which is schematically shown in Figure 5.1. In consideration of atomic and molecular activity in a microscopic scale, heat transfer can be viewed as the transfer of energy from energetic molecules to less energetic molecules as they collide. The means of heat transfer mainly concerns conduction, convection and radiation. Conduction is the most significant means of heat transfer in a solid, which generally carries out in two ways: phonons or electrons transfer. The electron is a fundamental subatomic particle that carries a negative electric charge and rotates around atomic nuclei that consist of protons and neutrons. The phonon is a quantised mode of crystal lattice vibration. In a rigid crystal lattice, atoms are vibrating instead of being fixed at rigid sites on the lattice. The vibration of atoms in a periodic structure is able to create a set of vibration waves propagating through the lattice. As the energy of vibrations is quantised, a phonon is used to label the quantum of vibrating energy, in analogy to photons for quantisation of the electromagnetic waves. Heat transfer in insulators is entirely dominated by phonon transport. In conductive metallic solid, electrons act the carrying role in nearly all heat flux. Less than 1% heat flux is carried by phonon vibrations. This is why metals always perform very well as both thermal and electrical conductors. Phonons tend to scatter when they collide with other particles such as phonons and electrons, defects or boundary surface in crystalline lattice. The anharmonic phonon-phonon or electron-phonon scattering is usually called Umklapp scattering, which mainly limits the thermal conductivity of low
defect crystalline materials. As soon as multi-phase structured composites are specifically concerned, strong phonon scattering at phase-phase interface dominantly limits the thermal conductivity. Reducing interfacial phonon scattering thus is key topic in expanding thermal limit in composite materials.

CNTs have exciting thermal conductivity due to their crystalline lattice structures with long free path that facilitate phonon transport. It is initially expected that percolated CNT networks formed in polymer matrix can facilitate phonon transport as well as electron transport. However, two types of interface could arise the strong phonon scattering in CNT/polymer composites: (1) CNT-polymer interface; and (2) CNT-CNT junctions. It is commonly considered that phonon scattering at CNT-CNT junctions is stronger than CNT-polymer interface [139]. Thus, the practical way to reduce phonon scattering is to reduce CNT-polymer interfacial area and increase CNT-CNT junctions.

![Diagram of heat transfer process](image)

**Figure 5.1** Schematic process of heat transfer

### 5.2.2 Thermal conductivity of MWCNT/PU composites

**Figure 5.2** shows the thermal conductivity of MWCNT/polyether-based PU composites as a function of the MWCNT content. The results show that the thermal conductivity reaches a plateau between 2wt% and 5wt% MWCNTs before rising sharply at 7 wt% MWCNTs. However, it can be seen clearly that with 7 wt% MWCNT, the thermal conductivity was only improved by ~86%. **Figure 4.9**
in last chapter has disclosed that the percolation threshold in the MWCNT/polyether-based PU composites is around 0.5wt%. It seems that the percolated CNT network does not significantly contribute to the enhancement of the thermal conductivity, which is in agreement with the findings from Gojny et al [8]. As mentioned in the mechanism of heat conduction, there are two types of heat carriers in solid: electrons and phonons. Phonon transport determines the heat transport in insulating materials, and electron transport determines the heat transport in conductive materials (e.g. metal). Gojny et al considered that phonon transport dominates the heat transport in semi-conductive CNT/polymer composites and electron plays side role in this case. Although the percolated CNT network in polymer matrix should facilitate phonon transport as well as electron transport, the strong phonon scattering at the nanotube-polymer interfaces and nanotube-nanotube junctions disables the percolated CNT network to transport phonon in CNT/polymer composites. This is the reason CNTs fail to

![Figure 5.2](image_url)

**Figure 5.2** Thermal conductivity of MWCNT/polyether-based PU composites as a function of MWCNT content
highly improve the thermal conductivity of polymers, which is totally opposite to people’s initial expectation. How to reduce the interfacial scattering is becoming the key challenge in expanding thermal limit in CNT/polymer composites. As mentioned in the part of “introduction”, the CNT/polymer with a continuous nanotube-rich phase can achieve relatively higher thermal conductivity than that with randomly-dispersed CNTs. In Du et al’s article, a detailed explanation was given to the contribution of the continuous nanotube-rich phase to the enhancement in the thermal conductivity of PS. They thought that the idea path for phonon transport is from one nanotube to another in CNT/polymer composite. The colloidal physics method is able to uniquely create a percolated CNT network going through the boundary area between latex particles. This percolated CNT network can be regarded as a continuous nanotube-rich phase in polymer matrix and is different from the percolated CNT network formed by randomly-dispersed CNTs. The nanotube-polymer interfacial area could be reduced since the continuous nanotube-rich phase only is distributed in the boundary area among latex particles.

Although the colloidal physics method has shown its advantage in the reduction of the interfacial phonon scattering in comparison with other methods in which CNTs are randomly dispersed in polymer matrix, the MWCNT/polyether-based PU composites fail to observe the exciting improvement of the thermal conductivity. Can we go further?

A phonon is a quantum of crystal vibrational energy, which have two fundamental lengths; wavelength and mean free path. Amorphous phase without long-range crystalline structure limits the free length of path for phonon transport in solids. We consider, in CNT/polymer composites, amorphous interface is inclined to arise the stronger interfacial phonon scattering than crystalline interface. “Repairing” amorphous interface could be an effective way to reduce the interfacial phonon scattering. Nucleating ability of CNTs in semi-crystalline polymer has been
practically applied to form crystalline layers around CNTs. It was found that the crystallites at CNT-polymer interface could enhance the performance of CNTs in improving the thermal conductivity of a CNT/PE composite [138]. In the colloidal physics method, our focus moves from amorphous latex to semi-crystalline latex since the improvement in the thermal conductivity of the MWCNT/polyether-based PU composite is not exciting. A semi-crystalline PU dispersion that was synthesized from polycaprolactone (PCL) was used as latex host to accommodate CNTs via the colloidal physics method. A much higher improvement of the thermal conductivity was found in comparison with the polyether-based PU composites.

Figure 5.3 Thermal conductivity of the MWCNT/PCL-based PU composites as a function of MWCNT content. All the samples were consistently loaded with 1wt% SDS

Figure 5.3 shows the thermal conductivity of the MWCNT/PCL-based PU composites with constant loading of 1wt% SDS as a function of the MWCNT content. The weight fraction of SDS and nanotubes were both calculated based on
the PU matrix. The thermal conductivity increases from 0.15 \( \text{Wm}^{-1}\text{K}^{-1} \) to 0.39 \( \text{Wm}^{-1}\text{K}^{-1} \), by \( \sim 160\% \), when the PU is loaded with 1.5wt\% MWNCTs. But the thermal conductivity exhibits a slight decrease to 0.32 \( \text{Wm}^{-1}\text{K}^{-1} \) when the incorporation of the MWCNTs reaches 2wt\%. It has been known that decreasing weight ratio of SDS to CNTs has negative impact on the dispersion of the CNTs in water [178]. The worse distribution of the nanotubes in the PU matrix could explain why the composite filled with 2wt\% MWCNTs performed lower thermal conductivity in comparison with that containing 1.5wt\% MWCNTs. It was experimentally found that the MWCNTs were not able to be dispersed in water well when the weight ratio of SDS to MWCNTs exceeded 1:3. In order to prepare the composites with higher incorporation of the MWCNTs, another group of the MWCNT/PCL-based PU composites were also prepared with fixed weight ratio (1:1) of SDS to MWCNTs. Figure 5.4 shows the thermal conductivity of the MWCNT/PCL-based PU composites as a function of the MWCNT content. The thermal conductivity increases from 0.15 \( \text{Wm}^{-1}\text{K}^{-1} \) to 0.47 \( \text{Wm}^{-1}\text{K}^{-1} \), by \( \sim 210\% \), as the addition of the MWCNTs increases to 3wt\%. Similarly, the thermal conductivity undergoes a slight decrease when MWCNTs and SDS content both increases over 3 wt\%. In the PU latex, the free space among latex particles accommodating the MWNCTs is limited. With increasing MWCNT concentration, the settlement of more single MWCNT in the void space among latex particles could increase the size of MWCNT bundles that result in more nanotube-nanotube interfacial phonon scattering. It could be concluded that the thermal conductivity of the PCL-based PU almost was tripled with the incorporation of 3wt\% MWCNTs. These results started to lighten our assumption regarding the strategies to reduce the interfacial phonon scattering via latex technology. As mentioned above, the continuous nanotube-rich phase created by the colloidal physics method is one point. Compared with our previous result that less than 100\% enhancement of the conductivity was obtained for the amorphous PU filled with 7wt\% nanotubes, it also could reach the conclusion that the PCL crystallites nucleated at
the nanotube-polymer interface showed the advantage in the effective reduction of interfacial phonon scattering over amorphous interface because lattice vibration was inclined to be destroyed by disordered structure. It has to be pointed that the use of surfactant wrapping around the CNTs strongly increased the interfacial phonon scattering, and was the obstacle for this method to make the improvement of the thermal conductivity meet our high prediction no matter in the amorphous or semi-crystalline PUs.

![Graph](image.png)

**Figure 5.4** Thermal conductivity of the MWCNT/PCL-based PU composites as a function of MWCNT content. All samples were prepared with consistent weight ratio (1:1) of SDS to MWCNTs

### 5.2.3 SEM imaging the morphology of MWCNT/PCL-based PU composites

A SEM image of the MWCNT(3%wt)/PCL-based PU composite with low magnification is shown in **Figure 5.5(a)** to disclose almost homogeneous dispersion of the MWCNTs that are represented by bright dots although some big nanotube bundles still exist in the PU matrix. **Figure 5.5(b)** shows a magnified SEM image focusing on the framed area in **Figure 5.5(a)**. Apparently, a few
micro-sized nanotube bundles still can be seen in the fractured surface. It is difficult to totally avoid these big nanotube bundles even though surfactant acts as de-aggregating role because the nanotubes are inclined to aggregate as the nanotubes are automatically pushed into the boundary among the latex particles during the film formation. However, these big nanotube bundles give a clear view of the nanotube-rich phase in the PU matrix. In combination with a TEM image of the nanotube-rich phase in poly(vinyl acetate) previously released by Grunlan et al, the colloidal physics method could produce a cellular structure with the continuous nanotube-rich phase locating in the interstitial areas between latex particles. Figure 5.5(e) shows the enlarged area with the well-dispersed nanotube bundles in the fractured surface. In Figure 5.5(d and e), the bright dots observed on the top surface represent the nanotube bundles in vertical direction. It can be seen that that the thickness of the nanotube-rich phase in the composite varied from several nanometres (single tube and nanotube bundles) to micron (the large-area CNT arrays).
Chapter 5 Latex technology as a simple route to improve the thermal conductivity of a carbon nanotube/polymer composite
Figure 5.5 FESEM images of the MWCNT(3wt%)/PCL-based PU composite. a, b and c are the fractured surface images; d and e are the top surface images.
5.2.4 Study of the crystalline morphology of MWCNT/PCL-based PU composites

Crystallisation process consists of two steps: the formation of nuclei, and, crystal growth. The formation of nuclei is the first step, in which polymer chains start to gather into clusters in the nanometre scale. These stable clusters constitute the nuclei as the clusters reach a critical size. The crystal growth is the subsequent growth of the nuclei, in which long chain segments fold themselves together to form lamellar structures. Amorphous region exists between the crystalline lamella, which means there is no 100% crystallinity in polymers. The formation of nuclei is called nucleation, which can be categorised as homogeneous nucleation and heterogeneous nucleation. Homogenous nucleation means that the formation of nuclei takes place spontaneously only due to supercooling without existing nuclei. Heterogeneous nucleation refers to the formation of nuclei in presence of existing nuclei in polymer solution or melts. The existing nuclei generally refer to preexisting/residual nuclei surviving from initial melt or dissolution conditions, or any “impurity” existing in polymer solution or melts. Nanofillers are commonly regarded as one kind of the “impurity”, which have shown their nucleating ability for crystalline polymers. The crystalline morphology and crystallisation behaviour of polymers could be significantly changed in the presence of nanofillers.

As one-dimensional nanofillers with tubular structures, the nucleating ability of CNTs for polymers has been reported in many articles [73][147][179] [180]. The nucleation of polymer crystallites around CNTs has been considered a practical route to engineer the nanotube-polymer interface. Coleman et al [20] discovered that the crystalline coating around CNTs made a significant contribution to the stress transfer from CNTs to polymers. In combination with Haggenmueller et al’s [138] discovery, we also considered that the function of the nucleated crystallites could be extended to reduce the interfacial phonon scattering because the nanotube-polymer interface is being crystallised. This assumption has been
Figure 5.6 Polarised optical microscopy images of the MWCNT/PCL-based PU composites. a: the pure PU; b: the MWCNT(1wt%)/PU composite (—— 20μm)

partially confirmed by comparing the thermal conductivities of the MWCNT/polyether-based PU composites and the MWCNT/PCL-based PU composites. The aim of this part is to confirm the existence of crystallites nucleated by CNTs in the MWCNT/PCL-based PU composites by using POM and
Chapter 5 Latex technology as a simple route to improve the thermal conductivity of a carbon nanotube/polymer composite

DSC techniques.

(1) Polarised optical microscopy study of the crystalline morphology of MWCNT/PCL-based composites

The POM images of the MWCNT/PCL-based PU composites are shown in Figure 5.6. The crystalline morphology of the pure PU exhibits a type of big ringed spherulites. It can be seen that the addition of the MWCNTs results in a significant damage of the big spherulites. A large number of smaller spherulitic and needlelike crystals appear in the PCL-based PU containing 1wt% MWCNTs. This phenomenon is attributed to the nucleating ability of the MWCNTs for crystalline polymers. The incorporation of one-dimensional tubular nanofillers acting as nuclei significantly affects the growth of spherulites. In another aspect, the POM images can confirm the formation of the PU crystallites nucleated by the MWCNTs. In this system, the it is difficult to observe the crystallites nucleated by

![Figure 5.6](image)

**Figure 5.6** PE/MWCNT NHSK structure produced by crystallisation of PE on MWCNTs at 103°C in p-xylene for 0.5h: a) SEM image shows that MWCNTs are decorated by dis-shaped PE single crystals and PE-functionalised MWCNTs MWCNTs can therefore be achieved. b) TEM image of enlarged PE/MWCNT NHSK structures. a) and b) show that periodicity of the kebabs is ~50-70nm. c) Schematic representation of the PE/CNT NHSK structure [181].

105
CNTs directly using electron microscopy. Li et al [181][182] studied the CNT-induced polymer crystallisation in the extremely diluted solution of PE and achieved the electron microscopy images of CNT-nucleated crystallites as shown in Figure 5.7. It can be seen that PE periodically grows on the surface of CNTs and forms 'nanohybrid shish-kebabs' (NHSKs). This discovery clearly confirms the nucleating ability of CNTs for crystalline polymers, and can support the POM images on the micro-scale revealing that the growth of spherulites are significantly affected by the incorporation of MWCNTs.

(2) DSC study of crystallisation of MWCNT/PCL-based PU composites

DSC technique was further used to detect the existence of the crystallites around the CNTs. DSC technique, as an important thermal analysis method, has been widely used to study the morphology of polymers. DSC curves are very informative to disclose the second order glass transition, the first order melting transition and the fraction of crystallinity in polymers. The crystalline morphology of polymers typically presents a lamellar structure. Thompson-Gibbs (TG) equation is proposed to describe the linear relationship between melting temperature and lamellar thickness:

$$T_m = T_m^0 \left(1 - \frac{2\sigma}{L_c \Delta H_f^0}\right)$$

where $\sigma$ is the fold surface interfacial free energy, $L_c$ is the lamellar thickness, $T_m^0$ is the equilibrium melting temperature of the polymer, $\Delta H_f^0$ is the bulk enthalpy of melting per unit volume of crystals. Coleman et al [20] used the fact that the crystallinity increased with increasing addition of the CNTs to confirm the formation of the crystallites around CNTs. Typical DSC curves of the MWCNT/PCL-based PU composites are shown in Figure 5.8. The crystallinity calculated based on melting peaks failed to increase with increasing addition of the MWCNTs obviously. However, it can be seen that, compared with the pure PU, a new melting peak appears around 27°C, which can be attributed to some
crystallites with thinner lamellar thickness formed around the nanotube bundles. The differential signals of heat flow shown in Figure 5.9 can identify this new melting peak more clearly. Furthermore, it was found that the thermal conductivity

Figure 5.8 Typical DSC curves of the PCL-based PU and MWCNT/PCL-based PU composites; A: all samples with consistent loading of 1wt% SDS; B: all samples with consistent weight ratio (1:1) of SDS to MWCNTs
Figure 5.9 Derivated DSC curves of the PCL-based PU and MWCNT/PCL-based PU composites; A: all samples with consistent loading of 1wt% SDS; B: all samples with consistent weight ratio (1:1) of SDS to MWCNTs of the composites roughly varied with the areas of these new peaks. Figure 5.8(A) reveals the DSC curves of the composites which have shown their thermal conductivity in Figure 5.3. At 1.5wt% MCWNTs, the biggest new peak around
27°C corresponds to the highest thermal conductivity. Similarly, it can be seen from Figure 5.8(B) and Figure 5.4 that 3wt% MWCNTs yields the composite with the biggest peak around 27°C and the highest thermal conductivity. These details helped us make better understanding of the contribution of the crystallites around nanotubes to the enhancement of the thermal conductivity. The nanotube is a super thermal conductor due to its unique structure. Nanotube netwok acting as an ideal pathway for phonon transporting in polymer matrix is expected to significantly enhance the thermal conductivity of polymers. The phonon scattering in the CNT-polymer interface is the barrier between the expectation and the reality. In comparison with the amorphous interface, the crystallites formed in the CNT-polymer interface could be responsible for enhancing the orderliness of the interface and reducing the interfacial phonon scattering. Less loss of phonon during the thermal transporting, higher thermal conductivity of CNT/polymer composites will be achieved.

5.3 Conclusions

A universal recognition that the interfacial phonon scattering that is hardly eliminated is the bottleneck for CNTs to perform as ideal thermal conductors in the polymer composites has been compromised. How to reduce the interfacial phonon scattering technically is regarded as a big challenge for the development of the thermally conductive CNT/polymer composites. Latex technology has been applied to fabricate the electrically conductive composites with very low percolation threshold. In this chapter, latex technology was applied to achieve high improvement of the thermal conductivity. It was found that the thermal conductivity almost was tripled with the incorporation of 3wt% MWCNTs into the semicrystalline PCL-based PU, whereas the incorporation of 7wt% MWCNTs only resulted in a nearly 86% increase in the thermal conductivity of the amorphous polyether-based PU. The continuous nanotube-rich phase and polymer crystallites nucleated at interface were two main factors for the effective reduction
of the interfacial phonon scattering. It convinces that latex technology will be a simple and promising route ahead to functional CNT/polymer composites.
Chapter 6 Study of thermal-induced crystalline interface for the load transfer in a carbon nanotube/polymer composite

6.1 Introduction

CNTs are known to have an extremely high Young's modulus of up to 1 TPa and tensile strength approaching 60 GPa [2][10], which are considered to be ideal candidates for mechanical reinforcement of polymers [11]. Two issues needs to be considered in the development of highly strong CNT/polymer composites: (1) uniform dispersion of CNTs in polymer matrix; (2) a strong interface between CNTs and polymers. It seems the uniform dispersion of CNTs is not a big challenge any more in labs as chemically functionalised CNTs are widely used. How to form a strong interface between CNTs and polymers currently presents to be the biggest challenge in this field. The functional groups or macromolecules attached onto CNTs are capable of enhancing the compatibility between inorganic components (CNTs) and organic components (polymers) [91][106][145]. The covalent bonding between CNTs and polymers until now is commonly considered as a kind of strong interface for the load transfer. Very recently, Coleman and co-workers made significant efforts to understand the mechanism of the load transfer across the non-covalent interface. They found that a polymer crystalline layer nucleated by CNTs acted as an effective interface for the load transfer, which results in nearly 400% improvement in the Young's modulus of PVA only with the incorporation of 0.6 vol% CNTs [147]. This finding was confirmed by the much lower reinforcement of a non-crystalline PVK with a similar CNT loading [147]. Coleman et al's discovery has pointed a novel approach to engineer the non-covalent interface, which can lead to highly strong CNT/polymer composites. We noticed that Coleman et al's discovery was only based on the composites prepared via the solution processing. In the solution system, flexible macromolecule chains could have enough time and space to organize well-ordered structure on the surface of CNTs and form an optimised crystalline layer during
slow drying of the solution. However, it is not clear how to fabricate an optimised crystalline layer around CNTs from polymer melts, although the nucleating role of CNTs in crystalline polymers has been commonly recognised. In this chapter, the crystallisation behaviour of polycaprolactone (PCL) in presence of CNTs with different thermal treatments was investigated, and we aimed to find out a proper thermal method to optimise the crystalline layer surrounding CNTs from PCL melt. The improvement in the Young’s modulus of the CNT/PCL composites before and after the thermal treatment was also comparatively studied to disclose the role of the crystalline layer in the load transfer between stiff CNTs and soft polymers.

6.2 Results and discussion

6.2.1 Dispersion of MWCNTs-OH in PCL matrix

The preparation of the composites with good dispersion of CNTs is the first step in studying their structure-properties relationship. In this work, the solution method was used to prepare the MWCNT-OH/PCL composites, in which good dispersion of the nanotubes was firstly achieved in DMF. The characterisation of the stable MWCNT-OH/DMF dispersion has been revealed in chapter 3. Here, SEM technique was used to investigate the dispersion of the nanotubes in the PCL matrix. The SEM images shown in Figure 6.1 prove that the nanotubes are successfully incorporated into the PCL matrix at nanoscale level. However, with the incorporation of the 2wt% nanotube, some nanotube bundles can be obviously observed. So, the dispersion and distribution becomes worse with increasing incorporation of the nanotubes.

6.2.2 DSC study of the crystallisation behaviour of MWCNT-OH/PCL composites

In order to understand the formation process of the crystalline layers surrounding the nanotubes from the composite melts, DSC technique was used to study the
non-isothermal and isothermal crystallisation of the MWCNT-OH/PCL composites. Figure 6.2 shows the non-isothermal DSC curves of the MWCNT-OH/PCL composites. It can be seen that the crystallisation temperature of the PCL increases.

Figure 6.1 SEM images of (a) PCL, (b) MWCNT-OH(0.1wt%)/PCL composite, (c) MWCNT-OH(0.5wt%)/PCL composite, (d) MWCNT-OH(1wt%)/PCL composite and (e) MWCNT-OH(2wt%)/PCL composite.
as the incorporation of the nanotubes increases up to 2wt%, which indicates the strong nucleating ability of the nanotubes. Table 6.1 shows the non-isothermal parameters including crystallisation temperature ($T_c$), melting temperature ($T_m$) and heat of fusion ($\Delta H_m$). The biggest increase of $T_c$, nearly 11°C, was witnessed in the MWCNT-OH (2wt%)/PCL composite. The nucleating role of CNTs in crystalline polymers has been reported [183]. There is no doubt that the PCL crystallites can grow on the surface of the nanotube during the cooling process. But, it seems that the crystalline layer cannot be optimised at quick cooling rate. $T_m$ and $\Delta H_m$ shown in Table 6.1 were found to be almost unchanged, and even the shapes of melting peaks look quite similar. Coleman et al used the increase of crystallinity as a strong evidence to support the existence of the crystalline layer in CNT/PVA composites [14]. Different from solution-crystallization, the motion of polymer chains is more restricted in polymer melts. As the melts are cooled very quickly, it is difficult to achieve the optimisation of the crystalline layer although the nucleating behaviour of the nanotubes is very obvious.

![Non-isothermal DSC curves of the MWCNT-OH/PCL composites](image_url)

**Figure 6.2** Non-isothermal DSC curves of the MWCNT-OH/PCL composites
Figure 6.3 DSC curves of heat flow vs temperature after completion of the isothermal crystallisation in the MWCNT(1wt%)/PCL composite at three temperatures

We do believe a slow crystallisation rate could facilitate the optimisation of the crystalline layer. In polymer melts, isothermal crystallisation is a common approach to slow down the crystallisation rate. The isothermal crystallisation temperature generally should be carefully selected to ensure the isothermal crystallisation will not be affected by the non-isothermal crystallization. Firstly, we used $T_c$ as base point to select three appropriate temperatures to conduct the isothermal crystallisation for the MWCNT-OH(1wt%)/PCL composite. After melting pre-existing crystals at a high temperature nearly 85°C, the samples were cooled to the temperature set for the isothermal crystallization, which were 45°C, 51°C, 53°C, respectively. After completion of the isothermal crystallization, the rescanning of the samples was performed at a heating rate of 5°C. The rescanning DSC curves are shown in Figure 6.3. It can be seen that the treating temperature of 51°C widens the melting peak and creates a small shoulder on left of the melting
peak in comparison with 45°C. Obviously, this small shoulder turns to a tiny peak as the isothermal crystallisation was conducted at 53°C. It is well-known that the lamellar thickness closely connects with the melting temperature. Thompson-Gibbs (TG) equation is proposed to describe the linear relationship between melting temperature and lamellar thickness. The details of this equation were given in Chapter 4. The tiny peak could be attributed to the formation of a new lamellar structure belonging to the crystalline layer surrounding the nanotubes with short lamellar thickness.

Figure 6.4 shows the DSC curves tracking the process of the isothermal crystallisation for the MWCNT(1wt%)/PCL composite. Nearly half crystallisation has been completed when the sample approaches the treating temperature of 45°C. At higher temperature, the crystallisation rate slows down and the whole peak of the isothermal crystallisation can be seen in Figure 6.4. In combination with Figure 6.3, it indicates that the crystalline layer is formed in the early stage of the isothermal crystallisation due to the nucleating behaviour of the CNTs in the PCL matrix. As the treating temperature is more closed to the melting temperature, it was found that the isothermal crystallisation failed to complete due to the equilibrium between the crystallisation and melting. Therefore, it was considered that the treating temperature, 14°C higher than $T_c$, was appropriate to induce the crystalline layer surrounding CNTs in the composite melts. Here, we named the condition of this thermal treatment as the "14°C" rule. The "14°C" rule was also applied to other composites with different nanotube concentration. Figure 6.5 shows the rescanning DSC curves (heat flow vs temperature) of the composites with different nanotube concentration after completion of the isothermal crystallization. It also can be seen that the area and position of the tiny peak on the shoulder of typical peak of PCL appears increasingly large as a function of nanotube concentration. A similar phenomenon was observed in CNT/PmPV composites by Ryan et al as well [184]. The crystallisation took place during the drying process of the CNT/PmPV solutions. In the DSC curve (first heating), they
attributed a new melting peak around 73 °C that was higher than the typical melting peak of the PmPV to a more ordered crystalline conformation of the PmPV nucleated by the CNTs. After melting and quick cooling, the new melting peak was absent on the shoulder of typical melting peak in the second heating. This evidence also confirmed that the crystalline layer is not easy to be optimised at very quick crystallisation rate from polymer melts.

![DCS curves of heat flow vs time for the 1wt%MWCNT-OH/PCL composite, which are tracking the whole process of the isothermal crystallisation](image)

**Figure 6.4** DCS curves of heat flow vs time for the 1wt%MWCNT-OH/PCL composite, which are tracking the whole process of the isothermal crystallisation

In our system, the increase of crystallinity was not found to be as a function of the nanotube concentration. The melting peaks of the PCL composites reflect two parts: (1) the crystalline layer associated with the nanotubes; and (2) the crystalline region not associated with the nanotubes. Coleman and his co-worker [14][147] viewed the increase of crystallinity as a strong evidence for the existence of the crystalline layer in the system of polymer solutions. Our results showed that the formation of the crystalline layer in a bulk polymer presented another way in comparison with polymer solutions. The area of new melting peak attributed to the
well-ordered crystalline layer increased with increasing nanotube concentration, but the crystallinity of the bulk polymer failed to increase.

Figure 6.5 DSC curves of the MWCNT-OH/PCL composites after completion of isothermal crystallization. The isothermal crystallizations were performed based on the “14°C” rule for all samples.

Table 6.1 Crystallisation parameters in the MWCNT-OH/PCL composites.

<table>
<thead>
<tr>
<th></th>
<th>Tc(°C)</th>
<th>Tm(°C)</th>
<th>ΔHm(J/g)</th>
<th>Tm</th>
<th>ΔHm(J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>28.7</td>
<td>58.1</td>
<td>56.1</td>
<td>57.8</td>
<td>58.2</td>
</tr>
<tr>
<td>0.1%CNT/PCL</td>
<td>32.1</td>
<td>58.1</td>
<td>56.2</td>
<td>59.8</td>
<td>59.9</td>
</tr>
<tr>
<td>0.5%CNT/PCL</td>
<td>37.3</td>
<td>59.0</td>
<td>54.4</td>
<td>62.7</td>
<td>58.0</td>
</tr>
<tr>
<td>1%CNT/PCL</td>
<td>39.1</td>
<td>58.4</td>
<td>58.9</td>
<td>62.8</td>
<td>58.6</td>
</tr>
<tr>
<td>2%CNT/PCL</td>
<td>40.1</td>
<td>57.7</td>
<td>57.2</td>
<td>62.0</td>
<td>58.2</td>
</tr>
</tbody>
</table>

[a] and [b] represents the crystallisation parameters obtained from the non-isothermal and isothermal DSC curves, individually.
6.2.3 Morphological study of the PCL crystals in MWCNT-OH/PCL composites

Polarised optical microscope (POM) was used to observe the morphology of the PCL crystals in the composites. Figure 6.6(a) shows a typical image of PCL spherulites with a cross-like extinction classically named “Maltese Cross”. In Figure 6.6(b-d), it can be obviously seen that the size of crystals is much smaller in the composites in comparison with pure PCL. This is due to the nucleating role of the nanotube is PCL matrix. In Figure 6.6(e), it is interesting to see that the size of PCL crystals in the MWCNT-OH(2wt%)/PCL composite is much bigger than that of the other composites, but smaller than that of pure PCL. Avrami equation [185] is a common tool to analyze the growth of crystals under isothermal condition. Generally, Avrami equation is written as followed:

\[ X(t) = 1 - \exp(-Kt^n) \] (10)

where \(X(t)\) is the relative crystallinity, \(t\) is the crystallisation time, \(K\) is the kinetic rate constant depending on the nucleation and growth rate, and \(n\) is the Avrami exponent determining the shape of the growing crystalline body. The relative crystallinity \(X(t)\) can be calculated following the equation:

\[ X(t) = \frac{A(t)}{A(total)} \] (11)

where \(A(t)\) is the partial area of the peak at a time \(t\) and \(A(total)\) is the total peak area. The relationship between \(X(t)\) and \(t\) is plotted in Figure 6.7. All data inside were fitted into Avrami equation using Origin software to obtain the values of \(n\) and \(K\), as shown in Table 6.3. As mentioned, \(K\) relies on the nucleation and growth rate. 0.1 wt% nanotubes increase the nucleation and growth rate nearly by a factor of 20. In comparison with the curve belonging to pure PCL in Figure 6.7, the curve of the MWCNT-OH(0.1wt%)/PCL composite reveals that its initial
Figure 6.6 Optical microscopy images of the (a) the PCL, (b) the MWCNT-OH(0.1wt%)/PCL composite, (c) the MWCNT-OH(0.5wt%)/PCL composite, (d) the MWCNT-OH(1wt%)/PCL composite and (e) the MWCNT-OH(2wt%)/PCL composite taken by built-in digital camera during the isothermal crystallisation that follows the “14°C” rule for all samples. (20µm — )
crystallisation is faster before the crystallinity reaches 50%, and the crystallisation rate is slower after that. At low nanotube concentration, the nanotubes could be exfoliated into single nanotubes in the PCL matrix. It seems single nanotube with a diameter of 20-30nm plays significant nucleating role as an inorganic phase in the PCL matrix. Also, the mobility of polymer chains is slightly restricted by small amounts of the single nanobutes. With the more incorporation of nanotubes, the value of K presents a downturn trend, which even is smaller than that of pure PCL. Although the nucleating role of the nanotubes still works, the existence of the nanotubes significantly hinders the mobility of polymer chains to form the crystalline structure.

Table 6.2 Relationship between Avrami exponent and shape of crystals [185][186]

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Avrami Exponent</th>
<th>Restriction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheres Sporadic</td>
<td>4.0</td>
<td>3 dimension</td>
</tr>
<tr>
<td>Predetermined</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Discs Sporadic</td>
<td>3.0</td>
<td>2 dimension</td>
</tr>
<tr>
<td>Predetermined</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Rods Sporadic</td>
<td>2.0</td>
<td>1 dimension</td>
</tr>
<tr>
<td>Predetermined</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3 Values of parameters (n and K) in Avrami equation

<table>
<thead>
<tr>
<th>CNT weight fraction(%)</th>
<th>n</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.94±0.03</td>
<td>0.00496±0.000029</td>
</tr>
<tr>
<td>0.1</td>
<td>1.16±0.03</td>
<td>0.10942±0.00548</td>
</tr>
<tr>
<td>0.5</td>
<td>1.55±0.02</td>
<td>0.00351±0.00024</td>
</tr>
<tr>
<td>1</td>
<td>1.87±0.01</td>
<td>0.00035±0.00002</td>
</tr>
<tr>
<td>2</td>
<td>2.04±0.03</td>
<td>0.00027±0.00004</td>
</tr>
</tbody>
</table>
As seen in Table 6.3, the value of $n$ for PCL is nearly 3, which shows that the shape of PCL crystals is 2-dimentional discs. In presence of the nanotubes acting as preexisting nuclei, the predetermined nucleation solely dominates the isothermal crystallization. The shape of PCL crystals is significantly changes with the incorporation of 0.1wt% nanotubes into PCL. It is reflected by the value of $n$ and POM image (Figure 6.6(b)). The value of $n$ for the MWCNT-OH(0.1wt%)/PCL composite is close to 1, which indicates that the shape of PCL crystals is transformed to rods. The PCL crystals might grow along with the axial direction nanotubes. The value of $n$ increased with increasing incorporation of the nanotubes. The value of $n$ is 1.55 and 1.87 for the composite with 0.5wt% and 1wt% nanotubes, respectively, which reflects the mixed shape (rods and discs) of PCL crystals. The value of $n$ for the MWCNT-OH(2wt%)/polymer composite rises up to 2.04, which indicates the disc

![Figure 6.7 Relative crystallinity $\chi_c$ as a function of time for the MWCNT-OH/PCL composites](image)

Figure 6.7 Relative crystallinity $\chi_c$ as a function of time for the MWCNT-OH/PCL composites
shape of PCL crystals. This can be directly observed in the POM image in Figure 6.6(e). This phenomenon could be explained by the worsening dispersion and distribution with increasing incorporation of the nanotubes that has been mentioned above. At high nanotube concentration, the nanotubes tend to aggregate to form nanotubes bundles in the PCL matrix, possibly resulting in the separation between the nanotubes and PCL matrix. This could explain why the shape of PCL crystals gradually recovered to disc-like shape from needle-like shape with higher incorporation of the nanotube than 0.1 wt%.

6.2.4 Understanding of the contribution of the crystalline layer surrounding CNTs to the Young's modulus of CNT/polymer composites

(1) Physical mechanism of the load transfer across the well-ordered crystalline layer

The improvement in the Young's modulus of CNT/polymer composites generally is used to measure the efficiency of the load transfer across the interface between CNTs and polymer matrix. The macromolecule chains covalently attached to the surface of CNTs and the crystalline layer around CNTs are commonly considered as two types of effective interfaces for the load transfer. Theoretically, Krenchel’s rule of mixture is usually used to predict the mechanical enhancement if CNTs perfectly bond to the matrix [14]. The difference between theoretical prediction and experimental values gives a clue to understand the transferring efficiency of the interface. Generally, Krenchel’s rule of mixture for predicting the Young's modulus of CNT/polymer composites is written as:

$$Y_c = \eta_0 \eta_1 Y_N V_f + (1 - V_f) Y_p \quad (12)$$

Where $Y_C$, $Y_N$, and $Y_P$ are the Young's modulus of the composite, CNTs, and polymer matrix, respectively, $V_f$ is the nanotube volume fraction in composites, and $\eta_0$ and $\eta_1$ are efficiency factors related to fibre orientation and length. The
Chapter 6 Study of thermal-induced crystalline interface for the load transfer in a carbon nanotube/polymer composite

Theoretical in-plane value of $\eta_0$ is equal to $3/8$ as the nanotubes randomly distribute in the plane of composite films. The fibre length efficiency factor is given by Cox's equation:

$$
\eta_1 = 1 - \frac{Tanh\left(\frac{l_{ef}\beta}{2}\right)}{2} \quad (13)
$$

Where $l_{ef}$ is the nanotube effective length and $\eta$ is given by

$$
\beta = \sqrt{-\frac{4G}{R^2Y_N\ln V_f}} \quad (14)
$$

where $R$ is the nanotube radius, $V_f$ is the nanotube volume fraction, and $G$ is the polymer shear modulus which was found using the expression: $G = \frac{Y}{2(1+\nu)}$, where $\nu$ is the Possion's ratio.

Coleman et al [14] experimentally found the contribution of the crystalline layer surrounding CNTs to the enhancement in the Young's modulus of CNT/PVA composites. Fitting the experimental values into the Krenchel's rule was of being failure. It was in agreement with the previous recognition that Krenchel's rule was not suitable for predicting the mechanical enhancement of CNT/polymer composites. This is because a perfect interface is assumed in the Krenchel's rule.

In order to understand the fundamental mechanism of the load transfer across the imperfect interface, a simple model was developed by Coleman et al [187] to describe the ordered assembly of polymer monolayers on the surface of CNTs. In this model, two energetically competing factors were considered in this model to calculate the amount of energy required to wrap polymer strands around a nanotube: (1) the van der Waals-based binding energy between the nanotubes and polymer strands; and (2) the elastic-energy cost required to bend the polymer
strands. The binding energy per unit length of polymer is angle independent and given by \( B = -\sigma \omega \), where \( \omega \) represents the width of a semi-flexible continuous stripe (polymer) and \( \sigma \) is a measure of average binding energy per unit polymer. In terms of the elastic energy cost named coiling energy \( C \), it can be defined as \( C = D\kappa^2 \), where \( D \) is the stiffness constant of the polymer and \( \kappa = \sin^2 \theta / R \) is the respective curvature of its helicoidal path. The stiffness constant relates to the so-called persistence length \( L_p \) of the polymer following \( D = L_p k_B T \), \( k_B T \) is the thermal energy. Conclusively, for a single polymer strand, the total energy per unit length of polymer was written as followed: \( E_1(\theta) = B + C = -\sigma \omega + D\sin^4 \theta / R^2 \).

Considering the situation of many polymer strands wrapping around the nanotube, the binding and coiling energies were scaled up with the number of the strands. Based on the geometrical constraint as seen in Figure 6.8, the maximum number of strands covering the nanotube is constrained to be \( m = \text{INT}(2\pi R \cos \theta / \omega) \), where \( \text{INT}(x) \) stands for the integer part of the argument \( x \). The dimensionless angle-dependent coverage is defined as \( \beta(\theta) = m \omega / (2\pi R \cos \theta) \), which corresponds to

\[ Figure 6.8 \] (a) Schematic representation of a single polymer strand coiling along the axis of a nanotube. (b) In the two-dimensional depiction, the unwrapped tube is represented by an infinitely long stripe of width \( 2\pi R \) and the coiling angle \( \theta \) defines a unit cell of length \( 2\pi R / \tan \theta \). The black stripe of width \( \omega \) symbolizes the polymer strand [187].
Figure 6.9 (a) Total energy as a function of the coiling angle \( \theta \) for PA (solid line) and PmPV (dashed line) wrapped around a 1nm long nanotube of 1.3nm diameter. (b) Corresponding probability density. The parameter for PA and PmPV are \( \sigma = 378 \text{meV/nm}^2 \); \( \omega = 0.48 \text{nm} \); \( D = 32.5 \text{meVnm} \) and \( \sigma = 770 \text{meV/nm}^2 \); \( \omega = 2.1 \text{nm} \); \( D = 250 \text{meVnm} \), respectively [188].

the proportion of the unit-cell surface that is maximally covered by the polymer strands with a width of \( \omega \). As a function of the angle \( \theta \), the coverage intermittently reaches 100% whenever the unit-cell surface area is an integer multiple of the surface area of one polymer strand. In both ends of the nanotube, this full-coverage configuration is then followed by a discontinuous change in \( \beta(\theta) \), which means that some polymer strands partially fit onto to the wall of the nanotube. The total energy per unit length of the nanotube was written as \( E_c(\theta) = (2\pi R \beta(\theta)/\omega) E_1(\theta) \). Figure 6.9 shows the total energy \( E \) as a function of \( \theta \) for a nanotube (diameter:1.3nm; length:1nm) coated with polyacetylene (solid line) and PmPV (dashed line), respectively. For narrow polyacetylene strands (\( \omega = 0.48 \text{nm} \)), small variations on the coverage and total energy are disclosed, which indicate narrow polymer strands do not have any clear preferential coating angle. For wide PmPV strands (\( \omega = 2.1 \text{nm} \)), the much larger fluctuations present two distinct energy minima as a function of \( \theta \) (48° and 70°). Coleman et al proposed this simple model to clarify the templating mechanism of CNTs for polymer stands. Energetically,
polymer strands are templated on the surface of CNTs following a favourable coiling angle due to geometric constraints. The coiling angle is relevant to the stiffness of polymer strands and the diameter of CNT. For amorphous coating (soft polymer strands), the coverage of nanotube lattice is less ordered and never can reach 100% in comparison with crystalline coating (stiff polymer strands). This model suggested that the load transfer was determined by only a fraction of polymer layers templated on the surface of the nanotube, and more coverage of the nanotube by polymer layers would result in better load transfer.

On the base of this finding, Coleman and co-workers [188] proposed a modified Krenchel’s rule of mixture to predict the improvement of Young’s modulus. In this model, a templating fraction $T_f$ defined by averaging over all possible coiling angles was introduced, which reflected the percentage of polymer stands experiencing the stiffness of nanotubes. The modified Krenchel’s rule of mixture was written as followed:

$$Y_c = T_f V_f Y_n + (1 - V_f) Y_p$$  \( (15) \)

where $Y_N$ and $Y_P$ are the Young’s modulus of CNTs and polymers, respectively, $V_f$ is the nanotube volume fraction in composites and the coefficient $\eta = 3/8$ accounts for the random distribution of CNTs in the plane of polymer films. $T_f$ was found to be a function of the natural bond length of polymer strands and nanotube radius. It was mentioned that the selection of a reliable way to calculate $T_f$ was very important to make a good prediction for the improvement of Young’s modulus. We noticed that the disagreement between experimental and predicted values was still obviously. It could be attributed to the difficulty in obtaining an accurate value of $T_f$.

However, their theoretical study gave us a clue to propose an empirical equation for the prediction of the Young’s modulus of the CNT/polymer composites with a crystalline interface induced by CNTs. In the empirical equation, a coefficient was
introduced to Krenchel's rule of mixture in order to general describe the degree of mismatch between the stiffer nanotubes and the softer polymer matrix (imperfect interface). The modified Krenchel's rule of mixture could be written as follows:

$$Y_c = \phi V_f Y_N + (1 - V_f) Y_P \quad (16)$$

Where $Y_N$ and $Y_P$ are the Young's modulus of CNTs and polymers, respectively, $V_f$ is the nanotube volume fraction in composites. $\phi$ is the coefficient of load transfer between CNTs and polymer matrix. According to Coleman's theoretical study, we considered that $\phi$ might have potential connection with Young's modulus of polymers since Coleman's theoretical study revealed that stiffer polymer strands could have more coverage on the surface of CNTs, which lead more fractions of polymer strands to join in the load transfer. In the published literature, it has been reported that an optimised crystalline layer surrounding CNTs was successfully formed in PVA [14], CIPP [14] and polyester-based PU [73]. These satisfied samples which were well thermal treated for forming the crystal layer surrounding CNTs were selected to disclose the relationship between $\phi$ and the Young's modulus of polymers. According to published value of $dY_c/dV_f$ disclosed in these three polymers, the calculation of $\phi$ was performed as $Y_N$ was taken as 1TPa. The values of $\phi$ are displayed in Table 6.4. As the variation of $\phi$ against $Y_P$ was plotted in Figure 6.10, the relationship between $\phi$ and $Y_P$ could be empirically generalized as followed:

$$\phi = 399(GPa)^{-1} Y_P \times 10^{-3} \quad (17)$$

Figure 6.11 gives a comparison of experimental values of Young's modulus with the predicted values by the empirical equation for the CNT/PVA, CNT/CIPP and CNT/polyester-PU composites. It can be found that the empirical equation can
Table 6.4 Values of the Young’s modulus ($Y_p$) and the coefficient ($\phi$) for PVA, CIPP and polyester-based PU in published literatures

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$Y_p$ (GPa)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA [14]</td>
<td>1.92</td>
<td>0.7559±0.09292</td>
</tr>
<tr>
<td>CIPP [14]</td>
<td>0.22</td>
<td>0.0720±0.00772</td>
</tr>
<tr>
<td>Polyester-based PU[73]</td>
<td>0.007</td>
<td>0.0035±0.00021</td>
</tr>
</tbody>
</table>

Figure 6.10 Relationship between the coefficient ($\phi$) and the Young’s modulus of polymers ($Y_p$)

predict the enhancement of the Young’s modulus for these three composites. It can be concluded that higher Young’s modulus of semi-crystalline polymer is, higher the coefficient of load transfer and lower mismatch between CNTs and polymer matrix. This empirical relationship is only valid for the CNT/semi-crystalline polymer composites with an optimised crystalline layer surrounding CNTs. Figure 6.12 provides a comparison of the Young modulus of a CNT/PVA composite
without an optimised crystalline layer surrounding CNTs with the prediction. It is clear that the optimised crystalline layer surrounding CNTs for reducing the mismatch between CNTs and polymer matrix is extremely important.
Chapter 6 Study of thermal-induced crystalline interface for the load transfer in a carbon nanotube/polymer composite

Figure 6.11 Comparison of experimental data with the model prediction for and the CNT/polyester-based PU and the CNT/PVA composites with an optimised crystalline layer surrounding CNTs.

Figure 6.12 Comparison of experimental data with the model prediction for the CNT/PVA composites without an optimised crystalline layer surrounding CNTs. The experimental data are provided from the reference [188].
(2) Comparative study on the Young's modulus of MWCNT-OH/PCL composites before and after thermal treatments

In order to study the effect of the crystalline layers on the load transfer in this system, the Young's modulus of the PCL composites were obtained from the stress-strain curves. Two groups of samples for tensile testing were prepared by the compression moulding. Group A was prepared under very quick cooling rate (Untreated). The preparation of Group B followed the process of the isothermal crystallisation at the treating temperatures that are 14°C higher than $T_c$ (thermally treated). Figure 6.13 shows the Young's modulus of the PCL composites as function of nanotube volume fraction. Nanotube volume fraction was calculated from nanotube weight fraction based on the density of the nanotubes (2.15g/cm$^3$) and the PCL (1.05g/cm$^3$). It can be seen that the improvement in the Young's modulus of the thermally treated composites is higher than that of untreated.

![Figure 6.13 Young's modulus of the MWNCT/PCL composites as a function of the nanotube volume fraction (■: the thermally treated composites; ●: the untreated composites)](image-url)
composites. It indicates that the load transfer has been enhanced by the thermal treatment. According to the empirical equation above, the coefficient of interfacial load transfer $\phi$ could be calculated to be around 0.10374 (the Young’s modulus of the PCL was taken as 260 MPa) if an optimised crystalline layer surrounding CNTs is formed. In Figure 6.13, the dash line shows the theoretical prediction by the empirical equation as $\phi$ was taken as 0.10374. The gap between theoretically predicted and experimental values can be obviously seen. It discloses that the crystalline layer was thickened but not optimised as the compression moulding was used for the thermal treatment. This is because it was difficult for the compression moulding with an open system to provide a stable and accurate temperature for the thermal treatment. So it is difficult to exactly repeat the whole process of the isothermal crystallisation obtained by DSC in the compression moulding. The scanning of the samples prepared by the compression moulding

![DSC curves](image)

**Figure 6.14** DSC curves (a) of heat flow vs temperature as a function of the nanotube weight fraction. The samples are prepared using the compression moulding following the "14°C" rule.
was also performed in DSC to detect the existence of the crystalline layer. In the DSC curves shown in Figure 6.14, the tiny peak relating to the crystalline layer is not clear in comparison with that in Figure 6.5. Only a small shoulder is observed on the left of the melting peak. The coating thickness was roughly measured using built-in bar in the SEM images shown in Figure 6.15. Considering the nanotube diameter is 20-30nm, it is found that the coating thicknesses of the crystalline layers are not uniformly created using the compression moulding especially at high nanotube concentration, and most of the crystalline layers have a thickness of less than 20nm. In the system of the PVA, CIPP and polyester-based PU, it was disclosed that an optimised crystalline layer could be around 20nm [14][73]. From the DSC and OM analysis above, it was disclosed that the 0.1wt% nanotubes imposed most significant influence on the crystallisation rate and crystalline morphology. Here, the SEM image in Figure 6.15(a) shows the coating thickness uniformly grows to nearly 20nm at 0.1wt% nanotube. It was considered that the low incorporation of nanotubes could result in the ideal dispersion and slightly restrict the mobility of polymer chains. These two factors could make the growth of the crystalline layer surrounding the nanotubes easier even if the thermal environment of the compression moulding was not as “perfect” as DSC. That could be why the improvement of the Young’s modulus followed the theoretical prediction very well at low incorporation of the nanotubes, and the gap between theoretical and experimental values was bigger for the higher incorporation of the nanotubes.

6.3 Conclusions

In this work, the MWCNT-OHIPCL composites were prepared using solution method. It was found that the thermal treatment (or isothermal crystallization) was a feasible approach to form the crystalline layer surrounding the nanotubes in PCL melts. The Young’s modulus of the PCL composites was studied to understand the contribution of the crystalline layer to the load transfer between the CNTs and the
Chapter 6 Study of thermal-induced crystalline interface for the load transfer in a carbon nanotube/polymer composite

PCL matrix. We considered several conclusions could be drawn in this chapter finally: (1) the good dispersion of the MWCNTs-OH in the PCL matrix was achieved, however, the dispersion worsened with the incorporation of the nanotubes reached 2wt%; (2) the non-isothermal crystallisation showed that the $T_c$ increased with increasing incorporation of the nanotubes, and the $T_m$ and $\Delta H_m$ were almost unchanged. The $T_c$ of PCL increased by $\sim$11°C with the incorporation of 2wt% nanotubes; (3) the isothermal crystallisation showed the temperature, 14°C higher than the $T_c$, was an appropriate one to optimise the crystalline layer in
Study of thermal-induced crystalline interface for the load transfer in a carbon nanotube/polymer composite

Figure 6.15 SEM images of the (a) MWCNT-OH(0.1wt%)/PCL composite, (b) MWCNT-OH(0.5wt%)/PCL composite, (c) MWCNT-OH(1wt%)/PCL composite and (d) MWCNT-OH(2wt%)/PCL composite. All samples are prepared in the compression moulding following the "14°C" rule.

(4) the DSC and OM studies showed that the incorporation of 0.1wt% nanotubes significantly affected the rate of crystal growth and crystalline morphology. For more incorporation of the nanotubes, the rate of crystal growth
and crystalline morphology was less affected; and (5) the contribution of the crystalline layer to the load transfer was disclosed via the comparative study of the improvement in the Young's modulus of the composites before and after the thermal treatment.
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

7.1 Introduction

Carbon nanotubes (CNTs) have been considered as an ideal nanofiller to improve the mechanical [14][91], electrical [6][7] and thermal properties [27] of polymers. Very recently, the role of CNTs in polymer composites is strongly challenged by much cheaper graphene sheets, which have similar properties to CNTs [17][189]. It is very difficult to strip graphene sheets from graphite due to the strong bonding between the sheets. Introduction, by means of strong oxidation, of oxygenated groups into graphite can reduce this mutual bonding, allowing the exfoliation of graphite oxide (GO) in water by assistance of ultrasonication [190]. However, it has been found that GO cannot be exfoliated in organic solvents. Stankovich et al [191] used phenyl isocyanate to terminate oxygenated groups in GO and achieved single layer isocyanate-functionalised graphene sheets in DMF. Furthermore, Stankovich et al [192] yielded a homogenous dispersion of the isocyanate-functionalised graphene sheets in polystyrene solution, chemically restored the destructive carbon structure of the isocyanate-functionalised graphene sheets by hydrazine in polystyrene solution, and obtained electrically conductive polystyrene composites with a percolation threshold of 0.1vol%. McAllister et al [193] found that pre-treatment of GO by rapid thermal expansion can facilitate the exfoliation of the GO in an organic solvent. Ramanathan et al [15] found that these exfoliated graphite oxide sheets significantly improve the glass transition temperature of PMMA, and show a strong capability in the reinforcement of PMMA. Expandable graphite (EG), known as a graphite intercalation compound, is produced by intercalating sulfuric acid into natural flaked graphite via chemical or electro-chemical processes. It can expand up to a hundred times in volume at high temperature. Our previous report [194] disclosed that the GO prepared by the oxidation of EG can be exfoliated into graphite oxide nanoplatelets (GONPs) in
DMF by ultrasound directly. This type of GO was specifically called expandable graphite oxide (EGO) in order to differentiate it from the GO prepared from natural graphite. In this chapter, this new method was introduced. With this method, it is not difficult to prepare GONP/polymer composite with good dispersion of the GONPs in polymer matrix.

As discussed in the chapter of literature review, the strong interface generally includes non-covalent interface (the crystalline layer surrounding the nanofillers) and covalent interface (chemical bonding). Similar to last chapter, we firstly selected semi-crystalline PCL as polymer matrix to explore if a crystalline layer could be formed on the surface of the GONPs from the GONP/PCL melt under a specific thermal treatment. The relationship between this non-covalent interface and the mechanical performance of the composites was investigated. Oxygenated groups attached to the GONPs cannot only facilitate the dispersion but also provide active sites to form chemical bonding that is an ideal interface between the GONPs and appropriate polymers. PU is an appropriate polymer that can form the chemical bonding with the GONPs via the reaction between isocyanate groups in the end of PU chains and oxygenated groups on the GONPs. Therefore, another aspect of this chapter is to engineer a covalent interface between a NCO-terminated PU and the GONPs and investigate its contribution to the mechanical performance of the GONP/PU composites.

7.2 Results and discussion (Part A): characterisation of GONPs

The board scan XPS spectra of EG and EGO are shown in Figure 7.1. The elemental analysis illustrates that C/O atomic ratio (12.9) of EG is higher than that (2.7) of EGO, which confirms that oxidation of EG is successfully conducted by the Hummers method. The C 1s XPS spectra of EG and EGO demonstrated in Figure 7.2 also can confirm the degree of oxidation. The C 1s XPS spectrum of EG can be split into two peaks locating at 285eV and 287eV, respectively. Similarly, the C 1s XPS spectrum of EGO is split into three peaks (285eV, 287eV,
and 288eV). The peaks at 285eV, 287eV and 288eV are attributed to carbon atoms in different functional groups including the non-oxygenated ring C, the C in C-O bond and carbonyl C in C=O bond, correspondingly. It is calculated that weight percent of non-oxygenated C in EG (90.1%) is lower than that (58%) in EGO, which also can indicate the degree of oxidation.

Figure 7.1 Broad scan XPS spectra of EG (A) and EGO (B)
Figure 7.2 C 1s XPS spectra of EGO (A) and EGO (B).

Figure 7.3 shows digital pictures of the EG/DMF and EGO/DMF dispersions with a same concentration of 10mg/g taken after two months. In the EG/DMF dispersion, all EG powder is clearly observed to precipitate at the bottom of the glass container after ultrasonic treatment. It was found that the EGO/DMF dispersion can be long-term stabilized, and even there was no precipitates.
appeared at the bottom of the glass container. The digital pictures are the hand-touched evidence to prove the possibility that the EGO is able to be fully exfoliated in the organic solvent. Transmission Electron Microscopy (TEM) was employed to observe the existence of the GONPs in DMF. From the TEM images demonstrated in Figure 7.4, it can be seen that the EGO was fully exfoliated into the GONPs by ultrasonic treatment. Rouff et al used atomic force microscopy to identify the thickness of both GONPs in water and chemically modified GONPs in organic solvent as \( \sim 1 \text{nm} \) [191]. In the TEM images, the thickness of the GONPs cannot be exactly measured, but can be roughly identified as several nanometres. Interestingly, the structure of exfoliated GONPs is observed as well in TEM images. Since the edge of the GONPs layers is observed to be folded, toughness of the GONPs is confirmed to be extremely high. From the folded edge of the GONPs in the high magnification TEM images, the thickness of the GONPs can be estimated to be several nanometres.

Regarding the exfoliation of GO in organic solvents, Stankovich et al [191] assumed that strong hydrophilicity and interlayer hydrogen bonds formed by oxygen groups attached to neighboring layers of GO could prevent the entrance of organic solvent molecules into interlayer space of GO not as water. Based on this assumption, reaction between organic isocyanate and hydroxyl groups was applied to chemically treat GO, which results in the decrease of hydroxyl groups in GO. With the assistance of ultrasonic treatment, isocyanate-treated graphite oxide can be fully exfoliated in polar organic solvents.

EG consists of carbon layers intercalated by sulfuric acid, which is also named as graphite intercalation compounds [195]. Expandable graphite is made from natural flake graphite treated by chemical or electro-chemical process [195]. It has been reported that d-spacing of expandable graphite can be increased in comparison with natural graphite due to intercalation of a variety of atoms and molecules [196][197]. Compared to nature graphite, it is reasonably assumed that oxidant
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

Figure 7.3 Digital pictures of expandable graphite /DMF (left) and expandable graphite oxide /DMF dispersions (right).

used in Hummers method can enter into interlayer space of EG more easily. Combined with the original intercalated oxidant such as sulfuric acid, EG is supposed to be introduced more functional groups into the inner galleries between carbon layers than natural graphite. The functional groups inside galleries and increased d-spacing presumably make the graphite oxide prepared by EG more accessible to organic solvents without any chemical treatment.

Figure 7.5 shows the XRD patterns of EG powder (Short Dash Dot), EGO powder (Short Dash) and EGO/DMF dispersion (Solid). The diffraction peak at about \(2\theta=10.9^\circ\) corresponding to the (001) plane reflection of GO is lower than the diffraction peak at about \(2\theta=26^\circ\) to EG, which confirms the successful oxidation of EG as well as the XPS results. From comparison between the X-ray diffraction patterns of EGO powder and EGO/DMF dispersion, it could be concluded that
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

EGO has been fully exfoliated in DMF due to the absence of diffraction peak of EGO.

Figure 7.4 TEM images of exfoliated graphite oxide nanoplatelets in DMF

Figure 7.5 X-ray diffraction patterns of EG powders, EGO powders and GONP/DMF dispersion
7.3 Results and discussion (Part B): GONP/PCL composites

7.3.1 Uniform dispersion of GONPs in PCL matrix

The fully exfoliation of the GONPs in DMF had been discussed above. The SEM images shown in Figure 7.6 prove that the GONPs are successfully incorporated into PCL matrix at nanoscale level. However, it has to point out that, it is very difficult to achieve single layer graphene sheets with 1nm thickness in PCL matrix although the fully exfoliation has been done in the organic solvent.

Figure 7.6 SEM images of the GONP(0.1wt%)/PCL composite (a), the GONP(0.5wt%)/PCL composite (b), the GONP(1wt%)/PCL composite (c) and the GONP(2wt%)/PCL composite (d)
7.3.2 Non-isothermal crystallisation of GONP/PCL composites

The non-isothermal DSC curves of the GONP/PCL composites are shown in Figure 7.7, in which it can be seen that the crystallisation temperature ($T_c$) of PCL is increased as the addition of GONPs increases up to 2wt%. Table 7.1 presents all data collected from the DSC curves including the crystallisation temperature ($T_c$), melting temperature ($T_m$) and fusion of heat ($\Delta H$). The $T_c$ of PCL displays a big increase by $\sim 9^\circ$C as 2wt% GONPs is incorporated. The $T_m$ and $\Delta H$ of all composites were found to be almost unchanged. Non-isothermal crystallisation kinetics was further analyzed based on the crystallisation peaks in DSC curves (Figure 7.7), whose results are shown in Figure 7.8. It can be seen that the non-isothermal crystallisation rate of the GONP/PCL composites gradually slows down with increasing incorporation of the GONPs. Therefore, it is clear to see that the GONPs can act as nucleating agents in the semi-crystalline PCL, and the GONPs impose strong restriction on the mobility of polymer chains to form crystalline structures. These results were similar to those found in the CNT/PCL.
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

composites. We considered that the quick cooling rate could be the reason for the failure of forming the crystalline layer on the surface of the GONPs although the nucleation of the GONPs was obvious. The following investigation would focus on the isothermal crystallisation of the GONP/PCL composites with slower crystallisation rate in comparison with the non-isothermal crystallization.

Figure 6.8 Non-isothermal crystallisation kinetics of the GONP/PCL composites

Table 7.1 Non-isothermal crystallisation parameters of the GONP/PCL composites

<table>
<thead>
<tr>
<th></th>
<th>Tc(°C)</th>
<th>Tm(°C)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>28.7</td>
<td>58.1</td>
<td>56.1</td>
</tr>
<tr>
<td>0.1%GONP/PCL</td>
<td>33.1</td>
<td>57.42</td>
<td>57.5</td>
</tr>
<tr>
<td>0.5%GONP/PCL</td>
<td>34.0</td>
<td>57.11</td>
<td>57.6</td>
</tr>
<tr>
<td>1%GONP/PCL</td>
<td>35.7</td>
<td>57.69</td>
<td>58.2</td>
</tr>
<tr>
<td>2%GONP/PCL</td>
<td>37.8</td>
<td>57.25</td>
<td>58.4</td>
</tr>
</tbody>
</table>
7.3.3 Isothermal crystallisation of GONP/PCL composites

In chapter 6, it had been revealed that the isothermal crystallisation under a specific temperature could create a polymer crystalline layer surrounding the nanotubes in the composite melts. The nucleating ability of the nanotubes is the original cause of this phenomenon. Non-isothermal crystallisation analysis above disclosed that the GONPs can take the nucleating role in the PCL as well as the nanotubes, but the nucleated crystalline layer cannot be optimised at very quick cooling rate in the GONP/polymer composites. Here, we did a similar study on the isothermal crystallisation of the GONP/polymer composites. Based on the $T_c$, three temperatures were selected to do the isothermal crystallisation to find out an appropriate crystallisation temperature to optimise the crystalline layer on the surface of the functionalised graphene sheets, which were 42°C, 49°C and 52°C. As shown in Figure 7.9, it can be seen that a new peak on the shoulder of the

![Figure 7.9](image)

**Figure 7.9** DSC curves of heat flow vs temperature after completion of the isothermal crystallisation of the GONP(2wt%)/PCL composite at three temperatures
Figure 7.10 DSC curves of the GONP/PCL composites after completion of isothermal crystallization. The isothermal crystallizations were performed based on the "14°C" rule for all samples.

melting peak appears increasingly big as the treating temperature increases, which, as we discussed before, could be attributed to the formation of the crystalline layer with a certain thickness the surface of the graphene sheets. It is interesting to find out that the "14°C" rule could be suitable for optimising the crystalline layer in the GONP-PCL interface. As the "14°C" rule was applied to thermally treat other GONP/PCL composites, Figure 7.10 shows the DSC curves (heat flow vs temperature) of the GONP/PCL composites after the thermal treatment. It also can be been that the area of the tiny peak on the shoulder of typical peak of PCL appears increasingly large as a function of GONP concentration. Table 7.2 shows the ΔH and Tm obtained from the rescanning DSC curves after the completion of the isothermal crystallization. Considering the crystallinity $\chi_c = \Delta H / \Delta H^0$ ($\Delta H^0$ is the heat of fusion for 100% crystallisation of PCL, which was taken as 136J/g [198]). Figure 7.11 shows nearly linear increase in the crystallinity ($\chi_c$) with the
incorporation of the GONPs in the range of 0% and 1wt%. At 2wt% GONPs, the worsening dispersion could be reason that $\chi_e$ fails to follow the linear increase. Conclusively, DSC study on the non-isothermal and isothermal crystallisation showed that the crystalline layer could be thermally induced on the surface of the 2D graphene sheets under a specific thermal treatment. It is interesting to see all these phenomena have been similarly observed in the CNT/polymer composites. It seems that the "14°C" rule is suitable for this PCL material to form optimised crystalline layers on the no matter 1D nanotubes or 2D graphene sheets from the composite melts. The difference between two systems is that the crystallinity of the CNT/PCL composites does not increase with increasing incorporation of the CNTs. This could be attributed to the dimensional difference between 1D nanotube and 2D graphene sheets. In chapter 6, templating mechanism of CNTs for polymer strands was discussed. We considered that the templation of polymer strands on the surface of 2D graphene sheets could be different although the theoretical study in this field has not been disclosed. The theoretical investigation on the templating mechanism of 2D graphene sheets is not in the scope of this thesis. The following studies using OM and DSC experimentally disclose the effect of 2D graphene sheets on the morphology of the PCL crystals, which is different from that of 1D nanotubes.

<table>
<thead>
<tr>
<th>Table 7.2 Isothermal crystallisation parameters of the GONP/PCL composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>PCL</td>
</tr>
<tr>
<td>0.1wt%GONP/PCL</td>
</tr>
<tr>
<td>0.5%GONP/PCL</td>
</tr>
<tr>
<td>1wt%GONP/PCL</td>
</tr>
<tr>
<td>2wt%GONP/PCL</td>
</tr>
</tbody>
</table>
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

Figure 7.11 Relationship between the crystallinity ($\chi_c$) and GONP concentration (wt%). Straight line is for eye guide.

7.3.4 Morphological study of the PCL crystals in GONP/PCL composites

Polarised optical microscope (POM) was used to observe the morphology of the PCL crystals in the composites, which is shown in Figure 7.12. In Figure 7.12b, it can be seen that the morphology of the PCL spherulites is slightly affected with the incorporation of 0.1wt% GONPs. In Figure 7.12 (c-e), it can be obviously seen that the size of crystals is much smaller in the composites in comparison with the pure PCL, which is due to the nucleating role of the GONPs in PCL matrix. It is interesting to see that 0.1wt% GONPs does not impose the most significant influence on the morphology of the crystals, which is different from the CNT-based composites. We considered it could be result of the geometrical difference between the graphene sheets and nanotubes, and the long 1D nanotubes show stronger nucleating ability than wide 2D graphene sheets. Here, we also used Avrami equation which was introduced in chapter 6 (Page 119) before to analyze the kinetics of the isothermal crystallisation. The relationship between $X(t)$ and $t$ is
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

Figure 7.12 Optical microscopy images of the (a) PCL, (b) GONP(0.1wt%)/PCL composite, (c) GONP(0.5wt%)/PCL composite, (d) GONP(1wt%)/PCL composite and (e) GONP(2wt%)/PCL composite taken by built-in digital camera during the isothermal crystallisation that follows the "14°C" rule for all samples. (20μm ——) plotted in Figure 7.13. All data inside were fitted into Avrami equation using Origin software to obtain the values of n and K, as shown in Table 7.3. The decrease in K obviously confirms that the incorporation of the GONPs slow down the growth rate of crystals, although the GONPs act as nucleates in the PCL matrix.
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

Table 7.3 Avrami parameters (n and K) of the GONP/PCL composites

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>3.03±0.01</td>
<td>0.00389±0.0001</td>
</tr>
<tr>
<td>0.1%GONPs/PCL</td>
<td>2.71±0.02</td>
<td>0.00061±0.00003</td>
</tr>
<tr>
<td>0.5%GONPs/PCL</td>
<td>2.57±0.01</td>
<td>0.00099±0.00003</td>
</tr>
<tr>
<td>1%GONPs/PCL</td>
<td>2.41±0.01</td>
<td>0.00046±0.00002</td>
</tr>
<tr>
<td>2%GONPs/PCL</td>
<td>1.75±0.00</td>
<td>0.00084±0.00000</td>
</tr>
</tbody>
</table>

Figure 7.13 Relative crystallinity $\chi_c$ as a function of time for the GONP/PCL composites

This supports the kinetic of the non-isothermal crystallization. We considered that the strong restriction of 2D graphene sheets on the mobility of polymer chains is the result of slowing down the growth rate. n overall decreases with increasing incorporation of the GONPs. As the incorporation of the GONPs is below 1wt%, the value of n is always above 2, which indicates the shape of crystals is like disc. At 2wt% GONPs, the value of n is around 1.75, which reflects the mixed shapes of
crystals (rod and disc). It indicates that a part of crystals grow in one-dimensional direction along the surface of the functionalised graphene sheets. Again, it is interesting to see the difference in the crystallisation behaviour between the CNT-based and GONP-based composites as the nanotubes could be considered as the rolling-up of the graphene sheets.

7.3.5 Comparative study on the Young’s modulus of the GONP/PCL composites before and after the thermal treatments

Two groups of samples for tensile testing were prepared by hot compression. Group A is prepared under very quick cooling rate (Untreated). The preparation of Group B followed the process of the isothermal crystallisation under the preset temperatures, 14°C higher than T_c (thermally treated). Figure 7.14 shows the Young’s modulus of PCL composites as a function of GONP weight fraction. It can be seen that the improvement in the Young’s modulus of thermally treated composites (●) is higher than that of untreated composites (■), which could

![Graph showing Young's modulus vs GONP weight fraction](image_url)

*Figure 7.14 Young’s modulus of the GONP/PCL composites as function of GONP weight fraction. ■ represents the samples without the thermal treatment; ●*
experimentally indicate that the crystalline layer on the surface of the GONPs makes significant contribution to the load transfer. The Young’s modulus of the treated composite with 2wt% GONPs increases by nearly 64% and the untreated one displays a nearly 32% increase in the Young’s modulus. The improvement in the Young’s modulus almost doubled after the thermal treatment. Physical mechanism of the load transfer across the crystalline interface between the CNTs and polymer matrix had been detailed discussed. Here, we found this transferring mechanism is available to explain the higher improvement in the Young’s modulus of the GONP/PCL composites with an optimised crystalline interface. The samples treated in compression moulding were also scanned using DSC at a heat rate of 5°C. The DSC curves in Figure 7.15 show, to some extent, the similarity with the DSC curves in Figure 7.10. The similarity is placed on the small melting peak attributed to the crystalline layer on the shoulder of the typical melting peak. It

![DSC curves](image)

**Figure 7.15** DSC curves (a) of heat flow vs temperature as a function of GONP weight fraction. The samples are prepared using compression moulding following the “14°C” rule.
indicates that the thermal treatment in compression moulding could works out the crystalline layers on the surface of the GONPs as the sheet samples are being prepared. It also needs to point out that it is difficult to exactly copy the whole process of the thermal treatment in the DSC cell to the compression moulding machine with an open system. represents the sample with thermal treatment following the “14°C” rule.

7.4 Results and discussion (Part C): GONP/PU composites

7.4.1 Morphology of the GONP/PU composites

The dispersion of the GONPs in the PU matrix did not present difficulties since in our previous work we succeeded in fully exfoliating the GONPs in DMF. The SEM images of the fracture surface in Figure 7.16(b and c) show the layer-structured GONPs are dispersed in the PU matrix with nanoscale thickness.

Figure 7.16 SEM images of the PU (a) and the 4.4wt%GONP/PU composite (b,c)
Figure 7.17 MDSC curves of heat flow against temperature: (a) the PU; (b) the 4.4wt%GONP/PU composite

PU is a polymer well-known for its two-phase microstructure containing alternative soft and hard segments. It was revealed that the hard segment with glassy or a lamellar crystalline structure acts as physical crosslinkers for the rubbery soft segment in PU [199]. Phase separation resulting from the thermodynamic incompatibility between the soft and hard segment plays a key role in their versatile physical properties. Thermal analysis and infrared spectra were used to investigate the effect of the GONPs on the phase separation. Firstly, MDSC was used to investigate the effect of the GONPs on the hard segment. In Figure 7.17, line (a) shows that the melting-like transition temperature relating to the hard segment of the PU appears around 200°C. As the incorporation of the GONPs increases to 4.4wt%, it can be seen in line (b) that the melting-like transition completely disappears and is replaced by recrystallisation transition. This finding indicates that a sufficient amount of the GONPs can even result in damage to the crystalline structure of the hard segment, which may be due to the
fact that the two dimensional structure of large graphene sheets prevents the formation of the lamellar structure in the hard segment. DMA was further used to investigate the interaction between the GONPs and the soft segment. Figure

![Graph showing storage modulus and damping factor as a function of temperature](image)

**Figure 7.18** Storage modulus (A) and damping factor tanδ (B) of the PU (a) and 4.4wt%GONP/PU composite (b) as a function of temperature
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

7.18A shows that the storage modulus of the PU composite containing 4.4wt% GONPs is about 30% higher than that of the PU at -60°C. Figure 7.18B shows no shift in the transition peak of damping factor (tanδ) associated with the glass transition temperature of the soft segment, which demonstrates the interaction between the GONPs and the soft segment is very weak. However, the huge decrease in damping capacity (amplitude of tan δ) indicates the greatly restricted motion of PU chains, resulting from the crosslinking function of the GONPs for isocyanate-terminated PU chains. Cooper et al. provided a method to estimate the phase separation using FTIR technique [200]. The degree of phase separation (DPS) can be calculated by an equation: DPS=R/(R+1) [201]. R in the equation represents hydrogen bonding index, which can be defined as A_{1701}/A_{1726}. The peak at 1701 cm\(^{-1}\) is attributed to hydrogen bonded –C=O and the peak at 1726 cm\(^{-1}\) belongs to free –C=O. Figure 7.19 shows the FTIR spectra of the PU and 4.4wt%GONP/PU composite. The area of the peaks around 1701 cm\(^{-1}\) and 1726 cm\(^{-1}\) were calculated by Microcal Origin software. R and DPS of the PU are

![FTIR spectra](image)

**Figure 7.19** FTIR spectra of the PU (a) and 4.4wt%GONP/PU composite (b). R is hydrogen bonding index and DPS is the degree of phase separation.
valued as 1.7 and 0.63, respectively, and those of the PU composite are equal to 1.3 and 0.57, respectively. This indicates that the reduction of the phase separation is caused by the incorporation of the GONPs. The GONPs, therefore, perform two roles in respect of the morphology of the PU: (1) the chemical crosslinker for isocyanate-terminated PU; and (2) the destroyer of the crystalline hard segment. These two roles affect the mechanical properties of the PU in opposite ways.

7.4.2 Mechanical properties of the GONP/PU composites

The mechanical properties were comprehensively obtained from tensile and nanoindentation tests. Figure 7.20 shows the typical stress-strain curves of the PU and 4.4wt%GONP/PU composite. Figure 7.21 illustrates the mechanical properties of the PU and 4.4wt%GONP/PU composites including Young’s modulus, elongation at break and tensile strength. It can be clearly seen that the Young’s modulus of the PU composite is nearly ten times higher than that of the pure PU, which can be attributed to efficient load transfer between the GONPs and the PU matrix resulting from the chemical bonding. About 60% decrease in the elongation at break occurs with the incorporation of 4.4wt% GONPs, which is in agreement with DMA results with regard to the reduction of the damping capacity. This means the elastic deformation can be reduced due to the crosslinking of PU chains by the GONPs. The tensile strength decreases nearly 19% with the incorporation of 4.4wt% GONPs, which is unexpected but understandable. As mentioned above, the GONPs play two roles in the two-phase microstructure of the PU, which affects the tensile strength in two opposing ways. The destruction of the hard segment that means a reduction of physical crosslinking for the rubbery soft segment dominates the decrease in the tensile strength in this specific case. Nanoindentation that refers to depth-sensing indentation testing is a useful technique to measure the mechanical properties of polymer composites in small dimension using nano-sized or micro-sized indenters. Figure 7.22 shows the nanoindentation results in terms of hardness and elastic modulus. With the
Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

Incorporation of 4.4wt% GONPs, the hardness and elastic modulus increases ~327% and ~182%, respectively, which show the similarity with the varying trend of the Young's modulus. In nano-scratch test, the scratch depth of the indenter in the sample was recorded along with the scratch length at a certain scratch rate, which reflects the protective ability of the surface coatings for the substrates. Figure 7.23 shows the scratch depth profiles of the PU and 4.4wt%GONP/PU composites against the scratch length. At a scratch rate of 3μm/s, the curve of the PU in Figure 7.23A reveals a scratch depth of about 2790nm at a scratch length of 100μm. The incorporation of 4.4wt% GONPs results in a nearly 80% decrease of the scratch depth to about 845nm at the same scratch length. At a scratch rate of 5μm/s, the scratch depth also decreases nearly 80% with the incorporation of 4.4wt% GONPs, as shown in Figure 7.23B. This characteristic makes the GONP/PU composite show strong potential in protecting metallic surface, such as airplanes and wind turbines.

Figure 7.20 Typical strain-stress curves of the PU and 4.4wt%GONP/PU composites
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

**Figure 7.21** Mechanical properties of the PU and 4.4wt%GONP/PU composite

**Figure 7.22** Nanoindentation results of the PU and 4.4wt%GONP/PU composites
Chapter 7 Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotub...}

Figure 7.23 Nano-scratch depth profiles for the PU and 4.4wt%GONP/PU composite at a scratch rates of 3μm/s(A) and 5μm/s(B), respectively.

7.4 Conclusions

In this chapter, our main objective was to find out a strong substitute for CNTs in
Chapter 7  Graphite oxide nanoplatelets: a strong and affordable substitute for carbon nanotubes in mechanical reinforcement of polymers

the mechanical reinforcement of polymers, which is GONPs also named as functionalised graphene sheets. In the first part, we focused on the fabrication of the exfoliated GONPs in an organic solvent. This step is quite vital for the preparation of polymer composites with good dispersion of the GONPs. It was discovered that the expandable graphite oxide can be directly exfoliated in DMF with the assistance of ultrasonication. The expandable graphite oxide was prepared using Hummer’s method, in which expandable graphite was used as starting materials instead of natural graphite. This method is much simpler than some published methods. With this method in hand, two kinds of polymers including semi-crystalline PCL and amorphous PU were selected to be incorporated with the GONPs using the solution method.

The creation of the crystalline layer was considered as a promising way to engineer a strong non-covalent interface for the load transfer. In the GONP/PCL composites, the crystallisation behaviour was mainly studied to find out a suitable thermal treatment to engineer a strong semi-crystalline interface for the load transfer. The study on the non-isothermal crystallisation illustrated that the GONPs showed strong nucleating ability in the PCL matrix, but would slowed down crystallisation rate of the PCL. The isothermal crystallisation behaviour showed that the thermal treatment under the “14°C” rule could be available to create an optimised crystalline layer on the surface of the GONPs from the composite melts, which was quite similar to that found in the CNT/PCL composites. The increase in the Young’s modulus of the treated GONP/PCL composites confirmed that the crystalline layer nucleated on the surface of the GONPs makes significant contribution to the load transfer across the non-covalent interface.

In the GONP/PU composites, the GONPs bearing oxygenated groups had the innate ability to form the chemical bonding with the isocyanate-terminated PU, which led to a significant increase in modulus and hardness. It was observed that the GONP/PU composites exhibited a marked improvement in anti-scratch
property, which is a key requirement of surface coatings. It was also found that the two-dimensional structure of large graphene sheets resulted in the destruction of the ordered hard segment and in decrease in the tensile strength. Nevertheless, this two-dimensional structure has its advantages, mainly improvement of barrier properties, which is another key requirement of surface coatings. In conclusion, the GONPs can be a powerful and affordable nanostructured material in the development of high performance surface coatings.
Chapter 8 Conclusions and future work

8.1 Conclusions

This project mainly concerned the development of novel engineering approaches to optimise the physical properties of the polymer composites with low incorporation of carbon nanotubes (CNTs).

Considering the fabrication of semi-conductive CNT/polymer composites, the colloidal physics and coating methods were applied to fabricate semi-conductive CNT/polymer composites with low percolation threshold. PU latex and UHMWPE powder was used in the colloidal physic and coating method, respectively. The core idea of these two methods is to engineer a unique micro-structure in which the settlement of CNTs in polymer matrix is limited to boundary area since particulate hosts are exclusive for CNTs. The percolation threshold of the MWCNT/PU composites prepared by the colloidal physical method and MWCNT/UHMWPE composites prepared by the coating technology were both lowered to around 0.5wt%.

A universal recognition that the interfacial phonon scattering that is hardly eliminated is the bottleneck for CNTs to perform as ideal thermal conductors in the polymer composites has been compromised. How to reduce the interfacial phonon scattering technically is regarded as a big challenge for the development of the thermally conductive CNT/polymer composites. Latex technology has been applied to fabricate the electrically conductive composites with very low percolation threshold. Here, latex technology was applied to achieve high improvement of the thermal conductivity. It was found that the thermal conductivity almost was tripled with the incorporation of 3wt% MWCNTs into the semicrystalline PCL-based PU, whereas the incorporation of 7wt% MWCNTs only resulted in a nearly 86% increase in the thermal conductivity of the amorphous polyether-based PU. The continuous nanotube-rich phase and polymer
crystallites nucleated at interface were two main factors for the effective reduction of the interfacial phonon scattering. It convinces that latex technology will be a simple and promising route ahead to functional CNT/polymer composites.

The polymer crystalline layer nucleated by CNTs was considered as one kind of strong interface for the load transfer. In this project, the study on the crystallisation behaviour of the CNT/PCL composites showed that the isothermal crystallisation at the temperature, 14°C higher than the $T_c$, could optimise the crystalline layer surround the CNTs from the composite melts. An empirical equation was proposed to predict the improvement in the Young's modulus of the CNT/polymer composites with an optimised crystalline layer, in which the coefficient of the interfacial load transfer was used to measure the transfer efficiency of the semi-crystalline interface. It was found that the coefficient of the thermally treated CNT/PCL composite was obviously improved in comparison with that of the composites without the thermal treatment.

Finally, it was revealed that the functional graphene sheets could be a strong and affordable substitute for CNTs in the mechanical reinforcement of polymers. Two kinds of polymers including semi-crystalline PCL and amorphous PU were selected to be incorporated with the GONPs using the solution method. In the GONP/PCL composites, the study on the isothermal crystallisation showed that the thermal treatment under the “14°C” rule could be available to create an optimised crystalline layer on the surface of the GONPs from the composite melts, which is quite similar to that found in the CNT/PCL composites. The role of the crystalline layer as a strong non-covalent interface was confirmed by the increase in the Young’s modulus of the treated GONP/PCL composites. In the GONP/PU composites, the GONPs bearing oxygenated groups have the innate ability to form chemical bonds with the isocyanate-terminated PU, leading to a significant increase in modulus and hardness. The GONP/PU composites exhibited a marked improvement in anti-scratch property, which is a key requirement of surface
coatings. It was also found that the two-dimensional structure of large graphene sheets resulted in the destruction of the ordered hard segment and in decrease in the tensile strength. Nevertheless, this two-dimensional structure has its advantages, mainly improvement of barrier properties, which is another key requirement of surface coatings. We believe that the GONPs can be a powerful and affordable nanostructured material in the development of high performance surface coatings.

### 8.2 Future work

Outcomes of this project has led us to have better understanding the relationship between the microstructure and the physical properties of the composites, which could guide us to fabricate high performance CNT/polymer composites for the industrial application. However, the biggest challenge is placed on moving forward to industrial application from laboratorial experiment. To my best knowledge, the methods developed in labs are still complicated for industrial users, and simplifying processing methods for achieving uniform dispersion and strong interface could be the developing direction in this field.

In the aspect of the semi-conductive polymer composites, the tunnelling behaviour is still being the challenge for the maximizing the electrical conductivity of the composites although the very low percolation threshold was achieved. The low value of the maximal electrical conductivity could restrict the application of this functional material such as the bipolar plate which is a key component in fuel cells.

Similarly, the improvement of the thermal conductivity also needs to be maximized, which relates to the maximal reduction of the interfacial phonon scattering. This strategy could be implemented as we could control the morphology of the crystallites in the interface such as the thickness of the crystallites. The modelling work could help understand the relationship between
the morphology of the crystallites and the reduction of the interfacial phonon scattering.

In regard to the mechanical reinforcement, the work could be extended to study the mechanical behaviour of the composites under high strain rates. It could point out the application of the polymer composites in the military protection such as body armour.

The research on the GONP/polymer composite is still in its early stage. The exciting results found in this stage drive us to dig out more application of this new nanomaterial in the polymer composites.
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