POLYMER GRAFTED CARBON NANOTUBE REINFORCED ULTRA HIGH
MOLECULAR WEIGHT POLYETHYLENE FIBRE

by

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Abstract

In this research, a series of experiments have been conducted to develop a high performance ultra-high molecular weight polyethylene (UHMWPE) fibre with improved mechanical properties. A novel process was developed whereby polyethylene grafted multi-walled carbon nanotubes (PE-g-MWCNTs) were used to reinforce UHMWPE fibre. PE-g-MWCNT/UHMWPE fibres with remarkable modulus and tensile strength of 125.5 GPa and 4.0 GPa, respectively, were successfully fabricated and showed definite potential for reducing the weight of body armour.

A systematic study was carried out to investigate the effects of gel spinning conditions on tensile properties and morphologies of UHMWPE fibre. Spinning parameters, including polymer concentration, spinning temperature and winding-up speed, were selected and studied systematically and the spinning condition of UHMWPE fibre was optimized by design of experiment.

Intensive experiments were conducted to investigate the feasibility of reinforcing UHMWPE fibre with pristine multi-walled carbon nanotubes (MWCNTs). Various mechanical methods include ultra-sonication, ball milling, microfluidizing, etc. were applied for dispersing pristine MWCNTs. Studies on tensile properties and morphologies of formed MWCNT/UHMWPE fibre demonstrated that pristine MWCNTs tend to exist in micro-meter size agglomerations and no improvement in tensile properties of the MWCNT/UHMWPE fibres was found.

Finally, chemical functionalization of MWCNTs using a coupling agent and polymer grafting technology was studied. The effective modulus and strength of MWCNTs were calculated based on the ‘rule of mixture’. Compared to coupling agent functionalization, polymer
grafting has been found to be more effective in improving reinforcement of MWCNTs in UHMWPE fibre due to a stronger load transfer on the interface. The reinforcement mechanism of polymer grafted MWCNTs was analyzed based on experimental observations.
Preface

This thesis presents the results of several studies on the preparation of strong UHMWPE fibre reinforced by MWCNTs, which were performed as part of the research project ‘Lightweight Composite Armour for IED Protection’ funded by CRTI (chemical, biological, radiological and nuclear, CBRN, Research and Technology Initiative). The project was conducted through a collaboration of researchers from the Canada National Research Council, McGill University and Allen Vanguard Incorporation with the objective of developing a strong, stiff fibre that could be used to reduce the weight of armour for IED protection.

Chapter 8 reveals results of a study on grafting polyethylene on MWCNT to improve the load transfer between MWCNT and UHMWPE. That study is a refined extension of a method developed by Dr. Jingwen Guan from the National Research Council of Canada. I extended the concept by developing a simpler and more effective approach for grafting polyethylene and applied it as reinforcement for gel spun UHMWPE fibre. A version of Chapter 8 has been published in the Proceeding of the American Society for Composites 27th Technical Conference, 15th US-Japan Conference on Composite Material. I organized and conducted all the testing and wrote the manuscript.
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**List of Abbreviations**

The following table describes the significance of various abbreviations used throughout the thesis. The page on which each one is defined or first used is also given.

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<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
<th>Page</th>
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<tr>
<td>CNF</td>
<td>Carbon nanofibre</td>
<td>32</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
<td>1</td>
</tr>
<tr>
<td>CRTI</td>
<td>Canada Research and Technology Initiative</td>
<td>xviii</td>
</tr>
<tr>
<td>Decalin</td>
<td>Decahydronaphthalene</td>
<td>96</td>
</tr>
<tr>
<td>EOD</td>
<td>Explosive ordnance disposal</td>
<td>1</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
<td>45</td>
</tr>
<tr>
<td>IED</td>
<td>Improvised explosive device</td>
<td>1</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
<td>37</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
<td>ii</td>
</tr>
<tr>
<td>NaDDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
<td>36</td>
</tr>
<tr>
<td>nm</td>
<td>Nano mater</td>
<td>23</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
<td>5</td>
</tr>
<tr>
<td>PE-g-MWCNT</td>
<td>Polyethylene grafted multi-walled carbon nanotube</td>
<td>ii</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
<td>38</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
<td>37</td>
</tr>
<tr>
<td>PPD</td>
<td>P-phenylene diamineLL</td>
<td>15</td>
</tr>
<tr>
<td>PPTA</td>
<td>p-phenylene terephtalamides</td>
<td>15</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
<td>27</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
<td>36</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecylsulphate</td>
<td>37</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single walled carbon nanotube</td>
<td>6</td>
</tr>
<tr>
<td>TCL</td>
<td>Terephthaloyl chloride</td>
<td>16</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
<td>40</td>
</tr>
<tr>
<td>TPU</td>
<td>Thermoplastic polyurethane</td>
<td>30</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultra high molecular weight polyethylene</td>
<td>ii</td>
</tr>
</tbody>
</table>
Acknowledgments

I would like to take this opportunity to thank all those who have helped and inspired me during my doctoral studies.

First and foremost, I would like to express my sincere gratitude toward my supervisor Prof. Frank Ko for his enthusiastic supervision and guidance during my studies at the University of British Columbia. My interest in textile composite material came as a result of reading the book *Textile Structural Composites* written by Prof. Frank Ko while I was an undergraduate student at Donghua University in China. I sincerely thank Dr. Ko for providing such a wonderful research opportunity studying nano-composite material at a world-class university. Dr. Ko provided insightful discussions about the research. In addition, he set an example for me as a researcher through his passion about research.

The thesis is based on a research project in collaboration with the National Research Council (NRC) of Canada. The experience working with researchers from the NRC broadened my perspective on the practical aspects in industry. I would like to thank all researchers from NRC for their technical discussions. In particular, I would like to thank Dr. Jingwen Guan from for his advice and unsurpassed knowledge of nano-materials.

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Finally, my deepest gratitude goes to my parents and husband for their love and support through the past five years. I am forever indebted to them for always being supportive. This dissertation would have simply been impossible without their understanding, endless patience and encouragement.
Dedication

To my parents
Chapter 1- Introduction

1.1 Background

The increase of terrorist events involving Improvised Explosive Devices (IED) is a significant threat to all military and law enforcement. Explosive Ordnance Disposal (EOD) bomb disposal suit is worn as the first line of defense once an IED is identified. Current full body coverage EOD ensembles provide acceptable protection. However, the weight of these EOD ensembles is in excess of 30 kilograms which results in increased fatigue, heat stress and reduced mobility[1]. Thus, both military and civil defence organizations are looking for stronger fibre to further reduce the weight and improve the protection body armour provides.

Motivated by the need for lightweight IED protective armour, a research program (Lightweight composite armour for IED protection: A carbon nanotube solution) was funded by the Government of Canada through the CRTI (Chemical, Biological, Radiological-Nuclear, and Explosives Research & Technology Initiative) with the objective of reducing the weight of body armour used in IED protection by 25%. The feasibility of reducing armour weight by the integration of carbon nanotubes (CNTs) to either new material or currently used materials for IED application was explored.

1.2 Fibre with high ballistic performance

The performance of textile body armour is evaluated by $V_{50}$, which is the velocity at which impacting projectiles are expected to defeat a system 50% of the time. Soft textile ballistic armour dissipates the impact energy by wave propagating along the fibres. The relationship between material properties and armour performance has been studied by many researchers in
the past thirty years. Several analytical models and semi-analytical models have been developed that could effectively simulate the penetration process and predict ballistic performance. In the 1990s, Cunniff [2] proposed a set of simple and effective parameters to provide critical guidance to fibre developers in order to optimize textile-based body armour systems as shown in Equation 1.1. Dimensional analysis indicates that the performance index of interest is $U^*$, which is the product of fibre toughness and sonic wave velocity as shown in Equation 1.2. The $U^*$ allows for an estimation of the performance of an armour system based solely on the quasi-static fibre mechanical properties [3].

$$\Phi \left( \frac{V_{50}}{(U^*)^{1/3}}, \frac{A_d A_p}{m_p} \right) = 0$$

Equation 1.1

Where:

$U^*$ - Fibre ballistic performance index

$A_d$ - System areal density

$A_p$ - Projectile presented area

$m_p$ - Projectile mass

$$U^* = \frac{\sigma \varepsilon}{2 \rho \sqrt{\rho}}$$

Equation 1.2

Where:

$\sigma$ – Fibre tensile strength

$E$ - Fibre Young’s modulus

$\varepsilon$ - Fibre tensile strain

$\rho$ - Fibre density
As shown in Equation 1.2, \( U^* \) is directly proportional to fibre tensile strength, strain, and Young’s modulus, and inversely proportional to fibre density. Thus, fibres with high modulus, strength and strain are preferred for producing armour with better performance. The two most widely used high performance fibres that possess high enough tensile properties to protect a soldier from ballistic impact are para-aramid fibres such as Kevlar® and UHMWPE fibres such as Spectra®. Typical tensile properties and the ballistic performance index \( (U^*)^{(1/3)} \) of these two fibres are listed in Table 1.1.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Strength (( \sigma )) (GPa)</th>
<th>Failure Strain (( \varepsilon )) (%)</th>
<th>Modulus (E) (GPa)</th>
<th>( U^*(1/3) ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar®KM2</td>
<td>3.40</td>
<td>3.55</td>
<td>82.6</td>
<td>682</td>
</tr>
<tr>
<td>Spectra® 1000</td>
<td>2.57</td>
<td>3.57</td>
<td>120</td>
<td>801</td>
</tr>
</tbody>
</table>

\( V_{50} \) velocity of armour made of Spectra® 1000 fibre with various areal densities were tested as shown in Figure 1.1 and the \( V_{50} \) velocities of armour with other areal densities are approximated with a regression fit to the data. From the fitting curve, the dimensionless parameter \( 100A_d*A_p/m_p \) needed for armour made of Spectra 1000® to obtain a \( V_{50} \) of 550 m/s, which is a typical value for high performance personal armour can be obtained. To reduce armour weight by 25%, the parameter \( 100A_d*A_p/m_p \) will need to be 25% lower than the value for armour made of Spectra 1000®. By calculating the ratio between the \( 100A_d*A_p/m_p \) of the two armour system, the \( U^*(1/3) \) of high performance fibre needed to reach the goal of reduce armour weight by 25% while maintaining \( V_{50} \) of 550 m/s can be calculated according to Cunniff® model.
1.3 Unavailability of stronger and tougher fibres

The mechanical properties of high performance fibres increased remarkably from the 1940s to the 1980s with the invention of Nylon®, para-aramid fibre such as Kevlar®, and UHMWPE fibre such as Spectra® through continuing improvement in the spinning process. However, it seems that the fibres’ properties have reached a plateau after years of development. In the last three decades, no significant improvement in fibre mechanical properties has been made [6]. In applications such as body armours, where a high specific Young’s modulus and strength is critical, there is a desperate need to reduce weight by developing stronger and tougher fibre.
1.4 Development of stronger fibre

Although, the properties of these high modulus, high strength fibres are still far behind the theoretical value, few significant breakthroughs in fibre properties have been made in recent years. One of the most promising newly developed high performance fibres is M-5, which has a similar chemical structure to Kevlar® but modulus and tensile strength as high as 310 GPa and 5.8 GPa, respectively [3]. However, the fibre has been unavailable in a pre-commercialized status until now. From previous experience, it took twenty to thirty years for the commercialization of both Kevlar® fibre and Spectra® fibre. Thus, it is expected that M-5 fibre will not be available on the market in the foreseeable future.

Besides developing new high performance fibre, using strong reinforcements to produce composite fibre is another approach for obtaining fibre with improved mechanical properties. In recent years, carbon nanotubes (CNTs) with excellent mechanical properties have attracted the attention of researchers for reinforcement in polymer composite.

Mechanical properties of CNTs have been determined by theoretical calculation and experimental measurements. Large variations in the reported mechanical properties of CNTs have been found due to different production processes and various testing methods. However, it is generally accepted that CNTs have tensile strength of ~300 GPa, Young's modulus ~1000 GPa, and tensile strain as high as ~30% [7]. Because of their superior mechanical properties, CNTs have been considered as ideal reinforcement fillers and are of great interest in ballistic armour application.

In the past twenty years, various researches have focused on using CNTs to reinforce polymer fibres, such as Nylon-6® [9-16], polyethylene [17-27], and polyacrylonitrile(PAN) [28-32]. Significant improvements in the mechanical properties of these polymeric fibres have been
observed. For example, by adding 1 wt% single wall carbon nanotube (SWCNT), carbonized SWCNT/PAN fibers exhibited 64% higher tensile strength and 49% higher tensile modulus than the carbonized control PAN fibre [8]. However, it has been found that most of these researches focused on commodity fibres, which have tensile strength lower than 1 GPa, which is far lower than high performance fibres such as Kevlar® and Spectra®, which have strength of around 3 GPa [35].

In order to develop fibre with a higher $U^{*(1/3)}$ which will lead to a 25% weight reduction in ballistic armour, it is of great interest to focus on incorporating CNTs into high performance fibres. As one of the most widely used high performance fibres in body armour application, it is thus of great interest to investigate the feasibility of producing CNT reinforced UHMWPE fibre with improved mechanical properties.
Chapter 2- Scope of this study

Although a fair amount of research has been carried out on reinforcing polymeric fibre with CNTs, very few studies focused on using CNTs to reinforce high performance fibres, such as UHMWPE fibre. The aim and scope of this thesis is to explore the feasibility of producing UHMWPE fibre with improved mechanical properties by utilizing the extraordinary mechanical properties of CNTs.

Compared to commodity fibres, which consisted of partially aligned molecules, UHMWPE fibre with highly aligned molecules has a much different macro-molecular structure. In order to obtain such a structure, UHMWPE fibre is produced through a unique gel spinning process in which a low-concentration polymer solution in gel form is used as spinning dope. Thus, a systematic study on the effect of spinning conditions on fibre properties is necessary.

Besides the unique spinning process, one of the obstacles in processing CNT-reinforced UHMWPE fibre is obtaining a uniform dispersion of CNTs in the polymer matrix. However, the dispersion of CNT can be very challenging due to the high viscosity and non-polarity of its solvent. A thorough study on improving CNT dispersion in UHMWPE is critical for producing CNT-reinforced UHMWPE fibre with improved mechanical properties.

Compatibility between CNT and the polymer matrix is the other important factor affecting reinforcing efficiency. Owing to their inert nature, the interaction between CNTs and UHMWPE molecules is via Van der Waals forces and a hydrogen bond, which leads to a weak interfacial adhesion. In order to improve the CNT’s reinforcing efficiency, the chemical functionalization of CNT will be investigated.
2.1 Scope of the research

The organization of the research is listed below:

(1) Determine effect of spinning conditions on gel spun UHMWPE fibre properties and morphology

(2) Study dispersion of pristine CNTs in mineral oil and the feasibility of reinforcing UHMWPE fibre by pristine CNTs

(3) Seek improvement in CNT dispersion and reinforcing efficiency in UHMWPE through functionalization by a coupling agent

(4) Seek improvement in compatibility between CNTs and UHMWPE through polymer grafting on the surface of CNTs

2.2 Organization of the dissertation

This study starts with investigating the effect of the spinning condition on gel spun fibre properties, and then analyzing the feasibility of using pristine CNTs to reinforce UHMWPE fibres. Two chemical methods—including using a coupling agent and polymer grafting to functionalize CNTs—were utilized with the purpose of improving CNT dispersion in UHMWPE and the load transfer on the CNT and UHMWPE interface. Various methods were used to characterize the degree of dispersion of CNTs, the functionalization on the surface of CNTs, and the tensile properties, as well as the morphology of composite fibres. A summary of the element of this study is shown in Figure 2.1.
Chapter 2: Scope of This Study

Task 1---Optimize spinning process by studying the influence of various spinning parameters on fibre morphology and properties

Task 2---Investigate the feasibility of reinforcing UHMWPE fibre using pristine MWCNTs methods by different mechanical methods

Task 3---Study the effect of coupling agent functionalization on MWCNT dispersion and the reinforcing effect on UHMWPE fibre

Task 4---Improve compatibility and load transfer on the interface between MWCNT and UHMWPE by polymer grafting.

Functionalization of CNTs or use pristine CNTs directly.

Dispersion of MWCNT in mineral oil

(1) Gel preparation
(2) Spinning
(3) Extraction
(4) Post drawing

Characterization of UHMWPE fibre: tensile test, SEM, TEM

Characterization of CNTs by TEM, FTIR, XPS and TGA, etc.

Figure 2.1 Flow chart sequentially showing the various tasks conducted in this study
The thesis is organized into nine chapters. Chapters 1 and 2 provide an introduction of the background and aim of the study. The literature on UHMWPE fibre, CNT-reinforced polymeric fibres, and especially CNT-reinforced UHMWPE fibres are reviewed in Chapter 3. In Chapter 4, the details of the materials, process, and characterization methods are described. The investigation of the effects of various spinning conditions and optimization of the gel-spun fibre are discussed in Chapter 5. In Chapter 6, the possibility of using pristine CNTs to reinforce UHMWPE fibre is investigated. Several mechanical methods (including ultra-sonication, ball milling, and micro-fluidization) were applied to assist dispersion of CNTs in UHMWPE. In Chapter 7, the CNTs were functionalized with a titanium derived coupling agent and the mechanical properties and morphology of formed CNT/UHMWPE composite fibre were characterized. In Chapter 8, the preparation of polyethylene grafted CNTs and morphology and tensile properties of the composite fibre are shown. The reinforcing mechanism is revealed and the reinforcement efficiency is calculated based on the ‘rule of mixture’. Finally, Chapter 9 draws general conclusions and gives suggestions for future research.

2.3 Significance of the study

In this study, the concept of CNT-reinforced UHMWPE is demonstrated with the goal of producing fibre with improved ballistic performance index \( U^{(1/3)} \). UHMWPE fibre is one of the most widely used high performance fibres in body armour where high tensile properties and low weight is critical. Successful demonstration of the reinforcing concept, the CNT/UHMWPE fibre will lead the mechanical properties of high performance fibre to a new level. The CNT/UHMWPE fibre will significantly reduce the body armour's weight while maintaining a high level of ballistic performance, thus enforcing the development of light weight armour for IED protection as well as a wide range of impact protection products for the civilian market.
Chapter 3- Literature review

3.1 General review

Different from the traditional commodity textile fibres, high performance fibres are engineered for specific applications that require exceptional mechanical properties, heat resistance, or chemical resistance [35]. For example, fibres with ultra-high strength, stiffness such as carbon fibre, para-aramid fibre, and ultra high molecular weight polyethylene (UHMWPE) fibre have been developed since the 1970s and widely used in various applications including transportation, aerospace, protective clothing, marine (ropes and sails), automobile and others [36-40].

Compared to other strong materials, high performance fibres such as carbon fibre, para-aramid fibre and UHMWPE fibre have much higher specific strength and modulus due to their low density, as shown in Figure 3.1. Due to their relatively low density and high specific strength and modulus, high performance fibres find applications in areas where weight is critical, such as advanced composite material in airplanes and ballistic armours, etc. The usage of high performance fibres in these areas greatly reduces the weight of these products and improves their performance. One good example of reducing product weight using high performance fibre is in the area of life protection, such as ballistic body armour, vehicle and property protection panels.
3.2 Theory of high strength fibre

These high performance fibres are made from various polymer materials and spinning methods. However, all of these high performance fibres feature one unique structure, which is a highly oriented and largely extended molecular chain structure. Figure 3. 2 shows a comparison of polymer chain orientation between injected molded polymer material, textile grade fibre, industrial grade fibre and high performance fibre. Compared to injection molded polymer materials, which consist of randomly distributed molecular chains, polymer chains in fibre structure usually show a certain level of orientation, especially for high performance fibre in which molecules are perfectly aligned. Orientation offers great advantages for increasing the strength and stiffness because tensile strength and modulus along fibre direction are controlled
by the intrinsic strength of the carbon-carbon bond in polymer chains and the cross sectional area of molecular chains. Thus, the strength and modulus of fibre consisting of polymer molecules that are stretched and orientated in the direction of the fibre axis will be much higher than conventional fibre, which is made of partially aligned polymer chains [41-45].

<table>
<thead>
<tr>
<th>Form</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection molded</td>
<td>0.08</td>
<td>2.5</td>
<td>Random</td>
</tr>
<tr>
<td>Textile-grade fibre</td>
<td>0.43</td>
<td>2.5</td>
<td>Medium</td>
</tr>
<tr>
<td>Industrial-grade fibre</td>
<td>0.92</td>
<td>4.5</td>
<td>High</td>
</tr>
<tr>
<td>High performance fibre</td>
<td>3.50</td>
<td>186.0</td>
<td>Near Perfect</td>
</tr>
</tbody>
</table>

Figure 3. 2 Molecular structure of different types of fibre [35]

### 3.3 Spinning of high performance fibres

During the development of high performance fibres, questions such as "How strong can polymer fibres be and how can they be produced?” were often raised. Research has been carried out to investigate the structure required to obtain high strength and high modulus. The theoretical strength and modulus of polymeric fibre is calculated as 20-30 GPa and 200-400 GPa by various methods [46-48]. However, such an idealized arrangement of macromolecules cannot be obtained since the achievement of a perfect crystalline structure is impeded by the presence of chain ends, entanglements, and by the tendency of polymers to undergo folding during crystallization. As a result, the mechanical properties of experimental fibres are much lower than theoretical limits. A comparison of theoretical and achieved properties of various fibres is shown in Table 3.1. As can be seen, the achieved fibre properties are far lower than theoretical values; in particular, tensile strength is only about 1/10 of the theoretical value.
Table 3.1 Theoretical and achieved tensile properties of polymeric fibres [35]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Strength (Gpa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Commercial</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>32</td>
<td>3.6</td>
</tr>
<tr>
<td>Aramid</td>
<td>30</td>
<td>3.3</td>
</tr>
<tr>
<td>PA-6</td>
<td>32</td>
<td>0.9</td>
</tr>
<tr>
<td>PES</td>
<td>28</td>
<td>1.1</td>
</tr>
<tr>
<td>PP</td>
<td>18</td>
<td>0.6</td>
</tr>
</tbody>
</table>

In order to obtain a polymeric fibre with a highly extended molecular chain and high orientation, various methods have been investigated by scientists, including liquid crystalline spinning of rigid rod polymer and super drawing of flexible linear polymer, etc.

3.3.1 Liquid crystalline spinning of rigid rod polymer

Liquid crystalline spinning was invented in the early 1970s with the development of an aramid fibre by Dupont® [49]. Aramid fibres are made of polymers with 'rigid rod'-like molecules. Because the molecules are rigid, as the concentration of polymer increases, a saturation level of these rigid rod-like molecules is attained. Continual increase of polymer concentration to a certain level will lead to a parallel arrangement of these molecules, which is termed 'nematic'. The nematic liquid crystalline solution, which consists of domains in which polymer chains are oriented in the direction of spinning, will be extruded through a spinneret. The shear-flow field existing inside the spinneret will cause the rigid molecules to align. After spinning, an external force induced by an elongational flow will be applied on the spin line to
further orientate polymer chains in the as-spun fibre. A schematic illustration of the spinning process is shown in Figure 3.3.

![Schematic of liquid crystalline spinning process](image)

**Figure 3.3 Liquid crystalline spinning process [35]**

The polymer used in liquid crystalline spinning is prepared by the reaction between an amine group and a carboxylic acid halide group. Simple AB homopolymers can be obtained through the reaction as shown in Equation 3.1 [49]:

\[
nNH_2\text{-Ar-COCl} \rightarrow -(NH\text{-Ar-CO})_n + nHCl \quad \text{Equation 3.1}
\]

Kevlar® is made of p-phenylene terephthalamides (PPTA), which are the simplest form of the AABB aromatic polymer and are usually synthesised via a low-temperature polycondensation reaction based on p-phenylene diamine (PPD) and terephthaloyl chloride (TCL), with a structure as shown in Figure 3.4.
3.3.2 Super drawing of polymer with flexible molecular chain

The high mechanical properties of Kevlar® fibre are attributed to its unique rigid rod-like molecular composition, which could be aligned during the spinning process. Most polymer fibres are composed of flexible molecules that usually show partial or random orientation, even after post-drawing, as shown in Figure 3. 5 [50, 51]. It is of great interest to develop a method that could align the flexible polymer chains.

Figure 3. 4 Molecular structure of p-phenylene terephalamides (PPTA) [49]

Figure 3. 5 Polymer chain alignment during spinning [35]
To improve molecular orientation, fibres are post-drawn after extrusion. The draw ratio is used to determine the degree of stretching during the orientation of a fibre or filament, expressed as the ratio of the cross-sectional area of the undrawn material to that of the drawn material. In the conventional melt spinning process, the post-draw ratio is usually only around 5, due to the severe molecular entanglements. The structure of the polymeric fibre from conventional spinning methods was found to consist of the complex structure of the coexistence of the crystal region and the amorphous region, as shown in Figure 3. 6. It has been widely accepted that in order to produce high strength and high modulus fibre from polymers with flexible molecular chains, a much higher post-draw ratio is necessary. In order to reach a high post-draw ratio, polymers with linear molecular structure and fewer branches are favoured.

![Molecular model of polymeric fibre](image)

**Figure 3. 6 Molecular model of polymeric fibre [35]**

In the 1980s, DSM® researchers started the super drawing (draw ratio>30) of polyethylene fibre, which consists of long flexible molecular chains [52-54]. Its molecular chain is connected by a strong carbon-carbon covalent bond which has been estimated to have a theoretical strength of 20-30 GPa and modulus 200-300 GPa [55-59]. However, the interaction between the molecular chains is via the weak van der Waals force. In order to transfer the load
between molecular chains through Van der Waals forces, ultra-long molecular chains with a high overlap length are required. Thus, researchers focused on spinning polyethylene with an average molecular weight of one million or more, which is known as ultra-high molecular weight polyethylene.

It is known that polymer viscosity increases with polymer molecular weight. The Mark–Houwink equations can be used to relate the intrinsic viscosity of polymer to its average molecular weight as indicated in Equation 3.2. A critical molecular weight, $M_c$, is defined as the molecular weight above which chain entanglements occur in a polymer melt. In a polymer melt, when molecular weight is lower than $M_c$, zero shear melt viscosity, $\eta_0$, is roughly proportional to molecular weight. At molecular weights above $M_c$, $\eta_0$ increases with molecular weight to the power of 3.4.

\[
\begin{align*}
M_w < M_c & \quad \eta_0 = K_1 M \\
M_w > M_c & \quad \eta_0 = K_2 M^{3.4}
\end{align*}
\]

Where:

$K$ and $a$ are empirically determined constants

$M_w$ - molecular weight of the polymer

$M_c$ - critical molecular weight

UHMWPE with molecular weight around 3,000,000 to 6,000,000 shows melt viscosity as high as $10^8$ Pa $\cdot$ s and a melt flow rate (MFR) close to 0 when conventional testing methods were employed. A modified testing method to determine the elongational stress instead of MFR was developed which tests the stress required to elongate the testing polymer by 600% in an
elongation time of 10 minutes. The elongational stress values determined for fibre grade UHMWPE resin is around 0.7 MPa [60].

3.4 Techniques to produce UHMWPE fibre

Considerable research has been conducted to produce high modulus, high strength fibre using polyethylene with ultra-high molecular weight. Various methods, including solid state extrusion, surface crystal growth and gel spinning were developed.

3.4.1 Solid state extrusion

In solid state extrusion, UHMWPE melt has to be extruded through a spinneret under pressures as high as 0.2- 0.3GPa because of its high melt viscosity [61]. The polymer chains in as-spun fibre will be aligned along the fibre axis during the post-drawing process. Severe polymer chain entanglements due to the extremly high molecular weight have been observed in the fibre spun from solid state extrusion process and the fibre's tensile strength is only 1.94 GPa [62-63]. Besides the low fibre tensile properties, the stringent requirements for spinning equipment due to the high pressure needed during the spinning process also limited the application of the solid state extrusion process in large scale production.

3.4.2 Surface growth

The surface growth method was developed by Zwijneburg and A.J. Pennings in the late 1970s in which UHMWPE fibres were prepared by flow-induced crystallization in a Couette apparatus [64]. In order to orient the molecules, a drum rotates in a cylindrical bath of a polymer solution as shown in Figure 3. 7. Diluted UHMWPE solution with concentration as low as 0.5wt% is used to reduce the number of polymer chain ends and thus the chain entanglement. With the rotation of the roller insides, a thin layer of UHMWPE molecules is adsorbed on the
surface of the rotor. Crystal seeds are then added into the solution and longitudinal polyethylene crystals start to grow from the macromolecules in close contact on the surface of the rotor. Since fibres are pulled out at the same speed as the crystal growth and in the opposite direction of the rotation of the roller, the growing crystal and the rotor surface experiences a continuous strain which prevents the polymer chains from returning to the coiled conformation.

![Diagram of Coutte flow apparatus for producing an oriented UHMWPE fibre](image)

Figure 3. 7 Coutte flow apparatus for producing an oriented UHMWPE fibre [65]

The formed UHMWPE fibres were found to have a shish kebab structure, which is a typical morphology for high polymer weight polymers formed under a force that is often via a flow field, as shown in Figure 3. 8. The shish structure, which appears as the shaft part of the polymer, is crystallized from extended polymer chains. The shish structure acts as a nucleating template for the coiled chains to form kebab structures. Fibre obtained from this process has tensile strength and modulus as high as 5 GPa and 150 GPa respectively [66]. The major
disadvantage of the surface growth process is that, until now, the production rate of the longitudinal crystals is far below commercially viable speeds.

Figure 3. 8 Shish kebab structure of UHMWPE fibre [67]

3.4.3 Gel spinning/drawing

In order to reduce the entanglements of UHMWPE molecular chains and thus obtain a higher post-draw ratio, a new spinning process named gel spinning was invented by Smith in the late 1970s [68]. In this new process, diluted UHMWPE solution in gel form is used as spinning dope, instead of the polymer melt used in solid state extrusion. The main steps in the gel spinning process include: polymer solution preparation, spinning of the solution, coagulation, removal of the remaining solvent in the fibre, and super-drawing the formed fibre. After super-drawing at a draw ratio of over 100, fibres with a high level of macromolecular chain orientation, high crystallinity (>90%) and high tensile properties (3.0 GPa in tensile strength, 90 GPa in Young’s modulus) can be attained [68]. The gel spinning process is shown in Figure 3. 9.
In laboratory, UHMWPE fibres with tensile strength and Young’s modulus up to 7.0 GPa and 200 GPa, respectively, have been produced [69]. UHMWPE gel spinning has received considerable attention since the 1980s. The effect of processing parameters such as polymer concentrations [70], winding speed [54] and the post-drawing process [53] on the properties and structure of UHMWPE fibres has been widely studied. Jian [71] studied the effect of temperature on the viscosity of UHMWPE gel and found that when the temperature reaches 120°C-140°C, there is a tremendous increase in shear viscosities of UHMWPE gel solutions and the shear viscosity values approach the maximum at 140°C. Yeh [72] studied the influence of draw ratios of gel-spun UHMWPE fibres on resultant morphologies and tensile properties and found that the crystal structure of UHMWPE fibre changed from the constrained orthorhombic into hexagonal crystals during post-drawing. The melt temperature of the fibre increased to 148–154°C, which is the melting of the hexagonal crystals during post-drawing.

As-spun UHMWPE fibres contain a high content of solvent which needs to be removed through solvent extraction before post-drawing. Xiao [73] found that phase separation of UHMWPE and mineral oil is most significant in the first hour and reaches equilibrium state after
about 48 hours. The critical extraction time and the optimum bath ratios of extraction agent to gel fibres are 2 min and 10 mL/g, respectively. It was found that fibre spun from high concentration solution has much denser morphological structure, as shown in Figure 3.10, which leads to lower maximum draw ratio and tensile properties.

![Figure 3.10 (a)](image1)
![Figure 3.10 (b)](image2)

Figure 3.10 As-spun UHMWPE fibre spun from various polymer concentrations [7]

(a)8%, (b)16%

The UHMWPE fibre produced by the gel spinning process was first commercialized by DSM® with the trade name Dyneema® in the 1990s. There are currently two main manufacturers for UHMWPE fibre besides DSM®: Honeywell® in the US with trade name Spectra®, and Toyobo® in Japan with trade name Dyneema®.

3.5 Molecular model of UHMWPE fibre

Based on experimental observations, it has been observed that UHMWPE fibres obtained from high ratio post-drawing process exhibit a microfibrillar structure. UHMWPE fibre is made of fibrils with diameters around 100 nanometer (nm), which themselves are composed of
microfibrils 10nm in size. Microfibrils consist of alternating crystalline and non-crystalline zones, as shown in Figure 3.11.

![Fibrilar model of UHMWPE fibre](image)

**Figure 3.11** Fibrilar model of UHMWPE fibre [74]

Peterlin [75] pointed out that fibre tensile properties, such as modulus and tensile strength, are not the consequence of the crystal lattice orientation but of the connection of the crystals by a great many taut tie molecules that bridge the amorphous layers which alternate with the crystals in the axial direction of the fibrous material, as shown in Figure 3.12. Peterlin also argued that the number of taut tie molecules increases during the post-drawing process and, as such, the fibre modulus increases. Penning [76] verified Peterlin’s model through experimental results that showed that fibre tensile strength is determined by the fraction of load carrying chains in the disordered domains. The elongation at break and modulus are largely determined by the ratio of disordered domain length to crystal block length.
3.6 Polymeric composite fibre reinforced by carbon nanotube

It is well known that stronger material can be obtained by incorporating reinforcements into the matrix material. In order to produce stronger fibre, researchers are constantly looking for proper reinforcement materials. Carbon nanotubes (CNT) have been thought of as one of the most promising reinforcement materials for polymer materials due to their unique properties.

3.6.1 Carbon nanotube

CNTs were discovered by Ijima [77] in 1991. The structure of CNTs can be thought of as a rolled-up graphene sheet. The strong sp$^2$ in-plane bonds of the CNTs bind the atoms in the plane and results in the high stiffness and strength of CNTs. Based on their molecular structure, theoretical analysis predicts that CNTs should possess extremely high tensile properties. There are two main types of CNTs: multi-walled (MWCNTs) and single-walled (SWCNTs), as shown in Figure 3.13. MWCNTs consist of several layers of graphite shell, which are in a co-axial cylindrical shape, with an adjacent shell separation of approximately 0.36 nm. SWCNTs consist of a single graphite sheet wrapped into a cylindrical tube with a diameter of about 1.2 nm [78].
Because of their extremely small size, it is difficult to directly measure the mechanical properties of CNTs. In recent years, with the help of scanning electron microscopy (SEM), atomic force microscopy (AFM) and the scanning tunneling microscope (STM), researchers have successfully measured the strength, Young’s modulus and other properties of CNTs, as shown in. As is clear from Table 3. 2, CNT's Young’s modulus is in the range of 800-1300 GPa. Strength is more difficult to measure than modulus, thus there are few published data for CNT strength. Yu [7] used AFM and SEM to measure the strength of MWCNTs and the result is around 63 GPa.

Table 3. 2 Mechanical properties of carbon nanotubes, measured using SPM

<table>
<thead>
<tr>
<th>Young’s modulus (GPa)</th>
<th>Nanotube type</th>
<th>Deformation method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300±600</td>
<td>MWCNT</td>
<td>Lateral bending</td>
<td>[80]</td>
</tr>
<tr>
<td>1000±600</td>
<td>SWCNT</td>
<td>Normal bending</td>
<td>[81] [82]</td>
</tr>
<tr>
<td>870±400</td>
<td>MWCNT</td>
<td>Normal bending</td>
<td>[81]</td>
</tr>
</tbody>
</table>
3.6.2 Carbon nanotube fibre and yarn

Motivated by the exciting properties of CNTs, there are intensive efforts to convert CNTs directly into linear assemblies [83-93]. However, CNTs do not melt and they are not soluble in organic or aqueous solvents. Spinning of CNTs using traditional spinning methods has been proved to be challenging. In the past few years, pure CNT fibres have been spun by four general types of spinning processes: coagulation, solid-state, liquid crystalline and gas state.

(1) Coagulation spinning

In coagulation spinning, CNTs are homogeneously dispersed in water by sonication with the help of sodium dodecylsulphate (SDS) as a surfactant. The aqueous dispersion of CNTs is injected into a poly-vinyl alcohol (PVA) flowing bath using a set-up shown in Figure 3. 14. The coagulated fibre contains PVA in the matrix which will pass through a series of washing stages to remove it. CNT filaments produced from this method show tensile strength over 1 GPa and modulus 9-15 GPa [94].

![Schematics of the experimental set-up for coagulation spinning](image)

Figure 3. 14 Schematics of the experimental set-up for coagulation spinning [95]
(2) Solid-state spinning

In the solid state spinning process, CNTs act as the constituent fibre in the yarn, in a similar way as conventional fibres such as cotton and wool [89, 90, 96, 97]. CNTs are drawn continuously from CNT forests. The CNT “trees” in the forest are over 50,000 times longer than their diameter. An array of vertically aligned CNTs is shown in Figure 3.15.

![Carbon nanotube yarn formed from solid state spinning](image)

Figure 3.15 Carbon nanotube yarn formed from solid state spinning [89]

(3) Liquid crystalline spinning

Smalley and other researchers [98-101] found out that CNTs have similar properties to the rigid rod molecules, such as poly (p-phenyleneterephthalamide) (PPTA), which can form a liquid crystalline solution in sulfuric acid above a certain concentration. Thus, a similar process to produce aramid fibres was used to produce CNT filaments (shown in Figure 3.16). However, the tensile properties of CNT filaments made from this process are far lower than expected. For example, in Erison’s work, the tensile strength and modulus of the formed CNT yarn is only 0.116 GPa and 120 GPa, respectively [101].
(4) Gas state spinning

During CNT synthesis through chemical vapor deposition, CNTs become entangled in the gas-phase due to van der Waals forces. The entangled CNTs form black smoke and are called “aero gel” which can be continuously drawn out of the reactor and wound as film or twisted to form a fibre. The strength and modulus of the CNT fibres produced by this method are around 1 GPa and 50–100 GPa, respectively [103, 104].

While these processes are promising, the properties of individual CNTs are far from being fully realized in these CNT-based fibres. For example, the highest strength achieved with any of these spinning methods is around 1 GPa, much lower than the strength of individual SWCNTs which have been measured up to 60 GPa [7]. This could be partly attributed to the lack of sufficient load transfer among individual nanotubes. The load transfer among CNTs is through van der Waals interaction which is much weaker compared with the sp² in-plane bonds, thus CNTs tend to slip under tension before reaching the ultimate strength of individual tube. To facilitate stress transfer, the concept of CNT co-extrusion/co-spinning with a polymer to form
composite fibres was conceived. A series of CNT-reinforced polymer composite fibres have been produced.

3.6.3 Carbon nanotube reinforced polymeric composite fibre

The extremely small size and exceptional mechanical properties of CNTs make them ideal candidates for tailoring mechanical properties of polymer materials. Significant improvements in mechanical properties of the polymer composite have been observed with the addition of a small CNT weight percentage, compared to their unreinforced counterparts [28, 105-107]. In addition, from a cost standpoint, the CNT-reinforced polymer composite is an attractive way to make commercially viable CNT-based materials.

A number of studies have focused on producing CNT/polymer composite fibres by melt spinning. Chen et al. [108] spun MWCNT-reinforced thermoplastic polyurethane (TPU) elastomeric fibre using a twin crew extruder. The resulted MWCNT/TPU composite fibres showed a significant increase in mechanical properties. The fibre's Young’s modulus increased from 49.6 MPa of the unfilled TPU fibre to 135.1 MPa of fibre with 17.7% CNT. Andrews et al. [109] prepared SWCNT-reinforced carbon fibre by adding purified SWCNTs into pitch fibre and removing the solvent after sonication. The fibre was melt spun, drawn, and subjected to heat treatment in air and nitrogen. Carbon fibres with 5wt% of SWCNT showed a 90% increase in tensile strength and 150% increase in Young’s modulus. Sreekumar et al. [110] produced polyacrylonitrile (PAN)/SWCNT composite fibres. Fibres with 10wt% SWCNTs showed 43.5% and 105% higher tensile strength and Young’s modulus, respectively, compared to the properties of the pure PAN fibres.
3.6.4 Carbon nanotube reinforced UHMWPE fibre

With its low density and excellent mechanical properties, UHMWPE fibre has become one of the most widely used high performance fibres. Research has been conducted to reinforce UHMWPE fibre with CNTs. The high viscosity of spinning dope makes reinforcing UHMWPE with CNTs very challenging. In order to obtain a significant reinforcing effect, a good dispersion of CNTs in the matrix is necessary. Zhang [111] developed a new method to improve CNT dispersion in UHMWPE by spraying an aqueous solution of SWCNTs onto fine UHMWPE powder. These SWCNTs adhered on the surface of the UHMWPE and the CNT-coated UHMWPE powders were used in compression molding to make CNT/UHMWPE film. Gao [112] further developed Zhang’s method by using alcohol as a solvent to disperse the CNTs. After alcohol evaporated, UHMWPE particles covered with a layer of CNTs were obtained. Subsequently, the powders were compression molded into composite board. Test results indicated that the MWCNTs/UHMWPE composites formed a 2-dimension conductive network at a very low percolation of 0.072 vol%. Martinez [113] incorporated 1, 3 and 5 wt.% pristine MWCNTs into UHMWPE using a ball milling process. The tensile tests showed a 38% increase in the Young’s modulus in the reinforced nano-composites and a small decrease in toughness (5%), as shown in Figure 3.17.
Weston J. Wood [114] developed a paraffin-assisted melt-mixing method for improving carbon nanofibre (CNF) dispersion. A CNT/UHMWPE composite prepared by paraffin oil assisted mixing exhibited much higher wear resistance compared to a composite prepared through a dry mixing process, as shown in Figure 3. 18. Maksimkin [115] used a planetary activator with steel vials filled with steel balls to produce 0.1% and 1% MWCNT/ UHMWPE composite. The mixture was then thermo-pressed and post-drawn to form solid samples. Remarkable 130% and 20% increases in tensile strength and yield strength were obtained, respectively, for UHMWPE by adding 0.1% MWCNT.
Most of the above studies focused on CNT-reinforced UHMWPE composite film or plate. Very limited research focused on reinforcing gel spun UHMWPE fibre using CNTs. This could be because UHMWPE fibre is composed of highly oriented molecules and has very high crystallinity (>90%); the requirement for CNT dispersion in UHMWPE fibre is thus more stringent. However, the studies by Ruan’s group at Hongkong Poytechnic University and by Wang’s group at Donghua University in China were notable. Ruan et al. [24] investigated the feasibility of reinforcing the gel spun UHMWPE with pristine CNT using decahydronaphthalene (decalin) as a solvent. By adding 5wt% MWCNTs, ultra-strong fibres with tensile strength of 4.2 GPa and strain at break of approximately 5% (which corresponds to a 19% increase in tensile strength and 15% increase in ductility) could be produced. Wang et al. [26] used 1% of purified and coupling agent functionalized MWCNTs to reinforce the UHMWPE fibre and found that the strength and modulus of the composite fibre increased by about 9% and 14%, respectively.

Figure 3. 18 Wear rate of CNF/UHMWPE composite [114]
3.7 Carbon nanotube reinforcing mechanism

As various polymer fibres [19-21, 112, 114-120] showed significant improvement after CNT reinforcing, it is of great interest to investigate the reinforcing mechanism of these CNT composites.

Ye and Ko [121] pointed out that enhancement in fibre tensile properties arises when the oriented CNTs bridge crazes and the subsequent cracks that propagate normal to the applied uniaxial stress, which is schematically represented in Figure 3.19. By partly replacing the crazing fibrils, CNTs strengthen the weakest part of the fibre. On the other hand, randomly oriented CNTs will allow unimpeded crack propagation across regions that are similar to a neat polymer matrix, thereby the reinforcement of randomly oriented CNTs will not be as high as aligned CNTs. Compared to bulk material, CNTs exhibit much better alignment in polymer fibre due to the post-drawing process. As shown in Figure 3. 20, CNTs align perfectly along fibre axis.

![Diagram of crazing and rupture mechanism](image)

Figure 3. 19 Crazing and rupture of a CNT/polymer composite fibre [122]
Homogeneous CNT dispersion throughout the polymer matrix and adequate interfacial bonding is critical for load transfer in CNT–polymer composites. However, it has been found that CNTs are very difficult to properly disperse in organic matrices in their pristine state due to their inert nature. Great efforts have been made to improve CNT dispersion through both mechanical methods and chemical functionalizations.

### 3.8 Functionalization of carbon nanotubes

Many studies have been carried out to develop methods that improve CNT dispersion. Such methods can be divided into two categories: mechanical methods and functionalization methods (which include physical (non-covalent treatment) and chemical (covalent treatment) functionalization). The mechanical dispersion methods include ultrasonication, ball milling, high shear mixing, etc.. While these methods can significantly improve CNT dispersion, they can also fragment the tubes and decrease their aspect ratio. More often, these mechanical methods are applied in combination with chemically functionalized CNTs.
3.8.1 Non-covalent functionalization of CNTs

In non-covalent functionalization, the modified polymer molecular chains are physically bound to the surface of the CNTs by wrapping around the CNTs or adsorbed on the surface. For example, polyvinylpyrrolidone (PVP) is able to wrap around CNTs (as shown in Figure 3. 21) and wrapped CNTs can be easily dispersed in polar solvents like water. In addition to wrapping a polymer onto the CNT surface, using a surfactant is another widely used method to improve CNT dispersion.

![Figure 3. 21 PVP-wrapped CNT [124]](image)

The molecule of a surfactant usually consists of both polar and apolar groups which enable them to be absorbed on the interface between immiscible bulk phases, such as oil and water, air and water, or particles and solution. Surfactants such as sodium dodecylsulfate (SDS), Triton X-100 and sodium dodecylbenzenesulfonate (NaDDBS) have been widely used to improve CNT dispersion in an aqueous solvent [125-135]. These surfactants form micelles on the non-polar CNT surface and result in a greater hydrophilic character of the surface (shown in Figure 3. 22).

The advantage of non-covalent functionalization is that it keeps the original CNT structure intact, thus the mechanical properties do not change. However, the forces between the wrapping molecules and the nanotube surface may be weak and the efficiency of the load transfer may be low. Therefore, non-covalent functionalization is not suitable for some load-bearing applications.
3.8.2 Covalent functionalization of CNTs

In the covalent functionalization method, polymer chains are either “grafting to” or “grafting from” the CNT surface. Grafting long polymer chains onto CNTs can improve their solubility in solvents and increase miscibility in polymer matrices. Because of the higher energy of the covalent bond, a more favourable load transfer between CNTs and the polymer matrix can be obtained through this method. There are two types of polymer grafting functionalization: “grafting to” and “grafting from” [137-146]. “Grafting to” is based on the reaction between the pre-formed polymer molecules and the functional group (such as amino, hydroxyl, epoxy, or a radical group) on the CNT surface. In the “grafting from” method, the polymer grafting is realized by the covalent immobilization of polymer precursors on the CNT surface and subsequent polymerization in the presence of monomeric species. One good example of the “grafting from” process was developed Baskaran et al. [147] who functionalized MWCNTs with 2-Bromo-2-methylpropionyl bromide, as shown in Figure 3.22. The functionalized MWCNTs could then react with methyl methacrylate (MMA) to form the polymethyl methacrylate (PMMA).
grafted MWCNTs with good solubility in tetrahydrofuran (THF) and chloroform (CHCl₃). Similar methods have also been used to graft polystyrene and some other polymers [147].

![Figure 3. 23 Grafting MMA from MWCNTs via living radical polymerization [147]](image)

The “grafting to” method has also been used by many researchers for CNT functionalization. The carboxyl and hydroxyl group can be attached to the CNT tip and surface through a reaction with a strong acid or oxidant. The hydroxyl group on the CNT surface reacts with the amine and alcohol group through an acylation and condensation reaction to form amide or ester bonds through which polymers can be grafted onto CNTs. Because of the diversity of reactions between the hydroxyl group and the polymers, various polymers have been grafted onto CNTs. Haddon [148] used acylated MWCNTs to react with octadecylamine. Yoon [149] grafted polylactic acid (PLA) on acylated MWCNTs and found that the molecular weight of PLA has a significant influence on the coverage of PLLA on the MWCNT surface.

These methods generate surface modifications that are chemically bonded to CNTs. Compared to non-covalent bonding using polymer wrapping or a surfactant, the load transfer through these chemically bonded polymers is much higher [150]. Thus, in the applications where highly reinforced efficiency is required, CNT modification through polymer grafting is favoured.
Chapter 4- Materials and methods

The materials, experimental methods and characterization methods used in this thesis are listed and described in detail in this chapter.

4.1 Materials

The solvents, polymers and other materials used in this research are listed in Table 4.1, Table 4.2 and Table 4.3, respectively. All the materials were used as received unless otherwise stated. Ultra-high molecular weight polyethylene (UHMWPE) from Sigma Aldrich with a molecular weight of $3\sim6 \times 10^6$ was used in all the spinning experiments in the thesis. Mineral oil was used as a solvent to dissolve UHMWPE for all the gel spinning experiments. Xylene was used as an extracting solvent for mineral oil from the as-spun UHMWPE fibre in all extraction processes. Carboxyl functionalized MWCNTs (COOH-MWCNT) with a length around 1µm and a diameter about 8 nm was from Cheaptubes Inc. Ethanol was used as a solvent to disperse MWCNTs during functionalization with a titanium-derived coupling agent. Ethylene diamine was used to react with the carboxyl group functionalized MWCNTs to produce amino functionalized MWCNTs. PE-g-MA with 0.5wt% maleic anhydride content was used as a polymer to be grafted on the surface of MWCNTs. N,N-Dimethylformamide was used to disperse CNTs to prepare samples for scanning microcopy (SEM) and transmission electron microscopy (TEM).
Table 4. 1 Characteristics of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Source</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>Sigma-Aldrich</td>
<td>$M_w=3\times10^6$~$6\times10^6$</td>
</tr>
<tr>
<td>PE-g-MA</td>
<td>Sigma-Aldrich</td>
<td>0.5wt% MA content</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>Fluka</td>
<td>absolute, $\geq$99.5% (GC)</td>
</tr>
</tbody>
</table>

Table 4. 2 Characteristics of solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Source</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Fisher</td>
<td>$&gt;$99.5%</td>
</tr>
<tr>
<td>Mineral oil (light)</td>
<td>Sigma-Aldrich</td>
<td>Cat. No.330779</td>
</tr>
<tr>
<td>Xylene</td>
<td>Sigma-Aldrich</td>
<td>ACS reagent, $\geq$98.5% xylenes</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>Sigma-Aldrich</td>
<td>HPLC, $\geq$99.9% (Sigma-Aldrich)</td>
</tr>
</tbody>
</table>

In order to avoid UHMWPE oxidization at elevated temperatures, 2, 6-di-tert-butyl-4-methylphenol (BHT) was used in this study as an anti-oxidant. A type of titanium-derived coupling agent was used to functionalize the surface of the CNTs.

Table 4. 3 Characteristics of other materials

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Source</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH-MWCNT</td>
<td>Cheaptubes.Inc</td>
<td>95wt%, diameter=5-10nm, length~1µm</td>
</tr>
<tr>
<td>2, 6-di-tert-butyl-4- methylphenol</td>
<td>Sigma Aldrich</td>
<td>$\geq$99.0%</td>
</tr>
<tr>
<td>tri(dioetylpyrophosphoryloxy) isopropyl titanate</td>
<td>Nanjing Shuguang Chemical Plant of China</td>
<td>CAS # 67691-13-8 Product number: NDZ201</td>
</tr>
</tbody>
</table>
4.2 Experiment and characterization

4.2.1 Gel spinning

In this thesis, MWCNTs were functionalized by a coupling agent and a polymer grafted by PE-g-MA with the purpose of improving dispersion and reinforcing efficiency in the UHMWPE. Detailed functionalization processes are described in Chapter 7 and Chapter 8.

(1) CNT dispersion

MWCNTs were dispersed in mineral oil by sonication for about 10 hours using the Branson 2510 bath sonicator. UHMWPE was added to the MWCNT/mineral oil dispersions. The mixtures were sonicated for 1 more hour.

(2) Gel preparation

The UHMWPE/mineral oil mixture or the MWCNT/UHMWPE/mineral oil mixtures were heated up in an oil bath from room temperature to 100°C at 5°C/min, and then from 100°C to 110°C at 1°C/min under constant stirring and nitrogen protection using a set-up as shown in Figure 4. 1. At 110°C, the UHMWPE started swelling in the mineral oil. Magnetic stirring was stopped when swelling was observed, as shown in Figure 4. 2. The temperature was kept at 110°C for 1 hour. After the UHMWPE fully swelled, the temperature of the oil bath was further increased from 110°C to 160°C with magnetic stirring at 5min/min and kept at 160°C for another 2 hours to form uniform UHMWPE/mineral oil or MWCNT/ UHMWPE/mineral oil gel. The air trapped in the gel was removed by vacuuming it for 24 hours.
(3) Spinning

A laboratory mixing extruder (LME) from Dynisco Co., Ltd. was used for the gel spinning process. The MWCNT/UHMWPE/mineral oil gel was fed into the hopper and the gel passed through an annular zone formed by a rotating screw inside the extruder where the actual melting took place. The temperature in the annular zone was kept at 150°C, 180°C and 210°C, according to the experimental design. As rotation continued, the molten gel driven by shear force flowed to the spinneret, which had a 3 mm diameter. A 10 cm air gap was used between the spinneret and the water bath. The extruded fibres were then solidified in a cold water bath and wound on a take-up roller. The gel spinning set-up is shown in Figure 4. 3.
(4) Extraction

The as-spun fibre containing a high proportion of mineral oil was extracted using xylene. The as-spun UHMWPE fibres were wound on a metal frame to avoid fibre shrinking after extraction. The fibres wound on the metal frame were immersed in 50ml xylene and sonicated 3 times at a duration of 15, 10 and 5 minutes, respectively. Fresh xylene was changed after each extraction run to make sure that all the mineral oil was removed.

(5) Post-drawing

Extracted fibres were post-drawn using a homemade post-drawing system consisting of two rollers and a heated oven, as shown in Figure 4.4. The oven was kept at a desired temperature in the range of 110°C to 140°C with the optimum conditions obtained in Chapter 5. By adjusting the speed of the two rollers, different draw ratios could be applied during the post-drawing process. The draw ratio and temperature used in this study are shown in Figure 4.6.

![Post-drawing process](image)

**Figure 4.4 Post-drawing process**

<table>
<thead>
<tr>
<th>Post drawn condition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draw ratio</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>110°C</td>
<td>120°C</td>
<td>130°C</td>
<td>140°C</td>
</tr>
</tbody>
</table>

**Table 4.4 Post-drawing condition UHMWPE fibre**
4.2.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a method used to determine the elemental composition of a material’s surface. The Perkin Elmer PHI 5600 XPS using the Mg Kα X-ray line of 1253.6 eV excitation energy, 300W, 15 kV was used in this study for characterizing the MWCNT functionalization. The vacuum base pressure was approximately $1 \times 10^{-8}$ Torr. The binding energy of the C$_{1s}$ of graphite, 284.5 eV ($\pm$0.35 eV energy resolution of the spectrometer at the settings employed) was taken as the reference. MWCNT samples were set on indium foil and then placed on the sample holder for analysis in the XPS surveys and multiplex. Prior to individual elemental scans, a survey scan was taken for all the samples in order to detect the elements present. Carbon, oxygen and titanium analysis were carried out on each sample.

4.2.3 Transmission electron microscopy (TEM)

TEM images were taken on a FEI Tecnai G2 electron microscope at 200 KV. A droplet of the MWCNT/dimethylformamide (DMF) dispersion was deposited on a microscopy copper grid covered with a holey silicon dioxide film and the solvent was evaporated in air at room temperature.

4.2.4 Raman spectroscopy

Raman spectroscopy is one of most widely used spectroscopic techniques for analyzing nano-material. It is based on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near-infrared or near-ultraviolet range. The laser light interacts with molecular vibrations and photons of the laser light are absorbed by the sample and then re-emitted. The energy of the laser photons shifts up or down to provide information about vibrational, rotational and other low-frequency transitions in molecules. In this study, a
Renishaw 1000/2000 Raman micro-spectrometer equipped with a 514.5 nm argon ion laser as the excitation source was used for all the analyses. The laser power was reduced to <0.1 mW (50 × objective) to prevent overheating of the fibre sample.

4.2.5 Fourier transform infra-red (FTIR)

In the FTIR test, infrared radiation is passed through a sample and some of it is absorbed by the sample while the other is passed through (transmitted). The resulting IR spectrum creates a molecular fingerprint of the sample with absorption peaks that correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each material is a unique combination of atoms, no two compounds produce exactly the same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. This makes infrared spectroscopy useful for material composition analysis. FTIR spectra of MWCNTs were recorded from 400 cm⁻¹ to 4000 cm⁻¹ with a Perkin Elmer FT-IR spectroscopy instrument by KBr pellets.

4.2.6 Thermogravimetric analysis (TGA)

TGA is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Measurements are primarily used to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can be used to characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. TGA of a functionalized MWCNT sample was performed using a TA Instrument Q500TGA. A 5mg sample was heated at 20°C min⁻¹ from room temperature to 600°C in a dynamic nitrogen atmosphere (flow rate=50ml/min).
4.2.7 Tensile test

The sample for the single fibre tensile test was prepared by placing the fibre on a rectangular paper frame and affixing it with epoxy glue, as shown in Figure 4.5. According to ASTM D3379-75, a gauge length of 25 mm was used for the UHMWPE fibre, which has a tensile strain of 3-4%. After placing the sample on the tensile tester, the paper frame was cut to initiate the testing frame. 25 fibres were tested for each sample and the average strength, modulus, and strain were used for data analysis.

![Figure 4.5 Preparation of single fibre tensile test sample](image)

Single fibre tensile tests were carried out using a KES-G1 tensile testing machine with a 50 Newton load cell. Tests were performed at a crosshead speed of 20 mm/min according to ASTM D3379-75. The breaking load in Newton and time duration in seconds needed for breaking the fibre were recorded. The diameter of the fibre was measured by the average of the three readings from the optical microscopy image. The modulus of the fibre was calculated from the slope of the initial linear section of the stress-strain curve. A typical stress-strain curve of UHMWPE fibre is shown in Figure 4.6.
Figure 4.6 Typical stress-strain curve of UHMWPE fibre
Chapter 5- Optimization of gel spun UHMWPE

5.1 Introduction

The tensile properties of gel spun UHMWPE fibre are influenced by spinning conditions, including polymer concentration, spinline draw ratio (draw ratio between spinneret and winder), and spinning temperature. For example, the viscosity of spinning dope is highly sensitive to spinning solution concentration and extrusion temperature because of the high molecular weight. Besides spinning temperature, winding speed has been found to have a significant effect on the fibre properties as well [151]. The probability of introducing structural defects into the as-spun fibre increases with winding speed. If formed, these defects are difficult to remove during the hot drawing step, thus leading to the production of fibres with poor tensile properties.

In order to investigate the influence of the spinning conditions on the morphology and mechanical properties of gel spun UHMWPE fibres, polymer concentration, spinning temperature, and winding speed were studied systematically using a design of experiment. The aim of this part of the study is to find the optimum spinning condition that could be used in subsequent spinning experiments for this thesis.

5.2 Effect of spinning conditions on morphology and property of UHMWPE fibre

During gel spinning, polymer gel was forced through the spinneret and quenched in a water bath. Winding of the as-spun fibre applied initial drawing to the fibre. A high percentage of solvent exists in as-spun fibres and is removed through solvent extraction. The purpose of these processes is to prepare the fibre with disentangled molecular chains, thus facilitating the
subsequent super-drawing process. During super-drawing (draw ratio $>$100), these disentangled molecular chains were extended and aligned along the fibre axis, thus giving the fibre ultra-high strength and modulus. Throughout the whole gel spinning process, weak polymer gel with randomly oriented polymer chains was transformed to the fibre with high tensile properties. It was expected that the processing parameters would have great influence on the properties of the gel spun fibre. Among various parameters, polymer concentration, spinline draw ratio, and spinning temperature were found to be the three most important factors [152]. In this chapter, the effects of these parameters on the tensile properties and morphology of gel spun UHMWPE were studied systematically according to a design of experiment.

5.2.1 Polymer concentration

Polymer concentration has a significant effect on the density of the molecular chain entanglements contained in the spinning dope. In order to obtain fibres with a highly aligned structure, the optimal polymer concentration should be the concentration at which just enough entanglements exist to maintain spinning and drawing stability. Lower than the optimal polymer concentration, the intermolecular entanglement network cannot sustain the spinline stresses (which leads to constant breakage). In this study, 2wt% UHMWPE/mineral oil was found to be the lowest concentration at which gel spinning could be conducted. Based on this observation, polymer concentration ranging from 2wt% to 5wt% were used for analyzing the effects of polymer concentration on UHMWPE fibre properties.

5.2.2 Spinning temperature

Spinning temperature is one of the most important parameters for the spinning process because it has great influence on the viscosity of the spinning dope. Figure 5.1 shows how the
shape of a spinline of a 1.5% UHMWPE/mineral oil gel changes with increasing temperature. It was found that when the temperature is too high, the viscosity of the spinning dope decreases to such a point that continuous spinning of the fibre cannot be carried out and the spinline will fracture frequently due to the low coherence between the molecules, resulting in serious capillary failure. However, a certain temperature is needed because an increase in temperature will reduce the elongation rate at which molecular scission occurs. Based on published results and preliminary experimental results in our laboratory, three temperature levels (150°C, 180°C and 210°C) were selected for this study.

![Figure 5.1 Viscosity of fibre at various spinning temperatures](image)

(a) 150°C  (b) 180°C  (c) 210°C

5.2.3 Winding speed

Spinline fractures can also happen as a consequence of high winding speed due to high stress from rapid deformation of visco-elastic materials. This high stress can lead to stress-induced crystallization, which in turn increases the elasticity of the extrudate. Based on some preliminary tests, three levels of winding speed levels (5, 10 and 20 feet/min (FPM), which correspond 12.7, 25.4 and 50.8 meter/min, respectively) were selected for this study.
5.2.4 Orthogonal experiment design

To understand the effect of spinning condition on fibre properties and morphology and to find an optimal spinning condition, a 3-factor, 3-three level design of experiment was applied. The factors and levels of the experimental design are shown in Table 5.1. For a complete 3-factor, 3-level factorial experiment design, twenty-seven experiments are required for all possible level combinations. As described in last chapter, the entire gel spinning process includes gel preparation, spinning, extraction, post-drawing, and a tensile test. In order to study the effect of the spinning condition on fibre tensile properties more efficiently, a design of experiment must be considered.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Polymer concentration (wt%)</th>
<th>Spinning temperature (°C)</th>
<th>Winding speed (FPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levels</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>180</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>210</td>
<td>20</td>
</tr>
</tbody>
</table>

Among various design of experiment (DOE) methods, orthogonal experimental design, which is one type of fractional factorial experiment, was chosen for this study due to its efficiency and suitability for the various natures of the factors. Orthogonal experimental design is an optimization method that utilizes orthogonal tables to arrange the experiment for systematically researching various factors and levels. The advantage of using orthogonal design is that only representative tests will be performed according to the orthogonality. As such, it has the capability of sampling a smaller amount but representative set of level combinations. For example, a 3-level, 4-factor optimization will need to test eighty-one combinations. By using orthogonal design according to orthogonal array L9_3_4 (the 3-level, 4-factor design array) as
shown in Table 5.2, only nine representative combinations are necessary. In the L9_3_4 orthogonal matrix, each row represents a designed level and each column represents a factor. In an orthogonal matrix, each level is repeated the same number of times and any combination of two factors is combined with the third factor at three levels, respectively. As shown in Figure 5.2, the experiment points of orthogonal design are evenly distributed among all factors and levels; for example, A_1B_1 has a combination with C_1, C_2 and C_3.

Table 5.2 L9_3_4 Orthogonal experiment design

<table>
<thead>
<tr>
<th>Experiment NO.</th>
<th>Combination</th>
<th>Polymer Concentration</th>
<th>Spinning Temperature</th>
<th>Winding Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A_1B_1C_1</td>
<td>2%</td>
<td>150°C</td>
<td>5FPM</td>
</tr>
<tr>
<td>2</td>
<td>A_1B_2C_2</td>
<td>2%</td>
<td>180°C</td>
<td>10FPM</td>
</tr>
<tr>
<td>3</td>
<td>A_1B_3C_3</td>
<td>2%</td>
<td>210°C</td>
<td>20FPM</td>
</tr>
<tr>
<td>4</td>
<td>A_2B_1C_2</td>
<td>3.5%</td>
<td>150°C</td>
<td>10FPM</td>
</tr>
<tr>
<td>5</td>
<td>A_2B_2C_3</td>
<td>3.5%</td>
<td>180°C</td>
<td>20FPM</td>
</tr>
<tr>
<td>6</td>
<td>A_2B_3C_1</td>
<td>3.5%</td>
<td>210°C</td>
<td>5FPM</td>
</tr>
<tr>
<td>7</td>
<td>A_3B_1C_3</td>
<td>5%</td>
<td>150°C</td>
<td>20FPM</td>
</tr>
<tr>
<td>8</td>
<td>A_3B_3C_1</td>
<td>5%</td>
<td>180°C</td>
<td>5FPM</td>
</tr>
<tr>
<td>9</td>
<td>A_1B_3C_2</td>
<td>5%</td>
<td>210°C</td>
<td>10FPM</td>
</tr>
</tbody>
</table>

Figure 5.2 3-factor, 3-level orthogonal experimental design
5.2.5 Statistical analysis of orthogonal experimental design results

The analysis of variance conducted by an F-test determines if the variance in experimental results is coming from the variance of factors or from experimental error and the significance. If the null hypothesis is true, statistical analysis will show that factor has no significant influence on testing properties. If the null hypothesis is false, then we will reject the null hypothesis and consider that the factor has no significant effect on the testing results.

5.3 Results and discussion

UHMWPE fibres spun from gels with different polymer concentrations and at different spinning conditions were prepared. Tensile properties were tested according to the methods described in Chapter 4. From the tensile test results, it was found that diameter has a significant influence on the tensile strength of gel spun UHMWPE fibre, as shown in Figure 5.3. A similar phenomenon has been observed by many researchers. The earliest study was conducted by Griffith [153] in the 1920s when he tested tensile strength of glass fibres at different diameters, as shown in Figure 5.4. He pointed out that material strength was greatly affected by the size of defects which initiate cracks under tension due to stress concentration. Fibres with a bigger diameter showed lower tensile strength because larger pre-existing cracks could statistically exist in larger samples.
Figure 5.3 Variation of tensile strength with UHMWPE fibre diameter


g(x) = 5.5878e^{-0.029x}
R^2 = 0.9473

Figure 5.4 Variation of tensile strength with glass fibre diameter [153]

In the post-drawing of UHMWPE fibre, fibre diameter decreased from 100-200µm to 20-30µm. To avoid the influence of fibre diameter on tensile test results it is necessary to compare a
fibre with the same diameter. In this study, great efforts were made to control fibre diameter. However, due to the equipment limitations, variations in fibre diameter still existed as fibres with diameters in the range of 20-25 µm were tested, which is one of the reasons for the variance in tested fibre properties.

5.3.1 Optimization of spinning process

The orthogonal table L9_3_4 (as shown in Table 5. 2) was used to arrange the optimization experiments. UHMWPE fibres were prepared according to orthogonal experimental design. For each sample, 25 fibres with diameters in the range of 20-25 µm were tested. The fibre ballistic performance index $U^{*\text{(1/3)}}$ value, which is calculated according to Cunniff’s model as shown in Equation 1.2, was used as the response for the optimization since the objective of this study was to obtain fibre with the highest anti-ballistic properties. Tensile test results including fibre strength, strain, modulus and $U^{*\text{(1/3)}}$ are listed in Table 5. 3.
### Table 5.3 Tensile properties of UHMWPE fibre spun at different conditions

<table>
<thead>
<tr>
<th>Experiment NO</th>
<th>Polymer concentration</th>
<th>Temperature (°C)</th>
<th>Winding speed (RPM)</th>
<th>Error</th>
<th>Diameter (μm)</th>
<th>Strength (GPa)</th>
<th>Modulus (GPa)</th>
<th>Strain (%)</th>
<th>$U^{\frac{1}{3}}$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2%</td>
<td>150</td>
<td>5</td>
<td>1</td>
<td>21.97</td>
<td>1.72</td>
<td>51.40</td>
<td>4.40</td>
<td>656.64</td>
</tr>
<tr>
<td>2</td>
<td>2%</td>
<td>180</td>
<td>10</td>
<td>2</td>
<td>21.66</td>
<td>1.98</td>
<td>56.01</td>
<td>3.94</td>
<td>673.34</td>
</tr>
<tr>
<td>3</td>
<td>2%</td>
<td>210</td>
<td>20</td>
<td>3</td>
<td>21.66</td>
<td>0.94</td>
<td>21.51</td>
<td>4.26</td>
<td>459.97</td>
</tr>
<tr>
<td>4</td>
<td>3.5%</td>
<td>150</td>
<td>10</td>
<td>3</td>
<td>20.95</td>
<td>2.92</td>
<td>92.06</td>
<td>4.23</td>
<td>852.03</td>
</tr>
<tr>
<td>5</td>
<td>3.5%</td>
<td>180</td>
<td>20</td>
<td>1</td>
<td>21.55</td>
<td>2.62</td>
<td>58.12</td>
<td>4.79</td>
<td>794.34</td>
</tr>
<tr>
<td>6</td>
<td>3.5%</td>
<td>210</td>
<td>5</td>
<td>2</td>
<td>21.29</td>
<td>1.96</td>
<td>63.92</td>
<td>4.12</td>
<td>696.80</td>
</tr>
<tr>
<td>7</td>
<td>5%</td>
<td>150</td>
<td>20</td>
<td>2</td>
<td>21.71</td>
<td>1.54</td>
<td>40.00</td>
<td>4.91</td>
<td>629.70</td>
</tr>
<tr>
<td>8</td>
<td>5%</td>
<td>180</td>
<td>5</td>
<td>3</td>
<td>20.61</td>
<td>1.78</td>
<td>55.22</td>
<td>4.17</td>
<td>661.10</td>
</tr>
<tr>
<td>9</td>
<td>5%</td>
<td>210</td>
<td>10</td>
<td>1</td>
<td>20.84</td>
<td>1.06</td>
<td>24.96</td>
<td>4.17</td>
<td>499.51</td>
</tr>
</tbody>
</table>
An F-test was done to investigate if these factors had significant influence on $U^{* (1/3)}$. From the F-test results (as shown in Appendix A), it can be seen that among the three factors investigated, polymer concentration and spinning temperature had significant influence on $U^{* (1/3)}$ at 99% confidence, while winding speed had significant influence at 90% confidence. Thus, it is important to study the effect of these factors on fibre tensile properties and morphology and find the optimal level of these three factors so as to spin UHMWPE with the highest $U^{* (1/3)}$. The optimum spinning conditions were found to be with a polymer concentration of 3.5%, a spinning temperature of 150°C, and a winding speed of 5 FPM.

### 5.3.2 Effect of spinning condition on fibre morphology

Besides affect fibre tensile properties, spinning condition also has significant influence on the morphology of gel spun fibres. Fibre morphology was studied using scanning electron microscopy (SEM) to understand its relationship with fibre tensile properties. Post-drawn fibres were initially used as samples for morphology study. However, it was found that the morphology of fully post-drawn UHMWPE fibres spun from different conditions looked quite similar even though they were spun at various conditions, as shown in Figure 5.6. During hot drawing, all the porous structures in as-spun fibres are converted into fibres with smooth fibrils. It is known that the main factor determining the drawability is the entanglement network in the as-spun fibres, which is strongly affected by the flow conditions in the extruder. Thus, as-spun fibres were used as samples to investigate the effect of the spinning condition on fibre morphology.
Figure 5.5 Morphology transformation during post-drawing

Figure 5.6 Morphology of UHMWPE fibre after post-drawing
After UHMWPE fibre was extruded from the spinneret, the polymer was immersed in a cold water bath to be quenched and crystallized, during which the structure would be completely solidified. Tension applied on the as-spun fibre during crystallization is determined by the winding-up speed. Thus, the morphology of as-spun fibres is affected by winding speed as well. From an examination of the morphology of UHMWPE fibres winding up at different speeds it was found that although the as-spun UHMWPE fibres showed a shish-kebab structure, there was a distinct difference in the nature of the backbone materials. Figure 5.7(a) shows UHMWPE fibre that was wound up at 5 FPM. It can be seen that all the kebab structures formed closely folded molecular chains and no extended fibrils were discerned in between. Meanwhile, in Figure 5.7(b), which is the fibre winding-up at speeds of 10FPM, it can be seen that the fibrillar entities have average lateral dimensions of about 500 nm and the length of the kebab structure is around 100 nm. When the winding speed was increased to 20 FPM, the lateral dimension of the kebab structure decreased to about 100nm while the length between each kebab became even bigger, as shown in Figure 5.7(c). This observation implies that winding speed greatly affects the morphology of as-spun fibre, as the elongation of the kebab structure is proportional to the deformation rate during spinning.
Figure 5.7(b)

Figure 5.7 (c)

Figure 5. 7 Morphology of UHMWPE fibre drawn at various winding speeds

(a) Winding at 5 FPM (b) Winding at 10 FPM (c) Winding at 20 FPM

It was found that UHMWPE showed certain level of oxidization when heated-up at atmosphere for longer than four hours. As shown in Figure 5. 8, the colour of the spinning gel was found turning from white to yellow when the spinning temperature was increased to 210°C. UHMWPE oxidization can be avoided in practice by using nitrogen to protect the heating zone in the commercial production condition however was not achievable in lab scale in this study. This could be another reason that a lower spinning temperature is preferred in this study.
5.3.2 Optimization of extraction process

Because the UHMWPE concentration in the spinning dope used in the gel spinning process is only about 2-5wt%, the as-spun fibre contains a high concentration (95–98%) of mineral oil. The necessity of removing the mineral oil before the hot drawing process has been argued by researchers such as Roukema [52] and Peterlin [154]. Roukema pointed out that the mineral oil could have a similar effect as a plasticizer which has been used in other fibre production and is believed to increase the maximum draw ratio through diffusion into the amorphous regions and a decrease in the cohesion between the molecules. On the other hand, Peterlin found that it was much more effective to align polymer chains by post-drawing them in the solid state rather than the liquid state because the relaxation phenomena counteracting the molecular orientation in the solid state is negligible comparing to those in the liquid state.

In this study, gel spun UHMWPE fibres were hot drawn with and without the extraction of the mineral oil. The fibre's drawability and tensile strength was measured to evaluate the necessity of the extraction process. The extracted sample was prepared according to the method described in Chapter 4. As-spun fibre was used as an un-extracted sample. Both samples were post-drawn using a homemade post-drawing system. A very low constant post-drawing speed
Chapter-5 Optimization of Gel Spun UHMWPE fibre

(1cm/min) was used in the post-drawing process to avoid stress build-up, which can lead to premature breakage of the fibre. The samples were drawn until they broke. The final length of the sample was measured and compared with the original length to calculate the draw ratio using Equation 5.1.

\[
\text{Draw ratio} = \frac{\text{Final length}}{\text{Original length}} \quad \text{Equation 5.1}
\]

It was found that fibre strength and modulus increased significantly with the post-draw ratio. This can be explained using Peterlin’s model which relates fibre strength with the number of taut tie molecules in a cross section area. During the post-drawing process, the molecules gradually aligned along the fibre axis and the fibre diameter become smaller. Thus, there are more taut tie molecules in the unit's areal on the fibre's cross section. A fibre with a higher post-drawn ratio is thus more desirable. As evident in Figure 5.9, the fibre extracted before post-drawing showed a maximum draw ratio of about 21, as opposed to 14 for the un-extracted fibre.

The tensile strength and modulus of UHMWPE fibre at different draw ratios is shown in Figure 5.10. This figure shows how the fibre strength and modulus increase sharply as the diameter decreases. At the same draw ratio, fibre that is post-drawn without mineral oil showed much higher strength and modulus compared with fibre with mineral oil. This could be explained by the fact that the fibre without extraction contained a high content of mineral oil, and therefore not enough fixing points. Entangled molecules tend to slip over each other instead of being straightened when they are pulled under tension. Thus solvent removal in as-spun UHMWPE fibre using solvent extraction is necessary.
Figure 5.9 Maximum post-draw ratio of UHMWPE fibre with and without mineral oil

Figure 5.10 (a) and (b)

Figure 5.10 (a) and (b)

Figure 5.10 Effect mineral oil on UHMWPE fibre tensile properties

(a) Tensile strength (b) Young modulus

5.3.3 Optimization of post-drawing process

During the gel spinning process, UHMWPE gel exits the capillary of the spinneret and is quenched in a water bath. The stretching of the spinline due to the winding up mechanism
Chapter-5 Optimization of Gel Spun UHMWPE fibre introduced a limited amount of orientation to as-spun fibre. In order to further straighten and align polymer chains, a post-drawing process is necessary. During post-drawing, the relatively weak as-spun UHMWPE fibres were transformed into fibres with improved molecular orientation and tensile properties.

Temperature is one of the most important factors affecting the effectiveness of post-drawing [155]. In order to obtain high tensile properties, the fibre has to be drawn at a temperature that is high enough to prevent molecular scissioning, yet low enough to prevent slip and relaxation. From practical experience, the optimum drawing temperature seems to be several degrees below the polymer's melting temperature [156, 157]. For the UHMWPE used in this experiment, it was found that polymer starts to melt at a temperature of about 145°C, thus, the highest temperature used in the post-drawing process was set to be 140°C, which is 5°C lower than the melting temperature. In order to evaluate the effect of temperature on fibre drawability and tensile properties, four different temperatures were applied in the post-drawing process. The detailed descriptions of the post-drawing conditions are listed in Table 5.4

<table>
<thead>
<tr>
<th>Post-drawn condition</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25°C</td>
<td>110°C</td>
<td>140°C</td>
<td>110°C for fist draw 120°C for second draw 130°C for third draw 140°C for fourth draw</td>
</tr>
</tbody>
</table>

The maximum draw ratios of UHMWPE fibre post-drawn at different temperatures are shown in Figure 5.11. It is evident that the maximum draw ratio of fibre post-drawn at room temperature was much lower compared with fibre drawn at elevated temperatures. This is
because room temperature could not provide enough energy for the molecules to disentangle.

Post-drawing at room temperature led to the formation of tight knots of entangled molecules as drawn ratio increased which ten caused stress concentration at certain points and initiated fibre breakage at low strain.

Figure 5.11 Effect of temperature on maximum draw ratio

(A) 25°C  (B) 110°C  (C) 110/120/130/140°C  (D) 140°C

The typical morphology of fibre drawn at room temperature is shown in Figure 5.12. It is clear that large clusters consist of un-oriented molecules that are bridged by a few tie molecules. Because these clusters were covered by more than one bundle of fibrils, they could be easily broken up into several smaller units as draw ratio increased.
Figure 5.12 Morphology of UHMWPE fibre drawn at room temperature
(a) Draw ratio=1, (b) Draw ratio=3, (c) Draw ratio=6
Chapter-5 Optimization of Gel Spun UHMWPE fibre

At room temperature, the fibre elongation was obtained by stretching fibrils that connect the clusters of folded molecules bundles. These fibrils broke at a low draw ratio and snapped back to random coil conformation immediately, which led to the generation of elastic turbulences. As a result, the connection between these un-oriented clusters was partially destroyed. Thus, fibres post-drawn at room temperature showed poor drawing and tensile properties.

Higher draw ratio was observed for UHMWPE fibres drawn at elevated temperatures of 110°C and 140°C. Fibre drawn with a stepwise increased temperature (110,120,130,140°C) showed the highest draw ratio. Lower temperature is preferred at the start of post-drawing because that lower temperature helps keep the 'fixing points' in the entangled molecular structure. Thus, the molecules in between these fixing points can be straightened. As the post-drawing ratio increases, the molecules gradually align along the fibre axis and fibre crystallinity increases accordingly. At the same time, the melting point of the polymer increases, and as such the higher temperature is needed to provide enough energy for molecules to continue to disentangle. On the other hand, when a higher temperature is used from the beginning, molecules are easily pulled out of entanglements and snap back to their random coil conformation. The breakage of the network gives rise to stress concentrations in neighbouring molecules. Therefore, when the temperature used in post-drawing is too high, not only does disentangling take place but also chain scissoring.

The tensile properties of UHMWEP fibre post-drawn at different temperatures are shown in Figure 5.13. Similar to draw ratio, fibre post-drawn in three stages by gradually increasing the temperature showed the highest strength, modulus, and $U^{*(1/3)}$. 


Figure 5.13 Effect of post-drawing temperature on UHMWPE fibre tensile properties

(a) Tensile strength  (b) Modulus  (c) strain  (d) \( U^{*\{1/3\}} \)
5.4 Validation of optimization of gel spinning process

The gel spinning process (which includes spinning, solvent removal and post-drawing) was studied and optimized. The optimum spinning condition was optimized through DOE using the orthogonal method. It was found that the optimum spinning condition to obtain higher $U^{*(1/3)}$ was 3.5wt% UHMWPE/mineral oil gel, spin at 150°C and winding at 5 FPM. UHMWPE fibres were produced under this optimum condition and the morphology and tensile properties of the resulted fibre is shown in Figure 5.14 and Table 5.5. UHMWPE fibre processed in these optimum conditions showed $U^{*(1/3)}$ of 883, which is significantly higher compared to fibre processed in other conditions. This demonstrates that the optimization process performed in this experiment was successful.

Figure 5.14 Morphology of UHMWPE fibre spun at optimum condition
Chapter-5 Optimization of Gel Spun UHMWPE fibre

Table 5. 5 Tensile strength of UHMWPE fibre spun at optimal conditions

<table>
<thead>
<tr>
<th>Diameter (μm)</th>
<th>Strength (GPa)</th>
<th>Modulus (GPa)</th>
<th>Strain (%)</th>
<th>( U/n ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>22.17</td>
<td>3.37</td>
<td>101.93</td>
<td>3.84%</td>
</tr>
<tr>
<td>STDEV</td>
<td>2.80</td>
<td>0.35</td>
<td>16.29</td>
<td>0.56%</td>
</tr>
</tbody>
</table>

5.5 Summary

In this chapter, the gel spinning process was optimized by studying the influence of the three most important factors through the design of experiment: polymer concentration, spinning temperature and winding speed. The influence of these factors on fibre morphology, and the influence of extraction and the post-drawing process on fibre post-draw ratio was also studied in this chapter. UHMWPE fibre was produced under the optimum spinning, extraction and post-drawing conditions and the tensile properties were tested. This optimum spinning condition will be used for all subsequent experiments in which carbon nanotubes (CNTs) are added to pure UHMWPE fibre as a reinforcement.
Chapter 6- MWCNT reinforced UHMWPE fibre

6.1 Introduction

Carbon nanotubes (CNTs) are now widely recognized as excellent reinforcement filler for polymer composites because of their outstanding mechanical, thermal and electrical properties. In recent years there has been an explosive growth in research activity in CNT-reinforced polymer composite materials. It is also widely recognized by researchers that the reinforcement effectiveness of CNTs in a polymeric matrix depends on their volume ratio and their dispersion in the hosting medium. In order to utilize the excellent properties of CNTs, one of the most important challenges is to obtain a uniform dispersion of CNTs in the polymer matrices. In spite of many reports claiming successful reinforcement of polymers by CNTs, the reinforcing efficiency is far below expectations. This is primarily due to the strong interaction forces that cause the formations of bundles and clusters in as-produced CNTs.

Although there are various methods of producing CNTs such as arc discharge, chemical vapor deposition, laser ablation, high pressure carbon monoxide (HiPco) and electrolysis, the CNTs produced from these methods are always physically entangled or adhere to each other in the form of bundles, as shown in Figure 6.1. The cohesion energy between two parallel CNTs is about $-0.095 \text{ eV/Å}$, as calculated by Girifalco et al. using a continuum model [158]. Since the thermal energy at room temperature is only about $0.025 \text{ eV/Å}$ (which is much lower than the cohesion energy between CNTs) the CNT de-bundling from an existing bundle on their own under room temperature is unlikely. In some cases, those CNT bundles will further aggregate into entangled networks, which have been found to act as a obstacle for realizing the extraordinary mechanical and electrical properties of individual tube [94, 159]. Because of the
strong inter-tube van der Waals forces, the as-produced CNTs usually align parallel to each other and pack into crystalline bundles, which are typically composed of 100-500 tubes. Thus, improving CNT dispersion has been widely recognized as a crucial issue for fully utilizing the enhancement potential of the CNT in CNT/polymer composites.

![Figure 6.1 (a)](image1.png)  ![Figure 6.1 (b)](image2.png)

Figure 6.1 Morphology of as-produced CNTs [160, 161]
(a) CNT ropes produced by discharge method  (b) CNTs grown by plasma-enhanced chemical vapour deposition

### 6.1.1 Importance of CNT dispersion in UHMWPE fibre

A good dispersion of CNTs is especially important for reinforcing UHMWPE fibre. This is because the fibrils of UHMWPE fibre, with a size of around 100nm to 1µm, are extended and tightly aligned along the fibre axis during the post-drawing process and any micro-meter size nanotube agglomeration could form structural defects. As fibre is under great tension during drawing, any stress concentration due to structural defects may lead to crack initiation and thus the fibre's rupture. CNT agglomerates will also lead to premature breakage of UHMWPE fibres during the post-drawing process. Thus, the molecules in the fibre consisting of these agglomerates cannot be fully drawn to obtain a highly extended and aligned structure. Since tensile properties of UHMWPE fibre are greatly determined by the fibre's draw ratio and
diameter (as discussed in Chapter 5), fibres with lower draw ratio or larger diameter usually show lower tensile properties.

6.1.2 Methods to disperse CNTs in solvent

Considering the importance of separating CNTs’ bundles and agglomeration, there have been intensive efforts to develop methods that will enable CNT solubilization, dispersion and separation. These methods can be organized into two categories: chemical methods and mechanical methods. The chemical approach includes chemical modification of the CNT surface by attaching functional groups, or functionalization by wrapping the CNT with long polymer chains. The mechanical method usually refers to nanotube separation using shear mixing or ultrasonication, which can transfer local shear stress to break down aggregates. Due to its simplicity and efficiency, mechanical dispersion is usually preferred. In this study, the feasibility of achieving a good dispersion of CNTs in UHMWPE fibres by mechanical methods was investigated. MWCNTs dispersed by ultra-sonication and ball milling were used as reinforcements for UHMWPE fibres. Fibre morphology and tensile properties were used as criteria for evaluation of CNT dispersion in UHMWPE fibres.

6.2 Dispersing by ultra-sonication

Ultra-sonication is one of the most widely used methods to disperse nanoscale materials and has been shown to be very effective in breaking up CNT aggregates and dispersing CNTs [162-169]. CNT dispersion through high-intensity ultrasonic waves is caused by cavitation during which very high temperatures (approx. 5,000K) and pressures (approx. 2,000atm) can be reached locally [170]. Implosion of cavitation bubbles also creates high velocity liquid jets with a velocity up to 280 m/s that overcomes bonding forces between CNTs and de-agglomerate
CNTs [171]. The fluid flow caused by the bubble collapse depends on the solvent's boiling point and viscosity.

### 6.2.1 Materials and experiment

Acid purified MWCNTs with a carboxyl group (COOH-MWCNTs) with a diameter of about 8nm and a length of 1μm were used for this study. Detailed information for the materials including the UHMWPE, mineral oil and anti-oxidant used in this study can be found in Chapter 4.

From the optimization of the gel spinning process in Chapter 5, it was discovered that the optimum UHMWPE concentration of mineral oil was 3.5wt%. In this study, UHMWPE fibres with a MWCNT concentration of 0.5, 1.0 and 1.5wt% were prepared. MWCNTs were dispersed in mineral oil by bath ultra-sonicating(Model: Misonix3000) for 10 hours before adding UHMWPE into the mixture. UHMWPE powders and anti-oxidants were then added to the MWCNT/mineral oil mixture. The mixture of MWCNT, anti-oxidant, UHMWPE and mineral oil was then heated up to form a uniform gel. 3.5wt% UHMWPE/Mineral oil with MWCNT concentration of 0.5, 1.0 and 1.5wt%, respectively, was extruded into the fibre at 150°C with a winding speed of 5FPM, which was the optimum spinning condition determined in Chapter 5.

### 6.2.2 Results and discussion

The tensile properties of MWCNT/UHMWPE composite fibres with various MWCNT contents were tested using the methods described in Chapter 4. Pure UHMWPE fibres were also prepared and tested under the same conditions and used as reference samples. The tensile strength, modulus and strain of MWCNT/UHMWPE composite fibres containing 0.5, 1.0 and 1.5wt% MWCNTs are shown in Figure 6.2 (a), (b), (c), respectively.
Figure 6.2 Tensile properties of MWCNT/UHMWPE fibre prepared by ultra-sonication

(a) Tensile strength  (b) Modulus  (c) Tensile strain  (d) $U'^{(1/3)}$

As can be seen in Figure 6.2(a) and (b), the tensile strength and modulus of UHMWPE fibre decreased significantly after adding MWCNTs, which were dispersed by ultra-sonication. Tensile strain increased slightly after adding 0.5 and 1.0% MWCNTs but decreased when the MWCNT content increased to 1.5wt%, as shown in Figure 6.2(c). However, the increase in strain is not statistically significant at a confidence level of 95%. Due to the decrease in tensile
strength and modulus, the $U^{(1/3)}$ of MWCNT/UHMWPE fibre is even lower than pure UHMWPE. The decrease in fibre tensile properties after adding MWCNTs could be attributed to the non-uniform dispersion of MWCNTs, which was examined by optical microscopy and shown in Figure 6.3. Apparently, MWCNTs were not uniformly dispersed in the UHMWPE matrix. MWCNT agglomerations with a size of 10-20μm could be found even at 5 × magnifications. The agglomeration worsened as the CNT concentration increased. According to the stress concentration theory, these CNT agglomerates will behave as structural defects and cause stress concentration under tension, thus leading to inferior mechanical properties. Assuming that the CNT agglomerations have a circular shape, the stress on the edge of the CNT agglomerations could be at least three times of the tension applied on the fibre during post-drawing. These CNT agglomerates create discontinuity in the UHMWPE matrix, especially when the fibre diameter decreases during post-drawing, thus leading to adverse effects in mechanical performance. MWCNT clusters with a size similar to fibre diameter were found protruding from the fibre surface, as shown in Figure 6.4.

Figure 6.3 Morphology of MWCNT/UHMWPE fibre prepared by ultra-sonication
(a) Pure UHMWPE (b) 0.5% (c) 1.0% (d) 1.5% MWCNT/ UHMWPE
During ultra-sonication, CNT agglomerates are subjected to local shear stress generated by the flow of the solvent determines the dispersion of CNTs. The solvent flow is caused by cavitation of the micro air bubbles. In order to successfully debundle CNT agglomerates, the local energy density in the solvent generated by sonication must be higher than the binding energy that holds CNTs together. The binding forces for CNTs can be evaluated by the van der Waals interaction between them. In order to simplify the calculation, a pair of CNTs was modeled by a pair of parallel rods [172]. It was estimated that the energy density $\varepsilon$ required to separate a pair of parallel tubes is around 100MPa [173]. The shear rate generated in a ultrasonic bath is through the of cavitation collapse of bubbles which could reach as high as $10^9$ s$^{-1}$ [174, 175]. The viscosity of mineral oil at room temperature is around 0.05 Pa·s. The local shear stress in the vicinity of the cavitation should be around 50 MPa. Thus, it was expected that there would not be sufficient energy to separate tubes from the bundles during sonication. In order to improve CNT dispersion, alternative dispersion methods that can provide a higher level of shear energy, such as ball milling, were sought.
6.3 Dispersing by ball milling and sonication

Ball milling is a mechanical process by which high-energy forces by colliding balls reduce the material to a fine powder. It has been widely used in industry as a key piece of equipment for grinding materials to produce powders such as cement and silicates. Laboratory scale ball milling machines usually consist of cylindrical capped milling jars that sit on drive shafts. The milling jars are partially filled with the material to be ground and the grinding medium rotates around a vertical axis. It has been demonstrated that the size of the CNT agglomerations can be decreased after the ball milling process [176]. However, side effects such as CNT shortening and destruction have also been reported [177]. Kukovecz [178] performed a systematic study on the morphological and length changes experienced by MWCNTs during long-time ball milling. Samples were collected after ball milling for 1, 80, and 140 hours. It was evident that SWCNT entanglement significantly improved and the SWCNT length was maintained after 1 hour of ball milling, as shown in Figure 6.5 (b). However, longer ball milling durations such as 40 hours and 140 hours did shorten the SWCNT length significantly, as shown in Figure 6.5 (c), (d).
In another study, N. Pierard [179] investigated the effect of ball milling on the structure of SWCNTs. SWCNTs were ball milled for 1 hour, 8 hours and 50 hours, respectively, and it was found that there was no significant nanotube destruction for the first 3 hours, as shown in Figure 6.6 (a). However, longer milling times progressively disrupted the SWCNTs' structure and transformed them into multilayered polyaromatic carbon structures, as shown in Figure 6.6 (b), (c).
6.3.1 Materials and experiment

The ball milling machine from Retsch (Model: Planetary Ball Mill PM 200) is shown in Figure 6.7 with 50ml stainless steel grinding jars and stainless steel grinding balls (2mm in diameter) used in this study. 1.75 grams of MWCNT/UHMWPE mixtures with MWCNT concentrations of 0.5, 1.0, 1.5wt% were fed into the grinding jars. Grinding balls were fed into grinding jars until they took about half of their volume. The rotation speed was set to 3000 rpm and milling duration was fixed at 15 minutes. After ball milling, the mixture (including MWCNT and UHMWPE) was dispersed in mineral oil by sonication using a bath sonicator (Model: Misonix3000) under a power level of 80 Walt's for three hours. Anti-oxidant BHT was added to the MWCNT/UHMWPE mixture and sonication was subsequently continued for another hour. The mixtures of MWCNT/UHMWPE/mineral oil with different MWCNT concentrations were heated up in an oil bath to form spinning gels. A laboratory mixing extruder was used for the gel
spinning process. Detailed information regarding gel preparation, spinning and post-drawing processes has been detailed in Chapter 4.

Figure 6.7(a)  Figure 6.7(b)

Figure 6. 7 Retsch ball mill machine
(a) planetary ball mill machine  (b) grinding jar

6.3.2 Results and discussion

Contrary to the previous experiments which used ultra-sonication as the only method for dispersing MWCNTs, a ball milling process was added before ultra-sonication with the purpose of further improving MWCNT dispersion in UHMWPE. The tensile properties of the MWCNT/UHMWPE composite fibres containing 0.5, 1.0 and 1.5wt% MWCNT were tested and analyzed, as shown in Figure 6. 8. There was a slight increase in tensile strength, however no improvement in modulus and strain was observed. Accordingly, the $U^{*(1/3)}$ did not show significant change after adding MWCNT into UHMWPE either, as shown in Figure 6. 8(d).
The CNT dispersion in UHMWPE fibre processed by ball milling and the ultrasonication process was examined by optical microscopy, as shown in Figure 6.9. The dispersion of MWCNTs was still not uniform as agglomerates the size of about 10μm were easily observed under the microscope. As most MWCNTs exist in the form of agglomerates, very few individual nanotubes were dispersed in the UHMWPE matrix to act as reinforcement, thus the reinforcing efficiency was very low.
In conclusion, ball milling could not efficiently disperse UHMWPE in UHMWPE fibre. The reinforcement of UHMWPE fibre using MWCNTs dispersed through ball milling could not be realized. Other mechanical dispersion methods such as micro-fluidizing and a solvent assisted MWCNT spray method have also been studied and the results are shown in Appendix C.

Figure 6.9 Morphology of MWCNT/UHMWPE fibre prepared by ball mill process
(a) Pure (b) 0.5% (c) 1.0% (d) 1.5% MWCNT/UHMWPE

6.4 Conclusion

The feasibility of reinforcing UHMWPE fibre using MWCNTs without chemical functionalization was investigated. Mechanical methods (including ultra-sonication and ball milling) were used to disperse MWCNTs in mineral oil. The MWCNT dispersion and tensile properties of MWCNT/UHMWPE composite fibres with 0.5%, 1.0% and 1.5% MWCNT were examined. It was found that both ultra-sonication and ball milling were not able to disperse MWCNTs uniformly in mineral oil, and thus 10μm to 20μm MWCNT agglomerations were found in the UHMWPE fibre. Compared to using ultra-sonication alone, MWCNTs dispersed
through both ball milling and ultra-sonication showed improved dispersion. However, no statistically significant improvement in tensile properties was observed. Other methods including the newly developed microfluidizing technology and a solvent assistant dispersion were also studied, as shown in Appendix C. However, again, no significant increase in tensile properties was found. Thus, it is concluded that UHMWPE fibre reinforcement using MWCNTs cannot be realized through simple mechanical dispersion. In the following two chapters, the feasibility of dispersing MWCNTs through chemical functionalization is investigated.
Chapter 7 - Coupling agent functionalized MWCNT reinforced UHMWPE fibre

7.1 Introduction

Coupling agents are chemicals that have two functional groups with different reactivity. One of the two functional groups reacts with organic materials and the other reacts with inorganic materials. The special structure of the coupling agent enables the linkage between fillers and a polymer matrix. Traditionally, coupling agents have been widely used in composite industry to improve the dispersion of inorganic fillers in a polymer matrix and the mechanical performance of some filler/polymer composites [180-183]. In recent years, coupling agents have also been used in surface modification of nano-particles for improving dielectric properties in organic–inorganic nano-composites. For instance, Cheng’s group applied a silane coupling agent to MWCNTs to increase the degree of interaction between a polyimide and MWCNTs for further improvement in the mechanical properties and the thermal stability of the polyimide/MWCNT nano-composites [184]. Lin et al. [185] improved the tensile modulus of the polypropylene nano-composites by functionalization of nano silicon dioxide using silane coupling agents.

In this study, a titanium derived coupling agent was used to functionalize the surface of the MWCNTs. The coupling reaction was achieved in the MWCNTs by taking advantage of the carboxyl groups on the surface of the acid-treated MWCNTs. These results in the formation of matrix-compatible organic monomolecular layers consist of a long alkyl chain on the MWCNT surface.
7.2 Experimental

7.2.1 Functionalization of MWCNTs

The titanium derived coupling agent isopropyl tri(dioctylpyrophosphate) titanate has the chemical form $R_0\text{-Ti-(ORT)}_3$, where $R_0$ is a functional group and $R$ is a hydrolysable alkyl group. The titanium derived coupling agent used in this work has the structure

$$
\text{CH}_3\text{-CH-O-Ti} \left[ \text{O-} \right] \text{Ti} \left[ \text{O-C_8H_{17}} \right]_3.
$$

The coupling reaction was achieved by taking advantage of the carboxyl groups on the MWCNTs, resulting in the formation of matrix compatible organic monomolecular layers consisting of long alkyl chains on the CNT surface, according to the chemical mechanism shown in Figure 7.1. The reaction was confirmed by XPS and Raman spectroscopy.

![Figure 7.1 Reaction between coupling agent and COOH-MWCNTs [26]](image)

Following Wang’s [26] method, the carboxyl group functionalized multi-walled carbon nanotubes (COOH-MWCNTs) reacted with a titanium derived coupling agent by adding COOH-MWCNTs into a coupling agent/alcohol solution. The mixture was stirred with a magnetic stirrer at 60°C for 30 minutes followed by sonication for 3 hours at 65°C. The functionalized MWCNTs (identified as Ti-MWCNTs) were then separated by filtration and dried in a vacuum oven at
110°C for 1 hour to allow a complete evaporation of alcohol. The resulting Ti-MWCNTs were washed thoroughly with acetone to eliminate any non-reacted coupling agent.

### 7.2.2 Gel spinning and post-drawing

UHMWPE gel with 0.5%, 1% and 1.5% Ti-MWCNTs was prepared by dispersing Ti-MWCNTs and UHMWPE in mineral oil first and then heated up in an oil bath under nitrogen protection to 160°C. The gel was vacuumed for 24 hours to eliminate air bubbles and then was cut into small pieces. The small pieces of MWCNT/UHMWPE gel were fed into the extruder and spun into fibre. The spinning, extraction, and post-drawing was performed using the methods described in Chapter 4. Spinning and post-drawing were carried out at the optimum spinning conditions discussed in Chapter 5.

### 7.2.3 Characterization of MWCNT

X-ray photoelectron spectroscopy (XPS) and a field emission analytic transmission electron microscope (FE-TEM) were used to characterize the changes in MWCNT chemical structure and surface morphology during functionalization. Single fibre tensile tests were carried out using a KES-G1 tensile testing machine and the diameter of the filament was measured using an optical microscope. The detailed methods are described in Chapter 4.

### 7.3 Results and discussion

#### 7.3.1 XPS

XPS is a useful tool for chemical surface analysis. Figure 7.2 depicts XPS survey scans of a COOH-MWCNT and Ti-MWCNTs in wide scan mode. Compared to the COOH-MWCNT, the
spectrum for Ti- MWCNTs shows a sharp Ti1p peak at 457 eV, which is attributed to the titanium element in the R0-Ti-(ORT)3 coupling agent.

![XPS spectrum of an MWCNT and a coupling agent treated MWCNT](image)

Figure 7.2 XPS spectrum of an MWCNT and a coupling agent treated MWCNT

The elemental compositions obtained from the XPS spectra of the COOH-MWCNT and the coupling agent functionalized MWCNTs are summarized in Table 7.1. The COOH-MWCNT has an oxygen-to-carbon (O/C) atomic ratio of 0.19, while the O/C ratio of the Ti-MWCNT is 0.62. The increase in the oxygen-to-carbon (O/C) atomic ratio should be attributed to oxygen in the coupling agent, which confirms the reaction between MWCNTs and the coupling agent.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O/C</th>
<th>Ti/O</th>
<th>Elemental compositions (mol%)</th>
<th>Binding Energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O</td>
<td>C</td>
</tr>
<tr>
<td>COOH-MWCNT</td>
<td>0.19</td>
<td>0.00</td>
<td>16.27</td>
<td>83.73</td>
</tr>
<tr>
<td>Ti-MWCNT</td>
<td>0.62</td>
<td>0.70</td>
<td>30.04</td>
<td>48.79</td>
</tr>
</tbody>
</table>
Figure 7.3 shows the high resolution C$_{1s}$ spectra of a COOH-MWCNT and a Ti-MWCNT. The C$_{1s}$ peak could be deconvoluted into two fitting curves: C$_1$ at 284 eV represents C-C or C-H and C$_2$ at 285 eV, which corresponds to C-O. These results are summarized in Table 7.2. After treatment by the coupling agent, MWCNTs exhibited a different intensity in the C$_{1s}$ peak. The increase in the relative intensity of C$_1$ peak at 285 eV suggests the formation of more C-O bonds, which further confirms the presence of long alkyl chains on the MWCNT surface after reactions.

![Figure 7.3 (a) COOH-MWCNT](image)

![Figure 7.3 (b) Ti-MWCNT](image)

Figure 7.3 Deconvoluted high resolution C$_{1s}$ spectra of COOH-MWCNT and Ti-MWCNT
Table 7.2 Analysis of C$_{1s}$ peaks of the COOH-MWCNT and Ti-MWCNT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analysis of C$_{1s}$ peaks(%)</th>
<th>Binding energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_1$</td>
<td>C$_2$</td>
</tr>
<tr>
<td>COOH-MWCNT</td>
<td>54.81%</td>
<td>45.19%</td>
</tr>
<tr>
<td>Ti-MWCNT</td>
<td>42.99%</td>
<td>57.01%</td>
</tr>
</tbody>
</table>

7.3.2 Raman spectrum

MWCNT defects were analyzed by Raman spectroscopy. Raman spectra of a COOH-MWCNT and a Ti-MWCNT are shown in Figure 7.4(a) and (b). In both cases, two bands at 1310 cm$^{-1}$ (D band) and 1589 cm$^{-1}$ (G band) appear. The shift of peak at 1585 cm$^{-1}$ can be assigned to the G band which is related to the vibration of sp$^2$-bonded carbon atoms in a two dimensional hexagonal lattice, indicative of the formation of crystalline graphite phase. The D band, at 1310 cm$^{-1}$ is usually attributed to the structural disorder or the presence of amorphous carbon in the MWCNTs. Thus, the intensity ratio of the D and G bands has been used as an indication of the number of defects on the carbon nanotube structure.

Figure 7.4 Raman spectra of (a) COOH-MWCNT (b) Ti-MWCNT
As can be seen, there is no significant change of intensity ratio of the D/G bands between the COOH-MWCNT and Ti-MWCNT, which indicates that the functionalization of MWCNTs by a titanate coupling agent does not introduce extra defects onto the MWCNT structure.

<table>
<thead>
<tr>
<th>CNT</th>
<th>Intensity of D peak</th>
<th>Intensity of G peak</th>
<th>D/G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>2696.9</td>
<td>2499.5</td>
<td>1.08</td>
</tr>
<tr>
<td>Ti-MWCNT</td>
<td>663.94</td>
<td>635.80</td>
<td>1.04</td>
</tr>
</tbody>
</table>

**7.3.3 TGA**

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature. TGA is one of the most straightforward methods to characterize CNT reinforced polymer composites. CNTs cannot be easily decomposed at high temperatures, whereas most polymers will completely decompose at temperatures over 500 °C. Therefore, TGA can be used to provide quantitative information about nanotube functionalization.

Figure 7. 5 shows a representative TGA spectra under the nitrogen atmosphere of the COOH-MWCNTs and the coupling agent treated MWCNTs. The TGA curve of the COOH-MWCNTs is steady, without significant weight loss below 600°C. The slight mass loss (5 wt%) below 600°C was caused by the decomposition of amorphous carbon and free carboxylic and hydroxyl groups on the sidewall of the MWCNTs at elevated temperatures. In comparison, the TGA curve for the Ti-MWCNTs shows a distinct weight loss of 3wt% from the beginning to 120°C, followed by a gradual mass loss to 20 wt% as the temperature reached 260°C. A more significant mass loss from 20 to 58% was observed between 260°C and 600°C, which can be attributed to the decomposition of the coupling agent covalently attached to the MWCNTs.
distinguishable weight loss was observed below 120°C for coupling agent treated MWCNTs due to the covalent bonding formed between the coupling agent and the carboxyl groups on the surface of the MWCNTs.

![TGA of COOH-MWCNT and Ti-MWCNT](image)

**Figure 7.5 TGA of COOH-MWCNT and Ti-MWCNT**

### 7.3.4 Dispersion of MWCNTs

The dispersion of 0.05wt% MWCNTs and Ti-MWCNTs in mineral oil was prepared by sonication for 10 hours. These two solutions were allowed to stand for 30 minutes. It was clear that MWCNTs without coupling agent functionalization completely precipitated from the mineral oil while the dispersion of Ti-MWCNTs was still stable after 30 minutes of precipitation, as shown in Figure 7.6. This observation demonstrated that the functionalization by a coupling agent significantly improved MWCNT suspension stability in mineral oil. This could be
explained by the improvement in affinity of MWCNTs with mineral oil through the alkyl chain on the MWCNT surface.

![CNT suspension in mineral oil](image)

**Figure 7.6** CNT suspension in mineral oil

### 7.3.5 Tensile properties

Ti-MWCNT/UHMWPE composite fibres with 1%, 2%, and 3% Ti-MWCNTs were prepared according to the gel spinning process described in Chapter 4 under the optimum processing conditions obtained from the design of experiment detailed in Chapter 5. Tensile strength of UHMWPE with 3wt% Ti-MWCNTs increased from 3.38 GPa to 3.73 GPa, which corresponds to a 10.5% increase. This increase is statistically significant at 95% confidence level. The increase in tensile strength alone could be explained by the improvement in fibre structure and crystallinity by adding MWCNTs. It has been found that with good compatibility between CNTs and UHMWPE, CNTs could help UHMWPE molecules to disentangle and align along the fibre axis during post-drawing. However, no significant improvement in modulus and strain was observed, which suggested a lack of good load transfer on the interface of CNTs and UHMWPE.
To further improve the tensile properties of UHMWPE fibre, higher Ti-MWCNT content is needed. A 4wt% MWCNT/UHMWPE mineral oil solution was prepared but MWCNTs were found starting to precipitate on the bottom of the bottle. Thus, MWCNT concentration in UHMWPE fibre through coupling agent functionalization was limited to 3wt%.
7.4 Conclusion

Compared to mechanically dispersed COOH-MWCNTs, functionalization of MWCNTs using a coupling agent significantly improved MWCNT dispersion in mineral oil. An enhancement of the mechanical properties of the UHWMPE composite fibres can be obtained at low nanotube loading, which indicates a uniform dispersion of MWCNT in the UHWMPE matrix. As a representative example, a 10.5% improvement in tensile strength was achieved by the addition of only 3 wt% functionalized nanotubes.

However, considering the extraordinary properties of MWCNTs, the reinforcing efficiency of MWCNTs in UHWMPE fibre is still relatively low. Also, it was found that higher concentrations could not be obtained since the MWCNTs started to precipitate at concentrations higher than 3wt%. Thus, it is difficult to further improve the mechanical properties of UHWMPE fibre using coupling agent functionalized MWCNTs. The reinforcement in polymer composite depends on both CNT dispersion in a polymer matrix and the load transfer through the interface. In order to further improve the tensile properties of UHWMPE fibres, the load transfer on the MWCNT and UHWMPE interface must be improved.
Chapter 8- Polymer grafted MWCNT reinforced UHMWPE fibre

8.1 Introduction

In recent years, there have been many attempts to use CNTs to reinforce UHMWPE fibre. One of the most successful works came from Ruan’s group [24]. In their study, the strength and modulus of UHMWPE fibre were increased by 19% and 12%, respectively, when reinforced with 5 wt% MWCNTs. However, the solvent used in their study was decahydronaphthalene (decalin), which is not only flammable but also toxic. Efforts have been taken to develop MWCNT/UHMWPE composite fibres using mineral oil as a solvent, but the result was disappointing as the tensile strength of the composite fibre decreased from 4 GPa to around 1 GPa when 5 wt% MWCNTs were added. According to Ruan, the main reason is that the MWCNT dispersion in mineral oil is not as uniform as in decalin due to mineral oil's high viscosity. Large MWCNT clusters were found in composite fibres which prevent MWCNTs from exfoliating and thus compromise their significant potential. It has been found by many researchers that CNTs dispersion in the matrix and the adhesion between the nanotube and the matrix are the two critical factors in capitalizing the strength of the nanotubes. In Chapter 7, CNT dispersion in mineral oil was improved by functionalizing with a titanium derived coupling agent. A better dispersion of CNTs in a UHMWPE matrix was obtained. However, there is no significant improvement in ballistic performance $U^{*}(1/3)$ of composite fibre containing 3wt% functionalized MWCNTs, compared to pure UHMWPE fibre. The low reinforcing efficiency is attributed to the inadequate interfacial load transfer between the CNTs and the polymer matrix, which is crucial for the properties of a CNT reinforced composite. In order to transfer the
properties of CNTs to the composite material, stronger bonding between CNTs and UHMWPE is needed. Among others, grafting long polymer chains onto CNTs has been regarded as a promising method for improving the miscibility of CNTs in polymer matrices. Through the high energy of the covalent bond formed during polymer grafting, a higher interfacial strength and thus a more favorable load transfer between the CNTs and the polymer can be obtained.

8.2. Experimental

8.2.1 Functionalization and polymer grafting of MWCNTs

Composite science has proven that the lack of compatibility between reinforcement and the polymer matrix inhibits the load transfer from the matrix to reinforcement. This is also true for carbon nanotube reinforced polymer composite. Great efforts have been made to improve the compatibility between CNTs and the polymer matrix. In this study, the carboxyl groups on the sidewall of the CNTs enable the grafting of molecules onto the CNT surface so as to increase the compatibility and realize the load transfer between the matrix and the CNTs [149].

100mg of as-received carboxyl group functionalized MWCNTs (COOH-MWCNTs) were reacted with 100ml ethylene diamine to form amino group functionalized MWCNTs (NH$_2$-MWCNT). The COOH-MWCNTs were added into ethylene diamine with the presence of a coupling agent. The mixture was sonicated for 4 hours at 50°C. After the reaction, the mixture was filtrated to separate the resulting NH$_2$-MWCNTs. These NH$_2$-MWCNTs were washed extensively with methanol until the solution was neutral to get rid of the ethylene diamine. The NH$_2$-MWCNTs were then dried overnight in a vacuum oven at 80°C.

The covalent grafting procedure is shown in Figure 8. 1. 100mg NH$_2$-MWCNTs were dispersed in 10ml toluene and sonicated for 2 hours to break up MWCNT agglomerations.
500mg PE-g-MA was dissolved into 10ml toluene under a nitrogen atmosphere at 120°C. NH2-MWCNTs/toluene solution was then mixed with a PE-g-MA/toluene solution and then stirred for 24 hours. The grafting reaction was accompanied by the formation of bubbles, indicating the release of water vapour during imidization reaction. The reaction was complete after the formation of bubbles ceased. The grafted MWCNTs were separated by filtration through a 0.8 μm polytetrafluoroethylene (PTFE) membrane and thoroughly washed with methanol several times. The grafted CNTs were finally dried overnight in a vacuum oven at 80°C to remove the residue solvent. Through this process, polyethylene grafted multi-walled carbon nanotubes (PE-g-MWCNTs) were obtained and were ready to be used as reinforcement for UHMWPE fibre.

![Figure 8.1 Polyethylene grafted maleic anhydride functionalized MWCNT](image)

**8.2.2 Gel spun PE-g-MWCNT reinforced UHMWPE fibre**

The PE-g-MWCNTs were used to reinforce UHMWPE in the gel spinning process with various concentrations. PE-g-MWCNTs were dispersed in mineral oil by sonication. 3.5wt% UHMWPE was added into MWCNT/mineral oil dispersions and heated up to form the spinning
gel. UHMWPE fibres with different PE-g-MWCNT concentrations were spun under the conditions described in Chapter 4.

### 8.2.3 Characterization

Transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR) were used to study the polymer grafting process. Single fibre tensile tests were carried out using the KES-G1 tensile testing machine. The diameter of the filament was measured using an optical microscope. Detailed characterization methods can be found in Chapter 4.

### 8.3 Results and discussion

#### 8.3.1 TEM and SEM

The TEM images of the COOH-MWCNTs as well as PE-g-MWCNTs are shown in Figure 8. 2. The diameters of the COOH-MWCNTs measured in Figure 8. 2 (a) are 8-10 nm. After polymer grafting, it was found that the diameter of PE-g-MWCNTs increased to around 20 nm, which is about twice the diameter of COOH-MWCNTs. The thickness of the coated polymer on the surface of the MWCNTs was about 6 nm, as shown in Figure 8. 2 (b) which is direct evidence that the polyethylene chains were grafted efficiently to the nanotube surface.
Figure 8. 2 TEM of COOH-MWCNT and PE-g-MWCNT

(a) MWCNT before polymer grafting,  (b) polymer grafted MWCNT

By controlling the amount of grafting, carbon nanotubes with different grafting thickness were obtained. For example, a much thicker polymer grafted carbon nanotube was observed under SEM, as shown in Figure 8. 3.

Figure 8. 3 PE-g-MWCNT with thicker grafting layer
8.3.2 FTIR

The FTIR spectroscopy of the COOH-MWCNT, NH₂-MWCNT and PE-g-MWCNT are shown in Figure 8.4. The spectrum of COOH-MWCNT presenting a peak at ~1716 cm⁻¹ is attributed to the C=O stretch of the carboxylic group. The spectrum of the amide-functionalized MWCNT samples shows the disappearance of the peak at 1716 cm⁻¹ and a corresponding appearance of the peak with lower frequency at 1635 cm⁻¹, which can be attributed to the stretch mode of the amide carboxyl C=O. In addition, the peaks at 1415 cm⁻¹, 2849 cm⁻¹ and 2918 cm⁻¹, which belong to the stretch and scissor mode of C-H, respectively, further confirm the presence of the amide functional group. In the spectrum of PE-g-MWCNTs, the presence of a new peak at 1260 cm⁻¹ represents the stretch mode of the methyl group from the end of the grafted polyethylene chain. The two new peaks at 800 cm⁻¹ and 717.8 cm⁻¹ represent the bending mode of aromatic C-H formed from the maleic anhydride group in PE-g-MA. In addition, the peaks at 1463 cm⁻¹, 2849 cm⁻¹ and 2918 cm⁻¹ corresponding to the scissor and stretch mode of alkane C-H became stronger due to the grafting of the polyethylene chain. These results clearly indicate that polyethylene polymer chains were successfully grafted on the surface of the MWCNTs.
Figure 8.4 FTIR spectrum of COOH-MWNT, NH$_2$-MWCNT and PE-g-MWCNT
8.3.3 Tensile properties

The tensile properties of UHMWPE fibres reinforced by PE-g-MWCNT with concentrations of 1wt%, 2wt% and 3wt% were tested and compared with pure UHMWPE fibre. As shown in Chapter 5, fibre diameter has a significant influence on tensile properties. During the post-drawing process, it was found that the UHMWPE fibres reinforced by PE-g-MWCNTs showed better drawability and were easier to be drawn into a smaller diameter compared to pure UHMWPE fibres and Ti-MWCNT reinforced UHMWPE fibres. For example, the minimum diameter of pure UHMWPE fibres and Ti-MWCNT/UHMWPE fibres was around 20-25 µm after post-drawing, which corresponds to a draw ratio of around 45. However, PE-g-MWCNT reinforced UHMWPE fibres showed a much higher maximum draw ratio. For example, 3wt% PE-g-MWCNT/ UHMWPE fibre could be drawn to a draw ratio of 125 with a diameter around 15 µm. The tensile strength, modulus and strain to failure of the 3wt% PE-g-MWCNT/UHMWPE fibre is about 5.0 GPa, 150 GP and 3.7%, respectively, which is almost 50% higher than commercial UHMWPE fibres such as Dyneema® and Spectra®. A typical stress-strain curve of the small diameter fibre is shown in Figure 8. 5(a).

More interestingly, fibre with a diameter as small as 11 µm could be obtained when the temperature in the fourth pass of post-drawing was increased from 140°C to 150°C. As fibre tensile properties increased sharply with the decrease in diameter, significantly higher tensile properties were observed on those small diameter fibres. Tensile strength as high as 7.3 GPa were observed as shown in Figure 8. 5 (b).
The increase in the draw ratio of PE-g-MWCNT/UHMWPE fibre could be attributed to the improvement in molecular disentanglement during the post-drawing process. It has been demonstrated by other researchers that the draw ratio of UHMWPE fibre can be improved by adding polyethylene with a smaller molecular weight—e.g. high density polyethylene (HDPE)—as shown in Figure 8.6 [186]. This is because polymers with shorter molecular chains are easier to disentangle during the post-drawing process, thus avoiding the breakage of UHMWPE molecules due to stress concentration. By adding PE-g-MWCNTs which have compatible surface with UHMWPE and thus can be uniformly dispersed in the UHMWPE matrix, a similar phenomenon is expected.
To analyze the reinforcement of PE-g-MWCNTs on UHMWPE fibre, the tensile properties of 3wt% PE-g-MWCNT/UHMWPE fibre were compared with pure UHMWPE fibre. As shown above, fibre diameter has great influence on tensile test results, too. Thus, only fibres with the same diameter (20 to 25 µm) such as pure UHMWPE fibre were used for the comparison so as to investigate the influence of CNTs on fibre tensile properties. Twenty fibres were tested for each sample using the test method described in Chapter 4 and the results are shown in Figure 8.7.

It was found that both tensile strength and modulus of the composite fibres increased significantly as the MWCNT loading increased from 1wt% to 3wt%. At 3wt%, the tensile strength and modulus of PE-g-MWCNT/UHMWPE fibre reached 4.02 and 125.5 GPa, respectively, which represented a 19% and 23% increase compared to pure UHMWPE fibre. The fibre's ballistic performance index $U^{*(1/3)}$ calculated from Cunniff’s model also increased to 996.4
m/s, which is higher than the requirement for the objective of a 25% weight reduction in body armour.

Figure 8.7 (a) Figure 8.7 (b)

Figure 8.7 (c) Figure 8.7 (d)

Figure 8.7 Tensile properties of gel spun UHMWPE and MWCNT/UHMWPE fibre
(a) Strength (b) Modulus (c) Strain (d) $U^{(1/3)}$

In order to compare the reinforcement of MWCNTs to UHMWPE fibre quantitatively, the reinforcing efficiency was calculated using “rule of mixture” equations which are based on the
weighted contribution of the fibre and the matrix. The “rule of mixture” was first developed for fibre reinforced composite and is widely used to predict the modulus and strength of fibre reinforced composites. The simplest form of the “rule of mixture” is shown in Equation 8.1, which assumes that load is perfectly transferred between the fibre and the matrix. The density of composite $\rho_c$ can be calculated based on the volume fraction of reinforcing fibre $V_f$ and matrix $V_m$.

$$\rho_c = \rho_f V_f + \rho_m V_m$$

Equation 8.1

Where the density of reinforcing fibre and matrix $\rho_f$ and $\rho_m$ are known. For unidirectional composites, the Young’s modulus of the composite $E_c$ can be calculated using Equation 8.2.

$$E_c = E_f V_f + E_m V_m$$

Equation 8.2

In this equation, the Young’s modulus of reinforcing the fibre and the matrix, referred as $E_f$ and $E_m$, respectively, are known. However, since CNTs are discontinuous and are not perfectly aligned, a modified version of the “rule of mixture” is needed. Cox [187] introduced the concept of the effective Young’s modulus for short fibre embedded into a matrix by defining the length efficiency factor $\eta_l$ and the orientation factor $\eta_0$ as the reduction ratio of the filler’s intrinsic Young’s modulus. According to Cox’s modification, the modulus of CNT reinforced composite can be calculated by Equation 8.3. A similar equation formulated for strength is shown in Equation 8.4.

$$E_c = \eta_l \eta_0 E_{CNT} V_{CNT} + E_m (1 - V_{CNT})$$

Equation 8.3

$$\sigma_c = \eta_l \eta_0 \sigma_{CNT} V_{CNT} + \sigma_m (1 - V_{CNT})$$

Equation 8.4
The CNT length efficiency factor $\eta_l$ can vary between 0 and 1. The orientation factor $\eta_0$ is equal to 1 for fully aligned CNTs. Equations 8. 5 and 8. 6 can be used to evaluate the contributions of CNTs to the composite properties if the properties of the matrix, the composite and the CNT volume fraction are known. According to the equation, the effective modulus, strength can be defined as:

$$E_{\text{eff}} = E_{\text{CNT}} \eta_l \eta_0$$  \hspace{1cm} \text{Equation 8. 5}$$

$$\sigma_{\text{eff}} = \sigma_{\text{CNT}} \eta_l \eta_0$$  \hspace{1cm} \text{Equation 8. 6}$$

The orientation of PE-g-MWCNTs in gel spun UHMWPE fibre was analyzed by SEM. As shown in Figure 8. 8, polymer grafted MWCNTs were very well aligned along the fibre axis in the UHMWPE fibre. From the evidence of the SEM picture, an assumption that the orientation factor $\eta_l$ of PE-g-MWCNTs is equal to 1 has been made. Hence, an effective nanotube modulus (or nanotube strength), which incorporates only the length efficiency of the nanotubes, can be calculated as $E_{\text{eff}} = E_{\text{CNT}} \eta_l$ and $\sigma_{\text{eff}} = \sigma_{\text{CNT}} \eta_l$.

A good orientation of PE-g-MWCNT that existed in gel spun UHMWPE fibre can be explained by two reasons.

(1) The extended-chain conformation of polyethylene matrix.

In gel spun UHMWPE fibre, the linear polyethylene polymer chains are perfectly aligned along fibre axis which are rare in polymer materials. During the post drawing process with drawn ratio as high as over 100 times, polymer chains gradually aligned along fibre axis which create opportunity for carbon nanotubes with similar diameter as polyethylene micro-fibrils to change their orientation as well. Compared with melt spun textile fibre which consists of partial
orientated polymer chains, orientation of carbon nanotube is much easier in gel spun UHMWPE fibre.

(2) The compatibility between the polymer grafting layer on CNT and polyethylene matrix

The compatibility between the polymer grafting layer on CNT and polyethylene matrix allows the polyethylene chains to interact with PE-g-MWCNTs more readily and nucleate on PE-g-MWCNT surfaces due to epitaxy. For this reason, PE-g-MWNTs are potentially easier to align parallel to the axis direction compared with normal MWCNTs.

![Figure 8. 8 PE grafted MWCNTs bridge the crack of UHMWPE fibre](image)

The effective modulus and strength of polymer grafted MWCNTs are calculated and summarized in Table 8. 1. Effective CNT modulus and strength was found to be equal to 1244 GPa and 35 GPa, respectively, by using Equations 8. 5 and 8. 6. The experimental measurements of Young’s modulus and strength by scanning probe microcopy were in the range of 400-1900 GPa and 11-63 GPa, as shown in Table. 8. 2 [188]. Thus, it is reasonable to use the “rule of mixture” model to calculate reinforcing efficiency.
Table 8. 1 Effective modulus and strength of PE-g-MWCNT

<table>
<thead>
<tr>
<th>Fibre tensile properties</th>
<th>Modulus</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property increase</td>
<td>22.9%</td>
<td>19.0%</td>
</tr>
<tr>
<td>From 102.12 to 125.51GPa</td>
<td>From 3.375 to 4.02 GPa</td>
<td></td>
</tr>
<tr>
<td>PE-g-MWCNT effective properties</td>
<td>1244.4 GPa</td>
<td>34.7GPa</td>
</tr>
</tbody>
</table>

Table 8. 2 shows the effective modulus and strength of various types of carbon nanotubes summarized from various literature [188]. Compared to effective modulus and strength of CNTs from the literature, the polymer grafted MWCNTs obtained in this study showed higher values. This demonstrates that a high reinforcing efficiency to UHMWPE was achieved through polymer grafting on MWCNTs.

Table 8. 2 Effective modulus and strength of CNTs from literature [188]

<table>
<thead>
<tr>
<th>Type of CNT</th>
<th>$d_e$ [nm]</th>
<th>$E_{eff}$ [GPa]</th>
<th>$\sigma_{eff}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>1.4 nm</td>
<td>971 GPa</td>
<td>126 GPa</td>
</tr>
<tr>
<td>MWCNT</td>
<td>15 nm</td>
<td>929 GPa</td>
<td>121 GPa</td>
</tr>
</tbody>
</table>

To compare the reinforcing efficiency of polymer grafted MWCNTs with the coupling agent functionalized MWCNTs studied in Chapter 7, the effective modulus and strength of coupling agent functionalized MWCNTs were calculated and shown in Table 8. 3. The effective modulus and strength of coupling agent functionalized MWCNTs were calculated to be 240 GPa and 21 GPa, respectively, which are much lower than polymer grafted MWCNTs. From this comparison, it was demonstrated that a higher reinforcing efficiency to UHMWPE fibres can be realized by MWCNT polymer grafting.
Table 8. 3 Effective modulus and strength of Ti-MWCNT

<table>
<thead>
<tr>
<th>Property increase</th>
<th>Modulus</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.76%</td>
<td>10.5%</td>
</tr>
<tr>
<td></td>
<td>From 102.1 to 104.9 GPa</td>
<td>From 3.375 to 3.73 GPa</td>
</tr>
</tbody>
</table>

PE-g-MWCNT/UHMWPE fibres with different MWCNT volume fractions were prepared and the slope of increase in modulus versus CNT volume fraction \( \frac{dY}{dV_{CNT}} \) proposed by Coleman was used in this study to quantify the enhancement in Young’s modulus [189]. By adding 0.67 v% (1 wt%) of PE-g-MWCNTs in to UHMWPE, a dramatic increase in Young’s modulus from 102.1 GPa to 117.3 GPa was observed and \( \frac{dY}{dV_{CNT}} \) was calculated to be as high as 2246 GPa. However, \( \frac{dY}{dV_{CNT}} \) was found to decrease as higher CNT volume fractions were applied (as shown in Table 8. 4). The decrease in CNT reinforcement efficiency with volume fraction can be explained by the deterioration of CNT dispersion as volume fraction increased. Researchers have shown that the enhancement in mechanical properties of CNT reinforced composites is strongly dependent upon the level of CNT dispersion. It is thus believed that the dispersion deteriorates when the CNT volume fraction is higher than 0.67%, which slows that increase in composite’s tensile properties.

Table 8. 4 Effective modulus of PE-g-MWCNT as a function of volume fraction

<table>
<thead>
<tr>
<th>CNT volume fraction</th>
<th>0.67 v% (1 wt%)</th>
<th>1.35 v% (2 wt%)</th>
<th>2.05 v% (3 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{dY}{dV_{CNT}} ) (GPa)</td>
<td>2246</td>
<td>1588</td>
<td>1142</td>
</tr>
</tbody>
</table>
8.3.4 Morphology and microstructure

Figure 8. 9 shows a SEM image of fracture surfaces of the PE-g-MWCNT/UHMWPE fibre after the tensile test. It is evident that nanotubes coated by thick layers of polymer protrude from the composite fracture surfaces. Fractured PE-g-MWCNTs were found pulling out from the matrix, which suggests a strong interface bonding exists between the polyethylene grafted carbon nanotube and the UHMWPE matrix.

![SEM image of fracture surfaces](image)

**Figure 8. 9 Cross section image of PE-g-MWCNT/UHMWPE fibre**

8.4 Reinforcing mechanism of polymer grafted CNTs

In this study, polyethylene molecular chains were successfully grafted onto the surface of MWCNTs to improve the compatibility between MWCNTs and the UHMWPE matrix. PE-g-MWCNTs exhibited higher reinforcing efficiency than coupling agent treated MWCNTs. The improvement in the tensile properties arises from several factors, including improvement of CNT dispersion and interface bonding.
(1) Improvement in CNT dispersion

Due to their high surface energy, CNTs tend to form bundles, as was found in Chapter 5 where pristine MWCNTs were used as reinforcement for UHMWPE fibres. With PE molecular chains grafted on the MWCNT surface they have better affinity with the UHMWPE matrix and can thus be better dispersed in the matrix, allowing a more uniform load distribution. As can be seen in Figure 8. 10, individual nanotubes can be found in the fractured surface of the UHMWPE fibre. Good alignment along fibre axis was observed which is critical for higher reinforcement efficiency.

(2) Improvement load transfer on interface

It is expected that the PE molecular chains grafted onto MWCNTs could enable a more efficient load transfer from the matrix to the nanotubes. In Chapter 7, a coupling agent was used to functionalize MWCNTs and improvement in mechanical properties was found. Compared to the short alkyl chains grafted on MWCNTs through the coupling agent used in Chapter 7, the molecular chains of polyethylene grafted on the MWCNT surface are much longer. Thus, it is expected that the load transfer layer, which contains the entanglements of molecules from grafted polymer and matrix polymer, has stronger bonding and will provide more efficient load transfer on the MWCNT and UHMWPE interface.

![Figure 8. 10 Interface between PE-g-MWCNT and UHMWPE](image-url)
8.5 Conclusion

In this study, PE-g-MWCNT/UHMWPE composite fibres with significantly improved tensile properties have been successfully prepared through the gel spinning process. FTIR characterization indicated that polyethylene molecular chains were covalently grafted to MWCNTs. TEM images of PE-g-MWCNT showed that the thickness of the grafted PE molecules is controllable to as thin as 6 nm. The SEM of the cross section of PE-g-MWCNT/UHMWPE fibre confirmed a strong bonding between MWCNTs and the UHMWPE matrix on the interface.

UHMWPE fibre with improved drawability was observed after adding PE-g-MWCNTs. Maximum post-draw ratio increased from around 45 to 125 and the diameter of fibre decreased from 25 μm to 15 μm. 3wt% PE-g-MWCNT/UHMWPE fibre with a diameter of 15 μm was obtained under the same post-drawing conditions as pure UHMWPE fibre and showed tensile strength and modulus of 5.0 GPa and 150 GPa, respectively. By optimizing post-drawing conditions, fibre with a diameter as small as 11 μm can be obtained. The tensile strength of the resultant fibre is over 7 GPa, which is the highest tensile strength of UHMWPE fibre from gel spinning process that has been reported.

To investigate the reinforcement of CNTs on UHMWPE fibre, PE-g-MWCNT/UHMWPE and UHMWPE fibres with the same diameter were tested and compared. The Young's modulus and tensile strength of composite fibre kept increasing up to at least 3 wt% and an enhancement of 23% and 19% was observed. The effective Young’s modulus and strength was calculated based on the “rule of mixture”. Compared to the effective modulus and strength calculated from coupling agent functionalized MWCNTs (as shown in Chapter 7), PE-g-MWCNTs showed much higher properties. The significantly higher reinforcing efficiency
suggests that an improved dispersion and load transfer achieved in the PE-g-MWCNT/ UHMWPE composite fibre and the surface modification on MWCNTs by polymer grafting is a successful method for producing strong MWCNT/UHMWPE composite fibre. The fibre's ballistic performance index $U^{*(1/3)}$ also increased to 996.4 m/s. According to theoretical calculation, $U^{*(1/3)}$ of only 862 m/s or higher is needed to reach the objective of a 25% weight reduction in body armour. Thus, reinforcing UHMWPE fibre with PE-g-MWCNTs is a feasible method to reach the goal of the CRTI project.
Chapter 9- Summary and suggestion for future work

9.1 Major achievements of the present thesis

This thesis is part of the research project for developing strong fibre material with the objective to reduce the weight of IED body armour by 25%. In order to reduce the weight of body armour, high performance fibres with higher tensile properties are needed. Motivated by this urgent need, an extensive study has been conducted to develop and optimize new processes to improve CNT dispersion and compatibility between CNTs and the UHMWPE matrix.

In the beginning of the study, the feasibility of using pristine CNTs to reinforce UHMWPE fibre was discussed. However, no statistically significant improvement in tensile properties was found after adding up to 1.5% MWCNTs. These results demonstrated the necessity of chemical functionalization to improve MWCNT dispersion in the UHMWPE matrix. A coupling agent (which is one of the most commonly used substances to improve the capability between fillers and the polymer matrix in the composite industry) was applied to CNTs with a similar purpose. The UHMWPE fibre reinforced by a 3% titanate coupling agent treated MWCNT showed a 10.5% increase in tensile strength. However there is no improvement in the ballistic performance index $U^{*1/3}$ compared to pure UHMWPE fibre.

An innovative polymer grafting MWCNT was used to reinforce UHMWPE fibre for the first time, with the objective to further improve interface compatibility and reinforcing efficiency. It was found that the drawability of UHMWPE fibre was significantly improved by incorporating PE-g-MWCNTs. Compared to pure UHMWPE fibres with a diameter of 25μm, fibres with a much smaller diameter of 15 μm can be obtained. The tensile strength, modulus and strain of 3wt% PE-g-MWCNT/UHMWPE fibre is 5 GPa, 150 GPa and 3.7%, respectively. Since fibre
Chapter 9- Summary and Suggestion For Future Work

diameter has a strong effect on fibre tensile properties, only PE-g-MWCNT/UHMWPE fibre with the same diameter as pure UHMWPE fibre were compared to investigate the reinforcing effect of CNTs. At 3% load level, the tensile strength, modulus and strain increased by 19%, 23% and 9%. The reinforcing efficiency of MWCNTs was significantly improved by polymer grafting, compared to pristine MWCNTs and coupling agent functionalized MWCNTs. The ballistic performance of the 3wt% PE-g-MWCNT/UHMWPE reached around 966.4 m/s, which is much higher than required to reduce the weight of body armour by 25%, according to Cunniff’s model. Thus, the objective of the CRTI project was successfully achieved. The major achievements of this thesis are summarized in detail in the following:

9.1.1 Effect of spinning conditions on fibre tensile properties and morphology

UHMWPE fibre is produced through the gel spinning process due to its extremely high polymer chains. It was found that the fibre properties and morphology were very sensitive to spinning conditions. It is therefore very important to discuss the effects of various spinning parameters on the tensile properties of gel spun fibre and to find the optimum spinning conditions for spinning conducted using laboratory scale spinning systems.

In this study, the effect of the three most important spinning parameters on fibre properties were studied: polymer concentration, spinning temperature and winding speed. The optimum spinning conditions were found to be with a polymer concentration of 3.5%, a spinning temperature of 150°C and a winding speed of 5 FPM. Under these conditions, as-spun UHMWPE fibre showed an open shish kebab structure which was found to have adequate strength to endure the tension during the post-drawing process and loose enough to be easily unfolded and straightened. The optimization process is very important because it helped to understand the relationship between UHMWPE tensile properties and morphologies. Also,
finding the optimum spinning conditions builds up a good calibration foundation for future spinning experiments.

9.1.2 Feasibility of reinforcing UHMWPE fibre by pristine nanotubes

Compared to chemical functionalization, physical methods are preferred in some applications because they will not cause the disruption of CNT structure. In addition, mechanical methods are relatively easy to apply and the cost is usually lower than chemical treatment. Since UHMWPE fibre is a widely used high performance fibre, the treatment of CNTs as reinforcement for UHMWPE fibre should be easy to apply in industry, which is why the mechanical method was taken into consideration in the first place. In this study, various widely used mechanical methods for dispersing particles were studied including sonication, ball milling, and microfluidizing. In addition, an innovative water spray method was studied. Results showed that ultra-sonication was not a sufficient method for dispersing pristine CNTs, as larger agglomerates found in fibres and tensile properties dropped after incorporating these CNTs. Ball milling is more effective in decreasing the size of CNTs agglomerates than ultra-sonication as tensile properties of the MWCNT/UHMWPE showed a slight increase after adding 1% MWCNTs. However, statistical analysis showed that these improvements in tensile properties were not significant. Other methods such as microfluidizing and solvent assistant dispersion were similarly unable to obtain uniform and stable dispersion. The conclusion is therefore that chemical functionalization of carbon nanotubes is necessary for better dispersion and higher reinforcing efficiency.
9.1.3 Reinforced UHMWPE fibre by coupling agent functionalized CNTs

CNT dispersion and reinforcement in UHMWPE fibre was improved after being functionalized by a coupling agent. MWCNTs with a concentration as high as 3wt% can be dispersed in UHMWPE. Tensile strength of MWCNT/UHMWPE composite fibre increased by 10.5% by adding 3wt% Ti-MWCNTs, compared to using pure UHMWPE fibre. However, no improvement in Young’s modulus and strain was observed, which led to little improvement in $U^{*(1/3)}$.

9.1.4 Polyethylene grafted CNTs reinforced gel spun UHMWPE

This is the first study focusing on using a polyethylene grafted CNT to reinforce gel spun UHMWPE fibre. Through grafting polyethylene molecular chains onto CNTs, the CNT compatibility in the UHMWPE matrix greatly improved. Compared to pristine CNTs (which formed agglomerates the size of micrometers), individual nanotubes were found after polymer grafting, indicating a uniform dispersion. PE-g-MWCNT reinforced UHMWPE fibres were found to have tensile strength, modulus and strain approximately 19%, 23% and 9% higher, respectively, than pure UHMWPE fibre at 3wt% CNT loading. The effective modulus and strength of polyethylene grafted MWCNTs was calculated from the “rule of mixture” and was found to be 419% and 667.5% higher than coupling agent functionalized MWCNTs, which demonstrated a significant improvement in reinforcing efficiency by polymer grafting. The ballistic performance index $U^{*(1/3)}$ was calculated to be 966.4 m/s which is much higher than what is needed to reach the goal of reducing the weight of body armour by 25%

More significantly, the maximum draw ratio of UHMWPE fibre was found to greatly increase from 45 to 125 by incorporating 3wt% PE-g-MWCNTs. Fibre with tensile strength and modulus of 5 GPa and 150 GPa, respectively, were obtained under the same spinning and post-
Chapter 9- Summary and Suggestion For Future Work

drawing conditions as pure UHMWPE fibre. By further improving the post-drawing conditions, fibres with a diameter as small as 11μm were obtained with tensile strength over 7 GPa, which is within the same level of the strongest UHMWPE ever developed by researchers.

Commercially available UHMWPE fibres are produced by two different processes that use decalin and mineral oil, respectively, as solvents. It is therefore of great interest to develop processes to reinforce UHMWPE fibre through CNTs using the two solvents. Ruan’s [24] group proved that acid purified MWCNTs significantly improved the mechanical properties of UHMWPE fibre when decalin was used as a solvent. However, similar results could not be obtained when mineral oil was used as a solvent. Due to the high viscosity, it is more difficult to debundle and disperse CNTs in mineral oil. The current study developed an innovative process that could significantly improve CNT dispersion and load transfer on the CNT/UHMWPE interface. Significant improvement in the tensile properties of UHMWPE fibre was observed by reinforcement with PE-g-MWCNTs using mineral oil as a solvent. The methods introduced in this thesis can be easily adopted on an industry scale production of UHMWPE fibre with improved tensile properties.

9.2 Suggestion for future work

9.2.1 Characterization of CNT alignment in gel spun UHMWPE fibre

In this study, preliminary evidence of CNT alignment was found in UHMWPE fibres through SEM images. However, it will be of great interest to study how the alignment of CNTs in UHMWPE was obtained during the post-drawing process using characterization methods such as polarized Raman spectroscopy.
9.2.2 Quantitatively study load transfer between CNT and UHMWPE

In Chapter 8 of this study, it was found that by grafting MWCNTs with PE molecular chains the tensile properties of the composite UHMWPE fibre significantly improved. Through the SEM analysis of the fractured surface of the composite fibre it was observed that strong adhesion was achieved on the interface. In the future, a quantitative measurement of the load transfer on the CNT and UHMWPE interfaces could give more direct information for improvement in compatibility between CNTs and UHMWPE by assessing different surface functionalization properties.

9.2.3 Gel spun CNT reinforced UHMWPE fibre using commercial production line

All the experimental results presented in this thesis are based on a laboratory scale extruder and homemade post-drawing equipment. Gel spinning is a complex spinning process that depends a great deal on the processing equipment. Thus, more efforts are needed to reproduce the results on a production line. It is expected that with better processing control, composite fibres with heightened properties could be obtained by applying a similar method on a large-scale commercial production line.
References


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Appendices

Appendix A Statistical analysis of orthogonal design of experiment

The result of orthogonal design of experiment was analyzed by calculating following parameters as shown in Equation A.1-A.4.

\[ T = \sum_{i=1}^{n} t_i \]  
Equation A.1

\[ CT = \left( \frac{\sum_{i=1}^{n} t_i}{n} \right)^2 \]  
Equation A.2

\[ O_j = \frac{1}{r} \sum_{i=1}^{m} k_{ij}^2 - \frac{CT}{n} \]  
Equation A.3

\[ s_j^2 = \frac{O_j}{f_j} \]  
Equation A.4

Table A.1 Analysis of orthogonal optimization using \( U^{(1/3)} \) as response

<table>
<thead>
<tr>
<th>Experiment NO</th>
<th>Concentration</th>
<th>Temperature</th>
<th>Winding speed</th>
<th>Error</th>
<th>( U^{(1/3)} ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>656.64</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>673.34</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>459.97</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>852.03</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>794.34</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>696.80</td>
</tr>
<tr>
<td>Experiment NO</td>
<td>Concentration</td>
<td>Temperature</td>
<td>Winding speed</td>
<td>Error</td>
<td>$U^{*1/2}$ (m/s)</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------</td>
<td>-------------</td>
<td>---------------</td>
<td>-------</td>
<td>-----------------</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>629.70</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>661.10</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>499.51</td>
</tr>
<tr>
<td>K1j</td>
<td>1789.94</td>
<td>2138.36</td>
<td>2014.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2j</td>
<td>2343.17</td>
<td>2128.77</td>
<td>2011.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K3j</td>
<td>1777.30</td>
<td>1643.28</td>
<td>1884.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K1j^2</td>
<td>3203901.44</td>
<td>4572596.12</td>
<td>4058353.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2j^2</td>
<td>5490457.64</td>
<td>4531680.63</td>
<td>4047634.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K3j^2</td>
<td>3158795.00</td>
<td>2700367.90</td>
<td>3549486.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Kij: sum of test result of fibre spun with factor j at level i.

The influence of each factor on the objective will also be determined. Total variance $Q_r$, degree of total freedom $f_r$, square deviation for factor $S^2_{\text{factor}}$, square deviation for error $S^2_e$ can be calculated from Equations A.5 to A.9.

$$Q_r = Q_{\text{factor}} + Q_e$$  \hspace{1cm} \text{Equation A.5}

$$Q_r = \sum_{i=1}^{n} x_i^2 - \left( \frac{\sum_{i=1}^{n} x_i}{n} \right)^2, \quad Q_j = \frac{1}{r} \sum_{i=1}^{n} K_{ij}^2 = \left( \frac{\sum_{i=1}^{n} x_i}{n} \right)^2 (j = 1,2,..,k)$$  \hspace{1cm} \text{Equation A.6}

$$f_r = f_{\text{factor}} + f_e$$  \hspace{1cm} \text{Equation A.7}
\[ S_{\text{factor}}^2 = \frac{Q_{\text{factor}}}{f_{\text{factor}}} \]  
Equation A.8

\[ S_e^2 = \frac{Q_e}{f_e} \]  
Equation A.9

Where \( Q_{\text{factor}} \) is the variance for factor, \( Q_e \) is the variance for error, \( f_{\text{factor}} \) is the degree of freedom for factor, \( f_e \) is the degree of freedom for error, \( S_{\text{factor}}^2 \) is the square deviation for factor, and \( S_e^2 \) is the square deviation for error. The F value for each factor is calculated using Equation A.10.

\[ F_{\text{factor}} = \frac{S_{\text{factor}}^2}{S_e^2} \]  
Equation A.10

An F test was applied to analyze the significance of the influence of factors on fibre \( U^{*2} \).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Sum of squares ( SS_i )</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F</th>
<th>( F_\alpha )</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>67969.95</td>
<td>2</td>
<td>33984.97</td>
<td>167.01</td>
<td>( F_{0.01}(2,2)=99 )</td>
<td>99%</td>
</tr>
<tr>
<td>B</td>
<td>50638.63</td>
<td>2</td>
<td>25319.31</td>
<td>124.43</td>
<td>( F_{0.025}(2,2)=39 )</td>
<td>99%</td>
</tr>
<tr>
<td>C</td>
<td>4109.71</td>
<td>2</td>
<td>2054.86</td>
<td>10.10</td>
<td>( F_{0.05}(2,2)=19 )</td>
<td>90%</td>
</tr>
<tr>
<td>Error</td>
<td>406.98</td>
<td>2</td>
<td>203.49</td>
<td></td>
<td>( F_{0.1}(2,2)=9 )</td>
<td>90%</td>
</tr>
</tbody>
</table>
# Appendix B Statistical analysis of tensile test data

Table B.1 F-test and T-test of tensile properties of UHMWPE fibre reinforced by sonication dispersed MWCNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average(GPa)</td>
<td>STDEV(GPa)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
<td></td>
</tr>
<tr>
<td>UHMWPE</td>
<td>3.375</td>
<td>0.353</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%MWCNT/UHMWPE</td>
<td>2.108</td>
<td>0.218</td>
<td>0.018</td>
<td>4.10054E-20</td>
<td></td>
</tr>
<tr>
<td>1%MWCNT/UHMWPE</td>
<td>2.677</td>
<td>0.234</td>
<td>0.033</td>
<td>5.5259E-11</td>
<td></td>
</tr>
<tr>
<td>1.5%MWCNT/UHMWPE</td>
<td>2.220</td>
<td>0.260</td>
<td>0.088</td>
<td>2.85412E-16</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Modulus</th>
<th>Average(GPa)</th>
<th>STDEV(GPa)</th>
<th>P(F&lt;=t)</th>
<th>P(T&lt;=t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>102.120</td>
<td>16.083</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%MWCNT/UHMWPE</td>
<td>68.958</td>
<td>14.591</td>
<td>0.3383</td>
<td>3.04E-09</td>
</tr>
<tr>
<td>1%MWCNT/UHMWPE</td>
<td>85.196</td>
<td>11.461</td>
<td>0.0633</td>
<td>0.000178941</td>
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<tr>
<td>1.5%MWCNT/UHMWPE</td>
<td>51.547</td>
<td>7.659</td>
<td>0.0009</td>
<td>1.13162E-18</td>
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<table>
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<tr>
<th>Strain</th>
<th>Average(%)</th>
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<th>P(F&lt;=t)</th>
<th>P(T&lt;=t)</th>
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</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>0.038</td>
<td>0.006</td>
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<td></td>
</tr>
<tr>
<td>0.5%MWCNT/UHMWPE</td>
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<td>0.3105</td>
<td>0.06227854</td>
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<td>1%MWCNT/UHMWPE</td>
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<td>1.5%MWCNT/UHMWPE</td>
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<td>0.007</td>
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Table B.2 F-test and T-test of tensile properties of UHMWPE fibre reinforced by sonication and ball mill dispersed MWCNTs

<table>
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<tr>
<th>Sample</th>
<th>Tensile strength</th>
<th>Modulus</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average(GPa)</td>
<td>STDEV(GPa)</td>
<td>P(F&lt;=t)</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>3.375</td>
<td>0.353</td>
<td></td>
</tr>
<tr>
<td>0.5%MWCNT/UHMWPE</td>
<td>3.530</td>
<td>0.398</td>
<td>0.260</td>
</tr>
<tr>
<td>1%MWCNT/UHMWPE</td>
<td>3.561</td>
<td>0.539</td>
<td>0.013</td>
</tr>
<tr>
<td>1.5%MWCNT/UHMWPE</td>
<td>3.212</td>
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<td>0.266</td>
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</table>

<table>
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<tr>
<th></th>
<th>Average(GPa)</th>
<th>STDEV(GPa)</th>
<th>P(F&lt;=t)</th>
<th>P(T&lt;=t)</th>
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</thead>
<tbody>
<tr>
<td>UHMWPE</td>
<td>102.120</td>
<td>16.083</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%MWCNT/UHMWPE</td>
<td>95.98</td>
<td>16.80</td>
<td>0.435</td>
<td>0.169</td>
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<tr>
<td>1%MWCNT/UHMWPE</td>
<td>103.279</td>
<td>25.538</td>
<td>0.026</td>
<td>0.797</td>
</tr>
<tr>
<td>1.5%MWCNT/UHMWPE</td>
<td>86.49</td>
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<th>P(T&lt;=t)</th>
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<tr>
<td>UHMWPE</td>
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<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5%MWCNT/UHMWPE</td>
<td>0.035</td>
<td>0.004</td>
<td>0.037</td>
<td>0.016</td>
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<td>1%MWCNT/UHMWPE</td>
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<td>1.5%MWCNT/UHMWPE</td>
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Table B.3  F-test and T-test of tensile properties of UHMWPE fibre reinforced by coupling agent functionalized MWCNTs

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<th>Sample</th>
<th>Tensile strength</th>
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<tr>
<td></td>
<td>Average(GPa)</td>
<td>STDEV(GPa)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
<td></td>
</tr>
<tr>
<td>UHMWPE</td>
<td>3.375</td>
<td>0.353</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%MWCNT/UHMWPE</td>
<td>3.466</td>
<td>0.348</td>
<td>0.468</td>
<td>0.343</td>
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<tr>
<td>2%MWCNT/UHMWPE</td>
<td>3.563</td>
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<tr>
<td>3%MWCNT/UHMWPE</td>
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<table>
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<tr>
<th>Sample</th>
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<th></th>
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<tbody>
<tr>
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<td>Average(GPa)</td>
<td>STDEV(GPa)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
<td></td>
</tr>
<tr>
<td>UHMWPE</td>
<td>102.120</td>
<td>16.083</td>
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<tr>
<td>1%MWCNT/UHMWPE</td>
<td>102.700</td>
<td>13.335</td>
<td>0.138</td>
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<tr>
<td>2%MWCNT/UHMWPE</td>
<td>102.792</td>
<td>13.564</td>
<td>0.150</td>
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<tbody>
<tr>
<td></td>
<td>Average(%)</td>
<td>STDEV(%)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
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</tr>
<tr>
<td>UHMWPE</td>
<td>0.038</td>
<td>0.006</td>
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<tr>
<td>1%MWCNT/UHMWPE</td>
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<td>2%MWCNT/UHMWPE</td>
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<td>3%MWCNT/UHMWPE</td>
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<td>0.006</td>
<td>0.554</td>
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Table B.4 F-test and T-test of tensile properties of UHMWPE fibre reinforced by polymer grafted MWCNTs

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<th>Tensile strength</th>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Average(GPa)</td>
<td>STDEV(GPa)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>3.375</td>
<td>0.353</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%MWCNT/UHMWPE</td>
<td>3.617</td>
<td>0.292</td>
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<td>2%MWCNT/UHMWPE</td>
<td>3.770</td>
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<td>3%MWCNT/UHMWPE</td>
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<td>0.372728</td>
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<table>
<thead>
<tr>
<th>Sample</th>
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</thead>
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<tr>
<td></td>
<td>Average(GPa)</td>
<td>STDEV(GPa)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>102.120</td>
<td>16.083</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%MWCNT/UHMWPE</td>
<td>117.305</td>
<td>11.527</td>
<td>0.081427</td>
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<table>
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<th>Sample</th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average(%)</td>
<td>STDEV(%)</td>
<td>P(F&lt;=t)</td>
<td>P(T&lt;=t)</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>0.038</td>
<td>0.006</td>
<td></td>
<td></td>
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<tr>
<td>1%MWCNT/UHMWPE</td>
<td>0.041</td>
<td>0.004</td>
<td>0.032912</td>
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<td>0.004</td>
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<td>0.042</td>
<td>0.006</td>
<td>0.263781</td>
<td>0.072041</td>
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Appendix C Dispersing MWCNTs through mechanical methods

1. Dispersing MWCNT in mineral oil by microfluidizing

Microfluidizing is a high shear fluid process that has been used in recent years for particle de-agglomeration, dispersion and size reduction. In this process, high pressures are used in order to generate high shear which forces CNT dispersion to go through specially designed micro channels at high flow rates to pull CNT agglomerates apart. The process pressure and the channel geometry control the velocities inside the channels, and therefore modulate the energy dissipation.

1.1 Material and experiment

MWCNT/mineral oil mixtures samples with MWCNT concentrations of 0.5wt% were prepared and sent to Microfluidics Co., Ltd. for processing. The feed material was driven at constant pressure through the interaction chamber which has micro-channels with unique fixed-geometry inside the microfluidizer. The microfluidizer processor (model M-110P) was used to process the MWCNT/mineral oil dispersion. Different levels of shear forces were applied to the sample by varying the pressure from 10,000 to 30,000 psi and passed from 1 to 3 during the processing, as listed in Table. C.1.

Table C.1 Processing condition of Mircofluidizer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure(Psi)</th>
<th>Pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low shear</td>
<td>10K</td>
<td>1pass</td>
</tr>
<tr>
<td>Medium shear</td>
<td>30K</td>
<td>1pass</td>
</tr>
<tr>
<td>High shear</td>
<td>30K</td>
<td>3pass</td>
</tr>
</tbody>
</table>
1.2 Results and discussion

The dispersion of MWCNT in mineral oil after treatment by microfluidizer was examined by optical microscopy. As can be seen in Figure C.1, big MWCNT agglomerations with a size of about 10μm can be found after treatment under low shear conditions. These extra-large agglomerates disappeared after two more passes in the microfluidizing machine at the same pressure level.

![Image of MWCNT dispersion](image.png)

(1) Low shear mode  (2) Medium shear mode  (3) High shear mode

Figure C.1 MWCNTs dispersion in mineral oil processed by microfluidizer

The particle sizes of MWCNTs processed by the microfluidizer under different conditions were estimated by photon correlation spectroscopy (PCS) using a Zetasizer™ (Malvern Instruments Worcestersher, UK). It was observed that with when low shear force was used, the size of CNT agglomerates was almost the same as CNTs dispersed by ultra-sonication. As shear force increased, the size of MWCNT agglomerates decreased slightly from about 3400nm to 2560 nm under the high shear mode treatment. The size of MWCNT agglomerates processed by microfluidization was about 1/3 smaller than those processed by ultra-sonication, as shown in Table.C.2. However, neither process is effective enough to debundle MWCNT agglomerates.
### Table C.2 Average particle size in MWCNT/UHMWPE solution

<table>
<thead>
<tr>
<th>Sample treated by</th>
<th>Average Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonication</td>
<td>3400</td>
</tr>
<tr>
<td>Microfluidizer</td>
<td></td>
</tr>
<tr>
<td>Low shear</td>
<td>3063</td>
</tr>
<tr>
<td>Medium shear</td>
<td>2915</td>
</tr>
<tr>
<td>High shear</td>
<td>2596</td>
</tr>
</tbody>
</table>

2. **Dispersing MWCNT in mineral oil by solvent assistant spraying method**

In this method, an aqueous solution of carbon nanotube with surfactant was made and sprayed onto the surface of fine powder UHMWPE. The carbon nanotubes were adsorbed on the surface of the UHMWPE powders. The UHMWPE that adsorbed the CNTs were then dissolved in solvent and the MWCNTs/UHMWPE composites (in the form of film) were prepared from the solution. Similar methods were used in this study to disperse MWCNTs in UHMWPE to produce composite fibre.

#### 2.1 Material and experiment

The UHMWPE and MWCNTs used in this study are the same as those listed in Chapter 3. Distilled water was used as the solvent to disperse MWCNTs with sodium dodecylbenzene sulfate (SDS) as a surfactant. 10 mL solutions containing 12.5, 25 and 37.5 mg of MWCNTs and 1 wt % SDS based on H₂O were ultrasonicated using a bath sonicator for 3 hours and then centrifuged at 3000 rpm for 20 min. The MWCNT coated UHMWPE powders were then dried overnight in a vacuum oven under 80°C. 5wt% MWCNT coated UHMWPE powders were
dissolved in mineral oil and heated up to prepare gel for gel spinning. The gel preparation, spinning, and post-drawing processes are detailed in Chapter 3.

2.2 Results and Discussion

The surface morphology of UHMWPE powder used in this work was observed under SEM. Instead of solid particles with smooth surfaces, the UHMWPE powder consisted of many nano-scale particles and fibrils. The diameter of the nanoparticles was around 800-900 nanometers while the diameter of the nanofibrils was around 100 nanometers, as measured from Figure C.2. Because of the above microstructure, many micro-voids form on the surface of the UHMWPE particles. These microvoids provide the channels for MWCNT/water solution to penetrate the whole particle, thus forming an even distribution of MWCNTs in the particle. Furthermore, the micro particles' and fibrils' structures greatly increased the surface area of the UHMWPE particle, which made it easy to adsorb MWCNTs.

![UHMWPE powder before and after spraying with MWCNT](FigureC.2)

(a) Before

(b) After

Figure C.2 UHMWPE powder before and after spraying with MWCNT
However, it was found that after spraying only 0.1wt% of MWCNTs, the surface of the UHMWPE particle was covered completely, as shown in Figure 2(b). Thus, the MWCNT/UHMWPE composite material made through this method is too low to improve the mechanical properties.