PHYSICAL AND CHEMICAL MODIFICATIONS OF CARBON NANOTUBES FOR THE DEVELOPMENT OF ADVANCED POLYMER NANOCOMPOSITES

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Abstract

There is a great need for advanced functional materials such as light-weight and high strength materials, super capacitive materials, highly conductive materials for many advanced engineering applications. Carbon nanotube (CNT)/polymer composites are a new class of materials with a wide range of properties for engineering applications. However, the major challenges for CNT/polymer composites are to attain a uniform dispersion of CNTs in polymer matrices and an efficient interfacial adhesion between CNTs and matrices.

Therefore, the objective of this thesis is to fabricate CNT/polymer composites for various engineering applications using a melt-mixing technique. The modifications, such as physical and chemical functionalisations, of multiwalled carbon nanotubes (MWCNTs) were also made. The properties of the CNT/polymer composites, such as electrical, thermal, mechanical, morphological and rheological properties, and the relevant mechanisms have been studied systematically. The improved interfacial adhesion between MWCNTs and a matrix polymer as well as the uniform dispersion of MWCNTs in the polymer matrix were achieved by means of functionalisations of MWCNTs. Moreover, a complementary effect between MWCNTs and conductive carbon black (CCB) was found to promote the formation of electrically conductive network of the carbon fillers in the polymer matrix, resulting in a dramatic increase in the electrical conductivity of the resultant composites.
Acknowledgement

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[8] N. G. Sahoo, H. K. F. Cheng, H. Bao, Y. Pan, L. Li, S.H. Chan, J. Zhao,


# List of Abbreviations

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<td>Alternating current</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2,1-azobisisobutyronitrile</td>
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<td>ATRP</td>
<td>Atom transfer radical polymerisation</td>
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<tbody>
<tr>
<td>CCB</td>
<td>Conductive carbon black</td>
</tr>
<tr>
<td>CED</td>
<td>Cohesive energy density</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>-COOH</td>
<td>Radical of carboxylic acid</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethyl ammonium</td>
</tr>
<tr>
<td>CTVB</td>
<td>Cetyl trimethylammonium 4-vinylbenzoate</td>
</tr>
</tbody>
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## D

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DTAB</td>
<td>Dodecyltrimethylammonium bromide</td>
</tr>
</tbody>
</table>

## E

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ET</td>
<td>Ethylene acrylate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>H</td>
<td>Radical of hydroxyl benzoic acid</td>
</tr>
<tr>
<td>HiPCO</td>
<td>High pressure carbon monoxide</td>
</tr>
<tr>
<td>HTAB</td>
<td>Hexadecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>iPP</td>
<td>Isotatic polypropylene</td>
</tr>
<tr>
<td>LCMN</td>
<td>Liquid crystalline polymer composite with hydroxyl functionalised multiwalled carbon nanotube</td>
</tr>
<tr>
<td>LCR meter</td>
<td>Inductance, capacitance and resistance meter</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer by layer</td>
</tr>
<tr>
<td>LCP</td>
<td>Liquid crystalline polymer</td>
</tr>
<tr>
<td>LDS</td>
<td>Lithium dodecyl sulphate</td>
</tr>
<tr>
<td>MTS</td>
<td>Mica-type silicates</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multiwalled carbon nanotube</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>Hydroxyl functionalised multiwalled carbon nanotube</td>
</tr>
</tbody>
</table>
MWCNT-HBA  Hydroxyl benzoic acid functionalised multiwalled carbon nanotube
MWCNT/NaDDBS  Sodium dodecyl benzene sulphonate treated multiwalled carbon nanotube
MWCNT/SDS  Sodium dodecylsulphate treated multiwalled carbon nanotube

N
NaDDBS  Sodium dodecyl benzene sulphonate

O
-OH  Hydroxyl radical

P
PA6  Polyamide 6 (Nylon 6)
PAB  Polyamide 6 composite with conductive carbon black
PABN  Raw multiwalled carbon nanotube/polyamide 6 composite with 10 wt% conductive carbon black
PAMN  Polyamide 6 composite with hydroxyl functionalised multiwalled carbon nanotube
PAN  Polyamide 6 composite with raw multiwalled carbon nanotube
PANI  Polyaniline
PASN  Polyamide 6 composite with sodium dodecylsulphate treated multiwalled carbon nanotube
PE  Polyethylene
PLMN  Liquid crystalline polymer/polyamide 6 blend composites with hydroxyl functionalised multiwalled carbon nanotube
PMMA  Poly(methyl methacrylate)
PP    Polypropylene
PPCN  Polypropylene composite with sonicated multiwalled carbon nanotube
PPMN  Polypropylene composite with hydroxyl functionalised multiwalled carbon nanotube
PPN   Polypropylene composite with raw multiwalled carbon nanotube
PPNN  Polypropylene composite with sodium dodecyl benzene sulphonate treated multiwalled carbon nanotube
PPSN  Polypropylene composite with sodium dodecylsulphate treated multiwalled carbon nanotube
PPy   Polypyrrole
PS    Polystyrene
PU    Polyurethane
PVA   Poly(vinyl alcohol)

S
SC    Sodium cholate
SDC   Sodium deoxycholate
SDS   Sodium dodecylsulphate
SLS   Sodium lauryl sulphate
STDC  Sodium taurodeoxycholate
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TETA</td>
<td>Triethylene tetramine</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TTAB</td>
<td>Tetradecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Background

Carbon nanotube/polymer composites are a new class of materials which has a wide range of properties for various applications. Moreover, the research and development of carbon nanotube/polymer composites have greatly increased in recent years for several reasons. The main reason is related to the discovery of carbon nanotubes (CNTs) by Iijima in the early 1991.\textsuperscript{[1]} Subsequently, the polymer nanocomposite using CNTs as fillers was firstly reported by Ajayan in 1994,\textsuperscript{[2]} followed by many researchers over the world. Besides, some of the CNT/polymer composites were reported showing unpredicted combinations of properties due to the unique properties of CNTs.\textsuperscript{[3]} Finally, recent significant development in chemistry (such as chemical modifications of CNTs), which has also created an almost unrestricted possibility to improve the interfacial interaction between CNTs and a polymer matrix, has brought to the remarkable control over the morphology of such CNT/polymer nanocomposites.

For those reasons, this is an appropriate time to study CNT/polymer composites, not only due to their outstanding combinations of properties but also due to their high potential for successful commercial development of advanced materials. Unfortunately, CNTs usually agglomerate themselves due to the van der Waals forces among them and as a result, it is extremely difficult to disperse CNTs in a polymer matrix. Therefore, the main challenges in developing high performance CNT/polymer composites are to improve the dispersion of CNTs in polymer matrices and to enhance the interfacial adhesion between CNTs and polymers. Surface modification of CNTs seems to be a straight-forward method to prevent CNTs from aggregation, which helps not only to
disperse but also stabilise the CNTs within a polymer matrix. More precisely, the chemical modification of CNTs may greatly modify the interactions at the CNT-polymer interface and thus solves the issue of weak interfacial adhesion.\textsuperscript{[4]}

Therefore, in this thesis, the advanced ways to attain a uniform dispersion of CNTs in a polymer matrix and to achieve an effective molecular interaction between CNTs and polymer molecules will be focused. In addition, the important factors of the fabrication of carbon nanotube/polymer composites will be discussed. Moreover, the carbon nanotube/polymer composites developed in this work are targeted to be used in various applications such as interior parts for aerospace and naval industries, printed circuit boards and housings for electronic devices, and bipolar plates for low-temperature fuel cells.

1.2 Objective and scope

The main objectives of this project are:

1. To develop high-performance carbon nanotube/polymer nanocomposites by modifying carbon nanotubes either physically or chemically, and/or by optimising the processing methods and parameters, and

2. To characterise the properties of such polymer nanocomposites to understand various effects and their relevant mechanisms.
Therefore, the scope of the project consists of three parts as follows.

1. Modifications of carbon nanotubes

   The modification of CNTs is done by two ways: either physically or chemically. Physical modification of carbon nanotubes mainly involves surfactants. Two types of anionic surfactants, namely sodium dodecylsulphate (SDS) and sodium dodecyl benzene sulphonate (NaDDBS), are used in this study. Besides, the physically modification of carbon nanotubes using conductive carbon black (CCB) is performed to study the complementary effect between the CNTs and the CCB in their polymer composites. For the chemical modification of carbon nanotubes, carbonxyl-functionalisation (-COOH) of CNTs, is firstly used, then followed by the hydroxyl benzoic acid (HBA) functionalisation of CNTs as an innovative and specific approach. This is the unique and foremost achievement for the carbon nanotubes being chemically attached with the hydroxyl benzoic acid (HBA) groups on their surfaces.

2. Fabrication and characterisation of CNT/polymer composites

   As properties of CNT/polymer composites strongly depend on the dispersion of CNTs in polymer matrices and the interaction between CNTs and polymer molecules, this part concerns the effect of fabrication methods on CNT/polymer nanocomposites and the characterisations of the nanocomposites for understanding of relationships among composition, dispersion and property. The characterisations include mechanical, electrical, thermal, optical, rheological and morphological properties.
3. Study of different factors influencing the properties of CNT/polymer composites

The following factors influencing the properties of CNT/polymer composites are systematically studied.

(1) Surfactants

(2) Chemical functionalisations of carbon nanotubes

(3) Processing methods

(4) Compatibilising effect of chemically functionalised carbon nanotubes

(5) Complementary effect of carbon nanotubes and conductive carbon black.

1.3 Structure of the thesis

This thesis comprises nine chapters. The review on the history of CNT/polymer composites, the surface modifications of CNTs, the processing methods for CNT/polymer composites, the properties and applications of CNT/polymer composites is given in Chapter 2, while the materials and experimental methods used in this study are described in Chapter 3.

Chapter 4 focuses on the effects of surfactants on the properties of CNT/polymer composites. Subsequently, Chapter 5 reports the effect of chemically functionalised carbon nanotubes on the properties of CNT/polymer composites. Chapter 6 examines the effects of processing methods on the properties of CNT/polymer composites. Chapter 7 deals with the compatibilising effect of functionalised carbon nanotubes on an immiscible polymer blend, while Chapter 8 studies the complementary effects of multiwalled carbon nanotubes and conductive carbon black on the formation of electrical conductive network in the polymer matrix. Finally, the conclusions on this research are drawn in Chapter 9. References are provided at the end of the thesis.
Chapter 2 Literature Review

2.1 Polymer-based nanocomposites

Polymer composites, consisting of additives and polymer matrices, including thermoplastics, thermosets and elastomers, are considered to be an important group of relatively inexpensive materials for many engineering applications. Two or more materials are usually combined to produce composites which possess properties those are unique and cannot be obtained by each material alone. For example, high modulus carbon fibres or silica particles are added into a polymer to produce reinforced polymer composites that exhibit significantly enhanced mechanical properties including strength, modulus and fracture toughness. Therefore, due to their unique and superior properties as well as ease of production at low cost, polymer-based composites are currently important engineering materials with many applications which include high-performance composites even used in aerospace application, filled-elastomers for damping, electrical insulators, thermal conductors, and other special applications in which a particular superior property is needed.
Figure 2.1 Schematic of nanofillers.[3]

Special materials with extraordinary properties are chosen to create composites with desired properties; for example, high-modulus but brittle carbon fibres are added to low-modulus polymers to create a stiff and light-weight composite with a reasonable degree of toughness. In recent years, although, the highest level of optimisation of composite properties with traditional micrometre-scaled fillers has been reached, a large bundle of opportunities has been opened to overcome the limitations of traditional polymer composites by using newly available nanometre-scaled fillers – polymer nanocomposites in which the filler is < 100 nm in at least one dimension as shown in Figure 2.1.[3]

Unlike traditional polymer composites containing micro-scale fillers, when the small amount of nano-scale fillers, such as carbon nanotube tubes (CNTs) or nano-clay flakes, are incorporated into a polymer system, the properties of such nanocomposites can be largely modified even at an extremely low content of filler due to a very short distance between the fillers. Although, polymer nanocomposites can be considered as a new class
of materials, some nanofillers, such as carbon black\textsuperscript{[5]} and fumed silica,\textsuperscript{[6,7]} have been used for more than a century for the fabrication of polymer-based nanocomposites. However, the research and development of polymer nanocomposites have greatly increased only in the recent years for the following reasons.

Firstly, some of the polymer nanocomposites showed unpredicted combinations of properties.\textsuperscript{[8]} For example, the incorporation of equi-axed nanoparticles in thermoplastics, and particularly in semicrystalline thermoplastics, increases the yield stress, the tensile strength, and Young’s modulus\textsuperscript{[9]} compared to pure polymer. A volume fraction of only 0.04 mica-type silicates (MTS) in epoxy increases the modulus below the glass transition temperature by 58 % and the modulus in the rubbery region by 450 %.\textsuperscript{[10]} In addition, the permeability of water in poly(e-caprolactone) decreases by one order of magnitude with the addition of 4.8 % silicate by volume.\textsuperscript{[11]} Yano et al.\textsuperscript{[12]} showed a 50 % decrease in the permeability of polyimides at a 2.0 wt % loading of MTS. Many of these nanocomposites are optically transparent and/or optically active.

The second reason for the large increase in research and development efforts was related to the discovery of carbon nanotubes by Iijima in the early 1990s.\textsuperscript{[1]} Although there is an argument that carbon nanotubes have been observed since the 1960s,\textsuperscript{[13]} it was only in the mid-1990s that they became popular to the researchers and the scientists around the world, due to the ability to produce them in the quantities required for property evaluation of composites. The unpredictably sophisticated properties of these carbon nanotubes, especially their superior mechanical and electrical properties over those of the traditional fillers, offer an exciting potential for new composite materials.
Finally, recent significant development in the chemistry, such as click chemistry,\textsuperscript{[14]} has brought to the remarkable control over the chemical modification of carbon nanotubes and the in-situ process for polymer nanocomposites. It has also created an almost unrestricted possibility to control the interfacial interaction between the polymer matrix and the filler.

2.2 Carbon nanotube/polymer composites

One of the well-known nanofillers for polymer nanocomposites is the carbon nanotubes. Due to the outstanding properties of CNTs, they have become an attractive candidate for scientists to develop advanced polymer nanocomposites with multifunctional features. The first polymer nanocomposites using CNTs as fillers were reported by Ajayan et al. in 1994.\textsuperscript{[2]} Since then, there has been a lot of research dealing with fabrication of CNT/polymer composites. On the basis of extraordinary physical properties as well as the large aspect ratio of CNTs, most of CNT/polymer composites show unexpected properties in many aspects such as mechanical, electrical and thermal properties. In general, the homogeneous dispersion, alignment and content of CNTs in polymer matrices are the key parameters to enhance the physical properties of CNT/polymer composites.

For example, CNTs are used in the development of the stiff and light-weight polymer nanocomposites. CNT/polymer composites show considerably improved mechanical properties even at a low CNT content. For example, with an addition of 0.5 wt % MWCNTs, the tensile strength and modulus for high density polyethylene nanocomposite films remarkably increased by ~30% and ~20% respectively.\textsuperscript{[15]} CNTs can also be used as a nucleating agent for crystallisation of polymers. Several groups
have been studied the crystallisation of polypropylene in the presence of CNTs.\textsuperscript{[16-18]} Assouline et al.\textsuperscript{[19]} studied the non-isothermal crystallisation of MWCNT/isotactic polypropylene (iPP) composites. The crystallisation behaviour of MWCNT/iPP composite was significantly different from that of the neat iPP. With an addition of 1.0 wt \% MWCNTs into iPP, the crystallisation rate was increased with evidence of fibril crystal growth rather than spherulite growth. Many research groups have observed the improved thermal stability in CNT/polymer composites. For example, Kashiwagi et al.\textsuperscript{[20]} reported that the addition of MWCNTs into polypropylene enhanced the thermal stability of PP both in nitrogen and in air. Besides, the MWCNTs could significantly reduce the heat release rate of PP. Generally, the thermal stability of the CNT/polymer composites increases due to the higher thermal conductivity of MWCNTs that facilitates heat dissipation within the composites.\textsuperscript{[21]} The results show a great potential for the use of CNTs as a flame retardant for polymer materials.

Therefore, in the following sections, the synthesis and unique properties of carbon nanotubes will be described. Besides, several approaches for surface modifications of CNTs, such as chemical modifications and physical modifications, as well as the processing methods used to fabricate CNT/polymer composites will be reviewed. Finally, the thermal, mechanical and electrical properties and applications of CNT/polymer composites will also be covered.

2.3 Carbon nanotubes

Carbon nanotubes were firstly discovered as a by-product of a synthesis of fullerenes ($C_{60}$) using an arc discharge method. However, being different from other carbon materials, such as graphite, diamond and fullerene ($C_{60}$, $C_{70}$, etc.), CNTs are one-
dimensional carbon materials which can have an aspect ratio greater than 1000. They can be envisioned as cylinders composed of rolled-up graphene planes with diameters in a nanometre scale. The cylindrical nanotube usually has at least one end capped with a hemisphere of fullerene structure.\(^{[22,23]}\) Therefore, a carbon nanotube is defined as a hexagonal network of carbon atoms rolled up into a seamless, hollow cylinder, with each end capped with half of a fullerene molecule. There are two main types of carbon nanotubes: single-walled carbon nanotubes (SWCNTs)\(^{[24]}\) and multiwalled carbon nanotubes (MWCNTs)\(^{[1,25]}\) An SWCNT comprises cylinders of one (concentric) graphene sheet, whereas an MWCNT consists of several concentric cylindrical shells of graphene sheets. The specific surface area of an MWCNT depends on the number of walls, and to a lesser extent on the diameter of the inner tube.

Although, CNTs are synthesised in a variety of ways, such as arc discharge,\(^{[24]}\) laser ablation,\(^{[26]}\) high pressure carbon monoxide (HiPCO),\(^{[27]}\) and chemical vapour deposition (CVD),\(^{[28,29]}\) there are only two main methods or processes for synthesis of CNTs:

1. Sublimation of graphite with subsequent desublimation and

2. Decomposition of carbon-containing compounds.\(^{[30-32]}\)

The first type of processes is associated with high temperature (up to 4000 \(^{\circ}\)C) which can be obtained by electric arcs,\(^{[33-37]}\) by the process of laser ablation,\(^{[13,37-41]}\) by focused solar radiation\(^{[41,42]}\) or by resistive heating of graphite. The second types of methods includes pyrolysis of gases (chemical vapour deposition),\(^{[13,37,43]}\) low-temperature pyrolysis of solids (e.g., pyrolysis of polymers)\(^{[44-47]}\) and spray pyrolysis of
aqueous solutions (hydrothermal synthesis),\cite{48,49} or organic solutions (e.g., supercritical toluene).\cite{50}

The chemical bonding of an ideal CNT is composed entirely of sp$^2$ carbon-carbon bonds. This bonding structure, which is stronger than the sp$^3$ bonds found in diamond, provides CNTs with extremely high mechanical strength.\cite{51} It is well known that the mechanical strength of CNTs exceeds those of any existing materials.\cite{52-54} For example, the bulk modulus of super-hard phase SWCNTs is 462-546 GPa, even higher than that of diamond (420 GPa for single-crystal diamond).\cite{55} Although there is no consensus on the exact mechanical properties of CNTs, theoretical and experimental results have shown unusual mechanical properties of CNTs: for example, Young’s modulus as high as 1.2 TPa and tensile strength of 50–200 GPa.\cite{53} These make CNTs the strongest and stiffest materials on earth.

In addition to the exceptional mechanical properties of CNTs, they also possess many advantages over other carbon materials in terms of electrical and thermal properties. These properties offer CNTs great potentials for wide applications in field emission, conducting plastics, thermal conductors, energy storage, conductive adhesives, thermal interface materials, structural materials, fibres, catalyst supports, biological applications, air and water filtration, ceramics and so on.\cite{54,56-58} The exact magnitude of the properties of CNTs depends on the diameter and chirality of the nanotubes and whether they are single-walled or multiwalled. The typical properties of CNTs are presented in Table 2.1.\cite{57,59-62}
Table 2.1 Typical properties of CNTs.[57,59-62] (*Theoretical properties)

<table>
<thead>
<tr>
<th>Property</th>
<th>SWCNT</th>
<th>MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength* (GPa)</td>
<td>50-500</td>
<td>10-60</td>
</tr>
<tr>
<td>Elastic modulus* (TPa)</td>
<td>~ 1.0</td>
<td>0.3-1.0</td>
</tr>
<tr>
<td>Elongation at break* (%)</td>
<td>5.8</td>
<td>-</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.3-1.5</td>
<td>1.8-2.0</td>
</tr>
<tr>
<td>Electrical conductivity* (S/m)</td>
<td>~10⁶</td>
<td></td>
</tr>
<tr>
<td>Thermal stability (°C)</td>
<td>&gt;700 (in air)</td>
<td></td>
</tr>
<tr>
<td>Typical diameter (nm)</td>
<td>1.0-1.2</td>
<td>~20</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>150-1600</td>
<td>40-500</td>
</tr>
</tbody>
</table>

2.3.1 Challenges for CNTs as reinforcing fillers in CNT/polymer composites

Although, the main advantages of adding CNTs into polymer matrices are enhanced stiffness, modulus and tensile strength as well as improved thermal stability and electrical conductivity, CNTs tend to form stable aggregates or bundles in a polymer matrix due to the very strong van der Waals forces among them.[4] Therefore, they are difficult to be separated into individual nanotubes and dispersed homogeneously in a polymer matrix, which hampers the mechanical and electrical properties of fabricated nanocomposites.

Many research efforts have been made in the production of CNT/polymer composites for functional and structural applications.[56-60] However, even after a number of decades of research, the potential for CNTs as reinforcing fillers has been brutally restricted due to the drawback associated with dispersion of entangled CNTs during a
fabrication process and poor interfacial interaction between CNTs and a polymer matrix. As CNTs are characteristic of small diameter in nanometre scale with high aspect ratio (>1000) and thus extremely large surface area, their nature of poor dispersion in a polymer matrix is rather different from that of other conventional fillers, such as spherical particles and carbon fibres. Therefore, the agglomeration of CNTs in a polymer matrix can be considered as the main reason for the reduced mechanical, thermal and electrical properties of their nanocomposites as compared with theoretical predictions based on individual CNTs. The critical challenge is, therefore, how to incorporate individual CNTs, or at least relatively thin CNT bundles or disentangled CNTs, into a polymer matrix. In other words, dispersion of CNTs is not only a geometrical problem due to the length and size of the CNTs, but also relates to a method for how to separate individual CNTs from CNT agglomerates and stabilise them in a polymer matrix to avoid the secondary agglomeration.[51] In addition, the most suitable processing conditions are required for the efficient transfer of either mechanical load or electrical charge among individual carbon nanotubes in a polymer matrix towards a successful fabrication of CNT/polymer composites.[4]

2.4 Surface Modifications of carbon nanotubes

As mentioned above, the agglomeration of CNTs in a polymer matrix and the poor interfacial interaction between the CNTs and the polymer molecules are the most critical issues in the fabrication of CNT/polymer composites. Fortunately, there are several possibilities to improve the dispersion of CNTs in polymer matrices such as solution mixing, melt blending, and in-situ polymerisation methods. Moreover, several methods are also available to enhance the interaction between the CNTs and the polymer
molecules. Especially, the surface modification of CNTs is an effective way to prevent the carbon nanotube aggregation by improving their chemical compatibility with the polymer matrixes, which helps CNTs to disperse better and stabilise within a polymer matrix. There are mainly two approaches for surface modification of CNTs namely: physical modification (noncovalent functionalisation) and chemical modification (covalent functionalisation).

2.4.1 Noncovalent functionalisation

Noncovalent functionalisation of CNTs, also known as physical modification, is particularly attractive because it does not spoil the physical properties of CNTs, but improves their compatibility with a polymer matrix, dispersion and processability. This type of functionalisation mainly involves surfactants. CNTs can be well dispersed in water using anionic, cationic, and non-ionic surfactants.\cite{63-65} During a dispersion process, ultrasonication may help a surfactant to debundle CNTs after an absorption of the surfactant on the CNTs surfaces by steric or electrostatic repulsion.\cite{66} The high shear environment of the ultrasonicated solution causes the ends of CNT bundles to separate. These split ends of CNT bundles are then propagated along the bundle length due to surfactant absorption and diffusion, thereby separating the individual nanotube from the bundles.\cite{67} The noncovalent functionalisation of CNTs is summarised in Table 2.2.
Table 2.2 Noncovalent functionalisation of CNTs by using cationic, anionic, and non-ionic surfactants.

<table>
<thead>
<tr>
<th>Type of Surfactant</th>
<th>Functionality</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cationic surfactants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetyltrimethyl ammonium bromide (CTAB)</td>
<td>-N^+Br^-</td>
<td>Ultrasonication</td>
<td>[68]</td>
</tr>
<tr>
<td>Cetyl trimethylammonium 4-vinylbenzoate (CTVB)</td>
<td>-CO_2^-N^+</td>
<td>Sonication</td>
<td>[69]</td>
</tr>
<tr>
<td><strong>Anionic surfactants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylsulphate (SDS)</td>
<td>-SO_4^2Na</td>
<td>Ultrasonication</td>
<td>[70, 71]</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulphonate (NaDDBS)</td>
<td>-SO_3^2Na</td>
<td>Ultrasonication</td>
<td>[63, 64]</td>
</tr>
<tr>
<td><strong>non-ionic surfactants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Octyl-phenol-ethoxylate (Triton X-100)</td>
<td>Phenyl, Ethylene oxide</td>
<td>Ultrasonication</td>
<td>[72]</td>
</tr>
<tr>
<td>Polyoxyethylene (30) 4-(1,1,3,3-tetramethylbutyl) phenyl ether (Triton X-305)</td>
<td>Ether, phenyl</td>
<td>Ultrasonication</td>
<td>[73]</td>
</tr>
</tbody>
</table>
The nature of a surfactant and its concentration play a major role in the dispersion of CNTs. In general, the ionic surfactants are preferable for CNT/water solutions, whereas the non-ionic surfactants are used for organic solvents. Anionic surfactants such as sodium dodecylsulphate (SDS) and sodium dodecylbenzene sulphonate (NaDDBS) are commonly used to decrease CNT aggregation in water. Particularly, SDS has a weaker interaction with the nanotube surface compared to that of NaDDBS because it does not have a benzene ring. Indeed π-π stacking interaction between benzene rings of NaDDBS and CNTs increases the binding and surface coverage of surfactant (i.e.; NaDDBS) molecules to CNTs significantly. As a result, the stronger interaction between NaDDBS and MWCNTs may greatly reduce the agglomeration of MWCNTs.

Many other surfactants such as lithium dodecyl sulphate (LDS), sodium deoxycholate (SDC), sodium taurodeoxycholate (STDC) and sodium cholate (SC) as anionic surfactants, dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (HTAB) as cationic surfactants, and TritonX-100, Tween-20, Tween-40 and Tween-60 as non-ionic surfactants have been used for the dispersion of CNTs.

Noncovalent functionalisation of CNTs is determined by the interaction between the surfactant molecules and CNT surfaces through hydrophobic, π-π, CH–π, and charge transfer interactions. In general, a strong and specific interaction between the carbon nanotube surface and surfactant molecules via π-π stacking is more favourable over the non-specific hydrophobic interaction.
2.4.2 Covalent functionalisation

The CNTs are relatively reactive because of the π-orbital of the sp\(^2\) hybridised C-atoms, and therefore they have a high tendency to covalently react with chemical groups.\[89\] In the case of covalent functionalisation, the translational symmetry of CNTs is disrupted by changing sp\(^2\) carbon atoms to sp\(^3\) carbon atoms, and the properties of CNTs such as electronic properties are varied from original CNTs.\[90\] But this functionalisation of CNTs can improve solubility as well as dispersion in solvents and polymers.

The most common and simple method for the covalent functionalisation of CNTs, usually described as chemical modification, is to chemically introduce carboxylic acid (-COOH) groups on the surface of CNTs. These carboxylic acid groups are usually introduced by oxidation using concentrated sulphuric acid, nitric acid, aqueous hydrogen peroxide, or acid mixture.\[90\] The acid treated MWCNTs possess some defects on the surface, which are caused by the formation of -COOH groups, while the raw MWCNTs have smooth surfaces because of their perfect lattice structure of carbon-carbon bonds.\[91-93\] The amount of -COOH groups on the surface of CNTs depends on the oxidation procedure, oxidising agent,\[94\] processing temperature and time.\[92\] For example, the concentrations of -COOH groups after treatment with oxidising reagents, H\(_2\)SO\(_4\)/H\(_2\)O\(_2\), NH\(_4\)OH/H\(_2\)O\(_2\) and HNO\(_3\) are 2.0, 1.6 and 3.8 mmol/g, respectively.\[94\] The presence of these carboxylic acids can be further employed for the covalent attachment of organic or inorganic groups (Scheme 2.1), leading to highly soluble materials.\[95\] The sidewalls of the nanotubes could be also functionalised with a fluorination reaction.\[96\] For example, the fluorinated SWCNTs exhibited the improved solubility in isopropanol or dimethyl
formamide by ultrasonication.\textsuperscript{[97,98]} Fluorinated CNTs can be further functionalised by alkyl groups using Grignard reagent or alkylithium compounds that are soluble in chloroform.\textsuperscript{[99]} Direct side-wall functionalisation of CNTs can also be achieved by reactions with carbenes,\textsuperscript{[100]} nitrenes,\textsuperscript{[101]} radicals,\textsuperscript{[102]} etc.

Scheme 2.1 Covalent functionalisation of CNTs.

Covalent functionalisation of CNTs with polymer molecules (polymer grafting) is particularly important because the grafted polymer chains may help to dissolve the CNTs into a wide range of solvents even at a low degree of functionalisation. There are two main methodologies for the covalent grafting of polymers to carbon nanotubes, which are defined as “grafting to” and “grafting from” methods.\textsuperscript{[4]}

The “grafting to” approach involves the attachment of as-prepared or commercially available polymer with reactive groups to the CNT surface by chemical reactions, such as amidation, esterification, radical coupling, etc. Generally, in this
approach, the preformed polymer chains react with the surface of pristine, oxidised or functionalised CNTs. The grafting of CNTs with a polystyrene copolymer was reported by Hill et al.\[103\] They mixed a solution of poly(styrene-co-p-(4- (4'-vinylphenyl)-3-oxobutanol)) in tetrahydrofuran with acyl chloride-activated nanotubes.

The main limitation of the “grafting to” method is that the content of grafted polymers is quite low not only due to the relatively small fraction of active sites on the CNTs but also due to the depressing effects of steric hindrance on the reactivity of a polymer.\[104\] For example, the grafting efficiency by direct free radical addition of the grafted polymers was below 1.0 % for MWCNTs\[105\] and ranged from 0.6 % to 13.4 % for SWCNTs.\[106\] But Wang et al.\[107\] grafted the poly(methyl methacrylate) (PMMA) onto SWCNTs in poor solvents of PMMA, where the grafting efficiency increased up to 40 % for SWCNTs. Peng et al.\[108\] reported a new “grafting to” method for the functionalisation of MWCNTs, exhibiting a high grafting efficiency. The grafting efficiency was as high as 65.7 % for poly(polysoap-co-MMA) covalently attached to MWCNTs.

Many other linear polymers such as poly(sodium 4-stryrenesulphonate),\[109\] poly(methyl methacrylate),\[110\] polyimide,\[111,112\] poly-(2-vinylpyridine),\[113\] and Poly(ethylenimine-ethylene imine)\[114\] as well as dendrons,\[115\] dendrimers,\[116\] and hyperbranched polymers\[104\] have been successfully bonded to CNTs using this method.

On the other hand, in the “grafting from” approach, the polymer is bonded to the CNT surface by in-situ polymerisation of monomers in the presence of reactive CNTs or CNT supported initiators. In comparison with “grafting to” methods, “grafting from” methods exhibit significantly higher grafting efficiencies (especially for living
polymerisation), because the polymer chains can be grafted more densely from their monomers onto the CNTs surfaces.\textsuperscript{[117,118]} Sakellariou et al.\textsuperscript{[117]} reported the grafting efficiency for living anionic surface-initiated polymerisation of styrene and isoprene on MWCNTs can be even as high as 100 \%. However, in this ‘grafting from’ method, it is necessary to control the amounts of initiators, monomers, and reaction conditions for polymerisation.

Chen et al.\textsuperscript{[119]} functionalised the CNTs using a simple “grafting from” method. They functionalised MWCNTs with carboxyl groups, acyl chloride, and amide, and finally polyurethane was covalently coated onto the sidewalls (or surfaces) of the MWCNT by in-situ polymerisation of 2,4-toluene diisocyanate under ultrasound in the presence of MWCNT-NH$_2$. The results show that the amount of grafted PU is about 34 wt \%.

In a different approach, Qin et al.\textsuperscript{[120]} attached an initiator on the carboxylic functionalised CNTs for atom transfer radical polymerisation (ATRP). The grafting of n-butyl methacrylate monomer on the CNT surface was achieved using the initiator. The nanocomposites were soluble in a variety of solvents. The same strategy was followed for the functionalisation of MWCNT with acrylate polymers by in-situ ATRP.\textsuperscript{[121]}

This “grafting from” approach has also been used to graft many polymers such as polyamide 6,\textsuperscript{[122,123]} poly(methyl methacrylate),\textsuperscript{[124,125]} polystyrene,\textsuperscript{[126,127]} poly(acrylic acid),\textsuperscript{[128]} poly-(tert-butyl acrylate),\textsuperscript{[129]} poly(N-isopropylacrylamide),\textsuperscript{[130]} poly(4-vinylpyridine)\textsuperscript{[131]} and poly(N-vinylcarbazole)\textsuperscript{[132]} on the CNT surface via radical, cationic, anionic, ring-opening, and condensation polymerisations.
2.5 Preparation Methods for Carbon Nanotube/Polymer Composites

It is well-known that the desired reinforcing effects of CNTs in polymer composites will be only achieved when they do not form aggregates and are well dispersed in polymer matrices. Therefore, a solution to the homogeneous dispersion of CNTs is to use a method for the fabrication of CNT/polymer composites. Currently there are several methods used to improve the dispersion of CNTs in polymer matrices which include solution mixing, melt mixing, and in-situ polymerisation.

2.5.1 Solution mixing

This is a common method usually used in laboratories for preparing the CNT/polymer composites. In this approach, CNTs and a polymer (or polymers) are dissolved in an appropriate common solvent. The CNT/polymer composites are obtained by precipitation or by evaporation of the solvent.

The main advantage of this method is the high possibility to achieve a good dispersion of the CNTs in a suitable solvent. As it is still very difficult to disperse pristine CNTs properly in a solvent by simple mechanical stirring, a high power ultrasonication process is more effective for the dispersion of CNTs. Ultrasonication has been extensively used in dispersing, emulsifying, and activating solid particles. By taking the advantage of ultrasound, the aggregates and entanglements of CNTs can be effectively broken down. However, using high power ultrasonication for a long period of time may reduce the length of carbon nanotubes and therefore, decrease their aspect ratio, which will deteriorate the properties of resultant nanocomposites. Thus, there is a trade-off between the dispersion and degradation of CNTs, and the control of the parameters for
the sonication process, such as sonication time and sonication power, is important for this trade-off.

For example, Li et al.\cite{133} used a solution–precipitation technique to improve the dispersion of CNTs in a polycarbonate solution by sonication at a frequency of 20 kHz for 10 min. They found that the CNTs were uniformly dispersed in the polycarbonate matrix under this condition. Sahoo et al.\cite{134} fabricated MWCNT/PU composites with a good dispersion of CNTs up to 20 wt % in PU using the method consisting of solution mixing, casting and drying. In this research, raw MWCNTs with or without surfactant, and carboxylic functionalised MWCNTs were incorporated into PU. This PU containing functionalised MWCNTs showed the improved mechanical and thermal properties, as well as increased crystallinity than other composites filled with the same raw MWCNTs, in the presence or the absence of a surfactant and pure PU.

Using the modified CNTs, either covalently or noncovalently modified ones, with solution mixing will give an additional benefit over the traditional solution method. Using noncovalently functionalised CNTs, which contain surfactants, is an efficient method to disperse higher loading of carbon nanotubes.\cite{135,136} The use of non-ionic surfactants such as polyoxyethylene-8-lauryl has been demonstrated to improve the dispersion of MWCNTs in epoxy resins and resulted in the strong interaction between MWCNTs and epoxy resins.\cite{137} However, sometimes using surfactants to improve the CNTs dispersion can be problematic because the surfactants remain in the resulted nanocomposites and they might degrade the properties of nanocomposites.\cite{138} For example, the thermal conductivity of the SWCNT/epoxy composite with surfactant is much lower than that of the composite without surfactant at the same loading.\cite{139}
With the solution mixing method, CNTs tend to agglomerate back again in the composite during the slow evaporation of the solvent. The evaporation time can be reduced by putting the CNT/polymer suspension on a rotating substrate or a hot substrate.\textsuperscript{[140,141]} Du et al.\textsuperscript{[142]} proposed an alternative approach i.e.; coagulation method that involves pouring a CNT/polymer suspension into a large excess of nonsolvent. The precipitating of polymer chains entrapped the CNTs and prevented them from bundling.

Many other polymer nanocomposites such as CNT/polystyrene composite,\textsuperscript{[143,144]} CNT/epoxy composite,\textsuperscript{[145]} CNT/poly(vinyl alcohol) composite,\textsuperscript{[146]} CNT/p(MMA-co-EMA) composite,\textsuperscript{[147]} CNT/polyacrylonitrile composite\textsuperscript{[148]} and CNT/polyethylene composite\textsuperscript{[149]} have been fabricated by this method.

2.5.2 Melt mixing

For solution mixing, the matrix polymer must be soluble in at least one solvent. Unfortunately, as most polymers are insoluble in many organic solvents, it is difficult to choose an appropriate solvent for a given system. Therefore, this is the major drawback of the solution mixing method for many polymer nanocomposite systems.

On the other hand, the melt mixing technique is a simple and industrial-friendly method, especially very useful for most of thermoplastic polymers. In melt processing, CNTs are mechanically dispersed into a polymer matrix using a high temperature and high shear force mixer, extruder or compounder.\textsuperscript{[68]} This approach is straight-forward and compatible with current industrial practices. Carbon nanotubes are disaggregated in the molten polymer with high-shear forces provided by the mixer. However, the melt mixing method is less effective as compared to solution mixing to disperse the CNTs in the
polymer matrix and it is also limited to lower contents of CNTs because the higher the loading of CNTs is, the higher the viscosities of the nanocomposites will be.

McNally et al.\[^{[150]}\] prepared the MWCNT/PE composites using twin screw melt compounding and they found that the MWCNTs were very well distributed and dispersed in the PE matrix. The dispersion of the CNTs in the polymer matrix depends on the processing methods. Prashantha et al.\[^{[151]}\] prepared the MWCNT/PP composites by diluting a MWCNT/PP masterbatch using melt compounding with a twin extruder and obtained the optimum mechanical properties with 2.0 wt % MWCNTs.

Figure 2.2 Optical microscopic images of (a) 1.0 wt % pristine-MWCNT/PP; (b) 1.0 wt % acid treated MWCNT/PP; (c) 1.0 wt % pristine-MWCNT/PP-g-MA/PP; (d) 1.0 wt % acid treated MWCNT/PP-g-MA/PP.\[^{[152]}\]
Recently, Pan et al.\textsuperscript{[152]} prepared MWCNT/PP composites using a master-batch of MWCNT/PP-g-MA (maleic anhydride-grafted polypropylene) by melt blending with a twin-screw micro extruder and injection moulding. For pristine MWCNT/PP composites without a master batch (Figure 2.2a), several isolated large MWCNT agglomerates were observed. The large MWCNT agglomerates indicate that the tightly entangled MWCNTs in the powder form have not been separated and they remained in the state of entanglements. For pristine-MWCNT/PP composite prepared by the master-batch process (Figure 2.2c), even though the CNT agglomerates are still observed, they have become much smaller and dispersed uniformly. Besides, the chemical functionalisation of MWCNTs would help the dispersion of MWCNTs in a polymer matrix with the melt mixing. It can be seen in Figure 2.2b that the acid-treated MWCNTs have a better dispersion in the PP matrix compared with the pristine MWCNTs even without the master-batch process. Figure 2.2d presents the acid treated MWCNT/PP-g-MA/PP composite with the master-batch process. Based on the same master-batch method, the similar uniform dispersion with the smaller agglomerates was obtained compared with the acid-treated CNT/PP composites without a master-batch process, indicating that the master batch method with PP-g-MA has promoted the homogeneous dispersion of CNTs in the PP matrix.

Melt mixing has been applied for the preparation of different CNT/polymer composites such as CNT/linear low density polyethylene,\textsuperscript{[153]} CNT/high density polyethylene,\textsuperscript{[154]} CNT/polycarbonate,\textsuperscript{[155]} CNT/poly(methyl methacrylate),\textsuperscript{[156,157]} CNT/polyimide,\textsuperscript{[158]} CNT/polyamide 6\textsuperscript{[159]} and etc.
2.5.3 In-situ polymerisation

In-situ polymerisation is an efficient method to realise a uniform dispersion of CNTs in a thermosetting polymer. In this method, CNTs are mixed with monomers, either in the presence or absence of a solvent, and then these monomers are polymerised via addition or condensation reactions with a hardener or a curing agent at an elevated temperature. The major advantage of this method is that covalent bonding can be formed between the functionalised CNTs and the polymer matrix, resulting in significantly improved mechanical properties of nanocomposites through strong interfacial bonds. Another advantage of this method is the preparation of nanocomposites with polymers that cannot be processed by solution or melt mixing, e.g., insoluble and thermally unstable polymers.

Most of the epoxy nanocomposites prepared by this method, where the CNTs can be dispersed in a liquid epoxy precursor, and then, the mixtures can be cured with a hardener, such as triethylene tetramine (TETA), and upon the application of temperature.\textsuperscript{[160,161]} Scheme 2.2 illustrates a flowchart of typical processes used to produce CNT/epoxy composites.\textsuperscript{[162]} Ma et al.\textsuperscript{[163]} prepared epoxy nanocomposites by this method using functionalised MWCNTs with improved interfacial adhesion between the matrix and functionalised CNTs through covalent bonds, resulting in improved flexural and thermo-mechanical properties over those without functionalisation.
Another common usage of this method is in the fabrication of CNT/PMMA composites. Jia et al. synthesised PMMA by an in-situ radical polymerisation method where a free radical initiator, (2, 2, 1-azobisisobutyronitrile) AIBN, was used to initiate opening of π-bonds of CNTs to participate in the PMMA polymerisation, forming a strong interface between the CNTs and the PMMA matrix.

The in-situ polymerisation method has also been used for the preparation of CNT/polyurethane composites. Xia et al. studied the incorporation of poly(propylene glycol)-grafted MWCNTs into PU by in-situ polymerisation. Raw MWCNTs are difficult to be dispersed in dimethylformamide (DMF), and the MWCNTs aggregate with a size in a micron meter scale. MWCNT-graft-PU can be dispersed in DMF without forming aggregates after 5 min of sonication. MWCNT-graft-PU can also be well dispersed in 0.2 % SLS/water solution, where SLS stands for sodium lauryl sulphate.

As a novel approach, MWCNTs are also attached with certain conducting polymers using in-situ polymerisation method to improve not only their processability and compatibility, but also their properties such as electrical, magnetic and optical properties. Sahoo et al. described a simple approach to the synthesis of
MWCNT/polypyrrole (PPy) by the in-situ polymerisation of pyrrole on the CNTs using ferric chloride as an oxidant. They have reported that by changing the pyrrole to MWCNT ratio, the layer thickness of PPy could be easily controlled.

### 2.5.4 Other methods

The mechanical properties of polymer nanocomposites strongly depend on the content of fillers contained. When the content of CNTs is high, it is a great challenge for the preparation of CNT/polymer composites with a uniform dispersion of CNTs.

Layer by layer (LBL) assembly is one of the methods to produce the composites where the CNT/polymer ratio can easily be controlled and very high loading levels of CNTs can be obtained. In the LBL method, the composites are formed on solid substrates by the sequential deposition of oppositely charged polyelectrolytes and CNTs. In addition, this method is environmentally sound and cost-effective. This method is limited to those polymers that are capable of charge–transfer interaction with CNTs. Feng et al. reported a mixed-curing-agent assisted layer-by-layer method to synthesise CNT/epoxy composite films with a high CNT loading from ~15 to ~36 wt %. The electrical conductivity of the nanocomposites showed a value up to 12 S/m, which is much higher than that for CNT/epoxy composites with a low CNT loading prepared using the conventional methods. In other work, the LBL method was used to produce PVA/SWCNT+poly(sodium 4-styrene-sulphonate)-layered coatings and free-standing films, which exhibited high electrical conductivities and excellent mechanical strength.

Latex technology can be applied to prepare CNT/polymer composites. This method simply refers to drying a mixture of CNT aqueous dispersion and a polymer
latex. In this method, the electrically conductive CNT/polymer composites can be prepared with a lower percolation threshold than that by other traditional methods.\cite{176,177}

For example, Grossiord et al. prepared SWCNT/PS composites by this method with a very low percolation threshold of 0.3 wt % SWCNTs in a PS matrix.\cite{178} Grunlan et al. reported an even lower percolation threshold of about 0.04 wt % SWCNTs in poly(vinyl acetate) using the same method.\cite{168} Yu et al.\cite{179} prepared MWCNT/PS composites based on latex technology. MWCNTs were first dispersed in an aqueous solution of SDS and then mixed with PS latex. The MWCNT/PS composites were obtained by freeze-drying and compression moulding. The percolation threshold for electrical conduction was about 1.5 wt % of MWCNTs in the composites, and a maximum conductivity of about 1.0 S/m can be achieved. When SDS was replaced by a latex of poly(3,4-ethylenedioxythiophene):poly(styrene sulphonate) (PEDOT:PSS of 0.4 wt % PEDOT and 0.8 wt % PSS), which effectively stabilised individual SWCNTs in water and the composites prepared with these dispersions showed a lower percolation threshold value of 0.2 wt %.\cite{180}

O’Connor et al.\cite{181} developed a new fabrication method to obtain polymer composite films based on the swelling of polyethylene in nanotube/tetrahydrofuran dispersions, followed by carbon nanotube infiltration. These polymer films displayed conductivities of up to 66 S/m.
2.6 Properties of carbon nanotube/polymer composites

2.6.1 Electrical conductivity

As CNTs exhibit the high aspect ratio and high electrical conductivity, they are excellent candidates for fabrication of electrically conducting nanocomposites. While the electrical conductivity of individual carbon nanotubes has been measured to be in the order of $10^6 \text{ S/m}$, the maximum electrical conductivity of SWCNT films has been reported to be in the range of $10^4$ to $10^5 \text{ S/m}$ due to the contact resistance between the individual carbon nanotubes in the films. Therefore, the range of electrical conductivity of CNT/polymer composites is reported to be tremendously wide. On the other hand, this wide range advises that it is possible to control the electrical conductivity of CNT/polymer composites by varying the amount and degree of dispersion of CNTs in the composites. The CNT/polymer composites can be used for a variety of applications including electrostatic dissipation ($< 10^{-4} \text{ S/m}$), electrostatic painting ($10^{-4} \sim 10^{1} \text{ S/m}$), electromagnetic interference (EMI) shielding ($> 10^{1} \text{ S/m}$), printable circuit wiring and transparent conductive coatings.

Again, the electrical conductivity of CNT/polymer composites is widely defined by the percolation theory. The percolation theory predicts that there is a critical volume fraction at which nanocomposites containing conducting fillers in insulating polymers become electrically conductive. According to this theory, $\sigma_c = A (V-V_c)^\beta$, where $\sigma_c$ is the conductivity of a composite, $V$ is the CNT volume fraction, $V_c$ is the CNT volume fraction at the percolation threshold, and $A$ and $\beta$ are constant. So far, there are several publications documented on the progress of electrical conductivity of different CNT/polymer composites. The percolation threshold has been reported to range
from 0.0025 vol %\textsuperscript{[188]} to several vol %\textsuperscript{[189]} Therefore, it is difficult to draw definite conclusions about the mechanism of electrical conductivity of CNT/polymer composites from the literature. This is because the reported levels of CNT loading to achieve a percolation threshold vary widely. The electrical conductivity and percolation threshold of different CNT/epoxy composite systems are shown in Table 2.3. It seems that different systems give a wide range of percolation values. However, even for the same system, for example SWCNT/epoxy composites ($V_c = 0.0025$–$0.1\ \%$),\textsuperscript{[188]} a wide variation in percolation value was observed.\textsuperscript{[59]}

Table 2.3 Electrical properties of different CNT/epoxy composites.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>$V_c$ (vol %)</th>
<th>$\beta$</th>
<th>Maximum conductivity (S/m)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>0.074</td>
<td>1.3</td>
<td>$1.2 \times 10^{-3} \ @ 0.2 \text{ wt %}$</td>
<td>[190]</td>
</tr>
<tr>
<td>MWCNT-1</td>
<td>0.01</td>
<td>-</td>
<td>$5.0 \times 10^{-1} \ @ 0.1 \text{ wt %}$</td>
<td>[188]</td>
</tr>
<tr>
<td>MWCNT-2</td>
<td>0.0025</td>
<td>1.2</td>
<td>$2.0 @ 1.0 \text{ wt %}$</td>
<td>[188]</td>
</tr>
</tbody>
</table>

The mechanism for percolation threshold for electrical conductivity of CNT/polymer composites is determined by numerous factors, and a number of publications have reported the factors affecting the percolation mechanism of CNT/polymer composites. The common factors affecting the percolation threshold of electrical conductivity are: dispersion,\textsuperscript{[188,191,192]} alignment,\textsuperscript{[193, 194]} aspect ratio,\textsuperscript{[192,195,196]} degree of surface modification\textsuperscript{[92]} of CNTs, types and molecular weights of the matrix polymer\textsuperscript{[197,198]} and composite processing methods.\textsuperscript{[192]} The aligned CNTs in epoxy decrease the percolation threshold by one order of magnitude compared to entangled nanotubes.\textsuperscript{[188]} The electrical conductivity of SWCNT/epoxy composites with SWCNTs
aligned under a 25 T magnetic field was increased by 35% compared to similar nanocomposites without magnetically aligned SWCNTs.\textsuperscript{[193]}

In contrast, Fangming et al.\textsuperscript{[194]} found that the electrical conductivity of CNT/PMMA composite with 2.0 vol % CNTs was $10^{-10}$ S/cm with the aligned CNTs in the matrix and $10^{-4}$ S/cm with unaligned CNTs. This indicates that the alignment of the CNTs in the composite decreased the electrical conductivity. The reason is that there are fewer contact points between the CNTs when they are highly aligned in the composites, so CNT-aligned composites require more nanotubes to reach the percolation threshold. The aspect ratio of CNTs has a tremendous influence on the percolation threshold of CNT/polymer composites without changing other important parameters, such as the polymer matrix or the dispersion and aggregation state of the CNTs. On the other hand, it is well known that chemical functionalisation may disrupt the extended-conjugation of nanotubes and hence reduce the electrical conductivity of functionalised CNTs. For example, silane-functionalised CNT/epoxy composites showed a lower electrical conductivity than that of the untreated CNT composites at the same nanotube content.\textsuperscript{[199]}

Cho et al.\textsuperscript{[91]} reported that the electrical conductivity of the acid-treated MWCNT composites was lower than that of the untreated MWCNT composites at the same content of MWCNTs. This is attributed to increase defects in the lattice structure of carbon-carbon bonds on the nanotube surface as a result of the acid treatment. In particular, the severe modification of carbon nanotubes may significantly lower their electrical conductivity. However, there are several publications reporting that the functionalisation of CNTs can improve the electrical conductivity of the nanocomposites.\textsuperscript{[200,201]} Tamburri et al.\textsuperscript{[200]} found that the functionalisation of SWCNTs with -COOH and -OH groups
enhanced the nanocomposites’ electrical conductivity as compared to the use of untreated SWCNTs.

2.6.2 Thermal and rheological properties

The glass transition temperature ($T_g$) is a measure of the thermal energy required to allow polymer motion involving 10 to 15 monomeric units and corresponds to the softening of a polymer.\textsuperscript{[202]} Park et al.\textsuperscript{[112]} reported that $T_g$ did not change for their in-situ polymerised SWCNT/polyimide composites. The SWCNT/PMMA composites produced by the coagulation method have the same $T_g$ over a wide range of nanotube loadings.\textsuperscript{[203]} Therefore, it can be concluded that the addition of CNTs does not significantly change the glass transition temperature in CNT/polymer composites, because in the absence of strong interfacial bonds and at low nanotube loadings, the majority of polymer molecules are locally constrained only by other polymer molecules but not by CNTs.

On the other hand, in larger districts, carbon nanotubes do obstruct the motion of polymer molecules as measured by rheology. Rheological (or dynamic mechanical) measurements at low frequencies probe the longest relaxation time of a polymer which corresponds to the time required for an entire polymer molecule to change its conformation.\textsuperscript{[203]} Du et al.\textsuperscript{[203]} found that although it has little effect on polymer motion at the length scales comparable to or less than an entanglement length, the presence of CNTs has a substantial influence at large length scales corresponding to an entire polymer chain. The storage modulus, $G'$, at low frequencies becomes almost independent of frequency as CNT loading increases. This shows a transition from a liquid-like behaviour (which has short relaxation times) to a solid-like behaviour (in which the relaxation times will be infinite) with increasing CNT loading. By plotting $G'$ versus
CNT loading and fitting with a power law function, they reported that the rheological threshold of these nanocomposites was ~0.12 wt %. This rheological threshold could be attributed to a hydrodynamic CNT network that impedes the large-scale motion of polymer molecules. A similar phenomenon has previously been observed in nanoclay/polymer composites by Krishnamoorti et al.\cite{204} They reported that a network of nanoscale fillers restrains polymer relaxations, leading to a solid-like or non-terminal rheological behaviour. Therefore, any factor that changes the morphology of the CNT network will influence the low-frequency rheological properties of their nanocomposites.

The factors influencing the polymer chain mobility are the aspect ratio of CNTs, dispersion and alignment of CNTs in the polymer matrix and the molecular weight of the polymer matrix. Du et al.\cite{203} reported that higher aspect ratio, better dispersion and less alignment of the CNTs and longer polymer chains would result in more restraint on the mobility of the polymer chains; i.e., the onset of a solid-like behaviour occurs at lower nanotube contents. In addition to these factors, the content, size and interfacial properties of CNTs are expected to influence rheological properties of CNT/polymer composites. For example, at a fixed loading, nanotubes with smaller nanotube diameters and larger aspect ratios will produce a network with smaller mesh size and larger surface area/volume, which might restrain polymer motion to a greater extent.\cite{205} Experimental results support this hypothesis. Lozano et al.\cite{206} observed a rheological threshold of 10-20 wt % in carbon nanofibre/polypropylene composites in which the diameter of the carbon nanofibre is ~150 nm. The rheological threshold is ~1.5 wt % in MWCNT/polycarbonate composites,\cite{48} and only 0.12 wt % for the SWCNT/PMMA system.\cite{203} Even if these three systems have different polymer matrices as well as their
states of dispersion are unclear; the diameters among carbon nanofibres, MWCNT, and SWCNT differ by orders of magnitude. It can be concluded that if the diameter of filler decreases, the filler loading required for a solid-like behaviour increases significantly.

Figure 2.3 Optical micrographs using cross-polarisers of (a) pure PP and (b) a 0.8 wt % SWCNT/PP composite.[18]

The constraints imposed by CNTs on polymer matrices in nanocomposites are also evident in the polymer crystallisation behaviour. Bhattacharyya et al.[18] studied crystallisation in 0.8 wt % SWCNT/PP composites using optical microscopy (with cross-polars) and differential scanning calorimetry (DSC). From Figure 2.3, the spherulite size in PP is much larger than that in SWCNT/PP composites. The authors also reported that upon cooling, the SWCNT/PP composites began their crystallisation at the temperature which was about 11°C higher than that for PP’s crystallisation, suggesting that nanotubes acted as nucleating sites for PP crystallisation. They also observed that both melting and crystallisation peaks in the nanocomposite are narrower than those in neat PP. Therefore,
they proposed that higher thermal conductivity of the CNT as compared to that of the polymer, at least in part should be responsible for the sharper but narrower crystallisation and melting peaks, as heat would be more evenly distributed in the nanocomposite samples containing CNTs.

2.6.3 Mechanical properties

CNTs exhibit excellent mechanical properties with Young’s modulus as high as 1.2 TPa and tensile strength of 50-200 GPa.\textsuperscript{[53]} The combination of these exceptional mechanical properties along with the low density, high aspect ratio and high surface area make CNTs an ideal candidate of reinforcing fillers for fabrication of stiff and light-weight nanocomposites. Both SWCNTs and MWCNTs have been utilised for reinforcing thermoplastic polymers, such as polyethylene, polypropylene, polystyrene, nylon and polycarbonate, as well as thermosetting polymers, including epoxy, polyurethane, and phenol–formaldehyde resins. Generally the CNT reinforced nanocomposites can be considered as particulate composites or short fibre composites with the filler dimensions on the nanometre scale and a high aspect ratio. Therefore, the mechanics of CNT/polymer composites is governed by that of particulate composites or short fibre composites. On the other hand, unlike the macroscopic particulate composites, mechanical properties of CNT/polymer composites mainly depend on the dispersion state of nanofillers, apart from the properties of filler and matrix themselves. In addition to dispersion, there are other important factors that determine an effective reinforcement of CNTs in nanocomposites: they include a high aspect ratio, alignment and interfacial interactions between CNTs and polymer matrix.\textsuperscript{[207]} The aspect ratio must be sufficiently large to maximise the load-transfer between CNTs and the matrix, and thus, to achieve
enhanced mechanical properties. For example, polystyrene nanocomposites reinforced with well-dispersed 1.0 wt % CNTs of a high aspect ratio had more than 35 % and 25 % increases in elastic modulus and tensile strength, respectively.\textsuperscript{[143]} Similar promising results have also been reported,\textsuperscript{[208,209]} but other reports demonstrated only modest improvements in modulus and strength. For example, the impact resistance and fracture toughness of the CNT/epoxy composites containing CNTs of a larger aspect ratio were improved much better than those of the CNT/epoxy composites containing CNTs of a smaller aspect ratio.\textsuperscript{[210]} However, the corresponding tensile modulus and strength showed the very limited improvements of less than 5.0 %, probably due to weak bonds between the CNTs and the matrix molecules as well as agglomeration of CNTs. In reality, the dispersion is known as the foremost important issue in producing CNT/polymer composites. Many different techniques, including the functionalisation of CNTs and processing of CNT/polymer composites, have been employed for CNT dispersion, as discussed in Sections 2.3 and 2.4. A good dispersion not only makes more filler surface area available for bonding with a polymer matrix, but also prevents the aggregated filler from acting as a stress concentrator that is detrimental to mechanical performance of nanocomposites.\textsuperscript{[211]}

However, to obtain a uniform CNT dispersion in nanocomposites, some parameters, such as CNT content in nanocomposites, length and entanglement of CNTs as well as viscosity of matrix, are still needed to optimise. There were many reports\textsuperscript{[162,212-214]} showing that there is a critical CNT content in the matrix below which the strengthening effect for CNT/polymer composites increases with increasing CNT content. Above this critical CNT content, however, the mechanical strengths of
CNT/polymer composites decrease, and in some cases, they decrease below those of the neat matrix materials. These observations can be attributed to (i) the problems associated with uniform dispersion of CNTs at high CNT contents and (ii) lack of polymerisation reactions that are adversely affected by the high CNT content for an in-situ process. The latter effect becomes more pronounced when functionalised CNTs are employed to produce CNT/polymer composites. To a large extent, the technique employed for CNT dispersion can influence on the mechanical properties of CNT/polymer composites.

It should be noted the definition of a dispersion state of CNTs in a polymer matrix is totally dependent of the magnification or scale used for the analysis. According to the study by Li et al., using the term uniform or good dispersion to evaluate the CNT dispersion without any distinctive description may simply be misleading or inaccurate. This is because, for the conventional composites, uniform or good dispersion generally refers even distribution of fillers in a matrix medium without aggregation. However, for CNT/polymer composites, dispersion has two major aspects: (i) disentanglement of CNT bundles or agglomerates, which is referred as the nanoscale dispersion and (ii) uniform distribution of individual CNTs or their agglomerates throughout the nanocomposites, which is a micro- and macro-scale dispersion. From geometric consideration, the difference between random orientation and alignment of CNTs can result in significant changes in various properties of nanocomposites.

The storage modulus of the polystyrene composite films containing random and oriented CNTs were 10 % and 49 % higher than the unreinforced bulk polymer, respectively. The alignment can be regarded as a special case of CNT dispersion. A few techniques, including mechanical stretching, melt-spinning,
dielectrophoresis,\textsuperscript{[218]} application of an electrical or magnetic field,\textsuperscript{[219-221]} have been employed during the composite fabrication to align CNTs in a polymer matrix. The degree of CNT alignment in the composite can be governed by two factors: (i) aspect ratio of CNTs and (ii) CNT content. A smaller diameter of CNT can enhance the degree of CNT alignment due to the greater extensional flow; and a higher CNT content decreases their alignment because of the CNT agglomeration and restrictions in motion from neighbouring CNTs.\textsuperscript{[222]} While alignment is necessary to maximise the strength and modulus, it is not always beneficial because the aligned nanocomposites have very anisotropic mechanical properties, i.e., the mechanical strengths along the alignment direction can be enhanced, whereas these properties are sacrificed along the direction perpendicular to this orientation.

In addition, the interfacial properties between CNTs and matrix molecules play an essential role for mechanical properties of such nanocomposites. A strong interfacial adhesion corresponds to high mechanical properties of nanocomposites through enhanced load transfer from matrix to CNT. Chemical and physical functionalisations of CNTs have proven to enhance the interfacial adhesion. Table 2.4 summarises the effects of CNT functionalisation on the mechanical properties of CNT/polymer composites made from thermoplastic polymers. These results indicate clearly that functionalisation of CNTs can greatly enhance the modulus, strength as well as fracture resistance of CNT/polymer composites.
Table 2.4 Effect of CNT functionalisation on mechanical properties of CNT/polymer composites. [*The data are the percentage improvement in the mechanical properties of nanocomposites with pristine CNTs while the data in the brackets for those with functionalised CNTs compared to the neat polymer.]

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fabrication Process</th>
<th>Type of Functionalisation of CNTs</th>
<th>CNT content (wt %)</th>
<th>Improvement in mechanical properties *</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon (Polyamide, PA)</td>
<td>Twin-screwed extruder</td>
<td>Diamine treatment</td>
<td>1.0</td>
<td>6.1 (42) 5.3 (18)</td>
<td>[223]</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>Shear-mixing</td>
<td>Maleic anhydride and amine treatment</td>
<td>1.5</td>
<td>22 (75) 17 (33)</td>
<td>[224]</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>Ultrasonication</td>
<td>Undecyl radicals attachment</td>
<td>1.5</td>
<td>55 (84) 10 (13)</td>
<td>[225]</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>Ultrasonication</td>
<td>Butyl attachment</td>
<td>0.25</td>
<td>8.3 (25) 2.1 (50)</td>
<td>[226]</td>
</tr>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td>Ultrasonication</td>
<td>Polymer grafting</td>
<td>2.5</td>
<td>35 (40) 4.8 (17)</td>
<td>[227]</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>Ultrasonication</td>
<td>Polymer grafting</td>
<td>0.1</td>
<td>57 (104) 2.7 (86)</td>
<td>[228]</td>
</tr>
</tbody>
</table>
2.7 Comparison to other fillers

Other well-known alternatives for carbon nanotubes as reinforcing fillers for polymer nanocomposites are asbestos and nanoclays. Asbestos has been used as reinforcing fillers for polymer for many years in the engineering, aircraft, automotive, chemical and shipbuilding industries. Asbestos is in all its four main varieties – chrysotile (white asbestos), crocidolite (blue asbestos), amosite and anthophyllite.\[229\] Among them, chrysotile asbestos, a hydrated magnesium silicate \[\text{Mg}_3\text{Si}_2\text{(OH)}_4\], is the most commonly used and represents over 90-95 % of the world production of asbestos fibers.\[229, 230\] This is because the chrysotile asbestos short fiber has 30 nm in diameter, 1.0 mm in length, surface area of 1.7-60 m\(^2\)/g, 3780 MPa of tensile strength and 145 GPa of Young’s modulus. Moreover, the chrysotile asbestos short fibers are hollow.\[229\] Therefore, the geometry of the chrysotile asbestos short fibers is very much similar to that of the multiwalled carbon nanotubes. However, the multiwalled carbon nanotubes are 5-20 times stronger in tensile strength and 4-10 times stiffer in Young’s modulus compared to the chrysotile asbestos.

Similar to carbon nanotubes, asbestos is also difficult to disperse properly into polymers due to its tendency to agglomerate itself. One of the techniques used to disperse asbestos is to desolve it into water. Due to the instinctive property of asbestos, the positive charges will develop on its surface and as a result, it can suspend in the water individually. According to its size and tendency to agglomerate, asbestos can be considered as a micro-filler rather than a nano-filler. Besides, asbestos fibres are more commonly used to fabricate fibre-reinforced polymer composites or are sometimes used as secondary fillers for the glass-fibre/polymer composites.
Compared to the carbon nanotubes, asbestoses are non-conductive and lower mechanical properties. Additionally, due to their catalytic effect on the thermal degradation of the polymer, the asbestos-reinforced polymer composites need stabilisers for the polymer and inhibitors for the thermal oxidation.\textsuperscript{[229]} However, their main advantage over the carbon nanotubes is their low production cost and relatively good reinforcement for the polymer matrices.

Another type of famous reinforcing fillers for the polymers is nanoclays. Although, the incorporation of layered silicates into polymer matrices has been known for more than 50 years,\textsuperscript{[231]} the current industrial and academia interest on the nanoclay as reinforcing fillers for the polymer matrices was initiated by the finding of Toyota research group in 1990.\textsuperscript{[232]} Okada of the Toyota research group\textsuperscript{[232]} firstly reported that by the addition of very small amounts of montmorillonite nanoclay into the Nylon-6 matrix resulted in pronounced improvements of thermal and mechanical properties. Moreover, Vaia et al.\textsuperscript{[233]} reported in 1993 that it is possible to melt-mix polymers with nanoclays without using the organic solvents. After these reports, nanoclays, such as montmorillonite, hectorite and saponite, have been added into different thermoplastic polymers, including Nylon-6,\textsuperscript{[234]} polypropylene,\textsuperscript{[235]} polystyrene,\textsuperscript{[235]} poly(methyl methacrylate),\textsuperscript{[236]} polyvinyl alcohol\textsuperscript{[237]} and so on, to fabricate nanoclay/polymer nanocomposites.

The layer thickness of a pristine nanoclay sheet is around 1 nm and the lateral dimension of these layers may vary from 30nm to several microns or even larger depending on the particular layered silicate. The improvements in the physical properties of the nanoclay/polymer composites are related to the state of dispersion of the nanoclays.
in the polymer matrix often known as intercalated and exfoliated.\textsuperscript{[238]} Unfortunately, the pristine nanoclays usually tend to agglomerate and are difficult to disperse individually in a polymer matrix and therefore, the physical mixture of a polymer and layered silicates may not form a nanocomposite. In this situation, the poor physical interaction between the polymer (organic) and the layered silicates (inorganic) leads to poor mechanical and thermal properties. In contrast, pristine layered silicates usually contain hydrated Na+ or K+ ions\textsuperscript{[239]} and thus, they are only miscible with hydrophilic polymers, such as nylons or polyvinyl alcohol.\textsuperscript{[240]} Therefore, the layered silicates are usually modified with the organic groups on their surfaces and they are widely known as organoclays. After more than 2 decades of research and development, the organoclays are successfully commercialised and widely available in the market. The well-known organoclays are Cloisites with different varities, such as Na+, 10A, 15A, 20A, 25A, 93A and 30B.\textsuperscript{[241]} In general, the addition of an organoclay in a polymer matrix results in significant improvements of the mechanical properties.\textsuperscript{[242]} For example, Shelley et al.\textsuperscript{[240]} reported a 175\% improvement in yield stress accompanied by a 200\% increase in tensile modulus for a nylon 6 nanocomposite containing 5 wt\% of organoclay.

Different from carbon nanotubes, nanoclays are 2-dimensional nanofillers with very poor in the electrical conductivity. Therefore, the polymer nanocomposites with nanoclays as fillers can only enhance the mechanical and thermal properties yet there is no improvement in the electrical conductivity of the composites.
2.8 Application of carbon nanotube/polymer composites

Due to the superior mechanical properties of CNT/polymer composites, they have drawn great attention to the applications in the aerospace and defence industries. The most possible applications come with the significant weight reduction by using CNT/polymer composites in the design of airframes which requires materials with low density, high strength and modulus.

Carbon nanotubes were employed to reinforce the interfaces between ultrahigh molecular weight polyethylene particles, enhancing composite strength, stiffness, impact toughness as well as structural damping.\textsuperscript{[243]} Therefore, these nanocomposites are attracted for the applications in aerospace and naval engineering. The high strength and toughness-to-weight characteristics of CNT may also prove to be valuable as part of composite components in fuel cells which are deployed in transport applications, where durability is extremely important.

O’Donnell et al.\textsuperscript{[244]} studied the potential impact of CNT-reinforced polymer composites on commercial aircrafts. The CNT-reinforced polymer composite structured airframes were modelled through the utilisation of Euro Control’s Base of Aircraft Data and from traditional flight dynamics theory. In their model, weight reduction has positive effects on the aircraft performance, fuel saving, and efficiency. They reported that the average weight reduction was 17.3 % in the low initial take-off mass category (<7,000 kg) and over 10 % in the high initial take-off mass category (> 136,000 kg). The initial take-off mass is the maximum allowable mass at which the aircraft has been shown to meet all the airworthiness requirements applicable to it.\textsuperscript{[245]} The average fuel savings for all CNT-reinforced airframes was 9.8 %. 
Ren et al. studied the fatigue behaviour of unidirectional, aligned SWCNT-reinforced epoxy composites, and demonstrated the potential in long-term structural applications as well as in aerospace applications. Gu et al. investigated the CNT/bismaleimide hybrids for potential aerospace application. These nanocomposites are attractive for applications in aerospace and naval industries.

Moreover, CNTs are being used as fillers for electrically conductive adhesives because of their high aspect ratio, high electrical conductivity and high oxidation resistance. Generally, commercially available electrically conductive adhesives are filled with silver particles at very high loadings (generally, more than 80 wt%), which show high conductivity but very low shear strength. However, because of their high aspect ratio and high electrical conductivity, CNTs can be used at lower loadings with a minimal effect on the reduction of mechanical performance. Li et al. reported the CNT-filled adhesives as a replacement for tin/lead solder for aerospace applications. But conductive adhesive based on CNTs shows an unusually high resistance mainly due to the high contact resistivity at the adhesive-metal interface. Fortunately, Rosca et al. proposed a new method recently to reduce efficiently the contact resistivity by forcing a controlled amount of electric current through the bonded joint. They were successful in the reduction of the contact resistivity of CNTs-containing epoxy adhesives for aerospace applications.

Currently PU is primarily used for aircraft topcoats due to its light-colour, flexible, thermally stable, and chemically resistant properties with optimum exterior durability. In addition, the coatings should have sufficient electrical conductivity to mitigate electrostatic build-up which may cause considerable damage to surrounding
materials and electronics. Because of these, a surface resistance in the range of $10^6$-$10^{10}$ Ωm is needed.\textsuperscript{[251]} For these specific aerospace coating applications, Zhao et al.\textsuperscript{[252]} dispersed MWCNTs into a commercial topcoat PU matrix to produce nanocomposites for electrostatic dissipation and/or de-icing coatings. The DC electrical resistivity of MWCNT/PU composite films was $10^8$ Ωcm at 0.5 wt % MWCNTs and $10^7$ Ωcm at 3.0 wt % MWCNTs, which were sufficient for electrostatic dissipation applications.

The thermal transport properties of polymer nanocomposites can be improved with the addition of CNTs due to the excellent thermal conductivity of CNTs. These types of composite are quite attractive for usages as printed circuit boards, connectors, thermal interface materials, heat sinks, lids, housings etc.\textsuperscript{[253]}

CNTs are also widely used in actuators.\textsuperscript{[254,255]} The polyurethane nanocomposites with surface-modified MWCNTs showed the almost completely recovered original shape in at least 10 seconds when an electric field of more than 40 V was applied.\textsuperscript{[91]} The CNTs increased the modulus and electrical conductivity of polymers to show a good electroactive shape recovery. These nanocomposites may lead to the application of electroactive actuators, which is important in many practical applications, such as smart actuators for controlling microaerial vehicles. The addition of CNTs to PANI fibres increased the electromechanical actuation because the CNTs improved the mechanical, electronic, and electrochemical properties of PANI fibres.\textsuperscript{[256]} Polymer nanocomposites based on CNTs are studied for a variety of sensor applications.\textsuperscript{[139,140]} For example, polypyrrole or PANI deposited on single-walled CNT networks that can be used as solid state pH sensors.\textsuperscript{[141]} A DNA sensor was created from a composite of polypyrrole and CNTs functionalised with carboxylic groups to covalently immobilise DNA onto
CNTs. As another example, polypyrrole films doped with CNTs functionalised with oligonucleotides were implemented for DNA biosensors using direct impedance measurements. In general, the presence of CNTs tends to increase the overall sensitivity and selectivity of biosensors.

Conductive CNT/polymer composites also have a potential application in supercapacitors. The MWCNT/polyaniline composites electrodes showed much higher specific capacitance (328 F/g) than pure polyaniline electrodes. The capacitances of a CNT/polypyrrole+CNT/poly(3-methyl-thiophene) based supercapacitor prototype and a CNT+CNT/polypyrrole based hybrid supercapacitor prototype were 87 F/g and 72 F/g, respectively, which were much higher than that of 21 F/g for the CNT+CNT corresponding supercapacitor prototype due to the Faraday effect of the conducting polymers.

2.9 Summary

Polymers are usually modified by additives or fillers to improve their physical properties for specific applications. Among the available additives, CNTs provide unique opportunities to improve mechanical, electrical, and thermal properties of a variety of polymers. Although the CNT-filled polymers have shown improved properties for high-strength, light-weight and high performance nanocomposites, and potential applications, till now there have not been many industrial successes showing their advantage over traditional carbon fibres.

It is well-known that there are two major interconnected challenges that must be solved before such nanocomposites can be widely applied in real applications: namely (i) lack of solubility and dispersion when mixed with polymer matrices and (ii) poor
interfacial adhesion between CNTs and various polymers. The first issue is mainly related to the nanometre scale and high aspect ratio of CNTs. CNTs usually form stable bundles due to van der Waals interactions, and they are extremely difficult to disperse and align in a polymer matrix. The second one is due to the inherently inert nature of CNT surface which results in the insufficient interaction with the most polymers.

After reviewing on the literature, the following conclusions can be drawn in the area of fabrication of advanced CNT/polymer composites. Apart from the CNT content in a polymer matrix, the properties of CNT/polymer composites strongly depend on the dispersion of CNTs within the polymer matrix, the aspect ratio of the CNTs and the alignment of the CNTs within the polymer matrix. These quantities (such as dispersion, aspect ratio, and alignment of CNTs) are difficult and tedious to determine, and many publications fail even to attempt a qualitative description of these characteristics of their nanocomposites. The dispersion of CNTs in a polymer nanocomposite should be examined over a range of length scales from micro to nanometres. Despite various methods, such as melt processing, solution processing, and in-situ polymerisation, there are still opportunities and challenges to be found to improve dispersion and interfacial properties. Especially, a specific functionalisation of CNTs is a possible solution for strong interfacial adhesion between CNTs and a given polymer matrix, which may also simultaneously improve the dispersion of CNTs in the polymer matrix.

Additionally, mechanical properties of CNT/polymer composites may be compromised between the carbon–carbon bond damage and the increased CNT-polymer interaction due to the CNT functionalisation. Similarly, electrical conductivity of a CNT/polymer composite is determined by the negative effect of carbon-carbon bond
damage and the positive effect of the improved CNT dispersion. In either case, the choice and control of tailored functionalisation sites for chemical modification of CNTs are extremely necessary.

On the other hand, it is necessary to understand the mechanisms involved in the methods used to improve the properties of CNT/polymer composites. This will be helpful to select the appropriate polymers and the CNTs grafted with suitable chemical groups or polymer branches for the optimal dispersion of CNTs as well as the maximum adhesion at the CNT-polymer interfaces.

The concept of formation of CNT networks provides strong correlations between morphology of the nanocomposite and its properties. CNT networks are structures in which CNTs are interconnected to form an open and irregular framework of CNTs that span across the CNT/polymer composites. Such CNT networks are easily identified by dynamic mechanical (rheological) or electrical conductivity measurements. In reality, the formation of a CNT network provides a reliable measure but an indirect technique of the relative dispersion and aspect ratio of CNTs. For example, the evidence of a solid-like behaviour in the rheological properties indicates a better dispersion compared to another nanocomposite with the same loading and aspect ratio of CNTs which shows a liquid-like behaviour. The presence of CNT networks in polymer nanocomposites is appropriate for understanding rheological, electrical, and flame-retardant properties. However, it is inappropriate for other properties such as mechanical and thermal properties which are governed by the interfacial properties between the CNTs and polymer molecules.

Finally, CNT/polymer composites have confirmed their promising and straightforward potentials as multifunctional materials. By solving these challenges mentioned
above, CNT/polymer composites will maximise their applications in various areas for the coming decades as a new class of nanocomposites.
Chapter 3 Materials and Experimental

3.1 Materials

Materials used in this thesis are classified into three categories: polymers, fillers and chemicals.

Nylon 6 (PA6: Ultramid® B36 LN 01) was purchased from BASF, Singapore. Its density melting temperature and relative viscosity [1.0 % (m/v) in 96 % (m/m) sulphuric acid] were 1.12-1.15 g/cm$^3$, 220 °C and 3.49-3.71, respectively. Polypropylene (PP: Aldrich isotactic polypropylene, P/N: 427896) used in Chapter 4 was purchased from Sigma-Aldrich, USA. Its density, melt flow index, weight average molecular weight, polydispersity index and melting temperature were 0.90 g/cm$^3$, 35 g/10 min, ~190,000 g/mol, 3.8 and 160-165 °C, respectively. Polypropylene (PP, MS640) used in Chapter 6 was purchased from Tokuyama, Japan. Its density, melting temperature and melt flow index were about 0.90 g/cm$^3$, 160 °C and 6.0 g/10 min at 230 °C, respectively. The liquid crystalline polymer (LCP) used in this thesis was a copolymer of hydroxyl benzoic acid (HBA) and ethylene acrylate (ET), with a molar ratio of 80 % HBA to 20 % ET. The LCP was produced by Unitika, Japan, with a trade name of Rodrun LC-5000. According to Unitika, Rodrun LC-5000 had an excellent mouldability. Its weight average molecular weight, specific gravity, glass transition and melting temperatures were ~20,000 g/mol, 1.41, 90~100 °C and 280~305 °C, respectively.

The multiwalled carbon nanotubes (MWCNTs, Baytubes® C 150 HP) used in Chapters 4, 6 and 8, were purchased from Bayer Material Science, Germany. The Baytubes were produced in a high-yield catalytic process based on chemical vapour
deposition. According to the manufacturer’s specifications, the purity, diameter, length, number of walls and bulk density were ~99 %, 5.0-20 nm, 1.0-10 µm, 3.0-15 and 140-230 kg/m³, respectively. Iljin nanotubes, the MWCNTs used in Chapters 5 and 7, were purchased from Iljin Nanotech, Korea. Their diameter, length and density were 10-20 nm, ~20 µm, 90-150 kg/m³ respectively. These nanotubes (purity 95%) were produced by a chemical vapour deposition method. The conductive carbon black (CCB, ENSACO 350G) used in the Chapter 8 was kindly supplied from Timcal Ltd., Switzerland. The CCB had a density of 135 kg/m³ and its average particles size and volume resistivity were 45 nm and < 20 Ωcm, respectively.

Sulphuric acid (95-97 %), nitric acid (≥ 69 %), thionyl chloride (≥ 97 %), acetone (≥ 99.5 %), tetrahydrofuran (≥ 99.9 %), hydroxyl benzoic acid (≥ 99 %), N,N’-dimethylformamide (≥ 99.8 %), ammonium persulfate (≥ 98.0 %), hydrazine hydrate (50-60 %), sodium nitrite (≥ 97.0 %), ferric chloride (97 %), p-aminobenzoic acid (99 %), p-nitroaniline (≥ 99 %) and 2,2’-azoisobutyronitrile (98 %), were purchased from Sigma-Aldrich, Singapore. Sodium dodecylbenzene sulphonate and sodium dodecyl sulphate (≥ 99.0 %), were purchased from Sigma-Aldrich, USA.

3.2 Functionalisation of multiwalled carbon nanotubes

3.2.1 Sonication

The sonicated MWCNTs were prepared by a bath sonicator (Cole-Parmer 8890-16) with a frequency of 42 kHz. 100 ml of deionised water containing 1.0 g of raw MWCNTs was sonicated at room temperature for 2 hours. Then, the aqueous mixture was dried in a vacuum oven at 60 °C for 48 hours.
3.2.2 Noncovalent functionalisations

Two surfactants, sodium dodecylbenzene sulphonate (NaDDBS) and sodium dodecyl sulphate (SDS), were used in this study to functionalise the MWCNTs noncovalently. The surfactant-treated MWCNTs were prepared by a suspension method described as follows. 100 ml of aqueous solution containing 1.0 g of surfactant (either SDS or NaDDBS) was sonicated with 1.0 g of raw MWCNTs at room temperature for 2 hours by using a bath sonicator with a frequency of 42 kHz. Therefore, the ratio of MWCNTs to surfactant was 1:1 in weight in the prepared suspension. Then, the suspension was dried in a vacuum oven at 60 °C for 48 hours.

3.2.3 Covalent functionalisations

The most popular and simplest covalent functionalisation of carbon nanotubes is the carboxylic (-COOH) functionalisation. Generally, the carboxylic acid functional groups on carbon nanotubes are raised during the oxidation of the carbon nanotubes by oxygen, concentrated sulphuric acid, nitric acid, aqueous hydrogen peroxide, and acid mixture. Moreover, the carboxylic functionalisation of MWCNTs can be generally considered as an initiation process followed by a displacement reaction of the -OH groups of the carboxylic groups on the MWCNTs by other chemical moieties for the further functionalisation of MWCNTs. Two types of covalent functionalisation of MWCNTs, namely carboxylic functionalisation and hydroxyl benzoic acid (HBA) functionalisation, were used in this thesis.
(I) Carboxylic functionalisations

Scheme 3.1 Synthesis of MWCNT-COOH.

The carboxyl functionalised MWCNTs were prepared by oxidation of raw MWCNTs with a solution of concentrated sulphuric acid (H$_2$SO$_4$) and nitric acid (HNO$_3$) at 90 °C for 30 minutes with vigorous stirring according to Scheme 3.1.

A 250 ml beaker charged with 1.0 g of MWCNTs and an aqueous solution of concentrated H$_2$SO$_4$/HNO$_3$ (75ml/25ml) was heated in an oil bath to a temperature of 90 °C using a lab heater. The mixture was then magnetically stirred at the same temperature for 30 minutes. After being naturally cooled down to room temperature, the mixture was diluted with 500 ml of deionised water and then vacuum-filtered through a 200 nm PTFE membrane. The deposit was then washed with deionized water until the pH of the filtrate reached 7.0. The filtered solid was then dried under vacuum at 60 °C for 48 hours.
(II) Hydroxyl benzoic acid functionalization

Scheme 3.2 Synthesis of MWCNT-HBA.

After the MWCNTs were functionalised with carboxylic acid groups, their hydroxyl benzoic acid (HBA) functionalization was accomplished stepwise as shown in Scheme 3.2.

A mixture of the as-prepared MWCNT-COOH (1.0 g, 2.42 mmol/g of -COOH) and SOCl₂ (50 ml, 0.685 mol) were heated under reflux at 60-70 °C for 24 hours under a nitrogen atmosphere. The reaction mixture was then cooled down to room temperature naturally, followed by the filtration under a vacuum through a 200 nm pore-size membrane. The black deposit (MWCNT-COCl) was washed with dry acetone (500 ml). Then, this MWCNT-COCl was immediately added to a solution of HBA (2.0 g, 14.2 mmol) in dry THF (40 ml) in a 100 ml flask and was magnetically stirred at 50 °C for 24
hours. The reaction mixture was then filtered under a vacuum, and the solid deposit obtained was washed with dry THF (500 ml) and dried in a vacuum oven at 50 °C for 48 hours to give 0.612 g MWCNT-HBA (0.787 mmol/g, COOC₆H₄COOH).

3.3 Fabrication of carbon nanotube/polymer composites

Prior to mixing, polymers, fillers (MWCNTs and CCB) and additives (surfactants), were dried at 60 °C for 24 hours in a vacuum oven. The fabrication of carbon nanotube/polymer composites was carried out by three methods of melt-mixing followed by moulding.

In Method-I, compounding of the MWCNT/polymer composites was carried out in a micro-compounder (HAAKE MiniLab II), equipped with two counter rotating screws at a mixing temperature about 20-50 °C higher than the melting point of the polymer matrix. The screw speed was 60 rpm and the duration of compounding was 15 minutes. After being extruded from the micro-compounder, the composites were palletised and moulded at a selected moulding temperature and an injection pressure of 60 MPa using a mini-injection machine (HAAKE MiniJet II) into different test samples.

In Method-II, the carbon nanotube/polymer composites were compounded using an internal mixer (Haake polylab II) with two counter-rotating screws at a selected processing temperature. The screw speed was set at 30 rpm and the duration of compounding was 30 minutes. The moulding of the samples was carried out by compression moulding using a laboratory hydraulic hot press (Carver 4122, 12-12H) at the processing temperature of the composites under 10 bars for 10 minutes. The moulded samples were cut into required shapes for investigation of different properties.
In Method-III, the carbon nanotube/polymer composites were prepared by an extrusion process, followed by injection moulding. In this case, samples were melt-mixed using an industrial co-rotating twin screw extruder (Leistritz ZSE 27 HP). There were 3 temperature zones starting from the hopper to the die which were set according to the processing guideline by the material suppliers and the screw speed was fixed at 50 rpm. The extrudate was immediately quenched in a water bath at room temperature. The quenched samples were pelletised by a cutter. After being pelletised and dried, the composite samples were injection-moulded into different sample shapes using a 100 Ton injection moulding machine (Netstal HP 1000). The temperature of the barrel was set at the moulding temperature of the sample.

For Fourier transform infrared, Raman and optical microscopic measurements, the thin films with 1.0 µm thickness of the composite samples were fabricated by a lab-scale hot press (Carver 4122, 12-12H) at the melting temperature of the polymer matrix under 10 bars for 5 minutes.

### 3.4 Characterisation

X-ray photoelectron spectroscopy (XPS) analysis was carried out to elucidate the surface chemistry of MWCNTs before and after functionalisation. For this surface chemistry analysis, a Kratos Ultra XPS system was used with a monochromatic Al K$_a$ X-ray source operating at 15 kV and 10 mA. The core-level spectra were obtained at a photoelectron take-off angle of 90°, measured with respect to the sample surface.

Raman spectroscopy (Renishaw, RM1000) with the He-Ne laser (632.8 nm) as a light source was used to get essential information on the covalent functionalisations of MWCNTs. Raman analysis was performed on both powder and film samples.
Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical groups formed on the MWCNTs after the reactions as well as to determine the nature of the interaction between the MWCNTs and the polymer matrix. FTIR spectroscopic measurements were performed using an FTIR spectrometer (Thermo Nicolet Magna-IR 560 spectroscopy, USA) in a transmittance mode. The powder samples were prepared by the KBr method while the composite thin films were by hot pressing mentioned in the previous section.

The surface morphology of the tensile fractured samples was observed by field emission scanning electron microscopy (FESEM), after gold coating. The FESEM measurements were done using a Jeol JSM-5800 SEM at an accelerating voltage of 20 KV.

An inverted optical microscope (Olympus GX51) attached with a 3CCD camera (Sony DSP Exwave HAD) was employed to characterise the dispersion of the MWCNTs in the polymer matrix.

Transmission electron microscopic (TEM) analyses were performed on a JEM-2010F (Jeol Co., Japan) electron microscope. The MWCNT samples were prepared by sonicating about 1.0 mg of the MWCNT powder in 10 ml of ethanol at room temperature for 15 minutes using a bath sonicator (Cole-Parmer 8890-16) with a frequency of 42 kHz. A few drops of the resulting suspension were deposited on a TEM grid (200 mesh).

X-ray diffraction (XRD) was studied using an X-ray diffractometer (PW1830 series, Philips) with CuK$_\alpha$ radiation at a scan rate of 2.0 °/min. The percentage crystallinity ($\chi_c$) was determined using the equation:

$$\chi_c = \frac{i_c}{i_a+i_c} \times 100 \%$$  (3.1)
where $I_c$ and $I_a$ are the integrated intensities corresponding to the crystalline and amorphous phases respectively.

A thermal gravimetric analyser (TGA 2950, TA Instruments) was used under dry nitrogen over a temperature range of 25 to 600 °C at a heating rate of 10 °C/min.

Differential scanning calorimetric (DSC) measurements were carried out using a thermal analyser (TA DSC Q200) in a temperature range of 25 to 200 °C, at a ramping temperature of 10 °C/min in dry nitrogen. The first cooling and heating thermograms of DSC were used for the analysis. The crystallinity of sample ($\chi_c$) was determined with the following equation:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0 (1 - w_t)}$$

(3.2)

where $\Delta H_f$ is the heat of fusion, $\Delta H_f^0$ is the theoretical specific melting heat of 100 % crystalline matrix polymer and $w_t$ is the weight fraction of fillers.

Melt rheological measurements were performed on a rotational rheometer (Anton Paar Physica MCR 301) with the moulded composite samples ($\Phi$ 25 mm × 1.0 mm). The experiments were carried out in a frequency sweep mode at 5.0 % strain, using a parallel-plate geometry of a diameter of 25 mm with 1.0 mm gap, at a specific temperature in nitrogen environment.

Dynamic mechanical analysis of nanocomposites was conducted using a dynamic mechanical analyser (Perkin Elmer DMA 7) under a freely supported clamp arrangement in a bending mode. The dimensions of test samples were 15 mm × 5.0 mm × 1.0 mm. The storage modulus ($E'$) and loss tangent (tan $\delta$) for each sample were measured at a
frequency of 1.0 Hz in the temperature range from 25 to 200 °C at a heating rate of 10 °C/min.

Tensile tests were carried out on an Instron universal testing machine (Instron 5569) at room temperature with an extension speed of 5.0 mm/min and an initial gauge length of 35 mm using dumb-bell shaped samples.

Alternative Current (AC) electrical conductivity measurements (Conductivity-frequency) were carried out using an analytical cell test system (Solartron 1470E) equipped with a frequency response analyser (Solartron 1255B) at room temperature. The measured frequency range was varied from $10^5$ Hz to 0.1 Hz at a ramp of 10 Hz/s and the amplitude of voltage applied was ± 1.0 V.

Direct Current (DC) electrical conductivity measurements (voltage-current) were carried out at room temperature using a probe station of four–pointed fixture (CASCADE-REL 4800) combined with a precision LCR meter (HP Agilent-4284B) with four test channels and another precision LCR meter (HP Agilent-4284A) as an external power supplier. The voltage was varied from 0.01 to 1.0 V and the correspondent currents were measured. Five samples were tested for electrical measurements. Besides, the electrical measurements on each of the bulk sample were conducted at five different places. The capacitance mode was used to measure the DC conductivity ($\sigma$) of the sample. The following equation was used to calculate the DC conductivity ($\sigma$) of the sample.

$$\sigma = \frac{I}{V} \times \frac{t}{l \cdot w}$$  (3.3)
where I is the current measured in ampere (A), V the voltage applied in volt (V), and t, l, and w are the thickness, length and width of the bulk sample respectively. The DC conductivity was taken as the gradient of the best fit line on the V against I graph.
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Chapter 4 Effects of Surfactants

4.1 Introduction

The noncovalent functionalisation (physical modification) of CNTs is an effective way to prevent CNTs from aggregation, which promotes for better dispersion and stabilises the CNTs within a polymer matrix. Besides, the noncovalent functionalisation of CNTs is of particular interest because it does not reduce the physical properties, such as mechanical and electrical properties, of CNTs but improves dispersity and processability. In this method, various surfactants are used to disperse CNTs in a solvent, usually in water. The CNTs are surrounded by hydrophobic moieties of the corresponding surfactant micelles. The interaction becomes stronger when the hydrophobic part of the amphiphilic surfactants contains an aromatic group.\textsuperscript{[65]} CNTs can be successfully solubilised in organic\textsuperscript{[257]} or aqueous\textsuperscript{[258]} solvents after noncovalent functionalisation, which is partly attributed to the much better coverage of CNTs by functional groups.\textsuperscript{[259]} During the dispersion process, ultrasonication could help a surfactant to debundle CNTs by electrostatic repulsion and by absorption of surfactant molecules on the CNT surfaces. The main drawback of this modification method is that the forces between the wrapping molecules (the surfactant) and CNTs might not be strong enough to achieve high efficiency in load transfer between CNTs and a polymer matrix.\textsuperscript{[4]}
Therefore, the objective of this chapter is to examine the effects of surfactant-treated MWCNTs, MWCNT-SDS and MWCNT-NaDDBS, on the morphological, rheological, mechanical and electrical properties of MWCNT/PP composites using field emission scanning electron microscopy, optical microscopy, thermal analysis, rheometry, tensile and electrical conductivity tests.

In this chapter, MWCNT/PP composites with different compositions were prepared by Method-I as described in chapter 3 using Polypropylene (Aldrich) and MWCNTs (Baytubes). The mixing and moulding were carried out at 180 °C. Sonicated MWCNTs were prepared according to the prescription stated in section 3.2.1 while the noncovalent functionalization of MWCNTs were carried out as mentioned in section 3.2.2 using the surfactants, sodium dodecylbenzene sulphonate (NaDDBS) and sodium dodecyl sulphate (SDS).

The sample codes and compounding formulations for the nanocomposites prepared in this work are listed in Table 4.1 where PPCN2 with the sonicated MWCNTs was prepared for comparison to study the effects of sonication on the properties of the MWCNTs added in the PP.
Table 4.1 Compounding formulations.

<table>
<thead>
<tr>
<th>Code</th>
<th>PP (wt%)</th>
<th>MWCNT (wt %)</th>
<th>SDS (wt %)</th>
<th>NaDDBS (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PP</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPN2</td>
<td>98</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPN5</td>
<td>95</td>
<td>5</td>
<td>-</td>
<td>-</td>
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<tr>
<td>PPN10</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPSN2</td>
<td>96</td>
<td>2</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>PPSN5</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>PPSN10</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>PPNN2</td>
<td>96</td>
<td>2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>PPNN5</td>
<td>90</td>
<td>5</td>
<td>-</td>
<td>5</td>
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<td>PPNN10</td>
<td>80</td>
<td>10</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>PPCN2</td>
<td>98</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

4.2 Results and discussion

4.2.1 Ratio between surfactant and multiwalled carbon nanotubes

Thermogravametric Analysis (TGA) was used to determine the ratio between the surfactant and the multiwalled carbon nanotubes before the composites were fabricated. Figure 4.1 shows the thermographs of SDS, NaDDBS, raw MWCNTs, MWCNT/SDS and MWCNT/NaDDBS. From this figure, MWCNT showed no or little decomposition over the temperature range while the surfactants, SDS and NaDDBS showed the dramatical loss above 300 °C and 480 °C, respectively. Therefore, it should be considered that the weight loss in the surfactant-treated MWCNTs (i.e. MWCNT/SDS and
MWCNT/NaDDBS) was due to the decomposition of the surfactants during the experiments.

Figure 4.1 The TGA thermographs of SDS, NaDDBS, raw MWCNTs, SDS-treated MWCNTs and NaDDBS-treated MWCNTs.

Table 4.2 lists the weight loss in percentage for all the samples at 600 °C. From this table, the weight loss of SDS-treated MWCNT is 36.6 % which is about the half of that of pure SDS (73.1 %). Similarly the weight loss of NaDDBS-treated MWCNT is 26.5 % which is about the half of that of pure NaDDBS (53.1 %). From these results, it could be concluded that the weight ratios between the surfactants and MWCNTs were 1:1.
Table 4.2 The percentage weight losses of SDS, NaDDBS, SDS-treated MWCNTs and NaDDBS-treated MWCNTs at 600 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT</th>
<th>SDS</th>
<th>MWCNT/SDS</th>
<th>NaDDBS</th>
<th>MWCNT/NaDDBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss (%)</td>
<td>0.2</td>
<td>73.1</td>
<td>36.6</td>
<td>53.1</td>
<td>26.5</td>
</tr>
</tbody>
</table>

4.2.2 Effects of surfactants on multiwalled carbon nanotubes

Figure 4.2 shows the TEM images of the raw MWCNTs, SDS-treated MWCNTs and NaDDBS-treated MWCNTs used in this work. The existence of highly entangled network-like structure of MWCNTs is well evident from the micrograph. In Figure 4.2a, raw MWCNTs were found as bundles while the surfactant-treated MWCNTs were individually separated as shown in Figure 4.2b and 4.2c for SDS-treated MWCNTs and NaDDBS-treated MWCNTs respectively. This is because the surfactants were absorbed on the surfaces of CNTs during the dispersion procedure where the sonication might also help the surfactants to debundle CNTs.\(^{[75]}\)
Figure 4.2 TEM micrographs of (A) raw MWCNTs, (B) SDS-treated MWCNTs and (C) NaDDBS-treated MWCNTs.
4.2.3 Rheological properties of MWCNT/PP composites

Figure 4.3A represents the complex viscosity ($\eta^*$) of the pure PP and MWCNT/PP composites as a function of angular frequency ($\omega$). From this figure, the pure PP followed nearly a Newtonian behaviour over the frequency range studied while its nanocomposites, a non-Newtonian with shear-thinning one. This non-Newtonian behaviour was more pronounced for the composites with higher loading of MWCNTs. The complex viscosity increased with increasing MWCNT content, which was more prominent at lower frequencies. Kim et al.\cite{260} reported the similar observation and considered that the increase in the complex viscosity with increasing MWCNT content in the polymer composites was attributed to the increase in the interactions between CNTs and the matrix polymer. Thus, the higher viscosity and shear thinning behaviour of the MWCNT/PP composites reflected the better compatibility between MWCNTs and the PP matrix as well as the better dispersion of MWCNTs in the composites.

Therefore in this case, with the aid of the surfactants, NaDDBS or SDS, there was a better dispersion of MWCNTs in the PP matrix compared to the raw MWCNTs. The $\pi$-$\pi$ interaction between the benzene ring of NaDDBS with the MWCNTs contributed to the better compatibility between the NaDDBS-treated MWCNTs and PP.\cite{65} Therefore, it can be concluded that the NaDDBS-treated MWCNTs had a better compatibility as well as a better dispersion as compared to the SDS-treated MWNCNTs and the raw MWCNTs.
Figure 4.3 Rheological properties of pure PP, PPN, PSN and PPNN composites: (A) Complex viscosity, (B) Storage modulus and (C) Loss modulus – where (o) pure PP, (a) PPN5, (b) PPSN5, (c) PPNN5, (d) PPN10, (e) PPSN10, and (f) PPNN10.
In general, at the same loading of MWCNTs, the composites with surfactant-treated MWNCTs have higher viscosity than that of the composite with raw MWCNTs. The higher viscosity of the composites with surfactant-treated MWCNTs is considered to be mainly attributed to:

(1) Better compatibility between the surfactant-treated MWCNTs and PP and

(2) Better dispersion of the surfactant-treated MWCNTs in the PP matrix.

For example, it would be reasonably considered that the well dispersed nanotubes are able to form loose network-like clusters in the PP matrix, which may restrain polymer chains to flow and then increase melt viscosity. At the same time, these loose network-like clusters of MWCNTs will contribute to a higher electrical conductivity.

The storage modulus (G') and loss modulus (G'') versus angular frequency for the pure PP, MWCNT/PP, MWCNT-SDS/PP, and MWCNT-NaDDBS/PP composites at 200 °C are shown in Figures 4.3B and 4.3C. The G’ and G” of the composites dramatically increased with increasing angular frequency and the MWCNTs loading compared with that of the pure PP. These results indicate that there was a transition from a liquid-like behaviour to a solid-like behaviour with increasing the MWCNT loading. As the rheological measurements observed at lower frequencies represent the longer relaxation times of PP, the differences among these composites were more dominant at low frequencies, indicating that the rheological properties of PP had been differently modified by the addition of the different types of MWCNTs. The storage modulus, G’, at lower frequencies becomes almost independent of frequency as the MWCNT loading increases as shown in Figure 4.3B. This phenomenon is attributed to a dynamic network of MWCNTs which could delay the large-scaled motion of the PP chains.\textsuperscript{204} At 10 wt %
MWCNT loading, the composites with surfactant-treated MWCNTs (PPSN10 and PPNN10) show the higher storage moduli at the lower frequencies compared to the composite with raw MWCNTs (PPN10). Du et al.\cite{203} reported that better dispersion and less alignment of carbon nanotubes resulted in more restriction on the mobility of polymer chains at the same loading of carbon nanotubes in the polymer composites. Besides, the properties of MWCNTs, such as the size, aspect ratio, and interfacial properties, all influence the rheological properties of the composites. In this study, the frequency independent storage moduli of the composites with surfactant-treated MWCNTs could be related with the better dispersion of MWCNTs in the PP matrix.

Finally, the pure PP had near-terminal flow behaviour while the others, non-terminal ones. It is observed that the composites containing the surfactant-treated MWCNTs had the higher complex viscosity, storage and loss moduli than the composites with the same loading of raw MWCNTs. This result suggests that the surfactant-treated MWCNTs would have a better dispersion in the polymer matrix.\cite{261} Moreover, NaDDBS-treated MWCNTs contributed to the higher viscosity and storage modulus of the composites than SDS-treated MWCNTs at the same loading of MWCNTs. This is because NaDDBS-treated MWCNTs had better interfacial interaction via π-π interaction than SDS-treated MWCNTs. As a result, the stronger interaction between NaDDBS and MWCNTs greatly reduced the agglomeration of MWCNTs.

**4.2.4 Morphological properties of MWCNT/PP composites**

Figure 4.4 shows the optical micrographs of PPN2, PPSN2 and PPNN2 thin films with 1 µm thickness. From Figure 4.4a, there are some black dots, which are bigger than the size of 10 µm, showing that the raw MWCNTs still tend to agglomerate in the PP
matrix. But for PPSN2, the size of the black dots obviously becomes smaller as compared to that of raw-MWCNTs as shown in Figure 4.4b. Although there are still some small black dots and spots observed, the image of PPNN2 in Figure 4.4c is much clearer than the rest (PPN2 and PPSN2), indicating a better dispersion of MWCNTs. This shows that because of NaDDBS, most of the MWCNTs were dispersed uniformly in the PP matrix and as a result, the image is more apparent.

The SEM photographs of the cross-sectional fracture of the MWCNT/PP composites are shown in Figure 4.5. From Figure 4.5a, the larger agglomerations of raw MWCNTs are shown in the circle indicators while the individual raw MWCNTs dispersed in the PP matrix are highlighted in the circle-headed arrows. From this figure, it is significantly observed that the dispersion of raw MWCNTs was poor in the PP matrix and the MWCNTs tended to form aggregates in the PP matrix. Due to the agglomeration problem of raw MWCNTs, the overall performance of the composites filled with raw MWCNTs tends to be poor. This is because these agglomerates of raw MWCNTs reduced the interfacial area between MWCNTs and the polymer matrix, and interrupted the formation of network structure, which would affect efficient load-transfer between MWCNTs and the polymer matrix as further explained in the following section.

On the other hand, the composites filled with the surfactant-treated MWCNTs show the better dispersion in the PP matrix than the composite containing the same amount of raw MWCNTs. As shown in Figures 4.5b and 4.5c, the bright dots and some lines indicate that the ends of the broken surfactant-treated MWCNTs were dispersed in the PP matrix. This is because the surfactant molecules could serve as a link between the MWCNTs and PP matrix, providing hydrophobic interactions that can enhance the
Thus, as a consequence of this uniform dispersion of surfactant-treated MWCNTs, the composites with these types of MWCNTs had better mechanical performance than those with raw MWCNTs. Besides, it is interestingly observed from Figures 4.5d, 4.5e and 4.5f that the diameters of surfactant-treated MWCNTs are larger than those of raw MWCNTs. Generally, the thicker MWCNTs can be explained by two aspects:

1. Due to the excessive interfacial adhesion between the surfactant molecules and the MWCNTs, it is difficult to remove the surfactant molecules from the MWCNTs after surfactant treatment. Therefore, MWCNTs were coated with the surfactant molecules during the modification process and these surfactant molecules were not removed during the mixing and injection moulding process.

2. Due to the surface modification of MWCNTs by surfactant molecules, there could be a better compatibility between the polymer matrix and the MWCNTs so that those MWCNTs were coated with the polymer molecules during the fabrication process and these polymer molecules were not removed during mixing and injection moulding. This phenomenon was also reported even in the polymer composites with raw MWCNTs.

In this study, MWCNTs could be coated with the surfactant molecules during the surfactant treatment process. Then, these surfactant-treated MWCNTs were coated further with the polymer molecules during mixing due to the better compatibility between them. Finally, these coated polymer molecules were not removed after a tensile test. As a result, the significant increase in the diameters of the surfactant-treated MWCNTs could be observed as shown in Figures 4.5e and 4.5f.
Figure 4.4 Optical micrographs of composite thin films: (a) PPN2, (b) PPSN2 and (c) PPNN2.
Figure 4.5 FESEM micrographs of tensile fracture samples of composites at 10 k magnification: (a) PPN10, (b) PPSN10 and (c) PPNN10, and at 20 k magnification: (d) PPN10, (e) PPSN10 and (f) PPNN10.
4.2.5 Thermal properties of MWCNT/PP composites

To study the effect of different types of MWCNTs on PP crystallisation in the composites, DSC measurements were carried out. In Table 4.3, the crystallisation temperature ($T_c$), melting temperature ($T_m$), heat of fusion ($\Delta H_f$) and crystallinity ($\chi_c$) obtained from DSC studies are summarised. The values for crystallinity were calculated using equation 3.2 where the theoretical specific melting heat of 100% crystalline PP was taken as 209 J/g.\cite{265,266}

Table 4.3 Thermal properties of the composites prepared in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PP</td>
<td>112.4</td>
<td>148.5</td>
<td>80.5</td>
<td>38.52</td>
</tr>
<tr>
<td>PPN2</td>
<td>115.5</td>
<td>154.4</td>
<td>74.8</td>
<td>36.52</td>
</tr>
<tr>
<td>PPN5</td>
<td>117.7</td>
<td>155.3</td>
<td>72.2</td>
<td>36.36</td>
</tr>
<tr>
<td>PPN10</td>
<td>121.5</td>
<td>156.0</td>
<td>68.1</td>
<td>36.20</td>
</tr>
<tr>
<td>PPSN2</td>
<td>116.3</td>
<td>155.2</td>
<td>76.12</td>
<td>37.94</td>
</tr>
<tr>
<td>PPSN5</td>
<td>118.2</td>
<td>156.0</td>
<td>69.15</td>
<td>36.76</td>
</tr>
<tr>
<td>PPSN10</td>
<td>122.2</td>
<td>156.4</td>
<td>60.26</td>
<td>36.04</td>
</tr>
<tr>
<td>PPNN2</td>
<td>118.7</td>
<td>155.5</td>
<td>76.46</td>
<td>38.11</td>
</tr>
<tr>
<td>PPNN5</td>
<td>120.8</td>
<td>156.4</td>
<td>71.27</td>
<td>37.89</td>
</tr>
<tr>
<td>PPNN10</td>
<td>124.1</td>
<td>157.5</td>
<td>60.93</td>
<td>36.44</td>
</tr>
<tr>
<td>PPCN2</td>
<td>115.9</td>
<td>154.8</td>
<td>75.1</td>
<td>36.67</td>
</tr>
</tbody>
</table>
The melting endotherms (Figure 4.6A) show that PP had a main melting peak at 151.3 °C with an additional shoulder peak at 148.6 °C, corresponding to the melting behaviours of the α-form and β-form crystals, respectively.\textsuperscript{[267]} However, for the MWCNT/PP nanocomposites, the shoulder peak decreased in the presence of MWCNT, which was more obvious when the content of MWCNTs in the MWCNT/PP nanocomposites was higher. These results show that the presence of MWCNTs promoted the crystallisation of PP for the formation of α-crystals, but they had a less effect on that of the β-form. Zheng et al.\textsuperscript{[268]} observed the similar effects of clay on polymorphism of PP in the clay/PP nanocomposites. They reported that clay had an insufficient effect on the crystallisation rate of the β-form crystal. The composites studied here also followed their finding that there is no shoulder peak observed for the composites incorporated with MWCNTs and only the α-phase crystallites existed. The melting peak temperature of PP was affected by incorporation of MWCNTs. The melting temperature of PP tended to increase with addition of MWCNTs due to their nucleating effect on PP.\textsuperscript{[269]} It is observed that the melting temperature of PP shifted higher by 4.5 °C for PPN10, 5.1 °C for PPSN10 and 6.2 °C for PPNN10.

From Figure 4.6B, it can be seen that the pure PP shows only a crystallisation peak temperature at about 112.4 °C. The PP crystallisation temperature shifted to the higher temperature side while incorporated with MWCNTs. These results indicate that the carbon nanotubes may act as a nucleating agent, which promotes the crystallisation of PP during a cooling process. It is also observed that the crystallisation temperature increased with increasing the MWCNT content in the composites. Seo et al.\textsuperscript{[270]} reported that the addition of MWCNTs enhanced the nucleation of PP during a crystallisation
process. Bao et al.\textsuperscript{[271]} also reported the addition of MWCNTs into PP resulted in an improved heterogeneous nucleation effect. When the MWCNT loading increases in the PP matrix, more heterogeneous nucleating sites are available, and hence more polymer chains are induced to crystallise, which causes the crystallisation peak to shift towards the higher temperature. Therefore, the incorporation of the MWCNTs effectively enhanced the crystallisation temperature of the PP matrix through heterogeneous nucleation.

However, at the same loading of 10 wt% MWCNTs, the composites with SDS and NaDDBS surfactants (i.e.: PPSN10 and PPNN10, respectively) exhibit no significant effect on the crystallisation temperature compared to the composite without any surfactant (i.e. PPN10). It has been discussed in the previous chapter that at the same MWCNT loading, the presence of surfactant would not show any significant effect on the crystallisation behaviour of PP in the MWCNT/PP nanocomposites. There is a similar observation in the literature on the MWCNT composites with nylon 6 as the matrix.\textsuperscript{[75]} From those results, it is concluded that the presence of the surfactants did not virtually affect the crystallisation behaviour of PP whereas the incorporation of MWCNTs into PP was responsible for the changes in the crystallisation of PP. Moreover, it is found that both melting and crystallisation peaks in the nanocomposites were narrower than those in PP. This is due to the higher thermal conductivity of the MWCNTs in the composites.\textsuperscript{[269]} The higher thermal conductivity of the MWCNTs as compared to that of the PP matrix is responsible for the sharper and narrower crystallisation and melting peaks, as heat could be more uniformly distributed in the samples containing the MWCNTs.
Figure 4.6 DSC thermograms for pure PP, PPN10, PPSN10 and PPNN10 at the rate of 10 °C/min in dry nitrogen gas: (A) melting and (B) crystallisation.
The heat of fusion (ΔH_f) slightly decreased with increasing the loading of MWCNTs in the composites. The heat of fusion is proportional to the degree of crystallinity in the sample. The crystallinities of all the composites were lower than that of pure PP. This is because the addition of MWCNTs enhanced crystallisation temperature of the composites compared to pure PP, but reduced the molecular mobility of PP simultaneously. Consequently, the crystallinity of PP in the composites reduced slightly with increase in the loading of MWCNTs in the PP matrix. Therefore, the degree of crystallisation of all the composites decreased as compared to pure PP.

4.2.6 Mechanical properties of MWCNT/PP composites

Figure 4.7 shows the tensile properties for PPN, PPSN and PPNN composites. The presence of MWCNTs improved the mechanical properties of the PP matrix. Generally, the improvement in the mechanical properties of MWCNT/polymer composites can be attributed to either their enhanced crystallinity or the interaction of MWNCTs with the polymer matrix or both. But in this study, the degrees of crystallisation of the MWCNT/PP composites were lower than that of pure PP as discussed previously. Therefore, the enhanced mechanical properties of the composites in this study were only due to the better dispersion of MWNCT with the PP matrix.
Figure 4.7 Mechanical properties of PPN, PPSN, PPNN composites at different MWCNT loading.
From Figure 4.7a, the Young’s modulus of the pure PP increased from 800 MPa to 1050 MPa for PPN2, 1124 MPa for PPCN2, 1280 MPa for PPSN2 and 1481 MPa for PPNN2, respectively only at 2 wt % of MWCNT loading. The Young’s modulus increased with loading of MWCNTs for all composites. This is because, while being incorporated with MWCNTs, the mobility of the polymer chains was limited. The restriction in chain mobility increased with increase in the MWCNT loading. This reduced mobility of polymer chains made the composites more rigid and as a result, the composites had higher moduli than the unfilled PP. Compared to PPN2 containing raw MWCNTs, PPCN2 filled with sonicated MWCNTs shows the higher tensile modulus due to the better dispersion of the sonicated MWCNTs. Moreover, the tensile moduli of the composites with surfactant-treated MWCNTs were higher than those with raw MWCNTs treated with or without sonication. This is because the surfactant-treated MWCNTs, which dispersed more uniformly in PP matrix, would interact effectively with more neighbouring PP chains than the raw MWCNTs. Therefore, the mobility of the matrix molecules in the surfactant-treated MWCNT/PP composites was more restricted and they had higher moduli than the composites with raw MWCNTs.

It is observed from Figure 4.7b, that with the addition of 2 wt % MWCNTs, the tensile strength improved 27 % for PPN2, 33 % for PPCN2, 42 % for PPSN2, and 55 % for PPNN2, respectively. The tensile strength increased from 12.5 MPa for the pure PP to 19.9 MPa for PPN10, 22.5 MPa for PPSN10 and 26.1 MPa for PPNN10, respectively. It is found that the tensile strengths of the composites with surfactant-treated MWCNTs are higher than those of the composites with raw MWCNTs treated with or without sonication. The uniform dispersion of surfactant-treated MWCNTs in the PPSN
composites and the PPNN composites contributed to the reinforcing mechanism in those composites. However, for the PPN composites with raw MWCNTs, the MWCNTs were agglomerated due to the strong van der Waals forces among them. This agglomeration of MWCNTs has been verified from the SEM images in Figure 4.5. The big agglomerates were obviously present in the PPN composites while the PCN2, the PPSN composites and PPNN composites showed no or little agglomerations. The aggregation of raw MWCNTs reduces the total surface area of the carbon nanotubes, which interrupts the stress transfer from the polymer matrix to nanofillers.\textsuperscript{[266]} Moreover, the PPNN composites showed a higher tensile strength than the PPSN composites.

This phenomenon can be explained by two aspects:

1. Interactions among the components in the composite and
2. Dispersion state of MWCNTs with different surfactants.

NaDDBS has a stronger interaction with MWCNT surface and a better ability to disperse MWCNTs compared to SDS due to its headgroup and longer alkyl chain.\textsuperscript{[65]} As a result, the overall mechanical performance of the PPNN composites could be significantly improved.

Figure 4.7c shows the elongation at break for raw MWCNT/PP composites, SDS-treated MWCNT/PP composites and NaDDBS-treated MWCNT/PP composites. From Figure 4.7c, it is observed that the elongation at break decreased from 168 % for the pure PP to 18 % for PPN2, 21 % for PPSN2, and 27 % for PPNN2, respectively only at 2 wt % of MWCNT loading. Notably, the elongation at break dropped very much for all composite samples after the addition of MWCNTs into the PP matrix. These results
indicate that the MWCNT/PP composites were harder but much more brittle than PP. This is because the MWCNTs could act as defects in the composites, which reduced the homogeneity and continuity of the matrix PP. Compared to the PPN composites, PPSN and PPNN composites had slightly higher values of elongation at break. This is because the elongation at break of MWCNT/PP composites strongly depends on the dispersion state of MWCNTs in the PP matrix and the compatibility between MWCNTs and PP chains. For the PPNN composites, for example, the better dispersion of MWCNTs and the better compatibility between the NaDDBS-treated MWCNTs and PP chains resulted in the highest elongation at break among all the composites studied at the same MWCNT loading.

4.2.7 Electrical properties of MWCNT/PP composites

As carbon nanotubes exhibit the high aspect ratio and high conductivity, they can be the excellent candidate for the fabrication of conductive composites. The electrical conductivity of the MWCNT/PP composites as a function of MWCNT loading is shown in Table 4.4. The electrical conductivity of pure PP is $10^{-16}$ S/cm.\[272\] The composite with 5 wt % raw MWCNTs had an electrical conductivity of $4.5\times10^{-7}$ S/cm. The conductivity of the composites increased with increasing MWCNT content and the electrical conductivity of the composite with 10 wt % raw MWCNTs was increased to $2.09\times10^{-6}$ S/cm. At low contents, conducting fillers were dispersed as isolated clusters within the polymeric matrix. Above the percolation threshold, individual fillers tended to link together to form conductive networks. This led to significant increase in electrical conductivity of the composite.
Table 4.4 Electrical conductivities of pure PP, PPN, PSN and PPNN composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pure PP</th>
<th>PPN5</th>
<th>PPN10</th>
<th>PPSN5</th>
<th>PPSN10</th>
<th>PPNN5</th>
<th>PPNN10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>1×10^{-16}</td>
<td>4.5×10^{-7}</td>
<td>2.1×10^{-6}</td>
<td>2.4×10^{-6}</td>
<td>6.7×10^{-4}</td>
<td>2.6×10^{-6}</td>
<td>6.9×10^{-4}</td>
</tr>
</tbody>
</table>

The uniform dispersion of surfactant-treated MWCNTs in the composites resulted in the higher electrical conductivity than the composites with raw MWCNTs. The electrical conductivity of 2.4×10^{-6} S/cm at 5 wt % of MWCNTs and that of 6.7×10^{-4} S/cm at 10 wt % MWCNT, respectively, were achieved in the presence of SDS in the composites. Therefore, it is known that the treatment of MWCNTs with a surfactant played an important role in the homogeneous dispersion of MWCNTs in a polymer matrix so as to allow conductive networks to be formed more easily. For the composites filled with NaDDBS-treated MWCNTs, the electrical conductivity at 5 wt % and 10 wt % of MWCNTs were 2.6×10^{-6} S/cm and 6.9×10^{-4} S/cm, respectively. From these results, it is found that the electrical conductivities of NaDDBS-MWCNT/PP composites were not different from SDS-MWCNT/PP composites at the same loading of MWCNTs. Thus, it can be concluded that the use of different surfactants could not attribute directly to the electrical properties of the composites, although the surfactant molecules could help MWCNTs to disperse effectively in the PP matrix.
4.3 Summary

The effects of different surfactants on the properties of multi-walled carbon nanotubes (MWCNT)/polypropylene (PP) composites prepared by a melt mixing method have been investigated by means of the dispersion of MWCNTs, crystallinity, thermal stability, mechanical properties and electrical conductivity. The research on the MWCNT/PP composites studied in this chapter can be summarised in Scheme 4.1.

![Scheme 4.1 Flowchart for the summary of work on the MWCNT/PP composites.](image-url)
Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (NaDDBS) were used as a means of physical modification of MWCNTs to help them to be dispersed uniformly into the PP matrix. Furthermore, to study the effect of the MWCNT loadings on the properties of the MWCNT/PP composites, the amounts of the MWCNTs were varied from 0 to 10 wt%. It was found that the surfactant-treatment and micro-mixing resulted in a great improvement in the state of dispersion of MWCNTs in the polymer matrix, leading to a significant enhancement of Young’s modulus and tensile strength of the composites. Overall, NaDDBS showed the stronger effects on PP than SDS. For example, with the addition of only 2 wt % of SDS-treated and NaDDBS-treated MWCNTs, the Young’s modulus of PP increased by 61.1 %, and 86.1 %, respectively. Therefore, it is confirmed that the dispersion of the MWCNTs in PP and the interfacial interactions among MWCNTs, surfactant and PP matrix are the key factors that determine the overall performance of a MWCNT/polymer composite.
Chapter 5 Effects of Functionalisation of Carbon Nanotubes

5.1 Introduction

In the case of covalent functionalisation, some of sp\(^2\) carbon atoms of CNTs are changed to sp\(^3\) carbon atoms, so that the electronic properties of CNT are changed from that of the original CNT. A proper functionalisation of CNT may improve its solubility in solvents and dispersion in polymers. Besides, it is known that the dispersion of the CNTs as well as their compatibility would be better in a polymer matrix if the CNTs have been functionalised with the same type of group at their surface as the polymer matrix.

Therefore, in this chapter, to obtain a homogeneous dispersion of MWCNTs throughout a polymer matrix as well as an enhanced interfacial adhesion between MWCNTs and the polymer matrix, the MWCNTs (Iljin tubes) have been chemically functionalised with hydroxyl benzoic acid (HBA) groups on their surfaces as the matrix polymer used in this study, Rodrun LC 5000, is an LCP containing 80 % hydroxyl benzoic acid and 20 % ethylene acrylate (ET).

The covalent functionalizations of MWCNTs were carried out according to the prescription stated in section 3.2.3. The raw MWCNTs were first covalently functionalised with the carboxyl (-COOH) groups on their surfaces as shown in Scheme 3.1 and then, followed by a further functionalization with hydroxyl benzoic acid (HBA) groups as in Scheme 3.2.

Method-I for fabrication of composites was used with an operation and moulding temperature of 300 °C. The formulation and sample code of the composites fabricated for this work are listed in Table 5.1.
Table 5.1 Compounding formulation in weight percentage for MWCNT/LCP composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LCP</th>
<th>Raw MWCNT</th>
<th>MWCNT-COOH</th>
<th>MWCNT-HBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw MWCNT/LCP</td>
<td>99</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MWCNT-COOH/LCP</td>
<td>99</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>MWCNT-HBA/LCP</td>
<td>99</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

5.2 Results and Discussion

5.2.1 Carboxylic functionalisation and hydroxyl benzoic acid functionalisation of MWCNTs

The FTIR spectra for the raw and functionalised MWCNTs are shown in Figure 5.1. The very low-intensity characteristic peaks of the raw MWCNTs were present in the FTIR spectra at 3440 (OH) cm\(^{-1}\) and 1640 (C=O) cm\(^{-1}\), respectively. After the H\(_2\)SO\(_4\)/HNO\(_3\) treatment, the peaks of the modified MWCNTs appeared at a significantly higher intensity depending on the degree of modification. In addition to these peaks, a new peak at 1182 cm\(^{-1}\) was due to the C-O stretching. These results were attributed to the increased number of carboxylic acid groups generated at the surface of the MWCNTs after the treatment with H\(_2\)SO\(_4\)/HNO\(_3\). The acid-treated MWCNTs were further activated for a nucleophilic displacement reaction by treatment thionyl chloride (SOCl\(_2\)) to give MWCNT-COCl. The reaction between MWCNT-COCl and excess HBA gave MWCNT-HBA (as shown in Scheme 3.2). The use of excess HBA ensured the complete reaction of all the acid chloride groups. The successful functionalisation of MWCNT-COCl with HBA can be clearly seen in the FTIR spectrum of MWCNT-COOCH\(_4\)H\(_4\)COOH (Figure 6.1). The new intense peak at 1740 cm\(^{-1}\) could be assigned to the C=O stretching of ester.
linkage of the \(-\text{COOC}_6\text{H}_4\text{COOH}\) moiety while the new peak at 1510 cm\(^{-1}\) is attributed to the aromatic ring of the benzoic acid.\(^{[273]}\)

![FTIR spectra](image)

Figure 5.1 FTIR spectra for (a) raw MWCNTs, (b) MWCNT-COOH, and (c) MWCNT-HBA.

Raman spectroscopy was used to get essential and quick information for the evaluation of the covalent modification of the MWCNTs. In Figure 5.2, the band around 1580 cm\(^{-1}\) in the spectra can be assigned to the tangential mode (G-band) and associated with the ordered \(sp^2\)-hybridised carbon network. The disorder-induced D-band was observed at 1321 cm\(^{-1}\), which was related to local defects that originated from the structural imperfection and associated with the disordered \(sp^3\)-hybridised carbon network.\(^{[134,274,275]}\) The second-order overtone of the D-band, referred to as D\(^*\), appeared at 2638 cm\(^{-1}\).\(^{[276]}\) The D\(^*\)-band reflects a breathing vibration mode by which all atoms of
a graphene sheet undergo in-plane movement. The D-, G-, and D*- bands were observed for all samples as shown in Figure 5.2.

![Raman spectra for raw and functionalised MWCNTs.](image)

The D- and G-bands of the MWCNT-COOH and MWCNT-HBA were shifted to higher wavenumbers as compared to the raw MWCNTs, which should be associated with the covalent attachment of organic moieties to the MWCNT surface. However, the D-band intensity increased in the functionalised MWCNTs compared to the raw MWCNTs. The peak intensity ratios; $I_D/I_G = 1.53$ and 1.58 between D-band and G-band for MWCNT-COOH and MWCNT-HBA, respectively, exceeded that of raw MWCNTs ($I_D/I_G = 1.1$). This result indicates that some of the sp$^2$ C atoms (C=C) were converted to
X-ray photoelectron spectroscopy (XPS) analysis was carried out to elucidate the surface chemistry of MWCNTs before and after modification. Figure 5.3 shows the XPS survey spectra for MWCNT-HBA, the XPS spectra for the C 1s and O 1s core levels of MWCNT-HBA, and the XPS spectra for the C 1s core level of MWCNT-COOH. The XPS survey spectrum (Figure 5.3a) of MWCNT-HBA revealed the presence of only carbon and oxygen, and not hydrogen, which could not be detected by XPS. The relative atomic concentrations of carbon and oxygen were 96 % and 4 % for raw MWCNTs, 88 % and 12 % for MWCNT-COOH, and 86 % and 14 % for MWCNT-HBA, respectively. The C1s core level (Figure 5.3b) could be fitted to six fractional peaks with the peak binding energies at 284.4 eV, 285.3 eV, 286.4 eV, 287.2 eV, 288.9 eV, and 291.1 eV. The main peak at 284.4 eV was attributed to sp$^2$-hybridised graphite-like C atoms, whereas the peak at 285.3 eV was assigned to sp$^3$-hybridised diamond-like C atoms.\textsuperscript{[277]} The peaks at 286.4 eV, 287.2 eV, and 288.9 eV correspond to C atoms attached to one O atom by a single bond (e.g., alcohol, ether), to one O atom by a double bond (e.g., ketone, aldehyde), and to two O atoms (e.g., ester, carboxylic acid), respectively.\textsuperscript{[278]} Finally, the π-π$^*$ transition loss peak was detected at 291.1 eV.\textsuperscript{[94]} The O 1s peak (Figure 5.3c) was fitted into three peaks appearing at 531.7 eV, 533.0 eV, and 534.0 eV, which corresponded to O atoms bound to C atoms in functional groups, such as alcohols (C-OH), ketones (COC), and carboxylic acids (COOH and/or –OC-O-CO–), respectively.\textsuperscript{[278]}

The C 1s core level XPS spectrum of the MWCNT-COOH showed the same six components, but the relative percentage of each component was different as shown in
Table 5.2. Compared to raw MWCNTs, the number of sp\(^2\) C atoms is reduced while the number of sp\(^3\) C atoms is increased in the functionalised MWCNTs. This is in good agreement with the Raman spectra showing that acids led to the oxidation of MWCNTs by preferentially creating carboxylic functional groups.

Figure 5.3 (a) Survey XPS spectrum and XPS spectra of the (b) C 1s and (c) O 1s core levels of the MWCNT-HBA, and (d) XPS spectra of the C 1s core level of the MWCNT-COOH.
Table 5.2 Relative percentages of the components obtained from XPS curve fitting of the C 1s peaks for MWCNTs as illustrated in Figure 5.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>sp² [%]</th>
<th>sp³ [%]</th>
<th>-C-O [%]</th>
<th>-C=O [%]</th>
<th>-COO- [%]</th>
<th>π-π* [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw MWCNT</td>
<td>70.4</td>
<td>15.6</td>
<td>5.4</td>
<td>-</td>
<td>2.2</td>
<td>6.4</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>63.8</td>
<td>17.3</td>
<td>7.2</td>
<td>4.2</td>
<td>5.3</td>
<td>2.2</td>
</tr>
<tr>
<td>MWCNT-HBA</td>
<td>60.1</td>
<td>19.3</td>
<td>7.7</td>
<td>5.4</td>
<td>5.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

5.2.2 Interaction between MWCNTs and the LCP

The nature of interaction between chemical groups in the LCP and those on the MWCNT surface is usually probed by measuring the extent of shift in absorption wavelength of the groups after mixing them. Figure 5.4 shows the FTIR spectra of the LCP and MWCNT/LCP composites. One characteristic peak near 1743 cm⁻¹ due to -C=O stretching of the ester group of LCP can be seen (Figure 5.4a). It can be clearly observed that the peak for -C=O group slightly shifted from 1743 cm⁻¹ in the pure LCP to 1738 cm⁻¹ in the composites with raw MWCNTs. This indicates that there was a very weak interaction between the LCP and raw MWCNTs. This kind of shift was more prominent in the LCP composites containing the functionalised MWCNTs (MWCNT-COOH or MWCNT-HBA).
Figure 5.4 FTIR spectra for (a) pure LCP, (b) MWCNT-HBA/LCP, (c) MWCNT-COOH/LCP, and (d) raw MWCNT/LCP.

In these two cases, the C=O stretching peak (Figure 5.4b, c) shifted from 1743 cm\(^{-1}\) to a lower wavenumber (1727 and 1729 cm\(^{-1}\) for MWCNT-HBA/LCP and MWCNT/LCP, respectively), suggesting that there was a stronger intermolecular interaction between the LCP and the MWCNTs (MWCNT-HBA or MWCNT-COOH) than that between the LCP and raw MWCNTs. The red-shift of the IR absorbance peak of the C=O stretching implies that the C=O stretching of the LCP became not ‘‘free’’ in the presence of MWCNT-HBA or MWCNT-COOH.
To explain the red-shift of the C=O stretching, the possibility of hydrogen bonding between the LCP chains and MWCNT-HBA and between the LCP chain and MWCNT-COOH is proposed in Scheme 5.1. Here, the presence of the carboxylic groups on the sidewalls of MWCNTs is the key to open the possibility of hydrogen bonding with the –C=O groups of the LCP chains. As shown in Scheme 5.1, when the functionalised MWCNTs act as bridges connecting the LCP chains, the dispersion of the MWCNTs is expected to be much better than when using raw MWCNTs. This has also been supported well with the observed dispersion of the MWCNTs in the LCP matrix, which will be discussed later by means of optical microscopy and field-emission scanning electron microscopy (FESEM).
Scheme 5.1 Possible formation of hydrogen bonds between (a) LCP chain and MWCNT-HBA and (b) LCP chain and MWCNT-COOH.
Raman spectroscopy was used to further investigate the interactions between the polymer and MWCNTs. The interaction between CNTs and a polymer is often examined by the shift of the D*-band in a polymer nanocomposite relative to that of the pure carbon nanotubes.\textsuperscript{[160,278-280]} The D-, G-, and D*-bands for raw MWCNT, MWCNT-COOH, and MWCNT-HBA in the composites are shown in Figure 5.5 and Table 5.3. The D*-band for the neat MWCNT-COOH shifted to the higher wavenumber (2657 cm\textsuperscript{-1}) by 19 cm\textsuperscript{-1} as compared to that (2638 cm\textsuperscript{-1}) of the raw MWCNT. This may be due to the intercalated acids within the CNT bundles, which exerted some pressure on the CNTs.\textsuperscript{[281]} The D*-band of the raw MWCNTs shifted to the higher wavenumber or a positive shift in the composite, whereas MWCNT-COOH and MWCNT-HBA in the composites show a shift in the D*-band to the lower wavenumber or a negative shift from their pure forms. The positive shift in the D*-band for the raw MWCNTs in the composite and the negative shifts for the MWCNT-COOH and MWCNT-HBA in the composites indicate that both raw and functionalised MWCNTs interacted with the LCP matrix, but the origins of the interactions should be different.
Table 5.3 Raman spectra results for MWCNT/LCP composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D band (cm(^{-1}))</th>
<th>G band (cm(^{-1}))</th>
<th>D(^*) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw MWCNT</td>
<td>1321</td>
<td>1580</td>
<td>2638</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>1335</td>
<td>1599</td>
<td>2657</td>
</tr>
<tr>
<td>MWCNT-HBA</td>
<td>1332</td>
<td>1590</td>
<td>2665</td>
</tr>
<tr>
<td>Raw MWCNT/LCP</td>
<td>1326</td>
<td>1595</td>
<td>2657</td>
</tr>
<tr>
<td>MWCNT-COOH/LCP</td>
<td>1332</td>
<td>1594</td>
<td>2645</td>
</tr>
<tr>
<td>MWCNT-HBA/LCP</td>
<td>1325</td>
<td>1580</td>
<td>2638</td>
</tr>
</tbody>
</table>

Figure 5.5 Raman spectra for (a) raw MWCNT/LCP, (b) MWCNT-COOH/LCP and (c) MWCNT-HBA/LCP.
Wood et al.\textsuperscript{[277,279]} observed that the D*-band shifted to the higher wavenumber when the single-walled CNTs (SWCNTs) were dispersed in liquids, such as decane, formamide, propylene glycol, etc. The magnitude of this shift was related to the cohesive energy density (CED) of the liquid which can be considered similar to the internal pressure of a liquid. They suggested that a liquid with a higher CED may exert a higher pressure on the surface of CNTs, causing a larger positive shift in the D*-band. The positive shifts were also observed for SWCNTs mixed in polycarbonate\textsuperscript{[282]} and the copolymers of styrene and vinyl phenol.\textsuperscript{[34]} Rasheed et al.\textsuperscript{[276]} observed the positive shift in the D*-band in purified SWCNTs-filled poly(styrene-co-vinyl phenol) copolymer, whereas they also observed a negative shift in the D*-band for the same polymer filled with oxidised SWCNTs. The observations in this study are in good agreement with the findings by Rasheed et al. The positive shift in the D*-band can be explained in terms of the internal pressure experienced by carbon nanotubes in the presence of a surrounding polymer. The intertube spacing decreased due to the internal pressure from the polymer, hence stiffening the bonds between the carbon nanotubes. The negative shift in the D*-band for functionalised MWCNTs within the LCP indicates that there was a reduction in radial stress on the carbon nanotubes, which correlated with a decrease in bundle size or increase in the dispersion of MWCNTs,\textsuperscript{[276]} resulting in the enhanced interaction between the functionalised MWCNTs and the LCP matrix.
5.2.3 Dispersion of MWCNTs in the LCP

Optical microscopic images provide direct evidence for evaluating the quality of the composite samples. The dispersibility of raw and chemically modified MWCNTs in the LCP was examined by optical microscopy. Figure 5.6 shows the optical microscopic images of the composite samples containing the raw and functionalised MWCNTs.

The aggregates of carbon nanotubes are visible in the raw MWCNT/LCP composites (Figure 5.6a), which reflects the low dispersibility of raw MWCNTs in the LCP matrix. It is important to note that the preparation conditions for the nanocomposite were not optimal to break these aggregates. Under the same preparation conditions, however, the aggregate sizes of MWCNTs were reduced in the case of MWCNT-COOH/LCP composites (Figure 5.6b). Furthermore, a homogeneous and uniform dispersion of MWCNTs was achieved by the addition of MWCNT-HBA (Figure 5.6c). Thus, from the optical images of Figures 5.6b and 5.6c, it can be concluded that the dispersion of MWCNTs in the LCP matrix was significantly improved by the chemical functionalisation of MWCNTs. This is because the functional groups at the surface of the MWCNTs could interact with the polymer matrix, thus enhancing the interfacial bond between the matrix and the CNTs and simultaneously destroying van der Waals forces among the MWCNTs. The HBA-functionalised CNTs shows a higher homogeneity than the carboxyl-group-functionalised CNTs.
Figure 5.6 Optical microscopy images for (a) raw MWCNT/LCP, (b) MWCNT-COOH/LCP and (c) MWCNT-HBA/LCP.
As confirmed by FTIR, H-bonding existed between the LCP and MWCNT-HBA or MWCNT-COOH, which helped the nanotubes to be dispersed well in the LCP. In addition, in the MWCNT-HBA filled composite, benzene rings attached on the surface of the MWCNTs allowed for an increased compatibility with the LCP resulting in a better dispersion of MWCNT-HBA in LCP. This difference in dispersion could lead to the difference in the mechanical properties of the composites.

The cross-sectional fracture of the composites after tensile testing was investigated by FESEM to further verify the dispersion and the possible reinforcing mechanism of MWCNTs. In Figures 5.7a and 5.7b, it is shown that there are well-dispersed bright dots and lines, which are the ends of the broken MWCNTs. Moreover, the MWCNTs were broken rather than pulled out due to the strong interfacial bonding between the MWCNTs and the polymer matrix. It is also observed that the functionalised MWCNTs displayed a higher ability of dispersion in the LCP matrix compared to the raw MWCNTs (Figure 5.7c). In the case of MWCNT-HBA/LCP composites, a single MWCNT seemed to be broken (indicated by 1 in Figure 5.7b), with the other two ends were still embedded in the LCP matrix. This kind of breakage of the CNTs upon a tensile test reflects a strong interfacial adhesion between the MWCNTs and the LCP matrix, which allowed an adequate load transfer from LCP to MWCNTs. In addition, another belt-like nanotube is observed, which bridges two polymer lumps (indicated by 2 in Figure 5.7b).
Figure 5.7 Cross-sectional FESEM images of the surfaces of tensile-fractured samples: (a) MWCNT-COOH/LCP, (b) MWCNT-HBA/LCP and (c) raw MWCNT/LCP.
Furthermore, one of the CNTs (indicated by 3 in Figure 5.7b) was stretched out of the matrix surface with one end bent and tapered while the other end was still embedded in the LCP matrix. From Figure 5.7, the diameter of MWCNTs was higher than that indicated by the manufacturer’s specifications because the MWCNTs were wrapped by the LCP molecules. A similar morphology for the CNTs was also observed by Zhang et al.\cite{zhang2010}

Therefore, it can be predicted from these results that the existing strong interfacial adhesion would be responsible for the vigorous enhancement of mechanical properties of the MWCNT-HBA/LCP composites. This will be discussed in the next section.

5.2.4 Mechanical Strength of LCP Enhanced by MWCNTs

Tensile testing was performed to evaluate the effect of CNT functionalisation on the mechanical properties of the LCP composites. Figure 5.8 presents the stress-strain curves for the pure LCP and the MWCNT/LCP composites. The tensile strength and modulus were calculated from the stress-strain profiles and are shown in Figure 5.9. The results indicate that the reinforcing effect of the chemically modified MWCNTs was more pronounced than that of raw MWCNTs. The tensile strength and modulus of the composite with 1 wt % raw-MWCNTs was enhanced only by 6 and 28 %, respectively, as compared to the pure LCP. The chemically modified MWCNTs led to the increase in tensile strength, modulus, and elongation-at-break of LCP composites. Among these, HBA groups on the MWCNTs contributed to the highest enhancement in the tensile strength and modulus from 87.5 MPa in neat LCP to 123.5 MPa (an increase of 41 %) and 2.9-4.5 GPa (an increase of 55 %), respectively, as well as a higher elongation-at-break (reaching to nearly 9 % tensile strain).
Figure 5.8 Typical stress-strain curves for (a) pure LCP, (b) raw MWCNT/LCP, (c) MWCNT-COOH/LCP, and (d) MWCNT-HBA/LCP.

Several conclusions may be made from the results obtained so far. First of all, from the observation by optical microscopy and FESEM, it has been clearly seen that a good dispersion of MWCNT-HBA was achieved throughout the LCP matrix, which led to a significant increase in the tensile strength of the composite. Second, the incorporation of the functionalised MWCNTs into the polymeric matrix created some interactions between MWCNTs and polymer chains, thus being favourable for stress transfer to MWCNTs. For example, the carboxylic groups attached on the MWCNTs provided the stronger interaction with the LCP matrix, probably through the H-bonding.
Third, more specifically, the longer chemical moieties containing benzene rings attached on the surface of the MWCNTs imparted the ability to loosen and eventually individualise bundled carbon nanotubes and then provided the strong interactions with the LCP chains via $\pi-\pi$ interaction. Therefore, the strong interaction between the HBA-functionalised MWCNTs and the LCP matrix greatly enhanced the dispersion as well as the interfacial adhesion. As a result, the overall mechanical performance of the composite could be improved significantly.
Figure 5.9 (i) Modulus and (ii) tensile strength of (a) pure LCP, (b) raw MWCNT/LCP, (c) MWCNT-COOH/LCP, and (d) MWCNT-HBA/LCP composites.
5.2.5 Thermal stability of MWCNT/LCP composites

To investigate the thermal stability of the MWCNT/LCP composites, thermal gravimetric analysis (TGA) measurements were carried out, and the results are shown in Figure 5.10. In this study, the criteria for thermal stability were taken as the temperatures at which 2 % and 50 % weight-loss occurred in the samples. The 2 % and 50 % decomposition for pure LCP occurred at 405 °C and 495 °C, respectively. Compared to the pure LCP, the raw MWCNT/LCP composite shows a delayed decomposition. Thus, the thermal stability of LCP was improved by adding MWCNTs. This is because polymer chains near the CNTs may degrade more slowly. Another reason is the increased thermal stability of the polymer due to the effect of higher thermal conductivity of MWCNTs, which may facilitate heat dissipation within the polymer composite.\textsuperscript{138}

![TGA thermograms for (a) LCP, (b) raw MWCNT/LCP, (c) MWCNT-COOH/LCP and (d) MWCNT-HBA/LCP.](image)

Figure 5.10 TGA thermograms for (a) LCP, (b) raw MWCNT/LCP, (c) MWCNT-COOH/LCP and (d) MWCNT-HBA/LCP.
The 2 % and 50 % decomposition temperatures for the nanocomposite with MWCNT-COOH increased by 20 °C and 27 °C, respectively, as compared to the pure LCP and by 8 °C and 7 °C, respectively, as compared to the composite with the same content of raw MWCNTs. In addition, dispersed carbon nanotubes might hinder the flux of decomposition products and hence delay decomposition. The presence of more carboxylic groups on the CNT surface was likely to give the strong interfacial interaction between the polymer matrix and CNTs in the composites. Since thermal degradation of a polymer began with chain cleavage and radical formation, the MWCNT-COOH in the composite might act as radical scavengers to delay the onset of thermal degradation and hence improve the thermal stability of LCP.\[283\] MWCNT-HBA/LCP composite had the highest decomposition temperature as compared to the composites with the same loadings of raw MWCNTs and MWCNT-COOH. The 2 % and 50 % decomposition temperatures for the MWCNT-HBA/LCP composites increased by 27 °C and 38 °C, respectively, as compared to the pure LCP and 7 °C and 12 °C, respectively, as compared to the MWCNT-COOH/LCP composites. It is important to point out that the higher degree of interaction between the HBA-functionalised MWCNTs and the LCP matrix could be responsible for the higher thermal stability of the MWCNT-HBA/LCP composite.

5.3 Summary

In this work, a novel route to the fabrication of advanced polymer nanocomposites was presented and verified using MWCNTs as fillers, where MWCNTs were chemically functionalised to be well dispersed in a selected polymer matrix (LCP in this study) and at the same time to possess a strong interaction with the matrix polymer.
The good dispersivity of the functionalised MWCNTs was achieved through (1) weakening or destroying of van der Waals forces among the CNTs and (2) enhancing of the interaction (or compatibility) of CNTs with the matrix polymer. The good dispersion of the functionalised MWCNTs in the LCP matrix was demonstrated by optical microscopy and FESEM, where the HBA-modified MWCNTs showed the better dispersion than the carboxyl-modified MWCNTs. As expected, the LCP matrix filled with only 1 wt % functionalised MWCNTs showed the greatly improved mechanical and thermal properties over the same polymer filled with 1 wt % of raw MWCNTs. Based on the composition and results for the MWCNT/LCP composites, a mechanism for the improved dispersion of MWCNTs in the LCP matrix and the enhanced interactions between the functionalised MWCNTs and the polymer has been proposed and discussed.
Chapter 6 Effects of Processing Methods

6.1 Introduction

As carbon nanotube (CNT)/polymer composites are still under development, this chapter will focus on the effect of different processing methods on the properties of CNT/polymer composites. Although some of CNT/polymer composites have been commercially available in the market, the literature describing the processing is limited. Significant issues remained to be solved on CNT/polymer composites are the dispersion of CNTs in the polymer matrix and the interfacial interaction and load transfer between the CNTs and matrix polymer molecules. A number of reports in the literature have attempted to solve these problems using different approaches. As discussed in the previous chapters, the functionalisation of CNTs seems to be an effective way to prevent CNTs from aggregation to achieve not only a better dispersion of CNTs but also a stronger interface between CNTs and a polymer matrix.

Therefore, in this chapter, two methods of processing for the MWCNT/polymer composites have been used to study the effect of processing method on the properties of MWCNT/polymer composites. Moreover, a comparison between the covalent and noncovlent functionalisations of MWCNTs on the properties of MWCNT/polymer composites has been made.

Two types of polymer matrices, nylon 6 (PA6, Ultramid® B36 LN 01) and polypropylene (PP, MS640), were used to fabricate the MWCNT/polymer composites. Method-II and Method-III were used in this chapter to fabricate MWCNT/polymer
composites. The notations II and III will be followed the sample codes to identify the composites fabricated by Method-II and Method-III, respectively.

Two functionalization methods were used to modify the MWCNTs (Baytubes) not only for a better dispersion in the polymer matrices but also for a stronger interaction with the matrices. The first method was the noncovalent functionalisation of MWCNTs in which the raw MWCNTs were treated with the surfactant, sodium dodecylsulphate (SDS), as prescribed in section 3.2.2 and characterised in sections 4.2.1 and 4.2.2. The second method was the covalent functionalisation of MWCNTs. MWCNTs were chemically attached with the carboxyl (-COOH) groups on their surfaces by the oxidation of raw MWCNTs according to scheme 3.1 and the formation of -COOH groups onto MWCNTs has been confirmed in section 5.2.1.

The effect of processing methods as well as functionalizations of MWCNTs on the morphological, crystalline, dynamic mechanical, mechanical and electrical properties of MWCNT/polymer composites has been investigated by using field emission scanning electron microscopy, differential scanning calorimetry, dynamic mechanical analysis, tensile and electrical conductivity tests.

6.2 Carbon nanotube/nylon 6 composites

Method-II and Method-III were used to fabricate MWCNT/PA6 composites. With Method-II, the processing temperature for mixing and compression moulding was chosen at 245 °C while for Method-III, the temperature zones from the hopper to the die were set at 230 °C, 245 °C, and 240 °C, respectively and the barrel temperature of the injection moulding machine was set at 245 °C. The compounding formulations of the composites prepared in this work are tabulated in Table 6.1.
Table 6.1 Compounding formulations for MWCNT/PA6 composites.

<table>
<thead>
<tr>
<th>Component (wt %)</th>
<th>Both Method II and III</th>
<th>Method II only</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAN0</td>
<td>PAN1</td>
</tr>
<tr>
<td>PA6</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>Raw MWCNT</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SDS</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

6.2.1 Dispersion of carbon nanotubes in PA6 matrix

The representative FESEM photographs of the cross-sectional fracture surfaces of composites are shown in Figure 6.1. This figure illustrates that the dispersed MWCNTs are present as the bright dots and some lines are the ends of the broken MWCNTs. The dispersion of raw MWCNTs is found to be poor in the PA6 matrix as prepared by Method-III for the 10 wt % MWCNT composite (PAN10-III) as shown in Figure 6.1a. Furthermore, the agglomerates of MWCNTs are observed in the PA6 matrix, which may decrease the reinforcing effects of MWCNTs. The dispersion is somewhat better in the composite prepared by Method-II with the same MWCNT’s loading (PAN10-II). It is clearly observed from Figure 6.1b that the MWCNTs were broken (as indicated by the arrows), which is of great importance for making MWCNT reinforced polymer composites.

The SDS-treated MWCNTs show the better dispersion in the PA6 matrix (PASN10) as compared to the composite containing the same amount of raw MWCNTs. The homogeneous dispersion of MWCNTs is observed in the 10 wt % MWCNT-
COOH/PA6 composite (PAMN10) (Figure 6.1d), where the MWCNTs were broken rather than pulled out due to the strong interfacial bonding between the MWCNT-COOH and the polymer matrix. The carboxylic groups seemed to be able to stabilise the MWCNT dispersion by strong interactions with the PA6 matrix. This can be attributed to the increased polarity of the MWCNTs by the functional groups and the possible interaction of the carboxylic groups with -NHCO- of the PA6 matrix.

Figure 6.1 FESEM images of the cross-sectional fracture of composites: (a) PAN10-III, (b) PAN10-II, (c) PASN10 and (d) PAMN10.
It is very interesting to note that a belt like nanotube is observed which interconnected polymer lumps as indicated by the arrows in Figure 6.1d. This typical phenomenon also indicates that an efficient load transfer from the polymer to carbon nanotubes was attained by a strong interfacial adhesion between MWCNTs and the PA6 matrix.

6.2.2 Thermal and crystalline properties

The DSC thermograms and XRD patterns of pure PA6 and MWCNT/PA6 composites are presented in Figures 6.2 to 6.5. The crystallisation temperature ($T_c$), melting temperature ($T_m$) and heat of fusion ($\Delta H_f$) obtained from DSC studies are summarised in Table 6.2 while the values for crystallinity were calculated using equation 3.1 based on the XRD results.

Table 6.2 Thermal properties of MWCNT/PA6 composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN0-II</td>
<td>183</td>
<td>220</td>
<td>74</td>
<td>53</td>
</tr>
<tr>
<td>PAN1-II</td>
<td>188</td>
<td>223</td>
<td>78</td>
<td>56</td>
</tr>
<tr>
<td>PAN3-II</td>
<td>189</td>
<td>224</td>
<td>80</td>
<td>58</td>
</tr>
<tr>
<td>PAN10-II</td>
<td>191</td>
<td>227</td>
<td>88</td>
<td>66</td>
</tr>
<tr>
<td>PAN10-III</td>
<td>189</td>
<td>224</td>
<td>68</td>
<td>48</td>
</tr>
<tr>
<td>PASN10</td>
<td>190</td>
<td>227</td>
<td>86</td>
<td>64</td>
</tr>
<tr>
<td>PAMN10</td>
<td>191</td>
<td>230</td>
<td>71</td>
<td>52</td>
</tr>
</tbody>
</table>
The DSC melting endotherms (Figure 6.2) indicate that PA6 had a melting peak at 220 °C, corresponding to the melting event of the α-form crystals. The same melting peak is also observed in the curves of MWCNT/PA6 composites. It is also confirmed by the XRD results. The X-ray patterns of the PA6 and composites (Figures 6.4 and 6.5) display the presence of two main peaks at 2θ = 20.1 and 23.9 corresponding to the (200), (002) and (220) reflections, indicating that PA6 and all the composites had the α-form structure under these experimental conditions. The raw MWCNT/PA6 composites show the higher diffraction intensity compared to PA6. As a result, for the raw MWCNT/PA6 composites, the crystallinity became higher with increasing content of raw MWCNTs. This result indicates that MWCNTs promoted the crystallisation of PA6, which was prominent in the case of MWCNT/PA6 composite with 10 wt % raw MWCNTs prepared by Method-II.

The melting peak temperature of PA6 was affected by incorporation of MWCNTs in the matrix, which was evident in the case of the composites prepared by Method-II. The PASN10 composite did not exhibit any significant change in the melting temperature of PA6 compared to the composites with the raw MWCNT. It is also observed that the melting temperature of PA6 was shifted higher by 10 °C for the acid treated MWCNT/PA6 composites. This is due to the existence of a strong interaction between the acid treated MWCNTs and the PA6 matrix.
Figure 6.2 DSC thermograms on heating at 10 °C/min in nitrogen for: (a) PAN0-II, (b) PAN1-II, (c) PAN3-II, (d) PAN10-III, (e) PAN10-II, (f) PASN10 and (g) PAMN10.

From Figure 6.3, it can be seen that the pure PA6 shows only a crystallisation peak temperature at about 183 °C. The crystallisation temperature shifted to a higher temperature and the crystallisation temperature range became broader, when both acid treated MWCNTs and raw MWCNTs were incorporated in the PA6 matrix. The effect became more dominant in the presence of raw MWCNTs. At the same loading of raw MWCNTs (10 wt %), the composite in the presence of SDS surfactant (PASN10) did not exhibit significant change in the crystallisation behaviour of PA6 compared to the PAN10-II and PAN10-III composites. The fillers often have a positive effect on the
crystallisation of a polymer in the composite system.\textsuperscript{[250]} That is, they can have a nucleating effect, resulting in an increase in crystallisation temperature. It is very interesting to observe that a new crystallisation peak appeared at a higher temperature for the MWCNT/PA6 composites and this peak position shifted to the higher temperature side with increasing content of MWCNTs in the composites.

![DSC thermograms on cooling from melt at 10 °C/min for: (a) PAN0-II, (b) PAN1-II, (c) PAN10-II, (d) PASN10, (e) PAN10-III and (f) PAMN10.](image)

The magnitude of this crystallisation peak was also increased with increasing MWCNTs in the composites. These observations are in good agreement with the findings by Phang et al.\textsuperscript{[286]} while the DSC results showed two crystallisation exotherms for MWCNT/PA6 composites instead of a single exotherm for the neat matrix. They reported that the formation of the higher-temperature crystallisation peak is closely related to the
addition of MWCNTs. When the amount of MWCNT increases in the PA6 matrix, more heterogeneous nucleation sites are available, and hence more polymer chains are induced to crystallise, thus resulting in a more significant second crystallisation peak.

Figure 6.4 X-ray diffractograms for: (a) PAN0-II, (b) PAN3-II, (c) PAN5-II, and (d) PAN10-II.
The composite processing methods also affected the crystallisation temperature. The composites prepared by Method-II were of higher crystallisation temperature than those prepared by Method-III. These results suggest that the incorporation of the MWCNTs effectively enhanced the crystallisation of the PA6 matrix through heterogeneous nucleation, and the nucleation effect was more evident for the PA6 composites with the raw MWCNTs, as compared to other composites. The heat of fusion ($\Delta H_f$) and heat of crystallisation ($\Delta H_c$) increased with increasing the content of raw MWCNTs in the composites. The heat of fusion is proportional to the amount of crystallinity in the sample, which was also supported by the crystallisation behaviour of...
composites. However, the heat of fusion ($\Delta H_f$) and the heat of crystallisation $\Delta H_c$ for the composites with the functionalised MWCNTs were lower than those of pure PA6 and the composites with the raw MWCNTs at the same loading. This can be explained by the fact that the addition of functionalised MWCNTs enhanced crystallisation of the composites, but reduced the molecular mobility of PA6 at the same time. The functionalised MWCNTs had a stronger interaction with PA6 to result in a better dispersion of MWCNTs, but the better dispersion of MWCNTs in PA6 decreased the space hindrance of the PA6 mobility. Therefore, the degree of crystallisation for these composites decreased as compared to pure PA6. Finally, the heat of fusion for the composite PAN10-III was also lower than that of the pure PA6. This might be because the PAN10-III was prepared using Method-III in which the sample was rapidly cooled down from the melting state to room temperature. As a result of rapid cooling, there was no sufficient time for the composite to form more crystallites than the composites prepared by Method-II which allowed slower cooling.

To investigate the thermal stability of the MWCNT/PA6 composites, TGA measurements were carried out, and the results are shown in Figure 6.6. In this study, the criteria for thermal stability were taken as the temperatures at which 10 % and 50 % weight losses occurred in the system. It is observed from Figure 4.9 that the 10 % and 50 % decompositions of pure PA6 occurred at 424 °C and 467 °C, respectively. Compared to the pure PA6, the 1 wt % raw MWCNT/PA6 composite prepared by Method-II (PAN1-II) shows the slightly delayed decomposition. However, for the 10 wt % raw MWCNT/PA6 composite (PAN10-II) prepared by Method-II, the 10 % and 50 % decomposition temperatures extended to higher temperatures at 435 °C and 498 °C with a slower
decomposition rate and almost 87.2% of the sample degraded in this step. So, the thermal stability of the composites increased with increasing the content of MWCNTs in the composites. Polymer chains near the carbon nanotubes may degrade more slowly, which helps to shift the decomposition temperature to the higher side.

Figure 6.6 TGA thermograms of composites at a heating rate of 10 °C/min: (a) PAN0-II, (b) PAN1-II, (c) PAN10-III, (d) PAN10-II, (e) PASN10 and (f) PAMN10.

Other reason is the increased thermal stability of the polymer composites due to the effect of higher thermal conductivity of MWCNTs which facilitates heat dissipation within the composite.\textsuperscript{[138]} It is also observed that composite containing 10 wt % MWCNTs prepared by Method-II shows the more delayed decomposition as compared to the same MWCNT composition made by Method-III. Such an improvement can be associated with the better dispersion of MWCNTs by Method-II. The crystallinity also
influenced the thermal decomposition of the composites prepared by Method-II. The 10 % and 50 % decomposition temperatures of PASN10 composites increased by 21 °C and 36 °C, respectively, compared to pure PA6 and by 10 °C and 5 °C compared to PAN10-II composite. Dispersed carbon nanotubes might hinder the flux of decomposition product and hence delay the decomposition. The acid treated MWCNT/PA6 composite (PAMN10) shows the highest decomposition temperature as compared to the composites with the same loadings of raw MWCNTs (e.g. PAN10-II). The presence of the more carboxylic groups on the MWCNT surfaces was likely to give the strong interfacial interaction with the polymer matrix. Since polymer thermal degradation began with chain cleavage and radical formation, the MWCNT-COOH in the composite acted as radical scavengers, delayed the onset of thermal degradation and hence improved the thermal stability of PA6. It can be considered that the interaction between functionalised MWCNTs and PA6 matrix was responsible for the higher thermal stability of the PAMN10 composite.

6.2.3 Mechanical properties

The loss tangent (tan δ) versus temperature curves are presented in Figure 6.7. The tan δ of each composite has a wider distribution than that of pure PA6 matrix. In the presence of MWCNTs, the mobility of the polymer chain became more restricted by the MWCNTs. It is well known that the temperature corresponding to the maxima of a tan δ peak is normally associated with the glass transition temperature $T_g$. From the variation of tan δ with temperature (Figure 6.7), $T_g$ of pure PA6 appears at approximately 63 °C. The glass transition temperature of PA6 was shifted to the higher temperature side by the addition of MWCNTs, which was more evident for the functionalised MWCNT/PA6 composites (PAMN10). The glass transition temperature increased from
63 °C for the pure PA6 to 75 °C for the composite with 10 wt % MWCNT-COOH. This was due to the presence of MWCNTs which might have imposed restrictions on molecular mobility. This effect can also be explained in terms of decreasing free volume of polymer. From the concept of free volume, with the addition of MWCNTs, this free volume is evidently reduced.

Figure 6.8 shows the storage modulus versus temperature curves of MWCNT/PA6 composites. Generally, storage modulus can determine the stiffness of materials. The storage modulus of the composites dramatically increased when MWCNT-COOH or raw MWCNTs were incorporated into the PA6 matrix. The composite PAN10-III had about 42 % and 75 % increment of storage modulus in the glassy plateau region (-20 °C) and the rubbery plateau region (100 °C), respectively, as compared to pure PA6. But this improvement of storage modulus was even higher at the same level of MWCNTs in the composite PAN10-II, i.e. 52 % and 267 % in the glassy plateau region (-20 °C) and the rubbery plateau region (100 °C), respectively, over the pure PA6. The presence of SDS surfactant in the composite (PASN10) resulted in the higher storage modulus compared to the PAN10 composite. The improvement in storage modulus of MWCNT/PA6 composites was attributed to the effect of good dispersion and high performance of MWCNT filler.
Figure 6.7 Tan δ for the MWCNT/PA6 composites at 1 Hz: (a) PAN0-II, (b) PAN10-II, (c) PAN10-III, (d) PASN10, and (e) PAMN10.

The effect of MWCNT-COOH on the increase in storage modulus was more dominant than the unmodified MWCNTs. The storage modulus for the composite containing 10 wt % acid treated MWCNTs (PAMN10) increased by 74 % and 375 % in the glassy plateau region (-20 °C) and by 15 % and 30 % in the rubbery plateau region (100 °C), as compared to the pure PA6 and the PAN10-II, respectively. The enhanced storage modulus is considered to be due to the effect of the fine dispersing ability of the functionalised MWCNTs into the PA6 matrix and the enhanced interaction between the -COOH groups of MWCNTs and the matrix polymer.
Figure 6.8 Storage modulus for the MWCNT/PA6 composites at 1 Hz: (a) PAN0-II, (b) PAN1-II (c) PAN10-III, (d) PAN10-II, (e) PASN10, and (f) PAMN10.

Figure 6.9 presents the stress-strain curves for the the MWCNT/PA6 composites. The results indicate that the Young's modulus of the sample increased with loading of MWCNTs for all composites. This is because, while being incorporated with MWCNTs, the chain mobility of the polymer matrix was restricted. The limitation in the mobility of the polymer chain increased with increase in the MWCNT loading. This reduction in the mobility of the polymer chains would make the composites more rigid and as a result, the composites became stiffer and more rigid. For example, the Young's modulus of PAN1-II is 425 MPa while that of the pure PA6 (PAN0-II) is 370 MPa. This is about 15 % increment in the Young's modulus of the pure PA6 when 1 wt % of MWCNTs was added.
From Figure 6.9, it is obviously seen that the elongation at break for the composite samples had been reduced significantly compared to the pure PA6. For example, by adding 1 wt % of MWCNTs into the PA6 (PAN1-II), the elongation at break of the PA6 was reduced from 70 % to 7.2 %. Therefore, it can be concluded that the addition of MWCNTs in to PA6 would make the composites stronger but more brittle. Additionally, the reinforcing effect of the chemically modified MWCNTs was more pronounced than that of raw MWCNTs. This result indicates that the chemically modified MWCNTs could not only disperse uniformly in the PA6 matrix but also possess a stronger interaction with the PA6 molecules.

Figure 6.9 Tensile stress-strain curves for (a) PAN0-II, (b) PAN1-II, (c) PAN10-III, (d) PAN10-II, (e) PASN10 and (f) PAMN10.
The tensile strength for pure PA6 (PAN0-II) and MWCNT/PA6 composites are illustrated in Figure 6.10. It can be seen that the addition of MWCNTs into the PA6 matrix improved the tensile strength of the composites. The tensile strength of the composite with 1 wt % MWCNTs (PAN1-II) was enhanced by 22.5 % as compared to the pure PA6. The tensile strength of PAN10-II composite was enhanced by 77 % as compared to pure PA6, while an increase of 50 % was achieved by incorporating the same amount of raw MWCNTs into the PA6 matrix by Method-III (PAN10-III). From FESEM, it has been clearly observe that the better dispersion of MWCNTs in the PA6 matrix was achieved by Method-II. In this method, most MWCNTs were separated into individual tubes by shear force from the internal mixer. The PASN10 composite had a higher tensile strength than PAN10-II composite and PA6 because of the better dispersion and greater interfacial interaction in this composite due to the presence of the surfactant.

Finally, the tensile strength of the composites increased from 16.0 MPa in the PA6 to 36.2 MPa (an increase of 126 %) when the 10 wt % functionalised MWCNTs were incorporated to the PA6 matrix. The functionalised MWCNTs prepared by acid treatment contained many -COOH groups. The incorporation of functionalised MWCNTs into the PA6 matrix created some interaction between MWCNTs and polymer chains, thus being favourable to stress transfer to MWCNTs. Consequently, the hydrophilic functional groups on the MWCNTs were helpful in improving the interaction with –CONH- groups in PA6. Therefore, the strong interaction between the functionalised MWCNTs and the PA6 matrix greatly enhanced the dispersion as well as the interfacial
adhesion. As a result, the overall mechanical performance of the composites could be improved.

Figure 6.10 Tensile strength for the MWCNT/PA6 composites.

6.2.4 Electrical properties

Carbon nanotubes exhibit the high aspect ratio and high conductivity, which makes CNT an excellent candidate for fabrication of conducting composites. The electrical conductivity of the MWCNT/PA6 composites as a function of MWCNTs is shown in Table 6.3 while the electrical conductivity of pure PA6 is $10^{-14}$ S/cm.\textsuperscript{[287]}

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131
Table 6.3 Electrical conductivity (S/cm) of MWCNT/PA6 composites.

<table>
<thead>
<tr>
<th>Method</th>
<th>PAN5</th>
<th>PAN10</th>
<th>PASN10</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>$3.7 \times 10^{-6}$</td>
<td>$4.9 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>III</td>
<td>-</td>
<td>$3.1 \times 10^{-5}$</td>
<td>-</td>
</tr>
</tbody>
</table>

The PA6 composite filled with 5 wt % raw MWCNTs by Method-II had an electrical conductivity of $3.7 \times 10^{-6}$ S/cm. The conductivity of the composites increased with increasing MWCNT content. The electrical conductivity of the 5 wt % MWCNTs composite produced by Method-III was too low to be measured but the electrical conductivity of 10 wt % MWCNT composite prepared by Method-III was greatly increased to $3.1 \times 10^{-5}$ S/cm. At low contents, conducting fillers were dispersed within the polymeric matrix as isolated clusters. Above the percolation threshold content, independent fillers tended to link together to form conductive networks. This led to a significant increase in the electrical conductivity of the composite. From the experimental results, the electrical conductivity of the composites prepared by Method-III was lower than that of the corresponding composites prepared by Method-II.

This observation is in agreement with the findings by Lee\cite{288} who used carbon black as conducting filler for polymer composites. This is due to the break-down of the black aggregates under high shear and also the existence of a polymer-rich skin layer. Since injection moulded parts normally show a layered structure (i.e. skin-core structure), the conductivity distribution in injection moulded composites is expected to be more complicated. It was observed that the skin layer, i.e., high shear zones, had a substantially lower conductivity than the core zone. The high shear near the surface of the sample
disrupted the formation of conductive networks in the polymer matrix, resulting in poor electrical conductivity in the skin layer. The poor conductive layer, which surrounded the more electrical conductive core, contributed to a higher bulk resistivity. On the other hand, Method-II was capable of producing better electrical conductivity by adopting an internal mixer to efficiently mix the polymer and MWCNTs and then making the samples by compression moulding. The higher conductivity obtained with Method-II could be attributed to the efficient mixing using the Haake internal mixer.\textsuperscript{[289]} The agglomerated MWCNTs in the polymer could be broken down during the mixing process in the internal mixer leading to better dispersion of the MWCNTs as compared to that by Method-III. In addition, compression moulding allowed more time for the MWCNTs to rearrange themselves in the polymer matrix than in the injection moulding where the cooling process was rapid, severely lowering the mobility of the CNT particles.

The presence of SDS surfactant in the composites resulted in a higher electrical conductivity of 0.012 S/cm which was 2.5 times that of the composites with the same MWCNTs loading. The mixing of a surfactant with MWCNTs played an important role in the dispersion of the MWCNTs in the polymer matrix. These experimental results confirm the ability of the surfactant to unravel individual carbon nanotubes from the clusters so as to allow conductive networks to be formed more easily.

6.3 Carbon nanotube/polypropylene composites

For Method-II, the temperature for both mixing and compression moulding was chosen at 190 °C while in Method-III, the temperature zones for the extruder starting from the hopper to the die were set at 120, 180, and 190 °C, respectively. For the
injection moulding, the barrel temperature was set at 190 °C. The compounding formulations of the nanocomposites prepared in this work are tabulated in Table 6.4.

Table 6.4 Compounding formulations for MWCNT/PP composites.

<table>
<thead>
<tr>
<th>Component</th>
<th>Both Method II and III</th>
<th>Method II only</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PPN0  PPN1  PPN3  PPN5  PPN10</td>
<td>PPSN10  PPMN10</td>
</tr>
<tr>
<td>PP (wt %)</td>
<td>100  99  97  95  90</td>
<td>80  90</td>
</tr>
<tr>
<td>Raw MWCNT (wt %)</td>
<td>0  1  3  5  10</td>
<td>10  0</td>
</tr>
<tr>
<td>MWCNT-COOH (wt %)</td>
<td>0  0  0  0  0</td>
<td>0  10</td>
</tr>
<tr>
<td>SDS (wt %)</td>
<td>0  0  0  0  0</td>
<td>10  0</td>
</tr>
</tbody>
</table>

6.3.1 Morphological properties

The representative FESEM photographs of the cross-sectional fracture surfaces of the MWCNT/PP composites are shown in Figure 6.11. The bright dots and some lines indicate that the ends of the broken MWCNTs were dispersed in the PP matrix. The dispersion of raw MWCNTs is found to be poor in the PP matrix as shown in Figure 6.11a for the composite PPN10-III. It is also observed that the MWCNTs tended to form aggregates in the PP matrix during the preparation of composites. The aggregates reduced the probability for MWCNTs to form a network structure. The composite PPN10-II shows a better dispersion with a small quantity of aggregates.
The SDS-treated MWCNTs show the better dispersion in the PP matrix compared to the composite containing the same amount of raw-MWCNTs. The homogeneous dispersion of MWCNT-COOH in the PP matrix is also confirmed in the composite (PPMN10) (Figure 6.11d), where the MWCNTs were broken rather than pulled out due to the strong interfacial adhesion between the MWCNTs and the polymer matrix. The carboxylic groups seemed to be able to stabilise the MWCNT dispersion by the electrostatic repulsion among them.\cite{290}
6.3.2 Thermal properties

To investigate the effect of the incorporation of MWCNTs on PP crystallisation in the composites, DSC measurements were carried out, and the results are shown in Figures 6.12 and 6.13. The crystallisation temperature ($T_c$), melting temperature ($T_m$), heat of fusion ($\Delta H_f$) and crystallinity ($\chi_c$) obtained from DSC studies are summarised in Table 6.5. The values for crystallinity ($\chi_c$) were calculated using equation 3.2 where the theoretical specific melting heat of 100% crystalline PP was taken as 209 J/g.\textsuperscript{[265,266]}

Table 6.5 Thermal properties of MWCNT/PP composites. The heat of fusion ($\Delta H_f^0$) for 100 % crystalline isotactic PP is taken as 209 J/g.\textsuperscript{[265,266]}

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPN0-II</td>
<td>113.3</td>
<td>151.2</td>
<td>77.4</td>
<td>37.01</td>
</tr>
<tr>
<td>PPN1-II</td>
<td>116.6</td>
<td>153.5</td>
<td>75.7</td>
<td>36.20</td>
</tr>
<tr>
<td>PPN3-II</td>
<td>118.9</td>
<td>156.2</td>
<td>72.3</td>
<td>35.65</td>
</tr>
<tr>
<td>PPN10-II</td>
<td>122.7</td>
<td>156.3</td>
<td>68.4</td>
<td>36.36</td>
</tr>
<tr>
<td>PPN10-III</td>
<td>120.5</td>
<td>156.1</td>
<td>63.2</td>
<td>33.60</td>
</tr>
<tr>
<td>PPSN10</td>
<td>122.2</td>
<td>156.4</td>
<td>67.8</td>
<td>36.04</td>
</tr>
<tr>
<td>PPMN10</td>
<td>119.8</td>
<td>159.5</td>
<td>65.3</td>
<td>34.72</td>
</tr>
</tbody>
</table>

The DSC melting endotherms (Figure 6.12A) show that PP (PPN0-II) had a main melting peak with a shoulder peak around 151.2 °C and 148.5 °C, corresponding to the melting events of the $\alpha$-form and $\beta$-form crystals, respectively.\textsuperscript{[267]} These two peaks are also observed in the case of MWCNT/PP composites prepared by Method-II. The
shoulder peak was decreased in the presence of MWCNT which was more prominent in the case of higher amount of raw MWCNT present in the MWCNT/PP composites. These results show that MWCNTs might speed up the crystallisation process for the formation of $\alpha$-crystals in the PP matrix, whereas they had less effect on the crystallisation of the $\beta$-form crystals. Zheng et al.\cite{Zheng2012} studied the effects of clay on polymorphism of PP in PP/clay nanocomposites. They found that clay had an insufficient effect on the crystallisation rate of the $\beta$-phase crystal. These results also show that there was not any shoulder peak for the composite prepared by Method-III. Only the $\alpha$-phase crystallites existed in this composite. In Method-III, the samples were rapidly cooled down from the molten state to room temperature, so that the formation of $\beta$-phase crystallites was restrained.

The melting peak temperature of PP was affected by incorporation of MWCNTs in the matrix. The melting temperature of PP tended to increase with an addition of MWCNTs due to their nucleating effect and the methods used.\cite{Xu2012} The PPSN10 composite did not exhibit any significant change in the melting temperature of PP compared to the composites with the raw MWCNT. It is also observed that the melting temperature of PP was shifted higher by 8 °C for the acid treated MWCNT/PP composites.
Figure 6.12 DSC thermograms upon heating at 10 °C/min in nitrogen for: (a) PPN0-II, (b) PPN1-II, (c) PPN3-II, (d) PPN10-II, (e) PPN10-III, (f) PPSN10, and (g) PPMN10.
From Figure 6.13A, it can be seen that the pure PP had only a crystallisation peak temperature at about 113 °C. The PP crystallisation temperature shifted to the higher temperature side and the crystallisation temperature range became broader, when both MWCNT-COOH and raw MWCNTs were incorporated in the PP matrix; the effect being more dominant in the presence of raw MWCNTs. These results indicate that the carbon nanotubes might act as a nucleating agent, which allowed the crystallisation process to occur more easily when molten PP was being cooled down. It is also observed that the crystallisation temperature increased with increasing the MWCNT content in the composites. Bao et al.\cite{271} reported that the addition of MWCNTs content ≥ 0.5 wt % produced a high heterogeneous nucleation effect for PP. Seo et al.\cite{270} also reported that the addition ≥ 1 wt % MWCNT enhanced the nucleation process during PP crystallisation. When the content of MWCNTs increases in the PP matrix, more heterogeneous nucleation sites are available, and hence more polymer chains are induced to crystallise and result in a crystallisation peak shifted more towards the higher temperature.

At the same loading of raw MWCNTs (10 wt %), the composite in the presence of SDS surfactant (PPSN10) did not have a significant change in the crystallisation behaviour of PP compared to the PPN10-II and PPN10-III composites. The composite processing methods also affected the crystallisation temperature. The composites prepared by Method-II were of higher crystallisation temperature than those prepared by Method-III. These results suggest that the incorporation of the MWCNTs effectively enhanced the crystallisation of the PP matrix through heterogeneous nucleation, and the nucleation effect was more evident for the PP nanocomposites with the raw MWCNTs, as compared to other composites. The heat of fusion ($\Delta H_f$) slightly decreased with
increasing the raw MWCNTs in the composites. The heat of fusion is proportional to the
degree of crystallinity in the sample. The degree of crystallinity of PP reduced little with
the addition of MWCNTs in the PP matrix. Under the same processing condition, the
percent crystallinity for the composites with the functionalised MWCNTs was lower than
the composites with the raw MWCNTs at the same loading.

Similar observation was reported by Tabuani et al.\textsuperscript{[291]} According to them, the
addition of functionalised MWCNTs decreased the percent crystallinity and
crystallisation temperature of composites as compared to those of composites with raw
MWCNTs. This can be explained by the fact that the addition of functionalised
MWCNTs enhanced crystallisation temperature of the composites, but reduced the
molecular mobility of PP at the same time. The functionalised MWCNTs had a better
dispersion in PP, but the better dispersion of MWCNTs would decrease the mobility of
PP chains. Therefore, the degree of crystallinity for this composite decreased as
compared to pure PP.
Figure 6.13 DSC thermograms upon cooling from melt at 10 °C/min for: (a) PP, (b) PPN1-II, (c) PPN3-II, (d) PPN10-II, (e) PPN10-III, (f) PPSN10, and (g) PPMN10.
TGA results of the pure PP and MWCNT/PP nanocomposites are reported in Figure 6.14 and Table 6.6. In this study, the criteria for thermal stability were taken as the temperatures at which 10 % ($T_{10}$) and 50 % ($T_{50}$) weight losses occurred in the system. Both PP and its nanocomposites decomposed in a single step, but TGA curves of the nanocomposites shifted toward higher temperatures compared with pure PP (PPN0-II). It is observed from Figure 6.14A and Table 6.6 that the 10 % and 50 % decomposition of pure PP occurred at 354.3 °C and 407.3 °C, respectively. Compared to the pure PP, the $T_{10}$ and $T_{50}$ were significantly increased by about 56.1 °C and 66.4 °C for PPN5-II composite. However, for the composite PPN10-II, the 10 % and 50 % decomposition temperatures extended to higher temperatures at 446.4 °C and 485.2 °C with a slower decomposition rate and almost 79.2 % of the sample degraded in this step. So, the thermal stability of the composites increased with increasing the content of MWCNTs in the composites. Polymer chains near the carbon nanotubes may degrade more slowly, which helps to shift the decomposition temperature to the higher side. Other reason is the increased thermal stability of the polymer composites due to the effect of higher thermal conductivity of MWCNTs which facilitates heat dissipation within the composite.\textsuperscript{138}
Figure 6.14 TGA thermograms of composites at a heating rate of 10 °C/min: (a) PPN0-II, (b) PPN1-II, (c) PPN3-II, (d) PPN5-II, (e) PPN10-III, (f) PPN10-II, (g) PPSN10, and (h) PPMN10.
Table 6.6 TGA parameters of MWCNT/PP composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{10} ) (°C)</th>
<th>( T_{30} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPN0-II</td>
<td>354.3</td>
<td>407.3</td>
</tr>
<tr>
<td>PPN1-II</td>
<td>362.6</td>
<td>438.6</td>
</tr>
<tr>
<td>PPN3-II</td>
<td>368.3</td>
<td>439.2</td>
</tr>
<tr>
<td>PPN5-II</td>
<td>410.4</td>
<td>473.7</td>
</tr>
<tr>
<td>PPN10-II</td>
<td>446.4</td>
<td>485.2</td>
</tr>
<tr>
<td>PPN10-III</td>
<td>446.0</td>
<td>481.8</td>
</tr>
<tr>
<td>PPSN10</td>
<td>447.4</td>
<td>489.5</td>
</tr>
<tr>
<td>PPMN10</td>
<td>473.1</td>
<td>500.0</td>
</tr>
</tbody>
</table>

It is also observed that, in composite PPN10-III, the decomposition started at almost the same temperature but the decomposition was faster in this case as compared to the same MWCNT composition made by Method-II. The 10% and 50% decomposition temperatures of PPSN10 composites were slightly increased compared to PPN10-II composite. Dispersed carbon nanotubes might hinder the flux of decomposition product and hence delay the decomposition. The acid treated MWCNT/PP (PPMN10) composite had the highest decomposition temperature as compared to the composites with the same loadings of raw MWCNTs (e.g. PPN10-II). The residue for PPMN10 composite was also more than 20% due to the combination of MWCNT and the residue of some PP. The better dispersion of the MWCNT-COOH in PPMN10 composites could be responsible for its better thermal stability by distributing the heat uniformly throughout the sample.
6.3.3 Mechanical properties

The loss tangent (tan δ) and storage modulus versus temperature curves are presented in Figures 6.15 and 6.16. The glass transition temperature (T_g) and storage modulus obtained from DMA are summarised in Table 6.7. Dynamic mechanical analysis of polypropylene shows two relaxations at about 8 °C (α) and 100 °C (γ).[17,292] The γ-peak is generally attributed to the relaxation of a few chain segments in the amorphous regions and the α-peak represents the glass transition temperature (T_g) of PP. The glass transition temperature of PP was shifted to the higher temperature side by the addition of MWCNTs, which was more evident for the functionalised MWCNT/PP composites. The glass transition temperature increased from 8 °C for the pure PP to 26 °C for the composite with 10 wt % MWCNT-COOH (PPMN10). This is due to the presence of MWCNTs which may have imposed restrictions on molecular mobility. This effect can also be explained in terms of decreasing free volume of polymer. From the concept of free volume, with the addition of MWCNTs, this free volume is evidently reduced.
Figure 6.15 Tanδ for the MWCNT/PP composites at 1 Hz: (a) PPN0-II, (b) PPN1-II, (c) PPN3-II, (d) PPN10-III, (e) PPN10-II, (f) PPSN10, and (g) PPMN10.

Figure 6.16 Storage modulus for the MWCNT/PP composites at 1 Hz: (a) PPN0-II, (b) PPN1-II, (c) PPN3-II, (d) PPN10-III, (e) PPN10-II, (f) PPSN10, and (g) PPMN10.
It is clearly observed in Figure 6.16 that the storage modulus of PP in composites was increased with the addition of MWCNTs. The composite PPN10-III increased about 44% in storage modulus in the glassy plateau region (-70 °C) as compared to pure PP (PPN0-II). But this improvement of storage modulus was even higher at the same level of MWCNTs in the composite PPN10-II, i.e. 53% in the glassy plateau region (-70 °C) over the pure PP. The presence of SDS surfactant in the composite (PPSN10) had a higher storage modulus (19%) than the PPN10 composite. The improvement in storage modulus for MWCNT/PP composites was attributed to the effect of good dispersion and high performance of MWCNT fillers.

Table 6.7 Glass transition temperature and storage modulus at -70 °C for the MWCNT/PP composites prepared in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>Storage modulus at -70 °C (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPN0-II</td>
<td>8.0</td>
<td>$4.3 \times 10^9$</td>
</tr>
<tr>
<td>PPN1-II</td>
<td>9.5</td>
<td>$5.1 \times 10^9$</td>
</tr>
<tr>
<td>PPN3-II</td>
<td>11.0</td>
<td>$5.3 \times 10^9$</td>
</tr>
<tr>
<td>PPN10-II</td>
<td>13.6</td>
<td>$6.6 \times 10^9$</td>
</tr>
<tr>
<td>PPN10-III</td>
<td>13.2</td>
<td>$6.3 \times 10^9$</td>
</tr>
<tr>
<td>PPSN10</td>
<td>23.1</td>
<td>$7.5 \times 10^9$</td>
</tr>
<tr>
<td>PPMN10</td>
<td>26.0</td>
<td>$8.6 \times 10^9$</td>
</tr>
</tbody>
</table>
The effect of MWCNT-COOH on the increase in storage modulus was more dominant than the unmodified MWCNTs. The storage modulus for the composite PPMN10 had an increase of 100 % and 30 % in the glassy plateau region (-70 °C) as compared to the pure PP (PPN0-II) and the PPN10-II, respectively. This was due to the effect of a fine dispersing ability of the functionalised carbon nanotubes into the PP matrix and hence, a better anchoring between the MWCNT-COOH and the PP matrix.

Figure 6.17 presents the stress-strain curves for the MWCNT/PP composites. Similar to the MWCNT/PA6 composites, the Young’s modulus of the MWCNT/PP composites increased with loading of MWCNTs for all composites. The increase in the Young’s modulus of a sample is related to the chain mobility of the polymer matrix as mentioned before and as a result, the composites became stiffer and more rigid.

Similarly, the elongation at break for the MWCNT/PP composites had been reduced significantly compared to the pure PP. Unlike to the MWCNT/PA6 composite, by adding 1 wt % of MWCNTs into the PP (PPN1-II), the elongation at break of the PA6 was reduced from 168 % to 30 %. From Figure 6.17, PPN1-II still shows a little plastic deformation due the intrinsice properties of PP. Usually the more chain mobility of the PP allows the PP molecules to flow under a certain about of MWCNTs. But for the higher content of MWCNTs in PP, the plastic deformation would be vanished and the composites became more brittle. Additionally, the reinforcing effect of the modified MWCNTs was more pronounced than that of raw MWCNTs.

Compared to the physically modified MWCNTs, the chemically modified ones show better mechanical properties. This finding reveals that the chemically modified MWCNTs could disperse more uniformly in the PP matrix than the physically modified
MWCNTs. Unlike the MWCNT/PA6 composite, there was no possible interaction between the chemically modified MWCNTs and PP molecules because PP is not a polar polymer.

Figure 6.17 Tensile stress-strain curves for (a) PP0-II, (b) PPN1-II, (c) PPN10-III, (d) PPN10-II, (e) PPSN10 and (f) PPMN10.

Figure 6.18 shows the tensile strengths for pure PP and MWCNT/PP composites. The presence of MWCNTs improved the tensile properties of the PP matrix. It is observed from Figure 6.18, the tensile strength of PP was improved 32 % with an addition of 1wt % MWCNT (PPN1-II), but it increased slowly with further addition of MWCNT. The tensile strength increased only 21 % when concentration of MWCNT increased from 1 to 10 wt % (PPN10-II). The tensile strength increased from 12.5 MPa for PP to 19.9 MPa for the PPN10-II composite. In the case of PPN10-III composite, the
tensile strength was slightly lower than PPN10-II. From FESEM (Figure 6.10), it has been observed that the agglomerations were present in the composites with 10 wt % MWCNTs, which was more prominent in the case of PPN10-II composite. Aggregations reduce the surface area of the nanotubes that interrupts the stress transfer from polymer matrix to nanofillers.\cite{266}

![Graph showing tensile strength for PPN composites](image)

Figure 6.18 Tensile strength for the MWCNT/PP composites.

The PPSN10 composite had a higher tensile strength than PPN10-II composite and PP because of the better dispersion of MWCNTs in this composite due to the presence of the surfactant. Finally, the tensile strength of the composites increased from 12.5 MPa in the PP to 23.1 MPa (an increase of 85 %) when the 10 wt % functionalised
MWCNTs were incorporated to the PP matrix (PPMN10). The higher tensile strength of PPMN10 could be due to an efficient stress transfer from PP to MWCNTs. Because of the acid treatment, the functionalised MWCNTs could not only disperse more uniformly in the PP matrix but also could as anchors in the composite due to their rough surfaces resulting from the C-C bond defects. As a result, the overall mechanical performance of the composites could be improved.

### 6.3.4 Electrical properties

The electrical conductivity of the MWCNT/PP composites as a function of MWCNTs is shown in Table 6.8. The electrical conductivity of pure PP is $10^{-16}$ S/cm. The PP composite filled with 5 wt % raw MWCNTs by Method-II (PPN5-II) possessed an electrical conductivity of $4.5 \times 10^{-7}$ S/cm. The conductivity of the composites increased with increasing MWCNT content. The electrical conductivity of the 5 wt % MWCNTs composite produced by Method-III (PPN5-III) was too low to be measured but the electrical conductivity of 10 wt % MWCNT composite prepared by Method-III (PPN10-III) was greatly increased to $2.09 \times 10^{-6}$ S/cm.

<table>
<thead>
<tr>
<th>Method</th>
<th>PPN5</th>
<th>PPN10</th>
<th>PPSN10</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>$4.5 \times 10^{-7}$</td>
<td>$1.24 \times 10^{-4}$</td>
<td>$2.34 \times 10^{-4}$</td>
</tr>
<tr>
<td>III</td>
<td>-</td>
<td>$2.09 \times 10^{-6}$</td>
<td>-</td>
</tr>
</tbody>
</table>

At low contents, conducting fillers were dispersed within the polymeric matrix as isolated clusters. Above the percolation threshold, individual or aggregated fillers tended
to link together to form conductive networks. This led to significant increase in the electrical conductivity of the composite. From the experimental results, the electrical conductivity of the composites prepared by Method-III was lower than that of the corresponding composites prepared by Method-II. On the other hand, Method-II was capable of producing better electrical conductivity by adopting an internal mixer to mix the polymer and MWCNTs and then making the samples by compression moulding. The compression moulding allowed more time for the MWCNTs to link themselves in the polymer matrix. But in the case of injection moulding samples, the MWCNTs aligned in the injection directions, therefore impeding the contacts between carbon nanotubes which caused the reduction in the electrical conductivity.

6.4 Summary

The raw MWCNTs have been incorporated into both PA6 and PP by two methods of mixing to examine their effects on the morphological, crystalline, thermal, electrical, and mechanical properties of MWCNT/polymer composites. Besides, the other types of MWCNTs such as surfactant-treated MWCNTs and carboxyl-functionalised MWCNTs were also incorporated into the polymer matrices to study their effects on the properties of the polymer matrices. The amounts of MWCNTs in the composites were varied from 0 wt% to 10 wt% to evaluate the effect of the MWCNT loadings on the properties of the MWCNT/polymer nanocomposites. The flowchart for the research conducted in this chapter is as shown in Scheme 6.1.
It was found that the composites fabricated by Method-II exhibited better crystalline, mechanical, thermal as well as electrical properties than those prepared by Method-III. The surfactant-treated MWCNTs were able to be dispersed in a polymer matrix uniformly compared to the raw MWCNTs which gave their composites better thermal and electrical properties. Besides, the composites containing functionalised MWCNTs showed the improved mechanical and thermal properties over the composites filled with the raw MWCNTs due to their strong interaction with their matrix polymer molecules. Therefore, it has been proved that the crystalline, mechanical, thermal as well as electrical properties of MWCNT-filled polymers are strongly dependent on the state of dispersion and interfacial adhesion of MWCNTs with the polymeric matrix.
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Chapter 7 Compatibilising Effect of Functionalised Carbon Nanotubes in an Immiscible Polymer Blend

7.1 Introduction

CNT/polymer composites usually have higher melt viscosity than their polymer matrix. This is because carbon nanotubes constraint the motion of polymer molecules in the composites due to the common effect of fillers as in many other composite systems. Therefore, liquid crystalline polymers (LCPs) are usually added into the CNT/polymer composites to reduce their melt viscosity. The inclusion of LCP into a CNT/polymer composite may facilitate the dispersion of CNTs by reducing the melt viscosity of the composite.[293-296] On the other hand, most of thermoplastic polymers are generally immiscible with LCP at a molecular level.[297,298] The immiscibility between a matrix polymer and LCP will also make the composite thermodynamically less stable due to the weaker interfacial adhesion and as a result, the blend has poor mechanical properties compared to the matrix polymer and the LCP.

Fortunately, if the chemically modified MWCNTs behave like a bonding agent or a compatibiliser present at the interface between LCP and the matrix polymer, then the MWCNTs will possess an additional function over the reinforcing function of fillers. Besides, the compatibilisation effect of the chemically modified CNTs can enhance the fibrillation of LCP in the composites which can significantly increase the mechanical properties of the composites. However, raw MWCNTs are chemically inert and they need to be chemically functionalised to have interfacial interaction with a polymer matrix. As most of LCPs have electronegative groups (such as C=O), the polar groups (-COOH) on the carboxylic modified MWCNTs could show attractive forces to electronegative groups.
(such as oxygen atoms) in the LCP chains. Moreover, this -COOH groups of the MWCNT-COOH are also compatible with some of the polar polymers such as nylon. As a result, the chemically modified MWCNTs have a possibility to act as a compatibiliser at the interface between LCP and nylon.

For those reasons above, this chapter is to study the compatibilisation effect of carboxylic functionalised MWCNTs (MWCNT-COOH) on a blend of nylon 6 (PA6: Ultramid B36 LN 01) and LCP (Rodrun LC-5000). The effect of contents of MWCNT-COOH on the blend will be also discussed. MWCNTs (Iljin tubes) were covalently functionalised with -COOH groups on their surfaces according to scheme 3.1 and MWCNT-COOH were characterised as discussed in section 5.2.1.

### 7.2 Molecular interaction of PA6, LCP and their blend incorporated with functionally carbon nanotubes

Fabrication for composites of PA6, LCP and MWCNT-COOH was done by Method-I as described in chapter 3. The processing and moulding temperature was set at 300 °C. The compounding formulations for the composites are tabulated in Table 7.1.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PA6 (wt %)</th>
<th>LCP (wt %)</th>
<th>MWCNT-COOH (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAMN0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PAMN1</td>
<td>99</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>LCMN0</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>LCMN1</td>
<td>-</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>PLMN0</td>
<td>80</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>PLMN1</td>
<td>79.2</td>
<td>19.8</td>
<td>1</td>
</tr>
</tbody>
</table>
7.2.1 Rheological properties

The changes in viscosity with shear rate at 300 °C for the pure PA6, the pure LCP, the LCP/PA6 blend and the composites, MWCNT-COOH/PA6, MWCNT-COOH/LCP and MWCNT-COOH/LCP/PA6, are shown in Figure 7.1. The pure PA6 (curve e) shows a Newtonian behavior approximately over the range of shear rates. But pure LCP (curve a) shows a strongly shear thinning over the range of shear rates. It is also observed from Figure 7.1 that the viscosity of the LCP/PA6 (20/80 wt %) blend (curve c) was much lower than that of pure PA6. The viscosity of PA6 has been reduced from 55 Pa.s to 15 Pa.s at the shear rate of 10 s\(^{-1}\) and at 300 °C by adding 20 % LCP. The reduction in viscosity of the LCP/PA6 blend could be attributed to interfacial slippage between the two phases (i.e. PA6 and LCP phases) which were formed due to the immiscibility between PA6 and LCP. In addition, the inherently low viscosity of LCP enables the polymer to act as a processing aid to reduce the overall melt viscosity. The results shown in Figure 7.1 are in good agreement with the literatures.\textsuperscript{[299,300]} However as being expected, the viscosity of the composite gradually increased with increasing MWCNT content due to the common effect of fillers on viscosity and the stronger filler-polymer interaction, which could restrict the flow of the composites in the molten state.
Figure 7.1 Complex viscosity versus angular frequency for the composites at 300 °C: (a) LCMN0, (b) LCMN1, (c) PLMN0, (d) PLMN1, (e) PAMN0, and (f) PAMN1.

7.2.2 Dispersion of MWCNT-COOH

The FESEM images of different composites at 10,000 times of magnification are shown in Figure 7.2. Some locations of MWCNTs are indicated in the circles. From this figure, it is confirmed that the uniform dispersion of the modified MWCNTs in the matrices was achieved.
7.2.3 Morphological properties

The LCP phase can be seen as globular domains in the PA6 matrix as shown in Figure 7.3a. In Figure 7.3a, the blend has many large voids, where the LCP globules were pulled out from the PA6 matrix, indicating the poor interfacial adhesion between PA6 and LCP phases, which is in good agreement with the other polymer blends with different LCPs.\textsuperscript{301,302} However, Figure 7.3b shows that there was a difference in morphology of the composites by adding of MWCNT-COOH into the LCP/PA6 blend. After the addition of 1 wt % MWCNT-COOH into the LCP/PA6 blend, a new interesting morphology is observed in Figure 7.3b instead of voids and globules: i.e. LCP microfibrils appeared which indicated a better miscibility and strong interfacial adhesion between PA6 and LCP, in the existence of MWCNT-COOH, which will contributes to superior mechanical properties.
7.2.4 Mechanical properties

The tensile test results of the different samples are as shown in Figure 7.4 and their respective mechanical properties are listed in Table 7.2. From Figure 7.4, LCP (curve c) shows a stiffer and more brittle behaviour compared to PA6 (curve a) and their blend (curve e) processes an intermediate trend. After addition of MWCNT-COOH, the Young's moduli and tensile strength of the MWCNT-COOH/polymer composites were much higher than those of the corresponding polymer matrices. On the other hand, with an addition of MWCNT-COOH, the elongations at break of all the composite samples were tremendously decreased. This finding reveals that the MWCNT-COOH/polymer composites were stiffer but more brittle than their respective polymer matrices. For example, the improvements in Young’s modulus and tensile strength for PA6 by adding 1 wt% MWCNT-COOH were 18% and 34.4%, respectively. However, the elongation at break for PA6 declined from 68% for PLMN0 to 7.2% for PLMN1 (more than 75% reduction).
Table 7.2 Tensile properties of different composites, measured at 25 °C and a strain rate of 5 mm/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young’s modulus</td>
<td>% increase to the polymer matrix</td>
</tr>
<tr>
<td>PAMN0</td>
<td>371.4 ± 4.7</td>
<td>-</td>
</tr>
<tr>
<td>PAMN1</td>
<td>438.2 ± 6.3</td>
<td>17.99</td>
</tr>
<tr>
<td>LCMN0</td>
<td>2894 ± 32.5</td>
<td>-</td>
</tr>
<tr>
<td>LCMN1</td>
<td>3217 ± 42.2</td>
<td>11.16</td>
</tr>
<tr>
<td>PLMN0</td>
<td>428.5 ± 8.5</td>
<td>-</td>
</tr>
<tr>
<td>PLMN1</td>
<td>693.0 ± 10.4</td>
<td>61.72</td>
</tr>
</tbody>
</table>

Particularly, the significant improvements in Young’s modulus and tensile strength are observed for the MWCNT-COOH/LCP/PA6 composites (PLMN1): 62 % and 44 % increase over its corresponding blend (PLMN0) of LCP and PA6. This result confirms that the chemically modified MWCNTs (MWCNT-COOH) could act as a compatibiliser between LCP and PA6 and the miscibility between LCP and PA6 was significantly improved with the addition of MWCNT-COOH in the LCP/PA6 blend. However, the elongation at break still reduced from 17.7 % to 8.5 % (about 50 % decline).
Figure 7.4 Tensile stress-strain curves for (a) PAMN0, (b) PAM1, (c) LCMN0, (d) LCMN1, (e) PLMN0 and (f) PLMN1.
7.2.5 The role of MWCNT-COOH in the PA6, LCP and PA6/LCP blend

Figure 7.5 shows the possible interactions among PA6, LCP and MWCNT-COOH. The formation of hydrogen bonds between carboxyl groups of MWCNT-COOH and the polar groups of LCP and PA6 was the reason why MWCNT-COOH/polymer composites had better mechanical properties over their respective polymer matrices. The polar –COOH groups on MWCNTs could have attractive forces to electronegative groups (such as oxygen and nitrogen atoms) in PA6 and LCP chains. This mechanism explains how the modified MWCNTs perform as a compatibiliser across the interface between PA6 and LCP to improve the interfacial adhesion between PA6 and LCP. As a result of this mechanism, (i) the dispersion of LCP in the PA6 matrix could be improved and (ii) the dispersion of MWCNTs in the PA6/LCP matrix could be improved, too.

Figure 7.5 Schematic illustration for the formation of hydrogen bonds among PA6, LCP and MWCNT-COOH.
7.3 Effect of content of chemically modified MWCNTs on the LCP/PA6 blend

From the previous section, it has been verified that the chemically modified MWCNTs could improve the compatibility between LCP and PA6 in their blend. Therefore, in this section, the effect of different MWCNT-COOH contents on the properties of the LCP/PA6 blend is studied. The composites of LCP/PA6 with the different contents of MWCNT-COOH were prepared as shown in Table 7.3.

Table 7.3 Compounding formulation and sample codes for MWCNT-COOH/LCP/PA6 composites.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PA6</th>
<th>LCP</th>
<th>MWCNT-COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLMN0</td>
<td>4 g (80 wt %)</td>
<td>1 g (20 wt %)</td>
<td>-</td>
</tr>
<tr>
<td>PLMN1</td>
<td>4 g (79.2 wt %)</td>
<td>1g (19.8 wt %)</td>
<td>0.05 g (1 wt %)</td>
</tr>
<tr>
<td>PLMN2</td>
<td>4 g (78.4 wt %)</td>
<td>1g (19.6 wt %)</td>
<td>0.1 g (2 wt %)</td>
</tr>
<tr>
<td>PLMN3</td>
<td>4 g (77.7 wt %)</td>
<td>1g (19.4 wt %)</td>
<td>0.15 (2.9 wt %)</td>
</tr>
<tr>
<td>PLMN5</td>
<td>4 g (76.2 wt %)</td>
<td>1 g (19 wt %)</td>
<td>0.25 (4.8 wt %)</td>
</tr>
<tr>
<td>PLMN10</td>
<td>4 g (72.7 wt %)</td>
<td>1 g (18.2 wt %)</td>
<td>0.5 g (9.1 wt %)</td>
</tr>
</tbody>
</table>

7.3.1 Rheological properties

The changes in viscosity for the pure PA6, the LCP/PA6 blend, and MWCNT-COOH/LCP/PA6 composites with shear rate at 300 °C are shown in Figure 7.6. The pure PA6 shows a Newtonian behaviour at very low shears rate but the flow changes to a non-Newtonian behaviour when the shear rate is greater than 2 s$^{-1}$. But pure LCP shows a strongly shear thinning behaviour over the test range of shear rate. Over the range of shear rates applied, the LCP/PA6 blend and MWCNT-COOH/LCP/PA6 composites had
the non-Newtonian flow behaviours, which became more outstanding for the composites with higher loading of MWCNT-COOH. On the other hand, the viscosity of the composite gradually increased with increasing MWCNT-COOH content due to (1) the common effect of fillers on viscosity and (2) the stronger interaction between the modified MWCNTs and the polymers which could restrict the flow of the composites in the molten state.

Figure 7.6 Viscosity versus shear rate for MWCNT-COOH/LCP/PA6 composites at 300 °C, where from bottom to top: (a) PLMN0, (b) PLMN1, (c) PLMN2, (d) PLMN3, (e) PLMN5, (f) PLMN10, and (o) pure PA6.
7.3.2 Influences of MWCNT-COOH on melting and crystallization of PA6/LCP blend

To investigate the effect of the incorporation of LCP and functionalized MWCNTs on crystallization of PA6, DSC measurements were carried out, and the results are shown in Figure 7.7.

The crystallization temperature ($T_c$), melting temperature ($T_m$), heat of fusion ($\Delta H_f$) and crystallinity ($\chi_c$) obtained from DSC studies are summarised in Table 7.4. In Figure 7.7A, the unfilled PA6/LCP shows a melting peak around 220 °C and then the melting temperature shifted higher with adding the MWCNT-COOH. At 9.1% CNTs, the melting temperature increased by 6 °C. This is due to the existence of a strong interfacial adhesion between the acid treated MWCNTs and the polymers. In the cooling process (Figure 7.7B), the unfilled PA6/LCP blend showed a single and broad crystallization peak at about 175 °C. With adding the modified MWCNTs, the crystallization temperature shifted to the higher temperature side and the crystallization temperature range became narrower. These results imply that the nanotubes might act as a nucleating agent, which allowed the crystallization process to occur more easily when a PA6/LCP blend melt was cooled down.
Table 7.4 Melting and Crystallisation properties of MWCNT-COOH/LCP/PA6 composites.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>T_c (°C)</th>
<th>T_m (°C)</th>
<th>∆H_f (J/g)</th>
<th>X_c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLMN0</td>
<td>175</td>
<td>220</td>
<td>81.6</td>
<td>35.5</td>
</tr>
<tr>
<td>PLMN1</td>
<td>176</td>
<td>222</td>
<td>82.4</td>
<td>35.8</td>
</tr>
<tr>
<td>PLMN2</td>
<td>177</td>
<td>223</td>
<td>85.7</td>
<td>37.3</td>
</tr>
<tr>
<td>PLMN3</td>
<td>179</td>
<td>224</td>
<td>88.7</td>
<td>38.5</td>
</tr>
<tr>
<td>PLMN5</td>
<td>179</td>
<td>225</td>
<td>88.8</td>
<td>38.7</td>
</tr>
<tr>
<td>PLMN10</td>
<td>180</td>
<td>226</td>
<td>88.3</td>
<td>38.4</td>
</tr>
</tbody>
</table>

The heat of fusion (∆H_f) increased with increasing the amount of MWCNT-COOH, but it slightly decreased at 9.1% loading (PLMN10). Since the heat of fusion is proportional to the degree of crystallinity in the sample,[202] the crystallinity of PLMN10 was lower than other composites. This result can be explained by the fact that the addition of functionalized carbon nanotubes enhanced crystallization of the composites but reduced the molecular mobility of the polymer chains at the same time.
Figure 7.7 DSC thermographs (Endo up) for (a) PLMN0, (b) PLMN1, (c) PLMN2, (d) PLMN3, (e) PLMN5, and (f) PLMN10: (A) at a heating rate of 10 °C/min, and (B) at a cooling rate of 10 °C/min.
7.3.3 Morphological properties

FESEM was used to observe the morphology of the tensile fracture surfaces of the MWCNT-COOH/LCP/PA6 composites. In Figure 7.8, there were the differences in morphology, which were caused by an increase in the content of MWCNT-COOH. From Figures 7.8a through 7.8d, it is found that the size of LCP globules in the PA6 matrix was significantly reduced, compared to Figures 7.8a and 7.8b, showing that the miscibility and interfacial adhesion between PA6 and LCP was improved by adding the MWCNT-COOH. The finer dispersion of these LCP microfibrils in the PA6 matrix indicates that there was a better miscibility and strong interfacial adhesion between PA6 and LCP in the existence of MWCNT-COOH.

The FESEM images at the higher magnification are shown in Figure 7.8e and 7.8f where the locations of some MWCNTs are indicated with arrows. It is also seen that the uniform dispersion of MWCNT-COOH in the matrix was achieved. From these observations, it can be concluded that the functionalised MWCNTs could act as a compatibiliser for the LCP/PA6 blend.
Figure 7.8 FESEM images at 500x magnification for the tensile fractured surfaces of (a) PLMN2, (b) PLMN3, (c) PLMN5 and (d) PLMN10. FESEM micrographs at 7000x magnification for (e) PLMN5 and (f) PLMN10.
7.3.4 Mechanical properties

Figure 7.9 presents the typical stress-strain curves for the LCP/PA6 blend and the MWCNT-COOH/LCP/PA6 composites. And, the tensile mechanical properties for the samples are listed in Table 7.5.

Table 7.5 Tensile properties of MWCNT-COOH/LCP/PA6 composites, measured at 25 °C and a strain rate of 5 mm/min.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>% Elongation at Break</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLMN0</td>
<td>428.5±8.5</td>
<td>24.9±0.30</td>
<td>17.7±0.35</td>
</tr>
<tr>
<td>PLMN1</td>
<td>693.0±10.4</td>
<td>35.9±0.72</td>
<td>8.5±0.10</td>
</tr>
<tr>
<td>PLMN2</td>
<td>724.5±8.7</td>
<td>34.9±0.42</td>
<td>7.8±0.12</td>
</tr>
<tr>
<td>PLMN3</td>
<td>764.1±7.9</td>
<td>32.6±0.49</td>
<td>5.8±0.10</td>
</tr>
<tr>
<td>PLMN5</td>
<td>889.1±16.0</td>
<td>30.8±0.34</td>
<td>4.9±0.05</td>
</tr>
<tr>
<td>PLMN10</td>
<td>949.8±13.2</td>
<td>29.4±0.56</td>
<td>4.1±0.08</td>
</tr>
</tbody>
</table>

It can be seen that the Young's moduli of the MWCNT-COOH/LCP/PA6 composites were much higher than that of the corresponding LCP/PA6 blend. As discussed in section 7.2.4, by adding 1 wt % of MWCNT-COOH in to the LCP/PA6 blend, there was the significant improvements in Young’s modulus and tensile strength of 62 % and 44 % increase, respectively, over the blend of LCP and PA6. Then, Young’s modulus of the composites gradually increased with increase in MWCNT-COOH contents up to 3 wt %, whereas the tensile strength of the composites decreased. The increase in Young's modulus was no doubt to be due to the addition of the modified
MWCNTs. The functionalised MWCNTs containing -COOH groups could be helpful for improving the interactions between PA6 and LCP chains. The probable interaction among PA6, LCP and MWCNT-COOH has been schematically proposed in Figure 7.5. This mechanism explains how the modified MWCNTs acted as a compatibiliser across the interface between the PA6 and LCP to increase the interfacial adhesion between PA6 and LCP and to improve the dispersion of MWCNTs in the blend matrix. As a result, the overall mechanical performance of the composites was improved. However, it could be noticed that there is another significant improvement in Young’s modulus of the MWCNT-COOH/LCP/PA6 composites when the contents of MWCNT-COOH vary from 3 wt % to 5 wt % in the composites. Compared to PLMN3 and PLMN5, a 16.4 % increase in the Young’s modulus was observed. This sudden improvement in Young’s modulus of PLMN5 might be an effect from the change in the morphology of the composites as shown in Figure 7.8.
However, from Figure 7.9, it is clearly seen that the plastic deformation for the composites was gradually vanished with the increase in MWCNT-COOH loading. Consequently, the elongation at break dropped very much after addition of the CNTs. At the highest loading of MWCNT-COOH, the elongation at break was 4.1 % only. Besides, the tensile strength had a tendency to level off or even decrease with further increasing MWCNT-COOH loading while the Young's modulus still increased with MWCNT-COOH wt % which was associated with the transition from a tensile mode to a brittle one. These results indicate that the PA6/LCP had been modified into stiffer but more brittle materials after being incorporated with MWCNT-COOH.
Figures 7.10A and 7.10B represent the variation of tangent delta and storage modulus as a function of temperature for the unfilled LCP/PA6 blend and the MWCNT-COOH/LCP/PA6 composites. In Figure 7.10A, \((\tan \delta)_{\text{max}}\) is observed at 55 \(^\circ\)C for the LCP/PA6 blend. The temperature corresponding to the tan \(\delta\) peak maxima is generally considered as glass transition temperature \((T_g)\) of a polymer. Therefore, the \((\tan \delta)_{\text{max}}\) at 55 \(^\circ\)C of the LCP/PA6 blend is related to the \(T_g\) of PA6. The \(T_g\) shifted to the higher temperature side for the MWCNT-COOH/LCP/PA6 composites. For example, the glass transition temperature was 75 \(^\circ\)C for the composite with 9.1 wt % MWCNT-COOH, which increased by 20 \(^\circ\)C from that for the unfilled PA6/LCP blend. These results suggested the restraining of the molecular motion of the PA6 matrix by MWCNT-COOH.

When the functionalised MWCNTs were incorporated into the LCP/PA6 blend, a dramatic increase in storage modulus is observed in Figure 7.10B. Both the improvement in storage modulus and the significant increase in glass transition temperature are considered to be due to (i) the effect of uniformly dispersed functionalised carbon nanotubes in the LCP/PA6 blend as observed in Figures 7.8e and 7.8f, (ii) the reduction of free volume in the polymer blend, and (iii) the enhanced interaction between PA6 and LCP by the functionalised carbon nanotubes as illustrated in Figure 7.5.
Figure 7.10 (A) Tan $\delta$ and (B) storage modulus as a function of temperature for (a) PLMN0, (b) PLMN1, (c) PLMN2, (d) PLMN3, (e) PLMN5 and (f) PLMN10.
7.3.5 Electrical properties

CNTs exhibit the high aspect ratio and high electrical conductivity, which make CNTs excellent candidates for fabrication of highly conductive composites. Figure 7.11A shows the AC conductivity as a function of frequency with the various concentrations of MWCNT-COOH. At the MWCNT-COOH loadings of 0 wt% and 4.8 wt%, the conductivity increased with the frequency in a logarithmic scale, exhibiting a typical capacitor behavior. But at the loadings of 1 wt%, 2 wt%, 2.9 wt% and 9.1 wt%, the conductivity is nearly independent of frequency (in logarithmic scale). According to these results, one can predict that there were two distinct thresholds in the system.

This result is in good agreement with the observations from the DC conductivity measurement as in Figure 7.11B. From this figure, it is observed that the conductivity of the composites increased with increasing MWCNT–COOH content. The content of CNTs at which the sharp rise of electrical conductivity occurs is attributed to the percolation threshold. When the content of MWCNT reaches to the threshold, the electrical conductivity of the composites suddenly increased by many orders of magnitude. From Figure 7.11B, it is clearly seen that there were two obvious thresholds in the PA6/LCP/MWCNT-COOH composite system. The first threshold was present in the range from 0 % to 1 % CNTs while the second one appeared in the range from 3 % to 5 % of CNTs.
Figure 7.11 (A) AC Conductivity ($\sigma_{ac}$) versus frequency ($\omega$) of PA6/LCP/MWCNTCOOH composites; (a) PLMN0, (b) PLMN1, (c) PLMN2, (d) PLMN3, (e) PLMN5, and (f) PLMN10, and (B) DC electrical conductivity ($\sigma_{dc}$) of PA6/LCP/MWCNT-COOH composites as a function of MWCNT-COOH loading.
7.4 Summary

The molecular interaction among nylon 6, liquid crystalline polymer and multiwalled carbon nanotubes has been studied. Prior to the fabrication of composites, the MWCNT were chemically modified with carboxylic functional group on their surfaces. The schematic abstract for the research conducted in this chapter is shown in Scheme 7.1.

Scheme 7.1 Summary of the research work conducted in Chapter 7.
For a preliminary study, the composites of MWCNT-COOH/PA6, MWCNT-COOH/LCP and MWCNT-COOH/LCP/PA6 composites with 1 wt % MWCNT-COOH were fabricated by melt-mixing technique. Upon the systematic comparison among these composite systems, it was found that there was an improved interfacial interaction among the polymer matrixes and the MWCNT-COOH. Therefore, the MWCNT-COOH could serve as a compatibiliser to improve interfacial adhesion between PA6 and LCP. A schematic illustration for the possible interactions among PA6, LCP and MWCNT-COOH was also proposed.

Then, various amounts of MWCNT-COOH were incorporated into an LCP/PA6 blend to demonstrate their effects on the rheological, thermal, morphological, mechanical and electrical properties of MWCNT-reinforced composites. As the MWCNT-COOH could serve as a compatibiliser to improve interfacial adhesion between the matrix polymer (PA6) and LCP, the tensile strength and modulus of the MWCNT-COOH/LCP/PA6 composites were greatly enhanced, yet without significantly increase the melt-viscosity of the blend. The homogenous dispersion of functionalised MWCNTs in the polymer matrix and the strong interfacial bonding among the PA6, LCP and MWCNT-COOH were the key factors for the improvements in the mechanical and electrical properties.
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Chapter 8 Complementary Effect of Carbon Nanotubes and Conductive Carbon Black

8.1 Introduction

From the literature,\textsuperscript{[17, 134, 263, 301-306]} it is known that there are a great difficulty and an enormous challenge to produce a polymer composite with a very electrical high conductivity by adding a single type of fillers such as carbon nanotube (CNTs) or conductive carbon black (CCB) alone. This is because MWCNTs tend to agglomerate themselves due to their strong van der Waals force although they exhibit the high aspect ratio and high conductivity. Therefore, it is difficult for MWCNTs to form a conductive network and as a result, the polymer nanocomposites with MWCNTs as fillers have relative low conductivity. On the other hand, CCB has an ability to form a spider-lied 3D network structure. However, the conductivity of CCB is limited due to its intrinsic feature. Thus, it can be considered that the ternary composites with both MWCNTs and CCB might be the best solution to overcome these individual problems to obtain a complementary effect from MWCNTs and CCB. As a result, they would have a much higher conductivity.

Therefore, in this chapter, to develop advanced conductive polymer composites, both multiwalled carbon nanotubes and conductive carbon black have been added into a matrix of polyamide 6. The complementary effects of CCB and MWCNTs at different compositions on rheological, physical, morphological, thermal, dynamic mechanical and electrical properties of the ternary composites have been examined systematically. As a result, a complementary effect has surprisingly been verified to exist between MWCNTs and CCB in the polymer matrix, which endows the ternary composites with superior
electrical and thermal properties. The mechanism for the complementary effect of MWCNTs and CCB has been proposed and discussed.

The ternary polymeric composites of PA6 (Ultramid B36 LN 01), CCB (ENSACO 350G) and MWCNTs (Baytubes) with different compositions were fabricated by Method-I using the mixing and moulding temperature of 300 °C. The compounding formulations and sample codes for the composites studied are tabulated in Table 8.1.

<table>
<thead>
<tr>
<th>Code</th>
<th>PA6 (wt %)</th>
<th>CCB (wt %)</th>
<th>MWCNT (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PABN0</td>
<td>90</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>PABN1</td>
<td>89</td>
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<tr>
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<td>87</td>
<td>10</td>
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<tr>
<td>PAN20</td>
<td>80</td>
<td>-</td>
<td>20</td>
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</table>
8.2 Results and discussion

8.2.1 Thermal properties

To inspect the thermal stability of the PA6 composites incorporated with MWCNTs and CCB, TGA measurements were carried out, and the results are shown in Figure 8.1. In this study, the criteria for thermal stability were taken as the temperature at which 5 %, 10 % and 50 % weight losses occurred in the system. It is observed from Figure 8.1 that 5 %, 10 % and 50 % weight loss of pure PA6 occurred at 430 °C, 446 °C and 455 °C, respectively. Compared to the pure PA6, the 10 wt % CCB composite, i.e. PABN0, showed the 23 °C delay in decomposition at 50 % weight loss. By adding 5 wt % MWCNT and 10 wt % CCB into the pure PA6, i.e. PABN5, the 5 %, 10 % and 50 % weight loss temperatures of PABN5 composite extended to higher temperatures at 465 °C, 478 °C and 490 °C, respectively, with a slower decomposition rate and almost 85.2 % of the sample degraded in this step. So, the thermal stability of the composites improved with increasing the MWCNTs in the composites. This is because polymer chains near the fillers may degrade more slowly, which helps to increase the decomposition temperature.
Figure 8.1 TGA thermographs of PA6 based ternary composites with CCB and MWCNT, (a) PA6, (b) PABN0, (c) PABN1, (d) PABN3, (e) PABN5 and (f) PABN10.

Other reason is the increased thermal stability of the polymer composites due to the effect of higher thermal conductivity of MWCNTs which facilitates heat dissipation within the composite.\textsuperscript{[138]} However, by adding of 10 wt % MWCNT and 10 wt % CCB into the pure PA6 matrix, i.e. PABN10, the thermal stability decreased to 456 °C at 5 % weight loss, 465 °C at 10 % weight loss and 474 °C at 50 % weight loss. This results show that the addition of excessive fillers into the polymer matrix makes the composites worse in thermal stability. The similar result is also observed in other composites with CCB only (PAB20) and MWCNTs only (PAN20) as shown in Table 8.2.
Table 8.2. Thermal stability for PABN10, PAB20 and PAN20 composites, all at 20 wt % filler loading, where $T_5$, $T_{10}$, and $T_{50}$ are the temperatures at which 5%, 10% and 50% weight loss occurred respectively.

<table>
<thead>
<tr>
<th>Code</th>
<th>$T_5$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PABN10</td>
<td>455.6</td>
<td>464.8</td>
<td>473.8</td>
</tr>
<tr>
<td>PAB20</td>
<td>447.3</td>
<td>465.4</td>
<td>474.0</td>
</tr>
<tr>
<td>PAN20</td>
<td>446.5</td>
<td>464.3</td>
<td>473.2</td>
</tr>
</tbody>
</table>

The DSC thermograms of all the ternary composites are presented in Figure 8.2. The crystallisation temperature ($T_c$), melting temperature ($T_m$), heat of crystallisation ($\Delta H_c$), heat of fusion ($\Delta H_f$) and crystallinity ($\chi_c$) obtained from DSC studies are summarised in Table 8.3. For the calculation of crystallinity using equation 3.2, the theoretical specific melting heat ($\Delta H_0^f$) of 100% crystalline PA6 was taken as 230 J/g.¹³⁰⁷

The DSC melting endotherm (Figure 8.2A) indicates that PA6 had a melting peak at 220 °C, corresponding to the melting event of the $\alpha$-form crystals.¹⁴⁶,¹⁴⁷ The melting peak temperature of PA6 was affected by incorporation of MWCNTs in the CCB/PA6 composites (PABs). It is observed that the melting temperature of PA6 was shifted higher by 4 °C for the PABN10 composite. This is due to the existence of MWCNTs and CCB in the composites of MWCNT/CCB/PA6 (PABNs). On the other hand, the heat of fusion of the ternary composites increased with increasing MWCNT loading as shown in Table 8.4.
Figure 8.2 DSC thermograph of PABN composites: (A) melting and (B) crystallization:

(a) PA6, (b) PABN0, (c) PABN1, (d) PABN3, (e) PABN5 and (f) PABN10.
Table 8.3 Melting and crystallisation behaviours of PABN composites.

<table>
<thead>
<tr>
<th>Code</th>
<th>Melting</th>
<th>Crystallisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ ($^\circ$C)</td>
<td>$H_f$ (J/g)</td>
</tr>
<tr>
<td>PA6</td>
<td>217</td>
<td>59.8</td>
</tr>
<tr>
<td>PABN0</td>
<td>219</td>
<td>60.02</td>
</tr>
<tr>
<td>PABN1</td>
<td>220</td>
<td>60.52</td>
</tr>
<tr>
<td>PABN3</td>
<td>220.5</td>
<td>62.91</td>
</tr>
<tr>
<td>PABN5</td>
<td>222</td>
<td>60.99</td>
</tr>
<tr>
<td>PABN10</td>
<td>223</td>
<td>53.61</td>
</tr>
</tbody>
</table>

Table 8.4 Comparison of melting and crystallisation behaviours of different composites at 20 wt % of carbon loading.

<table>
<thead>
<tr>
<th>Code</th>
<th>Melting</th>
<th>Crystallisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ ($^\circ$C)</td>
<td>$H_f$ (J/g)</td>
</tr>
<tr>
<td>PAB20</td>
<td>216</td>
<td>59.59</td>
</tr>
<tr>
<td>PAN20</td>
<td>217.4</td>
<td>52.80</td>
</tr>
<tr>
<td>PABN10</td>
<td>223.0</td>
<td>53.61</td>
</tr>
</tbody>
</table>

From Figure 8.2B, it can be seen that the pure PA6 had a single crystallization peak temperature at about 184 $^\circ$C. The crystallisation temperature shifted to a higher temperature and the crystallisation temperature range became broader for all the composites (PABNs). This is because the fillers often have a positive effect on the crystallisation of a polymer in its composite system.[^308] That is, the filler particles can act
as nucleating agents, inducing an earlier crystallisation during a cooling process. It is very interesting to observe that the new crystallisation peak appeared at a higher temperature for the PABN composites and this peak position shifted to the higher temperature side with increasing content of MWCNTs in the composites. The magnitude of this crystallisation peak was also decreased with increasing MWCNTs in the PA6 composites with 10 wt % CCB loading. These observations are in good agreement with the previous report in literature.\cite{75} From this report, it has been known that when MWCNTs are added into a polymer, the crystallisation temperature of the polymer shifts to a higher temperature side and its crystallisation temperature range becomes broader. Phang et al.\cite{286} also reported while the DSC results showed two crystallisation exotherms for MWCNT/PA6 composites instead of a single exotherm for the neat matrix. They reported that the formation of the higher-temperature crystallisation peak was closely related to the addition of MWCNTs. When the amount of MWCNT was increased in the PA6 matrix, more heterogeneous nucleating sites were available, and hence more polymer chains were induced to crystallise, thus resulting in a significant second crystallisation peak. This unusual crystallisation behaviour was also found in the clay/PA6 nanocomposites as reported by Wu et al.\cite{309} And, it could be considered that this kind of crystallisation occurs via a heterogeneous nucleation, in which two different crystal structures are formed. This also agrees with the several reports in the literature,\cite{75,286,307,309,310} which described PA6 to have a polymorphism of $\alpha$ and $\gamma$ crystallites. In this study, the heat of fusion ($\Delta H_f$) and heat of crystallisation ($\Delta H_c$) increased with increasing the MWCNTs in the PA6 composites, with 10 wt % CCB loading, up to 3 wt % of MWCNT (i.e.; PABN3).
The heat of fusion is proportional to the degree of crystallinity in the sample, which was also supported by the crystallisation behaviour of composites. The larger heat of fusion indicates the higher crystallinity of the composites. As a result, for the MWCNT/CCB/PA6 composites (PABNs), the crystallinity became higher with increasing MWCNTs up to 3 wt %. MWCNTs promoted the crystallisation of CCB/PA6 binary composite (PAB10) as shown in Table 8.4. But the composites with 5 wt % (PABN5) and 10 wt % (PABN10) of MWCNTs had lower crystallinity than other composites. The comparison shows that the heat of fusion, crystallinity and heat of crystallisation of PABN10 were lower than those of PAB20 as seen in Table 8.4. This can be explained by the fact that the addition of functionalised MWCNTs enhanced crystallinity of the composites, but reduced the molecular mobility of PA6 at the same time.

8.2.2 Mechanical properties

The loss tangent (tan δ) versus temperature curves are presented in Figure 8.3A. It is well known that the temperature corresponding to the maxima of a tan δ peak is normally associated with the glass transition temperature $T_g$. From the variation of tan δ with temperature (Figure 8.3A), $T_g$ of pure PA6 appeared at approximately 63 °C. The glass transition temperature of PA6 shifted to the higher temperature side by the addition of CCB and MWCNTs. The glass transition temperature increased from 63 °C for the pure PA6 to 65 °C for the composite with 10 wt % CCB in PABN0 and 68 °C for the composite with 10 wt % CCB and 10 wt % MWCNT in PABN10.
When CCB and MWCNTs are incorporated in, the mobility of polymer chains is constrained by those rigid particles, so that a higher energy (i.e., higher temperature) is needed to make the chains move. The broadening and increase of $T_g$ observed in the organic-inorganic nanocomposites are generally ascribed to the restricted segmental motions near the organic-inorganic interfaces. Because polymer chains near and far from fillers have different mobilities, they will start moving at different temperatures. This effect can also be explained in terms of decreasing the free volume of the polymer matrix. From the concept of free volume, with the addition of CCB and MWCNTs, the free volume is obviously reduced, which will further result in a difficulty of the movement of the polymer chains. This phenomenon was also observed in other nanocomposites with MMT nano-clay. For example, it was reported that the $T_g$ of neat PA6 (ca. 63.7 °C) was broadened and shifted toward higher temperatures (ca. 65.5–67.3 °C) with the addition of MMT nano-clay.
Figure 8.3 Dynamic mechanical behaviours of PABN composites: (A) tangent delta and (B) storage modulus – where (a) PA6, (b) PABN0, (c) PABN1, (d) PABN3, (e) PABN5 and (f) PABN10.
Figure 8.3B shows the storage modulus versus temperature curves. Generally, storage modulus can describe the stiffness of materials. The storage modulus of the composites dramatically increased when MWCNTs were incorporated into the PA6 composite with 10 wt % CCB loading (PABNs). The composite PABN10 showed about 15 % and 60 % increase in storage modulus in the glassy plateau region (-20 °C) and the rubbery plateau region (100 °C), respectively, as compared to pure PA6, and about 8 % and 10 % increase in storage modulus in the glassy plateau region (-20 °C) and the rubbery plateau region (100 °C), respectively, as compared to CCB/PA6 binary composite (PABN0).

8.2.3 Rheological properties

Dynamic frequency sweep tests were used to explore structure and network formation of the composites. The changes in complex viscosity ($\eta^*$) with respect to angular frequency for the pure PA6, the CCB/PA6 composites (PABs), and MWCNT/CCB/PA6 composites (PABNs) at 300 °C are shown in Figure 8.4. The power law index for complex viscosity varies with the loading of carbon filler are listed in Table 8.5.

Over the range of angular frequency applied, the power law for complex viscosity, $\eta^*$, varied with carbon loading from $\omega^{0.03}$ for pure PA6 to $\omega^{0.93}$ for PABN10, $\omega^{1.00}$ for PAB20 and $\omega^{0.85}$ for PAN20. The power law index for pure PA6 is 0.03, which tells that the flow is almost a Newtonian one but the power law index increases as the carbon loading increase. These increases in power law index show that the flow behaviour changes from Newtonian to non-Newtonian. Pure PA6 showed the Newtonian flow
behaviour but all the composites exhibited the non-Newtonian flow behaviour, which became more outstanding for the composites with higher loading of MWCNTs.

As being expected, the viscosities of the composites gradually increased with increasing MWCNT content from which it could be concluded that a dense MWCNT + CCB network is formed in the polymer, as seen in Figure 8.4A. But in Figure 8.4B, compared to the CCB-alone composite (PAB20), the ternary composite (PABN10) has a higher viscosity but the viscosity of PABN10 is lower than that of the MWCNT-alone composite (PAN20). This is probably due to the fact that MWCNTs with a high aspect ratio could restrict the flow of the polymer chains in their molten state, while CCB with a spherical structure (in its powder-form) could have a less effect. As a result, the mixture of the high aspect ratio MWCNTs and spherical CCB results in the intermediate viscosity for ternary composites. On the other hand, the higher viscosity of MWCNT-alone composite (PAN20) increases the difficult in dispersing MWCNTs into the polymer matrix, thus leading to a relative worse dispersion than CCB in CCB-alone composite (PAB20) as discussed in the following sections.
Figure 8.4 Complex viscosity versus angular frequency for pure PA6, PAN20, PAB20 and PABN composites at 300 °C: (a) PA6, (b) PABN0, (c) PABN1, (d) PABN3, (e) PABN5, (f) PABN10, (g) PAB20 and (h) PAN20.
Table 8.5 Power law index of complex viscosity, slopes of $G'$ and $G''$ with respect to angular frequency in a log-log scale for PAB, PAN, and PABN composites.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Power law index of log $\eta^*$ vs log $\omega$</th>
<th>Slope of log $G'$ vs log $\omega$</th>
<th>Slope of log $G''$ vs log $\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>0.03</td>
<td>1.572</td>
<td>0.958</td>
</tr>
<tr>
<td>PABN0</td>
<td>0.73</td>
<td>0.225</td>
<td>0.394</td>
</tr>
<tr>
<td>PABN1</td>
<td>0.83</td>
<td>0.116</td>
<td>0.242</td>
</tr>
<tr>
<td>PABN3</td>
<td>0.86</td>
<td>0.167</td>
<td>0.150</td>
</tr>
<tr>
<td>PABN5</td>
<td>0.91</td>
<td>0.105</td>
<td>0.016</td>
</tr>
<tr>
<td>PABN10</td>
<td>0.93</td>
<td>0.103</td>
<td>0.013</td>
</tr>
<tr>
<td>PAB20</td>
<td>1.00</td>
<td>0.027</td>
<td>0.00</td>
</tr>
<tr>
<td>PAN20</td>
<td>0.85</td>
<td>0.221</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Similarly, addition of MWCNTs influences the frequency-dependence of storage modulus ($G'$) and loss modulus ($G''$), especially at low frequencies. The storage modulus and loss modulus versus angular frequency for pure PA6, PAB20, PAN20 and PABN composites at 300 °C are shown in Figures 8.5 and 8.6, respectively. Over the range of angular frequency applied, pure PA6 tended to exhibit a typical terminal flow behaviour with the scaling relations of $G' \approx \omega^2$ and $G'' \approx \omega^1$ as $\omega$ was approaching to zero in accordance with the theory of linear viscoelasticity. But for all the composite samples, the dependence of $G'$ on $\omega$ became weaker with increasing carbon loading. Thus, the polymer chain relaxation in the composites was effectively controlled by the presence of
carbon fillers. The decreases in the power law index, which is related to the dependency of $G'$ on $\omega$, with the loading of carbon fillers, are listed in Table 8.5.

The power law index for $G'$ decreased with increase carbon loading from 1.572 for pure PA6 to 0.103 for PABN10, 0.027 for PAB20 and 0.221 for PAN20, respectively. The loss moduli of the composites exhibited a similar trend to the storage moduli. The frequency dependency of $G''$ also decreased from $\omega^{0.958}$ for pure PA6 to $\omega^{0.013}$ for PABN10, $\omega^{0.001}$ for PAB20, and $\omega^{0.01}$ for PAN20, respectively. These decreases in the power law index for $G'$ and $G''$ indicated a transitional behaviour from a liquid-like to a solid-like viscoelastic behaviour. This phenomenon is mainly related to the interactions among filler particles and then, the network formation as the inter-particle distance decreases. A network of filler particles will significantly influence not only rheological properties but also electrical ones of the composites, which will be discussed in the following sections.
Figure 8.5 Storage modulus versus angular frequency for pure PA6, PAN20, PAB20 and PABN composites at 300 °C, where: (a) PA6, (b) PABN0, (c) PABN1, (d) PABN3, (e) PABN5, (f) PABN10, (g) PAB20 and (h) PAN20.
Figure 8.6 Loss modulus versus angular frequency for pure PA6, PAN20, PAB20 and PABN composites at 300 °C, where: (a) PA6, (b) PABN0, (c) PABN1, (d) PABN3, (e) PABN5, (f) PABN10, (g) PAB20 and (h) PAN20.
8.2.4 Electrical properties

The comparison of DC electrical conductivity between CCB/PA6 (PAB) composites and MWCNT/PA6 (PAN) composites is shown in Figure 8.7A. From this figure, PAB20 has a conductivity of 0.5 S/m while PAN20 has that of 0.04 S/m. So, the composites with CCB alone have higher DC conductivity than those with MWCNTs alone although electrical conductivity of MWCNTs is higher than that of CCB.

Surprisingly, when MWCNTs were added into the PA6 composite filled with 10 wt % CCB to make the ternary composites (PABNs), there was another percolation leading to a significant improvement in the electrical conductivity of the resulting ternary composites. The comparison of conductivity among the three different composite systems is shown in Figure 8.7B. The conductivity of the ternary composite (PABN5) is 0.4 S/m, which is 80 % of that of PAB20 (0.5 S/m). This is 10 times higher than that of PAN20 (0.04 S/m). At 20 wt % of carbon loading, the PABN10 (5 S/m) (the ternary composite with PA6, 10 wt % CCB and 10 wt % MWCNT) showed about 10 times higher in conductivity than PAB20 (0.5 S/m) (the binary composite with PA6 and 20 wt % CCB) and about 125 times higher in conductivity than PAN20 (0.04 S/m) (the binary composite with PA6 and 20 wt % MWCNT).
Figure 8.7 DC electrical conductivities for: (a) PAN, (b) PAB and (c) PABN composites at different carbon loadings.
Figure 8.8 shows the AC conductivity as a function of frequency for PABN composites with various contents of MWCNTs. With increasing the MWCNT loading from 0 to 5 wt %, the conductivity increased monotonously over the range of frequency in a logarithmic scale, exhibiting a typical capacitor-like behaviour. For the PABN0 composite (referring to the curve (a) in Figure 8.8), the AC conductivity tends to reach an upper limit (i.e. about 0.2 S/m) at the higher frequencies (starting from $10^4$ Hz onwards). But by adding the MWCNTs into the composite consisting of PA6 and 10 wt % CCB, the resulting ternary composites did not show such a limitation in the higher frequency region and the limit seemed to be shifted to the higher conductivity values as reflected in the curves (b-d) in Figure 8.8. Interestingly, at 10 wt % MWCNT (i.e. PABN10), the conductivity was nearly independent of frequency (in the logarithmic scale) and this phenomenon implies another percolation which makes the ternary composites more conductive electrically. This result is in good agreement with the observations from the DC conductivity measurement as given in Figure 8.7B.
Figure 8.8 AC electrical conductivity versus frequency for PABN composites at different MWCNT loadings: (a) PABN0, (b) PABN1, (c) PABN3, (d) PABN5, and (e) PABN10.

8.2.5 Dispersion of carbon nanotubes and conductive carbon black in the PA6 matrix

CCB has the high surface energy and the relatively high conductivity while MWCNTs exhibit the high aspect ratio and the excellent conductivity. Therefore, both CCBs and MWCNTs are outstanding candidates for the fabrication of conducting polymer composites. Figure 8.9 shows the FESEM micrographs of PAN, PAB and PABN composites. Referring to circles in Figure 8.9a, due to the agglomeration of MWCNTs resulted from the strong van der Waal forces and high viscosity of a MWCNT/polymer composite during a melt-compounding process, the dispersion of
MWCNTs cannot be reached a satisfactory level, so that MWCNT-based composites are of low electrical conductivity.

On the other hand, due to the inherent properties of CCB,\textsuperscript{305} it is possible for it to form a spider-like 3D network in a polymer matrix as indicated by the circles in Figure 8.9b. Then, according to Figure 8.9c, in the ternary composites of PA6, CCB and

![Figure 8.9 Scanning electron micrographs of (a),(d) PAN20, (b),(e) PAB20 and (c),(f) PABN10.](image-url)
MWCNTs, CCB still can maintain its spider-like 3D structure (denoted by the circle A) while there are some MWCNT agglomerates (indicated by the circle B) in the composites. Moreover, it is interestingly observed a connection between the CCB network and MWCNT agglomerates (denoted by the circle C), which would make the electrically conductive network in the ternary composites more perfect and as a result, they would have higher electrical conductivities.

8.3 Formation of an electrically conductive network by the complementary effects of MWCNTs and CCB.

![Schematic diagrams](image)

Figure 8.10 Schematic diagrams for possible conductive mechanisms of (a) PAN, (b) PAB and (c) PABN composites.

According to Figures 8.7 and 8.8, it has been proved that the ternary composites have better conductivities than the binary composites. From these results, a possible mechanism, why the electrical conductivity of ternary composites is higher than that of their correspondent binary composites, is proposed in Figure 8.10.

This proposed figure is an analytical sketch based on the FESEM micrographs from Figure 8.9. Although MWCNTs exhibit the high aspect ratio and high conductivity, MWCNTs tend to agglomerate themselves due to their strong van der Waals force and they are present as bundles in the polymer matrix as shown in Figure 8.9a (denoted by the
circles). Therefore, we can conclude that it is extremely difficult for MWCNTs to form a conductive network as illustrated in Figure 8.10a. As a result, the composites with MWCNTs as fillers have lower conductivity. On the other hand, CCB has an ability to form a spider-like 3D network structure as observed as the circles in Figures 8.9b and as demonstrated in Figure 8.10b. However, the conductivity of CCB is limited due to their intrinsic feature. Thus, according to Figure 8.7B, ternary composites might be the best solution to overcome these individual problems to obtain a complementary effect from MWCNTs and CCB, as shown in Figure 8.10c. As a result, the ternary composites showed much higher conductivity.

8.4 Summary

In this work, a novel way for the fabrication of ternary polymer composites using CCB and MWCNTs as fillers have been presented and verified, in which MWCNTs were incorporated into PA6 preloaded with 10 wt % CCB. The crystalline, thermal, morphological, mechanical, rheological, and electrical properties of the ternary composites of PA6 have been studied. It is showed that the ternary composites of PA6 have the improved mechanical and thermal properties over the binary composites filled with CCB or MWCNT alone. Electrical conductivity measurements suggest that CCB/PA6 composites made better conductive network structure in the presence of MWCNTs, which showed higher conductivity than the binary systems. A mechanism for why the properties of the ternary composite system are better than those of the binary systems has been proposed and discussed.
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Chapter 9 Conclusions

This thesis clearly reveals that the properties of MWCNT/polymer composites strongly depend on the degree of dispersion of MWCNTs in a polymer matrix, interfacial interaction between MWCNTs and polymer molecules, and formation of MWCNT network in a polymer matrix. Scheme 9.1 summerises the research work done during this PhD study.

Scheme 9.1 Flowchart of the research done in this thesis.

The chemical modification of MWCNTs can effectively enhance the mechanical properties of MWCNT/polymer composites by improving not only the interfacial interaction between MWCNTs and polymer molecule but also the dispersion of MWCNTs in the polymer matrix. It is also found that the enhanced dispersion and alignment of CNTs in polymer matrices due to an appropriate choice of method(s) (such as the fabrication process and/or the functionalisation of CNTs) can greatly change mechanical, electrical, thermal, and morphological properties of the resultant
CNT/polymer composites. Upon accomplishing this study, the following specific conclusions can be drawn.

9.1 The effects of surfactants

The effects of two surfactants, sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulphonate (NaDDBS), on the properties of MWCNT/PP composites prepared by a melt-mixing method have been investigated. The surfactant-treated MWCNTs resulted in the improvement in their state of dispersion in the polymer matrix and largely enhanced the mechanical and electrical properties of the composites. Besides, it was found that the surfactant-treatment of MWCNTs together with a micro-mixing process led to a great improvement in their state of dispersion in a PP matrix. The improvement in the dispersion state of the surfactant-treated MWCNTs in PP greatly influenced the mechanical and electrical properties of the composites. The enhancement in the mechanical properties of PP by NaDDBS was more evident than SDS as the former possess a better compatibility with PP than the latter. For example, with the addition of only 2 wt % of SDS-treated and NaDDBS-treated MWCNTs, the Young’s modulus of PP increased by 61.1 and 86.1 %, respectively. The improvement in electrical conductivity of PP filled surfactant-treated MWCNTs was also due to the homogeneous dispersion of MWCNTs in PP, which allowed conductive network to be formed relatively easily.

9.2 The effects of functionalisation of carbon nanotubes

A novel approach to chemical functionalisation of multiwalled carbon nanotubes (MWCNTs) for making advanced polymeric nanocomposites based on a liquid crystalline polymer (LCP) was made. In this approach, two types of chemical moieties (carboxylic (-COOH) group and hydroxyl benzoic acid (HBA) group) were selectively
introduced onto the sidewalls of the MWCNTs. It was found that the strong interaction between the functionalised MWCNTs and the LCP greatly improved the dispersion of MWCNTs in the polymer matrix as well as the interfacial adhesion. The reinforcing effect of the chemically modified MWCNTs is more pronounced than that of raw MWCNTs. For example, the tensile strength and modulus of the nanocomposite with 1.0 wt% raw MWCNTs was enhanced only by 6.0% and 28%, respectively, as compared to the pure LCP. The chemically modified MWCNTs led to the significant increase in tensile strength, modulus, and elongation-at-break of LCP nanocomposites. Among these, HBA groups on the MWCNTs contributed to the highest enhancement in the tensile strength and modulus by 41% and 55%, respectively, as well as a higher elongation-at-break (reaching to nearly 9.0% tensile strain).

The good dispersivity of the functionalised MWCNTs can be achieved through (i) weakening or destroying van der Waals forces among the CNTs and (ii) enhancing the interaction (or compatibilisation) of CNTs with the matrix polymer. The HBA-modified MWCNTs showed the better dispersion in LCP than the COOH-modified MWCNTs and raw MWCNTs. The enhancement in the mechanical properties of the LCP by the HBA-modified MWCNTs could be due to the several reasons as described below.

The first reason is related to the good dispersion of MWCNT-HBA throughout the LCP matrix, which led to a significant increase in the tensile strength of the nanocomposite. The second one is the strong interactions between MWCNT-HBA and LCP chains, which is important for the efficient stress transfer between the MWCNTs and the LCP. The strong interaction of MWCNT-HBA with the LCP matrix is attributed to the H-bonding between them. Third, the longer chemical moieties containing benzene
rings attached on the surface of the MWCNTs could have the strong $\pi-\pi$ interactions with the LCP chains. Therefore, the strong interaction between the HBA-functionalised MWCNTs and the LCP matrix greatly enhanced the dispersion of MWCNTs as well as the interfacial adhesion. As a result, the overall mechanical performance of the nanocomposite could be improved significantly.

9.3 The effects of processing methods

The effects of processing method on the morphological, dynamic mechanical, mechanical, thermal and electrical properties of MWCNT/polymer composites were investigated. It is well-known that an optimum method of processing leads to improvement in the physical and mechanical properties of the composites through uniform dispersion of CNTs. In this study, the composites fabricated by Method-II (see Chapter 3) exhibited the better properties than those prepared by Method-III (see Chapter 3) because the internal mixer used in Method-II has an ability to disperse MWCNTs more uniformly in the polymer matrices than the industrial extruder used in Method-III.

Apart from the processing method, the functionalisation of MWCNTs plays an important role on their state of dispersion in a polymer matrix as well as their interaction with the matrix molecules. For example, the homogeneous dispersion of MWCNTs in the polymer matrices was achieved by means of the both functionalisations of MWCNTs, either covalent or noncovalent. Therefore, the composites containing functionalised MWCNTs showed the improved mechanical properties over those filled with the raw MWCNTs.

Besides, the interaction between MWCNT-COOH and PA6 molecules is stronger than that between MWCNT-COOH and PP molecules. The $-\text{CONH}$- groups in PA6
chains can physically interact with the –COOH groups of the functionalised MWCNTs, thus being favourable for stress-transfer from the PA6 matrix to MWCNTs. However, no functional or active group is available on the backbone of PP and it is nonpolar. Therefore, the improvement in the mechanical properties of a PP composite containing MWCNT-COOH was less significant than that of PA6 composite filled with MWCNT-COOH.

The composites containing noncovalent functionalised MWCNTs exhibited a higher electrical conductivity compared to those with covalent functionalised ones. This is because the sp² carbon structure of MWCNTs was changed to sp³ carbon structure during the covalent functionalisation and thus, their excellent electronic structure was demolished. Therefore, to improve the electrical properties of MWCNT/polymer composites, an optimisation is required between the improved dispersion of MWCNTs in the matrix and the damages in their carbon-carbon bonds due to the covalent functionalisation. On the other hand, the noncovalent functionalisation of MWCNTs, in which an appropriate surfactant was physically mixed with MWCNTs, could improve the dispersion state of MWCNTs in a polymer matrix but without damaging their electrical properties.

9.4 The compatibilising effect of functionalised carbon nanotubes

The carboxyl-functionalised MWCNTs (MWCNT-COOH) were added into a blend of polyamide 6 (PA6) and liquid crystalline polymer (LCP) to make ternary composites. The compatibilising effect of MWCNT-COOH on the ternary composites has been studied. It was interestingly found that the MWCNT-COOH served as a compatibiliser between the LCP and the PA6 to increase the interfacial adhesion between
them. As a result, the significant improvement in the mechanical properties of PA6/LCP/MWCNT-COOH composites has been achieved. The homogenous dispersion of the MWCNT-COOH in the LCP/PA6 blend and the strong interfacial bonding among PA6, LCP and MWCNT-COOH are the key factors for the improvements in the mechanical and thermal properties. For example, the tensile strength and modulus of the composite with 1.0 wt % MWCNT-COOH were enhanced by 44 % and 62 %, respectively as compared to that of a pure PA6/LCP blend.

9.5 The complementary effect of carbon nanotubes and conductive carbon black

A new and innovative idea for preparation of superconductive ternary composites consisting of polyamide 6 (PA6), conductive carbon black (CCB), and raw multiwalled carbon nanotubes (MWCNTs) was proposed and examined. The ternary composites of PA6 showed the improved mechanical, thermal and electrical properties over the binary composites filled with CCB or MWCNT only. For example, the electrical conductivity of PA6 composite containing 20 wt % of MWCNTs is only 0.04 S/m while that of the composites filled with 20 wt % of CCB is 0.5 S/m. However, the ternary composites of PA6 containing 10 wt % MWCNTs and 10 wt % CCB showed an electrical conductivity of 5.0 S/m, which is 10 times that of the CCB/PA6 binary composite and 125 times that of the MWCNT/PA6 binary composite. Moreover, the findings by FESEM microscopy also supported that the higher electrical conductivity of the ternary composites resulted from the additional linkages between the CCB network and MWCNTs agglomerates in the PA6 matrix, which made the electrically conductive network in the matrix more continuous and denser. Therefore, a complementary effect between MWCNTs and CCB was obtained in the PA6 matrix by using a ternary composite system.
References


