

Improved yarns and composites from CVDgrown CNT forests

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Abstract

In this thesis, the effect of polymer infusion into a carbon nanotube (CNT) yarn or CNT web was investigated. A combination of morphological (scanning electron microscope (SEM) and transmission electron microscope (TEM)), thermal (thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC)) and mechanical (tensile testing) analysis techniques provided an understanding of the structure and properties of the polymer-infused CNT yarns and CNT webs.

In order to understand the interactions of the CNTs in the CNT web and yarn structures alone, various densification techniques including twisting and solvent were used. The CNTs were drawn from the CNT forests and formed a web of longitudinally oriented CNTs. Such CNT webs were then densified into the CNT yarns using the densification techniques including solvent (acetone and ethanol) and twist (constant-length and shrinking-length). The effects of the densification on the mechanical and morphological properties of the CNT yarns were then studied. It was found that the solvent densification using acetone was more effective than ethanol in compressing the CNT web into a yarn. The mechanical properties of such acetone-densified CNT yarns were shown to be higher than those of the ethanol-densified CNT yarns, as well as of the CNT web itself. The CNT yarns produced by two different twist methods (constant-length and shrinking-length) confirmed that the constant-length CNT yarn had higher mechanical strength compared to the shrinking-length CNT yarn. In addition, such constant-length CNT yarn had a more uniform and cylindrical structure compared to the shrinking-length CNT yarn. The combination of the solvent and twist densification methods was also investigated and characterised using the tensile testing. The results showed that the densification of the CNT web by the constant-length twisting followed by acetone densification produced CNT yarns with the highest mechanical strength of 1.8GPa in this thesis.

Various polymers namely polyethylene, polypropylene and nylon 6,6, were incorporated into the CNT yarns and CNT webs and the effects of polymer solution concentrations,

molecular weights and crystallinity on the morphological, thermal and mechanical properties of the polymer-infused CNT yarns and CNT webs were studied. It was found that the polymer molecules adhered to the CNTs and grew disk like structures around the individual and bundles of the CNTs in the polymer-infused CNT yarns. The disk size, namely disk diameter, thickness and gap between the adjacent disks, for each polymer was also quantified from the SEM images. Such disk size analyses revealed that the disk growth around the CNTs was directly dependent on the polymer solution concentration with a greater concentration producing larger size disks. In the studies of polyethylene, such disks were smaller in diameter and thickness and further apart for the lower polymer solution concentration (0.01w/w%) compared to those of the 1w/w%. Furthermore, it was found that polyethylene with the higher molecular weight produced larger disks compared to the lower molecular weight polyethylene as well as polypropylene and nylon 6,6. This is due to the fact that the longer molecular chain of the higher molecular weight polyethylene facilitated the adhesion of one end of the polyethylene molecule to the nuclei, formed on the CNT, and caused the growth of larger disks accordingly.

The TGA characterisation of such polymer-infused CNT yarns showed that indeed such yarns had a higher CNT content in their structures than the polymer, while the DSC results showed that such disks were of semi-crystalline nature. The tensile testing results found that the mechanical properties of the polymer-infused CNT yarns were improved in terms of the tensile load bearing compared to those of the neat CNT yarns.

Furthermore, the CNT webs were also used to produce polymer-treated CNT webs to study the effects of the spatial confinement observed in the polymer-infused CNT yarns. The CNT yarn had a more compact structure compared to the open CNT web, resulting in hindrance of the polymer molecules in penetrating deeper into the CNT yarn and form disks. Using the CNT web instead of the CNT yarn, the polymer molecules were able to access the open CNT web structure and form disks evenly throughout. This was confirmed by the SEM characterisation of the disks. Such polymer-treated CNT webs were then twisted to form yarn structures (named web-to-yarn). The mechanical analysis of such polymer-treated web-to-yarns showed that the load at break for such web-to-yarn structures did indeed increase significantly compared to the CNT webs and their polymer-infused CNT yarn counterparts. This indicates that such interconnected structures increased the CNT participation in the load transfer. The method of crystallising the disks onto the CNT web first, allowed much more successful nucleation and growth of such disks from the CNT surface which resulted in a greater load bearing ability of the polymer-treated CNT yarns.

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or any other institution and affirms that to the best of my knowledge, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Signature:

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Date: 23/06/2017

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List of abbreviations

AFM	atomic force microscope
CNT	carbon nanotube
CVD	chemical vapor deposition
DSC	differential scanning calorimetry
DWCNT	double wall carbon nanotube
GPa	giga pascal
Н	hour
HMWPE	high molecular weight polyethylene
LC	liquid crystal
LMWPE	low molecular weight polyethylene
MWCNT	multiwall carbon nanotube
Ny	nylon 6,6
PE	polyethylene
PP	polypropylene
SEM	scanning electron microscope
Std dev	standard deviation
SWCNT	single wall carbon nanotube
TEM	transmission electron microscope
TGA	thermal gravimetric analysis
vdW	van der Waals
XRD	x-ray diffraction

List of publications

- Ehsan Jazaeri, Stephen Hawkins, Robert Shanks, George Simon, Incorporation of high density polyethylene with CNT yarn for improved mechanical properties, *MRS Spring Meeting and Exhibit*, Phoenix Arizona USA, 2016.
- 2- Ehsan Jazaeri, Robert Shanks, George P. Simon, Stephen Hawkins, Discoidal polymer crystallites as a strengthening mechanism in directly spun carbon nanotube yarn, manuscript in preparation.

Chapter 1

Introduction

1.1. Carbon nanotube yarn

Carbon nanotube (CNT) yarn is a promising material that can be potentially used as structural material for reinforcement. The fabrication of strong CNT yarn and its polymer composite yarn has been the focus of many research groups. Unlike carbon fibre yarns that require high temperature furnace to convert polymer yarns into carbon fibres, the CNT yarns could be made at room temperature. The possibility of drawing CNT yarns from vertically grown CNTs on a silica substrate was first reported by Jiang *et al.* [1]. In this method, called forest spinning, the CNT forest is produced by the chemical vapor deposition (CVD) method in a tube furnace where the silica substrate is coated with iron nanoparticles and placed inside the furnace. A carbon rich gas is then flowed through the tube reactor. The furnace is heated up to 650-850°C, at which temperature the CNT growth starts. The CNT forest is then taken out and the CNT yarn spinning can commence by drawing a width of the CNT forest. Such CNT forests contain CNTs with diameters of 10-100nm and multiwall structures with mixed number of walls (usually 2-14 walls).

The mechanical properties of the forest-spun CNT yarns are relatively high compared to those of the other CNT yarn fabrication methods or those of the carbon fibres (4-6 GPa) [2]. However, despite extraordinary tensile strength (50-150GPa) and tensile modulus (1-1.2TPa) of the individual CNTs, so far only a small fraction of such strength has been captured in the CNT yarn (5-7%), compared to the strength of conventional textile yarns such as cotton or wool (70-90%) [3]. This is far less than what the CNTs can tolerate in terms of stress loading, mainly due to the stress transfer mechanism in the CNT yarns being fundamentally different. In the conventional textile yarns, the tensile stress breaks the chemical bonds in the fibres thus the fibre breakage is the result of the tensile force being greater than the tensile strength of the individual fibres. In the CNT yarns, however, the

tensile strength of the individual CNTs is very high (50-150GPa) compared to the tensile strength of the CNT yarn. Therefore, upon tensile stress, the individual CNTs do not break their covalent bonds when the yarn fails, but rather slide relative to one another. This is because the interfacial shear strength of the nanotubes produced by the van der Waals attractions (vdW) is very low hence the applied tensile stress on the nanotubes becomes greater than its shear strength. Although more than a decade of research has investigated the mechanism of load transfer in the CNT yarn [2, 3], there have only been modest increases in the failure loads. Therefore, there is a need for new strategies by which mechanically stronger CNT yarns can be produced. One of such strategies is the new concept of infiltrating polymers within the CNT yarn in order to lock the individual and bundles of the CNTs together and ensure better load transfer under the tensile force.

1.2. Infiltration of polymer with the CNT

The CNT yarns greatly suffer from poor inter nanotube load transfer which leads to low tensile strength in the yarn. Most research studies to date, on the CNTs and their polymer composite, have been primarily focused on the addition of the CNTs to a majority phase polymer such as polyethylene. Polyethylene with its semi crystalline structure [4-6] has been shown to align around a material and form disk shaped structures [7, 8]. Such disks are known as shish-kebab structures in the literature where shish refers to the disk and kebab refers to the CNT.

Some research of the polymeric disks (shish-kebabs) crystallising on the individual and bundles of the CNTs in the polymer and CNT solution state has been done by Li *et al.* [5] and Li *et al.* [9]. Such polymeric solutions, prepared by dissolution into formic acid, sulfuric acid [10] or glycerine [5], were mixed with the dispersions of the CNTs, where the same solvent was used as the dispersant for the CNTs. This resulted in a homogenous polymer/CNT mixture which was then used for the fabrication of polymer-CNT nanocomposites. The polymer-CNT nanocomposite materials produced by such mixing of the polymer solution and the CNT dispersion still contained a majority phase of polymer and a small amount (<5wt%) of the CNTs in their composition. It is noted that unlike using

the formic or sulfuric acids, the use of glycerine does not damage the CNTs due to the low temperature processing (185°C) and less aggressive nature of glycerine compared to formic or sulfuric acids and hence there is no harmful effect on the CNT mechanical or electrical properties [9].

In the polymer-CNT nanocomposite materials, where the polymeric disks grow on the surface of the individual CNTs in the polymer/CNT mixture, primarily by controlled cooling of the mixture, such physically adhered polymeric disk structures, such as those of the polyethylene, polypropylene and nylon 6,6 have been shown to improve the mechanical strength of the nanocomposite compared to the nanocomposite with structures without disks [11, 12]. Such promising results indicate that by incorporating the polymeric disks onto the CNTs, the CNT inter nanotube cohesion can be improved which in turn leads to an increase in the load bearing capacity of the CNTs. Hence, one may take advantage of the light weightiness and the strength of the CNTs and improve the properties of the polymer-CNT composite [6]. This is especially important since the CNT rich composite fibres present strong and light weight structures which can be comparable with commercially availbale products such as Kevlar and carbon fibres.

1.3. Aims of the Ph.D. project

Since the CNT yarns suffer from poor inter nanotube load transfer, the incorporation of polymeric disks around the CNTs can act as clamps and fasten the individual and bundles of the CNTs together, thus increasing the load transfer between them. Some studies suggest that such disks can significantly increase the tensile strength of the polyethylene-rich composite [5, 6]. However, this thesis seeks to look at the other end of the polymer concentration spectrum, where small amounts of polymer are infused into the CNT yarn and produce the CNT-rich composite. To maintain a lightweight structure, it is important to incorporate as little polymer as possible. To this end, the CNT yarns were treated in solutions containing very low concentrations of polyethylene, polypropylene or nylon 6,6, in order to ensure the lowest possible polymer weight increase, compared to that of the CNT.

In order to prepare the polymer-infused CNT yarns, dilute solutions of polymer were prepared, followed by dipping the CNT yarns into the solution to fabricate the disks around the CNTs. Such polymer-infused CNT yarns were then characterised using scanning electron microscope (SEM), transmission electron microscope (TEM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and tensile testing. The characterisation results showed that the polymer disks were able to grow and clamp around the CNTs in the polymer-infused CNT yarns and resulted in increase in the mechanical load bearing. There were, however, challenges in growing them homogenously throughout the network of the CNTs (i.e. the depth within the CNT yarn) so that the disks could effectively transfer stress from one CNT to the adjacent in the polymer-infused CNT yarn. To this end, the polymeric disks were also firstly grown onto the CNT webs and then twisted into the CNT yarns as a much higher number of the polymeric disks could grow onto the CNTs in the more open CNT web compared to the densified CNT yarns. A CNT web is a structure which has individual CNTs or bundles with very loose contact with each other. The web formation is the primary step in making the CNT yarn.

1.4. Structure of the thesis

Chapter 1 is an introduction to this thesis, and outlines the challenges that face the CNT yarn research and an overview of the challenges that were studied in this thesis.

Chapter 2 is a comprehensive literature review on the CNT structure, fabrication methods and assembling of the CNTs into yarns. A detailed study of the current mechanical properties of the CNT yarns as well as various approaches to improve the mechanical properties is demonstrated. In addition, the current literature in the incorporation of polyethylene, polypropylene and nylon 6,6 onto the CNTs in polymer-rich nanocomposite is presented.

Chapter 3 overviews the materials used in the experimental work and describes the methodology of the experimental and characterisation techniques.

Chapter 4 studies the process of the CNT yarn fabrication directly from the CNT forest, solvent densification using acetone and ethanol, densification by two twisting techniques namely shrinking length and constant length as well as characterisation of the CNT yarns that were subsequently produced from such methods. This provided the foundation for the following chapters, in order to study various proposed routes to enhance the CNT yarn properties by polymer infusion.

Chapter 5 investigates the incorporation of seven polyethylene samples of different molecular weights as well as polypropylene and nylon 6,6 infused into the CNT yarns. The disks were grown on the CNTs in the CNT yarn with three different polymer solution concentrations at three different cooling rates. The polymer-infused CNT yarns were then characterised using the electron microscopy and the disk properties namely disk diameter, thickness and gap between the adjacent disks quantified. A comprehensive comparison of the polymer types, molecular weights, polymer solution concentrations and cooling rates provided a broad and complete understanding of the mechanism by which the polymer disks and CNTs interacted in the polymer-infused CNT yarn structures.

Chapter 6 investigates the effect of polymer type, molecular weight, polymer solution concentration and cooling rate on a range of properties other than those studied in Chapter 5 in the polymer-infused CNT yarns. The studies of various polymer types, molecular weights, polymer solution concentrations and cooling rates, in Chapter 5, showed that the polymeric disks with different properties could be produced. Such different properties can affect the thermal, crystalline and more importantly mechanical properties of the polymer-infused CNT yarns. In this chapter a detailed investigation into the thermal, crystalline and mechanical properties of the polymer-infused CNT yarns was carried out and the results are discussed with relevance to the effect of the polymer disk interactions with the CNTs in the polymer-infused CNT yarns. The thermal properties of the polymer-infused CNT yarns were characterised using the TGA method, providing a method to determine the amount of polymer infused into the CNT yarn, while the crystalline and mechanical properties were characterised and studied using the DSC and tensile testing respectively. In addition, the

effect of highly densified CNT yarn as the starting point for the growth of polymer disks around the CNTs was investigated.

Chapter 7 studies the effect of using the loose structures of the CNT web itself as the substrate for the growth of polymeric disks around the CNTs as an alternative approach to the CNT yarn. It was established in the preceding chapter that the looser structure of the CNT web could be beneficial in terms of the polymer penetration deeper into the CNT structure leading to the distribution of the disks throughout the CNT web. In this chapter, the polymer-treated CNT webs were then able to be spun into the yarns. The morphological properties of such polymer-treated CNT webs and the subsequently spun yarns were characterised using the electron microscopy, while the mechanical properties were determined using the tensile testing.

Chapter 8 outlines the conclusions and suggestions for the future work related to this thesis.

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Chapter 2

Literature review

2.1. CNT structure

CNTs are cylindrical, nano-dimensioned carbon materials that have one dimensional tubular structure [1], the nano-dimension being in the radial direction (Figure 2.1). Single wall carbon nanotubes (SWCNTs) are the simplest form of CNT family and can structurally be described as single graphene sheets that are rolled up in a coaxial structure, with the hollow cylinders being a single carbon atom thick. If two or more graphene sheets are rolled up coaxially, the CNT is known as a double wall carbon nanotube (DWCNT) or multi wall carbon nanotube (MWCNT) if there are two or more nested tubes, respectively. The presence of MWCNTs was reported in experimental work in Japan by Ijima *et al.* in 1991 [2] and highlighted the outstanding properties of CNTs and captured the fascination of scientists. The strength of the individual CNTs has been determined to be as high as 500 GPa, with a modulus of over 1 TPa.

In MWCNTs, the distance between each wall is ~0.34nm while the C-C bond within each wall has a length of ~0.14nm. SWCNTs have only one layer of graphene and identical C-C bond length to MWCNT [4, 5]. The diameter of MWCNT ranges from ~10nm to a few hundred nm, while that of SWCNT can be from ~0.5nm to a few tens of nm. MWCNT can have from three nested layers up to several layers, usually 7-10 layers [6]. The length of CNT (including MWCNT and SWCNT) is mainly in the μ m range (1-500 μ m), although some researchers have reported production of mm or even cm long SWCNTs [6, 7].



Figure 2.1. SEM images taken from the bundles of CNT [3].

The hexagonally-arranged carbon atoms which make up the CNT walls can have various symmetries in relation to the CNT axis, and these variations are known as chirality [8] as shown in the Figure 2.2. The angle between the rolled-up graphene sheets and the CNT axis determines the electrical conductivity of the CNTs. As shown in the Figure 2.2, If θ =30° the CNT is called armchair and if θ =0° the CNT is called zigzag. For all other θ values, the CNT is called chiral which is the most abundant type of CNT produced today [8]. If n=3m, the CNT is conductive while n≠3m gives a semiconductive property to the CNT [8]. Therefore zigzag CNTs are the most conductive, and armchair CNTs are semiconductive. Generally, when CNTs are synthesised, a mixture of all chiralities is found in the mixture.



Figure 2.2. Chirality of the CNT.

2.2. CNT growth methods

Various methods of CNT production have been developed over the years [9] (Figure 2.3). Although some have been successfully commercialised, the CVD method remains the main production method for the CNT, as shown in the Figure 2.3 [1]. All of these methods consist of a carbon feedstock that is converted into the CNTs using different methods.



Figure 2.3. Schematic of the range of production methods of the CNT [10].

2.2.1. Arc-discharge method

In this method, a high current of ~50-120A is passed through a graphite anode or cathode inside an inert atmosphere, producing a high temperature plasma region [9]. The high temperature vaporizes the carbon atoms in one electrode and causes them to travel from the anode to the cathode, by virtue of a flowing inert gas. The carbon atoms condense in the cathode and form CNTs, soot and other impurities on the opposing electrode [11].

2.2.2. Laser ablation method

This method is similar to arc-discharge method in that two electrodes are used for vaporizing and condensing carbon atoms. The major difference is that in laser ablation method, the necessary temperatures are produced by a high energy laser source [9]. The CNTs produced by laser ablation method are similar in chirality to those produced by arc-discharge method. However, the laser ablation method is the only method that can produce armchair SWCNTs, unlike other methods that produce SWCNTs with a mixture of chirality. This method can produce SWCNTs and MWCNTs, depending on the temperature and the gas flow in the chamber.

2.2.3. CVD method

In the CVD method, a substrate containing metallic catalysts such as iron, nickel or copper is placed in a furnace and heated to above 700°C. A carbon-rich gas such as methane or ethane is then passed into the furnace, acting as the carbon feedstock for the CNT production. When in contact with the catalyst particles, the carbon atoms start to accumulate on the particle circumference and the CNT structures grow [9]. Once the desired length is achieved, the process is terminated by the flow of inert gas into the furnace.

There are three main variations of the CVD method, where different types of reactor are used for the CNT growth. If the catalyst particles are packed on a substrate and a horizontal
furnace is used, the method is called "bed-packed" CVD [1]. However, if the catalysts are packed in a cylindrical vertical reactor, the method is called "fluidized-bed" CVD [1]. In the latter method, the carbon rich fluid (gas or liquid) is flowed over the packed catalysts inside the vertical reactor at a controlled speed and at temperatures around ~1200°C [1]. In this method, the catalysts are not packed but flow with the carbon-rich gas. As the catalyst particles travel along the reactor, they absorb the carbon atoms on their surfaces, forming CNT aerogel. The CNT growth is terminated when they reach the other end of the reactor where the temperature is cooler. The aerogel containing the CNTs is then collected to spin CNT yarns directly from the CVD reactor.

2.3. Assembling of the CNTs

Since the CNT has been found to have superior properties over a wide range of conventional materials, many researchers have tried to develop products that utilise such properties by manufacturing them into engineering products that can be readily manipulated on a macro scale, such as buckypaper [12, 13], composite [14], membrane [14-16] and yarn [17-21]. However, before such products can become commercially available, there are challenges that need to be overcome. A primary aspect is the large number of intermolecular attractions that can occur between the CNTs (vdW attractions) which causes them to adhere together and form clusters (also known as bundles or aggregates). Due to the nano-dimensions of the individual nanotubes, there are many such interactions per nanotube which play an important role in determining their behavior. For example, in a polymer nanocomposite mixture, the ability to disperse the nanotubes well in a polymer matrix is generally the key to getting good properties for low concentrations (ca. 2–5w/w%), and thus to realise and/or optimise the sought electrical or mechanical properties.

The degree of importance of the vdW forces between the CNT arises from the atomic size of individual or small bundles of the nanotubes. The primary structure of the CNTs is a graphitic one, and as stated above is effectively two dimensional carbon sheets rolled up. While the sp² orbital hybridisation creates the sheet like structure of the graphene (a single layer), the π orbital that extends perpendicular to the sheet forms π - π bonds with the

neighboring graphene sheet [5] and the vdW forces. The same principle of inter planar π - π bonding applies between the walls within a MWCNT, as that occurs between outer walls of adjacent CNTs. Many studies have investigated the vdW forces between the walls on one CNT and between outer walls of adjacent CNTs [22-28]. In addition, as the diameter of the nanotube increases, the vdW forces between the outer walls of adjacent CNTs decrease due to the fact that many of the atoms on the outer walls of CNTs are further away from each other.

The main challenge in realising CNT products with enhanced properties is thus to assemble them in a controlled manner, with optimal selection of various parameters so that the individual CNTs can integrate into the structure more effectively. Such parameters which may influence the final properties of such products include the number of walls, the length and diameter of the CNT, possible chirality and presence of carbon impurities.

2.3.1. Buckypaper

Buckypaper is made by filtration of dispersions of CNTs so that paper like sheets of CNT are produced [29] shown in the Figure 2.4. These self-supporting sheets have shown thickness of 50-200µm and porosity of 70%.



Figure 2.4. SEM images of buckypaper surface [30].

In addition, polymers can be added to these sheets to form composite sheets with interesting properties [30]. Due to high porosity and low density, polymer can be used to fill these pores or produce layered structures. The electrical and thermal conductivities, the mechanical strength and absorption and filtration properties can also be modified (Figure 2.5) by the selection of appropriate polymers [30].



Figure 2.5. Flexible and strong buckypaper [31].

Since buckypaper is lightweight, strong and flexible (tensile strength of 76-293MPa and modulus of 6-42GPa), many applications have been proposed including smart clothing using conductive buckypaper wires [32] or water purification using highly porous buckypaper sheets [31].

2.3.2. CNT composites

2.3.2.1. CNT/polymer composite

Composite materials made of the CNT and polymers are usually found to contain less than 5w/w% CNT in polymer matrix [33]. The main purpose of researching such composite materials has been mainly to improve the properties of the polymer. The addition of the

CNT to a polymer matrix can significantly increase the electrical, thermal and mechanical properties of the resulting composite [33]. The mechanical properties of such composites are of special importance. There are four main factors influencing the mechanical strength of the CNT/polymer composites: (i) CNT aspect ratio, (ii) CNT alignment, (iii) CNT distribution in the polymer matrix and (iv) stress transfer at the interface [34]. Although an isotropic distribution in the polymer matrix is advantageous for bulk composite sheets, composite fibres need to have a directional distribution of CNTs along the fibre axis, allowing more stress transfer from the matrix to the CNTs. Higher shear strengths are desired between the interface of the nanotubes and the matrix which in turn improve the stress transfer.

Two main approaches are used in order to produce stronger interactions between the polymer matrix and the CNT sidewalls: (i) covalent bonding between polymer matrix and carbon molecules, and (ii) non-covalent or physical bonding between polymer matrix and carbon molecules [34]. In the former method, the mechanical properties of the composite are significantly improved due to the transfer of stress from the polymer matrix to the CNT walls via covalent bonds [35, 36]. Electron irradiation of around 200keV provides sufficient energy to crosslink atoms of one CNT to those of the adjacent CNT, thus producing a solid structure. The main disadvantage of such an approach is that it introduces defects into the CNT structure which reduces the mechanical strength of the CNT itself [37]. In addition, the flexibility of the crosslinked CNTs is significantly reduced compared to noncrosslinked assembly of the CNTs [38]. The non-covalent (physical bonding) approach utilises the free electron orbital in the polymer molecules and the carbon atoms in the outer wall of the CNTs to form π - π interaction at the polymer and CNT interface. Due to non destructive nature of this approach, both the polymer's and CNT's molecular integrity remains intact and no defects are introduced into the nanotube structure [39]. The disadvantage of the non-covalent approach is that the mechanical properties of the composite cannot be significantly increased due to the poor interfacial cohesion between the CNT and polymer.

Regardless of the polymer type or the method of composite fabrication, there are some critical factors that greatly influence the resulting composite properties. Among these, the homogeneity of the CNT distribution in the polymer matrix, the minimal aggregation of the CNT in the dispersion, the degree of alignment of the CNTs and the strength of interfacial interactions between the matrix and the CNT all have significant influences on the final composite properties [40].

The mechanical strength and modulus of CNT/polymer composite fibre can be calculated by the "rule of mixtures" [41]. In this approach modulus, Y_c , and tensile strength, σ_c , are calculated by:

$$Y_{c} = (\prod_{0} \prod_{1} Y_{f} - Y_{m}) V_{f} + Y_{m}$$
 Equation 2.1

where

$$\eta_{1} = \begin{cases} 1 & for \frac{L}{D} > 10\\ 1 - \frac{tanh(a, \frac{L}{D})}{a, \frac{L}{D}} & for \frac{L}{D} \le 10 \end{cases}$$
 Equation 2.2

where

$$a = \sqrt{\left(\left(\frac{-3Y_m}{2Y_f \ln V_f}\right)\right)}$$
 Equation 2.3

and

$$\Pi 0 = \begin{cases} 1 & \text{for aligned fibres} \\ \frac{3}{8} & \text{for plane aligned} \\ \frac{1}{5} & \text{for random oriented} \end{cases}$$

$$\sigma_{c} = \begin{cases} (\eta_{s}\sigma_{f} - \sigma_{m})V_{f} + \sigma_{m} \text{ for } L > L_{C} \\ \left(\frac{\tau L}{D} - \sigma_{m}\right)V_{f} + \sigma_{m} \text{ for } L < L_{C} \end{cases}$$
Equation 2.4

where

$$\eta s = 1 - \frac{L_c}{2L}$$
 Equation 2.5

$$Lc = \frac{\sigma_f D}{2\tau} \left[1 - \frac{D_{int}^2}{D_{ext}^2} \right]$$
Equation 2.6

where V_f is the volume fraction of the fibre, Y_f is the Young's modulus of the fibre, Y_m is the Young's modulus of the polymer and L is the length of the composite fibre. L_c is the critical length, and is defined as the nanotube length at which the transferred stress from the matrix can rupture the nanotube. At lengths greater than L_c , the fibre ruptures, whereas for fibre lengths smaller than L_c the nanotubes often preferentially slide through the matrix without breaking. Experimental works were undertaken to investigate the mechanical properties of composite materials using the equations 2.1 to 2.6. The works published by Palza *et al.* [42] on CNT/polyethylene, Allaoui *et al.* [43], Ajayan *et al.* [44] on CNT/epoxy and Chen *at al.* on the CNT/polyvinylalcohol composite materials have demonstrated that such critical lengths (L_c) influence the final mechanical properties. They showed that by increasing the amount of the CNT and varying their length, mechanical stiffness and strength can be manipulated.



Figure 2.6. Mechanical behaviour of a polyvinyl alcohol/CNT composite [45]. The image on the right shows the CNTs in the CNT forest. The image on the left shows that by increasing the amount of the CNT in the polyvinylalcohol from 46.4 wt% to 56.8 wt%, the tensile stress increased while further increasing the CNT content resulted in the decrease of the tensile stress.

In the case where the polymer matrix is semi-crystalline in nature, such as polyethylene, the nucleation of the polymeric crystalline phase can occur at the interface of the polymer and the CNT [46, 47]. This can significantly increase the tensile strength of the composite compared to that of a non-crystalline polymer since the shear strength at the interface of the nanotubes and polymer is greatly increased [45, 48]. Therefore, the crystallisation of polymer in the vicinity of the CNT strengthens the polymer/CNT interface, reducing the degree of CNT failure. In addition, the failure tends to occur away from the crystallised polymer [34].



Figure 2.7. Mechanical strength as a function of CNT weight content [45].

Typically, in order to combine the CNTs with polymers, they are either (i) dispersed (melt blended) in molten polymer and subsequently solidified on cooling [49] or (ii) dispersed in polymer solutions such as polyvinyl alcohol [50]. Most of the studies involve polymers being the majority phase with CNT volume content between 5-25%, with various structural, molecular and mechanical characteristics. This resulted in CNT composite materials showing tensile strength of 0.4-0.8GPa and modulus of 1.6-12.6GPa for CNT volume fraction of 5-25 % [41, 51] as shown in the Figure 2.6. The Figure 2.7 shows that increasing the CNT content resulted in decrease in the mechanical properties of the composite material. Such values for tensile strength and modulus come from the fact that the addition of the CNT into the polymer can enhance the properties of the composite materials when the CNT is isotropically distributed in the polymer matrix [52].

2.3.2.2. CNT/metal composite

The increasing demand for stronger and lighter materials has led to the increasing use of CNTs in metal composites [53, 54]. These composite materials are mainly used in automobile and aerospace industries. CNT/metal composites are manufactured by various methods such as powder metallurgy, electrochemical deposition, thermal spray and melting/solidification. Powder metallurgy and electrochemical methods are widely used during the polymer synthesis process mainly due to good composite properties and

production viability [55, 56]. Powder metallurgy method has been used for producing CNT/Cu, CNT/Mg or CNT/Al composites. In this method, metal particles are grinded and mixed with the CNTs through mechanical alloying such as ball milling [57]. Ball milling is an efficient step in homogenously mixing the CNTs with the metal particles while increasing interfacial interactions between the CNTs and the metal. The mixture is then solidified into monolithic objects either by compaction/sintering, cold isostatic pressing, hot isostatic pressing or spark plasma sintering [56].

The electrochemical method can be used for making thin coatings of 20-180µm or yarn like CNT/metal composite [56]. The fabrication of CNT/nickel, CNT/cobalt [58] and CNT/boron yarns has been studied using this method [59, 60]. In this method, metallic salts are thermochemically decomposed to release the metallic ions. These metallic ions then fuse with the CNTs to form the composite in inert atmosphere in order not to damage the CNTs. The temperature and pH of the decomposition bath are critical factors during composite fabrication both in terms of metal ionisation and maintaining CNT integrity. For nickel/phosphorus/CNT composite, the pH is usually maintained in 4.5-5 range while the temperature is kept at 350-360K [61, 62].

In both of the above mentioned methods, the mechanical strength of the composite material is achieved by good homogeneity and strong interfacial cohesion between the CNTs and the metal particles [63-66]. The interfacial cohesion is a critical factor in CNT/metal composite, as it facilitates the transfer of applied stress from the metallic matrix to the CNT. If the interfacial cohesion is poor, the composite will fail at lower stress due to inefficient utilisation of the CNTs in the matrix. The addition of the CNTs to the metal alloy increases the resultant composite mechanical properties such as hardness, bending strength, compressive strength and tensile strength [58, 67-69].

2.3.3. CNT yarn

The commercialisation of CNTs in various applications has been limited mainly due to the difficulties in handling and processing of the CNTs. The CNTs are currently commercially

used in a few applications such as in electronics for example in batteries and sensors [70, 71], or in composites or yarn structures such as reinforcements in polymeric matrices [72, 73] (Figure 2.8).



Figure 2.8. A wearable glove using embedded CNT yarns as sensors [71].

The CNT's excellent mechanical properties, when compared to other high strength materials such as steel or Kevlar, are very impressive and thus the possible improvements they can cause, when incorporating them into applications such as yarns, is highly attractive. Macroscopic assemblies of the CNTs into yarn, rope and sheet structures have been widely investigated in the literature [17, 21, 74, 75]. The CNT yarns can be produced by three major methods: (i) direct spinning [76], (ii) forest or dry spinning [77] and (iii) wet or coagulation spinning [75].

2.3.3.1. CNT yarn spinning methods

2.3.3.1.1. Direct spinning

Although direct spinning of the CNTs was first reported by Zhu *et al.* [18], it was Li *et al.* [76] who commercially developed this method. In this method, a carbon-rich gas such as ferrocene [Fe(C_5H_5)₂] or thiophene (C_4H_4S) is fed into a vertical furnace shown in the Figure 2.9. The furnace is then heated to 1050-1300°C. The CNTs then start to grow onto the iron nanoparticles that have been coated onto a silicon substrate. At the other end of the

furnace, a spindle collects the newly-formed CNTs and assembles them into a yarn structure. Due to continuous feeding, the CNTs can be spun into kilometer-long yarns [76].



Figure 2.9. Schematic of the direct spinning of CNT yarn from CVD furnace [76].

The initial tensile properties of directly spun CNT yarns were very low (~200MPa). However, research conducted over the years led to the improved tensile strength, modulus and toughness of 1.8-3.4GPa (2.2N/tex), 50-150GPa (160N/tex) and 121J/g respectively [78, 79] as shown in the Figure 2.10.



Figure 2.10. Mechanical strength of the CNT yarn produced by direct spinning method [76].

Various parameters were found to influence the properties of the CNT yarn produced by direct spinning method. These include the furnace temperature, the gas flow and the wind-up speed. Although these values show that the CNT yarns are comparable or even stronger than commercially-available Kevlar and carbon fibre, they are still much lower than the theoretical values for the CNTs [80].

2.3.3.1.2. Dry (forest) spinning

The possibility of drawing yarns from vertically-grown CNTs on a silica substrate was first discovered by Jiang *et al.* [77]. In this method, shown in the Figure 2.11, the CNT forest is first produced by the CVD method in a tube furnace where the silica substrate is coated with iron nanoparticles and placed inside the furnace with a carbon rich gas flow through the tube reactor. The furnace is heated up to 650-850°C at which temperature the CNT growth commences.



Figure 2.11. SEM images of a vertically aligned CNT forest [81].

The CNT forest is then taken out and spinning is commenced by drawing a width of forest, for example by using tweezers (Figure 2.12). The CNTs produced by this method, have diameters of 10-100nm and multiwall structure with mixed number of walls (usually 2-14 walls).



Figure 2.12. SEM images of the CNT forest used to draw a continuous length of CNT web [77].

It should be noted that not all CNT forests are drawable, as it took many years for researchers to develop drawable CNT forests [77, 82]. The only type of CNT forest that can produce a continuous web is the one that has vertically aligned CNTs with individual CNTs parallel to one another, at the appropriate distance, as shown in the Figure 2.12. Such individual CNTs then form bundles of CNTs which are connected by vdW forces and inter connectors. Pulling one bundle of CNT from the forest causes the adjacent bundles to bend and be taken up by the pulling force and form a web, as shown in the Figure 2.13 [77, 83, 84]. The tensile strength and modulus of forest spun CNT yarn has been reported to vary between 1.8-3.3GPa and 200-400GPa respectively, depending on the forest and the spinning conditions [85]. These values are still much lower than the theoretical strength and modulus of individual CNTs which are 100-150GPa and 1TPa, respectively [85].



Figure 2.13. Schematic of drawing a web from the CNT forest. Blue and red bars are vertically aligned CNT bundles while thinner lines are the interbundle CNTS or interconnections [84].

Although this method has great potential for commercialisation due to a lower growth temperature, higher purity of the CNT yarn, tunable yarn diameter depending on the width of the drawn web, and low yarn density, CNT yarns produced by forest spinning still have only moderate mechanical properties.



Figure 2.14. SEM images of twisting a length of CNT web from a vertically aligned CNT forest [87].

A number of techniques have been developed to improve the mechanical properties of the CNT yarns, including twist and solvent densifications [17]. The CNT webs (a single wedge or double wedge shaped structure) produced by drawing a length of web from the drawable CNT forest can be spun into a yarn by spinning one end of the web, whilst keeping the other end fixed shown in the Figure 2.14. The insertion of the twist in the web compresses the CNTs towards the centre of the web, hence forming a uniform structure as shown in the Figure 2.14 [86].

The solvent densification can also improve the mechanical properties by increasing the number of contacts between the CNTs. In this method solvents such as ethanol, acetone or NMP are used to compress the CNTs in the web structure and form tightly held yarn structure. It has been shown that such densification can improve the tensile strength compared to neat CNT web by a factor of 2 from 0.6GPa to 1.1GPa [88] (Figure 2.15). The twist and solvent densification methods will be further discussed in more detail in the Section 2.3.5.



Figure 2.15. Improvement in mechanical properties by solvent densification methods using acetone [88].

2.3.3.1.3. Wet (coagulation) spinning

The concept of wet spinning of CNT yarns was introduced almost simultaneously by Vigolo *et al.* [75] and Gommans *et al.* [89]. In this method, the CNTs are first dispersed in a dispersant such as sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP) or Dimethylformamide (DMF) schematically shown in the Figure 2.16.



Figure 2.16. Schematic of the wet spinning of the CNT yarn [90].

Due to the chemically inert and hydrophobic nature of the CNTs, various methods have been investigated to disperse the CNTs in the dispersants including ultrasonication, super acid treatments, high pressure and shear mixing. In the ultrasonication method, high energy ultrasonic waves travel through the dispersant and cause formation of cavities which then hit the bundles of the CNTs [91]. The implosion of the high energy cavities causes the bundles to break into even smaller bundles and eventually into individual nanotubes. The ultrasonic energy often also breaks the nanotubes in longitudinal direction and thus shortens the nanotubes. The CNT dispersion is then injected through a syringe into a coagulation bath containing a solvent for the dispersant but not for the CNT. The solvent dissolves the dispersant, leaving the CNTs to form a CNT yarn. The yarn is then taken out of the solution and dried before winding up.

In the super acid method, very strong acids such as sulfuric acid or nitric acid are used to disperse the CNTs [92]. Due to highly corrosive nature of such acids, the positively-charged functional groups attach to the outer walls of the CNTs and the static repulsion forces help the individual CNTs remain separate. This method is not as effective as the ultrasonication method due to the chemical interaction between the CNTs and the super acids creating defects such as Stone Wales and adatoms defects in the CNT walls [93]. In

addition, the CNT/super acid dispersion is very sensitive to water [94, 95] with the presence of minimal moisture causing the separation of the CNTs and the super acid phases. Such separation phenomenon occurs mainly due to the introduction of negatively-charged hydroxyl groups into the system.

Initially, wet spun CNT yarns showed poor mechanical properties such as tensile strengths of 140MPa and modulus of 15GPa [75]. Although later studies improved the mechanical strengths and modulus to 1.8GPa and 120GPa, respectively, these values are still much lower than those of forest spun CNT yarns [96]. The reason for this lies in the preparation stage of the CNT dispersion. All of the dispersion methods that manage to separate the CNTs in the solution inevitably damage the CNT structure and hence reduce the mechanical strength of the CNTs. Furthermore, there is little control over the diameter of the CNT yarn, other than the nozzle diameter and injection speed. With the average diameter of these yarns being 10-80µm, this method limits optimisation of the CNT yarn diameter for the maximum strength [17].

2.3.3.2. CNT yarn properties

2.3.3.2.1. Mechanical properties

Many studies focused on improving mechanical properties of the CNT yarns using the methods described above. The Table 2.1 shows such properties obtained by several research groups while the Table 2.2 shows the mechanical properties of the composite material containing CNT in their structure.

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Table 2.1. Reported mechanical properties of CNT yarns.

Production method	Reported linear density tex	Tensile strength GPa(N/tex)	Young's modulus GPa(N/tex)	Toughness J/g	Reference
Forest spun		-(3.5)			[83]
Forest spun		0.6(-)			[97]
Forest spun		0.5(0.6)			[86]
Forest spun		0.7(-)	12(-)	27	[87]
Forest spun		-(0.46)			[21]
Forest spun		1.3-3.3(-)	100-263(-)		[98]
Forest spun		1.1(-)	55(-)		[99]
Forest spun		1.9(-)	330(-)		[100]
Forest spun		1.2(-)	50(-)		[72]
Forest spun		1.4(-)	55(-)	100	[101]
Forest spun		0.46(-)			[102]

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Forest spun		1.2(-)	20(-)		[103]	
Direct spun	0.03-0.13	8.8(8)	357(200)		[79]	
Direct spun		0.35(0.35)	35(35)		[104]	
Direct spun	0.1	0.55(1)	22(40)		[73]	
Direct spun		2.9(-)	250(-)		[105]	
Direct spun		-(0.7)		40	[106]	
Direct spun		-(1.1-2.1)	-(60-142)	32-42	[78]	
Direct spun		1(-)	50-77(-)		[18]	
Direct spun		-(1.2)	(30)		[107]	
Wet spun		0.15(0.06)	-(12)		[90]	
Super acid spun		0.2(-)	130(-)		[19]	
Coagulation spun		0.12(-)	12(-)		[108]	

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Table 2.2. Mechanical properties of nanocomposites containing polymer as matrix and CNT as filler.

Production method	CNT fraction	Tensile strength	Young's modulus	Toughness J/g	Reference
	%	GPa(N/tex)	GPa(N/tex)		
Coagulation spun CNT/PVA	60 w/w	1.8(1.2)	78 (-)	600	[96]
Dispersion spun CNT/epoxy resin	0.0225 w/w		3-5(-)		[109]
Direct spun CNT/PVA	50 w/w	0.5(0.4)		870	[110]
Forest and wet spun CNT/PU	30 w/w	1.7(-)	85(-)		[111]
Direct spun and molding CNT/epoxy	17-26 v/v	0.253(0.23)	18.8(17.1)	1.9	[73]
Direct spun CNT/PVA	1 w/w	1.4-2.6(-)	60-70(-)		[112]
Forest spun CNT/PS	90 w/w	1.1(-)			[102]
Coagulation spun CNT/PVA	0.2 v/v	0.4-0.5(-)	30-40(-)	10-20	[113]
Gel spun CNT/UHMWPE	9 w/w	2.5(-)			[114]

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Forest spun and solution CNT/epoxy	5 w/w	1.5(-)	55(-)		[115]	
Dispersion spun CNT/PVA	5w/w	1.7(-)	92(-)		[116]	
Solution spun CNT/CF	1 w/w	2-4.5(1.4-2.5)	200-463(190-257)		[117]	
Solution spun CNT/UHMWPE	5 w/w	0.01(-)	1.35(-)		[118]	
Solution spun CNT/UHMWPE	3 w/w	-(2.9)	(89.44)		[119]	
Solution spun CNT/UHMWPE	5 w/w	4.2(-)	136.8(-)		[120]	
Melt extrusion CNT/HDPE	1 w/w	0.03(-)	1.2(-)		[121]	
Solution spun CNT/HDPE	0.44w/w	0.109(-)	1.34(-)	842	[122]	
Solution spun CNT/MDPE	1 w/w	0.004-0.007(-)	0.59-0.81(-)		[123]	
Melt spun CNT/LDPE	10 w/w	0.015(-)	0.44(-)		[124]	
Ball milling and molding CNT/LDPE	3 w/w	0.055(-)	0.48(-)		[125]	
Melt spun CNT/LDPE	1.5 w/w	0.02(-)	0.371(-)	129	[126]	

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Solution spun CNT/PP	1 w/w	1(-)	9.8(1.15)	[52]	
Melt spun CNT/PP	1 w/w	0.033(-)	1.1(-)	[127]	
Gel solution CNT/PP	5 w/w	0.018(-)	1(-)	[128]	
Extrusion CNT/PP	0.75w/w	0.035(-)	1.18(-)	[129]	
Solution spun CNT/Nylon6	1 w/w	0.37(-)	0.84(-)	[130]	
Solution spun CNT/Nylon6	0.5w/w	0.108(-)	0.79(-)	[131]	
Melt spun CNT/Nylon6	1 w/w	0.85(-)	2.02(-)	[132]	
Melt spun CNT/Nylon6	2w/w	0.04(-)	1.24(-)	[133]	

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The Table 2.1 shows that despite enormous efforts to make CNT yarns with high mechanical strength, the tensile strength and modulus of the CNT yarns still remain in the 1.8-3.4GPa and 100-200GPa ranges, respectively. The main reason for such values are due to the CNT structure [107]. Due to the nano dimension of the CNTs, the vdW attractive forces often cause them to aggregate and form bundles hence they do not interact with one another on an individual basis. As the result, the mechanical stress transfer between the nanotubes is not well optimised. The Table 2.2 shows that the mechanical properties of the polymer can be improved by addition of 2-25 w/w% CNT into the polymer. However, it is noted that the tensile strength remained at around 0.5-1.8 GPa with the exception of gel spun CNT/UHMWPE having a tensile strength of 2.5 GPa while the modulus shows a wide range of values with exceptionally high value reported for the solution spun CNT/CF composite yarn.



Figure 2.17. Representative tensile stress-strain curves of the CNT yarn obtained by forest spinning [87].

The tensile strength and modulus of CNT yarns are represented by a density factor called linear density instead of cross-section area [134]. This is due to the fact that the diameter changes along the length of the yarn, and thus it is hard to ascribe an average diameter to a length of yarn. The use of the linear density eliminates diameter variability, and so the mechanical strength of the yarn will be independent of the diameter [79]. It is known that the CNT chirality, length, diameter and number of walls affect the stress transfer between

the nanotubes in the CNT bundles [83], and thus these parameters must be optimised in order to increase the mechanical properties of the CNT yarn. Since the strength of the CNT yarn depends on the ability of the individual and bundles of CNT to transfer the stress between one another, the CNTs with a greater number of walls or larger diameters have less of such interactions. This results in a decrease in the ability of the CNTs to efficiently adhere together, and reduces the number of contacts [79, 83]. The tensile stress can be calculated from bulk and linear densities of the CNT yarn [134]:

$$\sigma = \rho_{\rm CNT} \times \frac{F}{\rm tex}$$
 Equation 2.7

where σ is the tensile strength (GPa), ρ is the CNT density (assumed 1.8 g/cm³) [135], F is the tensile force at break (N) and tex is the linear density of the CNT yarn defined as the weight of 1000m of CNT yarn in grams (g).

2.3.3.2.2. Electrical properties

Some CNTs can have high electrical conductivity of 8000S/m and electrical current density of 4×10^9 A/cm² [136]. Despite such high electrical properties, macroscopic CNT yarns show a very low conductivity (200-1000S/m) [21, 137]. This is due to the bundle formation in the CNT yarn which in turn increases the irregularities in longitudinal orientation between the bundles and thus greater resistance. This, among other reasons such as the presence of defects and metallic impurities in the CNTs, reduces electron transfer within the individual and bundles of the CNTs, thus increasing the resistivity of the CNT yarn. On the other hand, if maximum alignment is achieved in the CNT yarn, the minimal points of contact between the nanotubes are then obtained which in turn maximises the conductivity. The maximum electrical conductivity of the CNT yarns that has been reported to date is 8000S/cm from the work by Davis *et al.* [138].

2.3.4. Comparison of CNT yarn with conventional textile yarns

In the conventional textile industry, the twist is used for densification of the yarns [139]. Optimal twist depends on the yarn characteristics and diameter and is $20-23^{\circ}$ [140-142]. The number of fibres in the yarn cross-section depends on the yarn diameter but it is usually ~100 fibres for conventional yarns such as cotton and wool. It is noted that inserting too much twist into the yarn structure can lead to a dramatic loss of the mechanical strength [143]. The reason is that the twist causes the fibres to bend away from the axial direction of the yarn. In this case, fibres can no longer efficiently bear the tensile load as some fractions of the load will convert to torque.



Figure 2.18. SEM image of the failure points in the untwisted CNT yarn [144].

However, when the CNTs are used as the building blocks for the yarn, the twist can be a misleading concept (Figures 2.18 and 2.19). When Zhang *et al.* [21] used twist to increase the mechanical strength of the CNT yarn for the first time, they proposed that twist could be a major factor in increasing the CNT yarn mechanical strength in the same way as conventional textile yarns, on the basis that the twist can potentially increase the contacts between the nanotubes, which in turn increases the friction and allows the twist to penetrate into the CNT yarn core and lock the nanotubes.

Since 2004, when Zhang *et al.* [21] first reported twisted CNT yarns, other researchers followed by studying the effect of twist on the CNT yarns [145-149]. Surprisingly, it was emerged that the twist on its own cannot be a major factor in the CNT yarn mechanical enhancement. The reason is twofold; (i) unlike conventional textile fibres that have micron size diameter, the CNTs have nano-sized diameter. This has a strong effect since nano-sized nanotubes have a very high surface energy which causes strong molecular vdW attractions between the nanotubes. Hence, the movement of the nanotubes with respect to each other is very limited and (ii) unlike conventional textile yarns that have ~100 fibres in the yarn cross-section, the CNT yarn has in the order of million nanotubes in the yarn cross-section. Consequently, the twist cannot travel deep into the CNT yarn structure and only locks the nanotubes on the outer surface of the yarn [134].



Figure 2.19. SEM images of the failure point on the twisted CNT yarn [146].

This results in a core-sheath structure where the core has a higher density and the sheath has a lower density. At its best, the twist has been reported to be able to increase the mechanical strength by a factor of three, from 0.6GPa to 1.8GPa [85].

In the conventional textile yarns, the tensile stress at failure breaks the chemical bonds in the fibres and hence the failure is the result of the tensile force being greater than the tensile strength of individual fibres [141]. In the CNT yarns, however, the tensile strength of individual nanotubes is huge compared to the tensile strength of the yarn (50-150GPa). Hence, failure occurs not because the nanotubes undergo covalent bond failure, but instead slide relative to one another. This is because the interfacial shear strength of the nanotubes is very low compared to the strength of the covalent bonds, and the applied tensile stress on the nanotubes is greater than their relative shear strength [146].

CNT yarn properties depend not only on the spinning method (direct, dry or wet), but also on many other factors including the neat CNTs (number of walls, chirality, presence of defects, diameter, aspect ratio) and the yarn structure (diameter, CNT alignment, packing density, yarn diameter, twist angle, vdW interactions) [83, 107, 150]. While some factors such as chirality and defective walls cannot be controlled, optimisation of those factors that can be controlled such as mechanical strength and electrical or thermal conductivities will lead to enhancement of the CNT yarn properties. In general, the CNT diameter, yarn diameter and twist angle should be minimised, while CNT aspect ratio, alignment, packing density and vdW attraction should be maximised [83]. The diameters of the individual CNTs and the CNT yarn as a whole influence the amount of stress that individual and bundles of the CNTs can bear before sliding occurs, while the alignment and the density govern the amount of intermolecular interactions between the CNTs.

It seems that while the direct spun CNT yarns show higher electrical conductivity and mechanical strength, the forest spun CNT yarns have mechanical strength consistency and diameter uniformity across their lengths [17]. In addition, the forest spinning method produces CNTs with the highest possible length, purity and uniformity compared to the wet and direct spinning methods. As the result, the forest spun CNT yarns are commercially more viable and the forest spinning method has the potential to become a commercially available spinning method for the CNTs.

There exists a significant literature about the effects of the CNT diameter, forest length, the CNT yarn diameter, the yarn packing density, interfacial and intrafacial vdW interactions between the walls in the CNTs, the spinning method and their related parameters on the mechanical properties of the CNT yarns [20, 72, 83, 103, 145, 151-154]. Although these studies have identified influencing parameters about the CNTs and their yarns, none of these studies has successfully produced mechanically stronger yarns close to the theoretical values of the CNTs. All CNT yarns reported to date have, at the best, tensile strengths of ~1.8-3.4GPa and modulus of ~200GPa [85]. These values are only a few percent of the values for individual CNTs.

2.3.5. CNT yarn densification methods

Densification increases the interfacial CNT interactions within the CNT yarn. This is due to greater vdW attractions between the nanotubes. Since stress transfer occurs by having the nanotubes in close contact with each other, having a more packed structure (with higher volume density) with the nanotubes closer to each other enhances the mechanical strength. In addition, the greater surface contact between the nanotubes helps transformation of electrons and phonons which in turn increases the electrical and thermal conductivities in the CNT yarn, respectively [99].

2.3.5.1. Twist

Twist involves the insertion of a torsional torque in the CNT yarn structure so that individual and bundles of the CNTs can be laterally compressed and form a cylindrical structure [155] (Figure 2.20). Although twist is an effective way to densify the CNT yarn with volume density of 0.05-0.5 tex and increase the mechanical properties of the conventional textile yarns, it only affects the properties of the CNT yarns to a smaller degree [78].

The reason relates to the size of the individual CNTs. In the relaxed state, the nano-sized CNTs exert intermolecular vdW forces, thus reducing the relative motion between them.

This results in a lack of migration of the twist towards the center of the CNT yarn. Such a lack of migration leads to poor stress transfer between the CNTs, under tensile loads, and hence the mechanical strength remains low. The helix angle is defined as the angle between the CNT yarn and individual and bundles of the CNT axial directions and is an important factor to determine the stress utilisation of the CNTs in the yarn [97, 156].



Figure 2.20. SEM images of twist insertion in the CNT web, and the effect of the twist on the CNT yarn structure [156].

2.3.5.2. Solvent

The use of solvents such as acetone [99], ethanol [99] and NMP [157] has been studied with regards to the densification of the CNT yarns although the actual bulk density of the CNT yarns were not reported. In a dry state, the CNTs exert vdW forces to each other causing them to stick together. However, such solvents temporarily remove these forces

which cause the CNTs to separate schematically shown in the Figure 2.21. They then become straight and create more contact points with one another while still in the solvent. Evaporation of the solvent from the CNTs causes them to compress together, significantly increasing the number of contacts [93]. Therefore, the vdW interactions in the CNT yarn structure will be further increased and the mechanical properties improved.



Figure 2.21. Schematic mechanism of the separation of CNTs in the solvent [158].

Studies by Bergin *et al.* [157] have found that NMP and acetone are the best candidates for densification of the CNT yarns. They suggested that NMP and acetone would lead to a near zero enthalpy of mixing, which facilitates the dispersion of the CNTs in such solvents. The volumetric densities of the SWCNT and MWCNT were 1.3 and 2.1g/cm³ respectively.

2.3.6. CNT yarn alignment methods

2.3.6.1. Drafting

The idea of drafting or tensioning the CNT yarn has been borrowed from conventional textile technology [159]. However, the CNTs are intrinsically different from conventional fibres such as cotton or wool due to their nano-size dimensions and their intermolecular vdW attractive forces. Once the CNTs are drawn into a web structure, the draft cannot homogenously align the CNTs in the draft direction due to the strong vdW forces. The web

formation is the primary step in making the CNT yarn. Therefore, drafting has been found to have little effect in improving the CNT yarn properties [87, 134].

2.3.6.2. Fluid flow induced alignment

Various studies have used flow of gas or liquid in order to exert shear forces on the individual or bundles of the CNTs [160-162]. This in turn leads to a better alignment of the CNTs in the flow direction compared to untreated CNTs with more than 75% of the CNTs distributed within $\pm 2.5-5^{\circ}$ from the gas flow direction. In order to use this method, the CNTs were first dispersed in a dispersant. The CNT dispersion was then deposited on a substrate while an inert gas such as nitrogen [163] or argon [160] was passed over the CNT dispersion. The degree of alignment and the width of the CNT web could be controlled by appropriate adjustment of the gas flow rate and outlet orifice which resulted in 74% of SWCNT distribution within $\pm 5^{\circ}$ and 85% within 10° angular spread respectively. This led to a moderate improvement of the mechanical strength to 0.4GPa [75].

2.3.6.3. Liquid crystal induced alignment

Liquid crystals (LC) have been used for alignment of individual or bundles of the CNTs [95, 164]. Such alignment ability is due to the fact that the LC molecules can be readily aligned along the applied shear stress. When individual CNTs are dispersed in a LC, the LC molecules that were aligned in the shear stress direction force the CNTs to rotate and align accordingly in the stress direction. Such CNTs can then be processed to produce aligned CNT yarns by removing the LC from the CNTs. The alignment of the CNTs in the yarn is longitudinal in order to minimise the distortion of the aligned LC molecules and the free energy of dispersion [165]. For example, in the study by Lynch *et al.* [164], LC was used as dispersant for CNTs. The dispersion was then passed through two electrically charged porous films which aligned the LC molecules. This in turn aligned the CNTs in the same direction as LC molecules with the reported alignment of 0.7-0.9 where 1 is perfect alignment and 0 is random alignment [164]. The aligned CNTs were then processed into a yarn structure.

2.3.7. Polymer-CNT composite yarns

Composite yarns with majority polymer phase are produced in order to improve structural properties in the composite yarn. Conventional composite yarn is produced by adding 2-5w/w% CNT into the polymer matrix to increase the mechanical properties of the polymer [14, 33]. Two main approaches that are widely used in the composite yarn are melt-spinning and wet-spinning (also known as coagulation spinning) [14, 50].

2.3.7.1. Polyethylene-CNT composite yarns

Polyethylene consists of chains of hydrocarbon (Figure 2.22). It is produced by polymerisation of ethylene monomers in controlled temperature and pressure in order to obtain low molecular or high molecular weight polyethylene [166]. High molecular weight polyethylene (HMWPE) consists of long chains, whereas low molecular weight polyethylene (LMWPE) consists of short chains.

The branching on the chains determines the degree of crystallinity and thus the polymer density. High density polyethylene has minimal branching and thus causes increased amounts of the crystalline phase, compared to low density polyethylene. It is known that polyethylene can crystallise and form cylindrical structures known as "shish-kebab" [167]. Such structures are formed on the surface of nucleating agents, such as particles or in solution such as in xylene [168].



Figure 2.22. Schematic of the molecular structure of polyethylene.

The mechanism of such shish-kebab growth is well documented in the literature [168, 170]. It is believed that polyethylene molecules attach themselves by physical adsorption onto the surface of the nucleating agent forming nuclei. Such agents can be foreign particles or filaments. Shorter polyethylene chains or coils travelling in close vicinity of the nuclei are then attracted to the nuclei. As the nuclei grows in size, an increasing number of molecules attach themselves, creating a disk like structure as shown in the Figure 2.23.



Figure 2.23. SEM images of polyethylene shish-kebabs [169].

In the polyethylene-CNT composite, the vdW attractions exist between the two components. Such interactions are not strong, and thus the interface between the polyethylene and the CNT itself is weak. In order to increase the mechanical properties of the polyethylene-CNT composite yarns, the interfacial stress transfer between the CNTs and polyethylene needs to be increased [168]. In the conventional sense, two methods for the composite fabrication have been proposed: (i) covalent bonding between the CNT surface and polyethylene known as crosslinking [14] by using gamma rays [171, 172], plasma [173] and high concentration of nitric or sulfuric acid [174]. In this method, high energy gamma rays, plasma or strong acids create free radicals on the surface of the CNTs

before mixing them with polyethylene. By mixing them together in controlled environment, they form chemical bonds in the polymeric matrix. This results in an increase in the composite mechanical properties. Although covalent bonding of the CNT and polyethylene significantly increases the interfacial stress transfer, it also increases the number of defective sites on the CNTs [168]. This significantly reduces the mechanical strength of the CNT itself and hence offset the overall composite strength and (ii) non-covalent bonding involves physical gripping of individual CNTs by the polyethylene shish-kebabs [175]. The non-covalent bonding does not damage the CNTs, and thus the CNT mechanical properties can be more efficiently exploited into the composite structure [167].



Figure 2.24. Schematic of the shish-kebab structure and formation of disks [170].

Various research studies have been done on polyethylene-CNT composite yarns where a small amount of CNT was added to a majority phase polyethylene matrix [175-177]. The molten polyethylene molecules became aligned and formed disk shaped crystallites (Figure 2.24). These disks have been observed on CNTs [168] and cellulose nanofibres [178].

2.3.7.2. Polypropylene-CNT composite yarns

Polypropylene is a semicrystalline polymer synthesised from propylene gas [179]. Polypropylene is similar in structure to polyethylene, except that there is a methyl group attached to every second carbon in the backbone, as shown in the Figure 2.25.



Figure 2.25. Schematic of the polypropylene molecule.

Polypropylene is more rigid than polyethylene and has a higher melting point, although it has broadly similar mechanical behaviour to polyethylene at room temperature. It also has limited solubility in solvents, with hot xylene being one of the main solvents [179]. Polypropylene is widely used in filament production and also as composite matrix with CNT [180, 181]. Various studies found that the presence of 0.1-3w/w% CNT during polymerisation of polypropylene improved the rate of the crystalline growth of polypropylene, as well as the degree of crystallinity by 5.5%, hence acting as nucleating agents [41, 128, 182]. The mechanical strength and modulus of polypropylene/CNT composite were found to increase by about 20% by optimal alignment of the CNTs in the polymeric matrix and increased load transfer at the interface [183, 184]. In addition, the glass transition temperature (T_g) and viscosity of the composite changed in the presence of the CNT (Figure 2.26). For example, the addition of 1-3w/w% CNT resulted in a slightly higher T_g(5°C) and the rheology of the mixture became more non-Newtonian [185, 186].



Figure 2.26. TGA graph of the CNT and polypropylene composite [185].
Furthermore, a CNT mixing ratio of 1-3w/w% was found to optimally improve the mechanical properties of the composite yarns produced from CNTs as the filler and polypropylene as the matrix [52, 187]. The agglomeration of the CNTs for ratios higher than 3w/w% was believed to be the main reason in reduction of the mechanical properties of the polypropylene/CNT composite, compared to those of lower CNT ratios.

2.3.7.3.Nylon 6,6-CNT composite yarns

Nylon 6,6 is a semi-crystalline polymer with melting point of 240°C and is synthesised by condensation of hexamethylenediamine and adipic acid each containing 6 carbon atoms shown in the Figure 2.27. Three main methods have been used to incorporate CNTs into the nylon 6,6 as reinforcing agents.



Figure 2.27. Schematic of the molecular structure of nylon 6,6 [188].

In melt compounding method, CNTs are added to an already molten nylon 6,6 [189-191]. The molten polymer is then extruded to form filaments or other forms of nanocomposite [189, 190, 192]. Due to the lack of adhesion between the nanotubes and nylon 6,6 phases, surfactants or functional groups can be introduced to enhance the interactions between the CNT filler and nylon 6,6 matrix [189] through covalent or non-covalent bonds. In order to functionalise the CNTs, acidic solutions were prepared using nitric or sulphuric acids. Although such treatments of the CNTs result in improved dispersion of the CNTs in the polymer matrix, the functional groups such as carboxylic acid groups or the surfactants inevitably damage the CNTs structure and reduce the composite mechanical and electrical properties [193].

Another method of producing nylon 6,6 and CNT composite is via *in situ* polymerisation of nylon 6,6 in the presence of dispersed CNTs [194, 195]. In this method, both monomers and CNTs are firstly dispersed in identical solvents followed by controlled polymerisation of the monomers in the presence of CNTs. This approach maintains the CNT dispersion in the monomer solution and helps achieve uniform distribution of CNTs throughout nylon 6,6 matrix [189].

The third method to incorporate CNTs into nylon 6,6 matrix involves dissolution of the polymer in a solvent, usually formic acid, sulfuric acid [189] or glycerine [177], which are also able to disperse CNTs. A mixture of such dissolved polymer and dispersed CNTs results in a homogenous mixture which can then be used for fabrication of nanocomposite. The difficulty in using the dissolution method is that the mixture needs to be heated to above melting point of nylon 6,6 which makes formic acid or sulfuric acid extremely dangerous and combustible [196]. However glycerine requires a much lower temperature, thus, unlike using formic or sulfuric acids, the use of the glycerine does not damage the CNTs due to the low temperature (185°C) required for the fabrication process. Therefore, there is no harmful effect on the composite mechanical and electrical properties [197].

The formation of physically adhered crystalline structures around the CNT bundles has been shown to improve the mechanical robustness of the nanocomposite compared to noncrystalline nanocomposite, where nylon is the majority phase [198, 199]. The addition of 0.1-5w/w% of CNTs into a nylon 6,6 matrix has resulted in increase in the mechanical properties of the composite material [200, 201]. Another study found that the amount of the CNTs has an inverse relationship with the formation of nylon 6,6 crystalline disks [197]. It was shown that the addition of 2w/w% of CNTs into nylon 6,6 matrix led to the decrease in the size of the crystalline disks, indicating a hindrance in nylon 6,6 lamellar growth around the CNTs. An increase in the storage modulus and thermal stability of such composite has been also reported, whilst its tensile strength remained unchanged due to the inability of nylon 6,6 molecules to crystallise around the CNTs [199].

2.4. Conclusion

In this chapter, a critical literature review is presented and the works of CNT and polymers were studied in detail. It was established that the mechanical properties of the forest-spun CNT yarns are relatively high compared to those of the other CNT yarn fabrication methods. However, despite high tensile strength (50-150GPa) and tensile modulus (1-1.2TPa) of the individual CNTs, only a small fraction of such strength has been currently captured in the CNT yarn (5-7%), compared to the strength of conventional textile yarns such as cotton or wool (70-90%). This is despite the fact that the individual CNTs can bear much higher stress mainly due to the low stress transfer mechanism in the CNT yarns being fundamentally different to the conventional textile yarns. In the conventional textile yarns, the tensile stress breaks the chemical bonds in the fibres thus the fibre breakage is the result of the tensile force being greater than the tensile strength of the individual fibres. In the CNT yarns, however, the individual CNTs do not break their covalent bonds when the yarn fails, but rather slide relative to one another. This is because the interfacial shear strength of the nanotubes produced by the vdW is very low hence the applied tensile stress on the nanotubes becomes greater than its shear strength. Although more than a decade of research has investigated the mechanism of load transfer in the CNT yarn [2, 3], there have only been modest increases in the failure loads. Therefore, there is a need for new strategies by which mechanically stronger CNT yarns can be produced. One of such strategies is the new concept of infiltrating polymers within the CNT yarn in order to lock the individual and bundles of the CNTs together and ensure better load transfer under the tensile force.

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Chapter 3

Materials and methods

3.1. CNT yarn fabrication

The MWCNT forests were supplied by the CSIRO at Clayton on silicon made substrates typically 40×10 mm in length and width produced by the CVD method.



Figure 3.1. Schematic of the CNT growth in the CVD method [1].

In this method, as shown in the Figure 3.1, silicon substrates are first coated with iron nano particles and placed in a furnace where the temperature can reach 1000-2000°C. A carbon rich gas is then flowed through the furnace causing the carbon atoms to attach themselves to the iron particles. The combination of the temperature and flow results in carbon atoms assembling on top of one another forming long tubular CNT structure [2]. The supplied spinnable individual MWCNTs generally possessed the following properties: 7-15 walls, ~150µm lengths, 2nm inner and 20nm outer diameters confirmed by the SEM and TEM [3].

To fabricate the CNT yarn, a CNT web was first drawn from one end of the substrate using tweezers and attached to a stand (Figure 3.2). The stand was attached to a belt which was run by a DC motor. The movement of the belt drew the CNT web away from the forest, thus producing a length of the CNT web.



Figure 3.2. Schematic of the drawing a web of CNTs from the CNT forest, followed by twisting using a DC motor to form a CNT yarn

The substrate width was 10mm, and the CNT web initially retained this width immediately after drawing. However, downstream from the commencement of the drawing point, the web width reduced to \sim 2mm, largely due to the vdW forces. Upon tensioning the CNT web by pulling the end of the web, the width further shrank to ~0.5mm. This was the

minimum possible width value that could be achieved during the web formation process. Further tensioning of the web did not change the width, but led to the CNT web breakage. Typically, 30cm of the CNT web was drawn in order to perform the experiments.

3.2. Densification of the drawn CNT web

In order to produce the CNT yarns, the CNT webs were densified using twist and/or solvent. Two approaches were used to insert twist in the CNT web namely shrinking-length twist and constant-length twist. In addition, two solvents, acetone and ethanol, were used to densify the CNT web namely acetone and ethanol.

3.2.1. Densification by solvents

The CNT web was densified by using two solvents, acetone or ethanol. They were selected due to their efficient densifying ability, as established and discussed in Chapter 2. In order to densify the CNT web into the CNT yarn, a droplet of acetone or ethanol was dropped along the length of the CNT web whilst the web was horizontally held. The newly formed densified CNT yarn was then left at room temperature for 1h to allow any solvent residue to evaporate from the CNT yarn structure.

3.2.2. Densification by twist

The twist was used as a densification mechanism into the horizontally-held CNT web, in order to fabricate a twist-densified CNT yarn. The twist was inserted using two techniques: (i) in the first technique, the length of the CNT web was allowed to shrink during the twisting (named "shrinking-length" twist). In order to do so, one end of the CNT web could move while the other end was attached to a DC motor. Various amounts of twist were inserted in the CNT web before the motor was stopped, (ii) in the second technique, the length of the CNT web was kept constant during the twisting by fixing both ends of the CNT web at two points (named "constant-length" twist). For both twisting techniques, the motor was rotating at ~100rpm, inserting the twist in the CNT web converting it into a

CNT yarn. After the completion of the twist insertion, the CNT yarn was left in place for 10min to stabilise. No additional CNT web was drawn from the CNT forest during the spinning.

3.3. Densification whilst twisting in an acetone environment

In order to insert the twist in the CNT web while immersed in acetone, a new setup was designed and used as schematically shown in the Figure 3.3. In this setup, the DC motor was placed vertically so that the CNT web could hang vertically inside the acetone container. In order to fix the other end of the CNT web inside acetone, a small grip was placed at the bottom of the acetone container. The CNT web was first placed in the empty container and its end was fixed on the grip. The container was then filled with acetone. After the completion of the twist insertion, acetone was removed from the container before the CNT yarn could be taken out. The CNT yarn was then left in place to dry for 1h. The length of the CNT web remained constant during acetone densification.



Figure 3.3. Schematic of the set-up for producing twisted CNT yarn in acetone.

3.4. Polymer-infused CNT yarn fabrication

The polymer-infused CNT yarn is a general name, used in this thesis, to refer to the yarn structures that were produced by the infusion of different types of polymer into the CNT yarns in order to distinguish them from the neat CNT yarns. In this thesis, six types of polyethylene, a polypropylene and a nylon 6,6 were used to produce polymer-infused CNT yarns. In order to distinguish such infused yarns, produced by each polymer, and to eliminate any confusion in the following chapters, the "polymer" in the polymer-infused CNT yarn was then replaced with the appropriate polymer type accordingly.

3.4.1. Polyethylene-infused CNT yarn

Six types of polyethylene were used as received to fabricate the polyethylene-infused CNT yarns. The average molecular weights for each polyethylene are listed in the Table3.1.

Polyethylene	Molecular weight	Supplier
	g/mol	
HDPE0.83	158000	CSIRO
HDPE4.5	79000	CSIRO
HDPE20	54000	CSIRO
PE35000	35000	Sigma Aldrich
Polywax3000	3000	Baker Hughes
Polywax1000	1000	Baker Hughes

Table 3.1. Molecular weights of the polyethylene types.

The setup for the polyethylene infiltration into the CNT yarns consisted primarily of a hot plate for heating the silicon oil bath. A number of test tubes containing 10mL of xylene was

placed inside the oil bath, heating the xylene to 130°C. A solution of polyethylene and xylene was then prepared by adding the polyethylene beads into the hot xylene in the test tubes whilst stirring at 350rpm. Once a homogenous solution was prepared, the densified CNT yarn or the CNT web was dipped in the stirring solution and held stationary in the solution until the cooling process was completed. To keep the CNT yarn or web stationary in the solution during the cooling process, a purpose-made stainless steel frame was used and the CNT yarn was wrapped around it as shown in the Figure 3.4.



Figure 3.4. Frame for the wrapping of CNT yarn and dipping in the polymer solution with the CNT yarn or web wrapped around it.

The polyethylene-infused CNT yarn was then taken out of the polyethylene solution and left in the fume hood for 1h to remove the xylene residue. Three different cooling rates were used to study the effect of the cooling rate on the properties of the polyethylene-infused CNT yarns. The cooling rate of 1°C/min was achieved by turning off the hot plate while the CNT yarn was maintained in the solution and in the oil bath. The cooling rate of 10°C/min was achieved by taking the test tube containing the solution out of the oil bath and putting it in the fume hood while the CNT yarn was maintained in the solution. The cooling rate of 100°C/min was achieved by taking the CNT yarn out of the solution. The cooling rate of 100°C/min was achieved by taking the CNT yarn out of the solution and leaving it in the fume hood for 5min. The cooling time for the cooling rate of 1°C/min was 30min, 10°C/min was 3min and 100°C/min was 20s.

The resultant polyethylene-infused CNT yarn was washed with acetone at least three times to remove any polymer residue from the yarn surface. It was then left in the oven at 80°C for 1h, in order to remove any xylene or acetone residues from within the yarn structure.

Acetone does not dissolve polyethylene but was used to wash off any residue attached on the surface. The precipitation of the polyethylene during the cooling made some small chunks that were attached on the surface of the yarn. By using acetone, such residues were removed.

3.4.2. Polypropylene-infused CNT yarn

Polypropylene with an average molecular weight of 297000g/mol was obtained from Lyondell Basell Australia Pty. Ltd. and used as received. An oil bath was prepared using silicon oil on a hot plate. Xylene was used as the solvent for polypropylene in the test tubes. In a typical run, 10mL of xylene was used to dissolve polypropylene at 130°C while stirring at 350rpm. The CNT yarn or web was then placed inside the solution using a stainless steel frame and remained until the cooling process was completed. The polypropylene-infused CNT yarn was then removed from the solution and washed with acetone at least three times. This was done to remove any polymer residue from the yarn surface. Afterwards, the polypropylene-infused CNT yarn was placed in the oven at 80°C for 1h to remove any xylene or acetone residues from within the yarn structure.

3.4.3. Nylon 6,6-infused CNT yarn

Glycerine was purchased from Sigma Aldrich and used to dissolve nylon 6,6 and infuse this solution into the CNT yarn [4]. An oil bath was prepared on a hot plate using avocado oil due to its high smoking temperature (260°C). Between one and three test tubes containing 10mL of glycerine were placed in the oil bath heating it to 240°C. Nylon 6,6 beads with the average molecular weight of 22000g/mol were then added into the hot glycerine while the solution was stirring at 350rpm. Once a homogenous solution was prepared, the densified CNT yarn or undensified CNT web was placed inside the solution wrapped around the purpose-made stainless steel frame. The cooling of the solution to 185°C was achieved by turning off the hot plate. A cooling rate of 1°C/min was chosen for the preparation of the nylon 6,6-infused CNT yarn. The cooling time was 55min. After the cooling process was completed, the nylon 6,6-infused CNT yarn was then taken out of the solution and washed

with acetone at least three times in order to remove any polymer residue from the yarn surface. The yarn was then placed in oven at 80°C for 1h to remove any acetone from within the yarn structure.

3.5. Characterisation of the CNT web, CNT yarn and polymer-infused CNT yarn

3.5.1. Tensile properties

The tensile testing was performed on a Mini-Instron 5848 tensile tester with a load cell of 100N. The pneumatic grips firmly held the ends of the yarn with the upper arm moving at the extension rate of 0.1mm/min. The tensile gauges were 30×30 mm in dimension while the gauge length was 10mm. The sides of the gauge were cut so that the tensile force could be applied on the yarn, as shown in the Figure 3.5.

3.5.1.1. CNT Web

A sample of the CNT web with a length of typically 30cm was produced by drawing a length of the CNTs from the forest as shown in the Figure 3.2. The CNT web was then cut into specimens and placed on a tensile gauge which was custom made in the laboratory from paper sheet as shown in the Figure 3.5. Each paper gauge contained 1 specimen slot. Both ends of each CNT web specimen were then glued to the paper gauge using PVA glue, with the gauge length for each specimen being 10mm. The sides of the gauge were cut so that the tensile force could be applied on the yarn, as shown in the Figure 3.5.



Figure 3.5. Schematic of the tensile gauge with the slot in the middle prepared from paper sheet [5].

3.5.1.2. CNT yarn

A length of the CNT yarn was produced using one or more than one densification method. The CNT yarn was then cut into specimens and placed on a paper gauge containing 1 specimen slot. Both ends of each CNT yarn specimen were then glued to the paper gauge with PVA glue. Similar to the CNT web, the sides of the gauge, on which the CNT yarns were glued, were then cut so that the tensile force could be applied on the yarn.

3.5.1.3. Polymer-infused CNT yarn

The polymer-infused CNT yarn was placed in the middle of the paper gauge and glued to the gauge edge using PVA glue. Care was taken in order not to glue the yarn inside the gauge length since this could change the tensile strength and invalidate the data. The gauge length for each specimen was 10mm while an extension rate of 0.1mm/min was applied during the tensile testing. To commence the test, the sides of the gauge were firstly cut so that the tensile force could be applied on the polymer-infused CNT yarn

3.5.1.4. Calculation of the tensile strength and modulus for the CNT web, CNT yarn and polymer-infused CNT yarn

The tensile strength and modulus for the CNT webs, CNT yarns and polymer-infused CNT yarns were calculated using the following equations:

$$\sigma(\text{GPa}) = \rho_{\text{CNT}}(g/m^3) \times \frac{F(N)}{\text{tex}(\frac{g}{m})} (\frac{1GPa}{1x10^{9N}/m^2})$$
 Equation 3.1

$$E = \frac{\sigma}{e}$$
Equation 3.2
$$tex = \frac{w}{L}$$
Equation 3.3

where σ is the tensile strength (GPa), ρ is the CNT density and is assumed constant (1.8g/cm³) [6], F is the maximum load at break (N), *tex* is the linear density (tex), E is the tensile modulus (GPa), e is the maximum strain at break (%), w is the weight of a piece of the CNT web, CNT yarn or polymer-infused CNT yarn (mg) and L is the length of the CNT web, CNT yarn or polymer-infused CNT yarn (m).

3.5.2. SEM analysis

The morphological properties of the CNT webs, CNT yarns and polymer-infused CNT yarns were studied with the SEM using a FEI Nova NanoSEM 450 FEG SEM microscope. To allow imaging, a small amount of the sample was placed on a sample holder using a double-sided carbon tape. All images were taken using an acceleration voltage of 15-20kV. The SEM images were used to calculate the average yarn diameter and polymer disk size using Image J software.

3.5.3. TEM analysis

The TEM observations of the samples were undertaken on a JEOL JEM 2100F FEG TEM. In order to prepare the samples for the TEM, a small amount of the sample was placed onto a copper grid. The sample was then secured by gluing an empty copper grid, on top of the sample, to the copper grid underneath the sample. In doing so, the sample was sandwiched between the two grids which could then be inserted inside the TEM chamber for imaging. The TEM images were observed through a Gatan image filter at an accelerating voltage of 200keV.

3.5.4. TGA analysis

The thermal properties of the samples were investigated with a TGA using a Perkin Elmer SI1TGA model. The data gave information about the thermal characteristics of the material, that is, at which temperatures the molecule chains thermally degrade. Samples weighing 5-10mg were placed in an alumina crucible for measurement and the scanning performed in an air or nitrogen environment from 30° C to 800° C at the heating rate of 10° C/min.

3.5.5. DSC analysis

In order to study the phase transition and crystallisation of the polymer in the presence of the CNT, a Perkin Elmer Pyris 1 DSC instrument was used with Perkin Elmer 7 software. Typically, 0.2-2mg of CNT web, CNT yarn or polymer-infused CNT yarn was placed in an aluminum pan, and the sample was sealed by placing an aluminum cap on the top and pressing the sides of the container inward using a press to crimp the pan. Each sample was circular in shape and had dimension of around 1×1 mm. The atmosphere in the DSC chamber was nitrogen with a flow rate of 20mL/min and a hearing rate was 10° C/min.

3.5.5.1. Calculation of the degree of crystallinity of the polymer component in polymer-infused CNT yarn

The degree of crystallinity for the polymers and for the polymer component in the polymerinfused CNT yarn was calculated using the following equation:

$$X = \frac{\Delta H_{expt}}{\Delta H_0 \times W_{polymer}} \times 100$$
 Equation 3.4

where X is the degree of crystallinity (%), ΔH_{expt} is the enthalpy change obtained from the DSC experiment (J/g) and ΔH_o is the standard enthalpy change (J/g) of the 100% crystalline polymer (used as listed in the Table 3.2) and W is the weight fraction of the polymer in the polymer-infused CNT yarn obtained from the TGA results.

Polymer	ΔH_o	Reference
	J/g	
Polyethylene	293	[7]
Polypropylene	207	[7]
Nylon 6,6	256	[8]

Table 3.2. Standard enthalpy change (ΔH_o) of the 100% crystalline polymers.

3.5.6. Raman Spectroscopy

The Raman spectroscopy was undertaken to study the graphitic properties of the CNTs. The Raman spectra were obtained using an WITech alpha 300R Confocal Micro-Raman microscope with 514nm excitation from a Modu-Laser Stellar-Pro ML/150 argon ion laser through a X20 (0.4na) objective. The CNT web, CNT yarn, neat polymer and polymer-infused CNT yarn were mounted on a silicon wafer and placed in the microscope holder. An incident laser power of 1.0mW and coaxial backscattering geometry were employed to characterise the samples.

3.5.7. X-Ray Diffraction (XRD)

The XRD analysis was undertaken using a PXRD D2 Phaser instrument. X-ray was generated by Cu k α at 300W power, 40kV and 30mA. All the tests were undertaken at room temperature and atmospheric pressure. The samples were put on a zero diffraction

plate and flattened before the measurement. The spectrum was obtained by the reflection of the x-ray beams from the samples. The zero diffraction plate had no crystallinity in its structure and did not produce any diffraction peak associated with the plate. The degree of crystallinity was estimated using the Segal method [9]:

$$I_{\rm crys} = \frac{I_{\rm max} - I_{\rm min}}{I_{\rm max}} \times 100$$
 Equation 3.5

where I_{crys} is the degree of crystallinity (%), I_{max} is the maximum intensity of the characteristic peak and I_{min} is the intensity of the amorphous fraction.

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Chapter 4

Investigation into the CNT web and yarn drawn from CVD-grown CNT forest

4.1. Introduction

In this chapter, the results of a detailed study of the structure and properties of the CNT webs and yarns are presented. It was important to establish a benchmark for the properties of the CNT yarns used here, to allow comparison with the work in the following chapters where polymer was infused into these structures. The manipulation of the microstructure of the neat CNT yarns is in itself instructive and thus the work described here involves manipulating the forest drawn CNT webs using various methods of densification into the CNT yarns, such as by using twist or solvent. This provides some indication as to what morphology is important to get improved mechanical properties in the CNT yarns. Such structures were subsequently characterised and their morphological and mechanical properties studied.

From a detailed review of the literature, it is apparent that the mechanical properties of the CNT yarns will play a major role in improving the properties of any composite systems of polymer and CNT yarn. A number of studies reported to date has focused on improving the mechanical properties of the CNT yarns using the above mentioned densification methods. However, the tensile strength and modulus of the CNT yarns still remain in 1.8-3.4GPa and 100-200GPa ranges, respectively. It is believed that the main reasons for such drawbacks are due to the intrinsic structure of the CNT nanotubes [1]. Due to their molecular size, the CNTs have the vdW attractive forces which cause them to aggregate and form larger bundles. Therefore, the CNTs. This is because the strength of the CNT yarn depends on the ability of the individual and bundles of the CNTs to transfer the stress between one

another. The CNTs with a higher number of walls or larger diameters have less surface area thus less of such interactions per mass of the CNT. This results in a decreased ability of the CNTs to efficiently adhere together and to have the maximal number of contacts [2, 3]. Since the CNT yarn as a whole can be considered as an assembly of the bundles of the CNTs, that are elongated along the CNT yarn axial direction, such parameters affect the strength of the CNT yarn itself.

In order to increase the mechanical strength of the CNT yarns, two twisting methods and two solvent densifications, were employed. The characterisation methods such as SEM, TEM, TGA, DSC and tensile testing were undertaken to gain an understanding of the properties of the CNT yarns and to prepare the types of yarns that would be infiltrated by polymers in the following chapters.

4.2. CNT web properties

The CNT web was prepared by drawing a length of CNTs from the CVD-grown CNT forest. The detailed procedure to produce the CNT web is provided in the Section 3.1. Briefly, tweezers were used to grab one end of the CNT forest and draw the CNT web and attach it to a stand. The stand was attached to a belt which was run by a DC motor. The motor moved the belt which resulted in the CNT web being drawn away from the forest, thus producing a length of the CNT web.

4.2.1. Morphological properties

The Figure 4.1a shows an SEM image of the as-grown CNTs in the CVD-grown CNT forest before they were drawn from the substrate to form the CNT web. These CNTs grew vertically during the synthesis process and stood normal to the substrate. The inset of the Figure 4.1a shows some typical curvature and bending apparent on the individual and bundles of the CNTs. It can be seen that although a primary, longitudinal orientation was maintained along the direction of the growth, some individual or smaller bundles of the CNTs bridged larger bundles in a perpendicular manner and formed a number of contact

points in the structure. Such contact points are very important in drawability of the CNT forest [3, 6]. A continuous drawing process requires such an interconnection in the CNT web. The inset of the Figure 4.1b shows the CNT web drawn from the forest.



Figure 4.1. (a) CNT forest grown on a silicon substrate, (b) CNT web drawn from the CNT forest, (c) schematic of the web drawing from the CNT forest [4] and schematic of the mechanism of drawing process from the forest to the CNT web[5].

Zhu *et al.* [7] investigated the recruitment mechanism from the forest and reported that the CNT density and alignment in the CNT forest are crucial factors in maintaining a

continuous drawability. It should be noted that although the CNTs maintained a general directional orientation along the length of the CNT web, mainly due to the larger bundles of CNTs, a great deal of inter bundle entanglement and interlocking was also present as it was in the CNT forest prior to the drawing [6]. Such CNT interlocking results in the formation of a loosely connected structure, with vdW forces at the contact points maintaining the individual and bundles of the CNTs [8]. These contact points in the CNT web were important for effective stress transfer throughout the structure, leading to good mechanical strength in the CNT yarn that were produced from such CNT webs. The Figure 4.1c shows the schematic of the vertical alignment of the CNTs on the substrate and illustrates the mechanism by which the CNT web was produced [5].

4.2.2. Mechanical properties

The mechanical properties of the CNT web were measured using the tensile tester. The Figure 4.2 shows the load-strain curve of the CNT web, while the Table 4.1 presents the mechanical properties of the CNT webs, obtained using the tensile tester. It is noted here that the tensile modulus is calculated from the linear region of the stress-strain curve.



Figure 4.2. Tensile load-strain curve of the CNT web. The extension rate of 0.1mm/min and gauge length of 10mm were used for the tensile testing.

The curve shows two stages of load bearing in the CNT web. In the first stage, the load rapidly increased indicating stretching of the CNT web as a whole. In the second stage, the load increased to a lesser degree than the first stage, indicative of the stretching of the individual and bundles of the CNTs within the web [4]. Similar behaviour was observed by Zhang *et al.* [9] who concluded that the force is transferred from one bundle to another during the load bearing, causing slower slope in the load during the second stage. It can be also seen from the Table 4.1 that the strength of the drawn CNT web is around 0.41GPa and the strain is 4.2%. This shows that the CNT web had a lower strength compared to those of the CNT yarn in N/tex, the unit of GPa is widely used and reported in the literature. Thus, in this chapter both GPa and N/tex are reported in order to provide a better understanding of the mechanical properties of the CNT yarns.

It can be observed from the Table 4.1 that the tensile force and the extension at break required to break the CNT web were directly proportional to its linear density across most of the CNT webs. The tensile strength and modulus shown in the Table 4.1 confirm that the CNT webs had consistent strength across various forest substrates, when the linear density and the force at break were taken into account. Similar results were reported by Jia *et al.*[4] and Liu *et al.* [10] where the mechanical properties of the CNT webs were measured and they concluded that such properties can be increased by further shrinking the CNT bundles together and producing a more compact CNT yarn.

The average tensile strength and modulus values of 0.41GPa and 8.81 GPa for the CNT web is due to the vdW forces between the individual and bundles of the CNTs, thus indicating the strength of such intermolecular forces for a CNT web of ~0.5mm (500µm) in width. It should be noted here that the strength unit of N/tex is independent of the diameter because it takes into account the linear density of the CNT yarn or the web, rather than the cross-sectional area which varies along the length. This is especially useful, because using the cross-sectional measurements in the CNT yarn calculations would have added more uncertainty to the calculated strength. In addition, the tensile modulus was calculated from the linear region in the stress-strain curves.

Chapter 4 Investigation into the CNT web and yarn drawn from CVD-grown CNT forest

Table 4.1. Mechanical properties of the CNT webs produced from CVD grown CNT forests. The gauge length was 10mm and extension rate 0.1mm/min.

CNT forest	Number of	Linear	Load at	Strain at	Tensile	Tensile	Tensile
	specimens	density	break (std	break (std	strength	strength	modulus
	tested	tex	dev)	dev)	(std dev)	(std dev)	(std dev)
			Ν	%	GPa	N/tex	GPa
1	7	0.21	0.04(0.01)	3.99(1.3)	0.41(0.02)	0.22(0.02)	10.28(2.3)
2	5	0.15	0.03(0.01)	5.24(0.6)	0.44(0.05)	0.24(0.03)	8.4(1.02)
3	10	0.16	0.03(0.01)	5.39(0.5)	0.42(0.03)	0.22(0.03)	7.79(1.04)
4	3	0.12	0.02(0.01)	4.33(0.6)	0.38(0.01)	0.21(0.04)	8.78(1.14)

4.3. Crystallinity of the CNT

The Figure 4.3a shows the Raman spectrum of the CNT web and the Figure 4.3b shows the XRD curve to study the graphitic and crystalline structure of the CNT yarn. In previous Raman studies, Pierlot *et al.* [11] associated the peaks of the graphite at 1355cm⁻¹ to defect (D band) and 1589cm⁻¹ to graphitic (G band).



Figure 4.3. (a) Raman spectrum of the CNT web and (b) XRD curve of the CNT web.

The defect to graphitic ratio (I_D/I_G ratio) was calculated to be 0.85. This ratio for highly graphitic SWCNT is usually much lower due to single wall characteristic of such CNTs. However, the CNTs drawn from the CNT forest in our work contain of MWCNTs with 7-14 walls with characteristic curvature and bending as well as some amorphous carbon produced during the CVD process. This made the defect peak much higher, when compared to the graphitic peak. Similar results were observed and reported by Pirelot *et al.* who suggested the presence of impurity for the rather high defect peak [11.]

The XRD curve in the Figure 4.3b shows that our MWCNTs have very high internal order between the CNT layers, as the main (002) peak has a full width at half maximum of 0.0798, the highest intensity of 63.5161 and the baseline of 2.5172. Ducati *et al.* [12] and Thess *et al.* [13] investigated the crystallinity of MWCNTs using XRD technique and concluded that the main (002) peak at 22° determines the graphitic orientation within the

CNT structure. The calculation of the degree of crystallinity of our CNTs showed the degree of crystallinity of 96-97% (obtained from Equation 3.5).

4.4. CNT yarn characterisation

The CNT yarn was produced by the densification of the CNT web using twist, solvent and combinations of the two. Once a length of the CNT web was produced, two twisting techniques namely shrinking-length and constant-length twist were used to densify the web into a CNT yarn. In addition, two solvents, acetone and ethanol, were used to densify the web into a CNT yarn. In order to gain an understanding of the effects of such densification methods on the CNT yarn properties, the densified CNT yarns were then characterised using the SEM and tensile testing.

4.4.1. Densification of the CNT yarn by solvent

Two solvents were used to densify the CNT yarns, namely acetone and ethanol. They were selected due to their efficient densifying ability as established in Chapter 2 [10, 14]. Once a web of the CNTs was drawn from the CNT forest, a droplet of acetone or ethanol was drizzled along the length of the CNT web while it was horizontally held. The CNTs were likely held together by the capillary forces and the densification progressed by allowing the solvent to evaporate off the CNT web, thus compressing the CNT web and forming a denser yarn like structure. The CNT yarns were then left at room temperature for 1h to dry before subsequent characterisation.

4.4.1.1. Morphological properties

The newly-densified CNT yarns were left at room temperature for 1h to allow any liquid residue to evaporate from the yarn structure. The resultant CNT yarns shrank significantly from the initial CNT webs with the width of $520\mu m$ (Figure 4.4a) by an average factor of 29, to 18 μm in acetone (Figure 4.4b) and by an average factor of 25 to 21 μm in ethanol (Figure 4.4c).



Figure 4.4. SEM images of (a) CNT web, (b) acetone-densified CNT yarn and (c) ethanoldensified CNT yarn.

These results are in agreement with the results from Jia *et al.* [4] and Liu *et al.* [10]. In their studies, ethanol and acetone were used and they found that acetone had greater compression effect than ethanol by measuring the diameter of the CNT yarns before and after the densification. The volatility of acetone is greater than that of ethanol, thereby affecting the morphological properties of the CNT yarn [10]. The compression occurred due to the capillary forces of the solvent on the CNTs. While the CNTs were immersed in the solvent, the attractive vdW forces were temporarily reduced thus facilitating the CNTs to straighten and move closer together, increasing their contact points. This resulted in further compression of the CNT yarn. This result indicates that a more compact structure was obtained using acetone rather than ethanol which in turn increased the contact points between the individual and bundles of the CNTs within the yarn structure, as was also concluded by Jia *et al.* [4].

4.4.1.2. Mechanical properties

The acetone-densified CNT yarn was able to bear higher tensile load at failure compared to that of the ethanol-densified yarn by 20%, as shown in the Figure 4.5. Similarly, the tensile strength of the acetone-densified CNT yarn was also 20% higher than that of the ethanol-densified CNT yarn. It can be seen that the diameter of the acetone-densified CNT yarn is 20% smaller than that of the ethanol-densified CNT yarn as shown in the Figure 4.4, confirming that acetone is a more effective solvent in densifying the CNT webs into yarns.



Figure 4.5. (a) Load-strain curves and (b) stress-strain values of the undensified CNT web, acetone- and ethanol-densified CNT yarns.

CNT yarn	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
1	4	0.19	0.13(0.01)	3.02(0.1)	1.23(0.1)	0.68(0.06)	40.73(2.21)
2	3	0.2	0.13(0.01)	3.06(0.5)	1.16(0.1)	0.64(0.06)	37.91(2.81)
3	4	0.16	0.1(0.01)	3.05(0.2)	1.13(0.1)	0.62(0.07)	37.05(1.08)
4	2	0.14	0.05(0.01)	4.55(1.6)	1.11(0.3)	0.61(0.2)	24.4(2.19)
5	4	0.18	0.1(0.01)	2.9(0.2)	1.03(0.07)	0.57(0.04)	35.52(0.11)
6	4	0.15	0.1(0.01)	4.07(0.5)	1.04(0.07)	0.57(0.2)	25.55(1.43)
7	4	0.14	0.11(0.01)	3.44(0.4)	1.08(0.6)	0.59(0.3)	31.4(1.23)
8	10	0.12	0.07(0.01)	1.38(0.2)	0.75(0.3)	0.41(0.2)	54.35(1.15)
9	6	0.12	0.11(0.01)	2.3(0.2)	1.68(0.02)	0.92(0.01)	73.04(8.95)
10	7	0.24	0.13(0.01)	2.27(0.3)	1.05(0.01)	0.51(0.07)	46.26(5.82)

Table 4.2. Mechanical properties of acetone	-densified	CNT yarn.	The yarns	were produced	from identical	CNT forest.

CNT yarn	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
1	4	0.18	0.09(0.01)	2.5(0.3)	0.98(0.04)	0.54(0.02)	39.2(3.25)
2	4	0.17	0.08(0.01)	3.02(0.2)	0.92(0.03)	0.51(0.02)	30.46(1.19)
3	4	0.19	0.09(0.01)	2.4(0.2)	0.93(0.02)	0.51(0.02)	38.75(1.18)
4	2	0.19	0.09(0.01)	2.45(0.1)	0.88(0.07)	0.48(0.05)	35.92(2.76)
5	8	0.18	0.06(0.01)	2.56(0.3)	0.61(0.09)	0.34(0.06)	23.83(1.04)

Table 4.3. Mechanical properties of ethanol-densified CNT yarn.

The Tables 4.2 and 4.3 show the mechanical strength and modulus for the acetone- and ethanol-densified CNT yarns, respectively. It can be seen here that the strength of the acetone-densified CNT yarn is 10-20% higher than that of the ethanol-densified CNT yarn. The modulus of the acetone-densified CNT yarn is also 10-20% higher than that of the ethanol-densified CNT yarn. The reason is due to the better compression ability of acetone compared to ethanol which led to a higher stress transfer between the nanotubes as was confirmed by the SEM images (Figure 4.4).

The increase in the tensile strength in the acetone-densified CNT yarns compared to the ethanol-densified CNT yarns can be attributed to the higher volatility of acetone which compressed the CNT web more effectively than ethanol, producing a smaller diameter CNT yarn. The immersion of the CNTs in the solvent caused the attractive vdW forces to be temporarily reduced thus facilitating the CNTs to straighten and get closer together. This in turn resulted in further compression of the CNT yarn. Similar results were also reported by Liu *et al.* [10]. As a result, acetone-densified yarn had more inter nanotube contacts than ethanol-densified yarn. This has two effects: (i) an increased number of vdW attractions between the nanotubes and (ii) an improved load transfer between the individual and bundles of the CNTs due to the increased contact points created by further compression of the CNTs, thus increasing the tensile strength.

The maximum strain at failure of the acetone-densified CNT yarn was slightly higher than that of the ethanol-densified CNT yarn (~1%). The increase in the strain at failure as an indicator for the toughness of the CNT yarn shows that using acetone has increased the ability of the acetone-densified CNT yarn to elongate and absorb more energy before the failure, compared with the ethanol-densified CNT yarn. Hill *et al.* [8] found an inverse relationship between the CNT yarn diameter and its toughness. They concluded that large diameter CNT yarns require less energy to fracture than small diameter CNT yarns. Acetone compressed and reduced the CNT yarn diameter more effectively than ethanol thus increasing the toughness of the CNT yarn more than that of ethanol. The failure mechanism was investigated using the SEM for the acetone- and ethanoldensified CNT yarns. It was found that the failure mechanism for such CNT yarns is different from the conventional textile yarns such as cotton or wool, where the breakage of the covalent bonds leads to the ultimate failure of the yarn [15-17]. In the CNT yarn, since the main source of load transfer in the yarn structure is the contact points between the individual and bundles of the CNTs the load failure, upon tension, occurs due to the sliding of the CNTs relative to each other as shown in the Figure 4.6. The drawn line maps the conical formation at the tip while the scattering of some CNT bundles are due to the SEM sample preparation. The tensile loading of these CNT yarns was not sufficient to cause carbon bond failure in the individual CNTs which had a tensile strength of ~50GPa [18]. Therefore, sliding has been established as the key failure mechanism for the CNT yarns [18]. The failure of the CNT yarn under the tensile stress was also investigated by Sugano *et al.* [19] who found that the sliding and the pull out was the likely governing mechanism for such failure.



Figure 4.6. SEM images after tensile failure of (a) acetone-densified CNT yarn and (b) ethanol-densified CNT yarn.

4.4.2. Densification of the CNT yarn by twist

Twist was used to densify the CNT web into a yarn structure. Two types of twist were inserted into the CNT web namely, shrinking-length twist and constant-length twist. In the

shrinking-length twist, the length of the CNT web was allowed to shrink during the twisting. One end of the CNT web was moving while the other end was attached to a motor. In the constant-length twist, the length of the CNT web was kept constant during the twisting by fixing both ends of the CNT web at two points.

4.4.2.1. Shrinking-length CNT yarn

The shrinking-length CNT yarn was produced by holding one end of the CNT web fixed, while rotating the other end using a DC motor. The term shrinking-length is used in this thesis, to illustrate the fabrication method, as outlined in Chapter 3. Briefly, one end of the CNT web was fixed while the other end was attached to a DC motor which was held by a stand. The motor inserted twist on the CNT web producing the CNT yarns. The length of the CNT web was allowed to shrink during the twisting. It was observed that the resultant CNT yarn had a tendency to untwist in an attempt to regain its original untwisted state when the forces were released. However, the shrinking-length CNT yarn was not able to return to a completely untwisted state. This was understood by observing the CNT yarn after the twist was completed. This is due to the formation of new CNT contacts between the individual and bundles of the CNTs and thus stronger vdW interactions being formed by the twist, which in turn prohibited the CNT yarn to go back to an original twistless web. Although such intimate contact points may have been produced in the nanotubes on the outer surface as opposed to those on the inside of the CNT yarn, further analysis was not possible due to the limitations in the experimental equipment. In order to reduce the untwisting, the shrinking-length CNT yarn was kept fixed at both ends for 10min.

4.4.2.1.1. Morphological properties

The shrinking-length CNT yarn was formed by allowing the CNT web to contract along its length due to the twist, producing the coiled structure shown in the Figure 4.7a. The coil density (number of coils) and the homogenous distribution of the coils in the shrinking-length CNT yarn depended on the twist amount, as well as the speed of the free end of the CNT yarn moving towards the twisting end (shrinking speed).



Figure 4.7. SEM images of the shrinking-length twisted CNT yarn by contraction of the length leading to a coil formation (a) at shrinking speed of 60cm/min and (b) at shrinking speed of 30cm/min. A twist amount of 6000-7000 turn/meter was inserted into the yarns.

Keeping the twist amount constant, a slower shrinking speed (30cm/min) led to less coils being formed along the shrinking-length CNT yarn (lower coil density), while using a faster shrinking speed (60cm/min) led to more coils being formed (higher coil density). The helix angle, θ in the Figure 4.7b, on the shrinking-length CNT yarn was non-uniformly distributed along the yarn due to the non-uniform twist distribution, which caused some parts to twist more than others as is evident in the Figure 4.7. The speed was initially controlled by the pulling device shown in the Figure 3.2. However, since many samples were produced and characterised, it became clear that manual controlling by hand gave similar accuracy. Therefore, the samples presented in the thesis were all controlled manually by hand.

The shrinking-length method led to a nonuniform diameter distribution in the CNT yarn. The concentration of the twist on some points caused further compression of the CNT yarn and reduced the diameter. Lee *et al.* [20] and Lima *et al.* [21] studied the effect of shrinking-length twist on the CNT yarn and found that such CNT yarns had great mechanical actuation properties.

4.4.2.1.2. Mechanical properties

The Figure 4.8 shows the stress-strain curves for the shrinking-length CNT yarns before and after acetone densification. It can be seen that before acetone densification, the shrinking-length CNT yarn had a lower strength (0.25GPa) than CNT web (0.4GPa), while the strain was much higher (600%) compared to CNT web (4.5%).



Figure 4.8. Tensile strength of the shrinking-length CNT yarn (a) without acetone densification, and (b) with acetone densification. The yarns had twist of 6000turn/m. Acetone was applied after twist was inserted.

The mechanical properties of the shrinking-length CNT yarns produced with and without further acetone densification have been shown in the Tables 4.4 to 4.6. The shrinking-length CNT yarns were densified using acetone by running a droplet of acetone on the shrinking-length CNT yarn once (1-run) or 4 times (4-run). The shrinking-length CNT yarn (0.3-0.5GPa) showed no improvement in the tensile strength, compared to the CNT web (0.4 GPa), as shown in the Figure 4.2. Similar results were obtained for the force at break.

The twist did not increase the physical interactions between the individual and bundles of the CNTs, and thus the load transfer could not be increased in the CNT yarn, compared to the CNT web, which in turn led to the same tensile strength of 0.4 ± 0.02 GPa. Furthermore, due to a nonuniform distribution of the twist along the length of the shrinking-length CNT yarn, some stress concentration points occurred in the yarn which in turn caused the yarn to

fail under the tensile loading. It can be seen that using acetone increased the tensile strength from 0.3GPa in the Table 4.4 to 0.4GPa in the Table 4.5 and 0.5GPa in the Table 4.6.

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Twist turn/m	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
3000	7	0.18	0.03(0.01)	145.96(23.1)	0.31(0.09)	0.17(0.07)	0.21(0.11)
3000	4	0.22	0.04(0.01)	111.85(16.6)	0.32(0.1)	0.17(0.06)	0.29(0.21)
6000	6	0.21	0.03(0.01)	156.95(6.4)	0.27(0.07)	0.15(0.04)	0.17(0.11)
7000	5	0.17	0.03(0.01)	499.82(169.1)	0.33(0.1)	0.18(0.06)	0.07(0.01)

Table 4.4. Mechanical properties of the shrinking-length CNT yarn.

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Twist turn/meter	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
3000	9	0.16	0.04(0.01)	20.21(5.1)	0.44(0.1)	0.25(0.06)	2.18(0.21)
3000	9	0.18	0.05(0.01)	37.57(8.01)	0.56(0.03)	0.31(0.02)	1.49(0.14)
3500	10	0.19	0.01(0.01)	33.47(3.8)	0.16(0.02)	0.09(0.01)	0.48(0.13)
6000	5	0.18	0.04(0.01)	36.09(10.5)	0.45(0.05)	0.25(0.03)	1.24(0.15)
6000	5	0.18	0.04(0.01)	43.27(4.8)	0.46(0.04)	0.25(0.03)	1.06(0.11)
6000	5	0.18	0.05(0.01)	44.29(3.5)	0.49(0.01)	0.27(0.01)	1.11(0.11)
7000	9	0.19	0.04(0.01)	73.1(22.9)	0.45(0.02)	0.25(0.01)	0.61(0.18)
7000	5	0.17	0.05(0.01)	52.09(24.4)	0.58(0.05)	0.32(0.03)	1.11(0.14)

Table 4.5. Mechanical properties of shrinking-length CNT yarn followed by 1-run acetone densification.

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Twist turn/meter	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
1000	9	0.19	0.05(0.01)	7.38(0.66)	0.45(0.1)	0.25(0.07)	6.1(1.12)
1000	3	0.18	0.08(0.01)	6.76(1.83)	0.77(0.2)	0.43(0.1)	11.39(0.15)
1000	4	0.19	0.03(0.01)	1.38(0.99)	0.27(0.1)	0.15(0.06)	19.57(3.87)
2000	2	0.17	0.07(0.01)	7.33(0.25)	0.75(0.1)	0.41(0.06)	10.23(0.15)

Table 4.6. Mechanical properties of shrinking-length CNT yarn followed by 4-run acetone densification.

The increase in the tensile strength has been offset by the decrease in the ductility as indicated by the reduction in the extension at break from 228% in the Table 4.4 to only 5% in the Table 4.6. It can be also observed that within each experimental category, increasing the amount of twist for various shrinking-length CNT yarns resulted in an increase in the extension at break. The high strain at failure (up to 600%) is the result of the coils and twists being opened and increased the length of the yarn before the tensile force could be transferred into the individual and bundles of the CNTs. It is also noted that further acetone densification on the shrinking-length CNT yarns reduced the strain at failure (Tables 4.5 and 4.6) compared to shrinking-length CNT yarns. This may be due to the effect of acetone in reducing the CNTs' surface energy and aligning them along the direction of the CNT yarns, thus reducing the CNTs' bending and curvature. This may likely reduced the effective extension that the CNTs could travel within the yarn before breakage.

4.4.2.2. Constant-length CNT yarn

The constant-length CNT yarn was produced by fixing both ends of a drawn CNT web, while twisting one end relative to the other. Similar to the shrinking-length CNT yarn, the constant-length CNT yarn had a tendency to untwist when released. In order to avoid untwisting, the freshly twisted constant-length CNT yarn was kept fixed at both ends for 10min at room temperature.

4.4.2.2.1. Morphological properties

The Figure 4.9 shows the SEM images of the constant-length CNT yarn. It can be seen that the yarn diameter is even along the axial direction, with the cylindrical yarn cross-section shown in the Figure 4.9a.



Figure 4.9. SEM images of the constant-length CNT yarn showing (a) fully twisted yarn with uniform cross-section and a helix angle and (b) radial collapse during the compression by twist. The yarn was produced by inserting twist of 2400turn/m into a CNT web.

A helix angle of 8° was observed for the constant-length CNT yarn, due to the amount of the inserted twist in the yarn (2400turn/m). The helix angle increased as the amount of the inserted twist was increased. Since the inserted twist could not shrink the yarn axially, the force compressed the yarn radially. Hence, the diameter was reduced after the twisting (40µm), compared to the untwisted CNT yarn (80µm), as shown in the Figure 4.9b. It is shown that the insertion of the twist reduced the diameter of the CNT web into a yarn, as can be seen in the higher magnification inset.

A number of studies has investigated the properties of CNT yarns and found that although many factors influence the CNT yarn properties, it seems that the yarn diameter, twist angle, inter nanotube vdW interactions and the insertion of twist do enhance the uniformity across the length and cross-section of the CNT yarn [8, 22-24]. A study by Hawkins [25] showed that the twist on its own cannot induce CNT migration towards the centre of the CNT yarn but rather circularizes and compacts the CNTs on the outer surface of the CNT yarn which in turn improves the strain at break and minimises the stress concentration points. The constant-length CNT yarns produced here show a circular structure, indicating that a uniform twist distribution was achieved as shown in the Figure 4.9a.

Unlike the shrinking-length CNT yarn (Figure 4.7), the helix angle in the constant-length CNT yarn was very uniform across the length indicating a uniform distribution of twist in the CNT yarn. Obtaining a uniform distribution of twist is very important in achieving fewer stress concentration points along the length of the CNT yarn.

4.4.2.2.2. Mechanical properties

The Figure 4.10 shows the stress-strain values for the CNT web, and its twisted CNT yarns. The constant-length CNT yarn shows the highest tensile strength compared to the shrinking-length CNT yarn.



Figure 4.10. Tensile strength of constant-length CNT yarn compared to the CNT web and shrinking-length CNT yarn. The shrinking length and constant length CNT yarns were produced from identical CNT webs. The length of the CNT webs was also identical for both twisting methods. A twist of 2400turn/m was inserted in the length, followed by acetone densification.

The tensile strength of the constant-length CNT yarn significantly increased by a factor of 3 to just over 1.8GPa, compared to that of the shrinking-length CNT yarn (0.5GPa), as can be seen in the Tables 4.7 and 4.8. Such a significant increase in the tensile strength is due to the compression of the constant-length CNT yarn's lateral configuration which led to the

formation of more aligned and tightly packed CNTs within the CNT yarn. Hence, the stress transfer could be increased from, and to, the neighboring individual and bundles of the CNTs which improved the tensile strength of the constant-length CNT yarn. A number of researchers has reported the effects of changing various parameters such as the nanotube diameter, CNT forest length, CNT yarn diameter, CNT yarn packing density, interfacial and intrafacial vdW interactions between the CNT walls [3, 4, 8, 26-31], all of which influence the mechanical properties of the CNT yarn. However, their CNT yarns all remained to have, at the best, the tensile strength of ~ 1.8-3.4GPa and modulus of ~400GPa [32].

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Twist turn/m	Number of specimens tested	Linear density tex	Helix angle (°)	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
2400	5	0.21	6	0.17(0.01)	1.83(0.2)	1.43(0.1)	0.79(0.07)	78.14(3.1)
2400	5	0.21	6	0.17(0.01)	1.85(0.2)	1.41(0.1)	0.78(0.1)	76.21(2.12)
2800	5	0.24	8	0.23(0.01)	3.45(0.6)	1.72(0.1)	0.95(0.05)	49.86(3.84)
3300	10	0.21	9	0.22(0.01)	3.78(0.3)	1.81(0.1)	1.01(0.08)	47.88(2.39)
4800	5	0.21	10	0.13(0.01)	3.24(0.4)	1.11(0.1)	0.61(0.06)	34.26(1.11)
6000	10	0.24	12	0.2(0.01)	7.15(0.3)	1.5(0.08)	0.83(0.05)	20.98(0.11)
14000	5	0.21	30	0.05(0.01)	2.67(0.3)	0.42(0.1)	0.23(0.06)	15.73(3.29)

Table 4.7. Mechanical properties of constant-length CNT yarn without further acetone densification.

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Twist turn/m	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
2600	4	0.24	0.24(0.01)	3.56(0.2)	1.81(0.07)	1.01(0.03)	50.84(2.1)
2600	10	0.22	0.19(0.01)	1.97(0.3)	1.54(0.1)	0.86(0.05)	78.17(1.28)
2700	4	0.22	0.22(0.01)	3.65(0.3)	1.72(0.1)	0.96(0.04)	47.12(2.41)
3300	10	0.22	0.23(0.01)	2.39(0.1)	1.81(0.07)	1.01(0.04)	75.73(1.33)
3400	10	0.22	0.15(0.01)	2.25(0.1)	1.21(0.1)	0.67(0.06)	53.78(3.12)
3500	11	0.21	0.18(0.01)	4.03(0.7)	1.5(0.001)	0.83(0.06)	37.22(0.11)
3600	10	0.21	0.18(0.01)	3.47(0.3)	1.52(0.1)	0.84(0.06)	43.8(2.03)
4100	5	0.19	0.12(0.01)	3.1(0.2)	1.08(0.1)	0.61(0.07)	34.84(1.01)
4200	5	0.21	0.14(0.01)	2.54(0.13)	1.15(0.1)	0.64(0.07)	45.26(2.81)
5000	4	0.22	0.13(0.01)	3.29(0.12)	1.06(0.1)	0.59(0.05)	32.22(2.1)
6000	10	0.23	0.23(0.01)	5.37(0.24)	1.73(0.1)	0.96(0.08)	32.22(1.1)

Table 4.8. Mechanical properties of constant-length CNT yarn with acetone densification.

Conversely, the shrinking-length CNT yarns showed many macroscopic coils within the yarn structure, as can be seen in the Figure 4.7, whereas the constant-length CNT yarns showed a uniform cross-section across the length with individual and bundles of the CNTs stretched along the yarn axis as shown in the Figure 4.9. As the result, the shrinking-length CNT yarns failed at much higher strains than the constant-length CNT yarns. The results presented here indicate that the constant-length CNT yarns outlined above produced strong CNT yarns, comparable to those in the literature.

4.5. Effect of twist amount on the constant-length CNT yarn

The CNT yarns with various amounts of twist, between 2400-6000turn/m were produced in order to study the effect of twist on the morphological and mechanical properties of the constant-length CNT yarn.

4.5.1. Morphological properties

The Figure 4.11 shows the SEM images of the constant-length CNT yarns produced by 3 different twists. It can be seen that the constant-length CNT yarn with the highest twist (Figure 4.11c) had a higher helix angle compared to that with the lower twist (Figure 4.11a).

This is due to the transformation of the torsional force into the axial compression. Hence, the inter-tubular contacts in the constant-length CNT yarn increased, which in turn led to a smaller diameter. The insertion of more twists in the constant-length CNT yarn did not alter the uniformity of the diameter, as can be seen in the shrinking-length CNT yarn (Figure 4.7).



Figure 4.11. SEM images of constant-length CNT yarns with twist of (a) 2400 and (b) 3500 and (c) 6000turn/m.

4.5.2. Mechanical properties

The Figure 4.12a shows the load-strain curves of the constant-length CNT yarns produced by twists of 2400, 2600, 3000 and 6000turn/m, while the Figure 4.12b shows the stress-strain values for such yarns.

The mechanical properties of the constant-length CNT yarns with various amounts of twist, where acetone was also used to further densify the already twisted yarn, is also shown in the Tables 4.7 and 4.8. The amount of twist inserted in the constant-length CNT yarn increased the mechanical strength to 1.8GPa for the twist of up to 2800-3300turn/m, after which the strength decreased. It can be seen in the Table 4.8 that the tensile strength of the constant-length CNT yarn with further acetone densification stayed around 1.59 ± 0.21 GPa for twists of up to 3600turn/m, after which the tensile strength decreased.



Figure 4.12. (a) Load-strain curves and (b) tensile strength values of the constant-length CNT yarns with various twist amounts.

Miao [33] investigated the effect of twist on the CNT yarns produced from the CVD-grown CNT forests. Although the author did not specifically mention the method of twisting in the paper, constant-length or shrinking length, it is thought that the method used was effectively constant-length twisting, as the CNT yarns were very uniform in diameter, similar to our constant-length CNT yarns. Their twisted CNT yarns increased their tensile strength to 0.45GPa, compared to the untwisted CNT web of 0.35GPa. The author observed that the insertion of the twist increased the tensile strength of the CNT yarn up to 5000turn/m, above which the tensile strength started to decrease due to the introduction of stress concentration points in the CNT yarn from excessive twist.

The main mechanism for such an increase in the tensile strength was thought to be the result of an increase in the vdW interactions between the nanotubes in the CNT yarn. The research presented here, however, suggests that for a constant-length CNT yarn, an optimal twist amount of 2400-3000turn/m for both acetone-densified and non acetone-densified yarns can be applied to obtain a maximal tensile strength of 1.8GPa, as shown in the Table 4.8. The investigation of the extension at break for the constant-length CNT yarn with various amounts of twist showed that the extension increased linearly as the twist amount increased. It should be noted that it was found, during the many experiments over the 3year experimental period, that the twist of 2400-3300 turn/meter produced the highest tensile

strength of 1.8 GPa. Therefore, such values were chosen for the further work with the polymers. On the other hand, the higher twist amounts (6000 turn/meter or higher) did not produce consistent results thus were not chosen.

4.6. Combination of constant-length twist and solvent densification

The constant-length twist and acetone were combined and used to densify the CNT web into the CNT yarn structure. In one approach, the CNT web was firstly densified using the constant-length twist followed by further acetone densification, as described in Section 4.4.2.2. In another approach, the CNT web was firstly densified using acetone followed by further constant-length twist densification.

4.6.1. Application of solvent on constant-length CNT yarn (termed twist-then-acetone CNT yarn)

A CNT web was first twisted by the constant-length twist method, before acetone was used for further densification. Firstly, a twist of 2800turn/m was inserted into the CNT web producing the CNT yarn in order to increase the tensile strength of the yarn, as was described above. Secondly, in order to densify with acetone, a droplet of acetone was drizzled along the length of the CNT yarn while it was horizontally held. The CNTs were compressed together by the capillary forces and the densification progressed by allowing acetone to evaporate off the CNT yarn, thus compressing the CNT yarn against each other and forming a denser yarn structure.

4.6.1.1. Morphological properties

The Figure 4.13 shows the SEM image of the twist-then-acetone CNT yarn produced by constant-length twist of 2800turn/m followed by acetone densification. It can be seen in the Figure 4.13 that the twist-then-acetone CNT yarn had a similar surface morphology to that of the constant-length CNT yarn (Section 4.4.2.2.1), in that a circular structure with a

uniform cross-section was produced. A helix angle of 10° was measured on the twist-thenacetone CNT yarn, indicating a uniform distribution of twist along the length of the yarn.



Figure 4.13. SEM image of the twist-then-acetone CNT yarn. The CNT yarn was prepared by a twist of 2800turn/m into the CNT web followed by acetone densification.

4.6.1.2. Mechanical properties

The Figure 4.14 shows the load-strain curves and the stress-strain values of the undensified CNT web, twisted only and twist-then-acetone CNT yarns. The twist-then-acetone CNT yarns proved to have the highest tensile strength of 1.8GPa, compared to the CNT yarns with the twist as the only densification method as shown in the Figure 4.14, in addition to other experimental methods as shown in the Table 4.8.



Figure 4.14. (a) Load-strain curves and (b) tensile strength values of twist-then-acetone CNT yarn. A twist of 2800turn/m was used to prepare the twisted CNT yarns.

This value is ~20% higher than their twisted only counterparts and 500% higher than the shrinking-length CNT yarn. Furthermore, the extension at break of the twist-then-acetone CNT yarn showed consistency in the CNT yarns with various twist amounts. Tran *et al.* [23] densified their twisted CNT yarns with acetone and obtained a tensile strength of 1.2GPa using such densification methods. They concluded that by drawing the CNT web, while under tension, the tensile strength of the CNT yarn could be improved from 0.4-0.6GPa to 1.2GPa. Our results are in agreement with their finding, suggesting that the CNT drawing increases the CNT contact point within the CNT yarn hence increasing the stress transfer.

4.6.2. Application of constant-length twist on solvent-densified yarn (termed acetonethen-twist yarn)

A CNT web was first acetone densified, and then twisted using constant length twist method. The densification by acetone was accomplished by running a droplet of acetone along the length of the CNT web while the web was horizontally held. The CNTs were compressed together by the capillary forces and the densification was progressed by allowing the acetone to evaporate off the CNT web, thus compressing the CNT web and forming a denser yarn structure. The CNT yarn was then twisted using the constant-length twist method with a twist amount of 2800turn/m producing the acetone-then-twist CNT yarn.

4.6.2.1. Morphological properties

The Figure 4.15 shows the SEM image of the acetone-then-twist CNT yarn. It can be seen that the acetone-then-twist CNT yarn has similar morphology to that of the twist-then-acetone yarn (Figure 4.13) as both yarns have circular structures with uniform cross-sections. A helix angle of 10° was measured on the CNT yarn, indicating a uniform distribution of twist along the length of the yarn. The helix angle was similar to that of the constant-length CNT yarn.



Figure 4.15. SEM image of acetone-then-twist CNT yarn with a twist amount of 2800turn/m inserted in the CNT yarn.

4.6.2.2. Mechanical properties

The Figure 4.16 shows the load-extension curves and the tensile strength values for the CNT web, acetone densified, twist densified, twist-then-acetone and acetone-then-twist CNT yarns. It can be seen that the mechanical strength of the acetone-then-twist CNT yarn (0.02GPa) is significantly lower than that of the twist-then-acetone CNT yarn (1.8GPa).

Although twist is known to densify the CNT yarn and thus increase the mechanical strength of the CNT yarn [33], it appears to counteract the effect of acetone in increasing the inter nanotube contact points if it is applied after acetone densification.



Figure 4.16. (a) Load-extension curves and (b) tensile strength values of acetone-then-twist CNT yarn.

The Table 4.9 lists the mechanical properties of the acetone-then-twist CNT yarns from the tensile testing. It is shown that the twist, when applied after acetone densification, did not improve the mechanical properties of the CNT yarn and the tensile strength remained between 0.1-0.7GPa slightly higher than the untreated CNT web (0.4GPa). This is likely

because the twist is only inserted in the outer layer of the acetone-then-twist CNT yarn and since the CNT yarn has already been densified by acetone, the twist could not penetrate into the inner layers of the CNT yarn. Hence, a core-sheath structure was developed which hindered the improvement of the inter nanotube contact points.
Chapter 4	4 Inves	tigation	into the	CNT	web and	yarn	drawn	from	CVD	-grown	CNT	forest
		<i>(</i>)				2				<i>(</i>)		

Twist turn/m	Number of specimens tested	Linear density (std dev) tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
1200	6	0.2	0.06(0.01)	3.63(1.18)	0.62(0.01)	0.34(0.01)	17.08(1.43)
1185	5	0.19	0.04(0.01)	11.17(0.81)	0.37(0.1)	0.21(0.05)	3.31(1.02)
300	8	0.18	0.07(0.01)	3.48(0.28)	0.68(0.1)	0.38(0.06)	19.54(7.01)
3500	11	0.2	0.01(0.01)	4.02(0.71)	0.16(0.02)	0.08(0.02)	3.98(2.45)
3300	10	0.21	0.01(0.01)	3.85(0.65)	0.14(0.02)	0.08(0.01)	3.64(1.31)

Table 4.9. Mechanical properties of the acetone-then-twist CNT yarns.

4.7. Insertion of constant-length twist in the CNT yarn whilst submerged in acetone

In order to insert twist in the CNT web while immersed in acetone, a new setup was designed and used as shown in the Figure 3.3. In this setup, the DC motor was placed vertically so that the CNT web could hang vertically inside the acetone container, as described in the Section 3.3. Briefly, a small grip was placed at the bottom of the acetone container. The web was first placed in the empty container and its end was fixed on the grip. The container was then filled with acetone. After completion of the twist insertion, acetone was removed from the container before the CNT yarn could be taken out.

4.7.1. Morphological properties

The Figure 4.17 shows the SEM images of the constant-length CNT yarn produced by inserting the twist into the CNT yarn while the yarn was immersed in acetone. The characteristic twist lines around the CNT yarn clearly indicate the insertion of twist into the CNT yarn structure.



Figure 4.17. SEM images of the constant-length CNT yarn produced while the twist was inserted in acetone, (a) low magnification and (b) high magnification.

In addition, the Figure 4.17b shows that the CNT bundles were compressed together forming a tightly packed tubular structure. The helix angle of 10° was measured for these yarns, which were identical to those of the constant-length CNT yarns.

4.7.2. Mechanical properties

The Table 4.10 shows the mechanical properties of the constant-length CNT yarn twisted while being submerged in acetone. Compared to the twist-then-acetone CNT yarn, the tensile strength decreased from 1.8GPa to 1.35GPa, while maintaining a similar extension at break. It can be seen that among various twists, the degree of twist induced by 2500turn/m produced the highest strength of 1.35GPa as can be seen in the Table 4.10. The decrease in the tensile strength can be explained by the fact that the immersion of the CNT web into acetone prior to the twist caused relaxation of the CNTs due to the polarity and volatility of acetone [14], thus resulting in a loosely packed structure. Upon twisting, the CNT web was then compressed to form a CNT yarn but the twist was not sufficient to form a tight structure as seen in the twist-then-acetone CNT yarns. This prevented the CNT bundles optimally transferring the load, leading to a lower tensile strength than the twist-then-acetone CNT yarns.

Chapter 4 Investigation into the CNT web and yarn drawn from CVD-grown CNT forest

Twist turn/m	Number of specimens tested	Linear density tex	Force at break (std dev) N	Strain at break (std dev) %	Tensile strength (std dev) GPa	Tensile strength (std dev) N/tex	Tensile modulus (std dev) GPa
2500	8	0.23	0.17(0.01)	3.33(0.48)	1.35(0.05)	0.74(0.04)	40.54(5.13)
3100	2	0.22	0.11(0.01)	3.64(0.21)	0.86(0.04)	0.48(0.02)	23.63(1.37)
3200	5	0.21	0.12(0.01)	2.93(0.61)	1.03(0.1)	0.57(0.05)	35.15(6.33)
3500	2	0.19	0.12(0.01)	3.82(0.5)	1.09(0.1)	0.61(0.08)	28.53(3.11)

Table 4.10. Mechanical properties of constant-length CNT yarn twisted inside acetone.

4.8. Conclusion

In this chapter, the morphological and mechanical properties of the CNT web and their CNT yarns were studied. The CNT web showed a uniform longitudinal distribution of the individual and bundles of the CNTs along the length of the web, viewed by the SEM. The mechanical properties of the CNT web were determined using the tensile testing, demonstrating a moderate tensile strength of 0.4GPa. The CNT yarn was then produced by the densification of the CNT web using a variety of methods including solvent (using acetone and ethanol) and twist (shrinking-length and constant-length twist) and the combinations of the twists and the solvents.

It was found that acetone had higher densification ability than ethanol in compressing the CNT web into a yarn compared to ethanol. The mechanical strength of acetone densified CNT yarns increased to ~1.1-1.2GPa compared to that of the ethanol densified CNT yarn. The increase in the tensile strength can be attributed to a greater compression due to the capillary forces of acetone on the CNTs. Therefore, a more compact structure was obtained using acetone rather than ethanol which in turn increased the contact points between the individual and bundles of the CNTs within the yarn structure. The detailed analysis of the two different twist methods confirmed that the constant-length CNT yarn indeed produced higher mechanical strength as well as a more uniform and cylindrical structure compared to the shrinking-length CNT yarn. The combination of the twist followed by solvent (acetone) densification methods produced the CNT yarns with the highest mechanical strength of 1.8GPa confirming that such yarns were effectively densified. Such effective densification is attributed to the higher vdW interactions between the individual and bundles of the CNTs. This in turn resulted in the highest tensile strength in the CNT yarns produced in this work. Therefore, for later experimental work in polymer incorporation with the CNT yarns, acetone and constant-length twist were chosen to be the solvent and twisting methods, respectively, for the CNT web densification and the fabrication of the CNT yarns.

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Chapter 5 Incorporation of polymers into constant-length CNT yarn

5.1. Introduction

In the preceding chapter, it was established that the constant-length CNT yarn, followed by acetone densification produced the highest mechanical strength compared to the other methods described. In this chapter, the CNT yarns produced from such a fabrication method were chosen in order to incorporate various types of polymer into them and produce polymer-infused CNT yarns. It was intended to infiltrate the polymer in solution by cooling the polymer solution down and form polymeric disks between the nanotubes in the CNT yarn.

Six types of polyethylene, a polypropylene and a nylon 6,6 were used to produce polymerinfused CNT yarns. The experimental procedure for all polymers has been outlined in Chapter 3. Briefly, these polymers were firstly dissolved in their solvents at elevated temperatures while stirring. The constant-length CNT yarn was then dipped in the solution and kept for certain time until the cooling was completed. Three polymer solution concentrations were made by heating up the solutions and dissolving the polymer and were: 0.01, 0.1 and 1w/w%. Such polymer solution concentrations were chosen in order to maintain a relatively low amount of polymer in the CNT yarns and thus to maintain the light weightiness of the polymer-infused CNT yarns. In addition, three cooling rates of 1, 10 and 100°C/min were used to cool down the polymer solution and thus to produce polymeric disks around the CNTs in the CNT yarn. For polyethylene and polypropylene, the cooling time for the cooling rate of 1°C/min was 30min, 10°C/min was 3min and 100°C/min was 20s. These three cooling rates were chosen to study the effect of cooling on the polymer disk properties. For nylon 6,6, a cooling rate of 1°C/min was chosen. The polymer-infused CNT yarn was then taken out of the solutions, washed with acetone, dried in oven at 80°C and subsequently characterised.

5.2. Polyethylene-infused CNT yarns

Six types of polyethylene with different molecular weights (as listed in the Table 3.1) were dissolved in xylene at 130°C. A length of the constant-length CNT yarn was wrapped around the frame (shown in the Figure 3.4) and then placed inside the solution and kept stationary until the cooling process was completed. The polyethylene-infused CNT yarn was then taken out of the solution, washed with acetone and dried for 1h. In order to better describe the samples of the polyethylene-infused CNT yarns that were produced, a naming system was developed and is shown in the Table 5.1.

Sample ID	Polyethylene	Molecular	Polymer solution	Cooling rate
	type	weight	concentration	°C/min
		g/mol	w/w%	
I0.83-0.01-1	HDPE0.83	158000	0.01	1
I0.83-0.01-10	HDPE0.83	158000	0.01	10
I0.83-0.01-100	HDPE0.83	158000	0.01	100
I0.83-0.1-1	HDPE0.83	158000	0.1	1
I0.83-0.1-10	HDPE0.83	158000	0.1	10
I0.83-0.1-100	HDPE0.83	158000	0.1	100
I0.83-1-1	HDPE0.83	158000	1	1
I0.83-1-10	HDPE0.83	158000	1	10
I0.83-1-100	HDPE0.83	158000	1	100

Table 5.1. Description of the names for the different polyethylene-infused CNT yarns.

I4.5-0.01-1	HDPE4.5	79000	0.01	1
I4.5-0.01-10	HDPE4.5	79000	0.01	10
I4.5-0.01-100	HDPE4.5	79000	0.01	100
I4.5-0.1-1	HDPE4.5	79000	0.1	1
I4.5-0.1-10	HDPE4.5	79000	0.1	10
I4.5-0.1-100	HDPE4.5	79000	0.1	100
I4.5-1-1	HDPE4.5	79000	1	1
I4.5-1-10	HDPE4.5	79000	1	10
I4.5-1-100	HDPE4.5	79000	1	100
I20-0.01-1	HDPE20	54000	0.01	1
I20-0.01-10	HDPE20	54000	0.01	10
I20-0.01-100	HDPE20	54000	0.01	100
I20-0.1-1	HDPE20	54000	0.1	1
I20-0.1-10	HDPE20	54000	0.1	10
I20-0.1-100	HDPE20	54000	0.1	100
I20-1-1	HDPE20	54000	1	1
I20-1-10	HDPE20	54000	1	10
I20-1-100	HDPE20	54000	1	100
I35000-1-1	PE35000	35000	1	1
I3000-1-1	Polywax3000	3000	1	1
I1000-1-1	Polywax1000	1000	1	1

5.2.1. Morphological properties

The Figure 5.1 shows the SEM images of the polyethylene-infused CNT yarns produced from HDPE0.83 with an average molecular weight of 158000g/mol, polymer solution concentrations of 0.01, 0.1 and 1w/w% and cooling rates of 1, 10 and 100°C/min. The polyethylene disks are evident in the SEM images confirming that the disks grew perpendicularly around the individual and bundles of the CNTs. As the polymer solution concentration increased whilst the cooling rate was kept unchanged, the disks seemed to have grown in bigger sizes. This can be seen by visually comparing images of the Figure 5.1c, 5.11 and 5.1u. In addition, it should be noted that increasing the cooling rate resulted in a decrease in the disk growth rate. This was observed in the cooling rate of 100°C/min, as shown in the Figure 5.1i, 5.1r and 5.1aa, indicating that the cooling was too fast for the polyethylene molecules to be able to adhere to the CNT surfaces and grow disks.



I0.83-0.01-1 30000x(scale bar 2µm)



300000x (scale bar 200nm)



I0.83-0.01-10(scale bar 2μm)





(scale bar 200nm)

(scale bar 500nm)



I0.83-0.1-100(scale bar $2\mu m$) (scale bar 500nm)

(scale bar 200nm)



Figure 5.1. SEM images of the polyethylene-infused CNT yarns from HDPE0.83 (158000g/mol). For each yarn, an SEM image with 3 magnifications of 30000, 100000 and 300000 is shown. In the naming of the samples, the first number is the polyethylene type (listed in the Table 5.1, the second number is the polyethylene concentration in the solution and the third number is the cooing rate.

The Figure 5.2 shows the SEM images of the polyethylene-infused CNT yarns produced from HDPE4.5 with an average molecular weight of 79000g/mol, polymer solution

concentrations of 0.01, 0.1 and 1w/w% and cooling rates of 1, 10 and 100°C/min. Such polyethylene has lower average molecular weight than the HDPE0.83. The growth of the disk structures was also observed for HDPE4.5 similar to HDPE0.83 (Figure 5.1), with the disks also growing perpendicular to the axial direction of the individual and bundles of the CNTs, at regular intervals along their lengths. Such growth was observed across all polymer solution concentrations, for example the Figure 5.2c, 5.2j and 5.2q, as well as for varying cooling rates (Figure 5.2p, 5.2s and 5.2v).



I4.5-0.01-1 30000x (scale bar 2µm)



100000x (scale bar 500nm)



300000x (scale bar 200nm)



I4.5-0.01-10(scale bar 2µm)



(scale bar 500nm)



(scale bar 200nm)



I4.5-0.01-100(scale bar 2µm)





I4.5-1-100(scale bar $2\mu m$) (scale bar 500nm)

Figure 5.2. SEM images of the polyethylene-infused CNT yarns produced from HDPE4.5 (79000g/mol). For each yarn, an SEM image with three magnifications of 30000, 100000 and 300000 is shown.

The Figure 5.3 shows the SEM images of the polyethylene-infused CNT yarns that were made using HDPE20. The average molecular weight of this type of polyethylene was 54000g/mol while three polymer solution concentrations of 0.01, 0.1 and 1w/w% and three cooling rates of 1, 10 and 100°C/min were used to produce the polyethylene-infused CNT yarns. It can be seen in the Figure 5.3 that the polyethylene disks grew around the individual and bundles of the CNTs in similar fashion to HDPE0.83 and HDPE4.5.

The studies of the shish-kebab disk growth mechanism in polymer solutions have been documented in the literature [1, 2]. The widely accepted mechanism is that the polyethylene molecules attach themselves to the surface of the CNTs by physical adsorption. Such adsorbed molecules then form polymer nuclei. Shorter polymer chains or coils travelling in

close vicinity of the nuclei are then attracted to the nuclei facilitating the growth of the nuclei. Due to the flow of the solution, usually by the virtue of stirring, the molecule coils start to uncoil. While one end of the uncoiled molecule adheres to the nuclei, the other end takes up more molecules from the solution resulting in the growth of the nuclei. As the nuclei grow in size, more molecules attach themselves, creating disk like structures. Therefore, the growth of such disk like structures around the CNTs in the polyethylene-infused CNT yarns indicates that the disk growth is the preferred mechanism when in contact with the CNTs as opposed to filament growth [3].



I20-0.01-1, 30000X, (scale bar 2µm)



100000X, (scale bar 500nm)



300000X, (scale bar 200nm)



I20-0.01-10(scale bar 2µm)



(scale bar 500nm)

(f)

(scale bar 200nm)



I20-0.1-100(scale bar 2µm)

(scale bar 500nm)

(scale bar 200nm)



I20-1-100(scale bar 2µm)

(scale bar 500nm)

(scale bar 200nm)

Figure 5.3. SEM images of the polyethylene-infused CNT yarns produced from HDPE20 (54000g/mol). For each yarn, an SEM image with three magnifications of 30000, 100000 and 300000 is shown.

As discussed above, the morphological analysis of HDPE0.83-, HDPE4.5- and HDPE20infused CNT yarns revealed that the disk growth depends on the cooling rate and polymer solution concentration, among other parameters. In addition, the study of the three cooling rates and three polymer solution concentrations on the polyethylene-infused CNT yarns demonstrated that in order to increase the number of disks on the CNTs, it is important to have a slow cooling rate and a high polymer solution concentration. Therefore, for the subsequent polyethylene types, a cooling rate of 1° C/min and a polymer solution concentration of 1w/w% were used.

The Figure 5.4 shows the SEM images of the polyethylene-infused CNT yarn produced from PE35000 with an average molecular weight of 35000g/mol, at a polymer solution concentration of 1w/w% and a cooling rate of 1°C/min. At a low magnification of 30000x (Figure 5.4a) it can be seen that polyethylene has coated the entire outer surface of the CNT yarn, whilst the CNTs are still visible in some other parts. It can be clearly seen from the higher magnification image (Figure 5.4c) that the disks have bridged the adjacent CNT bundles, creating an interconnected structure.



I35000-1-1 30000X (scale 100000X (scale bar 500nm) 300000X (scale bar 200nm) bar 2μm)



The Figure 5.5a and 5.5b show the SEM images of the polyethylene-infused CNT yarns with Polywax1000 with an average molecular weight of 1000g/mol, while the Figure 5.5c and 5.5d show those of Polywax3000 with an average molecular weight of 3000g/mol at polymer solution concentration of 1w/w% and cooling rate of 1°C/min. It can be seen at low magnification images (Figure 5.5a and 5.5c) that a coating has occurred on I1000-1-1 and I3000-1-1 in similar fashion to I35000-1-1, with some areas covering the entire disk/CNT structure. Such an accumulation of polyethylene in some areas has resulted in

disks being completely covered. However, closer observation revealed that distinct disk growth perpendicular to the axial direction of the CNTs has occurred, as shown in the Figure 5.5b and 5.5d, bridging the neighbouring CNTs and creating an interconnected structure.



I3000-1-1, (scale bar 2µm)

(scale bar 500nm)

Figure 5.5. SEM images of the infused CNT yarns from Polywax1000 (1000g/mol) and Polywax3000 (3000g/mol) at 2 magnifications of 30000 and 100000.

The formation of the disk structures using such low molecular weight polyethylene (1000g/mol and 3000g/mol) is of particular interest. The nucleation and growth of the shish-kebab structures in the literature has been mainly limited to the high molecular weight polyethylene either in melt or solution states [8-13]. Zhang *et al.* [14] discussed that the shish-kebab disk growth, among other parameters, depends on the critical entanglement and the molecular weight. This means that the chain length is important in the formation and growth of the disks. While shorter length chains adhere to the surface of the CNTs forming nuclei, it is the longer chain molecules that uncoil and adhere to the nuclei, thus

facilitating the growth of the disks [7, 15, 16]. In this regard, such low molecular weights of Polywax1000 and 3000 (1000g/mol and 3000g/mol respectively) means that the chains are shorter compared to the higher molecular weight polyethylene, thus they cannot uncoil readily and adhere to the nuclei, and grow the disks to larger scales.

However, the results presented here confirm that Polywax1000 and Polywax3000 could indeed grow disks with similar morphological properties compared to the PE35000, HDPE20, HDPE4.5 and HDPE0.83. This indicates that although the molecular weight is an important factor, other factors may also contribute to the growth of the disks around the CNTs. Such factors may relate to the short length of Polywax1000 and Polywax3000 molecules that may eliminate the need for uncoiling, thus they readily adhere to the nuclei. The adhesion of such molecules to the nuclei may facilitate the growth of the disks around the CNTs as shown in the Figure 5.5.

5.2.2. Disk characterisation

The morphological analysis of the polyethylene-infused CNT yarns showed that the polyethylene disks grew perpendicular to the direction of the individual and bundles of the CNTs. In order to determine the effects on the disk properties of the polyethylene-infused CNT yarns, three parameters were varied. The polyethylene molecular weight, the concentration of the polyethylene in the solution and the cooling rate were found to be important parameters that were investigated. The SEM images were used to characterise the disk diameter, thickness and the gap between the adjacent disks using Image J software. The number of disks per 5.58mm² was measured from the SEM images with magnification of 300000, with each image viewing a sample dimension of 2.6mm ×2.2mm.

The Table 5.2 quantifies the data seen in the SEM images in terms of the diameter, thickness and gap between the disks. It can be seen that, for a given molecular weight and cooling rate, as the polyethylene solution concentration was increased, the disk diameter also increased and the gap between the adjacent disks decreased whilst the disk thickness did not change. This indicated a direct relationship between the disk size and polyethylene

solution concentration. Pennings [1, 4] studied the thermodynamics of the homogenous crystallisation and growth of polyethylene disks in xylene solutions without the presence of the nucleating agents such as CNTs. The author theorized that the homogenous disk crystallisation and growth is usually initiated by single molecules as the result of statistical thermal fluctuations. Furthermore, such a state is thermodynamically favorable for the polyethylene molecules, rather than remaining in the solution [1, 5]. Therefore, by increasing the polymer concentration in the solution, the disk has access to more polymer molecules, resulting in more polymer take up from the solution by the growing disks. Furthermore, for a given molecular weight and polyethylene solution concentration, as the cooling rate was increased, the disk diameter and the gap between the disks were decreased while disk thickness did not change, indicating an inverse relationship between the cooling rate and the disk size.

The heterogeneous crystallisation of polyethylene disks around the nucleating agents such as CNTs was studied by Mackley [6] who noted that polyethylene molecules can reach a lower energy state by physically adhering to the CNT surface. However, a faster cooling rate causes the polymer molecules to lose their energy much faster than when a slower cooling rate is applied to the solution. This loss of energy means that the molecules do not have tendency to adhere to the disks, thus resulting in smaller disks. It should be noted that there are some exceptions seen in the Table 5.2 that did not follow the above explanation. Such exceptions may be due to the limitations in experimental work in controlling the solution temperature and stirring although much attempt was done to design and undertake the experiments to the best available equipment and operators. Further analysis and experimentation revealed that the abovementioned trend was indeed happening for the samples and that studied parameters indeed affect the disks properties.

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Table 5.2. Polyethylene disk properties around the CNTs in the polyethylene-infused CNT yarns.

Infused CNT	Polyethylene	Molecular	Polymer	Cooling	Number of	Disk	Disk	Disk gap (std	Number of disks
yarn	component	weight	solution	rate	images from	diameter	thickness	dev)	per 5.58mm ²
		g/mol	concentration	°C/min	identical	(std dev)	(std dev)	nm	from each image
			w/w%		samples and	nm	nm		(magnification
					magnifications				300000)
I0.83-0.01-1	HDPE0.83	158000	0.01	1	2	47.3(11.5)	13.7(5.9)	29.9(10.3)	66
I0.83-0.01-10	HDPE0.83	158000	0.01	10	2	35.1(8)	3.8(1.3)	14.4(3.8)	30
I0.83-0.01-100	HDPE0.83	158000	0.01	100	1	Not seen*	Not seen*	Not seen*	0
I0.83-0.1-1	HDPE0.83	158000	0.1	1	4	40.5(7.8)	9.5(1.9)	33.7(15.7)	43
I0.83-0.1-10	HDPE0.83	158000	0.1	10	2	52.6(17.1)	18.6(7.2)	26.2(9.3)	34
I0.83-0.1-100	HDPE0.83	158000	0.1	100	1	Not seen	Not seen	Not seen	0
I0.83-1-1	HDPE0.83	158000	1	1	6	127.2(35.7)	14.5(3.7)	80.8(22.3)	47
I0.83-1-10	HDPE0.83	158000	1	10	3	133.1(33.6)	16.1(3.4)	68.6(28.7)	85

	1 1	1 2		U	2				
I0.83-1-100	HDPE0.83	158000	1	100	2	22.3(6.2)	6.1(1.5)	20.3(8.2)	4
I4.5-0.01-1	HDPE4.5	79000	0.01	1	1	39.4(10.1)	8.4(1.8)	31.8(13.4)	38
I4.5-0.01-10	HDPE4.5	79000	0.01	10	1	31.9(18.1)	6.3(1.3)	39.7(20.9)	43
I4.5-0.01-100	HDPE4.5	79000	0.01	100	1	Not seen	Not seen	Not seen	0
I4.5-0.1-1	HDPE4.5	79000	0.1	1	1	48.6(21.2)	17.1(4.1)	8.4(6.1)	58
I4.5-0.1-10	HDPE4.5	79000	0.1	10	1	31.2(14.3)	8.6(1.8)	16.3(6.2)	37
I4.5-0.1-100	HDPE4.5	79000	0.1	100	1	Not seen	Not seen	Not seen	0
I4.5-1-1	HDPE4.5	79000	1	1	2	127.1(20.7)	9.0(2.1)	68.9(25.4)	55
I4.5-1-10	HDPE4.5	79000	1	10	1	47.1(9.5)	8.7(2.1)	37.1(12.2)	78
I4.5-1-100	HDPE4.5	79000	1	100	1	Not seen	Not seen	Not seen	0
I20-0.01-1	HDPE20	54000	0.01	1	5	42.9(22.8)	12.8(5.1)	46.1(20.1)	21
I20-0.01-10	HDPE20	54000	0.01	10	5	74.7(19.4)	14.2(3.5)	36.4(12.7)	18
I20-0.01-100	HDPE20	54000	0.01	100	3	22.3(6.2)	6.1(1.5)	20.3(8.2)	20
I20-0.1-1	HDPE20	54000	0.1	1	4	53.3(14.3)	14.3(3.3)	39.1(10.6)	68

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I20-0.1-10	HDPE20	54000	0.1	10	6	88.7(29.3)	16.6(4.6)	46.8(16.1)	63
I20-0.1-100	HDPE20	54000	0.1	100	2	28.8(13.1)	8.9(3.2)	10.6(3.6)	28
I20-1-1	HDPE20	54000	1	1	6	165.1(43.4)	19.4(4.8)	73.1(21.7)	40
I20-1-10	HDPE20	54000	1	10	4	52.3(38.8)	12.5(3.4)	27.1(10.7)	58
I20-1-100	HDPE20	54000	1	100	1	38.8(7.7)	12.6(2)	28.4(10.6)	128
I35000-1-1	PE35000	35000	1	1	2	34.1(10.8)	8.7(1.9)	22.8(7.2)	75
I3000-1-1	Polywax3000	3000	1	1	2	86.7(34.9)	11.8(5.1)	41.2(20.7)	87
I1000-1-1	Polywax1000	1000	1	1	2	43.8(19.4)	11.2(2.4)	23.1(2.2)	119

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* Not seen: no disk was found in the image.

It was also found that the diameter, thickness and gap between the two adjacent disks are functions of the molecular weight. It can be seen that using HDPE20 (molecular weight of 54000g/mol) produced larger diameter disks than HDPE0.83 (molecular weight of 158000g/mol). The largest disks in terms of diameter and thickness were observed in I20-1-1 (HDPE20, polyethylene solution concentration of 1 w/w% and cooling rate of 1°C/min), while I0.83-1-1 yielded the next largest disks. Although the precise assignment of the disk dimension was difficult in some samples due to an inhomogeneous distribution of the disks along the yarn length, it was observed, by comparing the yarns of the same polyethylene solution concentration and cooling rate, that HDPE20-infused CNT yarns produced larger disks than those of the HDPE4.5- and HDPE0.83-infused CNT yarns, indicating an inverse relationship with the molecular weight and the disk size. In addition, for a given cooling rate, the gaps between the two adjacent disks were the largest for the HDPE20-infused CNT varns and polyethylene solution concentration of 0.01w/w%. It was also found that, for a given cooling rate, the highest number of disks per area was from the HDPE20-infusd CNT yarns followed by the HDPE0.83-infused CNT yarns at polyethylene solution concentration of 1 w/w%.

The increase in the number of disks as the polymer solution concentration was increased can be associated with the increased number of polymer molecules in the solution, increasing the polymer solution concentration, the number of polymer molecules with the right length and coil structure is subsequently increased. This results in an increased number of nuclei on the CNT surface, which results in an increase in the number of disks.

The disk size of PE35000 (molecular weight of 35000g/mol) in I35000-1-1 is also listed in the Table 5.2. Such disks were smaller compared to I20-1-1 (molecular weight of 54000g/mol, polymer solution concentration of 1w/w% and a cooling rate of 1°C/min) and I0.83-1-1 (molecular weight of 158000g/mol, polymer solution concentration of 1w/w% and a cooling rate of 1°C/min) by a factor of three in diameter and two in thickness. It seems that the diameter and thickness of the polyethylene disks are related to their molecular weights, since such values decreased with reducing the molecular weight. A decrease in the molecular weight had a direct effect on the growth of the disks. The growth

rate of the larger disks during the cooling process seemed to depend on the attraction of more molecules, preferably of higher molecular weight, due to this being more thermodynamically favorable. Furthermore, I35000-1-1 disks were close in diameter and thickness to the I20-0.01-1 (HDPE20, polymer solution concentration of 0.01w/w% and cooling rate of 1°C/min) and I0.83-0.01-1 (HDPE0.83, polymer solution concentration of 0.01w/w% and cooling rate of 1°C/min) as shown in the Table 5.2. This indicates that decreasing the polyethylene solution concentration has a similar effect to the decrease in the average molecular weight of polyethylene on the disk size.

The disk size of Polywax1000 (molecular weight of 1000g/mol) and Polywax3000 (molecular weight of 3000g/mol) grown on the CNT yarns are also listed in the Table 5.2. The I3000-1-1 disks measured to be larger than I1000-1-1 in diameter but identical in thickness, whereas the gaps remain similar for both. The comparison of the disk size of I1000-1-1 and I3000-1-1 with other polyethylene revealed that, for a given polymer solution concentration of 1w/w% and cooling rate of 1°C/min, the I35000-1-1 (molecular weight of 35000g/mol) and I3000-1-1 produced similar sized disks, while the disk diameters were three times smaller than those of the I20-1-1 and I0.83-1-1. This can be attributed to the difference in the average molecular weight of Polywax1000 and PE35000 compared to those of the HDPE20 and HDPE0.83.

5.3. Polypropylene-infused CNT yarns

Although polypropylene molecules are more rigid than polyethylene as well as higher melting point, it has broadly similar mechanical properties to polyethylene at room temperature. It also has limited solubility in solvents, with hot xylene being one of the main solvents. In order to produce the polypropylene-infused CNT yarns, polypropylene was first dissolved in xylene at 130°C while the solution was stirred at 350rpm. The constant-length CNT yarn was then placed in the solution. By cooling the polymer solution, while the CNT yarn was held inside, from 130°C to 100°C with the cooling rate 1°C/min, the polypropylene-infused CNT yarns were produced. Two polymer solution concentrations of

0.1w/w% and 1w/w% were chosen while the cooling rate of 1°C/min was used and the effect of different concentrations at such cooling rate was studied.

Sample ID	Molecular weight g/mol	Polymer solution concentration w/w%	Cooling rate °C/min
Ipp-0.1-1	297000	0.1	1
Ipp-1-1	297000	1	1

Table 5.3. Description of the names for polypropylene-infused CNT yarn.

5.3.1. Morphological properties

The Figure 5.6 shows the SEM images of the polypropylene-infused CNT yarns. At low magnification (Figure 5.6a and 5.6d) the coating of the infused CNT yarn by excess polypropylene is evident. The coating on the outside of the yarn length occurred very frequently making it difficult to locate and measure the disks contained within.

However, as shown in the higher magnification images (Figure 5.6c and 5.6f) where areas of disks could be located underneath the coating or those of the coating free areas, the disks can be seen around the CNT bundles indicating the growth of the polypropylene disks perpendicular to the axial direction of the CNT bundles. The disks, however, did not bridge the adjacent CNT bundles. Instead, the coating almost covered the entire outer surface of the polypropylene-infused CNT yarn.



Ipp-1-1(scale bar 2µm)

(scale bar 500nm)

(scale bar 200nm)

Figure 5.6. SEM images of the polypropylene-infused CNT yarns. An SEM image with three magnifications of 30000, 100000 and 300000 is shown.

The growth of disks of polypropylene in the melt state in pure polymer was studied by Varga *et al.* [17] and Dean *et al.* [18] who found that polypropylene chains adhere to the surface of the nucleating agents and form nuclei. Other polypropylene molecules then align along the direction of the shear flow, and adhere to the nuclei thus growing the disks. Zhou *et al.* [19] investigated the growth of the polypropylene disks produced in the injection molding of polypropylene. They observed that the disks were closely packed and concluded that such structures were produced due to the shear flow. The fabrication of the disks as shown in the Figure 5.6 indicates that the shear induced by the stirring of the polypropylene solution was likely the major parameter in producing the disks on the CNTs. The flow of the polymer solution meant that polypropylene molecules with shorter lengths could adhere

to the surface of the CNTs thus forming nuclei. The longer chain molecules were then able to adhere to such nuclei, stimulating disk growth.

5.3.2. Disk characterisation

The polypropylene-infused CNT yarns produced by two polymer solution concentrations of 0.1w/w% and 1w/w% and a cooling rate of 1°C/min were characterised with regards to their diameter, thickness and gap between the adjacent disks. The number of disks per 5.58mm² was measured from the SEM images with a magnification of 100000.

The Table 5.4 shows the disk properties of polypropylene around the CNTs in the polypropylene-infused CNT yarn. It can be seen that the disk diameter and thickness remained fairly constant for the two polymer solution concentrations, whilst the gap between the disks decreased on the polymer solution concentration of 1w/w%. While the standard deviations (std. dev.) for the diameter of the disks were high for both polymer solution concentrations, possibly due to the solution turbulence while stirring, the disks had diameters of 40-70nm comparable to I1000-1-1, I3000-1-1 and I35000-1-1 at the polymer solution concentration of 1w/w% and the cooling rate of 1°C/min (Table 5.2). The polypropylene disks were similar to those of polyethylene in geometry and perpendicular growth to the CNT axis.

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Infused	Polymer	Cooling rate	Number of	Disk diameter	Disk	Disk gap (std	Number of
CNT	solution	°C/min	images from	(std dev)	thickness (std	dev)	disks per
yarn	concentration		identical		dev)		5.58mm ²
	w/w%		samples and	nm		nm	(magnification
			magnifications		nm		100000)
Ipp-0.1-1	0.1	1	3	62.9(20.1)	7.1(2.2)	28.6(11.3)	86
Ipp-1-1	1	1	3	42.9(21.5)	4.3(1.8)	21.4(11.3)	38

Table 5.4. Polypropylene disk properties grown on the CNTs in the polypropylene-infused CNT yarns.

5.4. Nylon 6,6-infused CNT yarns

Nylon 6,6 was infused into the CNT yarn by dissolving nylon 6,6 in glycerine at 240°C while the solution was stirred at 350rpm. Three polymer solution concentrations of 0.01, 0.1 and 1w/w% were chosen in order to study the effect of concentration on the disk formation and their growth on the CNTs as shown in the Table 5.5. The solution was then cooled down to 185°C by reducing the hot plate temperature while the CNT yarn was maintained inside using a purpose made frame as shown in the Figure 3.4, at a cooling rate of 1°C/min, before removing the samples.

Sample ID	Molecular weight g/mol	Polymer solution concentration w/w%	Cooling rate °C/min
Iny-0.01-1	22000	0.01	1
Iny-0.1-1	22000	0.1	1
iny-1-1	22000	1	1

Table 5.5. Description of the names for the nylon 6,6-infused CNT yarns.

5.4.1. Morphological properties

The Figure 5.7 shows the SEM images of the nylon 6,6-infused CNT yarns. For each yarn, an SEM image with three magnifications of 30000, 100000 and 300000 is shown. The disks were observed in some areas in the nylon 6,6-infused CNT yarns where coating and accumulation of nylon 6,6 were also present. An example of the coating can be seen in Iny-1-1 at lower magnification (Figure 5.7g) where the whole yarn was coated by the polymer. Looking through the openings of the coated layer, the presence of the nylon 6,6 disk structures could be seen in the images with high magnifications, such as in the Figure 5.7i. The nylon 6,6 disks grew perpendicular to the axial direction of the individual and bundles

of the CNTs. However, the disks were not large enough to bridge the bundles, thus only locking the CNTs within one bundle as can be seen in the Figure 5.7c, 5.7f and 5.7i.



Iny-0.01-1 30000X (scale bar $2\mu m)$



100000X (scale bar 500nm)



300000X (scale bar 200nm)



Iny-1-1(scale bar 2µm)

(scale bar 500nm)

(scale bar 200nm)

Figure 5.7. SEM images of nylon 6,6-infused CNT yarns. An SEM image with three magnifications of 30000, 100000 and 300000 is shown.

The disk growth of nylon 6,6 on the surface of the nucleating agents such as carbon fibres has been reported in the literature [20, 21]. Li *et al.* [22] investigated the disks of nylon 6,6 on individual CNTs that were dispersed in glycerine by ultrasonication. They found that although nylon could grow disk structures on the CNTs, increasing the CNT content while maintaining the polymer solution concentration and the cooling rates constant resulted in hindrance of the disk growth due to the spatial (nano) confinement effect being the lack of space between the nanotubes. Such confinement effect then resulted in decrease in rate and cessation of the nuclei growth at an early stage [22]. The spatial confinement effect can be also attributed to the CNT yarn, as shown in the Figure 5.7. The CNT yarn was a compact structure with many individual and bundles of the CNTs closely held together. The introduction of nylon 6,6 molecules at high temperature (240°C) could indeed initiate the nucleation of such disks around the CNTs. However, further reduction in the temperature down to 185°C decreased the crystallisation kinetics, preventing the nuclei to grow to larger sizes.

5.4.2. Disk characterisation

The morphological analysis of the nylon 6,6-infused CNT yarns showed that despite heavy coating by the polymer on the CNT yarn, the disk structures could be evidently seen confirming that the nylon 6,6 disks could indeed grow on the surface of the CNTs. The characterisation of such disks with regards to their diameter, thickness and the gap between the adjacent disks was undertaken and discussed here. The Table 5.6 shows the disk properties of nylon 6,6 around the CNTs, as was observed in the SEM images.

As shown in the Table 5.6, it was found that the increase in the polymer solution concentration from 0.1w/w% to 1w/w% did not increase the diameter of the disks. This indicates that the formation of the disks around the CNTs did not increase as the polymer content in the solution increased. This is in agreement with the finding of Li *et al.* [22] that an increase in the CNT content hinders the nucleation and growth of nylon 6,6 disks where CNTs and polymer were dispersed in solutions.
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Infused	Polymer	Cooling	Number of	Disk diameter	Disk thickness	Disk gap (std	Number of
CNT yarn	solution	rate	images from	(std dev)	(std dev)	dev)	disks per
	concentration	°C/min	identical				5.58mm ²
	w/w%		samples and	nm	nm	nm	(magnification
			magnifications				100000)
Iny-0.01-1	0.01	1	4	Not seen*	Not seen*	Not seen*	0
Iny-0.1-1	0.1	1	4	45.4(28.1)	18.1(5.2)	36.6(15.8)	32
Iny-1-1	1	1	4	43.5(14.2)	10.8(3.2)	21.7(14.4)	86

Table 5.6. Disk properties of nylon 6,6 disks around the CNTs in the nylon 6,6-infused CNT yarns.

*Not seen: no disk was found in the image.

5.5. Measurement of the cross-section of polyethylene-infused CNT yarns

The polyethylene-infused CNT yarns showed disk growth on the outer layer of the yarns. However, they failed to grow deeper in the yarn structure, as shown in the Figure 5.8, where an image was taken from the failure point of the polyethylene-infused CNT yarn after the tensile testing. The tensile failure of the CNT yarn is due to the sliding of the CNTs against each other [23, 24]. This means that the CNTs at the tip of the failure point came from the regions closer to the yarn central axis. It can be seen that the disks failed to nucleate and grow on the CNTs deeper inside the yarn structure. This was the case for all polymers studied in this thesis including polypropylene and nylon 6,6. The Figure 5.8 is a representative of the polymer-infused CNT yarns studied regardless of the polymer solution concentration and the cooling rate.



Figure 5.8. Representative SEM image of the polyethylene disks on the outer surface of the polyethylene-infused CNT yarn taken from I20-1-1. The arrow indicates that disk nucleation and growth were limited to the outer CNTs rather than to the CNTs deeper inside the yarn structure. The yarn was fabricated using HDPE20 (molecular weight of 54000g/mol), with polymer solution concentration of 1w/w% and cooling rate of 1°C/min.

The penetration of polyethylene molecules into the CNT yarn structure is of great importance, since the disks were of suitable size to be used as the bridging components in the structure for an effective stress transfer between the CNTs. Therefore, the measurement of such layers on the outside was studied in an attempt to identify some of the parameters influencing the penetration of the polyethylene molecules into the yarn structure and their ability to form disks around the CNTs.

The SEM cross-section of the polyethylene-infused CNT yarn indicate that the disks only nucleated and grew on the outer CNTs, as seen in the Figure 5.9. This indicates that during the cooling process, most of the polyethylene molecules were taken up by the most outer CNTs in order to grow the disks. Once the entire surface of the individual and bundles of the CNTs was covered by the polyethylene molecules, new molecules were then recruited from the polymer solution to increase the dimensions of the already-grown disks, in particular the diameter.



Figure 5.9. Cross-section of the polyethylene-infused CNT yarn from (a) low to (d) high magnifications taken from I20-1-1.

This is confirmed from the diameter measurement of such disks (Table 5.2) where the higher polyethylene solution concentration resulted in the larger disks with little or no improvement in penetration of the polymer into the yarn structure.

It was initially thought that air or moisture pockets could have been trapped inside the yarn between the CNTs, thus preventing the polymer solution from penetrating into the CNT yarn and nucleating off the surface of the CNTs. Therefore, the neat CNT yarns were first placed in vacuum oven at 80°C for 1h in an attempt to extract air and moisture from the CNT yarns. The yarns were then infused with polyethylene using identical experimental procedure for polyethylene-infused CNT yarn fabrication.



Figure 5.10. Representative SEM image of the polyethylene-infused CNT yarn after vacuum drying at 80°C for 1h taken from the outer surface of I20-1-1. The growth of the disks are evident on the outer surface of the yarn as identified by the arrows.

However, the SEM and tensile testing results showed no improvement in the morphological and mechanical properties of the polyethylene-infused CNT yarn. The next approach was to encourage greater penetration by vacuum drying the polyethylene-infused CNT yarn at 80°C for 1h in an attempt to extract xylene or acetone from the CNTs deeper in the yarn structure. However, the SEM and tensile results also showed no improvement in the properties. In particular, the SEM studies showed that the growth of the disks remained limited to the outer CNTs in the polyethylene-infused CNT yarn, as shown in the Figure 5.10.

The investigation into the depth of polymer infiltration inside the yarn structure revealed that the spatial confinement could in fact be the influencing factor in the infusion of the polymers into the CNT yarns. This phenomenon can be explained by considering the mechanism by which the disks are nucleated and grown. Degennes [25] and later Keller et al. [15] discussed that the flow of polymers in solution causes the polymer molecules to uncoil to some degree. One end of the partially uncoiled molecule then adheres to the surface of the nucleating agent. When the flow reaches some critical value, the molecules uncoil and stretch along the direction of the flow and at the same time the hydrodynamic interactions between the polymer chains decrease. This results in further stretching and orientation of the polymer chains, which in turn results in the growth of the disks. In addition, Somani et al. [26, 27] suggested that longer molecular chains stretch more readily than shorter molecular chains, indicating that polymers with a higher average molecular weight can more readily nucleate and grow disks. Their findings suggest that in order to grow large enough disks, the polymer solution must be under directional flow and the polymer chains must have long enough chains to stretch and orient. However, the CNTs were tightly packed inside the CNT yarn structure, due to the fabrication of the constantlength CNT yarn described in Chapter 4, thus the polymer solution could not maintain its flow velocity deep inside the yarn. This resulted in significant reduction in polymer chain stretching and orientation deeper in the CNT yarn, which in turn hindered the nucleation and growth of the disks in the polyethylene-, polypropylene- and nylon 6,6-infused CNT yarns. Another possibility may be the poor wetting of the CNTs deeper inside the yarns due to the lack of polymer deposition during the cooling process as was observed on the outer surface of the yarns.

5.6. Conclusion

In this chapter various polymers were incorporated into the constant-length CNT yarns and the resultant polymer-infused CNT yarns and their polymeric disks were characterised using the SEM. The polyethylene disks were successfully grown in the vicinity of the individual and bundles of the CNTs. Such disks were smaller in diameter and thickness and further apart for the lower polyethylene solution concentration (0.01w/w%), while at the higher polyethylene solution concentration (1w/w%) they grew to larger diameters and closer together, with the disk thickness also increasing. This indicated a direct relationship between the solution concentration and the polyethylene disk size. As the polyethylene solution concentration increased, the disk size also increased. HDPE20 (molecular weight of 540000g/mol) produced the largest diameter and thickness disks, while HDPE0.83 (molecular weight of 158000g/mol) produced the second largest, for a given polyethylene solution concentration and cooling rate. This phenomenon can be related to the molecular weight of HDPE0.83. The longer molecular chains of HDPE0.83 meant more resistance to uncoiling and stretching that were found to be one of the main factors in the growth of the disks. Therefore, HDPE0.83 had smaller disks than HDPE20.

PE35000 (average molecular weight of 35000g/mol) was also used to infuse into the CNT yarns and produce polyethylene-infused CNT yarns. Such polymer produced disks with much smaller diameter and thickness, while the gap between the disks was also shorter compared to those of HDPE0.82, HDPE4.5 and HDPE20. Polywax1000 (average molecular weight 1000g/mol) and Polywax3000 (average molecular weight 3000g/mol) were also used to infuse into the CNT yarns. It was found that Polywax 3000 showed larger diameter disks compared to Polywax1000, while the thickness and gap remained identical.

The infusion of polypropylene into the CNT yarn produced disks around the CNTs in a similar fashion to those of polyethylene. The polypropylene solution concentration of 1w/w% produced larger diameter disks, whilst the thickness and gap distance remained unchanged compared to those of the 0.1w/w%. Furthermore, such disks were found around the individual and bundles of the CNTs, indicating the disk growth of polypropylene

perpendicular to the axial direction of the CNTs. It was also found that the disks were smaller in diameter compared to those of polyethylene. In addition, a thick coating covered most of the outer surface of the yarn.

Nylon 6,6 produced disks around the CNTs at the solution concentration of 1w/w%. Such disks grew in a non-uniform fashion, meaning it was difficult to locate such disks in the nylon 6,6-infused CNT yarn. The fabrication procedure of the constant-length CNT yarns meant that the CNT yarn was a compact structure with many individual and bundles of the CNTs closely held together. The introduction of nylon 6,6 molecules at high temperature (240°C) could indeed initiate the nucleation of such disks around the CNTs. However, further reduction in the temperature to 185°C may have decreased the crystallisation kinetics, preventing the nuclei to grow to larger sizes that were observed for polyethylene.

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Chapter 6

Investigation of the thermal and mechanical properties of polymer-infused CNT yarns

6.1. Introduction

Unlike conventional textile yarns such as cotton or wool [1, 2], where the tensile failure is due to the breakage of the chemical bonds in the individual molecules, the tensile strength of the individual CNTs is very large (50-150 GPa) compared to that of the CNT yarn. Hence, the CNTs do not fail because of covalent bond failure of the nanotubes, but rather fail by a mechanism of sliding relative to one another. This is because the interfacial shear strength of the nanotubes (vdW attractions) is comparatively low, and the applied tensile stress on the nanotube is greater than their shear strength.

In Chapter 4, it was shown that increasing the number of vdW attractions between the CNTs via solvent and twist densifications could enhance the stress transfer within the yarn, hence increasing the tensile strength of the CNT yarn itself. For example, a CNT yarn densified by acetone was 2 to 3 times stronger compared to the undensified CNT web. Furthermore, by inducing a twist into a CNT web, via constant-length twist method, the tensile strength of the CNT yarn increased by a factor of 3 compared to the CNT yarn of the shrinking-length twist method, and a factor of 5 compared to the undensified CNT web. All of these techniques ensured closer packing between the nanotubes in the CNT yarn, thus a greater number of secondary bonding interactions.

In Chapter 5, the morphological and geometrical properties of the polymer-infused CNT yarns were investigated. Six types of polyethylene with regards to their molecular weights, a polypropylene and a nylon 6,6, were incorporated into the constant-length CNT yarns.

The SEM analysis confirmed that the polymeric disks were nucleated and grown on the individual and bundles of the CNTs for such polymers. Such disks were quantitatively characterised in terms of their diameter, thickness and the gap between the disks. The growth of the disk like structures around the CNTs indicated that if such polymeric disks could grip the CNTs and also span individual and bundles of the CNTs in the polymer-infused CNT yarn structure, then there is the potential to improve the overall properties of the polymer-infused CNT yarn.

In the study using HDPE0.83 (158000g/mol), HDPE4.5 (79000g/mol) and HDPE20 (54000g/mol), a direct relationship was found between the polyethylene solution concentration and the disk size. The comparison of the polymer solution concentrations of 0.01, 0.1 and 1w/w% showed that at the lowest polymer solution concentration (0.01w/w%), the disks were smaller in diameter and thickness and further apart from each other than those observed for the higher concentration (1w/w%). It was also found that the average molecular weight of the polyethylene influenced the disk size, with lower molecular weight HDPE20 producing the largest disks in terms of diameter and thickness, while the higher molecular weight HDPE0.83 led to smaller disks. It is thought that HDPE0.83 may have had more resistance to uncoiling and stretching, which were found to be the main factors in the growth of the disks, and led to smaller disks compared to those of HDPE20.

The morphological analysis of the PE35000 (35000g/mol) revealed that the disks had much smaller diameter and thickness compared to those of HDPE20 while the gap between the disks was also shorter than those of HDPE20. Furthermore, Polywax1000 (1000g/mol) and Polywax3000 (3000g/mol) were also infused into the CNT yarns. The morphological studies showed that Polywax3000 grew larger diameter disks compared to Polywax1000, while the thickness and gap remained identical.

Polypropylene (297000g/mol) was also used to produce polypropylene-infused CNT yarns. It was found that the disks around the CNTs grew in similar fashion to those of the polyethylene. Furthermore, increasing the polypropylene solution concentration to 1w/w%

produced larger diameter disks, while the thickness and gap remained unchanged compared to those of the 0.1w/w%. Such disks were found around the CNT bundles, indicating the growth of the polypropylene disks perpendicular to the axial direction of the individual and bundles of the CNTs. It was also found that the disks were small in diameter (~30nm) compared to those of polyethylene, and thus did not bridge the adjacent CNT bundles. Rather, a coating almost covered the entire outer surface of the whole polypropylene-infused CNT yarn.

It was hypothesised that such polyethylene, polypropylene and nylon 6,6 disks around the CNTs could span across multiple individual and bundles of the CNTs and act as clamps, thus potentially increasing the stress transfer between the nanotubes. Importantly, to obtain these properties in an optimal sense and to maintain the light weightiness of the resultant polymer-infused CNT yarn, it was important to incorporate as little polymer as possible into the CNT yarn by maintaining the polymer solution concentration at 1w/w%. In addition, the polyethylene-infused CNT yarns produced from HDPE4.5 was found to have similar properties to those of HDPE20 and HDPE0.83. Therefore, HDPE20 and HDPE0.83 were further characterised and studied in terms of their thermal and mechanical properties.

In this chapter, the thermal and mechanical properties of such polymer-infused CNT yarns were characterised using the TGA (to determine the amount of polymer infused in the CNT yarn), TEM (to understand the microstructure of the disks and nanotubes), DSC (to understand the crystalline structure of the disks) and finally the tensile testing (to determine their mechanical properties). This led to a further understanding of the mechanism of polymeric disk incorporation into the CNT yarn, and their effects on the mechanical strength of the resultant polymer-infused CNT yarn.

6.2. Polyethylene-infused CNT yarns

Five types of polyethylene with different molecular weights were used to produce polyethylene-infused CNT yarns as shown in the Table 6.1. The experimental procedure for infusing such polymers into the CNT yarn was outlined in Chapter 3. Briefly, these

polymers were first dissolved in xylene at 130°C while stirring at 350rpm. The constantlength CNT yarn was then dipped in the solution and maintained in that solution, whilst the polymer was able to crystallise. Three polyethylene solution concentrations of 0.01, 0.1 and 1w/w% and a cooling rate of 1°C/min (cooling time 30min) were chosen. The polyethylene-infused CNT yarn was then taken out of the solution, washed with acetone, dried in an oven at 80°C for 1h and subsequently characterised. In order to better understand the properties of the polyethylene-infused CNT yarns, a naming system was developed, and is described in the Table 6.1.

Table 6.1. Description of the names of each polyethylene-infused CNT yar	n.
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Sample ID	Polyethylene type	Molecular weight g/mol	Polymer solution concentration w/w%	Cooling rate °C/min
I0.83-0.01-1	HDEP0.83	158000	0.01	1
I0.83-0.1-1	HDEP0.83	158000	0.1	1
I0.83-1-1	HDEP0.83	158000	1	1
I20-0.01-1	HDPE20	54000	0.01	1
I20-0.1-1	HDPE20	54000	0.1	1
I20-1-1	HDPE20	54000	1	1
I35000-1-1	PE35000	35000	1	1
I3000-1-1	Polywax3000	3000	1	1
I1000-1-1	Polywax1000	1000	1	1

6.2.1. TGA analysis

The Figure 6.1 shows a representative TGA weight loss curve and its first derivative thermogravimetric curve (DTG) for the CNT yarn and the polyethylene-infused CNT yarns. Such polyethylene-infused CNT yarns were produced from HDPE0.83 and HDPE20 with three polyethylene solution concentrations of 0.01, 0.1 and 1w/w% and subsequently oven dried at 80°C for 1h. All samples were then measured in an air atmosphere.



Figure 6.1. (a) TGA and (b) DTG graphs of the CNT yarn, HDPE0.83, HDPE20 and their polyethylene-infused CNT yarns in an air atmosphere.

The Table 6.2 lists the thermal degradation properties of polyethylene with different molecular weights, the CNT yarn and their polyethylene-infused CNT yarns extracted from the Figure 6.1. The CNT yarn showed a prolonged weight loss of 10% starting from 200°C, followed by thermal decomposition at 719.3°C with the DTG peak at 745.6°C. The initial weight loss may be due to the amorphous carbon produced during the CNT forest growth in the CVD method (Section 2.2.3). Similar results were also reported by Cui *et al.* [3]. HDPE0.83 and HDPE20 underwent similar thermal decomposition, both starting at ~460°C, with the DTG peaks at ~458°C.

Table 6.2.	Temperatures	at relevant	weight	losses,	weight	loss	values	and	derivatives	for
neat and po	olyethylene-inf	used CNT y	arns.							

Sample ID	Temperature	Temperature	First	Second	First peak	Second
	at first	at second	weight	weight	on DTG	peak on
	weight loss	weight loss	loss	loss	°C	DTG
	°C	°C	%	%		°C
CNT yarn	719.3	-	100	-	745.6	-
HDPE0.83	459.8	-	100	-	458.2	-
HDPE20	462.4	-	100	-	460.7	-
PE35000	437.3	-	100	-	452.2	-
polywax3000	456.4	-	100	-	451.2	-
polywax1000	443.9	-	100	-	450.5	-
I0.83-1-1	388.3	661.2	33	67	389.1	663.2
I0.83-0.1-1	369.8	636.4	15.8	84.2	376	642.8
I0.83-0.01-1	389.8	649	12.5	87.5	381. 9	649.9
I20-1-1	390.6	679.7	32.4	67.6	392.7	685.8
I20-0.1-1	408.4	661.2	16.1	83.9	410.7	666.7
I20-0.01-1	404.4	669.8	13	87	402.3	666.6
I35000-1-1	441.1	682.8	41.1	59	439.7	669.9
I3000-1-1	458.4	669.2	34.3	65.8	463.9	673.3
I1000-1-1	438.7	683.8	35.6	64.4	439.8	683.9

All the polyethylene-infused CNT yarns showed two weight loss stages, as identified in the Table 6.2. An initial weight loss occurred at 370-460°C, with the DTG peak at 376-464°C showing weight loss of 33%, 15.8% and 12.5% in I0.83-1-1, I0.83-0.1-1 and I0.83-0.01-1,

respectively. However, since the CNT yarn was reduced by 10% in this region, the actual weight losses associated with I0.83-1-1, I0.83-0.1-1 and I0.83-0.01-1 were calculated to be 23%, 5.8% and 2.5% respectively. Identical weight loss values were observed in I20-1-1, I20-0.1-1 and I20-0.01-1, respectively. This weight loss is associated with the decomposition and removal of HDPE0.83 and HDPE20 from such yarns respectively.

The graph in the Figure 6.2 shows that firstly the weight loss was directly proportional to the polyethylene concentration at a given cooling rate (1°C/min) for I0.83-1-1 and I20-1-1. Secondly, an identical weight loss was observed for both yarns indicating that regardless of the average molecular weight, a given concentration led to the same mass uptake of the polymer into the polyethylene-infused CNT yarn.



Figure 6.2. Polyethylene solution concentration vs the mass loss in I0.83-1-1 and I20-1-1 obtained from the TGA data.

In addition, it can be seen from the Table 6.2 that the second weight loss occurred at $\sim 650^{\circ}$ C with the DTG peak at 670° C. This decrease is due to the decomposition of the CNTs. A similar weight loss amount was also observed in I20-1-1, I20-0.1-1 and I20-0.01-1. This confirms that this weight loss was indeed due to the CNTs because at such temperature all the polyethylene has been already removed from the yarn. In their

experimental work, Cui *et al.* [3] reported similar weight loss behaviour from polyethylene and CNTs and they also concluded that the first and second weight losses were due to the decomposition of the polyethylene and the CNT, respectively.

It should be noted that if the solvent (xylene) is unintentionally retained in the polyethylene-infused CNT yarn structure, this can cause artifacts with regards to the quantification of these results. To this end, the above data was obtained after an initial investigation was undertaken in determining the degree of xylene removal. It was found that xylene could be removed by prolonged heating below the polyethylene melting point $(130^{\circ}C)$. The polyethylene-infused CNT yarns with identical polyethylene type and concentrations were prepared and oven dried at 80°C for 1h. These samples showed an initial weight loss of $5.9\pm0.2\%$ starting from $90\pm15^{\circ}C$ up to $200\pm10^{\circ}C$ with the DTG peaks at $130^{\circ}C$ indicating the physical cohesion of xylene with polyethylene during the dissolution process. Such trapped xylene was released when polyethylene was heated close to (but below) its melting point.

6.2.2. DSC analysis

The Figure 6.3 shows the DSC graphs of HDPE0.83, HDPE20, the CNT yarn and their polyethylene-infused CNT yarns. The Table 6.3 shows the melting and crystallisation temperatures and the degree of crystallinity of polyethylene and their polyethylene-infused CNT yarns obtained from the Figure 6.3. The degree of crystallinity was calculated using the standard ΔH_0 of polyethylene (293J/g [4]) for 100% crystalline polyethylene (Equation 3.4), as well as the weight component of polyethylene obtained by the TGA to normalise the data to the polymer phase. It was found that the crystalline properties of polyethylene in their neat form and in the polyethylene-infused CNT yarn remained the same.



Figure 6.3. DSC graphs of the CNT yarn, HDPE0.83, HDPE20 and their polyethyleneinfused CNT yarns at (a) first heating run and (b) first cooling run.

The Table 6.3 shows that HDPE0.83 and HDPE20 both had crystallinity of 44.6 % and 44.9 %, respectively. The polyethylene-infused CNT yarns showed the degree of crystallinity of 33-66%. Qiao *et al.* [5] investigated the degree of crystallinity of ultra high molecular weight polyethylene with the CNT and found that the presence of small amount of CNT in polymer could promote further increase in the degree of crystallinity of polyethylene may decrease when large CNT aggregates are present. They argued that well dispersed CNTs have high surface area thus enhancing the nucleating ability.

Table 6.3. Crystallinity calculation of polyethylene in their neat and incorporated forms in the polyethylene-infused CNT yarns obtained from the DSC first heating runs. The crystallinity was calculated using the standard ΔH_o of polyethylene (293J/g) as well as the weight component of polyethylene obtained by TGA.

Sample ID	Melting	Crystallisation	ΔH	Crystallinity
	temperature	temperature	J/g	%
	°C	°C		
HDPE0.83	130.8	116.7	169.9	44.6
HDPE20	131.8	115.9	171.6	44.9
PE35000	91.5	89.7	89.5	31.2
Polywax3000	112.6	105.6	218.3	38.4
Polywax1000	127.3	114.6	226.2	43.4
I0.83-1-1	128.9	120.7	22.1	66.5
I0.83-0.1-1	128.5	121.6	37.2	45.7
I0.83-0.01-1	No peak	No peak	-	-
I20-1-1	127.6	123.1	86.5	48.1
I20-0.1-1	128.1	122.1	20.8	32.9
I20-0.01-1	128.8	120.5	6.3	58.6
I35000-1-1	49.7	113.6	12.7	41.2
I3000-1-1	34.6	110.3	35.2	34.4
I1000-1-1	51.2	116.9	51.2	49.1

However, the results presented here indicate that the degree of crystallinity of polyethylene did not change significantly in the polyethylene-infused CNT yarn across all polyethylene types and the polymer solution concentrations shown in the Table 6.3. This may be due to the fact that the CNTs in the polyethylene-infused CNT yarns were well oriented along the direction of the yarn. Such axial orientation may in fact counteract the effect of agglomeration of CNTs in the yarn thus promoting their crystallisation ability. Miao *et al.* [6] studied the effect of the CNT in the melting temperature of polyethylene and found that the addition of the CNT did not significantly change the melting point. Their results are in

agreement with our findings where the addition of low amount of polyethylene into the CNT yarn maintained the degree of crystallinity of polyethylene in the polyethylene-infused CNT yarns.

6.2.3. TEM analysis

The Figure 6.4 shows the TEM image taken from the CNTs in the CNT web. It can be seen that the individual CNTs have multiwall structure (7-14 walls) with outer diameter of 15-20nm and inner diameter of 8-10nm.



Figure 6.4. TEM image of the CNTs taken from the CNT web. The CNT web was produced by drawing a length from the CVD-grown CNT forest.

The Figure 6.5 shows the TEM images of the polyethylene-infused CNT yarns (HDPE0.83 of 158000g/mol) produced with three polyethylene solution concentrations of 0.01, 0.1 and 1w/w% and a cooling rate of 1°C/min. It can be seen in these images that polyethylene disks were grown and clamped around the CNTs. It can be also seen that the disks firmly gripped bundles of the CNTs (Figure 6.5b, 6.5d and 6.5f) and that HDPE0.83 compressed the CNT walls towards the center of the disk. This is especially evident in I0.83-0.1-1 (Figure 6.5d) where the CNT walls have been compressed and bent towards the center of

the nanotube. Such compression behaviour of HDPE0.83 was observed for all three concentrations, with a similar degree of compression visually apparent.



I0.83-0.01-1 (scale bar 20nm) (scale bar 5nm)

Figure 6.5. TEM images of the polyethylene-infused CNT yarns produced with the infusion of HDPE0.83 into the CNT yarn. The arrows indicate HDPE0.83 coating in between the disks. A TEM image with low and high magnifications is shown.



I20-0.01-1 (scale bar 20 nm) (scale bar 5nm)

Figure 6.6. TEM images of the polyethylene-infused CNT yarns produced with the infusion of HDPE20 into the CNT yarn. The arrows indicate HDPE20 coating in between the disks. For each TEM image, low and high magnifications are shown.

The Figure 6.6 shows the TEM images of the HDPE20-infused CNT yarns (molecular weight of 54000g/mol) produced from three different polymer solution concentrations (0.01, 0.1 and 1 w/w%) and a cooling rate of 1°C/min. These images are similar in terms of morphological properties to those of the HDPE0.83-infused CNT yarns discussed above. It is seen that the disks were grown around the CNTs with each disk spanning and clamping several of the CNTs together (Figure 6.6a, 6.6c and 6.6e) creating a network of interconnected CNTs in the polyethylene-infused CNT yarn.

The Figure 6.7 shows the TEM images of the PE35000-infused CNT yarn (molecular weight of the 35000g/mol) into the CNT yarn. It can be observed in the Figure 6.7a that the polymeric disks were grown around the CNTs, with disks being sufficiently large to bridge several neighbouring CNTs, thus creating a network of disks inside the I35000-1-1. The high magnification image (Figure 6.7b) shows the typical CNT walls, as well as a polymeric disk grown perpendicular to the CNT axis.



I35000-1-1 (scale bar 20nm)

scale bar 5nm

Figure 6.7. TEM images of the polyethylene-infused CNT yarns produced with the infusion of PE35000 into the CNT yarn. The arrows indicate PE35000 coating in between the disks. A TEM image with low and high magnifications is shown.

A careful investigation into the disk structure (Figure 6.7b) also revealed interesting patterns in the disk itself using this method of analysis. In particular, some molecular

orientation can be observed around the CNT walls. These directional orientations are less than 1nm in length and indicate that the disk has some partial molecular orientation.

The Figure 6.8 shows the TEM images of the polyethylene-infused CNT yarns produced by the infusion of Polywax1000 and Polywax3000 (molecular weight of 1000 and 3000g/mol respectively). It can be seen in the Figure 6.8a and 6.8c that the disks were grown around and perpendicular to the axis of the CNTs. In addition, the disks gripped several CNTs together as shown in the Figure 6.8b.



I3000-1-1 (scale bar 20nm) (scale bar 5nm)





I1000-1-1(scale bar 20nm) (scale bar 10nm)

Figure 6.8. TEM images of the polyethylene-infused CNT yarns produced by the infusion of Polywax1000 and Polywax3000 into the CNT yarn. The arrows indicate the polymer coating in between the disks. A TEM image with low and high magnifications is shown.

The close examination of the polyethylene disks around the individual and bundles of the CNTs in the polyethylene-infused CNT yarns shows more clearly the mechanism by which the disks were grown and held the CNTs together. It was found that the disks gripped several individual and bundles of the CNTs together and bridged between them as was also observed by the SEM, discussed in Chapter 5. This created an interconnected structure, with the CNTs connected together at several points across their lengths. Such a structure was observed for all polyethylene types discussed above. However, HDPE0.83 showed an additional behavior with respect to the CNTs that was not observed for the other polyethylene types. The gripping of the CNTs by HDPE0.83 was so firm that the walls were compressed towards the center of the CNT, as seen in the Figure 6.9.



Figure 6.9. TEM image of a representative HDPE0.83 disk network in its HDPE0.83infused CNT yarn. The inset shows schematic firm gripping of the CNTs by the HDPE0.83 disks. (scale bar 20 nm).

Pennings [7] showed that homogenously crystallised polyethylene disks had high tensile strength of 4×10^4 kg/cm² while Cui *et al.* [3] experimentally showed that heterogeneously crystallised polyethylene disks around the CNTs could grip individual CNTs and compress the walls firmly. The results presented here are in agreement with their findings and suggest that not only such disks could firmly grip the individual CNTs but also were they strong

enough to compress several individual and bundles of the CNTs towards the center of the disk.

Furthermore, the high magnification TEM images of the disks in the Figure 6.7b revealed a molecular orientation in the disks. Such molecular orientations were more ordered closer to the CNT surface, compared to those further away from it. This indicated that the CNT could in fact induce orientation of the polyethylene molecules. A simulation study by Jeronimo *et al.* [8] showed that closer to the CNT surface, the polyethylene molecules become oriented along the CNT axis. They showed that as the disks grow, that is new polyethylene molecules are taken up from the solution and adhere to the nuclei resulting in the disk growth, the influence of the CNT on the newly attached molecules is reduced, leading to less molecular orientation further away from the CNT surface. The results presented here are in agreement with their findings, indicating that indeed such disks were semi-crystalline.

Although such a disk growth mechanism was observed for all of the polyethylene samples studied in this chapter, a thin layer of polyethylene with thickness of 0.5-1nm was also present in the gaps between the individual disks and around the nanotube surface, as is indicated by arrows in the Figures 6.5 to 6.8. This phenomenon is especially evident for the polyethylene-infused CNT yarns with polyethylene solution concentration of 1w/w% and cooling rate of 1°C/min (I0.83-1-1, I20-1-1, I35000-1-1, I3000-1-1), compared to those of 0.01w/w% (I0.83-0.01-1, I20-0.01-1, I35000-0.01-1, I3000-0.01-1 and I1000-0.01-1). This was also observed by Cui et al. [3] where a CNT rich (70w/w% CNT) composite yarn with a high molecular weight polyethylene was produced and characterised. Although the author did not mention about such a "thickening" effect, their SEM images clearly showed polymer coating around the CNTs. Jeronimo et al. [8] discussed that as the disks grow in size, the effect of the CNT is reduced, and that the longer chain molecules can then be attached to the disks growing the disks to larger dimensions. The TEM analysis on such thin layers in between the protruding disks here indicates that the shorter chain molecules may have primarily formed nuclei around the CNTs and taken up more molecules from the solution in order to grow. However, the

longer chain molecules may have also attached themselves to the surface of the CNT and aligned their length along the length of the CNT resulting in such coating phenomenon observed around the CNTs.

6.2.4. Mechanical properties

The Figure 6.10 shows the stress-strain curves for the polyethylene-infused CNT yarns produced from HDPE0.83, HDPE20, PE35000, Polywax3000 and Polywax1000. It can be seen that the tensile stress increased followed by the breakage of the polyethylene-infused CNT yarns at the maximal stress.



Figure 6.10. Stress-strain curves obtained from polyethylene-infused CNT yarns using (a) HDPE0.83, HDPE20 and (b) PE35000, Polywax3000 and Polywax1000. The extension rate of 0.1mm/min and gauge length of 10mm were used.

The Table 6.4 shows the representative data abstracted from the stress-strain curves for the CNT yarn, polyethylene and their polyethylene-infused CNT yarns. The CNT yarn has values of load at break, tensile strength and modulus of 0.24N, 1.88GPa and 32.98GPa, respectively, while those of the HDPE0.83 are 0.71N, 0.01GPa and 0.002GPa and of the HDPE20 are 1.73N, 0.02GPa and 0.005GPa, respectively.

Table 6.4. Mechanical properties of the polyethylene-infused CNT yarns. The gauge length was 10mm and extension rate 0.1mm/min. The weight percent of each component was determined using TGA results.

Sample ID	Number	Linear	CNT	Polymer	Average	Load at	Strain at	Tensile	Tensile
1	of	density	fractio	fraction	density	break (std	break (std	strength (std	modulus (std
	specimens	of the	n		of yarn	dev)	dev)	dev) GPa	dev)
	tested	yarn			g/cc	Ν	%		GPa
		tex							
HDPE0.83	3	50.81	0	1	0.96	0.71(0.07)	640(0.21)	0.01(0.001)	0.002(0.001)
HDPE20	3	75.24	0	1	0.96	1.73(0.06)	470(0.11)	0.02(0.001)	0.005(0.001)
PE35000	4	48.83	0	1	0.91	0.47(0.03)	149(0.14)	0.01(0.001)	0.006(0.001)
Polywax3000	4	12.97	0	1	0.98	0.13(0.04)	58(0.11)	0.01(0.002)	0.02(0.003)
Polywax1000	3	11.11	0	1	0.96	0.11(0.03)	38(0.09)	0.01(0.001)	0.03(0.002)
CNT yarn	120	0.23	1	0	1.8	0.24(0.06)	5.7(0.01)	1.88(0.03)	32.96(1.99)
I0.83-1-1	10	0.38	0.61	0.39	1.47	0.34(0.01)	3.1(2.1)	1.31(0.02)	42.41(3.98)
I0.83-0.1-1	10	0.33	0.69	0.31	1.55	0.19(0.01)	4.5(2.3)	0.89(0.11)	19.78(3.07)
I0.83-0.01-1	10	0.32	0.72	0.28	1.56	0.21(0.02)	3.3(1.1)	1.03(0.09)	31.11(4.22)
I20-1-1	10	0.36	0.64	0.36	1.49	0.34(0.05)	3.1(1.5)	1.41(0.05)	45.55(6.21)

I20-0.1-1	10	0.33	0.69	0.31	1.54	0.21(0.01)	3.8(1.56)	0.98(0.21)	25.86(3.76)
I20-0.01-1	10	0.31	0.74	0.26	1.58	0.19(0.01)	1.8(0.8)	0.97(0.09)	53.87(2.66)
I35000-1-1	10	0.42	0.55	0.45	1.39	0.18(0.02)	3.8(2.82)	0.59(0.11)	15.74(1.05)
I3000-1-1	10	0.35	0.66	0.34	1.52	0.19(0.01)	3.9(1.8)	0.82(0.26)	21.14(2.15)
I1000-1-1	10	0.31	0.74	0.26	1.58	0.21(0.03)	2.97(1.27)	1.07(0.04)	36.11(4.21)

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The addition of HDPE0.83 and HDPE20 to the neat CNT yarn led to an increase in the linear density of the polyethylene-infused CNT yarn which has resulted in slight increase in the applied breaking force. This increase was more evident for the infusion from a polyethylene solution concentration of 1w/w% compared to 0.1 and 0.01w/w%. The load at break of I0.83-1-1 and I20-1-1 both increased 70% to 0.34N, while those of the other samples remained close to 0.21N. The tensile strength and modulus values for the I0.83-1-1 and I20-1-1 show the highest compared with other polyethylene infused CNT yarns shown in the Table 6.4 indicating that the molecular weight of the polyethylene (fixed cooling rate and polymer concentration in the solution) has had an effect on increasing the stress and modulus.

On the one hand, the TEM analysis showed that the disks of I0.83-1-1 firmly gripped the CNT bundles which should have increased the shear stress of the polyethylene-infused CNT yarn. On the other hand, the SEM analysis showed that the polyethylene solution concentration of 1 w/w% covered the entire surface of the polyethylene-infused CNT yarn. While these results could, in principle, lead to a dramatic increase in the tensile strength of the polyethylene-infused CNT yarn, the results presented in the Table 6.4 show a decrease in such values.

The careful analysis of the tensile specimens at failure points revealed interesting phenomenon in the polyethylene-infused CNT yarns. It was discussed in Chapter 5 (Section 5.5) that the polymeric disks failed to grow deeper in the yarn structure in the polymer-infused CNT yarns produced from various polymers. The Figure 6.11 here shows a representative SEM image of the failure points of the polyethylene-infused CNT yarns after the tensile testing was completed.



Figure 6.11. A representative SEM image of the failure point of the polyethylene-infused CNT yarn taken from I20-1-1 (polymer solution concentration of 1 w/w% and cooling rate of 1° C/min) after the tensile testing. The arrow shows the disks only on the outer surface of the polyethylene-infused CNT yarn while no disk could be found deeper inside the yarn.

It has been previously established that the CNT yarn, in general, fails under the tensile stress due to the sliding of the CNTs against each other (Section 2.3.4) [9, 10]. The SEM examination of the failure surface can show the CNTs further deep in the polyethylene-infused CNT yarn structure and closer to the yarn center. Such examination can be done by focusing the SEM beam on the most outer surface of the polyethylene-infused CNT yarn. The CNTs that are slightly out of focus are those that are away from the focal point thus closer to the yarn center. It can be seen in the Figure 6.11, by the arrow, that the CNTs that were on the outer surface did have disks. However, the CNTs that were deeper inside the yarn did not have any disks. This revealed that the spatial confinement could in fact be the influencing factor in the infusion of polyethylene into the CNT yarn. This phenomenon can be explained by the mechanism by which the nucleation and growth of the disks occurs.

Degennes [11] and later Keller *et al.* [12] discussed that the flow of the solution containing polymer molecules causes such molecules to uncoil to some extent. The ends of the partially uncoiled molecules then adhere to the surface of the nucleating agent. When the

flow reaches some critical value, the polymer molecules are then able to uncoil and stretch along the direction of the flow, at the same time decreasing the hydrodynamic interactions between the polymer chains. This results in further stretching and orientation of the polymer chains, which in turn results in the growth of the disks. In addition, Somani *et al.* [14,15] suggested that the longer chain molecules stretch more readily than shorter chain ones, indicating that the polymer with a higher average molecular weight can more readily nucleate and grow disks. Their findings suggest that in order to grow large disks, the polymer solution must in fact be under a directional flow and the polymer chains must be sufficiently long to be stretched and oriented. However, in our study, the CNTs are tightly packed inside the CNT yarn structure, thus the polymer solution would not be able to maintain its flow velocity deep within the CNT yarn. This could have led to a significant reduction in polymer chain stretching and orientation within the CNT yarn, which thus hindered the nucleation and growth of the polyethylene disks.

6.3. Polypropylene-infused CNT yarns

A polypropylene with an average molecular weight of 297000g/mol was infused into the CNT yarns and the disks on the CNTs as well as the mechanical properties of the polypropylene-infused CNT yarns were investigated using the TEM and tensile testing respectively. In order to fabricate the polypropylene-infused CNT yarn, an oil bath was prepared using silicon oil on a hot plate. Xylene was used as the solvent for polypropylene. 10mL of xylene was used to dissolve polypropylene at 130°C inside test tubes while stirring at 350rpm. The constant-length CNT yarn was then placed inside the polymer solution using a stainless steel frame (Figure 3.4) and remained there, until the cooling process was completed. The polypropylene-infused CNT yarn was named Ipp-1-1 (polypropylene solution and washed with acetone at least three times in order to remove any polymer residue from the yarn surface. The polypropylene-infused CNT yarn was then placed in oven at 80°C for 1h to remove any xylene or acetone from the surface or from within the structure.

6.3.1. TEM analysis

The Figure 6.12 shows the TEM images of the polypropylene disks around the CNTs. Such disks resemble polyethylene disks in shape as these are cylindrical and grew perpendicular to the CNT axis.



Figure 6.12. TEM images of the polypropylene-infused CNT yarn at (a) low magnification and (b) high magnification. Polypropylene nucleated around the CNTs and disks grew perpendicular to the CNT axis (scale bar 20nm).

The high magnification TEM image (Figure 6.12b) shows that the polypropylene disks gripped several individual and bundles of the CNTs and clamped them together. In addition, a thin layer of polypropylene can be also observed on the CNT surface, between the protruding disks. This indicates that similar to the observations with polyethylene, the shorter chain molecules primarily formed nuclei around the CNTs and took up more molecules from the solution in order to grow. The longer chain molecules also attached themselves to the surface of the CNT and aligned their length along the length of the CNT. However, such longer chain molecules could not form nuclei and take up more polymer molecules from the solution due to the loss of their kinetic energy thus forming a thin layer of polypropylene along the length of the CNT instead.

6.3.2. Mechanical properties

The Figure 6.13 shows the stress-strain curve for the polypropylene-infused CNT yarn. The yarn was produced by using polypropylene solution concentration of 1w/w% and the cooling rate of 1° C/min.



Figure 6.13. Stress-strain curve obtained from Ipp-1-1. The yarn was produced from a polypropylene solution concentration of 1w/w% and cooling rate of 1°C/min. The tensile testing was done using an extension rate of 0.1mm/min and gauge length of 10mm.

The Table 6.5 shows the mechanical properties of polypropylene and polypropyleneinfused CNT yarn. The strength and modulus of polypropylene is about 0.008GPa and 0.009GPa, respectively. The polypropylene-infused CNT yarn demonstrated a strength and modulus of 1.06 and 33.23GPa, respectively. The SEM images of Ipp-1-1 in Chapter 5 showed more disks around the CNTs compared to Ipp-0.1-1 (polypropylene solution concentration of 0.1w/w% and cooling rate of 1°C/min). In addition, it can be seen that the Ipp-1-1 had a similar strength and modulus to I1000-1-1 and I0.83-0.01-1 and lower than those of the I0.83-1-1 and I20-1-1, indicating that their disk incorporation in the yarn resulted in an increase in the strength compared to other types of polyethylene.

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Sample ID	Number	Linear	CNT	Polymer	Average	Load at	Strain at	Tensile	Tensile
1	of	density	fraction	fraction	density	break (std	break	strength (std	modulus
	specimens	of the			of yarn	dev)	(std dev)	dev)	(std dev)
	tested	yarn			g/cc	Ν	%	GPa	GPa
		tex							
Polypropylene	5	21.4	0	1	0.9	0.18(0.01)	81(0.02)	0.008(0.001)	0.009(0.001)
Ipp-1-1	10	0.32	0.72	0.28	1.55	0.22(0.03)	3.2(0.01)	1.06(0.03)	33.23(4.08)

Table 6.5. Mechanical properties of polypropylene and polypropylene-infused CNT yarns.

6.4. Nylon 6,6-infused CNT yarns

A nylon 6,6 was infused into the CNT yarn. In order to achieve this, nylon 6,6 was dissolved in glycerine at 240°C at 1w/w% concentration, while the solution was stirred at 350rpm. The CNT yarn was contained while the solution was cooled down to 185° C, at a cooling rate of 1° C/min. The nylon 6,6-infused CNT yarn was named Iny-1-1 (nylon solution concentration of 1w/w% and the cooling rate of 1° C/min). The reason for choosing only one solution concentration was that it became clear after a number of experiments that this was the only concentration that produced more consistent samples with the nylon disks on the CNTs.

6.4.1. TGA analysis

The Figure 6.14 shows the TGA graphs of nylon 6,6 and nylon 6,6-infused CNT yarn in nitrogen atmosphere while the Table 6.6 lists the values for the temperatures and each weight loss stage.



Figure 6.14. TGA graphs of nylon 6,6 and nylon 6,6-infused CNT yarn under a nitrogen atmosphere. The heating rate was 10° C/min. A polymer solution concentration of 1w/w% and cooling rate of 1°C/min was used to prepare the nylon 6,6-infused CNT yarn.
For the Iny-1-1 the first weight loss is associated with the decomposition of nylon 6,6 at 380°C with the DTG at 318°C. The second weight loss is associated with the second stage of the decomposition of nylon 6,6 at 576°C with the maximum of the DTG occurring at 586°C. Similar results were reported by Shaffer *et al.* [16] and Sandler *et al.* [17]. Since the measurement was undertaken in nitrogen, the remaining weight of the Iny-1-1 qualitatively indicates that the amount of the CNT present in the yarn was around 23%.

Table 6.6. Thermal propert	ies of nylon 6,6 an	d nylon 6,6-infused	CNT yarns	obtained from
TGA graph.				

Sample ID	Temperature	Temperature	First	Second	First	Second
	at first	at second	weight	weight	peak on	peak on
	weight loss	weight loss	loss	loss	DTG	DTG
	°C	°C	%	%	°C	°C
Nylon 6,6	426.1	507.7	70.3	21.7	432.7	518.6
Iny-1-1	380.1	576.4	11.1	76.8	317.7	586.5

6.4.2. DSC analysis

The Figure 6.15 shows the DSC graph of nylon 6,6 and nylon-infused CNT yarn during a heating run and a cooling run, while the Table 6.7 lists the values of each run. The degree of crystallinity of nylon 6,6 was calculated to be 27%. However, the nylon 6,6-infused CNT yarn showed no peak during the heating and cooling, indicating hindrance in crystallisation of nylon 6,6 molecules in the vicinity of the CNTs.

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Figure 6.15. DSC graphs of nylon 6,6 and nylon 6,6-infused CNT yarn at (a) first heating run and (b) first cooling run.

Table 6.7. Crystallinity calculations for nylon 6,6 and nylon 6,6-infused CNT yarns obtained from the DSC first heating runs. The crystallinity was calculated using the standard ΔH_o of nylon 6,6 (230J/g) in the Table 3.2 ,as well as the weight component of nylon 6,6 obtained from the TGA.

Sample ID	Melting	Crystallisation	ΔH	Crystallinity
	temperature	temperature	J/g	%
	°C	°C		
Nylon 6,6	257.1	213.9	61.2	26.6
Iny-1-1	No peak	No peak	-	-

The SEM images in Chapter 5 showed that the Iny-1-1 more consistently produced disks around the CNTs compared to the Iny-0.01-1 and Iny-0.1-1. However, it is likely that the amount of such disks were not enough to display any peak in the DSC. It is therefore likely that such disks were of crystalline nature but abundant nucleation and growth throughout the nylon 6,6-infused CNT yarn were indeed prohibited by the yarn spatial confinement. The spatial confinement effect on the nucleation and growth of nylon disks was studied by Li *et al.* [18] who experimented with a mixture of nylon 6,6 and CNT both of which dissolved and dispersed in glycerine at 240°C. They then cooled down the mixture and studied the crystallisation of nylon 6,6 around the individual CNTs in the dispersion, and

concluded that an increase in the CNT content in the dispersion resulted in a decrease in the disk growth of nylon 6,6 as well as a reduction in the crystallinity of such disks.

6.4.3. TEM analysis

The Figure 6.16 shows the TEM images of the nylon 6,6-infused CNT yarn. The fringe layers of the CNT walls are evident while nylon 6,6 has covered the outer surface of the CNTs as well as thin layers of polymer around the CNT bundles. Although the SEM images revealed that the nylon 6,6 disks could grow on the CNTs (Figure 5.7i), many attempts to find such disks using the TEM were unsuccessful due to the scarcity of such disks.



Figure 6.16. TEM image of the nylon 6,6-infused CNT yarn (scale bar 20nm).

6.4.4. Mechanical properties

The Figure 6.17 shows the stress-strain curve obtained from the nylon 6,6-infused CNT yarn at the extension rate of 0.1mm/min and gauge length of 10mm. The nylon solution concentration was 1w/w% and the cooling rate was 1° C/min. The Table 6.8 shows the mechanical properties of nylon 6,6 and the nylon 6,6-infused CNT yarn. It is shown that the load at break of Iny-1-1 (0.21N) has doubled compared to nylon 6,6 (0.13N), while stayed unchanged compared to the constant-length CNT yarn (0.24N). In addition, the tensile

strength of the nylon 6,6-infused CNT yarn increased compared to nylon 6,6 while it decreased compared to the constant-length CNT yarn (1.88GPa).



Figure 6.17. Stress-strain curve obtained from the Iny-1-1 where the nylon 6,6 solution concentration of 1w/w% and the cooling rate of $1^{\circ}C/min$ were applied. The extension rate of 0.1mm/min and gauge length of 10mm were used for the tensile testing.

A similar trend is evident for the modulus of Iny-1-1 compared to the CNT yarn. These results indicate that the mechanical properties of nylon 6,6 have been significantly increased with the addition of 23w/w% CNT (as observed in the TGA). It is likely that the increase in the number of nylon 6,6 disks may have in fact increased the mechanical strength of the nylon 6,6-infused CNT yarn due to a higher load sharing by the linked individual and bundles of the CNTs which in turn increased the strength of the nylon 6,6-infused CNT yarn as a whole.

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Sample	Number	Linear	Load at	CNT	Polymer	Average	Strain at	Tensile	Tensile
ID	of	density	break (std	fraction	fraction	density	break	strength	modulus
	specimens	of the	dev)			of yarn	(std dev)	(std dev)	(std dev)
	tested	yarn	Ν			g/cc	%	GPa	GPa
		tex							
Nylon 6,6	3	12.33	0.13(0.02)	0	1	1.14	48(0.01)	0.01(0.001)	0.03(0.01)
Iny-1-1	10	0.38	0.21(0.03)	0.61	0.39	1.54	3.8(0.03)	0.85(0.02)	22.39(3.3)

Table 6.8. Mechanical properties of nylon 6,6 and nylon 6,6-infused CNT yarn.

6.5. Conclusion

In this chapter, the thermal and mechanical properties of various polymer-infused CNT yarns were investigated using the TEM, TGA, DSC and tensile testing. The TGA analysis of the polyethylene-infused CNT yarns showed that the CNT was in fact the major component of the yarn between 64-87%, confirming that the CNT rich yarns could be successfully produced. The DSC analysis of polyethylene also showed that the polymer components of the polyethylene-infused CNT yarns maintained a similar degree of crystallinity compared to the neat polyethylene. This was expected because the CNT itself is considered to be a nucleating agent which enhances the molecular orientation and growth of crystalline regions around the CNTs. Furthermore, the mechanical studies of the polyethylene-infused CNT yarns showed that the tensile force to failure increased, indicating that the load bearing of such polyethylene-infused CNT yarns was increased. However, the tensile strength and modulus were decreased which is associated with the overall weight of the polyethylene-infused CNT yarns.

Polypropylene was infused into the CNT yarns producing polypropylene-infused CNT yarns. The SEM analysis showed that polypropylene disks grew around the individual and bundles of the CNTs and produced a network of interconnected structure. The tensile testing also showed an increase in the load bearing of the polypropylene-infused CNT yarns compared to those of the neat polypropylene while lower than those of the CNT yarn.

Nylon 6,6 was also used to infuse into the CNT yarns. Such polymer produced disks around the CNTs as shown in the SEM images. These disks grew non-uniformly along the length of the CNT yarn meaning it was difficult to locate such disks in the nylon 6,6-infused CNT yarn especially in the TEM. This was attributed to the spatial confinement effect and the loss of kinetic energy of the nylon 6,6 molecules due to the cooling down of the nylon 6,6 solution. The dissolution of nylon 6,6 molecules at high temperatures (240°C) could indeed initiate the nucleation of such disks around the CNTs. However, further reduction in the temperature down to 185°C may have decreased the crystallisation kinetics thus stopping the nuclei to grow to larger sizes. The TGA results showed that nylon 6,6 underwent two

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distinct decomposition stages. The crystallinity of nylon 6,6-infused CNT yarn could not be quantified due to the lack of crystallites during the heating runs in the DSC analysis. The mechanical properties of the nylon 6,6-infused CNT yarn were also studied using the tensile testing. Although the tensile strength and modulus of the nylon 6,6-infused CNT yarn greatly improved compared to those of nylon 6,6, they did not change dramatically compared to the CNT yarn mainly due to added weight of nylon 6,6 into the nylon 6,6infused CNT yarn.

It was discussed in Chapter 5 that the polymeric disks (six types of polyethylene, polypropylene and nylon 6,6) could grow on the surface of the CNT yarn perpendicular to the CNT axis and in regular intervals. The analysis of such disks led us to hypothesise that the formation of the polymeric disks around the CNT bundles within the polymer-infused CNT yarn could act as clamps and fasten the individual and bundles of the CNTs together, thus potentially increasing the stress transfer between them. However, the mechanical analysis of such polymer-infused CNT yarns presented in this chapter revealed that although the load at break of such yarns increased compared to the CNT yarns, the calculated tensile strength rather decreased. Such results were consistently observed for polyethylene-, polypropylene- and nylon 6,6-infused CNT yarns. The reason is thought to be due to the added weight of the polymer (presented by the linear density) into the polymer-infused CNT yarns which in turn offset the increase in the load bearing in the Equation 3.1. Furthermore, the detailed SEM analysis also revealed that the polymeric disks grew only on the outer surface of the polymer-infused CNT yarns. This had an effect on the load transfer between the individual and bundles of the CNTs in the sense that only the nanotubes on the outer surface could effectively participate in the load bearing. Therefore, it is likely that the mechanical strength can be further increased once such polymeric disks could grow in depth of the polymer-infused CNT yarn structure.

Several attempts were made in order to further improve the disk growth deeper inside the polymer-infused CNT yarn. These included the removal of the trapped air or moisture pockets from between the CNTs inside the CNT yarns prior to the polymer infusion in order to facilitate the penetration of the polymer molecules thus nucleating off the surface

of the CNTs deeper in the yarns as was discussed in Chapter 5. In addition, attempts were made to vacuum dry the polymer-infused CNT yarns in order to extract xylene or acetone from the CNTs deeper in the polymer-infused CNT yarn structure.

The close examination into the growth of the polymeric disks deeper inside the yarn structure revealed that the spatial confinement could be the influencing factor in the infusion of such polymers into the CNT yarn. In order to grow large enough disks, the polymer solution must in fact be under a directional flow and the polymer chains must be long enough to allow them to stretch and orient. However, the CNTs were tightly packed inside the CNT yarn structure (due to the preparation of the CNT yarns discussed in Chapter 4, briefly constant-length twist followed by acetone densifications) thus the polymer solution could not maintain a high flow velocity deep within the yarn. This resulted in a significant reduction in polymer chain stretching and orientation deeper in the CNT yarn which in turn hindered the nucleation and growth of the polymeric disks in the polymer-infused CNT yarns.

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Chapter 7

Investigation of the growth of polymer disks directly onto the CNT web

7.1. Introduction

In the preceding chapters, it has been established that the polymeric disks could nucleate and grow from the individual and bundles of the CNTs in the CNT yarns, spun from the CVD-grown CNT forests. The thermal analyses of the polyethylene- and polypropyleneinfused CNT yarns confirmed that the majority of such yarns was the CNTs (>60w/w%). In addition, the mechanical properties of polyethylene-infused CNT yarns revealed that the load at break was increased by around 30% following the incorporation of HDPE0.83. A cooling rate of 1°C/min was found to produce disks with large diameter and thickness on the CNTs compared to the cooling rates of 10 or 100°C/min. However, a major drawback to further improvement of the polymer-infused CNT yarns was the observed limited penetration of the polymer solution into the dense CNT yarn structure, and thus the polymeric disks were not able to nucleate and grow deep within the CNT yarn. Rather, they only nucleated on the CNTs close to the outer surface. Some strategies were undertaken to try to overcome this issue, but were not successful.

In the work described in this chapter, the CNT web itself was used, rather than the CNT yarn, onto which the polymers could directly crystallise the disks. The properties of the CNT webs were discussed in Chapter 4. Unlike the CNT yarns, the CNT web is very loose in structure and the individual and bundles of the CNTs are relatively far apart from each other. In addition, the CNT web itself is much thinner (0.5-1 μ m) than the CNT yarn (20-40 μ m). These characteristic properties of the CNT web led us to hypothesise that using the CNT web instead of the CNT yarn could in fact increase the number of disks that could nucleate around the CNTs by providing a greater openness between the individual and

bundles of the CNTs. This would allow the disk growth on the CNT web, which could be subsequently fabricated into a CNT yarn by the virtue of spinning. In this chapter, polymeric disks using a range of polymer materials were crystallised onto the CNT webs, and subsequently spun into yarns (named web-to-yarn).

In order to produce a web-to-yarn, a CNT web was first drawn from one end of the CVDgrown CNT forest, using tweezers, and attached to a stand. The stand was attached to a belt which was then driven by a DC motor. The movement of the belt drew the CNT web away from the forest, thus producing a length of the CNT web. The CNT forest was grown on the silica substrate with the width of 10mm, and thus the web width, immediately after drawing was 10mm. However, further away from the start of the drawing point, the web width reduced to ~2mm, mainly due to the vdW forces. Upon tensioning the CNT web, the width further decreased to 0.5mm. This was the smallest width value that occurred during the CNT web formation process. Further tensioning of the CNT web did not change the width but rather led to the CNT web breakage. A polymer solution concentration of 1w/w% and a cooling rate of 1°C/min were used during the incorporation of all of the different polymers onto the CNT web.

In order to achieve the 1°C/min cooling rate, the hot plate was switched off. This allowed the oil bath and the polymer solution in the test tubes to cool down slowly. A thermometer in the oil bath near the test tubes demonstrated this degree of rate of cooling. The polymer-treated CNT webs were subsequently spun into the web-to-yarn structures. In order to spin the CNT webs into yarn, one end of the web was maintained fixed while the other end was spun to produce the twist. Due to the small length of the polymer-treated webs (2cm), the spinning was done by hand, with precise measurement of the amount of inserted twist being challenging due to the small length of the polymer-treated webs. The twist then travelled along the length of the polymer-treated CNT web to produce the final web-to-yarn. It should be noted that the TGA analysis of the web-to-yarn structures could not be performed due to lack of time. Of course if the data was available, a much clearer picture of the mechanical performance of these yarns could be shown in the context of conventional composite yarns.

7.2. Treatment of the CNT web with polyethylene

Four types of the polyethylene were chosen in order to produce the polyethylene-treated CNT webs and web-to-yarns as shown in the Table 7.1. HDPE0.83 had the highest molecular weight compared to other types of polyethylene used in this thesis and was selected due to its ability to efficiently grip and compress the individual and bundles of the CNTs, as described in the preceding chapters. This made them more suitable for bridging several bundles of the CNTs and creating an interconnected network within the CNT web.

Polyethylene	Molecular weight	Supplier
	g/mol	
HDPE0.83	158000	CSIRO
PE35000	35000	Sigma Aldrich
Polywax3000	3000	Baker Hughes
Polywax1000	1000	Baker Hughes

Table 7.1. Types and molecular weights of polyethylene used to treat the CNT webs.

The experimental setup for the polyethylene/xylene solution infiltration of the CNT webs consisted firstly of a hot plate for heating the silicon oil bath. One or up to three test tubes containing 10mL of xylene were placed inside the oil bath heating the xylene to 130°C. A solution of polyethylene and xylene was then made by adding the appropriate polyethylene beads into the hot xylene in the test tubes, with stirring at 130°C at 350rpm until polyethylene dissolved. Once a homogenous polyethylene solution was obtained, the CNT web was dipped into the stirring solution and held stationary until the cooling process was completed. The cooling time for the cooling rate of 1°C/min was 30min. It was shown in Chapter 5 that such a cooling rate could produce disks with large diameter and thickness (Table 5.2) in order to grip the individual and bundles of the CNTs together. To keep the CNT web stationary in the solution during the process, a purpose-built stainless steel frame was used (as shown in the Figure 3.4) and the CNT web was wrapped around it. Due to the

experimental procedure being manual twisting, it was difficult to accurately measure the amount of the twists. However, it is estimated that a twist of around 2000-3000 turn/meter was inserted into the yarn.

7.2.1. Morphological properties

The Figure 7.1 shows the SEM images of the CNT web produced from HDPE0.83 (molecular weight of 158000g/mol) and the spun web-to-yarn HDPE0.83 which was produced by the spinning the CNT web HDPE0.83. Due to the experimental procedure being manual twisting, it was difficult to accurately measure the amount of the twists. However, it is estimated that a twist of around 2000-3000 turn/meter was inserted into the yarn.



Web-to-yarn HDPE0.83 (1000x) (scale bar 20 µm)

35000x (scale bar 1 μ m)

100000x (scale bar 500 nm)

Figure 7.1. SEM images of the CNT web HDPE0.83 and the web-to-yarn HDPE0.83 produced by the spinning the CNT web HDPE0.83. An SEM image with three magnifications of 3500, 35000 and 100000 is shown.

The nucleation and formation of the disks can be clearly observed in the SEM images, especially those of the higher magnifications (Figure 7.1c and 7.1f). The width of the CNT web before the polymer treatment was around 500µm. After the polymer treatment, the resultant CNT web HDPE0.83 decreased to a width of around 100µm. This was expected as the HDPE0.83 solution contained xylene, which itself has a mild compressing effect on the CNT web during the drying process. The key advantage of using the CNT web instead of the twisted and densified CNT yarn for the fabrication of the CNT web HDPE0.83 and web-to-yarn HDPE0.83 was that the CNT web was very thin (0.5-1µm in thickness) which exposed all of the CNTs to the HDPE0.83 solution. As the result, in the CNT web form, all

(b)

of the nanotubes and bundles were exposed to the HDPE0.83 solution and there was much more significant crystallisation.





10000x (scale bar 5 µm)



100000x (scale bar 500 nm)



Web-to-yarn PE35000 (5000x) (scale bar 1 µm)

35000x (scale bar 5 μ m)

100000x (scale bar 500 nm)

Figure 7.2. SEM images of CNT web PE35000 and the yarn produced by spinning the CNT web PE35000. An SEM image with three magnifications is shown.

The Figure 7.2 shows the SEM images of the CNT web and the subsequently spun yarn after the treatment in PE35000 solution (molecular weight of 35000g/mol, polymer solution concentration of 1w/w% and cooling rate of 1° C/min). It can be observed that many disks were grown perpendicular to the direction of the CNT bundles, indicating the familiar disk growth mechanism in the polyethylene.

The Figure 7.3 shows the SEM images of the CNT webs and spun yarns produced from Polywax1000 (molecular weight of 1000g/mol) and Polywax3000 (molecular weight of

3000g/mol). Similar to observations for the other types of polyethylene, as discussed above, the disks of Polywax1000 and 3000 grew perpendicularly to the CNT axis, with regular gaps between the disks. In addition, the disks have bridged several CNT bundles thus producing an interconnected CNT structure, as can be seen in the high magnification images in the Figure 7.3c, 7.3f, 7.3i and 7.3l.



CNT Web PE3000 (3500x) (scale bar 20 μ m)



30000x (scale bar 3 μ m)

300000x (scale bar 200 nm)



Web-to-yarn PE3000 120x (scale bar 500 μ m)

35000x (scale bar 2 μm)

100000x (scale bar 500 nm)

Figure 7.3. SEM images of the CNT web PE1000 and CNT web PE3000 and the yarns subsequently produced by spinning such CNT webs. For each sample, an SEM image with three magnifications is shown.

The Table 7.2 shows the disk diameter, thickness and gaps in the CNT web HDPE0.83, CNT web PE35000, CNT web PE1000 and CNT web PE3000 and their spun web-to-yarns. It can be seen that, compared to the disks produced on the I0.83-1-1 (HDPE0.83-infused CNT yarn produced by the infusion of HDPE0.83 with molecular weight of 158000g/mol into a constant-length CNT yarn with HDPE0.83 solution concentration of 1w/w% and cooling rate of 1°C/min shown in the Table 5.2) the disks here are smaller in diameter (127.2nm), greater in thickness (14.5nm) and significantly closer together (80.8nm).

Chapter 7 Investigation of the growth of polymer disks directly onto the CNT web

Table 7.2. Characterisation of the disks of polyethylene-treated CNT webs and the web-to-yarns produced by spinning of such CNT webs.

Sample ID	Molecular	Polymer	Cooling	Number of	Disk	Disk	Disk gap	Number of
	weight of	concentration	rate	images from	diameter (std	thickness	(std dev)	disks per
	polymer	in solution	°C/min	identical	dev)	(std dev)	nm	5.58mm ² from
	g/mol	w/w%		samples and	nm	nm		each image
				magnifications				(magnification
								100000)
CNT Web HDPE0.83	158000	1	1	1	101.1(5.7)	23.6(5.9)	19.5(3.5)	20
Web-to-yarn HDPE0.83	158000	1	1	1	97.6(7.4)	19.3(6.1)	19(1.8)	10
CNT Web PE35000	35000	1	1	1	228.9(28.8)	34.4(7.7)	39.2(10.1)	8
Web-to-yarn PE35000	35000	1	1	1	214.1(14.8)	25.5(2.1)	39.8(3)	12
CNT Web PE3000	3000	1	1	1	127.3 (6.4)	24.9 (2.7)	47.9 (6)	3
Web-to-yarn PE3000	3000	1	1	1	129.3 (15.2)	37.6 (2.9)	39.1(4.2)	3
CNT Web PE1000	1000	1	1	1	238.6 (11.4)	33.3 (6.5)	103.8 (10.1)	6
Web-to-yarn PE1000	1000	1	1	1	218.9 (13.2)	31.7 (9.3)	98.6 (8.9)	7

The results here indicate that the nucleation and growth of the HDPE0.83 disks were more widespread throughout the CNT web structure than that of the I0.83-1-1 yarns, thus producing smaller disks with a higher disk density within the CNT web. As the result, it is thought that the HDPE0.83 molecules preferred to nucleate and grow disks on the CNTs rather than adhering to already made disks on the outer surface of the CNT web. The results here indirectly confirm that indeed the spatial confinement was clearly much less on the CNT web, compared to the constant-length CNT yarn, which was spun and densified before similar infusion.

It can be also seen in the Table 7.2 that the disks produced by PE35000 were bigger in diameter (34.1 nm), bigger in thickness (8.7 nm) and further apart from each other (22.8 nm), compared to the disks produced on the I35000-1-1 shown in the Table 5.3 which arose largely only at the outer surface of the I35000-1-1. Similarly, using the CNT web instead of the CNT yarn ensured that the web-to-yarn PE35000 had disks throughout the entire CNT structure. Furthermore, the Table 7.2 shows that Polywax1000 and Polywax3000 grew disks with different diameter, thickness and gaps, compared to those of the I1000-1-1 and I3000-1-1 as shown in the Table 5.5. It can be seen that the disks grown on the CNT web were significantly bigger (43.8nm on I1000-1-1 and 86.7nm on I3000-1-1), thicker (11.2nm on I1000-1-1 and 11.8nm on I3000-1-1) and further apart (23.1nm on I1000-1-1 and 41.2nm on I3000-1-1) from those of the CNT yarns discussed in Chapter 5. Such a clear difference in the disk size grown on the CNT yarns, and those of the CNT web indicate that indeed the use of the CNT web is more favorable for the polyethylene molecule chains to nucleate throughout the structure, rather than only on the outer surface of the polyethyleneinfused CNT yarn. The loose and open structure of the CNT web is indeed a factor in allowing the nucleation and growth of the disks in the CNT web.

7.2.2. Mechanical properties

The Figure 7.4 shows the tensile load-extension curves that were obtained from the web-toyarns produced from the polyethylene-treated CNT webs. The tensile extension rate was 0.1mm/min. It can be seen that the load at break and extension for the web-to-yarn HDPE0.83 was 0.3N and 0.72mm, respectively. Such a web-to-yarn increased the load and extension by approximately double, compared to the constant-length CNT yarn, which had a load at break of 0.22N and an extension of 0.41mm. In addition, the mechanical properties of the web-to-yarn HDPE0.83 showed that it could bear similar load to failure to I0.83-1-1 (load at failure of 0.34N and extension of 0.31mm). The results here clearly indicate that the load bearing ability of the web-to-yarn HDPE0.83 has increased due to the growth of more HDPE0.83 disks and the fact that they were more widespread throughout the web-to-yarn structure, compared to I0.83-1-1.



Figure 7.4. Tensile load-extension curves obtained from tensile testing of the web-to-yarns spun from spinning the polyethylene-treated CNT webs with the extension rate of 0.1mm/min.

Furthermore, the tensile load-extension curve obtained from the web-to-yarn PE35000 is shown in the Figure 7.4. The load at break and extension for the web-to-yarn PE35000 was 0.32N and 0.24mm, respectively. The comparison of the web-to-yarn PE35000 load and extension with those of the constant-length CNT yarn (discussed in Chapter 4) and I35000-1-1 (discussed in Chapter 6) shows that the web-to-yarn PE35000 roughly doubled the load bearing ability and extension (the CNT yarn with 0.22N and 0.41mm and I35000-1-1 with 0.18N and 0.38 mm, respectively). Such results indicate that the nucleation and growth of

more disks throughout the CNT web compared to the I35000-1-1 resulted in more CNT participation in the load transfer between the individual and bundles of the CNTs which in turn resulted in an increase in the stress transfer in the CNT network. Therefore, the web-to-yarn PE35000 had higher load bearing compared to I35000-1-1. The Figure 7.4 also shows the tensile load-extension of the web-to-yarn PE1000 and web-to-yarn PE3000. It can be seen that the load at break and extension for the web-to-yarn PE3000 were 0.5N and 0.2mm, respectively, while those of the web-to-yarn PE1000 showed a slightly lower load to failure, but higher extension of 0.4N and 0.23mm, respectively.

The comparison of the web-to-yarn PE1000 and the web-to-yarn PE3000 mechanical properties compared with those of the CNT yarn, I1000-1-1 and I3000-1-1 (0.22N, 0.21N and 0.19N respectively as discussed in Chapter 6) reveals that the load at break for such web-to-yarns has approximately doubled. These results confirm that the spatial confinement effect on the formation of the disks has been greatly reduced thus polyethylene disks could nucleate and grow on the individual and bundles of the CNTs throughout the CNT web structure. This in turn resulted in a higher load transfer between the CNTs.

7.3. Treatment of the CNT web with polypropylene

Polypropylene with the average molecular weight of 297000g/mol was used to produce the CNT web pp and spun yarn (web-to-yarn pp). The experimental procedure was identical to that of the polypropylene-infused CNT yarns. Briefly, polypropylene was dissolved in xylene at 130°C while the solution was being stirred at 350rpm. The CNT web pp was produced by placing the CNT web in the solution and cooling the polymer solution from 130° C to 100° C, with the cooling rate 1° C/min and the polymer solution concentration of 1w/w%.

7.3.1. Morphological properties

The Figure 7.5 shows the SEM images of the CNT web pp, and its subsequent spun webto-yarn pp. The disks were evident and perpendicular to the CNTs axis confirming that such disks were indeed nucleated and grown on the CNT web. Similar to the observations in Chapter 5, the growth of polypropylene disks was not widespread on the CNT yarn, but occurred largely at outer surface. In addition, a coating of the polypropylene was also evident over the CNT yarn (Figure 5.6a and 5.6d).



CNT Web pp (5000x) (scale bar 10 $\mu m)$

10000x (scale bar 5µm)

30000x (scale bar 3 µm)









100000x (scale bar 500 nm)

Figure 7.5. SEM images of the CNT web pp and the web-to-yarn pp produced by spinning the CNT web pp. An SEM image with three magnifications is shown.

15000x (scale bar 5 μ m)

The SEM results presented in the Figure 7.5 for the systems in which the CNT web was first treated with polypropylene solution, crystallised and then spun, show that such coating was still evident, even though the CNT web was infiltrated first. Nonetheless, when the CNT web was used, the growth of the disks was much more widespread, indicating that the spatial confinement of having a tight yarn like environment, had less influence on the growth of the disks. The initial CNT web was much more open compared to the CNT yarn,

which as with polyethylene allowed the polypropylene molecules to more freely access the CNTs in the CNT web and nucleate from the nanotubes surface.

The Table 7.3 shows the disk diameter, thickness and gap between the polypropylene disks grown off the surface of the CNTs in the CNT web pp and their subsequent spun web-toyarn pp. Various studies investigated the formation of the polypropylene disks [1-3] and found that coil to stretch phenomenon of polypropylene, induced by the shear stress, results in the attachment of shorter molecules to the nucleating surface creating nuclei. As the temperature is reduced, more molecules become attached to such sites, thus commencing the growth of the disks.

In our study, the CNT surface acted as the nucleating surface facilitating the attachment and growth of polypropylene disks. The disks grown on the CNTs in the CNT web pp structure had smaller diameter compared to those of the Ipp-1-1 (63nm), but similar in thickness (7nm) and gap (21nm) as discussed in Chapter 5. This indicates that the disks had access to more CNT surface compared to the CNT yarn. This resulted in a change in the abundance of the polypropylene disks on the CNTs in the CNT web compared to the CNT yarns.

Chapter 7 Investigation of the growth of polymer disks directly onto the CNT web

Table 7.3. Disk characterisation of the	CNT web pp and the we	b-to-yarn pp produced	d by spinning the CNT	web pp.
	11	~ 11 1		11

Sample ID	Molecular	Polymer	Cooling rate	Disk diameter	Disk thickness	Disk gap (std
	weight	concentration	°C/min	(std dev)	(std dev)	dev)
	g/mol	in solution w/w%		nm	nm	nm
CNT Web pp	297000	1	1	21.1(2.8)	10.1(1.7)	19.3(4.9)
Web-to-yarn pp	297000	1	1	24.1(3.3)	11(2.1)	18.8(3.2))

7.3.2. Mechanical properties

The Figure 7.6 shows the tensile load at break as a function of the extension for the web-toyarn pp produced by the spinning of the CNT web pp. The extension rate was 0.1mm/min and gauge length was 10mm. It can be seen here that the load at break for the web-to-yarn pp was 0.34N while the extension was 0.11mm. Although the load increased compared to Ipp-1-1 (0.22N), the extension reduced (0.32mm). The increase in the load at break demonstrated that the higher number of polypropylene disks in the web-to-yarn pp indeed increased the stress transfer between the individual and bundles of the CNTs during the tensile testing.



Figure 7.6. Tensile load-extension curve obtained from tensile testing of web-to-yarn pp spun by the spinning of CNT web pp. The extension rate was 0.1mm/min.

These results are in agreement with the findings of the polyethylene-treated web-to-yarns discussed above in that such yarns also showed higher load at break values compared to those of the polyethylene-infused CNT yarns.

7.4. Treatment of the CNT web with nylon 6,6

Nylon 6,6 was used to produce the CNT web ny and spun web-to-yarn ny. In order to prepare the CNT web ny and web-to-yarn ny, nylon 6,6 was first dissolved in glycerine at 240° C while the solution was stirred at 350rpm. The nylon 6,6 solution concentration was 1w/w%. The solution containing the CNT web was then cooled down to 185° C, at a cooling rate of 1° C/min. The reason for choosing a polymer solution concentration of 1w/w% was that this was the only concentration value that produced consistent samples with nylon disks on the CNTs as was discussed in Chapter 5.

7.4.1. Morphological properties

The Figure 7.7 shows the SEM images of the CNT webs decorated with the nylon 6,6 disks and their spun yarns. It is shown that the CNT web ny maintained their geometrical shape such as the width and thickness (Figure 7.7a), while the disks can be seen to have grown around the CNTs and perpendicular to the CNT axis (Figure 7.7c). It can be seen in the web-to-yarn ny that nylon 6,6 disks were able to grow around the CNTs (Figure 7.7f) although the web-to-yarn ny shows a coating layer of nylon 6,6.



CNT Web ny (120x) (scale bar 100000x (scale bar 500 nm) 200000x (scale bar 300 nm) 300 µm)



Web-to-yarn ny (1000x) (scale 30000x (scale bar 3 μ m) 100000x (scale bar 500 nm) bar 50 μ m)

Figure 7.7. SEM images of the CNT web ny and the web-to-yarn ny produced by the spinning of the CNT web ny. An SEM image with three magnifications is shown.

The Table 7.4 shows the disk diameter, thickness and gap between the disks grown on the CNT web ny and the subsequent web-to-yarn ny produced by the spinning of such a CNT web ny. It can be seen that the disk diameter, thickness and gap are similar to those found on the Iny-1-1 shown in the Table 5.6 (43.5, 10.8, 21.7nm, respectively). It was established in Chapter 5 that one challenge in producing the nylon 6,6 disks unlike HDPE0.83, PE35000, Polywax3000, Polywax1000 and polypropylene, in the constant-length CNT yarn was the fact that the CNT yarns were compact, and the inserted twist and acetone densifications added extra barriers for the polymer to penetrate into the yarn structure.

Chapter 7 Investigation of the growth of polymer disks directly onto the CNT web

Table 7.4. Disk characterisation of the CNT web ny and the web-to-yarn ny produced by the spinning the CNT web ny.

Sample ID	Molecular	Polymer	Cooling	Number of	Disk	Disk	Disk gap	Number of
	weight	concentration	rate	images from	diameter	thickness	from each	disks per
	a /m a 1	in solution	°C/min	identical	from each	from each	image (std	5.58mm ²
	g/moi	w/w%		samples and	image (std	image(std	dev)	(magnification
				magnifications	dev)	dev)		100,000x)
							nm	
					nm	nm		
CNT Web ny	22000	1	1	1	41(11.3)	15.3(1.9)	14.4(4.2)	8
Web-to-yarn ny	22000	1	1	1	41.7(15.2)	13.9(3.5)	12.2(4.6)	12

The analysis of the disks produced on the web-to-yarn ny as opposed to the constant-length CNT yarn indicate that the nylon 6,6 nucleation on the CNT did not affect the number and the size of the disks when a looser and open structure of the CNT web was used. In other words, although the effect of spatial confinement is eliminated, as discussed by Li *et al.* [4,5], and the disks were more abundant throughout the CNT web structure, the disk dimensions remained unchanged compared to the constant-length CNT yarns.

7.4.2. Mechanical properties

The Figure 7.8 shows the tensile load-extension curve obtained from the web-to-yarn ny at the extension rate of 0.1mm/min. The web-to-yarn ny was produced by the spinning of the CNT web ny. The load at break and extension for the web-to-yarn ny was 0.3N and 0.1mm. It is shown that the load at break has increased compared to the Iny-1-1 (0.21N), whereas the extension at break decreased (0.4mm). This indicates that the number of disks has increased compared to the Iny-1-1, due to the growth of more disks within the CNT web structure thus incorporating more CNT bridges into the network. This in turn resulted in more individual and bundles of the CNTs participating in the load transfer during the tensile testing.



Figure 7.8. Tensile load-extension curve obtained from the tensile testing of the web-toyarn ny spun from the CNT web ny. The extension rate was 0.1mm/min.

7.5. Conclusion

In this chapter various polymers were incorporated into the CNT webs, before spinning the resultant disk containing webs into web-to-yarns. It was found that by using the looser structure of the CNT web, compared to the constant-length CNT yarn, the polymer solutions were able to penetrate into the CNT web structure and produce more disks. Such disks could then nucleate and the resultant spun web-to-yarns had disks extended deeper into the yarn, not just having been formed on the outer surface. This was found to be the case for the disks produced by all the polymers studied in this chapter.

In addition, the disks were large enough to bridge between several bundles of the CNT, thus creating an interconnected structure. The mechanical analysis of these polymer-treated CNT webs and their web-to-yarns showed that the load at break for such web-to-yarn structures indeed increased significantly compared to the polymer-infused CNT yarns discussed in the previous chapters, indicating that such interconnected structures increased the load transfer between the individual and bundles of the CNTs, thus increasing the CNT participation in the load transfer. In the polymers such as nylon 6,6 and polypropylene, which had not previously produced abundant disks when infiltrating into the CNT yarns, the approach of using the CNT web for crystallising the polymeric disks allowed much more successful nucleation and growth of such disks from the CNT surface. It was also found that the main factor in the increase in the disk production in such polymers was likely due to the spatial confinement and that the use of the CNT web, instead of the densified CNT yarn, eliminated such confinement in the disk growth around the CNTs.

It was shown that the polymer-treated CNT webs, onto which the polymeric disks had nucleated and grown, could be spun into fairly uniform yarns. This is a significant progress in the production of high concentrations of polymeric disks around the CNT bundles as bridges for the improved stress transfer, potentially increasing the mechanical strength of such yarns.

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Chapter 8

Conclusion and future work

8.1. Conclusion

In this thesis, CNT webs and yarns, drawn from vertically grown CNT forests, were fabricated using various densification techniques and the effects of polymer infiltration into such web and yarn structures studied in detail. One of the major drawbacks in the commercialisation of the CNT yarns as structural materials is their low mechanical strength compared to commercially available yarns such as Kevlar. Therefore, this research was undertaken in an attempt to enhance the mechanical properties of the CNT yarns by exploring various CNT yarn fabrication methods as well as polymer incorporation into such yarns. The SEM and TEM analyses were undertaken in order to characterise the morphological properties of the CNTs and the polymeric disks while the TGA and DSC revealed information about the thermal and crystalline properties of such CNTs and polymeric disks. The tensile testing was undertaken to determine the mechanical properties and the results compared with the observed morphologies.

The first step in gaining a better understanding in the CNT yarns and their polymer incorporated yarns consisted of the fabrication of the CNT yarns from the CVD-grown CNT forests in order to establish a benchmark for further polymer incorporation studies. To this end, the CNT webs produced from such CNT forests showed a uniform longitudinal distribution of the individual and bundles of the CNTs along the length of the CNT web, as seen by the SEM, with a moderate tensile strength of 0.4GPa confirmed by the tensile testing. In addition, the Raman and XRD analyses showed that the CNTs were highly crystalline and graphitic. Further densification of the CNT web was undertaken in order to increase the mechanical properties using two densification methods namely solvent (acetone and ethanol) and twist (constant-length and shrinking-length). The detailed SEM analysis of such CNT yarns found that although acetone and ethanol produced CNT yarns

with similar morphologies, acetone had higher densification ability than ethanol in compressing the CNT web into a densified CNT yarn. The compression of the CNTs resulted in an increase in the mechanical strength of such acetone densified CNT yarn to ~1.1-1.2GPa due to the capillary forces of acetone on the CNTs being greater than that of ethanol. This resulted in a more compact CNT yarn structure using acetone rather than ethanol, which in turn increased the contact points between the individual and bundles of the CNTs within the yarn structure. Furthermore, the detailed analysis of the two different twist methods provided insight as to how the twist mechanism worked in the CNT yarns. The constant-length CNT yarns produced higher mechanical strength as well as more uniform and cylindrical yarn structures compared to the shrinking-length CNT yarns as confirmed by the SEM studies. This is attributed mainly to an increase in the inter nanotube cohesion in the CNT yarns as well as uniformity in the yarn structures which resulted in higher vdW interactions between the individual and bundles of the CNTs. In addition, the combination of the solvent and twist was also used in the fabrication of the CNT yarns. This study revealed that the combination of constant-length twist followed by the acetone densification could produce the CNT yarns with the highest tensile strength of 1.8GPa. Such effective densifications are primarily due to the higher vdW interactions between the individual and bundles of the CNTs. The detailed analyses of the fabrication methods of the CNT yarns, therefore, provided a benchmark, in this thesis, with regards to the CNT interactions with one another and the mechanical properties in the CNT yarn.

The constant-length CNT yarns were then infiltrated with different types of polymer. It was envisioned that such polymer infiltration could provide an improvement in the mechanical properties of the CNT yarns through the growth of the polymeric disks on the individual and bundles of the CNTs, gripping the CNTs together and allowing greater stress transfer in the CNT yarns. Six types of polyethylene with various molecular weights, a polypropylene and a nylon 6,6 were all used to produce the polymer-infused CNT yarns. Such polymers have been shown in the literature to produce disk like structures in the vicinity of the CNTs. In addition, three polymer solution concentrations (0.01, 0.1 and 1w/w%) and three cooling rates (1, 10 and 100° C/min) were also used and their effects on the polymeric disks were studied in detail. The SEM study of the polyethylene-infused CNT yarns showed that, for a

given molecular weight, the polyethylene disks could be successfully grown in the vicinity of the individual and bundles of the CNTs. Such disks were bigger in diameter and thickness and closer together for the polyethylene solution concentration of 1w/w% compared to the polyethylene solution concentration of 0.01w/w%. Therefore, a direct relationship between the polyethylene solution concentration and the polyethylene disk size was established. This is likely due to more polyethylene molecules being available in the polyethylene solution to be attached to the disks. The comparison of the disk size in polyethylene with different molecular weights provided information about the effect of the molecular weight of polyethylene on the disk size in the polyethylene-infused CNT yarns. It was found that the high molecular weight polyethylene, in particular HDPE0.83 (molecular weight of 158000g/mol), produced large disks which span across several bundles of the CNTs and created an interconnected network of disks within the polyethylene-infused CNT yarn. Polypropylene was also able to be infused in a similar fashion into the CNT yarns. The morphological study of such polypropylene-infused CNT yarns using the SEM also revealed invaluable information about the disk growth mechanism in the vicinity of the CNTs at varied polymer solution concentrations. The polypropylene solution concentration of 1w/w% produced larger diameter disks, whilst the thickness and gap distance remained unchanged compared to those of the 0.1w/w%. In addition, such disks were found around the individual and bundles of the CNTs, indicating the disk growth of polypropylene perpendicular to the axial direction of the CNTs. A thick coating on the outside of the polypropylene-infused CNT yarn proved challenging in terms of the observation of the disks under the SEM. The SEM study of nylon 6,6-infused CNT yarn showed that at nylon 6,6 solution concentration of 1w/w% the disks could grow in a non-uniform fashion in the sense that although visible if found, it was difficult to locate such disks in the nylon 6,6-infused CNT yarn.

The SEM studies of the infiltration of polymers into the CNT yarn revealed that such an approach was indeed successful in producing the CNT yarns with polymeric disks bridging the CNTs together and producing interconnected networks. This is an important achievement with regards to the fabrication of mechanically stronger CNT yarns. The tensile testing of the polymer-infused CNT yarns were undertaken in conjunction with the

TGA and DSC analyses in order to provide a comprehensive and complete understanding of the load transfer mechanism between the CNTs and the polymeric disks. The TGA analysis of the polyethylene-infused CNT yarns showed that the CNT was the majority phase in the yarn between 64-87% depending on the polymer solution concentration, confirming that such polyethylene-infused CNT yarns were in fact CNT-rich. In addition, the DSC analysis of polyethylene component in the polyethylene-infused CNT yarns showed that polyethylene maintained a similar degree of crystallinity compared to the neat polyethylene. This was expected since the CNT itself is considered to be a nucleating agent which enhances the molecular orientation and the growth of the crystalline regions around the CNTs. Furthermore, the mechanical studies of the polyethylene-infused CNT yarns showed that the tensile force to failure increased, which strongly indicated that the load bearing nature of the CNT yarns had increased likely due to the polyethylene disks acting as load transfer bridges between the CNTs. However, the tensile strength and modulus were decreased compared to the neat CNT yarn which is associated with the overall weight increase of the polyethylene-infused CNT yarns thus offset the load in the strength calculation (Equation 3.1). Similarly, the polypropylene-infused CNT yarns and nylon 6,6infused CNT yarns also showed promising results with regards to their tensile strength. The tensile study of such yarns also showed an increase in the load bearing compared to those of the neat polypropylene and nylon 6,6.

Despite such promising results in the load bearing ability of the polymer-infused CNT yarns, the detailed study into the tensile strength of such yarns also revealed new challenges mainly in terms of the polymeric disk growth only occurring on the outer surface of the yarns. This was more evident in polypropylene and nylon 6,6 studies where the disks grew non-uniformly along the length of the polypropylene- and nylon 6,6-infused CNT yarns as well as the formation of thick coating layers on the yarns. This had an effect on the load transfer between the individual and bundles of the CNTs in the sense that only the CNTs on the outer surface of the yarn could effectively participate in the improved load bearing under the tensile force. The Table 8.1 shows the summary of the mechanical properties of the CNT web, yarn and polymer treated CNT yarns produced in this thesis. It shows that although the tensile strength and modulus of the polymer-treated CNT yarns are indeed
advantageous over Kevlar and Carbon fibre considering the weight of the yarn, there still needs work to be done to further improve such properties.

After attempts to increase the polymeric disk growth deeper inside the polymer-infused CNT yarn structure, it was hypothesised that the spatial confinement within the CNT yarn could be limiting the infusion of polymers deep into the CNT yarn. In order to grow large disks throughout the CNT structure, the polymer solution must be under a directional flow and the polymer chains must be sufficiently long enough to allow them to stretch and orient along the flow direction. However, the fabrication method used for the CNT yarns (constant-length twist followed by acetone densifications) meant that the CNTs were tightly packed inside the CNT yarn structure. Hence, the polymer solution could not maintain a high flow velocity deep within the CNT yarn resulting in a significant reduction in the polymer chain stretching and orientation deeper in the CNT yarn, which in turn hindered the nucleation and growth of the polymeric disks in the polymer-infused CNT yarns.

 Table 8.1. The summary of the CNT yarns' highest mechanical vaules reported in this thesis for neat CNT yarn, polyethylene-, polypropylene- and nylon 6,6-infused CNT yarns.

 Vern type
 Tancila strength

Yarn type	Tensile strength	Tensile modulus
	(GPa)	(GPa)
Neat CNT web	0.44	8.4
Neat CNT yarn (shrinking length	0.77	11.39
Neat CNT yarn) (constant-length)	1.81	47.88
Polyethylene-infused CNT yarn	1.41	45.5
polypropylene-infused CNT yarn	1.06	33.23
Nylon 6,6-infused CNT yarn	0.85	22.39

In order to overcome this challenge, an alternative approach involved using the CNT web itself, rather than the CNT yarn, on which to crystallise the polymeric disks was proposed and studied. It was established that the CNT web itself was much thinner (0.5-1 μ m) than the CNT yarn (20-40 μ m). Since the CNT web was very loose in structure, the individual

and bundles of the CNTs were relatively far apart from each other and the structure quite open although the CNTs were still potentially close enough together to be gripped by the laterally grown disks. The studies of the growth of the polymeric disks around the CNTs in the CNT web showed that the polymeric disks were produced throughout the CNT web. In addition, the disks were large enough to bridge between several bundles of the CNT, thus creating an interconnected structure. The web-to-yarns could then be produced by subsequently spinning such disk loaded webs. The mechanical analysis of these polymertreated CNT webs and yarns showed that the load at break for such web-to-yarn structures indeed increased significantly compared to the polymer-infused CNT yarns. This indicated that such interconnected structures increased the load transfer between the individual and bundles of the CNTs, thus increasing the CNT participation in the load transfer. It also meant that the individual and bundles of the CNTs were close enough together in the web to allow the polymeric disks to grip multiple bundles. This approach of first crystallising disks onto the CNT web followed by spinning into yarn was particularly successful in nylon 6,6 and polypropylene, which had not previously produced abundant disks when infiltrated into the CNT yarns.

Such an approach for crystallising the polymeric disks allowed much more successful nucleation and growth of the disks from the CNT surface. This seems to indicate that the main factor in increasing the disk production in such polymers was in fact the spatial confinement and that the use of the CNT web, instead of the densified CNT yarn, eliminated such confinement in the disk growth around the CNTs. This represents a significant progress in the production of high numbers of polymeric disks around the CNT bundles as bridges for the improved stress transfer in such CNT yarns.

8.2. Future work

The future success of designing and fabricating mechanically strong CNT yarns relies on a number of issues. Since the CNTs are inherently susceptible to handling during the fabrication process, due care would have to be taken to minimise any interference with the CNTs in the CVD-grown forest as well as the CNT web. Further work could be performed

to investigate the parameters which affect the drawing of the CNTs from the web including the drawing angle and the speed of drawing in order to better understand the mechanism of the CNT recruitment into the CNT web. It would also be of interest to quantitatively investigate, in more detail, how the densification would change the vdW interactions between the nanotubes. This will lead to a better understanding of the mechanism of the CNT slippage under the tensile force. One approach would be to analyse the slippage of the nanotubes and measure the shear force under the SEM and atomic force microscope (AFM). This will be a difficult task, however, due to the fact that the CNTs have high surface energy and tend to agglomerate and form bundles of several nanotubes. One approach to tackle this challenge would be to disperse the CNTs in a solvent and select individual or small bundle of the CNTs for the SEM and AFM preparations. The force required for the slippage of the nanotubes under the SEM or AFM is equivalent to the vdW attractive forces between such CNTs.

An important challenge in the fabrication of the CNT yarns is to effectively insert the twist deeper into the CNT yarn structure. This challenge is more significant in the constantlength CNT yarns where the twist tend to remain only on the outer regions of the CNT yarns. By further penetration of the twist into the CNT yarn, much higher numbers of the individual and bundles of the CNTs would participate in the load bearing under the tensile force which would result in a much higher tensile strength in the CNT yarns. This could be achieved by producing the CNT yarns with much smaller diameter than those presented in this thesis. The minimisation of the CNT yarn diameter will be the key to integrate more of the nanotubes deeper inside with those on the outer surface of the CNT yarn structure by the twist. The execution of such a proposal is not a trivial task, however, and will involve a greater understanding of a possible pathway by which the twist can bypass the vdW interactions and travel deeper inside the CNT yarns.

The most significant issue in the fabrication of mechanically stronger CNT yarns is the issue of polymer infusion into the CNT yarns and the creation of polymeric disks around the individual and bundles of the CNTs. Although the fabrication of such disks was successfully executed in this thesis, there remain some challenges such as the formation of

polymer coating on the outer surface of the polymer-treated CNT webs as well as the optimisation of the twisting in such CNT webs. Further work would be undertaken to upscale the fabrication process of the polymer-treated CNT webs in order to produce longer CNT webs which could then be twisted using a motor. This would produce polymer-treated web-to-yarns with much higher uniformity in the structure. Furthermore, the study of the crystallinity of the polymeric disks is of much significance. Although attempts were made, in this thesis, to understand the type and degree of crystallinity of such disks using the DSC and TEM, further work can be done to analyse the crystalline regions in the individual disks using high resolution TEM (HRTEM) as well as the DSC. It should also be noted that the tensile strength and modulus of the web-to-yarns could not be calculated due to the lack of TGA data on the fraction of the polymers in the CNT yarns. Therefore, TGA should be used to understand the amount of the polymers in the web-to-yarns in order for the tensile strength and modulus to be calculated and compared with other results. Another important issue that should be investigated is the possibility of polymer molecule penetration into the internal space of the individual CNTs. Although in this thesis the polymer molecules were assumed too big to enter the space, further investigation such as TEM should be undertaken to confirm such an assumption. The amount of polymer in the yarns should also be accurately quantified using TGA. Moreover, further analysis should be done to understand the tensile properties of the polymer-treated CNT webs.

This thesis provided a step forward towards the development of mechanically strong CNT yarns. Such a goal could be achieved by further research into the interactions between the polymeric disks and the CNTs occurring in the CNT yarns under the tensile force. Such interactions can be understood by studying the crystallinity and shear strength of the individual polymeric disks. The use of the HRTEM and AFM could provide reliable means to accurately and quantitatively study such interactions in the nano scale. Further optimisation in the fabrication of highly crystalline polymeric disks around the CNTs, efficient bridging and clamping between the CNT bundles by such disks and more effective twist in the polymer-treated CNT webs could assist in the eventual realisation of commercially available CNT yarns.