Novel Electrospinning Techniques
with Nano-materials

By
Simon George King
Abstract

Modern society is ever in demand for higher performing materials, with increased efficiency. Recognising this need, the work discussed here details the steps taken to develop and engineer a cost-effective manufacturing process, which could be easily commercially scalable for the production of large-areas of aligned carbon nanotubes. These aligned carbon nanotubes can then be directly applied in areas such as advanced ‘multi-functional’ composites. Of the available routes, the electrospinning technique demonstrated to be one of extreme promise towards achieving this goal. This thesis guides and justifies the investigative steps taken in scientifically engineering a suitable electrospinning method to achieve high-aligned arrays of carbon nanotubes. This includes the design and development of a novel, large-area high-throughput needleless electrospinning system, which is capable of not only producing nano-fibres in excess of 160 g per hour (700 times faster than conventional single needle electrospinning), but also in an aligned orientation, using purely aqueous based polymeric solutions. This success has led to the successful production of the World’s first large area sheets of highly aligned arrays of single walled carbon nanotubes by electrospinning. The analysis of these sheets found substantial increases in both mechanical and electrical performance. For the aligned nanotube-loaded nano-fibres, the tensile strength increased up to 320%, ductility increased up to 315% and Young’s modulus increased up to 430% (compared to the original polymer performances). The realisation of the significant enhancements CNTs pose on a composite material, led to an investigation into the chemical interactions that lead to these results. This resulted in the discovery of a new small angle X-ray scattering peak, which we attributed to a crystalline interface between the polymer and carbon nanotubes, giving rise to the enhancements seen during mechanical testing. In addition to mechanical performance, there was also a significant increase in electrical conductivity of $10^8$ S/m, an improvement of 8 orders of magnitude compared to the original polymer. These results, combined with the realisation of industrially viable throughput, provide promise for impressive application into advanced multi-functional composites.

While the primary objectives of this research focused on large area electrospinning, the work outlined in this thesis also discusses investigations into other important aspects, and significant scientific discoveries. These scientific achievements include the introduction of a novel, micro-
centrifugal dispersion assessment method, for the efficient surfactant functionalisation of nano-materials. This method allows for a fast and effective assessment of a material suspension, without the need for any equipment other than a simple centrifuge and a balance. This process leads to fast and efficient use of surfactants, producing greater loadings of nano-materials which can be suspended within a solvent for further processing.

As a method to recover the nanotubes once they have been processed and aligned, this thesis also explores post processing of the aligned nanotube-loaded sheets using steam purification. This led to the complete recovery, and purification, of the high quality aligned CNTs, which were found to significantly increase the resulting nanotubes resistance to oxidation, increasing their oxidation temperature in excess of over 900° C, a previously unreported achievement. The mechanisms behind the underlying chemistry were further probed using Raman spectroscopic analysis, this revealed how selective oxidation of CNTs was limited to that of metallic CNTs, leaving the remaining material as only semi-conducting species. This selective oxidation process could lead to selective manufacture of specific CNT species, allowing for better suited application in electrical devices.
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Lastly I would like to thank my family, especially my fiancée, Rosanna Marie Wheeler for their emotional support through the good times and the stressful ones. Without their support I wouldn’t have had the drive to generate the accomplishments I can boast today, so once again, thank you.
Declaration

This thesis and its contents, are the results of my own efforts, and in all cases written in my own words. In cases where collaboration was required in order to gain access to necessary equipment or results, the collaborators have been acknowledged in the sections in which their input was required. Exception is given to Chapter 6.4, where although the work has be written in my own words, the scientific achievements/discoveries were gained with the collaborative efforts of Dr Liam McCafferty.

This thesis has not been submitted in whole, or in part, for any other academic degree or professional qualification. I agree, that the University of Surrey has the right to submit my work to the plagiarism detection service ‘TurnitinUK’ for originality checks. Whether or not drafts have been assessed, the University reserves the right to require an electronic version of the final document (as submitted) for assessment as above.

Simon George King

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1 Introduction

1.1 Background to the Project

A modern society needs highly functional materials that evolve with day to day needs. These advanced materials need to be produced with consideration of the environment, possessing increased efficiency, increased strength, and reduced weight. Due to their low-weight, high-strength properties, and having the ability to take on multi-functionalities, such as charge storage, composite materials are becoming increasingly the material of choice in modern applications. In most cases, the performance of a composite material can be maximised by decreasing the size and increasing the density of the reinforcement fibres loaded within it. However, this generalisation, only applies up to an optimum size to density relationship between the matrix and reinforcement materials. This optimisation of the loading between two materials, ensures that the beneficial properties of both matrix and reinforcement are combined within the final composite, acting as an entirely new material. In order to develop a new composite material that delivers the desired low weight and high strengths, new matrix reinforcements are being explored. The reinforcements providing the greatest scientific interest at present are cylindrical tubes of carbon, which have a diameter of one millionth of a millimetre, these are called carbon nanotubes. Due to their nano-sized structure, they have been known to have substantial surface areas, with one kilogram of single walled nanotubes having a surface area as large as 1.3 million metres squared (Peigney et al. 2001). More importantly, their strong scientific interest is a result of the remarkable properties which they possess, with: electrical conductivities being up to 1,000 times more conductive than copper, mechanical properties being up to 30 times that of steel, and thermal conduction properties up to 10 times that of copper. This makes them perfect options as a supplement or full reinforcement material for modern multi-functional composite materials.

Being cylindrical tubes, their primary strength and conductivity is one directional, down the length of the tube. However, the primary limitation with using carbon nanotubes, is the inability to be able to grow them to infinite lengths. This then presents the requirement to align them across large areas as sheets, so that their remarkable properties can be directed in much the same way as
conventional carbon fibres. However, until now, it has not been possible to align carbon nanotubes on a scale large enough to warrant using them in any significant structure or application. The reason behind this lack of progression is a result of a combination of challenges, each of which must be addressed. This first challenge is in carbon nanotube’s lack of natural solvents, meaning they must be functionalised in some fashion before they can be influenced. The second challenge is a result of their nano-scales dimension, rendering them almost impossible to align directly through a mechanical process. This then means, that the nanotubes must be essentially ‘forced’ into alignment, through the alignment of another material. This project utilises the process of electrospinning, initially discovered in the 17th century (Gilbert, 1628), which uses a point charge on a fluid to create a jet of material which spins into a nano-fibre. Based on a uniaxial stretching of a viscoelastic solution, electrospinning utilises electrostatic forces to stretch the solution as it solidifies, before being collected as a material with one or more dimensions of nano-size. By dispersing carbon nanotubes into the viscoelastic solution prior to electrospinning, the tubes are constrained and forced into alignment along the axis of the electro-spun fibre.

The standard electrospinning process is time consuming, with typical solution processing rates of 0.1g per hour (Ding et al. 2004). Re-engineering the concepts of electrospinning to utilise multiple jets of fibre would allow the process to be able to align carbon nanotubes on an industrial scale, achieving a square metre of aligned material in a few hours rather than a few days. This achievement would pave the way for the development of the next stage of advanced composite materials. Thomas Swan recognised these market needs and the potential of electrospinning, being the UK’s largest supplier of CNTs, they wanted to develop a route to align their single walled carbon nanotube material. With this in mind, the project was instituted, and the objectives were set.

The projects primary objective was to successfully investigate, and engineer a cost-effective industrially-scalable manufacturing process, which produces, regular large-area sheets of highly aligned carbon nanotubes. In order to keep production costs minimised, the secondary project objective outlined, was to limit the use of all solvent systems except water, which was currently a challenge when electrospinning. Meeting these objectives involves budgeting, designing and building of an innovative new electrospinning system, focused entirely on the goal of achieving carbon nanotube alignment by electrospinning aqueous based solutions. Fully exploring all of the electrospinning parameters needed for the nanotube alignment, and incorporating the results into a new rig, will ultimately lead to the World’s first production of large area arrays of aligned carbon nanotubes by process of electrospinning.
1.2 Structure of the Thesis

The thesis is organised as follows: Chapter 2 explores the literature review, background science and prior art required for the understanding of this project, including: composite materials, carbon nanotubes (CNTs) and their properties, and the electrospinning process. This was followed in Chapter 3 with a brief summary of the analytical methods used, taking care to outline any key parameters or considerations that were required when analysing the samples in this project.

In Chapter 4, with the aim of identifying any contaminant which could have undesired effects in a composite material, we explore and analyse Thomas Swan & Co.’s ‘Elicarb Single-Wall Carbon Nanotube Wetcake’ product using a variety of different analytical techniques, including: scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), time of flight secondary ion mass spectroscopy (ToF-SIMS) and Thermogravimetric analysis (TGA).

Chapter 5 details the various scientific investigations that led to the optimisation of the electrospinning process parameters, in order to obtain highly aligned arrays of CNT loaded nano-fibres. These investigations include:

- Controlling the solvent evaporation from the electrospinning jet in order to ensure the production of high quality nano-fibres.
- The measurement of the electrospun polymer jet velocity, for optimum collection drum speed, and nano-fibre alignment.
- The confirmation of CNT alignment by using polarised Raman spectroscopy, including assessment of potential damage to the nanotubes.
- The assessment of performance enhancements as a result of the introduction of aligned CNTs to the produced polymer nano-fibres.
- The analysis of the morphology of the polymer in the vicinity of the CNTs, using small angle X-ray spectroscopy (SAXS), which introduces a new scattering peak.

Chapter 6 will continue the details of the scientific investigations, but this time focusing on the optimisation of the CNT loading in the electrospinnable solution for high throughput. These investigations include:

- The performance assessment of various surfactants at high CNT loading, evaluating their CNT dispersant performance using a novel method, and assessing their compatibility with electrospinning and polymer systems.
- The effects of surfactant ionicity on the electrospinning process.
• How the CNTs can be recovered from the polymer nano-fibres using steam purification, in order to produce large areas of pure aligned CNTs.

In Chapter 7, we will explore how the process of electrospinning has been re-engineered through an innovative design to allow the CNT alignment process to be industrially scaled. This includes all design ideas and advancements, as we have progressed towards the project’s final goal of fully developing a scaled-up CNT alignment process. This chapter will include:

• The design and development of the large scale collection drum and its housing.
• The design and development of the needle-based spinneret electrospinning rigs, including single and multi-needle systems.
• The design and development of the high throughput needleless electrospinning rig.
• The redesign and development of a second prototype needleless electrospinning rig, which meets all of the projects objectives.
• A comparison between the engineered electrospinning rig designs, comparing nano-fibre throughputs, consistencies and alignment.

Chapter 8 summarises this thesis and concludes all the achievements made throughout this project. This thesis is then finished with an outline to the potential future research which could arise as a result of this project.
2 Literature Review

2.1 Introduction

Carbon nanotubes (CNTs) have been of scientific interest for several decades and are continually investigated for a wide variety of different applications (Baughman et al. 2002; De Volder et al. 2013). It has always been in dispute as to who and when initially discovered CNTs (Monthioux & Kuznetsov 2006), however it is widely accepted that the boom in scientific interest into CNTs was a result of the 1991 Nature publication by Iijima (Iijima 1991). In recent years, research into applications for this material has drastically increased; this has largely been due to a combination of increasing availability and realisation of this material’s outstanding electrical, thermal and mechanical properties. It has been well documented that, due to a combination of current limitations in manufacturing CNTs to infinite lengths, and to their disputed toxicity, the only way to harness their properties for large scale applications is to use the tubes within a composite material. To maximise the potential properties of the resultant material, the CNTs must be arranged into aligned arrays causing them to bind together, thus allowing the production of super-tough composite fibres (Dalton et al. 2003). Forcing the CNTs to contact one another and adhere in a similar a manner, also significantly increases conductivity within a resultant material, allowing for other applications such as super capacitors and electronics textiles (Vigolo et al. 2000).

CNTs can be produced in an ever increasing variety of ways, with each production method having its benefits and its drawbacks (Prasek et al. 2011). Typically, they are grown using some form of catalyst, or ‘seed’, usually in the form of a nano-particle comprised of metals such as iron, cobalt or nickel. These catalyst particles are then heated to temperatures in excess of 600°C in order to ‘activate’ them (depending on the catalyst chosen), while in a carbon rich atmosphere such as methane or acetylene (otherwise known as the ‘carbon source’) (Moisala et al. 2003). Providing the required parameters for growth are met, for the catalyst chosen (including temperature, gas concentration and catalyst size), the catalyst will ‘crack’ the carbon rich gas molecules and dissolve the carbon onto its surface. At the point at which the catalyst particle is saturated with carbon, it will begin to crystallise into a graphitic structure. As this graphitic structure is forming, it precipitates from of the surface of
the catalyst, pushing the catalyst particle away, leaving a graphitic tube along its path. This is otherwise known as the tip-growth model and an example of the process can be seen in Figure 2-1.

The variation across growth methods arises in both how the catalyst is supported, and how it is heated. Examples of different catalyst supports include: silicon wafers (Chen et al. 2011), within a porous bead (Li, Kinloch, Shaffer, et al. 2004), and suspended in a gas (Li, Kinloch & Windle 2004), to name a few. Whereas examples of different heat sources include (but not limited to): radio-frequency (Bower et al. 2000), photo-thermal (Ahmad et al. 2013) and arc discharge (Hutchison et al. 2001). Regardless of how they are produced, they are either grown vertically, as a ‘forest’, or as an entangled ‘bundle’. Typically, mass produced CNTs are only grown as entanglements and are nearly always supplied as such, meaning that they require disentanglement before they can be used for an application. Other than the fact they are tangled, the CNTs in a bundle are held together by an additional weak interaction known as the ‘van der Waals’ force. In order to manipulate the CNTs into alignment, this van der Waals force must be overcome and inhibited, preventing re-bundling of the nanotubes. However, this force must be permitted once the CNTs are aligned to re-enable the transfer of their extreme properties to a composite material. This can be achieved a number of ways which will be explored later in this thesis.

![Figure 2-1](image)

**Figure 2-1** – A schematic diagram of the widely accepted tip-growth mechanism of carbon nanotube production. Where in this example the catalyst is placed on a substrate, but this is not always the case. Once heated to the correct temperature, the catalyst activates and cracks a carbon rich gas to absorb its carbon (A), as the carbon diffuses through the catalyst it is precipitated as a graphitic cylindrical structure, pushing the catalyst along to form a tube (B).
Aligning CNTs has always been a challenge, especially if the tubes lack linearity, which can make disentanglement harder. There are currently very few methods of aligning CNTs, especially over large areas (Xie et al. 2005), these include: filtration (Heer et al. 1997), template growth (Hu et al. 2001), magnetic field induced (Hone et al. 2000), and CNT drawing (Zhang et al. 2010). However, another particularly cheap and simple method, which has the potential for large area alignment, is electrospinning. The first patent that described electrospinning was not issued until 1934, however it’s true potential wasn’t realised until the 1990s (D. Li & Xia 2004). In electrospinning, nano-sized fibres form based on the uniaxial stretching of a viscoelastic solution, where electrostatic forces stretch the solution as it solidifies, before being collected (Teo & Ramakrishna 2006). The process has been successfully used to produce polymer nano-fibres for a vast range of applications, including: air filtration (Qin & Wang 2006), protective textiles (Lee & Obendorf 2007), hydrogen storage (Im et al. 2008), cell cultivation (Sun et al. 2007), tissue growth (Matthews et al. 2002) and drug delivery (Zeng et al. 2003), to name a few. Numerous publications have already reported how electrospinning CNTs dispersed in a suitable polymer can produce aligned fibres containing the embedded nanotubes (Hou et al. 2005; Q. Zhang et al. 2007; Ge et al. 2004; Dror et al. 2003; Salalha et al. 2004). These CNT-embedded polymer nano-fibres have shown improvements in properties of up to more than 100% of the original values, depending on the polymer and type of CNT (Moniruzzaman & Winey 2006; Hou et al. 2005). However, the electrospinning process is largely slow and scalability is restricted; although there are scaled-up solutions for non-aligned nano-fibre systems, which will be discussed later, there are currently none for collecting aligned fibres.

The research conducted within this thesis, explores the scaled-up electrospinning systems currently reported in literature, and further develops the techniques as to allow for the collection of aligned nano-fibres across large areas. Introducing CNTs to the polymer systems used in this developed technique, will for the first time, also see the alignment of nanotubes across large areas. Providing the necessary high-performance reinforcements, for the next generation composite materials.
2.2 Composite Materials

2.2.1 Carbon Fibre and Multi-role Composites

Composites are becoming increasingly popular as the chosen material for use in most modern structures and applications. A good example of this is carbon fibre reinforced polymer (CFRP), used for its good strength-to-weight ratio. According to recent research, in 2012 carbon fibre reinforced polymer sales totalled approximately $14.6 billion, and are expected to grow to $36 billion by 2020 (Holmes 2013). A composite material by definition is generally made of two or more constituents, usually having very different physical or chemical properties. Which when these different materials are mixed, form a new material with combined characteristics, despite the constituents remaining as distinguishable separate entities. The constituent materials normally consist of a matrix, such as a polymer, and some form of reinforcement, such as fibre or particulate. Examples of this can be seen throughout material’s history, starting from straw mixed with mud to form bricks, to today’s methods of mixing steel rods with mortar, creating reinforced concrete. Composite materials can be engineered to possess various desired properties, depending on how they are manufactured. For example, a composite material consisting of long fibres could be engineered such that the fibres have uniform orientation (Tsai & Wu 1971), maximising the strength in the direction along the fibres for applications such as a boat mast (anisotropic material) (Quigley 1991). On the other hand, if the fibres used were shorter, the fibre-matrix solution could be injected into a mould or cavity, creating a material with properties generally equal in all directions (isotropic material) (Coleman et al. 2006). Anisotropic composites, such as carbon fibres, can be engineered in a way that exhibits quasi-isotropic properties, that are significantly better than those of a composite material injected into a mould (Trakas & Kortschot 1997; Ashby & Jones 2005a; Ashby & Jones 2005b). This process is called lamination and it involves laying sheets of aligned carbon fibres pre-impregnated with a semi-cured polymer, typically epoxy resin, in various different configurations, to achieve properties in specific directions (Quigley 1991; Moy et al. 2011). This method of lamination not only achieves significantly high mechanical strengths, but does so with a minimum amount of material, resulting in the outstanding strength-to-weight ratios seen in carbon fibre laminates (Ashby & Jones 2005a; Ashby & Jones 2005b). The extreme strengths of these materials are governed by the individual carbon fibres within the composite, therefore these fibres are drawn thin (minimising impurities and flaws) and packed tightly within a matrix which binds them together (Ashby & Jones 2005a; Ashby & Jones 2005b).

In the last several decades, there has been a big increase in the demand for high performance composite materials, with the development of both multi-role composites and composites for aerospace (Ashby & Jones 2005b; Mangalgiri 1999; Marks 2005). The aerospace industry has seen the largest increase in demand, with modern civil aircraft, such as the Airbus A380, using up to 20%
composite materials for its airframe, in a bid to lower weight and maximise the efficiency of the aircraft (Marks 2005). The defence sector within aerospace has also seen big developments, with the introduction of the Lockheed Martin F35 Lightning II, where 42% of its overall weight is composites [see Figure 2-2, A]. However, weight reduction is not the only advantage composites provide, they also allow for aircraft designs never before thought possible, further reducing drag and increasing lift, such as the Airbus A350’s vertically curved wingtips [see Figure 2-2, C].

In addition to the aerospace industry, the development of multi-role composites has also led to a rise in composite use in motoring, with these composites being engineered to provide both a light weight strong structure as well as providing charge storage, rendering the need for heavy batteries redundant in all types of vehicles (Greenhalg 2011). There have been several examples, from the motoring industry to the defence sector, of where the first generation of multi-role composites have been applied to vehicles and aircraft. One of the most successful of these being the Drayson Racing Le Mans car ‘Lola Drayson’, which utilises multi-role composites in its design and in July 2013 set the new land speed record for an electric vehicle [see Figure 2-2, C]. All these developments have the core target of maximising fuel efficiency, driven by ever rising fuel costs, leading to the need for new advanced high strength multi-role composite materials.

Figure 2-2 – Three examples of how the composite industry has seen new applications give rise to a significant increase in demand; the aerospace/defence industry with the introduction of composite airframes such as the F35 Lightning II (A), and advanced wing designs such as the Airbus A350 (C). Demands in the motoring industry caused by multi-role composites providing both structure and charge storage, such as the Lola Drayson (B).
If it were possible to create thinner, stronger fibres, then the material’s mechanical performance would be significantly increased. Multifunctional CNT-epoxy composites have already been shown to possess outstanding properties (Vilatela et al. 2012). It’s for this reason that this project investigates a cost effective way to align carbon nanotubes, allowing fibres to be packed within the matrix at a much higher density. More importantly, due to their size and chemical bonding, carbon nanotubes are well known for their outstanding strength and chemical properties.

2.3 Carbon Nanotubes

2.3.1 Carbon Nanotubes and Composites

Carbon Nanotubes (CNTs) are cylindrical nanostructures of carbon atoms that are quite often considered as single molecules, due to their small size and high aspect ratio (~nm diameter and typically ~μm length) (Guldi 2004). They are effectively graphitic (sp²) carbon sheets that have been rolled into a tube. The properties they possess depend on how these tubes are structured, which could consist of numerous variations including: - the tube diameter, the number of ‘walls’ they possess (single wall (SWNTs), double wall (DWNTs) or multiwall nanotubes (MWNTs)), and how they were structured as a crystal, i.e. if they possess the armchair structure, the zigzag structure or chiral structure. These different structures have been shown to possess remarkable strength and electrical properties, while being efficient thermal conductors. Different crystal structures can dictate whether the CNT possesses metallic-like electrical properties or that of a semiconductor. For example, compared to copper, certain CNTs can be ~1000x more electrically conductive (Hong & Myung 2007) and 10x more thermally conductive (Sinha et al. 2005), while being ~20x lighter and considerably stronger (Demczyk et al. 2002; Walters et al. 1999; Baughman et al. 2002). It’s these remarkable properties that make CNTs one of the most popular areas of research in many modern applications, such as nanotechnology, electronics, optics, materials science and architecture.

The mechanical performances of the different CNT types have been widely researched, and its published results have fuelled continued interest in advanced materials. CNTs have been reported to demonstrate tensile strengths of up to: 150 GPa for MWNTs (Demczyk et al. 2002), and up to 45 GPa for SWNTs (Walters et al. 1999; Baughman et al. 2002). Comparing these results to other materials such as the strongest high-strength steels exposes their significance, where the steels were only seen to display a tensile strength of 5 GPa, when in the form of a comparable fibre (Bhadeshia & Harada
Their interest as an alternative reinforcement material to conventional carbon fibres is due to them only having tensile strengths of up to 5 GPa, suggesting that CNTs could offer a considerable performance increase (Wu et al. 2009). It has already been shown that the mechanical properties of nano-composites with just 1% weight MWNTs are comparable to conventional fibre composites with 10% weight carbon fibres (Qian et al. 2000). When electrospinning MWNTs into aligned composite sheets, it has been demonstrated how it can improve the matrix polymer’s tensile modulus by up to 144%, depending on the degree of alignment (Hou et al. 2005). However, CNT composites have not fully replaced the currently used materials due to the high costs involved in acquiring the necessary linear high quality nanotubes. However, in this project we use Thomas Swan’s own CNT products which are made to a high quality at low cost (this material will be explored in Chapter 4).

This project will primarily use single and double-walled nanotubes, rather than multi-walled, as they are significantly smaller structures and have greater consistency in both size and linearity. Figure 2-3 illustrates an example of how an irregularly-shaped MWNT can prevent alignment during electrospinning. It is due of their morphological consistency that SWNTs/DWNTs align within the nano-fibres more efficiently, building a far greater array of aligned CNTs across the whole material, improving the materials anisotropic properties (Salalha et al. 2004). However, due to the smaller diameters, these types of CNT tend to aggregate much more easily as a direct result of the overall increase in the collective surface area; therefore, these types of nanotube are significantly harder to disperse.

Figure 2-3 – Transmission electron micrograph (TEM) of a single MWNT embedded within an electrospun PAN nano-fibre. This micrograph demonstrates the importance of linearity of the nanotubes in order to achieve CNT alignment during electrospinning. This image from Dror et al. was used with permission from Y. Dror et al. 2003 (Dror et al. 2003). Copyright 2003 American Chemical Society.
In order to successfully manipulate carbon nanotubes into alignment within polymer nano-fibres, they first require dispersing within a solution, prior to adding the polymer. This then prevents agglomeration, allowing freedom of movement for each individual tube while preventing them from interacting with each other. Extensive research and work has been carried out in order to understand how to maximise the CNT concentrations within the dispersions, thus allowing a considerable decrease in the time taken to process a larger mass of CNTs for any application (Hilding et al. 2003; Blanch et al. 2010; Rastogi et al. 2008; Shen et al. 2008). Dispersing carbon nanotubes can be somewhat of a challenge, especially in aqueous solutions (O’Connell et al. 2001). This is largely due to their extreme hydrophobicity, which drives them to interfaces as well as towards each other. Where, once they come close enough, strong van der Waals interactions between tubes bind them tightly together (Tucknott 2002; Girifalco et al. 2000). To obtain a good dispersion in any solution, the two key phenomena (hydrophobicity and van der Waals interactions) must be overcome and as such there are several ways this can be achieved. The most popular approaches have either involved chemical modification of the CNT surfaces (Chen et al. 2001; Bekyarova et al. 2004; Chen 1998; Kahn et al. 2002; Q. Zhang et al. 2007; Hou et al. 2005), which can also lead to damage to the tubes, altering their desirable properties (Wang et al. 2003; Chen 1998), or by applying surfactants or polymers to the nanotubes surface, otherwise known as non-covalent functionalisation (Islam et al. 2003; O’Connell et al. 2001; Cotiuga et al. 2006; Moore et al. 2003; Richard et al. 2003). However, using polymers or surfactants can restrict the achievable concentrations and may degrade properties, depending on the chemicals used (Moore et al. 2003; Zhang et al. 2005). These polymers or surfactants could also potentially interact with the final composite matrix as well as being problematic to remove (Ausman et al. 2000), once the dispersion has been used to manipulate the CNTs. For these reasons it is essential to critically choose the correct technique in order to disperse the CNTs within a polymer solution for alignment. In the next two sub-sections we explore the best dispersion methods for achieving the project goals.

2.3.2 Dispersing Carbon Nanotubes with Surfactants

One of the simplest and most common ways to disperse CNTs within an aqueous solution is by using a surfactant which adheres to the surface of the CNT, reducing the surface tension and increasing its wetting properties (Daintith 2004). There are four main types of surfactant available: - non-ionic, cationic, anionic and amphoteric, all of which exhibit a similar amphiphilic structural concept (meaning it has both hydrophilic and lipophilic (hydrophobic) properties). It is these chemical properties that cause the surfactant molecules to adhere to the CNTs surface and attach themselves
via van der Waals interaction at the lipophilic end, with the hydrophilic end oriented towards the aqueous phase (Richard et al. 2003). This therefore effectively places a surfactant molecule between individual CNT surfaces, reducing the inter-tube van der Waals interaction energies (Islam et al. 2003).

Two of the most commonly used surfactants are sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulphate (SDBS), which are both anionic surfactants. Figure 2-4 provides a visual example of the various different ways a surfactant molecule can position itself on the surface of the CNT, whether it be a uniform layer or a series of semi-micelles. However, although being the most widely used, SDS is not the most effective surfactant available for dispersing CNTs. Z. Sun et al. observed SDBS to produce higher stable concentrations of CNTs than SDS in an aqueous solution, observing enhanced stability factors, of the order of 10 to 100, when compared to other surfactants. This allowed extremely high concentrations of 20 mg/mL of CNTs to be achieved, as well as remaining in a stable solution for several months (Sun et al. 2008).

Figure 2-4 – This schematic diagram illustrates how the hydrophilic (red head) and lipophilic (blue tail) properties of a typical surfactant allow the surfactant molecules to adhere to the surface of the CNT, typically in these possible organisations; (A) the molecules could be attached perpendicular to the surface forming a monolayer, (B) the molecules could be attached at the base of the lipophilic part; forming half micelles along the length of the CNT, or (C) the molecules could be attached at the base of the lipophilic part; forming half micelles along the diameter of the CNT. This schematic diagram was adapted from “Supramolecular Self-Assembly of Lipid Derivatives on Carbon Nanotubes”, Richard et al. 2003. Reprinted with permission from AAAS.
Ionic surfactants are not the only option we are limited to, various other non-ionic surfactants have been reported to be extremely effective at dispersing CNTs and could also be applicable for use in our electrospinning systems. These include: polyoxyethylene glycol alkyl ethers (Brij), polysorbates (Tween), octylphenol ethoxylate (Triton X) and poloxamers (Pluronic F127) (Rastogi et al. 2008; Moore et al. 2003; Blanch et al. 2010), where each surfactant has a varying degree of success across literature. However, cationic surfactants are generally hazardous to health and result in poorer CNT dispersions, the best of these being reported as benzalkonium chloride (ADBAC), which tends to be used for filtration of CNTs as opposed to directly dispersing them (Rao et al. 1997).

One drawback to using surfactants is that they can be difficult to remove after the CNTs have been manipulated (Ausman et al. 2000). Almost all published work focuses on functionalising the CNTs in order to manipulate them, and then either uses acids for CNT recovery, which could damage the CNTs (Zhang et al. 2005) or simply leaves them functionalised. Leaving the surfactant attached to the CNT will prevent the CNTs from experiencing the maximum van der Waals interactions once aligned; this would therefore dramatically reduce the strength of the resulting composite material. However, it may be possible to evaporate the surfactant from the CNTs using a high temperature furnace. The majority of SDS evaporates in nitrogen at around 215°C (Swami et al. 2003) and SDBS at around 430°C (Gu & Tsai 2012), but both leave residue which could remain problematic for a composite.

2.3.3 Purifying Carbon Nanotube Materials

Once the CNTs have been manipulated into alignment it becomes necessary to recover them, removing both the electrospinnable polymer and surfactant, while maintaining alignment. Doing this allows the van der Waals interactions between CNTs to return, improving both mechanical and electrical properties. However, as previously mentioned, removing the polymer and surfactants after manipulation of the CNTs can be potentially problematic, especially if maintaining both alignment and CNT quality is a priority. Using surfactants to non-covalently functionalise the CNTs is the easiest way to achieve dispersions without introducing damage, but removing them presents several issues. Simply washing the CNTs with a suitable solvent could reduce alignment or completely remove the CNTs (if they remain functionalised). Equally, acid treatment will affect the CNT structure, oxidising defective parts of the nanotube as well as the surfactant, once again diminishing CNT quality and potentially adding unwanted chemical groups (Monthioux et al. 2001; Hu et al. 2003; Sun et al. 2002).
Thermal evaporation in an inert atmosphere could be the only potential alternative method for removing the surfactant (and electrospinnable polymer), from the surface of the CNTs. However, this process has been reported to result in a considerable amount of residual contaminants, depending on the chemicals used. For example SDS and SDBS contain sodium and sulphur, both of which will not be removed during this process and will result in the CNTs requiring further treatment. More problematic still, almost all of the surfactants and polymers thermally treated in this manner, will result in residual amorphous carbons left on the surface of the CNTs, which will continue to restrict the effects of the desired van der Waals forces between tubes.

However, Tobias et al. (2006) published a method for removal of these amorphous carbons while simultaneously evaporating the other materials. Simply by introducing steam to the baking chamber Tobias was able to remove the majority of the carbonaceous materials leaving just pure CNTs. It was revealed that, regardless of the fact that water molecules do not usually thermally degrade at temperatures below 2000°C (Srinivasan & Michael 2006), water molecules will react and breakdown on contact with carbon, through two key reaction processes, both of which reported to occur at elevated temperatures of approximately 750°C and above:

\[ C + H_2O = CO + H_2 \]
\[ CO + H_2O = CO_2 + H_2 \]

These reactions will preferentially take place with less ordered carbon, due to the lower energy required to break the chemical bonds, resulting in the selectivity of the oxidation reactions. On the contrary, assuming they are of high quality, CNTs are highly crystalline sp² carbon structures (along their length), and as a result require higher energy to break the chemical bonding, making them significantly more difficult to oxidise than amorphous carbon and polymeric carbon. However, this does not include any areas of the CNT where there are high concentrations of crystal defects, such as lattice defects (inclusions, displacements or exclusions), kinks or the nanotubes end-caps. This was demonstrated in Tobias’ work by oxidation of the highly defective tube ends (revealed through transmission electron microscopy), but not affecting the length of the nanotube, providing it was defect-free.

The process of steam purification has demonstrated numerous benefits such as, easy scalability to industrial sizes and volumes, the ability to be conducted at atmospheric pressure and not requiring harmful/hazardous reactants. Furthermore the treatment process has been proven not to introduce any chemical groups to the surface of the CNTs, unlike any other surfactant removal methods (Shao et al. 2007). The encouraging results and significant benefits make steam purification a promising technique for the complete recovery of the CNTs once they have been aligned into sheets by
electrospinning. However, steam purification will still not be able to remove any residual metals left over from the surfactant, such as the sodium from SDBS. This means that careful consideration of surfactant (and potentially polymer) composition needs to be done, to ensure that it does not leave unwanted residual contaminants within the sample. As an alternative, mild acids could be used to dissolve the sodium left on the CNTs, however it is not clear if this could still damage the CNT surface.

2.4 Electrospinning

2.4.1 Basic Principles

Today, electrospinning research and the nano-fibres market is extremely large, the global market for nano-fibre based products increased from $128.3 million in 2011, to $151.7 million in 2012, with an estimate growth to $570.2 million by 2017 (BCC Research 2013). Historically, the ‘electrospraying’ effect was discovered in the 16th century using electrostatics and water (Gilbert 1628), and it wasn’t until 1887 when the first reported process of electrospinning was published (Boys 1887). After numerous patents from various different people over several years, it wasn’t until 1938 when Nathalie D. Rozenblum and Igor V. Petryanov-Sokolov, working in Professor Nicolai A. Fuchs’ research group in the USSR, produced electrospun fibrous materials, which they later developed into filter material known as “Petryanov filters” (Lushnikov 1997). These filters were further developed to become filters within gas masks, leading to the first industrial electrospinning facility in 1939. By the 1960s during the cold war, the material named as ‘battlefield filter’ was claimed to have been produced in quantities as high as 20 million m² per year (Filatov et al. 2007). The electrospinning process was later explored in much finer detail between 1964 and 1969 by Sir Geoffrey Ingram Taylor, thus leading to the iconic electrospinning cone being named the ‘Taylor Cone’ [see Figure 2-5, A, for example of a Taylor cone] (Taylor 1969).

Sir Geoffrey Taylor noticed that, when a conductive liquid is subjected to a large electric field, the surface tension in the fluid causes the surface shape to deform into a coned shape, with a rounded tip. Using a Legendre polynomial and the assumptions that the cone has an equipotential surface as well as being perfectly round, Taylor derived the theory that when a certain threshold voltage is exceeded (which varies with viscosity), the rounded tip of the cone grows until it has an angle of 98.6º degrees, at which point it inverts to produce a jet of material (Taylor 1969). However, A L Yarin et al. (2001) illustrated that the Taylor angle can vary depending on the solution by witnessing angles as low as 67º, caused by an increase in the electric-field as the cone grows closer to the source. This cone formation mechanism is the driving force which creates the fibres during the electrospinning process.
Figure 2-5 – The schematic diagram is a basic set up to an electrospinning apparatus for collection of aligned fibre, where the introduction of a high voltage to a spinneret causes a solution fed from a syringe pump to form a Taylor cone (1 & A), which subsequently produces a jet of material which accelerates towards a collector at a known velocity, whipping and drawing into a nano-fibre (2 & B). Once the fibre has reached the collector it should have dried, where it is collected on a rotating drum at the velocity of the fibre, producing an aligned mat (3 & C). A typical scanning electron micrograph of aligned polyethylene oxide (PEO) nano-fibres produced from this typical equipment set-up is also shown (C).

The electrospinning process forms nano-fibres through ‘whipping’ or spinning the ‘jet’ of polymer solution, that is ejected from the tip of the Taylor cone. Once ejected, it is this whipping process which causes it to stretch, drawing it into a nano-fibre, before the solution solidifies and is collected (Teo & Ramakrishna 2006). A typical single-needle electrospinning rig [see Figure 2-5] will consist of a pump feeding a viscoelastic solution into a spinneret (at around 700 µl per hour), that is subjected to a large potential (typically +/- 10 to 30 kV), while positioned opposite an electrically-grounded conducting collection plate or a rotating drum (the choice of collector depends on if aligned fibre or random entanglement is desired). The spinneret is always located at a set distance from the collector to enable both constant electrostatic field strength, and adequate drying of the solution, preventing the fibre being collected undried, which would cause damage and inconsistency in the resultant fibres. Typical distances depend on the solvent used in the solution, as well as the atmospheric conditions that the fibre is produced within. As the solution is fed through the spinneret, it is subjected to the large potential, causing electrostatic forces that compress a droplet at the tip to form a ‘Taylor cone’, as previously mentioned. At the tip of this cone, a jet of material is produced,
which accelerates towards the collector as it solidifies; as it does so, the charged jet of material travels through the electrostatic field, causing it to flay out and form concentric circles in a spiral helix pattern. This behaviour causes the fibre to be stretched and drawn into nano dimensions, typically with a diameter that ranges between 50-500 nm (Chronakis 2005). The drawing process also promotes solvent evaporation, when eventually the nano-fibre dries before being collected.

Figure 2-6 – A schematic representation of the alignment of the CNTs within the nano-fibres during electrospinning. The CNTs will start of randomly oriented dispersed within the solution (1), as the fibre is drawn during whipping, the width of the fibre narrows, drawing the nanotubes along it (2). Once the array of fibres is collected, the aligned CNTs are locked within them (3).

The fibre is then collected at the collection drum or plate as, either an aligned sheet or randomly orientated entanglement. In specific situations, other more complex collection techniques can be implemented if required for the application, such as parallel plates (Beachley & Wen 2009) or yarn rollers (Ko et al. 2003). In any case, it is important to have a uniform collector, as any corners, sharp edges, kinks or scratches will cause point charges and subsequently cause an uneven build-up of fibre in these areas. Depending on the rig design and assuming that there are no disruptions, the fibre should be continuous for as long as there is a suitable solution feeding the jet. In reality, small variations in the solution consistency or premature solution drying will cause occasional fibre inconsistencies.

When electrospinning is used to produce aligned polymer nano-fibres loaded with CNTs, the CNTs are forced to align parallel to the fibre within it. This is caused by a combination of the high potential electric field as they pass through the spinneret, and the nano-sized width of the fibre, compared to the micro-sized length of the nanotube. Providing the CNTs are linear and without the kinks seen in Figure 2-3, they will be forced to align along the length of the nano-fibre [see Figure 2-6].
Unfortunately, although electrospinning using a single needle spinneret is consistently successful, it is an extremely slow process (typically processing about ~700 µl/hour). However the electrospinning equipment can be adapted to produce a substantially larger volume of fibre in a shorter time scale, by exploring other solutions and re-engineering the process, which is one of the main goals of this project (Niu et al. 2011).

2.4.2 Types of Electrospinning
The process of electrospinning can produce fibres in many different ways, for example from a needle spinneret, from a spiked surface or from a fluidised bed etc. Equally, fibres can also be collected in different ways, such as a rotating drum, or flat plate collector, to name a few. It is important to understand these various different approaches in order to engineer the method that best suits our project needs. Teo & Ramakrishna (2006) review the advantages and disadvantages of a significant number of modern designs for both producing the fibre, as well as collecting it, whether it is randomly oriented, aligned or interlaced. After careful consideration of all of these collection techniques [see appendix item A], it was decided that in order to achieve a large area of aligned fibre, the best technique for fibre collection in order to achieve our project goals, is by using a large, high-speed rotating uniform drum. This is due to the lack of scalability in other collection designs.

Figure 2-7 – This schematic diagram and photograph shows the basic set-up and workings of a simple needleless-electrospinning rig, using a smooth cylinder to produce fibres. In the photograph you can clearly see numerous jets of material streaming off of the drum, this is one of the advantages of needleless-electrospinning. This schematic diagram and image was adapted from “Needleless-electrospinning. I. A Comparison of Cylinder and Disk Nozzles”, Niu et al. 2009. Reprinted with permission from John Wiley and Sons.
Unfortunately, deciding on a suitable fibre production method is not as straightforward, as there are significant number of options that can be considered. For example, recently Petrik & Maly (2009) developed a needleless-electrospinning rig as a scaled-up solution, which was subsequently commercialised by Elmarco under the trademark Nanospider™. The Elmarco rig is currently one of the only scaled-up mass electrospinning rigs available on the market and is capable of spinning both aqueous and solvent based solutions at a rate of 160 g per hour (for a 4 x 1.6 m electrode system) (Elmarco 2010). However, this rig design is only capable of producing random entanglements of fibres across a large sheet, and although aqueous based solutions can be used, they require some hazardously high electrical potentials of over 120 kV. Potentials this high would require specialist safety equipment as a shock could be fatal, rendering this equipment unsuitable for this project.

As could be seen from the needleless design in Figure 2-7, electrospinning is not just limited to the use of a single needle spinneret; there are numerous different approaches to generating the necessary Taylor cones in order to produce electrospun material. These include, but not limited to: bubble electrospinning (Yang et al. 2009), rotary-cone electrospinning (Lu et al. 2010), conical wire coil electrospinning (Wang et al. 2009), smooth cylinder and disk electrospinning (Niu et al. 2009) and magnetic fluid electrospinning (Yarin & Zussman 2004). Almost all of these techniques rely on extremely high voltages (typically +/- 25 to 120 kV), in order to form Taylor cones and produce fibres. Electrospinning voltages this high are not only dangerous and require extensive equipment insulation, but also cause the nano-fibres to travel towards the drum at high velocities, making alignment challenging. Needleless-electrospinning techniques hold several advantages over traditional needle style spinnerets, such as the number of Taylor cones that can be generated in one instance is only limited by the size of the device, providing a scalable solution to the volume of material that can be processed in a limited time scale. Figure 2-7 was a prime example of this. Although multi-needle systems have been proposed, they are known to have interference issues with the neighbouring needles’ electrostatic fields, causing fibres to either fail to be produced or to be repelled away from the target collector (Theron et al. 2005). The other key advantage of not using a needle or a spinneret, is the avoidance of the constant risk of blockages, as well as eliminating the requirement for a suitable pump and length of tubing to supply a feed of solution, which when using CNT-loaded solutions could cause agglomerations. Based on the potential scalability, combined with the minimal risk of spinning interruptions, it was proposed that the development of a suitable needleless-electrospinning system would be best suited to meet the requirements of this project.

In order to electrospin using a needleless system, the spinning conditions must be optimised to produce adequate fibres. It has been reported that most needleless set-ups require a far greater
electrostatic potential, typically between 20 to 120 kV (Elmarco 2010; Niu et al. 2009). For this reason most needleless rigs are designed to produce fibre at collection distances ranging within 10 – 20 cm to maximise the electric field intensity. Although the collection distance can be increased with increasing the potential, it also means that the charged drum would need to be further away from any fume cabinet walls or floor, in order to ensure the collection drum is the nearest electrically-grounded object. Equally, the atmospheric conditions must also be carefully considered to ensure rapid solvent evaporation without diminishing the electrostatic field. However, understanding how the permittivity of air behaves with respect to both temperature and humidity can be complex.

2.4.3 Atmospheric Conditions

Gaining an understanding of the electrostatic properties of air is essential when attempting to tailor the atmospheric conditions for electrospinning. It has been previously reported in literature that maintaining temperature values within 20° to 30° C and the relative humidity between 20% – 40% would promote the evaporation of the solvent within the polymer solution, and as such prevent the wet lay that had been experienced (Niu et al. 2011). However, this could have more negative effects on the electrospinning process than positive, potentially rendering the process unable to produce any fibres. This is due to there being a fine balance between the humidity being low enough to ensure rapid evaporation and the humidity being so low that the permittivity of air reduces the strength of the electrostatic field to a threshold below that required for electrospinning. By understanding how varying both the temperature and humidity affects the permittivity of air, it is possible to tailor the electrospinning conditions without preventing the formation of fibres. Equally, this also allows easy avoidance of increasing the permittivity of the air to an excess, which could promote corona discharge.

The permittivity of air is complex, and varies with humidity, pressure and temperature, making it challenging to control. Norman Lea (1945) conducted an investigation which measured the permittivity of air in controlled atmospheres, and then compared the results to the following approximation:

\[
\kappa = 1 + \frac{211}{T} \left( P + \frac{48}{T} P_s H \right) \times 10^{-6}
\]

Equation 2-1

where \( \kappa \) is the permittivity of moist air, \( T \) is the absolute temperature (K), \( P \) is the pressure of the moist air (mm Hg), \( P_s \) is the pressure of saturated water vapour at \( T \) (mm Hg) and \( H \) is the relative humidity (%). The numerical values within this equation are experimentally defined constants. \( P_s \) can be approximated using the Antoine equation (Antoine 1889):
By assuming that pressure is constant at a specific location, for example the electrospinning laboratory, Equation 2-1 can be used to plot the permittivity of air against temperature for specific humidity. Figure 2-8 assumes that there is a constant pressure of 760 mm Hg to plot the permittivity of air against temperature for various specific relative humidity. This plot reveals how lowering the humidity will in turn lower the permittivity of air. Using the same assumptions and data, Figure 2-9 plots the permittivity of air against humidity for various specific temperatures, revealing that increasing the air temperature will increase the permittivity, except at very low humidity (<10%).

Investigating the relationship between the environmental conditions and the permittivity of air has shown that a hot, dry environment does not just promote solvent evaporation, but it also promotes Taylor cone formation, as long as the relative humidity is not lowered below 10%. These results clarify that any electrospinning rig must have some form of atmospheric control, in order to have complete control over the process.
2.4.4 Fluid Dynamics

Although set-up design is a key component to successful electrospinning, the properties of the solution must be suitable, or no fibres will be produced. During the spinning process, the fibre is drawn and stretched as it solidifies. For this reason, the solution is required to be sufficiently viscoelastic (which can be determined experimentally), in order to ensure an elastic strength that does not allow the fibre to tear (Regev et al. 2010). Having too little elasticity will cause the jet to disintegrate, while too much elastic strength will prevent the jet from being drawn and stretched. In order to achieve the required elasticity, the polymer solution can be adapted in different ways, such as: - varying the length of the polymer chains, varying the polymer concentration, heating the polymer, changing the atmospheric conditions to control the drying (by controlling temperature and humidity), changing the collector distance, varying the charge density and varying the solvent vapour pressure to name a few (Vrieze et al. 2008; Casper et al. 2003; Thompson et al. 2007; Megelski et al. 2002).

Figure 2-10 illustrates the effects that the polymer chain length has on the viscoelastic properties of the solution during electrospinning. Using a simple polymer such as polyethylene oxide (PEO), with an average molecular chain length of 2,000,000 $M_v$ (where $M_v$ is the viscosity average molecular weight of the polyethylene oxide polymer chain), Figure 2-10 (A) visually demonstrates how the right viscoelasticity of the solution (combined with the correct drum speed) can produce highly aligned uniform fibres (in this case, with an average fibre width of ~180 nm). Reducing the average PEO molecular chain length to 200,000 [see Figure 2-10, B], lowers the elastic strength of the solution,
proving insufficient to hold the fibre during the whipping/stretching and subsequently the solution disintegrated into small droplets (Mun et al. 1998). This process then becomes electrospraying, and is used for a variety of applications especially applying coatings (Burkarter et al. 2007).

Controlling the various different parameters not only allows for the production of fibres, but also allows for the manipulation of the jet in ways that affect the resultant fibre. For example, Casper et al. (2003) found that, when electrospinning polystyrene (PS), raising the humidity above 30% introduced nano-holes into the fibres, whilst varying the polymer chain length increased/decreased the pore size. These pores drastically increase the surface area of the fibres and have been found to be useful for many applications, including hydrogen storage (Im et al. 2008). Porous fibres aren’t the only nano-structures that can be produced via electro-spinning, others include, but not limited to: nano-ribbons (Chan et al. 2007), nano-beads (Fong et al. 1999), helical fibres (Yu et al. 2008) and hollow fibres (Dan Li & Xia 2004). It is important to optimise the electro-spinning conditions in order to avoid the possibility of creating any nano-structures within the CNT loaded fibres produced during this project, as any structures other than uniformly linear fibres could hinder the alignment of the CNTs within them.

For needleless-electrospinning, the design of the polymer solution is critical, especially when using aqueous soluble polymers. If the polymer concentration is too low, the polymer will either fail to form fibres or fail to dry before collection, destroying any previously collected fibre. If the concentration is too high, then the elastic strength of the Taylor cone becomes so high that it will not
produce a jet. Tang et al. (2010) found that when electrospinning from a drum using PEO (1,000,000 Mₘ) in an aqueous solution, any concentration below 8% failed to produce fibres, but also that upon increasing the polymer concentration, fibre consistency decreased and the average fibre diameter increased from 200 to 350 nm. F. Zhou et al. (2009) reported similar observations by changing the polymer molecular weight and by lowering the concentration to 6% weight PEO. This illustrates that, when needleless-electrospinning, we must choose the optimum polymer molecular weight, the optimum polymer concentration and the optimum atmospheric conditions, in order to produce consistent, uniform, aligned nano-fibres.

2.4.5 Jet Dynamics

Once the solution properties have been considered, the last key to achieving highly aligned fibres when electrospinning is matching the collection drum’s surface velocity to the velocity of the approaching electrospun fibres (Fennessey & Farris 2004; Kim et al. 2004). However, fibre velocity depends on both the viscosity of the solution and the electrostatic field strength applied to the spinneret (Regev et al. 2010). It is for this reason that jet velocities have been reported to be anywhere between 0.4 and 160 m/s (Bellan et al. 2007; Fennessey & Farris 2004; Reneker & Chun 1996). This is why, without a strong understanding of the jet dynamics of the solution system being used, achieving aligned fibres can be a challenge.

When an electrospun polymer jet travels towards the electrically ground collector, it begins to spiral, flaying out and drawing the fibres to significantly thinner diameters, as previously explained (Reneker et al. 2000). The centrifugal forces within these spirals increasing their diameter, further stretching the fibres as they dry. While in the spiralling phase, the polymer jet also accelerates in the direction of the collection drum. Upon drying, the stretching of the fibre is reduced and velocity continues to increase, acceleration slows, before finally being collected as a dry fibre (Wu et al. 2011). Literature has already shown how numerous factors influence the velocity of the electrospinning jet, which has highlighted that with each specific solution there are optimum parameters that produce the highest quality nano-fibres, and as such an optimum velocity that the collection drum should be rotated. Getting the velocity incorrect could result in either poor nano-fibre alignment or nano-fibre damage.
Figure 2-11 – This schematic diagram illustrates the theoretical effect that slower (1), equal (2) and faster (3) speeds of the collection drum (with respect to the jet of fibre) have on the electrospinning process.

For example a 2% PEO aqueous-based solution will have a specific drying time and as such will need to travel a minimum distance from the collection drum as to allow drying. As the PEO jet travels towards the collector, it will undergo an average number of spirals or loops before it dries and is ready to be collected. By spinning a collection drum at the velocity of this fibre at that point at which it is dry, will produce the highest quality, highly aligned fibres. To explain this further, Figure 2-11 illustrates with a schematic diagram how different drum velocities, with respect to the fibre velocity, will alter how the fibre is collected. When the surface velocity of the collection drum is slower than the fibre velocity [Figure 2-11, example 1], the loops will form a back log mid-flight, ‘buckling up’ on each other. As they are repelled by their identical charging, they will form a randomly oriented mat of fibres on the drums surface. When the surface of the drum exactly matches to the fibre arrival velocity [Figure 2-11, example 2], the fibre is collected after an average number of loops or spirals, exactly as the fibre dries. This avoids any form of buckling or pulling on the fibre (introducing stresses), thus ensuring high alignment and high quality. If the drum’s surface velocity is faster than the arrival velocity of the fibres [Figure 2-11, example 3], the jet will be pulled towards the drum immediately after initial attachment. This will reduce the number of loops and as such possibly introducing residual stresses and causing the fibres to be of inconsistent diameter as a result of plastic deformation. Equally, it has also been seen how overspinning the collection drum creates air turbulence, which would reduce the collection yields, fibre quality and the fibre alignment (Ayres et al. 2006; Kim et al. 2004).
The effects of the collector drum’s surface velocity being greater than the jet velocity can be predicted by rearranging the equation for Young’s Modulus to incorporate distance, speed and time. Using the equation for Young’s Modulus, we can substitute the measurement of length in for strain:

\[ E = \frac{\sigma}{\epsilon} = \frac{\sigma L}{\Delta L} \]  

Equation 2-3

where \( E \) is the Young’s Modulus (Pa), \( \sigma \) is the stress (Pa), \( \epsilon \) is the strain (a. u.), \( L \) is the original length (m) and \( \Delta L \) is the displacement length. The lengths can be calculated and substituted into this equation using the distance, speed and time equations:

\[ L = V_j \times t \]  

Equation 2-4

\[ \Delta L = (V_D - V_j) \times t \]  

Equation 2-5

where \( V_D \) is the drum surface velocity (m/s), \( V_j \) is the jet arrival velocity (m/s) and \( t \) is time (s). Substituting these equations into Equation 2-3 and subsequently rearranging, we can calculate the stress to the nano-fibres caused by the incorrect surface velocity of the collector drum:

\[ \sigma = E \left( \frac{V_D}{V_j} - 1 \right) \]  

Equation 2-6

Previously reported values for the Young’s Modulus of a PEO nano-fibres range from 45 to 59 MPa (Geng et al. 2006; Tan et al. 2005). Using either of these values in Equation 2-6 demonstrate that even a velocity difference of +2 m/s between the drum surface and the jet will introduce a residual stress within the nano-fibres of up to 5.9 MPa. A stress of this magnitude, when compared to the stress/strain curves for a PEO nano-fibre, will cause plastic deformation and even fracture, reducing the mechanical properties of the fibre and reducing alignment (Geng et al. 2006; Tan et al. 2005).

Figure 2-12 demonstrates an example of nano-fibres collected on a drum with a surface velocity greater than the arrival velocity of the fibres. The residual stresses this has placed within the nano-fibres can be seen in how they are constricting, exerting a tension on the paper they are attached to. Additionally, Equation 2-6 shows that, when the jet velocity is greater than the drum surface velocity, the stress then becomes negative, meaning that fibre begins to over-shoot the drum and buckle up on itself, also reducing the fibre alignment.

Obtaining the optimum electrospinning parameters cannot necessarily be found in literature. As previously explained, there are so many different variables that only experimentation will identify them for the apparatus and solutions used, literature can only help suggest what those optimum values might be.
Figure 2-12 – Nano-fibres collected on a high speed rotating drum, where the surface velocity of the drum was considerably higher than that of the fibres. The bend in the sample demonstrates how the fibre is under residual stresses, causing it to constrict which is exerting a tension on the paper substrate, causing it to buckle.

2.5 Prior Art

Previously, in chapter 2.4.1, it was explained how electrospinning has been developed over numerous decades; with this in mind, a prior art search was conducted exploring any patents that may have conflicting interest with this project. Patent searches were conducted across Google Patents (google.com/patents), the U.S. Patent and Trademark Office (uspto.gov) and the European Patent Office (epo.org), searching for both the alignment of CNTs via electrospinning and electrospinning system designs.

Across the stated patent offices searched, only two patents (one being an application) were found specifically relating to the electrospinning of CNTs, US 2007/0082197 A1 (Ko et al. 2004) and US7790135 B2 (Lennhoff 2010). US 2007/0082197 A1 specifically talks about the electrospinning of CNTs within spider or silk-worm silks, for the potential applications of biomedical devices (including those requiring electrical conductivity), and areas of blast and ballistic protection. This patent does not specifically declare any objectives for the alignment of the nano-fibres and CNTs, leading to the conclusion that this application does not directly conflict with the interests of this project. The patent did not reference any other patents and was referenced by three almost identical patents, US8187700 B2, US8435628 B2 and US8642167 B2, all by The Boeing Company, (Tsotsis 2012; Tsotsis 2013; Tsotsis 2014). These patents are based on the use of CNTs loaded within a carbon fibre reinforced composite (using polyacrylonitrile (PAN)), produced by melt-spinning. The patent also states why electrospinning is not suitable for their purpose and as such does not conflict with this project. US7790135 B2, the second of the first two patents mentioned, describes the process of electrospinning CNTs in PAN,
followed by heat treatment, to produce carbon nanostructures. Although this invention does describe a similar process to that of this project, it does not mention or make reference to any form of alignment or its potential benefits (as outlined in chapter 2.1, page 5), rendering it different to the goals of this project. This patent cited and was cited by various other patents, none of which were relevant, except the previously mentioned Boeing patent.

The prior art for needleless-electrospinning systems produced one patent in particular which describes a process for producing fibres over a larger scale, US7585437 B2 (Jirsak et al. 2009), which was commercialised by Elmarco and used to market the Nanospider™ system [see section 2.4.2]. Within this patent, Jirsak et al. describe the general working of a needleless system, focusing on the shape of the drum and how the air flow could be used to control the fibre deposition. The patent does give some examples of drum design, including a smooth and bevelled surface, but does not specify anything in particular [see Figure 2-13]. Furthermore, the patent does not allow for aligned fibre collection, focusing on high output fibre production. This patent also does not include any mention or references for electrospinning onto a drum style collector or for the alignment of the nano-fibres. This patent does reference several other patents, three of which are related to scaled-up solutions for

Figure 2-13 – Two figures taken from US patent: US 7585437 B2 (Jirsak et al. 2009), where a needleless-electrospinning design is proposed, including the various different spinneret drum designs. Note, it is not clear as to the drum design of 5e, as there are no references to it in the text.
needless-electrospinning: US4069026 A (Simm et al. 1978), US4143196 A (Simm et al. 1979) and US6604925 B1 (Dubson 2003). Each of these patents is based on similar needless-electrospinning systems, including cylindrical drums, semi-submerged within a polymer solution. The differences in these patents to the interests in this project, are in the how the fibre is collected; where none included rounded drums, that none made any mention or reference to alignment and the specified applications, which in most cases is for filtration (Simm et al. 1978; Dubson 2003; Simm et al. 1979).

Since the Jirsak et al. 2009 patent, there have been four other patent applications submitted by Elmarco, three of which relate to needless-electrospinning: US2008/0307766 A1 (Petras et al. 2006), US2008/0284050 A1 (Mares et al. 2006) and US8231822 B2 (Petras et al. 2012). The only patent (application) which is relevant to this project is US2008/0307766 A1, which describes the use of various different types of electrode which can be used for high-yield needless-electrospinning. These electrode designs were made to distribute the charge evenly across the drum for an even fibre deposition. The drum designs include a curved drum, an arrayed lamellar drum (in various tip designs including cylindrical, cuboid and flat tips) and a wave lamellar drum [see Figure 2-14 for examples of the tipped design and the curved design]. Once again all of these patents and designs, focus primarily on high-yield electrospinning and make no mention or reference to nano-fibre alignment or high
speed drum collectors. Furthermore in order to gain a uniform area of aligned CNT-loaded nano-fibres, it is important to design the electrode with respect to controlling field enhancement at pre-defined positions, as opposed to simply maximum output. Ensuring that the electric field is equal at specific, even points along the electrode. This guarantees that the nano-fibres produced will be subjected to the same electrostatic forces and therefore be identical, producing a final material uniform across its area. It is these objectives for this project which make this patent dissimilar in design objectives.

When designing the needleless solution in Chapter 7, we consider the results from this prior art search, ensuring that we achieve our goals of large area electrospinning of a uniform mat of aligned nano-fibres, and where possible engineering our design to be patentable. From the patents discussed in this section, it has been seen how a cylindrical drum, partly submerged in a polymer solution is a common design. The consistent variation across the various patents explored, has been in the design of electrodes on the spinneret drums surface (ranging from a smoothed surface to a complex series of lamellar) and how the nano-fibres are collected.

2.6 Conclusions
Reviewing the previous research, background science and prior art, has led us to gain a better understanding of how to approach accomplishing the goals set out by this project in chapter 1. Acknowledging previous attempts to produce CNT composites, whether it be by electrospinning or other, and with proper use of modern dispersion techniques, such as surfactant loading or polymer wrapping. This project aims to utilise a technique in which SWNTs can be dispersed within a suitable aqueous soluble polymer, and used to produce large-area, highly-aligned arrays of CNT-loaded nano-fibres by the process of electrospinning. Reviewing numerous publications and patents has led to a fundamental knowledge of the processes which are involved in designing and using a high-yielding needleless-electrospinning rig, capable of producing large arrays of aligned CNTs loaded nano-fibres. These processes include an appreciation of the various electrospinning parameters that must be defined experimentally, such as atmospheric temperature, humidity, collection drum speed and electrostatic field control, before CNT alignment can be achieved.
3 Analytical Methods

3.1 Introduction
Throughout this thesis numerous analytical methods were used to probe samples and build conclusions, leading to project progression. The major analytical methods used will be explained, focusing on the techniques that contributed the majority of the results. As well as explaining the general science and theory behind each technique, justification will also be made as to why the technique was desirable for this project’s success, and wherever possible how it can be used in combination with other techniques to gain better insight.

3.2 Electron Microscopy

3.2.1 Basic Principles
Much the same as light microscopy is the analysis of samples using light reflections/scattering from surfaces/interfaces within a microscope, electron microscopy is the analysis of samples using electrons. Electrons, despite having mass, can be treated as a wave or a particle, due to their extremely small mass and dimensions. By treating them as waves it is possible to image with them in a similar manner to imaging with light, but with a number of distinct differences that allow for higher imaging resolutions, while providing more information on the samples structure and composition.

Unlike light which can only vary in wavelength depending on its source, and has its limitations, Electrons produced from an electron-source do not have a limited wavelength. The wavelength of a beam of electrons (when treated as a wave), is controlled as a function of the electrostatic potential used to accelerate them (or accelerating potential). This gives rise to the main advantage for imaging with electrons; unlike with traditional light microscopy, which has at best a resolution of 200 nm (limited by the wavelength of the light being used), electrons can be accelerated to relativistic
velocities which result in wavelengths of that smaller than an atom, allowing atomic resolution (Browning et al. 1993).

For example, the wavelength of an electron, when considered as a wave, can be calculated using the de Broglie relationship:

\[
\lambda = \frac{h}{p} = \frac{h}{m_0 v}
\]

Equation 3-1

where, \( \lambda \) is wavelength (m), \( h \) is Planck’s constant (m\(^2\)kg/s), \( p \) is the momentum of the electron (kg m/s), \( m_0 \) is rest mass (kg) and \( v \) is velocity (m/s). Ignoring special relativity for the moment, the velocity of the electron can then be given as a function of accelerating potential:

\[
E = eV = \frac{1}{2} m_0 v^2
\]

Equation 3-2

\[
v = \sqrt{\frac{2eV}{m_0}}
\]

Equation 3-3

where, \( E \) is the kinetic energy of the electron (J), \( e \) is the charge of an electron (C) and \( V \) is the accelerating potential (V). Inserting Equation 3-3 into Equation 3-1 and simplifying gives us a non-relativistic approximation for the wavelength of an electron as a function of accelerating potential:

\[
\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_0 eV}}
\]

Equation 3-4

However, a typical electron microscope will accelerate the electrons to very high potential, usually tens of thousands of volts. This large accelerating potential causes the electrons to travel at very high velocities, often an appreciable fraction of the speed of light. For example, a scanning electron microscopy (SEM) typically operates with an accelerating potential of about 10,000 volts (10 kV), accelerating the electrons to approximately 20% of the speed of light. It is not uncommon for some microscopes to operate at potentials as high as 200 kV, which increases the electrons velocity to approximately 70% of light speed. With velocities this high, it becomes necessary to take into account the relativistic effects that increase mass and as such the momentum of the electrons involved. To do this we use the relativistic relationship between energy and momentum (Feynman et al. 2013):

\[
E^2 = p^2 c^2 + m_0^2 c^4
\]

Equation 3-5
where \( c \) is the speed of light. In order to obtain momentum as a function of accelerating potential as we did before, we need to both remember that when the electron is at rest energy \( (E_0) \), the momentum is zero, and that the difference between the rest energy and the final energy is equivalent to the accelerating potential, such that:

\[
\Delta E = E - E_0 = eV
\]

Equation 3-6

Equating Equation 3-5 for momentum using the stated rules and then substituting back into the de Broglie relationship (Equation 3-1), gives rise to the relativistic expression for the wavelength of an electron (for proof of derivation please see appendix item B):

\[
\lambda = \frac{h}{\sqrt{2m_0eV\sqrt{1 + \frac{eV}{2m_0c^2}}}}
\]

Equation 3-7

Recognise that the first half of the expression is the non-relativistic part derived before in Equation 3-4, and the second half is the relativistic correction factor. Using this formula the wavelength of electrons in a 10 kV electron microscope calculate to be 12.2 x 10^{-12} m (12.2 pm), while at 200 kV equates to 2.5 pm, both of which are well below the bonding between two atoms and as such demonstrating electron microscopy’s atomic resolution. It’s due to the SWNTs being only tens of atoms wide, that produces the requirement for this field of high resolution techniques.

Electron microscopy is a field of techniques that allows for different advantages depending on the analysis mode used. In this project the majority electron microscopy is either: scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) (which is a complementary form of electron analysis) and scanning transmission electron microscopy (STEM).

3.2.2 Scanning Electron Microscopy

Initially developed in 1933 (with limited success), scanning electron microscopy (SEM) has quickly become the most common form of electron microscopy (McMullan 2006), with ever increasing development they have slowly become smaller and more affordable, with some devices of a similar size to that of a desktop computer. As the name suggests, it builds an image by scanning a focused beam of electrons across the sample surface in the form of a raster pattern, constructing an image pixel by pixel [Figure 3-1, A]. Where magnification is altered by varying the area of the raster, unlike in optical microscopy which relies on the strength (focal length) of various optical lenses. This means
that once the microscope is calibrated, the imaging processes with respect to changing magnification, is largely repeatable and reproducible. Due to the nature of the beam of electrons this process has to typically be done under vacuum (high or low), with higher vacuums giving better resolutions as it minimises beam scattering off gas atoms. Furthermore, where the electron is a charged particle it is important to ensure that the sample is conductive, insulating samples can cause local charge build-up on the sample surface which will deflect the electrons, obscuring the image. These limitations aside, SEM offers considerable advantages, including minimal sample preparation (compared to other techniques), fast imaging time (with some systems boasting imaging in less than a minute), no limit on sample size or thickness and minimal sample damage. However, one of the biggest advantages is in the complementary information that can be simultaneously acquired while imaging.

![Figure 3-1](image)

**Figure 3-1** – A schematic diagram of how the electron beam is scanned across the sample surface in a SEM (A). Where the beam is focus on the sample the electrons will penetrate into it, with various depths yielding different information signals about the sample (B).

Unlike with light microscopy, the SEM technique can yield various forms of information about the sample, such as elemental composition. This is due to the electrons in the incident beam being of high energy and as such penetrating the sample surface and scattering within. Figure 3-1 (B) demonstrates a typical electron scatter paths you would expect within a sample, where the penetration depth depends on sample density, elemental composition and the accelerating voltage used. As the incident beam of electrons strike the sample surface they scatter, either elastically or inelastically. Depending on how they scatter, they can yield several different types of information.
Within this project we only focus on four types of information: secondary electrons, back-scattered electrons, X-rays, Auger electrons. Each of these signals, typically can only be detected at a maximum depth into the sample that’s being analysed. This is otherwise known as the ‘interaction volume’, and varies with sample density and composition. At any point within the sample, any of the used signals can be generated, however each signal varies with the typical maximum energy in which it can exit the sample to be detected. The deeper the incident electrons penetrates the sample, the more energy is required of the signal in order to exit the sample. It is this energy requirement that gives rise to the different signal regions seen in the sample interaction area in Figure 3-1 (B). Generally the deeper the electron beam penetrates that sample, the greater probability it (or a generated signal electron) will be absorbed into it, and the energy will be transformed into heat or electrical current. Signals produced deep within the sample can typically only escape as photons, such as X-rays.

Figure 3-2 – Four schematic diagrams of how different signals are produced during scanning electron microscopy, including: secondary electron emission (A), back-scattered electron emission (B), Auger electron emission (A then C) and X-ray emission (A then D). Note: the electron configuration is only a representation and not accurate for carbon.
As previously mentioned, there are two different types of electron scattering events, elastic and inelastic. Elastic electron scattering is described as any scattering event whereby the electron changes path and energy is conserved, such as scattering as a result of electrostatic attraction to the protons in an element's nucleus, or repulsion for its electron cloud. This is also known as Rutherford scattering and is the main form of scattering used in transmission electron microscopy (explained later in section 3.2.4), and back-scattered electron imagery. Inelastic scattering is unlike elastic scattering, in that energy is not conserved when the electron's path changes (usually by a measurable amount). Energy usually lost in the scattering event, is normally transferred to another electron, causing it to undergo a transition within the element. It is this form of scattering that is attributed to the most common form of SEM imaging modes; secondary electron imaging.

Auger electrons are the frequency of electrons that can be ejected from the sample being analysed, because of this they are only detected near the sample surface, where the incident beam is at its highest intensity. They are created when an incident electron removes a core 1s electron of an atom resulting in a vacancy [see Figure 3-2, A]. An electron from the 2s orbital of the affected atom then drops down into this vacancy to return the atom to the lowest energy state, in doing so a photon equivalent to the energy difference of these two levels must be emitted. In most cases this photon leaves the atom (normally as an X-ray, explained later), but in rare cases it is immediately absorbed by a 2p level electron in the same atom causing it to be ejected from the atom [see Figure 3-2, C] (Woodruff & Delchar 1994). This second ejected electron is called the Auger electron and its ejection kinetic energy yields information on the original atom it was ejected from. In relation to this project, Auger electron spectroscopy (AES) could be used to assess surface chemicals and composition in our composite materials.

Secondary electrons are low energy electrons that are ejected from the sample after having energy passed to them through an inelastic scattering event with an incident electron [see Figure 3-2, A]. These electrons are the most commonly used for imaging in an SEM, this is due to a combination of the high yields that they are produced in and the relatively low penetration depth that they originate from, allowing high resolutions to be achieved. The penetration depth of these electrons can be altered by simply changing the accelerating voltage. This can present a number of benefits when sample imaging, especially when imaging fibres which can be very small and have a low density. Lowering the accelerating voltage reduces penetration depth and allows for surface imagery, alternatively increasing the voltage allows imaging under the surface, avoiding any surface coatings such as amorphous carbon, that's not of immediate interest. When imaging polymer nano-fibres with secondary electrons, it is always best to keep the accelerating voltage low. This is due to a combination
of sample charging and sample heating. Sample charging is due to the poor conductivity of the sample, preventing the current to drain as electrons are absorbed, causing local charge build-up. This local charge build-up will then deflect incident electrons, obscuring any imagery. In some cases local charge build-up can be avoided by sputtering a fine conductive coating onto the sample, allowing the charge to drain (Li & Xia 2003) [see Figure 3-3, A]. Heating is caused by the incident electrons being absorbed into the sample and their kinetic energy is transferred as heat. As a nano-fibre is small, heating in this manner will cause the polymer to melt, damaging the sample and obscuring any analysis [see Figure 3-3, B]. This can be reduced by increasing the raster scan speed, which although will lower the image quality, will significantly avoid heating of the sample.

Back-scattered electrons are unlike secondary electrons in that they are generated as a result of typically a single elastic scattering event. However, also unlike secondary electrons, back-scattered electrons are the original incident electrons, as opposed to being ejected from a sample atom. When the incident electron from the beam penetrates the sample, it will typically undergo numerous inelastic scattering events before being absorbed by the sample. In some of these cases the incident electron is not absorbed into the sample, rather scattered elastically back out of the sample into a detector, hence the name back-scattered electron [see Figure 3-2, B]. Generally these electrons will maintain a large proportion of their initial energy, which results in their deeper penetration depths compared to secondary electrons. Imaging with back-scattered electrons poses a number of benefits, especially as additional information regarding the sample can be obtained. This additional information includes: composition (atomic number (Z) contrast), local surface inclination (topographic or shape contrast), crystallography (electron channelling) and internal magnetic fields (magnetic contrast) (Goldstein et al. 2011). With CNT samples, this contrast can be particularly useful with identifying residual heavy elements, such as the original catalyst used to grow them.
The final signal commonly received from an SEM is not electrons but rather X-rays. Previously, it was mentioned in the process of Auger electron production how a core electron is ejected from an atom in the sample, causing a higher level electron to drop into the vacancy, emitting a photon. When the photon is not reabsorbed by another electron in that atom (generating an Auger electron and previously explained), the photon is emitted from the sample (usually as an X-ray) and detected [see Figure 3-2, D]. Measuring the energy of these X-rays enables the accurate identification of the emitting element, as will be explained in the next section.

3.2.3 Energy Dispersive X-ray Analysis (EDX)

Illuminating a sample with a beam of highly focused, high-energy electrons will produce X-rays, as atoms that have had their core electrons removed return to a lower energy state. Every chemical element has unique energy levels that the electrons orbit the nucleus. When an electron from a higher orbital relaxes to fill a lower orbital state, it emits a photon of the exact energy difference between the orbitals. Detecting and measuring this photon's energy, and comparing it to a library of known photon energies, will reveal its element of origin. Doing this across a sample area will map the samples' elemental composition. Typically, the results are plotted as a series of peaks across a spectra, intensity against X-ray energy. Comparing the intensity of each of the peaks will also provide information on the samples' elemental composition (as a weight fraction or atomic percentage). A typical EDX spectra and corresponding elemental table can be seen in Figure 3-4.

![Figure 3-4 - An example of a typical EDX spectrum, where the labelled peaks can be compared to provide the table shown of relative compositions. This example was taken over an area of CNT filled nano-fibres.](image-url)
EDX of a sample can be performed in a number of different ways including: point analysis, line analysis (measuring the elemental composition from one point to another and plotting as a function of distance) and area analysis (measuring the elemental composition of an image pixel by pixel, producing images element by element). In order to obtain a spectrum which has a low ratio of noise, it is usually required to acquire the signals for several minutes, providing data which consists of over 10,000 counts. This means that line and area scans can take an extended length of time depending on the number of pixels being analysed. This can also mean that the sample can suffer damage as a result of the extended electron beam exposure. This means, when using EDX to analyse a sample various factors must be considered, such as beam intensity and scan time, for example. The most important of these is the penetration depth of the incident electron beam [Figure 3-1, B], if the item of interest is not thick enough, the majority of the electrons will pass straight through and the X-rays being analysed will originating from beneath the sample. This is particularly the case for some samples used in this project, as polymer nano-fibres and CNTs which are comprised of light atoms such as carbon and oxygen, contain few heavy elements (depending on the surfactant used). This means special consideration must be taken to ensure penetration depths are within the sample.

The use of EDX will be extremely useful when assessing the CNT samples. The combination of imagery and elemental analysis will enable careful assessment and identification of potential contaminates in the samples that could diminish the performance of any composite material. Furthermore, this will also allow the inspection for any residual contaminates after the aligned CNTs have been recovered, whether it be by the previously stated steam purification or another process.

3.2.4 Scanning Transmission Electron Microscopy

A sophisticated alternative to SEM is scanning transmission electron microscopy (STEM), which combines both SEM and transmission electron microscopy (TEM). This results in several simultaneous high resolution types of analysis: secondary electron, Z-contrast and transmission electron imagery. Unlike standard SEM equipment, STEM requires ultra-high vacuum, thinner samples (typically less than 100 nm thick) and significantly higher accelerating voltages (between 60 to 200 kV), enabling higher resolution imagery (as demonstrated with Equation 3-7). The requirement for thinner samples is necessary for successful TEM, which relies on the electrons passing through the sample purely by either a single inelastic scattering event or none at all. When electrons penetrate a sample they travel a typical distance, known as a ‘mean free path for inelastic/elastic scattering’, before they are scattered. In order for electrons to be transmitted through the sample for TEM, the
sample thickness must be of the order of one mean free path for inelastic scattering for that sample. The mean free path can vary depending on sample composition and density, but more so as a function of the energy of the incident beam of electrons, which gives rise to higher accelerating voltages used with this technique.

In complement to TEM, STEM can also explore high-angle annular dark field scattering events, also known as Z-contrast imaging. Electrons that pass through the sample, close to an atomic nucleus, will experience elastic scattering with a strength proportionate to the squared atomic number of that nucleus. Images can then be generated where the contrast is related to the proton number (Z) of the nucleus, revealing features of the sample that were otherwise unseen. This is particularly useful when imaging CNTs, as it will reveal any residual catalyst present in the sample.

### 3.3 Raman Spectroscopy

Raman spectroscopy is an analytical technique used to probe a material by studying the vibrational modes (or phonons) and other low frequency excitations of its molecular electronic states. It works by exciting an electron cloud that is shared across a chemical bond, using a monochromatic light source, usually a laser of a known wavelength. The light is then back-scattered off of the material, resulting in some of the light having its energy (or wavelength) altered by specific quantities, depending on the interaction with the material. The backscattered light is then collected and plotted as a function of the change in wavelength, when compared to the original incident light, against its intensity. Typically this then displays characteristic peaks in specific wavelength changes, which can be compared to a library of information, leading to the identification of specific chemical bonds within the sample (but only bonds with Raman active vibrations). For a vibration to be Raman active, the incident light needs to induce a specific change in the molecular electron cloud, such that it is now polarised. This polarisation effectively results in a one or many physical changes in the cloud, such as size, shape or orientation. Polarising the electron cloud across a chemical bond could then result in an alternating change in the bond angle or stretching/shrinking it, effectively causing it to act as a harmonic oscillator.

The Raman effect was initially discovered in 1928 by Indian physicist C.V. Raman and since then has been developed into one of today’s more powerful surface analytical techniques (Raman 1928). When light is incident on a material, specific resonance frequencies are absorbed, exciting an
electron in an atom or across a bond. As the atom relaxes back to its original energy level it re-emits the light photon of the same energy in any random direction (Baranska et al. 1987). This form of scattering is known a Rayleigh scattering, and contains no information about the material so is subsequently filtered out. However, an atom within the material will have electron excitation energy levels both higher and lower than the original energy level of the excited electron. Should any of these have an electron vacancy (possible due to further excitation), then in extremely rare events (1 in 1 million events), the excited electron can de-excite to this instead of its original energy level it started at, causing emission of a photon with either a shorter or longer wavelength compared to the incident light. These alterations to the incident lights’ wavelength are called Stokes (emission of a lower energy, longer wavelength photon), and anti-Stokes (emission of a higher energy, shorter wavelength), this is known as the Raman Effect [see Figure 3-6]. Generally, with Raman spectroscopy, only the Stokes interactions are used for analysis, due to the signal intensities typically being a factor of 2 to 10,000 greater (Moore 2001). This is because it is more likely you will have molecules in a ground state than excited.

Figure 3-5 – One of the Raman vibrational modes of carbon dioxide (CO$_2$). During this vibrational mode the oxygen – carbon bonds stretch and contract in an oscillation. This causes an intensity peak at Raman shift 1480 cm$^{-1}$.

Figure 3-6 – This is a schematic diagram of energy levels illustrates the three main types of scattering responsible for the Raman Effect. Each line dictates the energy of an electron within the cloud around the molecule, the first of each pair showing the absorption of the photon by an electron with resultant electron excitation and the second the emitted photon from the electron relaxation.
Typically the Raman effect is most easily observed when the material is illuminated with a laser, this is due to the high intensity of the beam of radiation and the good spatial resolution (Baranska et al. 1987). The Raman spectroscopy equipment available for use on this project is a Renishaw micro-Raman spectrometer, which is equipped with lasers at 514 nm (green) and 785 nm (red) and capable of scanning spectra between 170 cm\(^{-1}\) and 4000 cm\(^{-1}\). Before each spectrum is acquired, the equipment is calibrated using a silicon calibration sample and the first order silicon 521 cm\(^{-1}\) peak.

Unlike any other analytical technique, Raman analysis allows quick and easy examination of the CNTs within the samples, with the added bonus of being non-destructive, making this form of analysis essential for this project. CNTs can be challenging to analyse due to their size. However, Raman allows easy probing of numerous features, including: - the nanotube diameter (for SWNTs), the degree of structural defects, the CNT alignment, CNT agglomeration, electronic structure (metallic or semi-conducting) of SWNTs and number of walls to name a few. While there have been numerous reports and books related to Raman analysis of CNTs, here we will only provide a brief highlight of the useful information relevant to this project.

Raman spectra of materials can be acquired using a range of lasers however, with some materials, certain vibrations can only be detected when the molecules are excited with specific laser wavelengths. Within this project SWNTs are mainly used, and these can be analysed using different laser frequencies. However, they will only display clear signals from their weaker Raman vibrations when being analysed using a laser energy which is equal to the energy of the SWNTs resonance excitation; this varies depending on the nanotube’s type and diameter (Kataura et al. 1999). Figure 3-7 plots a typical Raman spectra that could be expected when analysing SWNTs that possess either metallic or semi-conducting properties.

The first feature of the Raman spectrum in Figure 3-7 is the region of the radial breathing mode (RBM), unique to CNTs with only single or double walls. It consists of a series of peaks corresponding to the radial contraction-expansion of the tube and whose positions vary with the SWNT diameter. The RBM can display broad peaks and narrow peaks, depending on the distribution of the CNT diameters across the sample, usually within the region of 100 to 500 cm\(^{-1}\). The peak positions correspond to the tube diameters and in some cases when there are more than one peak, it could indicate the presence of the inner tube and outer tube of the DWNT (Li et al. 2003; Souza Filho et al. 2006). The RBM can be used to estimate the nanotube diameter using the simple formula for bundled CNTs (Dresselhaus et al. 2005; Costa et al. 2008; Li et al. 2003):
where $\omega_{RBM}$ is the Raman frequency of the RBM peak, $d_t$ is the calculated CNT diameter and A & B are parameters that can be determined experimentally. For a typical CNT bundle $A = 234 \text{ cm}^{-1}$ and $B = 10 \text{ cm}^{-1}$, although these values can change with laser wavelength but can be calculated experimentally (Dresselhaus et al. 2005; Jorio et al. 2001). This change in Raman vibrational peak location with laser wavelength is common in carbon materials; this is called “dispersive” behaviour. An example of this type of behaviour can be found at the D-band at 1350 cm$^{-1}$ (explained later), where the frequency changes by 53 cm$^{-1}$ when changing the laser energy by 1 eV (Dresselhaus & Dresselhaus 2002; Thomsen & Reich 2000; Tuinstra 1970).

Ignoring the silicon and silicon dioxide peaks, denoted by the ‘*’ in Figure 3-7, the next two peaks on the spectrum are the D-band and G-band, which correspond to two different types of vibration within the graphitic structure of the CNT. The D-band is normally found around 1350 cm$^{-1}$ within a Raman spectrum (taken with a laser energy of 2.41 eV) and is a result of a vibrational mode of the symmetrical expansion/contraction of each of the graphitic carbon hexagons [see Figure 3-8] (Dresselhaus et al. 2005). This mode is forbidden in perfect graphite, as the vibration of each adjacent hexagonal ring of carbon effectively cancel each other out. This results in it only being existent in the
presence of crystal disorder, such as pentagons and defects within the CNTs graphitic structure, including the ends of tubes (Ferrari & Robertson 2000). The quality of the CNTs is typically assessed by comparing the peak intensity of the D-band to the G-band, given as a ratio of D to G, where values less than 10% are considered to be of high quality (Flahaut et al. 2003). This D-band/G-band ratio check is a quick and simple method used to ensure the quality of the CNTs before using them for this project. This guaranteed that only low defect tubes were used, avoiding issues like that seen in Figure 2-3. The G-band itself, found between 1550 to 1605 cm\(^{-1}\), is the main Raman feature present when observing graphitic structures. For SWNTs, it is split into two modes, where the lower frequency component (G\(_-\)) is associated with vibrations along the circumferential direction and the higher frequency component (G\(_+\)) is associated with the vibrations along the nanotube axis (Costa et al. 2008). However, in the presence of DWNTs it has been seen to display four peaks: G\(_+\) and 3 G\(_-\) modes (Li et al. 2003). The G-band is normally located at 1581 cm\(^{-1}\) and not dispersive (Dresselhaus et al. 2005), however, when CNTs are analysed in bundles or if there is a high concentration of defects, it can be shifted to a higher frequency. This is a direct effect of bundled CNTs interacting with each other (Ferrari & Robertson 2000). These bundling interactions have also been seen to affect the RBM, which could lead to slightly misleading calculations of the tube diameter (Yu & Brus 2001).

Figure 3-8 – These two schematic diagrams show the nature and directions of the bond vibrations within the D-band (disorder band) and the G-band (graphitic band) (Ferrari & Robertson 2000). Due to the nature of the D-band vibration it is forbidden in perfect graphite and is only allowed at sites of crystal defect, for example at the CNT ends.

The M-band found at around 1750 cm\(^{-1}\) only appears in the presence of bi-layer graphene (BLG) or few-layer graphene (FLG) as found in double-walled carbon nanotubes (DWNT) and multi-walled carbon nanotubes (MWNT, with only a few walls) (Cong & Yu 2010). This is attributed to a vibrational overtone of graphite (combination of vibrational modes), which would normally be found at 867 cm\(^{-1}\). Further features of DWNTs can also be seen around 1950 cm\(^{-1}\) as a very weak signal in the longitudinal optical (LO) and longitudinal acoustic (LA) branches, called the ‘LOLA’ or ‘iTOLA’ region; this peak has been associated with using acid treated DWNTs (Ellis 2006; Rao et al. 2010).
The final Raman features seen from CNTs are overtones, an example can be seen in Figure 3-7 labelled as G’, which corresponds to the D-band overtone (2D); this is sometimes called G' peak as it is the second most intense peak after the G-band (Dresselhaus et al. 2005). Common overtones are ‘2D’ and ‘2G’ peaks which correspond to the D-band and the G-band where the ‘2’ highlights that it has a Raman shift of twice the original band. Overtones are normally difficult to observe within Raman spectra (especially 2G), due to the lower probability of the double vibrational event needed for these modes, they are normally indistinguishable amongst signal noise. 2D is slightly more than just an overtone, as it involves not one but two vibrational phonons causing the peak to be twice the intensity of the D-band (Rao et al. 2010). This two vibrational phonon process is also known as a double resonant Raman process, which unlike the D-peak, is not cancelled out and continues to a second stage of the vibration, meaning it is allowed in the graphitic structure (Ferrari et al. 2006).

Although there are individual effects which can affect the peak width and location for each of the discussed CNT Raman features, there are situations which can affect the spectra as a whole. Across all of these peaks in the CNT’s Raman spectrum, pristine CNTs, i.e. with no defective sites along the length of the tube or any contaminate coating, will typically have a spectrum with well-defined, narrow peaks and with low background signal intensity. The presence of amorphous carbons and other such impurities will promote photon/phonon scattering through the sample, resulting in both broadening of the peaks and an increase in the level of background signal (Ferrari & Robertson 2000). In most cases, it is good practice to remove this background signal from a Raman spectrum, to allow more precise analysis of the peak heights and areas, however the background levels and peak full-width half-maximum (FWHM) (a measure of peak width), can provide a good indication of level of contamination or amorphous content in the samples.

3.3.1 Polarised Raman Spectroscopy

Polarised Raman spectroscopy is much the same as standard Raman spectroscopy except it measures the spectra in one plane of wave oscillation. Using a single plane polariser to polarise both the incident laser light and then the backscattered signal, it measures Raman signals generated in specific planes of orientation. Although there are numerous applications of this orientation dependant technique, for this project it has been widely used to measure the degree of alignment of an array of CNTs (Hwang et al. 2000; Gommans et al. 2000). By rotating the aligned array of CNTs from perpendicular to parallel to the plane of incident polarised light, all Raman features associated with
the nanotubes drastically increase from a minimum to a maximum. This orientation dependence in the Raman signal is the result of the CNTs extreme length to width ratio, leading to a one-dimensional quantum confinement of the electrons within the CNT (Rao et al. 1997). This leads to an orientation dependence of the absorption of light. With this in mind, Gommans et al. (2000) worked a simple Lorentzian oscillation model to show that the CNT Raman signal intensities increase and decrease, depending on orientation, in a manner that is proportional to \( \cos^4 \theta \) (for an ideal parallel CNT array), where \( \theta \) is the angle between CNT orientation and the laser’s plane of polarisation. This was confirmed experimentally by Hwang et al. (Hwang et al. 2000) [see Figure 3-9].

![Figure 3-9](image)

**Figure 3-9** – A demonstration of how the intensity of the CNT Raman features are expected to change in intensity, with respect to the excitation laser's plane of polarisation in relation to the orientation of the aligned CNTs. The plotted curve equates to \( \cos^4 \theta \).

For this project, polarised Raman is an essential method for assessing the alignment of the CNT arrays produced by electrospinning, where this technique will be used to check the alignment of the CNTs in Chapter 5.4. By measuring the intensity of a Raman feature unique to CNTs, such as the RBM, (as opposed to the D-band or the G-band which may also arise from graphitic or amorphous carbon debris), as a function of the sample orientation, will provide a true assessment of the degree of CNT alignment within our samples. The advantage of this technique is that it is non-invasive and that most other techniques involve imaging the CNTs, which can both prove difficult (especially when embedded within a polymer, due to lack of contrast between the two carbonaceous materials) and only show local orientation (Loos et al. 2005).
3.4 Small Angle X-ray Scattering Analysis

Small angle X-ray scattering (SAXS) is a technique where the elastic scattering of sub-nanometre wavelength X-rays from a sample is recorded at very low scattering angles (0.1° - 10°). This is particularly useful when studying the structural information of partially-ordered materials, particularly polymers and biological samples, which show structure over the nanometre scale (Glatter & Kratky 1982). SAXS is particularly useful in this project, as it allows an investigation into the polymer/surfactant/carbon nanotube interfaces, giving insight into how the loading of the CNTs into polymer nano-fibre systems affects the polymer structure and as such the mechanical properties of the material. Currently there is limited SAXS analysis of CNT systems in literature, possibly due to the scarceness of equipment availability, and its expertise. Despite this, we were able to gain access to the I22 SAXS beamline at the Diamond Light Source, in Didcot, and perform experiments to give us a crucial insight into the nano-structure.

The SAXS technique works by illuminating a sample with monochromatic X-rays, typically produced from synchrotrons known for their high intensity, high flux, high resolution and minimum beam divergence. As the incident beam of X-rays penetrates through the sample, a fraction of them are scattered. In this case, only the X-rays that are scattered to small angles are of interest, and a detector is positioned a few metres behind, allowing for an image of the diffraction pattern to be taken [see Figure 3-10]. Once the image has been acquired, the intensity of the diffraction pattern features can be measured as a function of angle (from the centre of the un-scattered beam spot in the centre). This produces a spectrum displaying peaks at specific diffraction angles, which can be related to the structure of the sample being analysed.

![Figure 3-10 – A schematic diagram of the basic working of a SAXS analyser, demonstrating a typical set-up and a crude example diffraction pattern that would be seen in a diffraction image.](image-url)
3.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a form of thermal analysis whereby changes in a samples weight are measured as a function of temperature (at a constant heating rate), or as a function of time (with a constant temperature or mass loss), in a controlled atmosphere (Coats & Redfern 1963). Typically, TGA is used to heat a sample at a fixed temperature rate, all the time while accurately measuring the weight of the sample. As the temperature increases, the sample will thermally degrade, whether that degradation be evaporation, sublimation or oxidation, to name a few. In some cases (especially when analysed in an oxidative atmosphere), a thermal degradation reaction may incur a weight gain, such as when a metal forms an oxide. At the end of the process, a plot is generated of sample weight against temperature, whereby reductions/gains can be measured as a percentage of the original sample’s weight at specific temperatures. The main benefit of TGA is the ability to conduct accurate analysis with only a few milligrams of material, reducing waste.

When using the TGA for comparative analysis between samples, it is important to ensure that sample sizes are similar. This is because the rates and temperatures of thermal decompositions can vary with both sample size and sample surface area. This is particularly the case when analysing in an oxidative atmosphere, where a large sample surface area allows for more oxidation reactions to take place simultaneously, and a small surface area could slow reaction rates, obscuring other reactions and increasing apparent reaction temperatures. Equally this is the same for the heating rate, where heating too fast may fail to reveal slower reactions, or reactions with several steps.

TGA can be used to analyse CNTs, providing information such as: sample CNT content, CNT quality, and CNT residual catalyst content. It has been widely reported how the TGA of CNTs in an oxidative atmosphere can give indication as to their quality, based on the temperature at which they oxidise at (Mansfield et al. 2010). This is because poorer quality CNTs having an increased occurrence of defective sites their graphitic structure, where the oxygen can attack the carbon, producing CO and CO$_2$. Typically CNTs can oxidise anywhere between 400°C and 700°C (Zhang 2003; Pang et al. 1993; Rinzler et al. 1998; Chiang et al. 2001), depending on their quality. This signifies that, within this project, comparing the oxidation temperature of the CNTs both before and after electrospinning can give indication as to any damage that could have been introduced. Further still, this will also allow the assessment of any CNT purification technique, such as steam purification (which was previously discussed in chapter 2.3.3), revealing any improvement in samples oxidation temperature (Rinzler et al. 1998). Using a TGA to assess any residual catalyst and amorphous carbon content is also widely used in determining the CNT sample purity, where typically amorphous carbons will burn at slightly lower temperatures and metal catalysts will remain as a residual (Shi et al. 1999).
3.6 Time of Flight Secondary Ion Mass Spectroscopy

Developed in the 1960s, time of flight secondary ion mass spectroscopy (ToF-SIMS) uses an ion gun (loaded with elements such as bismuth, gallium and caesium), to blast secondary ions and molecules from the sample surface. The time it takes for these ions to reach the detector depends on their atomic weight, and as such the sample atomic or molecular composition can be determined. Typically, the ion gun will fire in pulses at known times, upon each ion’s impact with the sample, sample ions and molecules will be ejected, in much the same way like splashing the surface of water, with larger molecules being ejected further from the impact site [see Figure 3-11]. In most cases, these ejected ions or molecules will be either positively or negatively charged (depending on if they have left electrons in the sample or taken extra electrons). ToF-SIMS exploits this and uses electrostatic attraction to pull the ejected matter towards a detector (in either positive or negative mode depending on the ions wanting to be analysed). Because the exact time the ion gun was fired is known, the time each ion takes to reach the detector can be calculated, where heavier ions will take considerably longer to reach the detector. This enables precise measurement of the ejected ion or molecule’s weight, resulting in a spectrum where mass is plotted as a function of intensity [see Figure 3-12 for example spectra].

![Figure 3-11](image)

**Figure 3-11** – A schematic diagram of the workings on ToF-SIMS, where the primary ion from the gun impacts the sample is the highest sample damage, resulting in individual ions ejected from the sample. As the distance from the original impact site is increased, damage is reduced and larger molecules are ejected.
The ion bombardment during the ToF-SIMS analysis can be paired with a heavier ion bombardment process, effectively milling the sample during the analysis. This allows for a double barrel effect whereby the sample can be analysed as a function of depth, otherwise known as depth profiling (Woodruff & Delchar 1994). This technique is particularly useful when analysing boundaries between two different materials, or to probe how a material differs under the surface. Due to the nature of the process in which the wetcake is produced, it is thought that residual catalyst or ceramic material may be residual inside the wetcake particles. Utilising ToF-SIMS and the depth profiling feature enables the full analysis of Thomas Swan’s wetcake product as a function of depth, allowing insight into the chemical make-up of the wetcake particles, and revealing any residual contaminate within. The results from this will be presented in Chapter 4.

Figure 3-12 – An example of typical ToF-SIMS spectra. These spectra were acquired of DNA- and RNA-functionalized SWNTs, corresponding to (A) and (B) respectively (Kim et al. 2014). In our case, this spectra is only available on the equipment itself, and for analysis is converted into another plot revealing the frequency on a molecule against time.

3.7 Conclusions

Each of the main analytical techniques used in this thesis have been introduced, highlighting their strengths and proper implementation techniques. Understanding the significances in the advantages and disadvantages of each analytical technique, enable proper and accurate analysis of any samples throughout this project. Although each technique is limited in the information it can provide, combining various techniques allow for full sample characterisation. This thesis continues with the characterisation of Thomas Swan’s ‘wetcake’ CNT product using the various modern analytical techniques explained in this chapter, verifying that the nanotubes are of the necessary low defect and high linearity needed for alignment within polymer nano-fibres.
4 Thomas Swan’s Single Walled Carbon Nanotubes

4.1 Introduction

As well as being the primary sponsors of this project, Thomas Swan & Co. Ltd. are also providing their own high quality manufactured CNTs for alignment within the polymer nano-fibres. Their Elicarb single wall CNT wetcake product is manufactured using a fully-scaled fluidized-bed chemical vapour deposition (CVD) process, which was developed in collaboration with the University of Cambridge (Li, Kinloch, Shaffer, et al. 2004). The manufacturing process employs microscopic porous ceramic magnesium particles, filled with an iron catalyst, allowing the growth of large volumes of CNTs. Once grown, the porous particles are removed in a hydrochloric acid bath, followed by a deionised water wash. This then leaves the CNTs in an aqueous scaffold, known as a ‘wetcake’ particle, which is the final product supplied for this project [see Figure 4-1]. A small sample of the wetcake (product number PR0920, batch 94890/591), was analysed using various techniques, in order to gain full characterisation of the material and chemistry within it. This then ensured effective implementation of the nanotubes within aligned nano-fibres by identifying any contaminant which could hinder the process, or alter any properties of the final composite material.

Figure 4-1 – A photograph of Thomas Swan’s CNT wetcake product, noting its caviar-like particulate appearance.
The characterisation techniques used were: - scanning electron microscopy (in order to probe the morphology of the CNTs within the wetcake), scanning transmission electron microscopy (to study the catalysts, contaminates, nanotube integrity and wall thicknesses), Raman spectroscopy (to measure the CNT diameters and quantify the level of structural defects), thermogravimetric analysis (to measure the CNT and residual catalyst content within the wetcake), energy-dispersive X-ray spectroscopy (to reveal and quantify the elemental composition of the wetcake, including any contaminant), and time of flight secondary ion mass spectroscopy (to study chemical compounds as a function of depth, through a wetcake particle).

### 4.2 Characterisation

#### 4.2.1 Scanning Electron Microscopy

Scanning electron micrographs where acquired on a Jeol JSM6610LB SEM (based at the Rutherford Appleton Laboratory), of a small particle of the wetcake material, which was previously squashed and dried in an oven at 100°C, for an hour. This ensured that there was no residual water within the material, minimising microscope contamination during evacuation, as well as creating a flatter surface for imaging. This flat surface allowed focused images to be taken, revealing a crusty layer on the outside of the sample, which initially did not look like carbon nanotubes, but rather some other contaminant within the solution, possibly amorphous carbon or remaining materials from the production process [see Figure 4-2]. In order to image within the wetcake, the dried sample was cut with a scalpel [see Figure 4-2, A], exposing the carbon nanotube scaffold-like structure under the surface [see Figure 4-2, B].

Examining the CNTs within the wetcake more closely [see Figure 4-3] allowed us to visually probe the quality of the material, getting indication to the tube lengths, diameters and linearity. Visually, the tubes appear to contain very few defects, with no obvious signs of kinks or diameter variation. They were generally found as nano-ropes (several CNTs bundled together in an aligned structure, held together by van der Waals forces), of lengths greater than 4 µm with no visual signs of any clusters of impurities or defective tubes. Although these results on the condition of the CNTs were not as definitive as other techniques, SEM provided a quick indication that the material was of a promising quality for alignment within nano-fibres.
Figure 4-2 – These two micrographs show (A) the dried cut CNT wetcake sample affixed to a carbon dot, and (B) a close up of the area marked by the red rectangle in the image A, displaying what appears to be a non-CNT outer shell and a CNT scaffold-like structure underneath.

Figure 4-3 – A close up of the CNT scaffold-like structure located under the wetcake surface, demonstrating; (A) the traced lengths of the CNT bundles or nano-ropes to be around 3-4 µm (orange lines), and (B) the diameter of the CNT bundles/nano-ropes averaging around 32 nm ± 4 nm.

4.2.2 Scanning Transmission Electron Microscopy

In order to gain further insight into the structural quality of the CNTs, scanning transmission electron microscopy was used for the significantly higher imaging resolution and structural insight it can provide. Analysis was performed on a small particle of the wetcake material, which was dispersed in methanol by ultrasonic bath irradiation. This was then filtered through a holey-carbon grid (from Agar Scientific) and held at 120°C for 10 minutes, to evaporate any remaining moisture from the sample, prior to insertion into the high vacuum within the microscope. The high resolution of the Hitachi HD-2300A microscope used at the University of Surrey, allowed the individual walls of the CNTs
to be seen [see Figure 4-4], revealing that the majority of the CNTs in the wetcake had either a single wall (SWNT) or double walled structure (DWNT). It was also seen that the individual SWNTs have diameters ranging from 1 – 2.5 nm, whereas the DWNTs had diameters ranging from 2 – 5 nm. As with the SEM micrographs, these images presented little/no sign of the presence of any defects along the lengths of the CNTs, indicating that they are of the required high quality.

Further probing of the sample using some of the equipment’s other techniques, such as Z-contrast imaging, revealed a relatively high presence of residual iron catalyst in the sample. Although the wetcake had been acid washed in an attempt to remove residual metals, this remaining iron was encased within the tip of the CNT (from the growth process), and as such had a protective carbon layer allowing it to survive the acidic processing (Baker 1989; Pumera 2007). Although this residual iron content will add unnecessary weight to any final composite, reducing the overall strength to weight ratio, it is not clear if this residual metal will have any other effects on a final composite material, whether that be negative or positive. However, Grimes et al. (2001) found that having the residual metal catalyst within a CNT composite can increase the conductivity of the overall material by several orders of magnitude. It was suggested that this increase in conductivity with the presence of the iron catalyst was a result of an increase in available conductive paths through the affected CNT (Grimes et al. 2001). This means that finding residual iron catalyst particles within the CNTs used in this project could have beneficial effects on the conductivity of the overall composite material, a property that is essential for high performance multi-role composites.

Figure 4-4 – A high-resolution bright-field image, revealing that the majority of CNTs are double-walled (indicated by the double lines seen when the image is magnified), with some SWNTs also present. There was little/no evidence seen of any defects along the length of these tubes.
4.2.3 Raman Spectroscopy

Raman spectroscopic analysis was conducted at the University of Surrey using a Renishaw micro-Raman spectrometer, equipped with the 782 nm (red) laser, which was found to be better suited (in resonance) for analysing the CNTs in the wetcake than the 514 nm (green) laser. The wetcake material (un-dried) was placed on top of aluminium foil (to maximise the Raman signal scattered back into the detector), and analysed at room temperature; the resultant spectrum is shown in Figure 4-5.

The initial appearance of the Raman spectrum suggests that the CNTs within the material are of high purity, with little amorphous carbon content (indicated by the low background level and the tall sharp peaks, where high levels of amorphous carbon would have the opposite effect) (Ferrari & Robertson 2000). Normally, it would be good practice to remove the background from a Raman spectra to allow accurate peak fitting, however in this case in the interests of assessing the sample it has not been removed, nor would it have been necessary to be removed.

Figure 4-5 – The Raman spectra acquired from the CNT wetcake when using the 782 nm laser (red). The largest plot (A), displays the full Raman spectra, with all regions of interest and key peaks labelled. A detailed region of the radial breathing mode (B), from which the CNT diameters were derived is also shown. All values of CNT calculated were done so using Equation 3-8, and had an associated error of $\pm 0.05$ nm. A zoomed plot of the G peak is also displayed (C), displaying how it splits into a transverse and a longitudinal mode, typical of SWNTs (Dresselhaus et al. 2005).
Focusing on the first feature of the obtained Raman spectrum, seen in Figure 4-5 (B), it corresponds to the region of the RBM, relating to the radial contraction-expansion of the tube [see Chapter 3.3]. The RBM shown displays four distinct broad peaks, indicating that there are four distinct general nanotube diameters, either as SWNTs or as part of a DWNT. By using Equation 3-8 (page 44), the RBM was used to calculate the tube diameters to be 1.61 nm, 1.23 nm, 1.07 nm and 0.93 nm, each with an error of ± 0.05 nm. When analysing the RBM of a DWNT, the tube diameters typically have a difference of approximately 0.68 nm, corresponding to the inner tube and outer tube (Li et al. 2003; Souza Filho et al. 2006). This signifies, that from our calculated RBM corresponding diameters, 1.61 nm and 0.93 nm must be the inner and outer tubes of a DWNT, with a size difference equivalent to 0.68 nm.

The next two peaks on the main spectrum are the disorder band (D-band) and the graphitic band (G-band). The quality of the CNTs can be related to the peak height of the D-band compared to the G-band (Dresselhaus et al. 2005). Figure 4-5 illustrates that, for this sample/batch, the D-band is considerably small compared to the G-band, with an average D to G ratio of 0.36, indicating that the CNTs have a low number of defects. Note: the D to G ratio will vary throughout this thesis with CNT batches, and will be re-measured for each batch.

![Graph showing Raman spectrum with labels and peaks](image)

**Figure 4-6** – These plots reveal the G-band splitting and the resultant Lorentzian fitted curves, as a direct result of the presence of DWNTs when conducting Raman analysis using a 782 nm laser. Each of the peaks have been labelled as to whether they are G+ or G- phonon vibrations.
The G-band is the most intense signal when analysing graphitic structures. Normally, for SWNTs the G-band consists of two peaks: G+ and G-. Whereas DWNTs have been seen to display four peaks: G+ and G modes (Li et al. 2003). This ‘splitting’ effect of the G-band can be seen in Figure 4-6, where the different signals have been modelled using the data analysis software ‘Origin 9.1’. The splitting of the G-band into peaks G+ and G, correspond to how the vibrational phonons propagate along the nanotube and around it [Figure 4-5, plot C] (Dresselhaus & Dresselhaus 2002). Closer inspection of the G-band reveals evidence as to how the wetcake is comprised of SWNTs and DWNTs. These four peaks are not well resolved, indicating a mixture of DWNTs and SWNTs, rather than one or the other. The G-band is normally located at 1581 cm⁻¹ however, in Figure 4-5, the G-band peak has been shifted to a higher frequency of 1586 cm⁻¹, which is a direct effect of bundled CNTs interacting with each other (Ferrari & Robertson 2000). The bundle interactions have also been seen to affect the RBM, which could lead to slightly misleading calculations of the tube diameter (Yu & Brus 2001).

The M-band found at around 1750 cm⁻¹ only appears in the presence of bi-layer graphene (BLG) or few-layer graphene (FLG), such as found in double-walled carbon nanotubes (DWNT) and multi-walled carbon nanotubes (MWNT, with only a few walls) (Cong & Yu 2010). This then means it is absent when scanning pure single-layer graphene (SLG), in the form of SWNTs. Although the signal in this result is weak, it confirms the presence of DWNTs, as seen in the STEM bright-field image in Figure 4-4. Further evidence of DWNTs can also be seen around 1950 cm⁻¹ as a very weak signal in the longitudinal optical (iTO) and longitudinal acoustic (LA) branch, called the ‘iTOLA’ region; this peak has been associated with surface vibrations of acid-treated DWNTs from the carbon hydrogen bond (Ellis 2006; Rao et al. 2010). Although these CNTs are not intentionally acid treated, acid is used to remove residual catalyst during manufacture, and would be expected to have a minor effect on the CNTs. This acid treatment effect on the CNTs could add OH groups to the CNTs at defective locations. Where OH groups are hydrophilic, it could promote CNT solubility when it is later required to disperse them for electrospinning. This will not only increase their dispersibility within an aqueous polymer solution, but more importantly increase their coherence to polymer chains in polymeric systems due to the introduction of hydrogen bonding (Dyke & Tour 2004; Moniruzzaman & Winey 2006). This would improve the mechanical performance of any final composite material by enhancing reinforcement-matrix interaction (Almgren et al. 2009). Furthermore, these OH groups could also be the reason why the wetcake particles hold so much water, as a result of the hydrogen bonding between these groups and the H₂O molecules. The water content in the wetcake is explored in the next chapter.
4.2.4 Thermogravimetric Analysis

TGA was performed on the wet cake material to identify the quantity of materials within the product [see Figure 4-7]; this was conducted on a TA Q500 TGA at the University of Surrey within the materials laboratory, using both nitrogen and air atmospheres to run two tests. Comparing the two results will highlight the volume of CNTs contained within the sample, as the CNTs should only burn in the presence of oxygen (Pang et al. 1993). The rate at which the CNTs burn off can be directly related to presence of defects within the CNTs (Mawhinney et al. 2000), as defect sites within graphitic structures decrease the oxidative stability of the material (Bom et al. 2002). This form of analysis should also provide information as to the water and catalyst content, enabling accurate formulation of the electrospinnable solutions later in this project.

![TGA plots](image)

Figure 4-7 – The TGA plots obtained from the wetcake material in both air and a nitrogen atmospheres. The average material content was calculated to be 94.8 ± 0.1 % weight of water (across both air and nitrogen), where analysing in air found there to be 3.7 ± 0.1 % weight fraction of CNTs and a residual weight of 1.5 ± 0.1 % which is potentially residual metal catalyst and amorphous carbon. The slight difference between the curves with respect to water is the result of water evaporation from the sample before analysis.
Across the two results there was a minor discrepancy in the measured water content [see Figure 4-7]. This was a result of a small percentage of the water content evaporating before it entered the equipment (resulting in slightly different values shown). The variation in the water evaporation temperature was a result of a slightly different sample size. However, on average, the wetcake contained 94.8 ± 0.1% weight fraction of water (across both air and nitrogen). The CNT content was deduced using the TGA data acquired in air, where the CNTs oxidise after the water content has evaporated. The wetcake was found to consist of 3.7 ± 0.1% weight fraction of CNTs, with final a residual weight of 1.5 ± 0.1% (which is potentially residual Iron catalyst within the CNTs). The residual material could not be analysed directly after the analysis due to the potential damage to the TGA’s platinum sample pans that attempting to remove it could cause. However, further chemical analysis in the next section by another technique confirms this residual to be the catalyst.

In this test it was found that the CNTs begin to burn off at 550°C in air, with an oxidation peak at 593°C. This is lower than other reported values of 600°C – 695°C for high quality CNTs (Zhang 2003; Pang et al. 1993). This could be due to the presence of the catalyst, where the metal catalyst used to grow the CNTs, can reactivate when exposed to certain conditions and work in reverse to break down the CNTs, effectively ‘unzipping’ them (Stolohan et al. 2006; Baker 1989; Figueiredo et al. 1988). The destructive catalyst reactivation could be avoided by purifying CNTs further, removing any residual catalyst, this would minimize any CNT damage during baking when trying to remove polymers from aligned nanotubes, or when curing a composite (as discussed in section 2.3.3).

### 4.2.5 Energy Dispersive X-ray Analysis

In order to provide clarification as to the potential elemental composition of the TGA residuals seen, EDX was utilised within the JEOL SEM based at the Rutherford Appleton Laboratory. Several random points on the surface of the sample were chosen, making sure not to take measurements too close to any edges or features as the interaction are within the sample could include these in the analysis (as explained in Chapter 3.2). The results from these points were compared [see Figure 4-8, image A], looking for any form of potential contaminant. All results were found to be consistent with each other, with no obvious sample irregularities across several sample areas, their average shown in Figure 4-8. The main features of Figure 4-8 only become visible when plotting on a logarithmic scale, due to the high carbon peak intensity. The calculated percentage weights of elements are: carbon 98.58 ± 0.05 %, chlorine 0.32 ± 0.02 %, iron 0.62 ± 0.03 %, silicon 0.41 ± 0.01 % and sodium 0.07 ±
0.01 %. The elements detected other than carbon, would contribute to the residuals seen in the TGA results. However, these results reveal significantly lower quantities than that suggested by the TGA. This could be a result of a poor local representation of the sample, as opposed to the bulk material which the TGA analysis, or it could be that the electron beam is failing to interact with most of the sample.

The iron detected within this sample would be residual catalyst from the manufacturing process. Whereas the sodium and chlorine, which could also contribute to the residue, is potentially in the form of sodium chloride (salt), a possible contaminant which entered the sample either during the CNT washing process or in the water that the CNFs are suspended within. The silicon could be a result of silica particles being created during the acid washing process, potentially caused by sample abrasion against the glass of the containers used. To guarantee that silicon peak was not a result of the silicon substrate used the substrate was changed and the sample reanalysed. Changing the substrate for aluminium saw no change in the results, confirming silicon’s presence in the sample.

![Figure 4-8 – The resultant plot when an EDX was taken of the imaged area (A), here the characteristic peaks of main elements located within the sample were measured and quantified, including: carbon 98.58%, chlorine 0.32%, iron 0.62%, silicon 0.41% and sodium 0.07%.

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4.2.6 Time of Flight Secondary Ion Mass Spectroscopy

In order to build a more accurate insight into the chemistry of the surface of the wetcake particles, where the CNTs were observed to be under a surface layer in Figure 4-2, a depth profile ToF-SIMS was performed at the University of Surrey using an ‘Iontof: ToF.SIMS’\(^5\). Once a particulate was compressed and dried within an oven, it was mounted upon a silicon wafer. An area of 98 x 98 µm\(^2\) was then scanned with a bismuth source at a potential of 25 keV, followed closely by sputtering with a caesium source at 3 keV. As previously explained in Chapter 3.6, ToF-SIMS works by accelerating an ion towards the surface of a sample, the resulting impact ejecting both positively and negatively charged ions which are collected (depending on the detector set-up). The time taken to travel the known length of the detector determines the atomic mass, which can be compared to a library of data. The scan was performed on two similar areas in both the negative ion spectrum [see Figure 4-9] and positive ion [see Figure 4-10] spectrum, giving an accurate indication as to the elemental and chemical composition of the negatively and positively ejected ions from the sample surface. There were a number of universal troughs found throughout both spectra (especially the negative spectrum, at 2000 and 5400 seconds); these are due to miss-fires of the ion gun, caused by a drop in the source potential (which was witnessed during testing).

![Depth Profile Over 6000 Seconds of CNT wetcake (Negative Ion Spectrum)](image)

**Figure 4-9** – This figure plots the ion count within a depth profile, obtained from an Iontof ToF.SIMS\(^5\) of the wetcake surface while scanning in the negative ion spectrum. While the spectrum is considerably weak due to the nature of the sample (low counts), it reveals the presence of various hydrocarbons, sodium, chlorine and silicon. Reading that fall off the bottom of the graph were readings of zero counts, this was especially the case for CH\(_3\) and Ca.
Throughout both Figure 4-9 and Figure 4-10 there were strong signals from both calcium and from magnesium and a weak signal from aluminium, whereas EDX failed to detect these metals. These contaminants could be residue from the ceramic catalyst holding beads used in the CNT growth process. It is also important at this point to note, that both the spectra had to be plotted as a logarithmic value of the counts detected. This was because the carbon signal was considerably higher than anything else, suggesting that any contaminants were very small in content. Both spectra show various multiples of carbon, such as C₂ or C₁₂ etc. (although not all data has been displayed on the graph), which was a direct result of fragments of CNT being ejected upon ion impact (Polizu et al. 2006). These multiples of carbon generally speaking become less common with increasing values of carbon atoms, this is simply due to the small probability that the sample with break into pieces of these exact sizes. Due to the violent nature of the ion bombardment, it is far more likely that smaller, in most cases single, atoms will be ejected, over larger molecules [see Chapter 3.6].

![Graph](image)

**Figure 4-10** - This figure plots the ion count within a depth profile, obtained from an IonToF ToF.SIMS® of the wetcake surface while scanning in the positive ion spectrum. This spectrum once again reveals the presence of various hydrocarbons, chlorine, silicon, iron, magnesium, sulphur and fluorine. The features seen at 2000 and 5400 seconds, are a result of miss-fires of the ion gun during analysis. '37Cl' relates to the isotope of chlorine, ³⁷Cl.
The negative ion spectrum in Figure 4-9, confirms the presence of hydrocarbons of various types (not all types are shown on the graph, just the strongest signals which were CH, CH$_2$ and CH$_3$) which were also detected in the iTOLE peak of the Raman spectrum in Figure 4-5 (page 56), confirming that some of the nanotubes have been functionalised during the acid washing process. Although sodium and chlorine where both detected as in the EDX [Figure 4-8, page 61] analysis, sodium chloride had only a weak signal, suggesting that there was only a low presence of salt. Silicon was again also detected, supporting the EDX results; this further suggests that silicon or silica is being introduced to the sample during the acid washing process from the glassware.

Figure 4-10, the positive ion spectrum, provided much stronger signals throughout, which displays further strong evidence for the presence of hydrocarbons, as well as OH groups, once again suggesting CNT functionalisation during the acid washing process. As the surface was profiled, it was seen that contaminants, such as chlorine (as well as its isotope $^{37}$Cl) and fluorine (F) fall in intensity, suggesting that the there is a higher concentration of these elements on the surface. However, it was not clear if this could be a natural formation of the wetcake surface, or created during the compressing and drying process prior to the analysis. The compressing and drying process could have possibly drawn these contaminates to the materials surface during water extraction and evaporation, giving the impression that they are on the surface. As the wetcake must be broken up and fully dispersed before it can be aligned, it was deemed unnecessary to determine if these contaminates where on the surface or not, this is because ultimately the contaminants would be dispersed within the sample regardless whether they originated from the wetcake surface or from within it. As a result no further testing was done.

4.3 Conclusions

Various analytical techniques were employed to characterise Thomas Swan’s wetcake product. It was found that the carbon nanotubes (CNTs) within it show little evidence of defects, while being considerably long, with bundled lengths $>$ 2 $\mu$m. More importantly, the CNTs demonstrated a consistently high linearity, which is ideal for producing highly aligned arrays within polymer nano-fibres. It was also found that, during the manufacturing and washing process, several contaminants are introduced to the material, including silicon, sodium and chlorine, which could have undesirable effects such as inducing agglomerations (Li et al. 2008). It was also found that, during the acid washing process, the CNTs gain a small degree of functionalization via the introduction of OH (oxygen-
hydrogen) and hydrocarbon groups to their defects. Which, where OH groups are hydrophilic, could promote CNT solubility when it is later required to disperse them for electrospinning. These OH groups could also be the reason why the wetcake particles hold so much water, as a result of the hydrogen bonding between these groups and the H\textsubscript{2}O molecules. However as there are few defects on these tubes, this was found to be rather low in occurrence. There was some concern over the potential decomposing effects of residual metals within this product especially during baking (Baker 1989; Stolojan et al. 2006). However the only true way to remove all of these metals is to use strong acids, which will damage the CNTs at the same time, potentially doing more harm than good to the final properties of a sample.

Across the different analytical techniques that were used to characterise the wetcake product, the majority of the conclusions agreed with one another, with only one disagreement. Scanning electron microscopy (SEM) suggested that the CNTs within the wetcake were of high linearity, with no obvious defects. It also revealed how the surface of the wetcake particles could contain other materials, and appeared to be a form of skin that the CNTs were located under. Scanning transmission electron microscopy (STEM) agreed with the SEM images, and revealed that some of the CNTs within the wetcake were actually double-walled (DWNTs). It was also suggested that residual metals remained within the sample after the manufacturing processes. Raman spectroscopic analysis found that the CNTs were indeed of high quality and consisted of a mixture of single and double-walled nanotubes, as the electron microscopy techniques had suggested. Evidence was also found to suggest that a small mass of the CNTs were functionalised. Thermogravimetric analysis (TGA) and energy dispersive X-ray analysis (EDX), both confirmed that the wetcake material contained contaminants, although they disagreed with each other as to the level of this contamination. With TGA finding a water content of approximately 95% and a CNT content of 3.7%, where the CNTs oxidised at around 590°C. Finally the wetcake was probed with time of flight surface ion mass spectroscopy (ToF-SIMS), where a depth profile analysis confirmed that there were indeed contaminants on the surface of the wetcake particles (as a form of skin), as originally suggested by the first electron micrographs. Although, the level of contamination was found to be very low.

The high degree of linearity and low defects frequency of the CNTs found within the wetcake product, enables us to conclude that these nanotubes are ideal for producing highly aligned arrays within polymer nano-fibres, and could potentially display higher mechanical properties than the material in previous literature [see Figure 2-3].

In the next section we use this material to investigate the various aspects of electrospinning capabilities and the parameters needed for producing highly aligned nano-fibres. We then use these
findings to electrospin the CNT wetcake material into aligned arrays. We then follow on to investigate how doping the electrospinnable polymer with the CNTs affects its overall properties; in particular the crystalline formation of the polymer at the CNTs-polymer interface.
5 Production of Highly Aligned CNT loaded Fibres

5.1 Introduction

To align carbon nanotubes (CNTs) using electrospinning, it is required to align the electrospun nano-fibres, which is an accomplishment not gained through the traditional process. This is achieved by reaching a fine balance between the numerous electrospinning parameters, such as: solution viscosity, operating voltage, and collection drum rotational velocity. Defining these variables allows the consistent production of aligned arrays of nano-fibres. In order to gain a uniform array of aligned CNTs, the subsequent nano-fibres that they embed within also have to be uniform, but in many other ways aside from orientation, this includes deposition distribution across an area, and the nano-fibre diameters. Only by carefully deciphering the optimum electrospinning parameters to achieve nano-fibres with these desirable attributes, can large areas of highly aligned arrays of CNTs be produced.

This chapter focuses on the various experimental steps taken, using a traditional single needle spinneret, to perfect the electrospinning process for the alignment of nano-fibres and ultimately the loaded CNTs. This is achieved by controlling the electrospinning jet dynamics (including solvent evaporation), in order to avoid beading or wet fibre deposition, and by matching the surface speed of the collection drum to the jet velocity in order to align the nano-fibres with minimal residual stresses.

This chapter is concluded by confirming that the CNT integrity is maintained throughout the process, and that they are aligned within the nano-fibres during the process. Mechanical and electrical testing is then used to probe the enhancements, which are brought in by addition of CNTs to the original polymer’s properties. Finally, in an effort to better understand the mechanisms behind the performance increases with the addition of the CNT, the CNT-polymer interface is probed using small angle X-ray scattering (SAXS), suggesting how the CNTs are affecting the polymer’s crystallinity.
5.2 Controlling Electrospinning Parameters for High Quality Polymer Nano-Fibres

5.2.1 Introduction

Within this project, high quality polymer nano-fibres are considered as those which possess a number of desirable attributes. These attributes include some that are individual to each fibre, and some that address the sheet of fibres as a whole. These attributes include: fibre linearity, consistent fibre diameter (along the length of the fibre), consistent fibre diameters (across the entire sheet), no undesirable fibre features along the fibre length (such as pores or beads), and no ‘spits’ or drips from the spinneret at any place on the sheet of material. In order to obtain high-quality fibres various electrospinning parameters need to be controlled, with the most important being the atmospheric humidity, and the solution’s viscosity.

Atmospheric humidity and solution viscosity are two of the most important parameters in electrospinning, this is because of the significant effects that they have on the process, and ultimately the final attributes of the nano-fibres. As well as the nano-fibres, variations in these parameters will also have significant effects on a number of aspects of the electrospinning process, this includes: variations in electrostatic field strength, variations in solvent evaporation rates, variations in fibre diameters and the introduction of potentially unwanted alternative fibre morphologies (such as beading). As previously mentioned in section [Chapter 2.4.4], these parameter variations in the electrospinning process could cause a variety of issues in the final mat of nano-fibres, especially those which result in the nano-fibres failing to dry and landing wet, damaging other previously spun fibres. In some extreme cases, failure to control the humidity and viscosity accurately can result in complete interruption of the electrospinning process altogether.

In order to explore these parameters and ensure that they are being applied correctly, a brief investigation was conducted at the start of this project, with the goal of exploring the effects these varying parameters had on a polyethylene oxide (PEO) aqueous solution. As PEO was the polymer chosen for this project, due to its low-cost and low-toxicity, it was important to grasp a much needed understanding on how to efficiently electrospin high quality nano-fibres with it, before continuing to the next steps and perfecting fibre alignment.
5.2.2 Solution Viscosity

The first electrospinning parameter that must be controlled is the solution viscosity, specifically the viscoelasticity; this governs how the solution will cope when subjected to electrostatic and centrifugal forces during the spinning process (Regev et al. 2010). The viscoelasticity of the polymer solution is necessary to provide a surface tension which can hold the jet together during the spinning process. Unlike other parameters, this is controlled outside of the electrospinning system, by controlling both the weight fraction and the chain length of the polymer that is being used.

Getting this parameter incorrect will most likely prevent any form of nano-fibre production. For example, if the solution’s viscoelasticity is insufficient, the jet of polymer solution will break up when subjected to the electrospinning whipping forces, leaving nothing more than droplets of polymer on the collection plate (this is otherwise known as electrospraying, and is used for the application of coatings). However, if the viscosity is too high, assuming the solution can both pass through the spinneret and form a Taylor cone, it will not undergo whipping at all, causing only a thick wet jet that saturates the collector. When changing polymers, polymer loading or solution constituents (e.g. adding CNTs), it is important to maintain this viscoelasticity; as a result, the spinnable viscosities were investigated for the polymer chosen for this project.

PEO with an average molecular weight of 2,000,000 M\textsubscript{v}, which had previously been found as being suitable for electrospinning, was blended into six aqueous based solutions at concentrations of 1%, 1.5%, 2%, 2.5%, 3% and 4% weight. With the help of Professor Spencer Taylor from the University of Surrey, a ‘Brookfield RS-CPS+’ rheometer was used to measure the viscosity of each of these samples. A measurement of Pascal seconds (Pa·s) was acquired using the cone and plate method at a temperature of 25°C, subjecting the solution to an increasing and then decreasing shear rate from 1 to 500 s\textsuperscript{-1}. The subsequent results for each sample were then plotted and analysed [see Figure 5-1], with a second plot generated for comparison of the viscosity of each sample, taken when the shear rate was at a value of 500 s\textsuperscript{-1} [see Figure 5-2].

After each of the samples were analysed and subsequently plotted, it was revealed that PEO in an aqueous solution is a pseudo-plastic (meaning it undergoes shear-thinning), dictated by the downward curves seen in Figure 5-1. This shear thinning phenomenon is the result of the viscosity of the solution decreasing as an increasing force is applied. This is caused by polymer chains aligning when the shearing force is applied, allowing the polymer solution to flow more freely (Xia & Callaghan 1991). This shear-thinning response will affect the electrospinning results, but not necessarily in a negative way. Provided that the surface-tension of the fluid after the shear-thinning remains strong enough to maintain the integrity of the polymer jet, nano-fibres will still be produced. As an added
bonus, the thinning of the jet as it undergoes the shearing forces in the electrospinning’s ‘whipping’ stage, will promote the whipping spirals to flay out over a larger circumference, effectivity increasing deposition area and decreasing the fibre diameter. Both of these effects are extremely beneficial when using electrospinning to align CNTs over a large area, as the decrease in the nano-fibres’ final diameter will aid CNT alignment within each fibre, and the deposition over a larger area will improve CNT distribution.

In addition to the results seen in Figure 5-1 for increasing shear, the viscosity of each sample was also measured for decreasing shear, in an attempt to find some form of hysteresis, which is sometimes a trait of viscoelastic materials (energy lost in the system, usually due to heating). Across all samples there were no evidence of hysteresis, the measured viscosity with both increasing and decreasing shear was virtually identical. Apart from the data for the 4% PEO solution which has been displayed as an example, this data was omitted from the plot in Figure 5-1.

![Figure 5-1](image)

Figure 5-1 – The measured viscosities of aqueous based PEO solutions which were subjected to increasing shear from 1 to 500 s\(^{-1}\). Plotted as logarithmic graph, the results reveal a downward curve which can be related to pseudo-plastic (shear thinning) behaviour. The results for the 4% PEO solution, are plotted for both increasing (+) and decreasing (-) shear, displaying no evidence hysteresis.

When comparing each of the solutions as a whole, Figure 5-2 demonstrates how the typical viscosity of the solutions change as a function of PEO concentration, when a shear rate of 500 s\(^{-1}\) is applied. Presenting the data in this manner reveals an exponential trend of an increase in viscosity with increasing polymer concentration. This behaviour in viscosity coincides with increasing polymer chain entanglement, where increasing the weight fraction of the polymer increases the force required to disentangle them (de Gennes 1971). On this same graph, the electrospinnable region has also been
highlighted. To decipher this, each of the solutions was electrospun and any produced fibres were analysed, looking for any undesirable attributes. Any solution concentration outside of the spinnable region marked on the plot, either failed to produce any fibres, or did so poorly with any of the previously mentioned undesirable attributes [see Figure 5-3 for examples of the nano-fibres produced]. The best nano-fibres where produced using either the 2% or 2.5% weight PEO concentrations (corresponding to viscosities of 0.15 and 0.26 ± 0.01 Pa·s respectively). However, when trying to maximise the CNT loading within nano-fibres, it is beneficial to keep the polymer content as low as possible. With this in mind, the 2% weight solution will be used as a preference.

**Figure 5-2** – At each of the concentrations the measured viscosity at a shear rate of 500 s⁻¹ was plotted as a function of PEO concentration. Each of these solutions were then electrospun and analysed, the solutions that produced ideal nano-fibres have been labelled within the marked area.

**Figure 5-3** – Scanning electron microscopy (SEM) micrographs taken at the same magnifications of polymer solutions mixed at 1%, 2% and 4% weight PEO. Where a clear difference in both fibre diameters and fibre morphologies is revealed. The 1% solution produced extremely narrow fibres, but in most case electro-sprayed forming polymer droplets. The sample mixed at 2% weight produced thicker fibres than 1% but of high quality, with no visible droplets. The sample mixed at 4% weight produce large fibres which show signs of wet collection in the melting between fibres. *Note: the scale bar is the same for each image.*
5.2.3 Atmospheric Humidity

Aside from the viscosity of the solution, it has been well documented in previous scientific literature that the humidity can significantly affect the final morphology of the electrospun nano-fibres (Casper et al. 2003; Vrieze et al. 2008). Without control measures in place, the humidity of any electrospinning apparatus is governed by the equipment’s surrounding environments, and will vary through the annual weather seasons. Within an air conditioned laboratory environment, the relative humidity was observed to range from as low as 25% to as high as 75% (with the passing of seasons and varying efficiency of air conditioning/heating). This can vary the electrospinning results considerably across the year, and in some extreme cases prevent spinning entirely.

The humidity of the atmosphere around the electrospinning rig dictates two key factors: the electrostatic field strength and the solvent evaporation rate from the jet. Alterations in the electrostatic field will ultimately vary both the Taylor cone size, and the acceleration of the jet of polymer material, changing the final velocity of the fibre before it is collected and varying the diameter of the spirals as the polymer undergoes ‘whipping’ (Tripatanasuwan et al. 2007). When electrospinning without regulated humidity, these affects make it hard to match the rotational speed of the collection drum to the fibres velocity (in order to achieve highly aligned nano-fibres), and varies the fibre diameter as the degree of stretching/whipping is changed.

As significant as these changes to the nano-fibres sound, they are only minor in variation across the variations in the electrostatic field strength. However, the major effects caused to the fibres by a humidity fluctuation, is due to the change in the solvent evaporation rate from the jet. Changes to the solvent evaporation rate essentially alter the length of time that the polymer jet remains as a fluid before it dries into a fibre (Tripatanasuwan et al. 2007). When using a solvent such a water, lower humidities will increase the evaporation rate of water from the jet, and high humidities decrease it. An atmospheric humidity that is too low will cause the solution to dry significantly faster once exposed to the atmosphere, resulting in the final fibres being far thicker, and in a severe case, causing the Taylor cone to dry, blocking the spinneret. An atmospheric humidity that is too high will result in the solution failing to dry at all, landing wet on the drum and damaging any fibres that did dry before collection. This will essentially allow the aligned CNTs to continue flowing/moving within the liquid material on the collectors’ surface, and will diminish alignment. The humidity required to successfully electrospin high quality nano-fibres varies for each sample, very much depending on solvent content within the polymer solution being used, as such this needs to be controlled for consistent fibre production.
In order to investigate this effect, a minor experiment was conducted that explored how humidity altered the nano-fibres produced from a standard PEO blended aqueous solution. Although accurate atmospheric control systems are generally very expensive, this investigation was conducted using a simple condenser dehumidifier purchased from Maplin Electronics. To reveal what effect the dehumidifier had on the fibres, two identical electrospinning sessions were run, where every attempt was made to ensure that the humidity was the only changed parameter. The solution used for both samples was 2% weight PEO (2,000,000 M\text{v}) in water. This was then electrospun through a single needle spinneret system, set up identically to the schematic diagram seen in [Figure 2-5]. The spinneret was charged at a potential of +12 kV, positioned 20 cm from a collection drum; where the drum was rotating with a surface velocity of 5 m/s. Although there is no control on the dehumidifier that was used, the system was left to dehumidify between samples until it reach a minimum (monitored using a USB atmospheric data logger), in this case relative humidity dropped to 40% from 65%. The electrospinning process was then repeated at the new humidity.

![Figure 5-4](image)

**Figure 5-4** – These two SEM micrographs (samples A and B) were taken of nano-fibres produced using identical spinning conditions (solution formula, potential, drum speed etc.), however the relative humidity was changed from 65% (A) to 40% (B). The fibres produced during high humidity show a different morphology with the inclusion of ‘beading’. **Note: the scale bar is the same for each image.**

Following the successful collection of both samples, each was imaged in a SEM revealing the nano-fibre morphologies and the conditions of the fibres. Figure 5-4 presents the two SEM micrographs taken, where image A reveals that the fibres spun at 65% relative humidity, have developed ‘beads’ during the spinning process. This ‘beading’ of the fibres has been known to occur when spinning aqueous based solutions in high humidity environments (Vrieze et al. 2008;
Tripatanasuwan et al. (2007). Tripatanasuwan et al. (2007) conducted a similar investigation with aqueous based PEO solutions, but at a concentration of 6% weight PEO and a polymer molecular weight of 400,000 M_w. In their investigation, they too found that PEO nano-fibres contain beads when electrospinning at higher humidity, and that the beading process occurs when electrospinning in any relative humidity over 50%. This result also appears to be concise with Figure 5-4 image B, where the nano-fibres produced at 40% humidity are of a higher quality, with no apparent beading. In the case of this project, the beading could hinder the fibre alignment process and lead to poorly aligned fibres and subsequently poorly aligned CNTs. This will be especially true for the nanotubes that are embedded within the bead themselves, as these will have avoided the stretching and drawing processes that pull them into alignment during the electrospinning process.

5.2.4 Conclusions

Two minor investigations were successfully conducted that explored how both solution viscosity, and atmospheric humidity effect the electrospinning process and the result fibres produced. From these investigations, it was firstly found that, when electrospinning a polyethylene oxide (PEO) based aqueous solution (with the PEO having a polymer molecular weight of 2,000,000 M_w), concentrations of either 2% or 2.5% weight PEO in the solution produced the best nano-fibres (corresponding to viscosities of 0.15 and 0.26 ± 0.01 Pa·s respectively). In the second investigation, although control over the dehumidifier was limited to ‘on’ or ‘off’, a clear difference was seen in the morphology of the fibres when produced at a lower humidity. A relative humidity of 40% produced nano-fibres with ideal attributes, but not at 65% relative humidity where beading was seen.

From this point forward, unless otherwise stated, all electrospun samples will be spun using PEO (2,000,000 M_w) at a concentration of 2% weight in an aqueous solution. Furthermore, before each sample is electrospun, the dehumidifier will be run for a time period in order to allow the humidity to fall to a stable, low level, and left running during the electrospinning process itself to remove any moisture created by the process. The results from this work allow the consistent production of high quality PEO nano-fibres needed for the alignment of carbon nanotubes (CNTs), however in order for the nanotubes to align, the nano-fibres themselves must be aligned. In order to achieve this, the collection drum must be rotated with a surface velocity that matches the approach velocity of the nano-fibre.
5.3 Measurement of Jet Velocity for Optimum Drum Speed and Alignment

5.3.1 Introduction

Now that the solution parameters have been agreed and chosen, the next step is to achieve highly aligned nano-fibres when electrospinning. This is accomplished by matching the surface velocity of a rotating collection drum to the approaching velocity of the electrospun jet (Fennessey & Farris 2004; Kim et al. 2004; Wu et al. 2007; Z. Sun et al. 2012). Gaining insight into the approach velocity of the polymer jet during electrospinning enables the correct drum collection speeds to be implemented on any electrospinning apparatus. However, as previously mentioned, nano-fibre velocity depends on a number of electrospinning parameters, including the viscosity of the solution and the humidity etc. (Regev et al. 2010). It is this multiple parameter variation from solution to electrospinning which results in polymer jet velocities being reported to be anywhere between 0.4 to 160 m/s (Bellan et al. 2007; Fennessey & Farris 2004; Reneker & Chun 1996).

In literature, previous attempts have been made to mathematically model the jet velocity. However, due to the sheer number of variables and parameters, and without making several assumptions, the only sensible way to decipher the velocity of an electrospinning jet is to measure it experimentally (Wu et al. 2011). This can be done via several different methods of determination, including: using high-speed cameras (Reneker et al. 2002), using laser Doppler Velocimetry (Buer et al. 2001), and by comparing fibre alignment against drum rotation velocity (Z. Sun et al. 2012; Wu et al. 2007). Due to equipment limitations within the project, the easiest of these methods to reproduce was that by which fibre alignment is compared against drum rotation velocity. With this in mind, an experiment was set up to measure the jet velocity on the electrospinning rig, when using the polyethylene oxide (PEO) aqueous solution chosen previously.

5.3.2 Theory

Chapter 2.4.5 has already explained the significance of matching the surface velocity of the collection drum to the approach velocity of the polymer jet, when trying to obtain high quality, highly aligned nano-fibres. It was demonstrated visually in Figure 2-11 how the jet (and resulting nano-fibre alignment) will be affected as the collection drum’s surface velocity varies in relation to the jet velocity, and furthermore how detrimental an incorrect surface velocity (which is too high) will be on the resultant fibres, through the introduction of internal stresses.
Electrospinning with a single needle spinneret can be a slow process, so gaining samples can be time consuming. Combining this with the fact that polymer jet velocities have been reported to be anywhere between 0.4 to 160 m/s, it becomes necessary to gain an estimate of the jet speed so that samples can be acquired within the immediate range of the ideal surface collection speed. However, as previously mentioned due to the complexity of all the fundamental forces influencing the polymer jet, it is almost impossible to accurately use logic to predict its final speed (Reneker et al. 2000). Equally due to their extreme velocities (metres per second, m/s) and sub-micron size they cannot be modelled empirically. Because of these facts, the speed of the electrospun nano-fibres can only be approximated using both a series of assumptions and ignoring complex principles. One of the simplest methods of approximating jet speed is by thinking of the jet as a single polymer particle, equating electrical potential energy \( E_{pot} \) (Equation 5-1), to kinetic energy \( E_{kin} \) (Equation 5-2), producing a crude expression for the final jet velocity (Equation 5-3):

\[
E_{pot} = eV
\]

Equation 5-1

\[
E_{kin} = \frac{1}{2}mv^2
\]

Equation 5-2

\[
v = \sqrt{\frac{2eV}{m}}
\]

Equation 5-3

where \( e \) is the charge of an electron (C), \( V \) is the applied electrical potential to the electrospinning spinneret (V), \( m \) is the mass of the jet particle (kg) and \( v \) is the velocity of the jet particle (m/s). This simple approximation predicts a final fibre velocity of \( v = 46.6 \text{ m/s} \), when approximating mass from the dimensions of the final fibres. However, this approximation assumes that the jet is a single free moving spherical particle travelling in a straight line, ignoring any whipping. It does not take into consideration the viscoelastic drag of the solution, air resistance or solvent loss, making the actual fibre velocity considerably slower. However, the most significant problem is this approximation also relies on mass remaining constant, which it isn’t due to solvent evaporation. By modelling how the solvent evaporates, a greater refined approximation can be built, which can then be further developed to include the other aspects, such as viscoelastic drag, allowing for a significantly more accurate approximation of the final jet velocity.

In order to address this issue of a non-constant mass, Wu et al. 2011 used a non-linear mass diffusion transfer model to describe dimethylformamide (DMF) solvent evaporation within the polymer jet during electrospinning; they found that solvent loss is exponential and accelerates with increasing fibre stretching. By plotting Wu’s data in an alternative way to that which it was given (as a
function of time rather than diameter), it was found that solvent evaporation, and as such jet mass, could be approximated using a sigmoid function (assuming DMF evaporates in similar ways to water). The sigmoid function (S-shaped function), was adapted to mimic the data of solvent evaporation, giving rise to the following approximation of the mass remaining within the jet as a function of time [see appendix item C for the sigmoid adaption, and appendix item D for derivation of expression]:

\[
m(t) = \left( \frac{P}{P_\%} \times 100 \right) - P \left( 1 - \frac{1}{1 + e^{(t-t_0)}} \right) + P
\]

Equation 5-4

where \( t \) is time (s), \( P \) is the final mass of the polymer (kg), and \( P_\% \) is the weight percentage of polymer in the original solution (%). The final mass of the polymer can be approximated from SEM images of previously spun fibre. This is achieved by measuring the nano-fibre’s diameter, and approximating its spherical mass from the polymer’s known density. It is this approximation which forces the model to be limited to modelling only a polymer particle, as opposed to the entire polymer jet. By using Equation 5-4 as a function of jet mass (taking into consideration solvent loss), and inserting this into Equation 5-3, it was possible to model the velocity of a free polymer particle as it dries as a function of time, which can be closely related to a section of the actual polymer jet of fibre [see Figure 5-5].

Figure 5-5 – This graph plots Equation 5-3 using Equation 5-4 to approximate the mass loss from solvent evaporation. The plot can be directly related to the electrospinning image in the background, showing the initial acceleration from the Taylor Cone (1), uniaxial drawing/stretching of the fibres (2), fibre drying/solvent evaporation (3) and nano-fibre collection (4). The background image was adapted from (www.plantandfood.co.nz 2013).
Figure 5-5 plots the modelled approximation for a polymer jet’s velocity, taking into consideration the solvent evaporation, but still ignoring air resistance and viscoelastic drag. This graph was overlaid over a picture taken of an electrospinning jet, allowing different parts of the model to be directly compared. The first section of the curve (area 1) shows the initial acceleration of the jet from the Taylor cone, this then leads to uniaxial drawing of the fibre, where the fibre flays out and is stretched into a nano-fibre (area 2), this narrowing significantly increases the solvent evaporation rate, decreasing mass and increasing in velocity. As the solvent begins to deplete the fibre dries (area 3) to become a solid where it is finally collected (area 4).

Although this approximation provides a good estimation of the fibre velocity, it is still only based on a sphere of free mass, ignoring the very fact that the fibre is a continuous chain of viscoelastic solution. The viscosity of the solution would cause a ‘drag’, much like a bungee cord, reducing the velocity of the jet significantly. This approximation also ignores air resistance, which at high drum collection speeds, could be an issue due to local air turbulences on the drum’s surface. Although it is practically impossible to accurately take these drags into account empirically, the viscosity measurements back in section 5.2.2 revealed that PEO (2,000,000 M$v$) at 2% weight fraction will have a viscosity of approximately ranging between 1 to 0.15 Pa·s when under stress. If we assume, that in the situation of our modelled free particle, the effective viscosity is zero, then the actual polymer jet’s velocity will be significantly lower, even while still ignoring air resistance.

Using our crude approximation for the velocity of the nano-fibre as it approaches the collection drum as an area of focus, this experiment aims to gain an accurate understanding of the final fibre velocity. Once an accurate measurement of the velocity of the nano-fibre has been measured, the previously introduced approximation can be compared, providing an indication of the significant decrease in velocity that the viscoelastic drag causes.

### 5.3.3 Experimental Procedure

A sufficient volume of aqueous based PEO (2,000,000 M$v$) solution at 2% weight fraction polymer was blended for this investigation; this same solution was used for each of the nano-fibre samples produced. At a set distance of 22 cm from the rotating collection drum, the single needle spinneret used was charged at a potential of +12 kV. Each time a nano-fibre sample was produced, exactly 4 ml of polymer solution was pumped to the spinneret, at a rate of 700 µl/hr. This solution then electrospun onto the rotating collection drum, where the surface velocity of the drum was set to
2.7, 5.4, 8.1, 10.8, 13.5, 16.2 and 19.0 metres per second (with the motor rotating the drum anti-clockwise), within the limitations of the motor control software. In order to allow easy removal of the collected nano-fibres, silicone coated paper was covered over the drum’s surface.

After each samples collection, they were analysed for their degree of alignment using two distinct methods: individual fibre analysis (where the orientation angle of each fibre in an image is measured by hand), and by analysing a Fast-Fourier transforms (FFT) of the image. The individual fibre analysis was conducted by acquiring an electron microrgraph of each of the nano-fibre samples, at a magnification of 10,000x (with approximately a field of view of 27 µm by 23 µm). By fixing the magnification to a specific value for each sample, enabled each of the images to be compared equally on the same microscope. It was also important to ensure at this stage that, for each of the samples, the individual nano-fibres could be easily distinguishable from the others, avoiding any measurement uncertainties caused by confusion when two nano-fibres cross paths. Image processing software, ImageJ, was then used to trace each of the nano-fibres seen crossing the edge of the micrograph, allowing each individual fibre’s angle of orientation to be measured as an angle to a normal [see Figure 5-6]. This data was then finally exported into data analysis suite, Origin 8.6, allowing a histogram for each sample to be plotted and finally fitted with an appropriate Lorentzian function. For each sample fitting, the full-width half-maximum (FWHM) was measured, revealing a comparison between the
orientation distributions for each collection speed; the narrower the Lorentzian distribution, the higher the degree of alignment.

However, it was noticed during this analysis that this is not only extremely time consuming, but also only providing data on small areas of fibre, possible leading to poor statistics. With this in mind, FFTs were also used, eliminating the need to measure each individual fibre in the micrograph. For each sample, a SEM image was acquired at a magnification of x1400, providing an image of a large area of fibres (of approximately 200 µm by 170 µm), allowing measurements to be more representative of the sample as a whole. Each micrograph was then opened in ImageJ and subjected to a FFT producing a second image of the transformation. Applying a FFT to an image converts its grey-scale components from the spatial domain to the frequency domain, effectively decomposing the image into its sine and cosine components. This means that any regular pattern, or in our case regular alignment, will be shown as bright spots/areas on the transformation and as such alignment can be quantified (Ayres et al. 2006).

Figure 5-7 – Starting with the micrograph of the spun fibres (1), a FFT was applied to the image revealing any regular ordering (2). This was then subjected to an oval profile plot which summed the grey value of the FFT as a function of angle (radially from the centre) (3). In the event of the fibres being randomly oriented, there would be no peaks in the oval profile plot, whereas the direct opposite (perfectly aligned fibres) would have a sharp peak. As such, measuring the peak FWHM in degrees can be considered a direct measure of nano-fibre alignment. The nano-fibre that has been traced with a dashed red line, gives an example of the corresponding arrowed intensity streak on the FFT, and the peak on the oval plot. This rogue single fibres are not indicative of the sample as a whole, and ignored as an anomaly.
Once the FFT image had been acquired, it was analysed using the ‘Oval Profile Plot’ plugin (available on ImageJ’s website). This plugin sums the grey value from the centre of an oval as a function of angle radially, where the number of measurements can be specified. For our analysis, a total number of 500 measurements were taken over the entire FFT. This then produced a corresponding graph and subsequent set of data points for grey value against angle for each of the samples [see Figure 5-7].

The oval profile values were then inserted into the data analysis software Origin, where any peaks found, such as the one at about 160° in Figure 5-7 (3), was fitted using a Lorentzian function, noting the fitting parameters such as its width. Where the width of the fitting represents the distribution of nano-fibre orientations compared to a normal (or to the peak orientation). The width of the distribution dictates the frequency of nano-fibres that are not aligned, such that a very narrow distribution indicates high degrees of alignment. The second large peak found in Figure 5-7 (3) at 340° was ignored, as it was a symmetrical repeat of the fitted peak. The several sharp smaller peaks seen at around 40° and 80° (including their reflections around 220° and 260°) were also ignored, this was because these peaks correspond to individual fibres seen cutting across the micrograph rather than contributing to the bulk of the sample signal. One of these nano-fibres in Figure 5-7 has been traced as an example, with arrowed indications of the influences it has of the FFT and oval profile plot. Once all of the samples had been analysed in this manner, the FWHM of each of the samples fitting was plotted against collection drum speed. The error bars were calculated by combining all of the propagating errors, including those from measurements and fittings.

In order to compare the diameters of the nano-fibres produced when collected at different drum surface velocities, another set of electron micrographs were taken of each sample at 20,000x magnification. This magnification was chosen because it produced a clear view of the fibres, including the edges, allowing them to be measured manually using ImageJ. It was important to make sure all images were taken at the same magnification in order to reduce the error in measurements, as the size of features measured by secondary electron images usually change by 2-3 nm with magnification, potentially leading to an incorrect measurement in the fibre diameters. Since all measurements are taken in the same way, comparisons remain valid. Once all of the data was collected, the average diameters were plotted against collection drum speed; the error bars were calculated from the standard error in measuring the same fibre 50 times.
5.3.4 Results and Analysis

The results in Figure 5-8 (A) revealed to be in agreement with the theory Chapter 2.4.5, when the collection drum speed is slower than the jet speed, alignment will be at a minimum. However, when the drum speed is increased the degree of alignment is also increased, but only up to an optimum speed, the speed of the approaching jet of fibre. Above this polymer jet speed, the fibres are pulled towards the drum upon contact, introducing stresses within the fibres. These stresses ultimately lead to plastic deformation and reduce the overall alignment of the array of fibres. Both approaches taken to evaluate the samples have shown almost identical trends, and agree with the theory. Both the manual and FFT methods found the jet speed to be within error or each other, producing values of 8.9 ± 1.2 m/s and 9.5 ± 1.2 m/s respectively, averaging to approximately 9.2 m/s. This confirms not only that both techniques used to measure alignment are reliable, but also that the FFT method is a quick and reliable approach to assessing the alignment of electrospun fibres. Due to programming limitations, the drum cannot be spun at exactly the same speed as the approaching polymer jet. However, the closest speed setting available to this value which can be used is 8.1 m/s. When comparing our measured polymer jet velocity of 9.2 m/s to the free particle approximation model in Figure 5-5, this measured velocity for the jet is approximately 80% slower. This reduced speed is a result of both the air resistance and viscoelastic drag of the polymer solution, reducing the final velocities.

![Figure 5-8](image)

Figure 5-8 – The alignment results (A), where by the lower the FWHM value, the higher the degree of alignment. These results were obtained both using the manual fibre measurement technique (red) and the FFT method (blue). Where they both show similar trends in fibre alignment; at slow speeds the fibres are poorly aligned, at the right speed they are highly aligned, and at fast speeds alignment is reduced (due to plastic deformation and air turbulence). Analysing the individual fibre diameters (B) found that the average diameter is reduced with drum speed (black); however it also found that the distribution in diameters was also increased with drum speed, giving rise to the increasing errors (blue).
Analysis of the average fibre diameter for each sample revealed how increasing the collection drum’s surface speed decreases the average fibre diameter, while simultaneously increasing the distribution of diameters. This effect could possibly have been caused by the increasing air flow around the drum as the surface speed is increased. This increasing air turbulence around the drum would progressively blow the fibres, and as such either increase whipping time, or stretch them around the drum before collection. A similar observation was made visually during testing, where fibres were seen to be blown onto the ceiling behind the drum when fibres were collected at extremely high drum speeds. This phenomenon could possibly be easily controlled with the addition of a wind breaker just before the area of fibre collection.

5.3.5 Conclusions

By electrospinning a 2% polyethylene oxide (PEO) aqueous solution, at various different collection drum surface velocities, it was possible to produce a collection of different samples that varied in degree of alignment. Using two different analytical methods, individual fibre analysis and Fast-Fourier transforms (FFT), the approach velocity of the polymer jet was measured to be approximately 9.2 m/s, with the two calculated values being 8.9 ± 1.2 m/s and 9.5 ± 1.2 m/s for measurements done manually and using FFT’s respectively. Due to programming limitations, the drum cannot be spun at exactly the same speed as the approaching polymer jet, however the closest speed setting to this value which can be used is 8.1 m/s. These measurements of the final polymer jet velocity enabled a drag correction to be applied to the approximation model detailed in the theory. The 80% reduction in the free particle velocity calculation in the approximation was attributed to both the air resistance, and the viscoelastic drag of the polymer.

Further analysis of the fibres found that the average fibre diameter decreased with increasing drum speed, but furthermore that as the fibre diameters decreased the distribution of fibre diameters increased. This decreasing in fibre diameter and increase in distribution is thought to have been caused by increasing air turbulence around the drum surface. In order to fully utilise this data, careful consideration and possibly retesting of the solution viscosity and electrospinning parameters should considered should there be a need to alter the solution or polymer systems at a later date.
Now that an in-depth grasp, of the polymer solution and electrospinning parameters necessary for producing high-quality, highly aligned nano-fibres has been acquired, the project can progress a step closer to achieving the final goal of producing large areas of highly aligned carbon nanotubes (CNTs). Using this knowledge gained for electrospinning PEO, CNTs can now be added to the solution to produce highly aligned arrays nano-fibres loaded with nanotubes.

5.4 Confirmation of CNT Alignment within the Nano-fibres

5.4.1 Introduction

Once it was possible to be able to consistently electrospin sheets of aligned high-quality polyethylene oxide (PEO) nano-fibres, our systems were ready for carbon nanotubes (CNTs) to be introduced. It was seen in Chapter 2.3, Figure 2-3, how irregular nanotubes fail to align within the electrospun fibres, however in Chapter 4 we have shown that Thomas Swan’s nanotubes are much the opposite, being of high quality and linearity, suggesting that they will lead to better alignment. This investigation was carried out to determine both to what degree the CNTs align within the fibre, and to what extent they are affected/damaged by solution mixing and the electrospinning processes.

It has been well documented in recent years that electrospinning can be used to align CNTs (Salalha et al. 2004; Gao et al. 2004; Hou et al. 2005; Yeo & Friend 2006). However, these results have seen varying degrees of success, depending on the quality/linearity of the nanotubes, and the extent of the damage caused by the solution/ dispersion preparation processes. Although it has been previously discussed how the quality of the nanotubes affects the alignment, it is not clear how the nanotubes will be affected by the dispersion processes, which is required to de-bundle the wetcake and allow movement into alignment. Currently, in order to disperse CNTs within a polymeric solution, they require intense tip ultrasonic irradiation in a surfactant loaded solution. Unfortunately, ultrasonic irradiation can also introduce damage to CNTs structure and as such lower the quality of the material, depending on the powers used (Dror et al. 2003; Kearns & Shambaugh 2002). In an effort to avoid these types of damages, sonication must be kept to the minimum power required, for a minimum duration. Probing into the sonication requirements will be explored in the next chapter.

As detailed in Chapter 3.3, Raman spectroscopy is an incredibly useful non-invasive technique, which can be used to probe the quality and attributes of CNTs. Using this technique to assess the
quality of the CNTs, both before and after any processing, will reveal any introduction of defects or damage to the nanotubes (through an increase in the D to G peak intensity ratio). If no damage has been introduced, then the peak ratios should remain constant before dispersing and after aligning (Costa et al. 2008). To probe the degree of CNT alignment, as previously explained in Chapter 3.3.1, we polarise the Raman laser, where at the point of the laser’s plane of polarisation being parallel to the one-dimensional quantum confinement of the CNTs, Raman signals will be at a maximum. Based on this theory, fixing the laser polarity and rotating the sample, taking spectra as a function of angle, should see CNT Raman features change in intensity, depending on the degree of alignment, where perfectly aligned CNTs will follow a \( \cos^4 \theta \) relationship (Gommans et al. 2000; Hwang et al. 2000).

5.4.2 Experimental Procedure

The CNTs used for this investigation were taken from the previously used wetcake material supplied by Thomas Swan & Co. Ltd. (PR0920, batch 94890/591), which was sonicated for 30 minutes, at 300 W, within a sodium dodecyl sulfate (SDS) aqueous solution. The solution was loaded at a ratio of 1:10, CNT to SDS respectively, as previously reported for being the ideal ratio of surfactant to CNT (Blanch et al. 2010; Islam et al. 2003). The solution was finally finished by dissolving PEO (2,000,000 M\(_v\)) overnight with a stirring bar. This resulted in a final solution consisting of: 2% PEO, 1% SDS and 0.1% CNT weight fractions. This solution would then effectively produce PEO nano-fibres that were loaded with 3.9% weight fraction of CNTs, assuming the fibre had completely dried (this was confirmed by TGA in Figure 5-13).

The solutions were then electrospun on the same rig as previously used, with the spinning parameters matching those which were already determined as being ideal. The dehumidifier was enabled until the relative humidity reached below 50%, and the high speed collection drum (covered in silicone paper) was rotated with a surface velocity of 8.1 m/s (as recommended in chapter 5.3). The atmosphere before this spin was measured as 22°C and 42% relative humidity. A total of 5 ml of solution was fed to a single needle spinneret, charged at +12 kV, and pumped at a rate of 700 \( \mu \)l per hour, from a syringe pump. Following a successful spin, the nano-fibres were removed and affixed to an aluminium foil-covered microscope slide, making every effort not to touch or damage the fibres throughout handling [see Figure 5-9].
Prior to any measurements on the Raman spectrometer, the software was first calibrated to the silicon 521 cm\(^{-1}\) Raman peak, to ensure that any measurements have peaks in correct positions. In order to perform polarised Raman, the polariser lenses must first be fixed into the correct position. This was achieved by rotating the polariser lens in 10° increments, in order to locate the lasers greatest polarised intensity. It was found that the laser was polarised at the 30° plane and the polariser was set to match it, this guaranteed that the polarised laser light was of maximum intensity, increasing the signals of the weaker CNT Raman vibrations. Once the laser was set, the polariser was secured and the sample was placed under the Raman spectrometer on a protractor [see Figure 5-9]. This enabled the oriented nano-fibre sample to be analysed at various specific angles. Although there were several CNT peaks that could be used, the radial breathing mode (RBM) was chosen as it is unique to the CNTs within the sample, as opposed to the G-band or D-band, which arise from any graphitic material. With this in mind, the intensity of the 202 cm\(^{-1}\) RBM mode was measured at each angle (to an original reference position). Several readings were taken at each angle at different sites, in a bid to average over any local variation in the CNTs orientation. In order to decipher the degree of damage that the CNTs sustained during the entire process (if any), full spectra were taken of both the processed CNTs and the un-processed wetcake for direct comparison.

The TGA performed on the nano-fibres was done so in air, in order to distinguish the temperature of the CNT oxidation peak, and the mass quantity lost. The analysis itself was conducted...
at a heating rate of 10°C per minute, up to an equipment-limited maximum of 900°C. The results were then plotted as percentage mass against temperature, with the differential plotted to identify peak centres/locations, which will help to identify if any defective sites have been introduced to the CNTs.

5.4.3 Results and Analysis

Comparing the Raman spectra acquired both before dispersing and then after electrospinning, reveals very similar results, displaying no evidence of the CNTs suffering any damage [see Figure 5-10]. Closer inspection of the two D-peaks, as well as the D to G ratio, reveals that these two spectra are practically identical. The D to G ratios measured, varied from 0.15 ± 0.2 taken before the CNTs were dispersed and electrospun, to 0.14 ± 0.3 afterwards. As these values are well within error of each other, it provides a strong suggestion that no defects or damage have been introduced to the CNTs as a result of the ultrasonic irradiation of the entire process. Although this result does not reveal whether the nanotubes are aligned, it does show that our dispersing and electrospinning processes can be used safely, without diminishing the quality of the CNTs within the material.

![Figure 5-10](image)

Figure 5-10 – These two Raman spectra (which have been spaced to allow comparison) show the results for both the wetcake (pre-processing, in blue) and the final PEO/CNT nano-fibres (post-processing, in red). A magnified D-band plot has been overlaid for comparison of the D-peaks. The D to G ratio for both of these spectra are 0.15 ± 0.2 taken before, and 0.14 ± 0.3 afterwards. This presents compelling evidence that no damage was induced on the CNTs during the dispersing or electrospinning processes. The slight smoothing of the G peak in the nano-fibre spectrum, is a result of a signal scattering off of the polymer.
Initially the results from the polarised Raman (Figure 5-11, red dashed plot), show that when embedded within the polymer the CNTs appear to not be as highly aligned as originally hoped. However, it was thought that this could be due to a depolarisation effect caused by the PEO, scattering the incident Raman laser and altering its polarity. In order to clarify this, the fibres were baked in a nitrogen oven for an hour at 400°C, removing the polymer and leaving the CNTs. Once cooled, the polarised Raman technique was used to reanalyse the baked sample [Figure 5-11, blue plot], this time producing a result well within error of the theoretical \( \cos^4 \theta \) plot for perfectly aligned CNTs [Figure 5-11, black dashed plot]. This not only reveals a depolarisation effect caused by the presence of PEO within the material, but more importantly, it confirms that electrospinning can be used to produce highly aligned arrays of CNTs, and furthermore that the CNTs remain highly aligned after baking.

In order to confirm that the CNTs were aligning because they were embedded in the nano-fibres, as opposed to residing on the surface or extruding from the fibre, transmission electron micrographs were taken at high magnification of a sample which still contained PEO. The STEM micrographs displayed in Figure 5-12 confirm both that the CNTs are embedded with the polymer nano-fibres, and that they have a length longer than the width of the fibres, confirming the alignment theory that they are forced into alignment by the drawing of the polymer. In Figure 5-12 it is also reveals how several tubes within the polymer fibres can overlap, in most cases in large linear ropes.
is also worth noting at this point, that although the CNTs in this micrograph appear to have large
diameters, this is in fact an image artefact caused by the surfactant loading on the surface of the tube.

![Figure 5-12 – A false colour transmission electron micrograph of double wall CNTs embedded within the PEO
electrospun nano-fibre (white arrow highlight the CNTs direction), imaged using a Hitachi HD-2300A STEM.
This image demonstrates that the high the electrospinning technique aligns the CNT within the polymer
nano-fibre, as opposed to CNTs being on the surface of the fibre, or sticking out at angles to the fibre axis.](image)

Finally, in order to confirm the CNT loading of the final electrospun nano-fibres, TGA was
employed to thermally assess the weight fraction that is oxidised during baking. Figure 5-13 displays
the TGA curve obtained from the fibre samples, where although the curve displays numerous complex
features, the labelled CNT oxidation peak can still be identified. The CNT oxidation peak equates to a
loss of approximately 3.9%, as expected. It is also interesting to note that the CNTs oxidised at around
551°C, which is around 42°C lower than the raw wetcake material, which oxidised at 593°C [see
Chapter 4, Figure 4-7]. Normally, a reduction in the oxidation temperature is a result of increased
areas of defective graphitic structures, which the oxygen can attack (Rinzler et al. 1998; Shi et al. 1999).
However, the Raman data revealed no evidence of the introduction of damage to the CNTs between
the before and after samples. This then suggests that perhaps the presence of the polymer and/or
surfactant is accelerating the nanotubes oxidation process, effectively lowering the CNTs oxidation
temperature. The cause of this effect is potentially because the CNTs are dispersed, meaning they are
spaced over a large area, increasing the surface area free for reaction, as opposed to the wetcake
particles where they were in tight bundles. An alternative suggestion is that this is also the result of
the oxygen rich surfactant which is now coating each of the entire CNT surfaces, acting as a local
oxygen source and promoting oxidation.
**5.4.4 Conclusions**

Using the previously optimised electrospinning parameters for producing highly-aligned nano-fibres, the first batch of aligned carbon nanotube (CNT) nano-fibre samples was produced. Conventional and polarised Raman spectroscopies were used to investigate whether the alignment by electrospinning (including dispersing by ultrasonic irradiation) can not only align the CNTs, but do so without damaging them; this includes an assessment of the damage caused by ultra-sonication. In both cases it was found that the electrospinning process can produce highly-aligned arrays of CNTs without inflicting any detectable damage. It was also discovered that the polymer, polyethylene oxide (PEO), causes a depolarisation of the Raman laser light, which resulted in the initial obscured alignment results; this was clarified by evaporating the polymer within a nitrogen oven.

TGA analysis of the nano-fibre samples confirmed that the final CNT loading of the fibres was, as theoretically predicted, at approximately 3.9% weight fraction. Further detailed analysis of the oxidation mechanism of the embedded CNTs revealed how they now oxidise at a lower temperature.
of around 551°C, as opposed to the original 593°C of the raw wetcake material. Although it has not been confirmed, with the Raman spectroscopic analysis demonstrating no evidence of an introduction of damage to the CNTs, it is thought that the reduction in the oxidation temperature is caused by another mechanism and not through an increase in CNT defects. It is assumed to be the cause of either the presence of the polymer or surfactant coating the surface of the CNTs, or the fact that the CNTs are now dispersed over an area, and have a significantly high reactive surface area for the oxygen to attack, compared to when they are in a bundle.

Proof of CNT alignment by the process of electrospinning was a crucial step for the success of this project. However, it is also important to explore how aligned CNTs affect the properties of the PEO fibres in which they are embedded within, in order to better understand potential beneficial or unwanted effects to mechanical or electrical properties. In the next section, using both mechanical and conductivity analytical techniques, we investigate the effect various percentages of CNT weights have on the resultant polymer nano-fibres. This will ultimately provide an indication, as to the stereotypical enhancements that the introduction of CNTs, would have within a composite material.

5.5 Mechanical and Electrical Properties of Carbon Nanotube Loaded Nano-Fibres

5.5.1 Introduction

The overall goal of this project is to engineer a process, ideally by electrospinning, to produce sheets of aligned arrays of carbon nanotubes (CNTs). In the previous chapter we demonstrated that this goal is achievable, with aligned CNT sheets being produced and structurally analysed. However, simply electrospinning CNTs into aligned nano-fibre sheets is only a part of the research, in order for this technology to be of commercial interest, there needs to be a suitable application. A current topical research field is in the use of CNTs to reinforce composite materials, with continuous research being publicised on a regular basis [see Figure 5-14] (Baughman et al. 2002; Bekyarova et al. 2004; Cotiuga et al. 2006; Kearns & Shambaugh 2002; Qian et al. 2000; Andrews & Weisenberger 2004; Cho et al. 2008; Ge et al. 2004; Salalha et al. 2004; Rein et al. 2010; X. Sun et al. 2012). The main focus of all of these publications was to investigate whether the addition of CNTs to any composite material has any
mechanical or electrical benefits. This research is driven by the need for ever greater performing materials, allowing efficiency improvements and new engineering potentials.

As we have already established the high quality of Thomas Swan’s CNTs, and that they align within nano-fibres to form a composite material, we will examine how changing the CNT weight fraction loading of the subsequent nano-fibres will affect the final mechanical and electrical properties of the composite fibres. Although there are many published scientific papers that have shown similar investigations, almost all of these use MWNTs and non-aqueous solvents, due to their easier dispersibility and processing (Hou et al. 2005). The goal of this experiment was to test the conductivity, ductility and mechanical strength of the fibres by using a multi-meter and a tensometer for polyethylene oxide (PEO) nano-fibres loaded with various loadings of CNTs.

![Figure 5-14 – The number of publications per year on the subject of carbon nanotube composites. Data acquired from the Web of Knowledge (http://apps.webofknowledge.com/).](image)

### 5.5.2 Experimental Procedures

The CNTs used in this investigation were again taken from the wetcake material supplied by Thomas Swan & Co. Ltd. (PR0920, batch 94890/591), and were used to blend three solutions consisting of 0%, 0.016% and 0.1% weight fraction CNT. The CNTs were dispersed by tip probe ultra-sonication for 30 minutes, at 300 W, within a sodium dodecyl sulfate (SDS) aqueous solution, mixed at a ratio of 1:10 (CNTs to surfactant), as before. Finally the solutions were prepared for electrospinning by dissolving in PEO (2,000,000 Mᵥ) overnight, with a stirring bar. This then should effectively produce PEO nano-fibres that were loaded with 0%, 0.7% and 3.9% weight CNTs, once the fibre had completely dried.
The three CNT-loaded polymer solutions were electrospun using the same rig set-up and spinning parameters that were used in the previous experiments. The dehumidifier was used to minimise humidity, and the spinneret was subjected to a potential of +12 kV, while being fed with solution at a dispensation rate of 700 µl/hour. The same silicone-coated release paper was again used as before, enabling quick fibre release from the drum and ease of removal for the analysis.

![Figure 5-15](image)

Figure 5-15 – These three photographs show the ‘TA XT Plus Texture Analyser’ equipment with a 5 kg cell module, running tensile tests on pure PEO samples (A and B) and CNT loaded PEO sample (C) (because the fibre is black it is hard to make out). The centre image shows where the paper was used to prevent the clamps cutting through the nano-fibre ropes.

Following nano-fibre production, electron microscopy was used to ensure that the nano-fibres had been collected with ideal attributes (i.e. were of high-quality and highly aligned, and there were no signs of beading or droplet spraying). Providing the samples were adequate, the fibres were carefully rolled parallel to the direction of fibre orientation, effectively like rolling up a carpet, producing a rope comprised of thousands of nano-fibres. Care was taken so as to both maintain fibre alignment and minimise the twist of the fibres around the axis of the rope. Any twist in the ropes would pose a negative effect on the mechanical performance of the sample by creating residual stresses, as well as creating a potential point of material failure. The nano-fibre ropes were secured into a ‘TA XT Plus Texture Analyser’ set up for use as a tensometer, using the clamps provided. Paper was employed to line the clamp surfaces, as it was found they were too sharp and cut into the fibres [see Figure 5-15, image B]. Efforts were taken to ensure each sample had a test length of 40 ± 1 mm, in order to allow fair comparison of the data post analysis. Each tensile test was conducted with a current room temperature of 21°C, at a testing speed of 0.5 mm/second. Stress/strain measurements were taken 50 times a second and plotted directly on a graph for comparison. Prior diameter
measurements of the ropes were used to plot the necessary stress/strain curves for each of the samples. These diameter measurements were challenging to acquire accurately, and required careful parameter control between samples. This was due to the possible voids that could be left within the rolled ropes of nano-fibres, potentially causing an over measurement of the ropes diameter, which would result in measured properties appearing lower than they actually are. In order to minimise this detrimental effect, and ensure a like-for-like comparison, samples were prepared in an identical fashion. This included controlling variables such as: electrospinning parameters, nano-fibre deposition thicknesses, and the same length of nano-fibre for each rope. For each electrospun sample, several ropes were made in order to assess the distribution in the results.

In order to measure conductivity, the nano-fibres had to again be rolled into ropes, which allowed conductive contacts to be easily added at 1 cm, 2 cm and 3 cm distances along the length of the nano-fibre rope. Cross-sectional area was again measured prior to any measurements being taken, this allowed the overall conductivity of the material post analysis. The samples were affixed onto a glass slide using a non-conductive tape, to both protect the sample from damage and ensure that they remained straight during the analysis. Current against Voltage (IV) curves were acquired on a ‘Keithley Digital Multimeter’, where measurements were taken between -0.9 to 0.9 V divided across 200 divisions. The IV curves for each of the three distances were used to gain a measure of total resistance across that specific probe separation. These values were then taken and plotted ‘total resistance’ against ‘contact separation distance over cross-sectional area’, where finding a linear line of best fit and the subsequent gradient and y-intercept, will reveal a measurement of both contact resistance (Ω) and resistivity (Ωm) or conductivity (Sm$^{-1}$).

For measurements of sheet resistance, an area of fibre was affixed to a 2.5 x 2.5 cm$^2$ glass substrate using double-sided adhesive tape. Two 25 mm wide contacts were then used to take measurements of resistivity at probe separation distances of 1 mm, 3 mm and 8 mm, where the results were then plotted as ‘total resistance’ against ‘contact separation distance over contact width’. Again finding the data linear line of best fit and the subsequent gradient and y-intercept, will reveal a measurement of both probe contact resistance (Ω) and sheet resistance (Ω$\square$m$^{-1}$).

5.5.3 Results and Analysis

The three CNT polymer solutions produced a good set of fibres of visually increasing shades of grey. However, it was noticed during electrospinning that, the higher the concentration of CNTs
loaded within the solution, the larger the area of fibre deposition. We observed that the nano-fibres were depositing over the entire electrospinning rig at high CNT loading, which ultimately lowered the volume of fibre that was collected. This effect could have been the result either an increase in the weight of the fibre which would increase the centrifugal forces, causing the spray helix to widen, or due to the higher conductivity of the solution as a result of the presence of CNTs. Ra et al. (2005) found that increasing the CNT concentration in the electrospinnable solution, subsequently increased solution conductivity, inducing large charge accumulation in the polymer jet, resulting in strong electrostatic repulsion, which increased the diameter of the jets whipping motion.

Figure 5-16 – The stress to failure results for PEO nano-fibre ropes, loaded with CNTs at 0%, 0.7% and 3.9% weight fractions. The measured corresponding Young’s Moduli were found to be 60 ± 2 MPa, 182 ± 5 MPa and 257 ± 8 MPa, respectively. The slight inflection point found just after the elastic region (A), is thought to correspond to polymer heating as a result of stress induced crystallisation. The area found just before failure for 0.7% CNT loading (B), corresponds to an area when a large number of fibres in the rope failed but the remaining fibres briefly continued before failing themselves. The variation in the results displays the degree of error arising from a combination of the error in measured diameter, and possible sample damage during preparation.

Using the tensometer, the stress vs. strain graphs were plotted for each sample, allowing the measurement of key mechanical properties of the nano-fibre materials. Figure 5-16 reveals how the introduction of CNTs to the nano-fibres drastically improves the mechanical performance of the material, increasing the ultimate tensile strength by up to 320% and increasing the ductility by up to 315% (from the measured 100% PEO samples). All of the samples successfully fractured in the centre of the rope, meaning that a true representation of the fibre’s mechanical properties was obtained. For any samples that didn’t, the results were discarded to ensure that the failure wasn’t caused by the
clamps. With some samples, individual fibres were seen failing (or fraying), without the complete failure of the entire sample, Figure 5-16 arrow B is an example of when this happened, and how it appears on the plotted curves.

From these plots it was possible to calculate the Young’s modulus of each nano-fibre rope. We found that the loading of CNTs within the PEO nano-fibres increased the Young’s modulus by up to up to 430%, from $60 \pm 2$ MPa (100% PEO), to $257 \pm 8$ MPa (3.9% CNT). Compared to literature, these results were comparable to previous CNT-loaded PEO composites tested (Yang et al. 2007). However, Yang et al. found that any further CNT loading above 1.5% was detrimental to the composite materials properties, and the material began to turn brittle. This affect was not seen in our samples, it is believed that this is due to the fact that the CNTs are aligned, as opposed to randomly orientated throughout the PEO matrix. This allows the remarkable properties of the CNTs to be directed in one direction, the direction of the stress loading. In addition to this, there is an added improvement that the CNTs used are of low defect and high linearity, both improving CNT performance and alignment within the composite material.

The stress-to-failure curves for 0.7% CNT and 100% PEO in Figure 5-16 also display another interesting feature, the slight dip near the beginning on the plastic region (labelled as A). It is thought that this softening of the nano-fibres is the result of either a release trapped residual solvent, as a result of the stretching in the plastic deformation region, or heating of the polymer from stress induced crystallisation (Guo & Narh 2002). A change in both the appearance and texture of the nano-fibre rope during the course of testing was noticed, and could be due to stress induced crystallisation (discussed later in this section).

Comparing the mechanical properties to other reported results can be extremely difficult, and in most cases not representative, where an example of this, is that PEO nano-fibres have been reported to have had measured Young’s moduli ranging from 45.1 MPa to 7.6 GPa (Geng et al. 2006; Tan et al. 2005; Bellan et al. 2005). This broad variation in results is due to two key factors. The first cause is the effect that a significant electrospinning parameter variation has on the final nano-fibres produced. As previously demonstrated, slightly altering controls such as humidity or viscoelasticity can have big consequences on the final nano-fibre morphology, ultimately changing its properties. The second cause, is the fact that producing fibres by electrospinning forces the polymer to undergo a stretching and drawing process, leading to small diameters and optimized molecular orientation of the polymer chains; reducing the polymer entanglement within the material which can lead to increased mechanical performance (Hou et al. 2005). This optimisation of the molecular polymer chains is again governed by the various electrospinning parameters, adding further variation to final
fibre performances across samples. This necessarily means that unless electrospinning parameters are strictly controlled, the same variation in results could be seen across the CNT samples produced in this investigation. To clarify, all of the samples tested for these results were done so under the same conditions, making comparison between our samples valid, however comparison of results with other publications will not necessarily be a fair representation.

To further add complication between material comparisons, sample preparation prior to the testing will also affect the results. In our investigation, several attempts were made to prepare the samples for testing, this included folding the fibres into coupons, leaving them as a thin film and rolling into a rope. Due to extreme difficulties in accurately measuring film thicknesses the rope option produced the only consistent results. However, using this method could have introduced internal stresses into the material and/or added voids between fibres, causing the cross-sectional area to be miss calculated. As all of our samples were prepared the same way, repeat measurements were consistent with each other, meaning the comparisons between samples in this investigation were valid. This means that the only true way to compare results with others publications is to tensile test individual fibres under strict conditions, usually with an atomic force microscope tip (AFM) (Bellan et al. 2005). However, for our investigation this was not an available form of analysis.

Further demonstration of the variations caused by both the error in diameter measurements and the introduction of possible sample damage during preparation, can be seen in the several repeat measurements that have been included in Figure 5-16. Comparing each of the repeated sample test profiles, reveals clear common trends between the different CNT loadings. However, it can be observed how the variation in results increase with the higher CNT loadings. There is a possibility that this was purely down to sample preparation, however it could also be suggested that this is a result of the higher CNT loading; possibly due to small agglomerations creating points of failure in the material. Further investigative work would be required in order to ascertain the exact nature of this observation.

During the tensile testing, both the appearance and morphology of the nano-fibres changed. Where the nano-fibre ropes were originally visually black in appearance, they transformed to light-grey as the material entered the plastic deformation stage (much the same as when stress is applied to a transparent plastic and it turns white). This process is usually the result of the polymer crystallising under stretching forces and it thought a similar process occurred in the nano-fibres (Mandelkern 2004; Sherwood et al. 1978). As previously mentioned, evidence of this can be seen in the 0% CNT (100% PEO) plot in Figure 5-16, where the curve dips after the elastic response, possibly due to heat released as a result of the crystallisation. It was also noticed that, after the CNT-loaded PEO fibres had fractured, that the fibre felt very stiff compared to the other fibres, again suggesting some form of crystallisation.
This stiffening of the fibres appeared to increase with CNT loading fraction, suggesting that the CNTs promote crystallisation. Comparing this result to literature, confirmed this was the case, where it was reported that the addition of CNTs to the polymer decreases the melting temperature, increasing crystallisation temperature and increases crystallinity in the material (Li et al. 2006; Chatterjee et al. 2005; Yang et al. 2007). In order to confirm this increase of crystallinity, a sample was submitted to the Diamond light source for further testing using SAXS analysis; this will be discussed in the next section, Chapter 5.6.

![Figure 5-17](image)

**Figure 5-17** – The electrical conductivity results from the 3.9% CNT loaded nano-fibres, where the resistivity of a rolled rope (A) was found to be $0.28 \pm 0.02 \Omega\text{m}$, with a contact resistance of approximately $8400 \Omega$, and the sheet resistance of film of fibres (B) to be $33.5 \pm 0.1 \text{k}\Omega$, with a contact resistance of approximately $87 \Omega$.

With the help of Laurent Sam and Iskandar Yahya from the University of Surrey, the electrical conductivity measurements conducted on the fibres revealed some exciting conclusions. For both the 100% PEO and 0.7% CNT nano-fibre ropes, resistance measurements failed to be obtained; this was due to the samples having a resistivity too high to measure on the equipment used. This resulted in a need to increase testing voltage, which in turn led to the sample heating, obscuring the results. However, for the 3.9% CNT loaded nano-fibre rope results were somewhat of a different story! Both measurements of resistivity for the rope, and sheet resistance of the thin film of fibres were obtained [see Figure 5-17]. The resistivity of the rolled rope was found to be $0.28 \pm 0.02 \Omega\text{m}$, corresponding to a conductivity of $3.57 \pm 0.24 \text{Sm}^{-1}$ (with a contact resistance of approximately $8400 \Omega$). In comparison, this result is an eight orders of magnitude increase on the reported value for the conductivity of PEO (Fanggao et al. 1996). This result, on top of the mechanical testing results, further demonstrates the significant improvements that just 3.9% weight fraction of aligned CNTs can have on a composite.
materials properties. The sheet resistance measurements of thin film of fibres [see Figure 5-17, B], was found to be $33500 \pm 100 \ \Omega \square^{-1}$, with a contact resistance of approximately $87 \ \Omega$. This is significantly higher that the resistivity of the rope and thought to be due to the thinness of the film, when compared to the rope which was rolled with at least twice the volume of nano-fibres.

As the nano-fibre rope measured in Figure 5-17 were rolled before measurements, as previously explained. There remains a high possibility that there are void or gaps within its structure that have led to an over measurement of the ropes diameter. This over measurement of the nano-fibre ropes diameter, will led to the measured resistivity’s appearing slightly higher than the results show. This is because the resistivity is directly proportional to the cross-sectional area. Equation 5-5 displays the general expression for the resistance of a material:

$$R = \frac{\rho l}{A}$$  \hspace{1cm} \text{Equation 5-5}

$$\rho = \frac{RA}{l}$$  \hspace{1cm} \text{Equation 5-6}

where, $R$ is the measured resistance ($\Omega$), $\rho$ is the materials resistivity ($\Omega m$), $l$ is the length of the material (m), and $A$ is the cross-sectional area of the material ($m^2$). Rearranging this equation to make resistivity the subject in Equation 5-6, reveals have an over measurement of the cross-sectional area ($A$), will increase the calculated resistivity. This suggests that the actual resistivity of our material could be less than these results suggest, but without definitive measurements of the ropes diameter this may not be achievable using this method.

The 0.7% CNT sample, was found to have resistivity too high for measurement, it is suggested that this was because the CNTs were distributed too far apart to allow conductance between nanotubes and current to flow. Referring to literature, it has been reported that there is a minimum loading of CNTs required within a polymer matrix composite system to allow for electrical conduction; this is otherwise known as the percolation threshold, and varies with how well the CNTs are dispersed in the matrix (Bauhofer & Kovacs 2009). It has been noted that at the point of this critical density of CNTs, i.e. the percolation point, being reached within the polymer system, the conductance will significantly increase. This phenomenon was not investigated any further (as it was not deemed necessary for this project); this could be something that is explored at a later date.
5.5.4 Conclusions

Once again electrospinning using previously defined parameters, this investigation has examined how varying the carbon nanotube weight fraction loading within polyethylene oxide electrospun nano-fibres affected the final mechanical and electrical properties of the composite material. A direct result of the introduction of the nanotubes to the polymer nano-fibres has revealed a significant enhancement to the materials mechanical and electrical properties. CNT introduction has also revealed other effects, such as the molecular changes in polymer crystallinity and material responses to stress.

Tensile testing has demonstrated how introducing as little as a 3.9% weight fraction of carbon nanotubes has altered mechanical properties of the matrix material, by increasing the ultimate tensile strength by up to 320% and increasing the ductility by up to 315%, when compared to 100% polyethylene oxide nano-fibres. These improvements also include an increase in the Young’s modulus by up to 430%, from 60 ± 2 MPa (100% PEO), to 257 ± 8 MPa. Although the mechanical properties of these ropes are relatively poor compared to other composite materials on the market, this is a good indication of the enhancements that the introduction of aligned carbon nanotubes could have on other such materials, like for example an epoxy resin system or as a bi-layer in a traditional carbon fibre system.

Electrical conductivity analysis provided insight into the effects that the nanotube loading had on the polymer nano-fibres. The measurements conducted on a rolled rope of nano-fibres loaded with 3.9% carbon nanotubes gave a resistivity of just 0.28 ± 0.02 Ωm, corresponding to a conductivity of 3.57 ± 0.24 Sm⁻¹, which is eight orders of magnitude higher than previously reported values for polyethylene oxide. The sheet resistivity of a thin film of these fibres however, was found to have a resistance of 33500 ± 100 Ω, significantly higher than that of the rope, which is assumed to be the result of a difference in materials volume.

In order to maximise these significant property improvements it is necessary to understand how the carbon nanotubes interface with the polymer and surfactant, so perhaps further enhancements can be made. As a result, in the next section we will probe the nano-structural information of the sample using small angle X-ray scattering (SAXS), in order to reveal how the nanotubes interacts with the crystalline structures at the polymer-nanotube interface.
5.6 SAXS Analysis

5.6.1 Introduction

The tensile testing analysis from the previous section revealed a significant increase in the mechanical performance of the polymer that the carbon nanotubes (CNTs) were loaded into. Typically, in a CNT loaded material, because CNTs cannot be grown to infinite lengths, the significant mechanical properties arise from van der Waals interactions between the nanotubes (X. Zhang et al. 2007). However, in our composite nano-fibres, the CNTs are still coated in surfactant, inhibiting these forces from creating the tube-to-tube interactions that promote stress transfer. This then means that the improvement in mechanical performance, from the introduction of CNTs into the polymer is a result of some form of CNT-polymer interface, allowing the polymer to transfer an applied stress to the CNTs, and as such improving its load bearing capabilities. With this in mind, we decided it would be beneficial to probe the molecular configuration of the composite nano-fibres, and the effects caused by the CNTs within the nano-crystalline structures of the polymer. By gaining an understanding of how the CNTs interface with the polymer-surfactant system, further property improvements may be possible.

In order to achieve this, access was gained to the small angle X-ray scattering (SAXS) equipment at the Diamond Light Source, Harwell Oxford. A small sample of some of the electrospun nano-fibres loaded with CNTs, as spun in Chapter 5.5, was subjected to SAXS analysis. SAXS is a technique which uses sub-nanometre wavelength X-rays to elastically scatter off of a sample at very low angles, and records the subsequent scatter pattern for analysis. This is particularly useful when studying the structural information of partially-ordered materials such a semi-crystalline polymers, which show structure over the nanometre scale (Glatter & Kratky 1982). With the professional help from Dr Nick Terrill and his team on the I22 Diamond beam line, SAXS was successfully utilised to reveal the nano-structures within the CNT-loaded polyethylene oxide (PEO) nano-fibres, providing evidence to suggest the type of CNT-polymer interface, and more importantly how they affect the polymer crystallinity with the material.

5.6.2 Experimental Procedure

The electrospun CNT-loaded PEO nano-fibres selected for this analysis were produced using the same parameters as used in the previous sections (see Chapter 5.5.2). The electrospinnable solution which was used consisted of 0.004% CNTs dispersed with SDS at a ratio of 1:10 (CNT to SDS), which was then blended with PEO (2,000,000 Mᵣ), effectively producing PEO nano-fibres embedded
with CNTs at 0.2% weight, once electrospun and dried. The resultant electrospun array of aligned CNT-loaded nano-fibres, was then secured across an open window between two cuts of card with double-sided adhesive tape [see Figure 5-18]. This was done as both a mesh and as a separately rolled rope, ensuring minimal twist (along the fibre direction, as done for the mechanical testing in the previous section, Chapter 5.5). Two samples were produced of each sample type for redundancy, this was because the nano-fibres were easily damaged, which could influence results.

![Figure 5-18](image)

**Figure 5-18** – A photograph of one of the aligned nano-fibre mesh samples produced for the SAXS analysis. The arrow highlights the nano-fibre direction, where the fibres have been affixed across the open window to allow the X-rays to pass through without any frame interaction. A similar sample holder was also used to secure the nano-ropes across the centre of the window, with the fibre direction remaining the same.

Before conducting SAXS, the X-ray detector was calibrated for the scattering vector ‘q’ using wet rat-tail collagen, which provides a primary spacing $d = 670$ Å (Bear 1944; Doyle et al. 1974; Folkhard et al. 1987; Fraser & MacRae 1981; Kaesberg & Shurman 1953; Tomlin & Worthington 1956). This ensured the equipment was configured for low ‘q’ experiments, ensuring that all measurements were accurate. The aligned nano-fibres were positioned horizontally in the sample housing, where initially the X-ray beam was scanned down the sample, in the direction perpendicular to the fibre axis. While scanning, several diffraction images were taken in 0.1 mm steps across the sample. This process was repeated for both the mesh and the rope, producing a set of diffraction patterns for each sample.

### 5.6.3 Results and Analysis

The first sample analysed was the rolled rope of nano-fibres, where Figure 5-19 displays a typical representation of the diffraction pattern obtained during one step of the SAXS scan. The diffraction pattern obtained displays a strong diamond shape in the centre, elongated in the vertical direction, which suggests the presence of oriented voids or gaps along the fibres, which could be air
or residual solvent (Crawshaw et al. 2002). These voids are most likely the result of the presence of space in between fibres, confirming that the diameter measurements in Chapter 5.5 were an over measurement, leading to our mechanical and electrical performances being lower than the actual values. As this result was consistent across all samples, it confirmed that the mechanical and electrical testing results were comparable between samples.

Figure 5-19 – This diffraction pattern (represented in black and white to highlight features, (A) displays a strong diamond shaped pattern with clear intensity streaks at low q values, indicating CNT alignment with the fibre axis. The same image (in its original colour scheme, (B) was then sector integrated over the highlighted region as a function of q, and plotted.

The diamond shape in the centre of the diffraction pattern seen in Figure 5-19 is not the only obvious feature, there are clear intensity streaks both above and below the centre at low q values, indicating some sort of long range ordering. In order to quantify the intensity of these features as well as expose any that are difficult to distinguish, a ‘sector integral’ was applied to the region marked in Figure 5-19 (B). A sector integral is a measure of signal intensity as a function of q, over a highlighted area (but corrected for angle). This gives a measurement of intensity as a function of q, allowing the diffraction pattern to be plotted as a series of signal intensity peaks, in much the same way as a Raman spectroscopy spectra.

The results from the sector integral, displayed in Figure 5-20, reveal several strong features that appear in each scanned step across the width of the nano-fibre rope. This gives several clues about the structure of the materials within the nano-fibres. Initially three clear peaks can be seen, as well as their second order peaks, however, in order to critically analyse the three main peaks, they were re-plotted after removing the background signal. Applying this technique revealed a fourth
minor peak [see Figure 5-21, peak 3]. By using the data analysis suite ‘Origin’, each of the peaks were modelled to a Lorentzian fit type, allowing the measurement of the centres of the peaks.

Peaks 1 and 2, corresponding to ‘d’ spacing’s of 3.92 nm and 2.41 nm, were found to be the result of the X-ray scattering from a structure formed by PEO and SDS (Dror et al. 2003). As suggested by Dror et al., the two chemicals form a two-layer lamella structure: a free SDS layer and an interacted PEO/SDS layer, leading to the long range order shown by the two peaks. The sharpness of these two peaks is an indication of a narrower distribution of lamella orientations of the PEO/SDS within the nano-fibres, perpendicular to the fibre direction (Dror et al. 2003). In Dror’s case, both peaks significantly broadened upon the addition of CNTs, which was attributed to using twisted/distorted CNTs, which disrupt the crystalline morphology in the fibre. In our case, peak 1 remains the same shape, with a similar peak width, whilst peak 2 has reduced in intensity and increased in width. However, despite these differences, in our samples both peaks are still present and distinguishable. This indicates that aligned linear nanotubes do maintain the crystalline morphology of the polymer-surfactant composite, confirming Dror’s suggested detrimental effects that occur when using non-linear CNTs. Maintaining this crystalline morphology within the polymer could also explain the increased mechanical properties observed in Figure 5-15.

Figure 5-20 – The results from the sector integration of X-ray signal intensity in the region specified in Figure 5-19, for equal steps across the nano-fibre rope, where plot 1 is the top of the nano-fibre rope and plot 7 is the bottom of the nano-fibre rope.
Peak 3 is of low intensity and barely visible through the signal noise, however by fitting the peak with a Lorenzian fit it has a peak at 5.15nm, which relates to micelle formation of the SDS within the polymer chains (Süss et al. 1995). Although this may not necessarily improve the mechanical performance of the nano-fibres, this could be a good indication of whether the surfactant loading on the CNTs is correct. In the event that too little surfactant is used, it is thought that this peak will not be present (as all SDS will be attached to the CNTs). However, if too much surfactant was used, this peak would be significantly larger, where more surfactant would be free to form micelles.

Figure 5-21 – A detailed plot of the four main peaks obtained from the sector integration in the region specified in Figure 5-15, with the baseline removed and the peaks fitted using a Lorentzian model. The results obtained from PEO/SDS nano-fibres by Dror et al. have been included for comparison to the obtained PEO/SDS/CNT results. Peaks 1 and 2 corresponding to 3.92nm and 2.41nm are from PEO/SDS interactions, while peak 3 corresponds to 5.15nm resulting from the formation of surfactant micelles. It is unclear as to exactly what peak 4 is the scattering result of (corresponding to 3.04nm). The data from Dror et al. were adapted with permission from Y. Dror et al. (2003). Copyright 2003 American Chemical Society.

Peak 4 has not been recorded in any previous work. As this peak does not appear in Dror’s data, it suggests that this is a result of a regular structural change caused by the presence of the CNTs. Additionally, being that this peak is extremely narrow across its distribution, it indicates that the signal is caused by a feature of specific and regular length scale. It is possible that the signal is a result of the presence of a helix type structure with a d spacing ratio of 1:2, which could indicate how the nanotubes are wrapped in the polymer chains (Striereck 1993; Wlochowicz & Eder 1984; O’Connell et al. 2001;
The evidence for this was found by locating the second order peaks shown in Figure 5-20, which were found to have also have a ratio of 1:2. This CNT polymer wrapping would result in an increase in the mechanical performance of the composite, by providing the polymer chains a “rigid scaffold” to bind on to, and as such preventing chain slippage when under stress. This theory is considered less likely, due to the low concentration for CNTs within the fibres. However, it has been observed in many examples that the introduction of CNTs to a polymer can both restrict and promote crystal growth in various ways (Shieh et al. 2005; Chatterjee et al. 2005; Haggenmueller et al. 2006; Jin et al. 2007). One manner in which the CNT promotes crystal growth, and could lead to the 3 nm peak, is by providing the polymer with a crystallisation nucleation point, which then acts as the centre of spherulite type crystal structures (Li et al. 2006). These crystal like formations that grow along the length of the CNT, are called ‘shish-kebabs’, with small formations arranged along the length of the nanotube.

This crystalline structure would provide the necessary interfaces which would promote the CNT/polymer binding, giving rise to the mechanical enhancements that we observe in Figure 5-15. This would also explain why the CNT samples stiffened and changed appearance during tensile testing. However, it could be argued that peak 4 is a result of the surfactant (SDS) forming structures on the surface of the nanotube. The SDS molecules could form semi-spheres in functional groups at points along the nanotubes, which has been reported to be up to 5nm in separation distance, depending on the surfactant length (Li et al. 2006; Dölle et al. 2010). However, the SDS micelle peak (peak 3), suggests that the SDS chains are of the wrong size. Peak 3 corresponds to a d-spacing of 5.15 nm, by which assuming the micelle is spherical, meaning that the SDS molecules used to disperse these CNTs are around 2.57 nm long. Furthermore, if peak 4 was a result of the surfactant on the surface of the CNTs, then Dror would also have seen a similar signal, which there wasn’t (Dror et al. 2003). Therefore, from the evidence found, it is postulated that the narrow peak (4) found at a d-spacing of 3.02 nm is a direct result of the polymer restructuring in the vicinity of the CNT/polymer interface, resulting in a structure which gives rise to the significant mechanical enhancements observed during tensile testing.

Efforts were made in an attempt to find definitive evidence to support this theory using analytical methods such as transmission electron microscopy, however nothing was found.

The results obtained from one of the two mesh samples were discarded, as no scattering data was obtained. It is thought that this is most likely due to the sample being too thin, resulting in either the X-ray beam scattering being too low to detect, or the sample being destroyed by it. Despite this, one of the mesh samples did provide an extremely weak scattering pattern [see Figure 5-22]. Due to the signals weakness, no features were found other than a circularly symmetric halo around the beam-
stop (the black centre). By once again conducting and plotting a sector integral scan of this symmetric halo, it became apparent that the halo intensity decays from the centre spot with an average power of -1.012. This is known to be caused by the scattering of the incident beam from cylindrical structures, this is most likely by the nano-fibres as a whole as opposed to the individual CNTs (Glatter & Kratky 1982). However, this does give evidence to suggest that the fibres are forming linear cylindrical structures and not buckling or twisting as a result of the CNT-loading.

![Scattering Pattern](image)

**Figure 5-22** – The scattering pattern obtained from the nano-fibre mesh sample and the subsequent intensity sector integration scan plot. The decay pattern from the centre decays with an average power of -1.012, highlighting the presence of cylindrical structures with the sample.

5.6.4 Conclusions

Small angle X-ray scattering was used to probe the structural information in the nanometre range of electrospun polyethylene oxide nano-fibres loaded with sodium dodecyl sulfate dispersed single wall carbon nanotubes. Evidence was found of a lamella two layer nano-structure, as well as a previously unreported peak, as a direct result of the introduction of carbon nanotubes to the polymer. The large scattered X-ray signal found at 3.04 nm appears to be a direct result of the polymer restructuring at the CNT/polymer interface, providing the polymer chains with a ‘rigid scaffold’ for the polymer to bind to. This binding process prevents the chains from slipping during the loading of stress onto the materials, and leads to the significant mechanical enhancements observed during mechanical testing.

The results from this investigation both conclude this chapter, and provide the necessary questions that lead into the next. From this investigation it demonstrated how the polymer can
interact with the surfactant, as well as the carbon nanotubes. It also revealed how the surfactant can form micelles with itself, in the event that it has not fully bound to the carbon nanotubes. With this result, it becomes a requirement to further explore, both the possibility of using other surfactants, and how that surfactant should be applied with regards to intensity of ultra-sonication irradiation.

5.7 Conclusions

This chapter has begun exploring the electrospinning aspects of this project, focusing on the use of the traditional single-needle approach to the process. Doing this has resulted in a number of investigations that have explored the numerous parameters that both govern the process, and dictate the attributes of the resultant nano-fibres. For example, exploring how the variation in solution viscosity affected the morphology of the final nano-fibres has revealed that the best viscosity for their production, which ensured they have ideal attributes, is \(0.15 \pm 0.01\) Pa·s (corresponding to a 2% weight fraction polyethylene oxide (PEO) (2,000,000 M\(_v\)) aqueous solution). This result was followed on by probing how humidity affects the qualities of the final array of nano-fibres, highlighting how the relative humidity of the atmosphere within the electrospinning rig is required to be below 50%. Above this, there was a high risk of beads forming on the fibres, which will reduce carbon nanotube alignment in the final material.

The final electrospinning parameter explored was the complexity of the electrospinning jet, where the investigation focused entirely on modelling the polymer jet’s velocity, as it accelerates toward the collection drum. By collecting arrays of nano-fibres at varying collection drum surface velocities, it was possible to accurately measure the final velocity of the approaching nano-fibres. For a 2% weight fraction PEO aqueous based solution, this was found to be \(9.2 \pm 1.2\) m/s, enabling the collection drum to be spun at the right speed for the best nano-fibre alignment. Due to equipment limitations, the closest available setting to this measured value which can be used is 8.1 m/s, which will be used for the remainder of the project.

Using the deciphered electrospinning parameters for ideal nano-fibres and high degree of alignment, this project then evolved to introduce carbon nanotubes (CNTs) into the polymer solution. Upon doing so, Raman spectroscopy and thermogravimetric analysis confirmed that not only were the nanotubes manipulated into highly aligned arrays, but they were done so without introducing any damage to their structure. However, thermogravimetric analysis did reveal how the carbon nanotubes now oxidise at a slightly lower temperature of 551°C, as opposed to the original 593°C of the raw wetcake material. This effect was attributed to either the CNTs being evenly distributed over a large
area (effectively increasing their immediate surface area), or to the oxygen rich surfactant that was coated on the nanotubes’ surface.

These newly produced highly aligned arrays of carbon-nanotube-loaded polymer nano-fibres, were then subjected to mechanical and electrical testing, in an attempt to expose how the introduction of aligned arrays of nanotubes would affect other typical composite systems. Tensile testing demonstrated how introducing just 3.9% weight fraction of carbon nanotubes to the polymer system increased the ultimate tensile strength by up to 320% and increased the ductility by up to 315%, when compared to 100% polyethylene oxide nano-fibres. These improvements also include an increase in the Young’s modulus by up to 430%, from 60 ± 1 MPa (100% PEO), to 257 ± 1 MPa (3.9% CNT). Electrical conductivity analysis demonstrated how a rolled rope of nano-fibres similarly loaded with 3.9% carbon nanotubes, was found to have a resistivity of just 0.28 ± 0.02 Ωm, corresponding to a conductivity of 3.57 ± 0.24 Sm⁻¹, eight orders of magnitude higher than previously reported values for the original PEO polymer material, despite the PEO still being present in the sample. The sheet resistivity of a thin film of these fibres, was found to have a resistance of 33500 ± 100 Ωμm⁻¹, significantly higher than that of the rope, which was assumed to be the result of a difference in the materials volume and density.

This chapter was then concluded by using small angle X-ray scattering to probe the structural information of the nanotube-polymer composite, in order to expose the molecular structure over the nanometre scale. Using this analytical technique provided insight into the materials molecular structure, especially around the vicinity of the carbon nanotubes. Evidence was found of a lamella two layer nano-structure, as well as a previously unreported peak at 3.04 nm parallel to the CNT orientation, as a direct result of the introduction of carbon nanotubes to the polymer. This peak was attributed to being a direct result of the polymer restructuring at the CNT/polymer interface, providing the polymer chains with a ‘rigid scaffold’ for the polymer to bind to, promoting stress transfer to the CNTs, down the length of the fibre. It was concluded that this binding process potentially prevents the chains from slipping during the loading of stress, and led to the significant mechanical enhancements observed during mechanical testing.

The results from these investigations have demonstrated both the outstanding results that can be achieved from the use of electrospinning carbon nanotube systems, and how the polymer can interact with the surfactant, as well as the carbon nanotubes. However, these investigations were only conducted with one specific type of anionic surfactant, we will further explore both the possibility of using other surfactants, and how that surfactant should be applied to achieve the highest loaded stable dispersions. The next chapter will investigate using other surfactants, especially non-ionic,
which have been proven to be easier to remove from the surface of the nanotubes, should the need arise. It will also follow on from this to confirm if ionicity (where the solution contains anions or cations), is a key factor to both the electrospinning and alignment processes. The next chapter will then conclude by using the findings from the surfactant investigations, to develop a process for fully recovering the carbon nanotubes from the polymer nano-fibres, leaving the nanotubes as an aligned array.
6 Optimising CNT Loading for High Throughput

6.1 Introduction

The previous chapter successfully demonstrated that carbon nanotubes can be manipulated into highly-aligned arrays by carefully controlling the many variables of the electrospinning process. These variables included: solution viscosity, atmospheric humidity and the collection drum’s surface velocity. Once the nanotube alignment was confirmed using Raman spectroscopy, small angle X-ray scattering was utilised to provide insight into how the aligned nanotubes interface with the polymer matrix to create a composite material, leading to the significant mechanical and electrical performances observed during the material’s testing.

In this chapter, we further develop the project towards its intended goals of large area carbon nanotube alignment, using the previous chapter’s achievements to explore the prospects of using alternative surfactants to disperse the carbon nanotubes. It is targeted that this will achieve a greater CNT loading, reducing CNT processing times, as well as presenting other benefits. Previously in literature, there has been no simple or successful techniques reported, other than visually, for assessment of the efficiency of surfactants. We introduce a novel micro-centrifugal precipitation method, which is used for the assessment of carbon nanotube dispersion performance of various ionic and non-ionic surfactants. Surfactants that demonstrate the ability to form uniform, stable dispersions of nanotubes will then be electrospun, allowing further assessments of both their compatibility with the polyethylene oxide polymer (needed for electrospinning), and of the effect it has on the electrospinning process itself. As electrospinning can be conducted with either a positive or a negative potential, the effects of the surfactant charge on the spinning process will also be of a particular focus, with the hope of identifying any electro-chemical effect caused as a result of the ionic surfactants and the high potentials of electrospinning.

Using surfactants best for both dispersing carbon nanotubes and electrospinning, this chapter will conclude by investigating the recovery of the aligned nanotubes by thermally evaporating the polymer, and the surfactant. As mentioned in Chapter 2.3.3, thermally evaporating the other carbonaceous materials in this manner will leave residual amorphous carbons in the sample. In order
to avoid this, the potential purification effects reported from the addition of steam into the baking chamber will be explored, applying the steam purification process to aligned CNTs for the first time. The processes will be fully understood by investigating the effects it has on the samples, with increasing temperature, in an attempt to achieve the highest quality arrays of highly-aligned CNTs.

6.2 Assessment of Surfactant Performance for High CNT Loading

6.2.1 Introduction

As demonstrated in the last chapter, carbon nanotubes (CNTs) can be successfully dispersed and aligned into arrays using the process of electrospinning. This was previously achieved by using the anionic surfactant sodium dodecyl sulfate (SDS) to non-covalently functionalise the CNTs, allowing for them to be dispersed in an aqueous solution and giving them the freedom of movement to be manipulated into alignment. SDS’s use with CNTs has been extensively researched in literature; it’s common use as a dispersant is a result of its broad availability and known reliable performance (Richard et al. 2003; Rastogi et al. 2008; Dyke & Tour 2004). Despite this, some items of literature claim that other surfactants may be more suitable for dispersing CNTs, achieving greater loadings, depending on the CNTs being used (Moore et al. 2003; Blanch et al. 2010). Regardless, throughout literature, there have been no methods, for quantifying surfactant performances in a way that is comparable between systems, other than visually. In this investigation, we propose a novel micro-centrifugal precipitation method to achieve this.

As this project’s primary aim is to produce aligned arrays of CNTs in an industrially scalable process, it becomes necessary to explore the potential of using other surfactants, in order to increase the CNT loading in solution, and as such maximise CNT processing rates. Furthermore, using different surfactants may present other added enhancements, such as: increasing composite performance (by improving matrix-surfactant compatibility), easier removal from the surface of the CNTs after alignment, or enhanced electrospinning capability as a result of an insulating sheath around the CNTs (where increased solution conductivity was seen to alter electrospinning results in Chapter 5.5). For example, Triton X-100’s potential as an alternative surfactant was included in this investigation due to its reported ability to disperse CNTs in aqueous solutions and its non-ionic chemical composition, meaning it could be easier to remove from the CNT surface (Bai et al. 2010; Blanch et al. 2010). In addition to this, Triton X-100 has also been reported to have some other added enhancements in improving a CNT-epoxy composite’s mechanical and electrical performance, by providing a bonding mechanism between CNTs and the epoxy (Geng et al. 2008).
This investigation aimed to expose the potential of using other surfactant systems to disperse the CNTs, as an alternative to the SDS used before. The main driving force behind this research was that SDS is an anionic surfactant, where most ionic surfactants usually contain ions in the form of metals. Such metals would be both difficult to remove and detrimental to any final composite material. With this, various other ionic and non-ionic surfactants were tested for both their dispersion performance (when applied to Thomas Swan’s wetcake material), and their ease of removal when thermally evaporated. The surfactants tested in this investigation include: Benzalkonium chloride (ADBAC), Brij 52, Brij 58, Pluronic F127, sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), Triton X-100, Triton X-405 and Tween 80, where the details of each surfactant can be found in Table 6-1. Each surfactant that was found to suitably disperse the CNTs, was blend with polyethylene oxide (PEO), assessing its compatibility with the polymer in solution. Assuming that the dispersion was stable, and there were no obvious signs of agglomeration, it was then electrospun to allow a final assessment of the resulting nano-fibres produced. By doing this, it was hoped that the best surfactant system would be identified to both enable high CNT throughput and their easy recovery.

Table 6-1 – A list of all the surfactants chosen to disperse carbon nanotubes, where in each case the elemental composition has been detailed, along with the surfactant type. Please note: †polyethylene glycol is also known as polyethylene oxide (PEO). *Triblock copolymer PEO-b-polypropylene glycol-b-PEO.

<table>
<thead>
<tr>
<th>SURFACTANT:</th>
<th>CHEMICAL NAME:</th>
<th>COMPOSITION:</th>
<th>TYPE:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADBAC</td>
<td>Benzalkonium chloride</td>
<td>C, H, N &amp; Cl</td>
<td>Cationic</td>
</tr>
<tr>
<td>BRIJ 52</td>
<td>Polyethylene glycol hexadecyl ether†</td>
<td>C, H &amp; O</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>BRIJ 58</td>
<td>Polyethylene glycol hexadecyl ether†</td>
<td>C, H &amp; O</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>PLURONIC F127</td>
<td>Poloxamer 407*</td>
<td>C, H &amp; O</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
<td>C, H, O, S &amp; Na</td>
<td>Anionic</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
<td>C, H, O, S &amp; Na</td>
<td>Anionic</td>
</tr>
<tr>
<td>TRITON X-100</td>
<td>Polyethylene glycol tert-octylphenyl ether†</td>
<td>C, H &amp; O</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>TRITON X-405</td>
<td>Polyethylene glycol tert-octylphenyl ether†</td>
<td>C, H &amp; O</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>TWEEN 80</td>
<td>Polyethylene glycol sorbitan monooleate†</td>
<td>C, H &amp; O</td>
<td>Non-ionic</td>
</tr>
</tbody>
</table>
6.2.2 Experimental Procedure

It was noticed, during the sonication of the Triton X-100 surfactant in a preliminary experiment, that sonication power made a big difference in how the surfactant performed (with regards to dispersion of the CNTs). Reducing the power of the ultra-sonic tip probe appeared to produce better dispersions, however reducing it too much saw the wetcake resist breaking up. Equally, if the sonication power was increased beyond a certain limit, there were indications that the surfactant was sustaining damage and the dispersion would begin to fail. With most surfactants, some consist of a ‘head’ and a ‘tail’ section of the molecule. For most of the surfactants used, the tail is similar in chemical structure to that of PEO, either being a PEO or alkyl chain. The premise is that, under high intensities of ultra-sonic irradiation, the surfactant would begin to fail due to scission of epoxide bonds (C-O-C) in the tail of the surfactant, where PEO has already been noted to be easily damaged under ultrasonic irradiation (Cotiuga et al. 2006).

To explore the range of stated surfactants, each was purchased from Sigma Aldrich, where a measured quantity of each was placed into 8 plastic 50 ml centrifuge tubes with Thomas Swan’s wetcake material and deionised water. To allow a direct comparison between each surfactant, aqueous based dispersions were mixed so that there was 0.1% weight fraction CNTs and 1% weight fraction of the chosen surfactant (so that the CNT to surfactant ratio was 1:10, as used with SDS in previous chapters). Each solution was formulated to be a total of 15 ml of material, except for the first sample which was required to be 30 ml, due to minimum power limitations on the sonicator, which required more solution in order to lower the power concentration per volume. Each solution was then sonicated with ‘Cole Palmer CPX750 750 W’ tip sonicator, equipped with a straight-tipped 13 mm diameter probe, at a various power concentrations, ranging from 5 to 40 W/ml, in 5 W/ml increments. Each of the samples was sonicated for a total of 30 minutes in pulse mode, consisting of pulses of 3 seconds ‘on’ and 3 seconds ‘off’, totalling a processing time of 1 hour per sample. In order to prevent the sample heating, which could result is either equipment or sample damage, each of the samples were submerged in a 400 ml glass beaker ice bath. Following the ultra-sonication, 1 ml of each sample was taken using a micropipette and placed into a 1 ml micro centrifuge tube, of a premeasured weight. The samples were then centrifuged at 5000 times gravity for 30 minutes. Once removed from the centrifuge, each sample was carefully drained of the dispersed CNT solution, leaving only the residual dropped out material as a wet solid in the bottom of the tube [see Figure 6-1]. This dropped out material was then weighed within the micro-centrifuge tube, where the tube’s pre-known weight could be subtracted, allowing the weight of only the residual to be plotted against sonication power. The resulting data was then processed in data analysis suite ‘Origin’, and fitted with a suitable distribution.
Following the dispersion analysis, thermogravimetric analysis (TGA) was conducted on a ‘TA Q500 TGA’ on each the surfactants, in both air and nitrogen atmospheres, providing both insight in what temperature the surfactants thermally degrade at and what residuals can be expected, giving an idea on how easily they can be removed from a CNT array. The heating rate was always fixed at 10°C per minute, up to a final temperature of 900°C, if it was necessary (limited by the equipment). An ideal surfactant would be one that completely thermally decomposes at a temperature significantly lower than that of the oxidation of the CNTs. This would then signify that the aligned CNT arrays could be recovered using just a simple high temperature oven in air, as opposed to needing a high temperature oven equipped with inert gases (or by using other techniques), lowering processing costs and increasing the process’s commercial viability.

![Image of dispersion assessment process](image)

Figure 6-1 – These four images demonstrate the dispersion assessment process, where in this case Triton X-100 was used. (A) The CNTs, surfactant and deionised water is added to a vessel at a specific recipe. (B) The recipe is sonicated at the specified power within an ice bath. (C) 1 ml of the dispersion is then added to a micro-centrifuge tube which is then centrifuged. (D) After centrifuging, the remaining suspension is removed, leaving only the dropped out material which failed to disperse.

Finally, any surfactant that suitably dispersed the CNTs (located in solution at the top of the centrifuge tube) was removed and placed into a new vessel, ready for the final two assessments: judging its PEO compatibility and how it electrospins. Once separated from the dropped out material, the stable dispersion was blended with PEO (2,000,000 Mₜ), using a magnetic stirrer. Lastly, if possible, the blended solutions were electrospun from a single needle spinneret at a potential of +12 kV, with the needle at a distance of 22 cm from a silicone paper coated collection drum, rotating with a surface speed of 8.1 m/s (identical conditions to those found as ideal in the previous chapter). Any nano-fibres produced were assessed for any obvious undesirable attributes.
6.2.3 Surfactant Dispersing Assessment

Once all of the surfactants were assessed for their ability to disperse CNTs, it was apparent that some were significantly better than others. Brij 52 appeared to be the only surfactant which failed to disperse the CNTs to any degree, and this was clear even without centrifuging, where significant dropout was seen immediately after sonication. Centrifuging any of the Brij 52 solutions resulted in total material dropout at the bottom of the centrifuge tube, leaving a clear aqueous solution at the top. For this reason, the results only varied with error, therefore the data for Brij 52 was omitted from the collective analysis in Figure 6-4.

In a similar fashion to Brij 52, Triton X-100 also saw relatively poor results, with a high volume of dropped-out CNTs (compared to the other samples) [see Figure 6-2]. This result contradicts some literature, which claims Triton X-100 to be extremely efficient at dispersing CNTs (Rastogi et al. 2008), but also agreed with others, that it isn’t (Blanch et al. 2010). This variation in results could be owed to the varying chain length of the PEO tail on the end of the molecule [see Figure 6-3]. Blanch et al. (2010) claimed that Triton X-100 wasn’t a good dispersant of CNTs due to the shorter molecular chain length of the sample they used, compared to Triton X-405 which they found had a longer chain. This may have been the case; however, it was found that the mass of material that dropped out after centrifuging reduced almost linearly with increasing sonication power [see Figure 6-4]. Unlike with the Pluronic F127 surfactant (discussed later), this reduction in the mass that dropped out during centrifuging did not appear to be a result of CNTs becoming increasingly dispersed, as visually the solutions remained a generic clear grey [see the example in Figure 6-2]. It is thought that this decrease
in residual mass was actually due to an increase in surfactant damage, whereby the hydrophilic polyethylene oxide tail section of the Triton X-100 molecule was becoming increasingly cleaved from the hydrophobic aromatic hydrocarbon head, and remained in the suspended solution. The hydrophobic head of the Triton X-100 molecule would then bind to another hydrophobic surface i.e. the CNTs or another hydrophobic molecule, and fall out of solution during centrifuging. Evidence was found of this cleavage of the Triton X-100 molecule when another two solutions consisting of just Triton X-100 and water (at 10% Triton X-100 by weight), were centrifuged in a similar fashion to the CNT samples in this investigation. However, one of the solutions was subjected to ultra-sonic irradiation at a power of 35 W/ml. Centrifuging this solution found a black residual at the bottom of the tube but not at the bottom of the non-sonicated solution. Where it is thought that this dropped out material is the cleaved hydrophobic aromatic hydrocarbon head of the Triton X-100 surfactant [see Figure 6-3, B]. It was suggested that Fourier transform infrared spectroscopy should be used in order to clarify this hypothesis. However, these speculations were not further investigated, and as such these findings should be further investigated as future work.

Triton X-100 and Brij 52 aside, the rest of the surfactants explored produced much more comprehensible results, where in most cases the data displayed a curve which followed a Gaussian distribution. Figure 6-4 plots the mass of residual material which has dropped out during centrifuging the solutions of CNTs dispersed with the remaining surfactants: ADBAC, Brij 58, Pluronic F127, SDS, SDBS, Triton X-100, Triton X-405 and Tween 80. Excluding the results for Pluronic F127, which will be
explained later, an average trend was observed for all other samples. This was attributed to three scenarios which vary with sonication power intensity. The first scenario is where the sonication power is not sufficient to fully de-bundle the CNTs within the wetcake, reducing the accessible surface area of the nanotubes for the surfactant to attach to. This results in both poor surfactant coating on the CNT surfaces, and in large heavy CNT bundles remaining in solution, which are prone to dropping out when centrifuging. As the sonication power increases, these effects are reduced down to a minimum; at this point, the maximum dispersion achievable with that surfactant is obtained, with the lowest amount of residue remaining after centrifuging. This corresponds to the lowest point of the curves seen in Figure 6-4. As sonication power increases past this point, damage is started to be introduced to the surfactant molecules, lowering their effectiveness. With the increase in damage to the surfactant, the mass of material that drops out of the solution during centrifuging increases, giving rise to the final upward curved shape seen in the results [see Figure 6-4].

![Graphs showing residual mass vs sonication power](image)

**Figure 6-4** – These two graphs present the results obtained from the dispersion investigation, displaying the mass of residual material that drops out of solution during centrifuging. In most cases, the mass that drops out varies as a function of sonication intensity, and the point of lowest drop out corresponds to the ideal sonication power for dispersing CNTs with that surfactant. Any missing data points are a result of no data being obtained due to the solution foaming. The graph on the right is a zoomed plot of the lower data.

Figure 6-4 displays all of the results from this surfactant sonication investigation, except for results obtained from Brij 52 as it failed to disperse any CNTs, as previously mentioned. Each of the data sets generally displayed a distribution with a lowest residual at a most ideal sonication power, except for the surfactants Pluronic F127 and Triton X-100. The approximations for ideal sonication power were profiled by using, where possible, a Gaussian distribution to find the distribution centre. Although it was not clear why, the samples made using surfactants Brij 58 and Triton X-405 did not follow a Gaussian distribution like the others, but still displayed an ideal sonication power.
Table 6-2 – This table displays the results from the sonication investigation which assess surfactant effectiveness as a function of sonication power intensity. The error is calculated from the standard error in the mean across multiple repeat measurements.

<table>
<thead>
<tr>
<th>SURFACTANT NAME</th>
<th>APPROXIMATE IDEAL SONICATION POWER (W/ml)</th>
<th>LOWEST RESIDUAL MEASURED FROM 1 ml OF SOLUTION (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADBAC</td>
<td>17.5</td>
<td>133 ± 4</td>
</tr>
<tr>
<td>Brij 58</td>
<td>18.5</td>
<td>1.28 ± 0.04</td>
</tr>
<tr>
<td>Pluronic F127</td>
<td>42.5</td>
<td>1.91 ± 0.06</td>
</tr>
<tr>
<td>Triton X-405</td>
<td>23.3</td>
<td>0.66 ± 0.02</td>
</tr>
<tr>
<td>Tween 80</td>
<td>18.5</td>
<td>8.20 ± 0.3</td>
</tr>
<tr>
<td>SDS</td>
<td>17.2</td>
<td>0.64 ± 0.02</td>
</tr>
<tr>
<td>SDBS</td>
<td>21.3</td>
<td>3.60 ± 0.1</td>
</tr>
</tbody>
</table>

The best surfactants were found to be Brij 58, SDS and Triton X-405, with SDBS and Pluronic F127 also proving to be very effective at dispersing the CNT wetcake. SDS demonstrated to be the best at dispersing the CNTs, however the solution foamed when subject to high sonication powers, giving cause for the two missing data points. Pluronic F127 also displayed an interesting trend by revealing increasing effectiveness with increasing sonication power. It is thought that this surfactant would follow the same Gaussian characteristic as the other surfactants with regards to eventual degradation after an ideal sonication power, but has an ideal power at an intensity higher than was achievable with the equipment used in this investigation. However, using a Gaussian approximation the ideal sonication power for Pluronic F127 was estimated to be 42.5 W/ml. Lastly Triton X-405 was also revealed to show a similar trend to the Pluronic F127, in the sense that increasing sonication intensity increased its effectiveness. However, unlike Pluronic F127, Triton X-405’s ideal sonication power was found. Unlike the other surfactants tested, Triton X-405 proved to be less affected by sonication powers above its ideal and failed to show any significant signs of damage beyond the ideal. Much the same as the research conducted by Blanch et al. (2010), Triton X-405 also revealed to be significantly more resilient to ultrasonic irradiation, and substantially more effective at dispersing CNTs than Triton X-100.
A table of the final results for the ideal sonication power intensities for each surfactant can be seen in Table 6-2. Each of the measured lowest residual values were taken from the same size sample centrifuged (1 ml), so can be used to directly compare the effectiveness of each surfactant. Errors in these measurements were calculated on a surfactant by surfactant basis, this was because each surfactant formed a solid at the bottom of the micro-centrifuge tube of varying densities. This resulted in some samples having a very soft residual drop out which was hard to separate from the dispersed solution, making high error likely on some surfactant systems. In order to minimise the error in each measurement, five identical samples were measured at each sonication power, so the error was calculated as an average error in the mean.

The ideal sonication power concentrations will vary depending on a number of situations. For example, the sonication tip used to define these values was worn, and as such a new tip would alter the energy transferred into the solution. Furthermore, in this investigation it was ensured that the same centrifuge tubes were used during sonication. This was because, the dimensions of the vessel, and its composition material, will also affect how much vibrational energy is either reflected back into the sample, or absorbed by the vessel (Nanzai et al. 2009). From the results we obtained, we purpose that the best surfactants to be used for the dispersion of the CNTs, is either Brij 58, SDS or Triton X-405. However, within this project, these recommendations are pending the outcome of the next few investigations, assessing each surfactants ability to be thermal removed, and its compatibility with the PEO polymer needed for electrospinning.

### 6.2.4 Surfactant Thermal Analysis

Once each surfactant’s ability to disperse Thomas Swan’s CNT wetcake product was assessed, the most effective surfactants were subjected to thermal analysis. TGA was performed on the surfactants in order to probe how they thermally degrade and what, if any, residual masses are left behind. This analysis was conducted in both air and nitrogen atmospheres on Brij 58, Pluronic F127, Triton X-405, Tween 80, SDS and SDBS. Figure 6-5 displays the 12 TGA curves obtained, revealing each surfactants oxidation/evaporation temperatures and any residue left behind.
The surfactant species can be split into two categories: non-ionic and ionic, whereby the ionic surfactants usually contain ions in the form of metals. This means that ionic surfactants would leave an increased residue after the TGA than the non-ionic ones, which can be seen when comparing the TGA data. SDS and SDBS are both ionic because they contain sodium ions, while the remaining non-ionic surfactants produced the best results, leaving little residue behind in both air and nitrogen. The metal content within the ionic surfactants, meant that it could not be fully removed by this process and large residues were seen. The surfactants easiest to remove were found to be Brij 58 and Pluronic F127.

Figure 6-5 – The TGA results for Brij 58, Pluronic F127, Triton X-405, Tween 80, SDS and SDBS when analysed in both air and nitrogen atmospheres. Non-ionic surfactants produced the best results, leaving little residue behind in both air and nitrogen. The metal content within the ionic surfactants, meant that it could not be fully removed by this process and large residues were seen. The surfactants easiest to remove were found to be Brij 58 and Pluronic F127.
surfants are non-ionic. As a direct result of the metal within SDS and SDBS, large residue can be seen in the TGA results [see Figure 6-5], and the rest of the surfactants have virtually no residue. Choosing a surfactant that does not leave any residue is crucial for producing CNT loaded nano-fibres where the CNTs need to be fully recovered. Using a surfactant such as SDS or SDBS would leave sodium containing residues on the CNT surfaces within the final material, potentially reducing CNT interaction and reducing the mechanical properties of any final composite material. This conclusion, despite the surfactants effectiveness at dispersing CNTs, renders SDS and SDBS unsuitable for use in the electrospinning solutions of this project, for samples that require the CNTs to be fully recovered.

The non-ionic surfactants all left very little residuals, with the biggest only having a residual of 2.78% of the original mass (Tween 80). Pluronic F127 left the lowest residual of 0.87% in nitrogen, with no visible residual deposits, indicating it has almost completely evaporated during heating. The remaining three other surfactants however, saw residuals of a 1 – 2% of the original mass, in the form of amorphous carbons species, but only when heated in nitrogen. When analysed in air all of the non-ionic surfactants left almost no residue material, with nothing visually noticeable remaining on the TGA sample crucible. Triton X-405 revealed the lowest residual when analysed in air, with just 0.12% of the original mass analysed remaining.

The thermal analysis of the non-ionic surfactants also revealed another advantage through the temperatures at which they oxidise. It was noticed that all of the non-ionic surfactants oxidise at temperatures lower than that of the CNT wetcake material [see Chapter 4], with Brij 58 oxidising at the lowest temperature of 265°C. By using a surfactant that oxidises at a temperature significantly lower than the 590°C of the CNTs, it enables the CNTs to be almost fully recovered within a standard oven, negating the need for air tight apparatus and inert gases. This advantage could significantly reduce process costs, increasing the commercial viability of the CNT alignment processes.

6.2.5 Surfactant-Polymer Compatibility and Electrospinning

Brij 58, Pluronic F127, Triton X-405, and Tween 80 were all chosen for continuing investigation due to their performance in both dispersing the CNTs and their minimal residual after thermal removal, as confirmed by TGA. However, the next stage of the comparison was to assess the compatibility of the surfactants with the PEO, which was needed to give the dispersion the viscoelasticity it required for electrospinning. To achieve this, dispersions were remade with each of the chosen surfactants at 0.1% weight fraction of CNT, ensuring that for each surfactant their ideal
sonication powers were used. 2% weight fraction of PEO (2,000,000 M<sub>n</sub>) was then added into each of the dispersion solutions, and left to dissolve over several hours.

Once dissolved, some results were immediately clear, Triton X-405 and Pluronic F127 saw agglomerations appear within their solutions [see Figure 6-6, image A]. This was found to be the result of a compensation effect, whereby the surfactant would leave the CNT surface in favour of the forming a micelle/lamella with the PEO (Qiao & Easteal 1998). Regardless of this effect, electrospinning was attempted on these samples but the agglomerations blocked the needle spinneret, any jets that were produced failed to whip and electro-sprayed instead. This ‘clouding’ mechanism with the PEO could potentially be avoided by using an alternative spinnable polymer such as polyvinyl alcohol (PVA), however this could increase production costs. Furthermore PVA is not as widely available as PEO in long chain lengths, meaning a higher weight fraction of the polymer would be needed, reducing the CNT content and increasing processing time.

Figure 6-6 – (A) A photograph of the CNT agglomerations found in the Triton X-405 solution after PEO was added, a similar reaction was also seen in the sample containing Pluronic F127. (B) The first areas of aligned CNTs using an alternative surfactant, Tween 80. Sheets like this were also made of the Brij 58 surfactant with similar success.

The remaining non-ionic surfactants, Tween 80 and Brij 58 both produced stable electrospinnable solutions with the PEO, with no noticeable agglomerations or any other kind of irregularity. These solutions were then electrospun without any issues, producing black nano-fibres loaded with CNTs [see Figure 6-6, image B]. As in the previous chapter, electron microscopy was used
to confirm that the nano-fibres are of high quality and that the CNTs in the sample are aligned. This advancement in the optimisation of the electrospinning solution is a key step to this project, whereby choosing the correct surfactant we have: ensured maximum CNT loading (by minimising the dropped out undispersed material), improved the process efficiency, and minimised processing time and cost with regards to CNT recovery. This research paves the way for the first time for full CNT recovery without using any acids or other damaging processes, in order to remove the surfactants from the CNT surface, which could otherwise diminish the CNT-to-CNT interactions which are responsible for their properties.

The mechanics of CNT recovery, its outcomes and how the process can be optimised, after the CNTs have been aligned via the electrospinning process, will be further explored in Chapter 6.4. However, before this, a brief investigation into how the surfactant species affect the electrospinning process will be conducted. This is because it was observed how surfactants can be either non-ionic, cationic or anionic, which could affect how they interact with the polarity of the electro-static potential subjected to the solution during spinning. Although it is fairly safe to assume that non-ionic surfactants will see little or no effect between electrode polarities, it is important to explore and expose any potential benefits from using ionic surfactants with the different polarities, such as jet control or electrostatic field enhancement. These ideas and questions will be explored next.

6.2.6 Conclusions

The surfactants: benzalkonium chloride, Brij 52, Brij 58, Pluronic F127, sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), Triton X-100, Triton X-405 and Tween 80, were assessed for their performances in various aspects of the electrospinning solution requirements. This included: their ability to disperse a high weight fraction of the CNTs found within Thomas Swan’s wetcake product, their thermal degradation profiles, leading to an assessment of how easy they are to remove from the CNT surface, and their compatibility when blended with PEO, to be subsequently electrospun into aligned nano-fibres.

Using a novel micro-centrifuge technique, each of the surfactants was assessed for their ability to disperse CNTs. Brij 58, Pluronic F127, SDS, SDBS, Triton X-405 and Tween 80 were found to be the best, with SDS producing the most stable dispersions. Triton X-100, despite being reported to be an effective CNT dispersant, was found to disintegrate under ultra-sonic irradiation, ultimately failing to disperse any of the wetcake’s CNT content. As well as their efficiency as a CNT dispersant, each surfactants ideal sonication power intensity was also revealed, with all surfactants (excluding Triton
X-100 and Pluronic F127) found to have an ideal power intensity between 17 to 24 W/ml. Pluronic F127’s ideal sonication power was found to be at a value higher than could be achieved with our equipment, but was estimated using a Gaussian fitting to be 42.5 W/ml. Note that these powers were measured at the controls of the sonicator, as opposed to using any form of microphone.

The surfactants that displayed the best results as a dispersant were then subjected to thermogravimetric analysis, assessing their ease of thermal removal from the CNT’s surface after the alignment process. This analysis was conducted, in both air and nitrogen atmospheres, on Brij 58, Pluronic F127, SDS, SDBS, Triton X-405 and Tween 80. The ionic surfactants SDS and SDBS were found to leave large residuals as a result of their metal content. Unlike the ionic surfactants, the non-ionic surfactants lacked metal ions in their chemical structure and left no residue, meaning that virtually full carbon nanotube recovery, without any contaminates, could be easily achieved. Furthermore, it was noticed that Brij 58 and Pluronic F127 almost fully evaporated from the CNT surface at temperatures significantly lower than the oxidation temperature of the CNTs, meaning almost full CNT recovery could be achieved in a standard oven in air, negating the requirement for specialist equipment or inert gases. Alternatively, combining the baking process with a later explained steam purification technique, in chapter 6.4, would also remove amorphous carbons and to purify the CNTs.

The final stage of this investigation was to assess the surfactant’s compatibility with the electrospinnable polymer polyethylene oxide (PEO). Brij 58, Pluronic F127, Triton X-405 and Tween 80 were assessed as the remaining surfactants, not eliminated at this stage in the investigation. Pluronic F127 and Triton X-405 were found to be incompatible with the PEO, where the presence of the polymer caused the surfactants to migrate from the CNT surface, resulting in eventual agglomeration. These agglomerations rendered the solution un-spinnable and as such lead to Pluronic F127 and Triton X-405’s elimination as potential surfactants for the project’s electrospinning solution systems. However, Brij 58 and Tween 80 both formed stable solutions that were electrospun to produce mats of aligned nano-fibres loaded with aligned CNTs. These discoveries signify that the Brij 58 and Tween 80 surfactant systems have paved the way for scalable CNT alignment and full 100% CNT recovery post-manipulating (whether this be electrospinning or else), something never before claimed in literature.

The next chapter in this thesis explores the effects that both surfactant charge and electrospinning electrode polarity has on the resulting nano-fibres. Although it is assumed that non-ionic surfactants will have little effect on the nano-fibres across electrode polarities, ionic surfactants could reveal some potential beneficial effects, such as jet control or electrostatic field enhancement.
6.3 Effect of Surfactant Ionicity on the Electrospinning Process

6.3.1 Introduction

Electrospinning can be conducted using either a positive or a negative electrode; the difference in using either polarity has been scarcely reported, with one previous publication reporting that there is little difference between the two (Kalayci et al. 2005). However, none of this research considers the effects of ionicity within the electrospinnable solution, and simply compares the difference that changing electrode polarity has on the resultant nano-fibres produced from a non-ionic polymer.

The process of electrospinning relies on the solution charging at the spinneret, whether it be positively or negatively. This charging then induces the bending instability seen during spinning through the mutually repulsive forces of the polymer jets. The degree of charging that is applied to the jet depends very strongly on the materials that the jet is composed of, and the electrical properties of these materials. Altering the constituent materials within the jet, and in turn the jets net charge density, will ultimately alter the resulting nano-fibres produced (Theron et al. 2004; Z. Sun et al. 2012).

A combination of the difference in effects between using either a positive or negative electrode being scarcely explored, and the significant difference across the chemistry of the surfactant systems, has warranted a short investigation within this project to be conducted. It is thought that the non-ionic surfactant systems will demonstrate no differences in the nano-fibres produces on either electrode polarities, much the same as the non-ionic polymers systems reported by Kalayci et al. (2005). However, ionic solutions could demonstrate differences between electrode polarities, depending on if the surfactant is cationic or anionic. For example, based on simple electrolysis theory, anionic molecules will be repelled from a negative electrode (cathode), and attracted to a positive electrode (anode), where the opposite applies for cationic molecules (Eagleson 1994). This same effect applies ionic surfactants, for example sodium dodecyl sulfate (SDS) has already been previously reported to behave in a similar fashion (Yüksel et al. 2009). However, with regards to electrospinning, this effect has not been previously explored, so it is not clear how the polarity of the spinneret will affect the resulting nano-fibres.

In this chapter we explore the effect that electrode polarity has on the resultant nano-fibres which are loaded with CNTs dispersed with either an anionic, cationic or non-ionic surfactant. Exposing any potential benefits or drawbacks in electrospinning jet control or electrostatic field enhancement, that could be a result from the electrostatic interactions between the solution and the electrode.
6.3.2 Experimental Procedure

In order to investigate the effects that surfactant ionicity and electrode polarity have on the electrospinning technique, a simple experiment was devised. Three aqueous based electrospinnable solutions were blended, where in each solution 0.1% weight fraction of CNTs was dispersed via ultrasonic irradiation, using 1% weight fraction of benzalkonium chloride (ADBAC) as the cationic surfactant, sodium dodecyl sulfate (SDS) as the anionic surfactant, and Brij 58 as the non-ionic surfactant. Each of the surfactants were utilised using the research from the previous chapter. Following successful CNT dispersing, 2% weight fraction of PEO (2 million Mₐ) was added to each solution, readying each one for electrospinning.

The electrospinning parameters were fixed so that only the polarity changed between samples. A single needle spinneret positioned approximately 22 cm from a rotating drum collector covered in silicone release paper, was charged by a power supply unit set to 12 kV, positive or negative. The solution was fed to the spinneret at a constant 700 µl/hr until a total of 4 ml of solution was delivered. Atmospheric temperature was measured to be 22°C, and humidity was kept low at around 42% relative humidity by a dehumidifier. During spinning, careful observations were made of the polymer jet, noting how it behaved between electrode polarities for each surfactant system.

Once the samples were produced, the resultant nano-fibres were then compared using both optical analysis and electron microscopy, looking for any obvious differences as a result of the polarity change between each of the surfactants used. In order to allow better demonstration of the sample morphology and quality, high resolutions grey scale scanners were also used to capture images of the nano-fibres in an ‘as they were collected’ fashion.

6.3.3 Results and Analysis

Across all samples, as expected, those made using the non-ionic surfactant saw no differences between electrode polarities. However, during the electrospinning process, visual observations were made of the polymer jet between the ionic samples. Studying the electrospinning jet shortly after it has left the spinneret, for each solution and polarity, revealed a notable difference between samples, as well as giving an indication as to the net density of charge within the jet. It was noticed that for the ionic surfactant systems, when a like-for-like polarity was used (i.e. negative polarity with the anionic surfactant containing solution), the jet travelled straight towards the collection drum. However, when using an opposite polarity (i.e. a positive polarity with an anionic surfactant containing solution) the jet path curved away from the electrode [see Figure 6-7]. This suggests that, when the solution
contains an electrolyte with a polarity opposite to the polarity of the electrode, it can carry a higher charge density, compared to when the polarities are equal. This effect could be because of the surfactant’s ionicity, meaning the solution would be less likely to charge when containing an electrolyte of the same polarity. Equally, in the case for SDS for example, a negatively charged spinneret could actually repel the negatively charged sulfate ions within the surfactant, and attract the positively charged sodium ions from it, in a similar manner to electrolysis. Being that the CNT’s surface is coated in the surfactant, if the surfactant is not driven from the surface of the CNT, the electrode would repel the CNT too. Evidence of this was seen on the sample collection paper, where spitting was seen after the spinning of the anionic SDS loaded solution had finished [see Figure 6-8].

Figure 6-7 – Two schematic diagrams depicting how the jet path changed depending on the electrode that was used with the SDS loaded solution, giving a good indication on which polarity charges the solution to a higher degree (as it is repelled from the electrode after charging).

Figure 6-8 demonstrates this suggested repulsion mechanism when using the SDS. Where electrospinning a solution containing an anionic surfactant with a negative electrode causes poor nano-fibres, whereas electrospinning with a positive electrode is unaffected. Unlike previously reported scientific literature, with respect to there being no difference between positive and negative electrospinning, this result shows the clear difference of using each electrode and how specking occurs when using an anionic surfactant and the negative polarity. The CNTs appeared to agglomerate at the needle and are ejected from the jet during whipping. This was evident as black specks were deposited all over the electrospinning rig, as well as the sample substrate, without any obvious preference. Closer inspection of the fibres revealed how the fibres were barely fibres at all but rather droplets of dried solution. As this ‘specking’ effect was not occurring with the non-ionic solutions, it was clear that this effect was caused by the anionic SDS used to disperse the CNTs.
Figure 6-8 – Grey-scale scanned images of electrospun PEO nano-fibres loaded with CNTs dispersed with SDS, where one sample was spun with a negative electrode displaying black spots where the CNTs have been repelled from the jet and subsequent poorly produced nano-fibres (A), and the other sample spun with a positive electrode shows good, regular nano-fibres, with no spots (B).

The cationic surfactant benzalkonium chloride (ADBAC) was used as a direct polar contrast to anionic SDS. Despite the fact that ADBAC was not as efficient at dispersing the CNTs (when compared to SDS), the results were still as predicted. The solution electrospun better with a negative electrode than a positive. Inspection of the fibres produced with the negative electrode found them to be significantly more homogenous than those produced with the positive electrode. Additional unwanted aspects of the nano-fibres produced with the positive electrode included: a high frequency of ‘spits’ or drips which resulted in final fibre damage, and vast areas of wet fibre collection (illustrated where the fibres had stuck together), where fibre sticking also demonstrated a lack of fibre to fibre repulsion from a lack of charge carried within the jets. Furthermore, the fibres produced with the preferred negative electrode ‘whipped’ across a larger area, again confirming that a greater density of charge was carried in the electrospun jet.

In order to fully appreciate these results, electron micrographs were acquired of the nano-fibres produced from each surfactant system, with each electrode polarity. Figure 6-9, reveals how the non-ionic surfactant system has no electrode preference, whereas both the anionic and cationic surfactants do. This result is extremely important for producing highly aligned fibres, and highlights how electrode polarity must be considered when changing the surfactant system (should the need arise).
6.3.4 Conclusions

Non-ionic, cationic and anionic surfactants: Brij 58, benzalkonium chloride (ADBAC) and sodium dodecyl sulfate (SDS) respectively, were used to disperse CNTs into aqueous-based solutions blended with polyethylene oxide (PEO) for electrospinning. They were each electrospun with the same spinning parameters using both a negatively and positively charged spinneret, where the difference between the nano-fibres produced between electrodes was compared both visually and with electron microscopy.

The results found that, when using a non-ionic surfactant to disperse the CNTs, either electrode polarity was found to be suitable to produce high quality nano-fibres. However, the same could not be said for the cationic and anionic surfactants. The sample containing CNTs dispersed with the cationic ADBAC surfactant only produced high quality nano-fibres when electrospinning with the negative electrode. The anionic SDS surfactant-loaded sample was found to prefer the direct opposite, and only produced desirable fibres when electrospun with a positive electrode. When using a non-preferred electrode polarity on the ionic surfactant systems, the fibres were found to be inconsistent
and defective, not ideal when the goal is the alignment of CNTs. Furthermore, the CNTs dispersed with SDS and electrospun with a negative electrode were found to be ejected or expelled from the electrospinning jet, depositing randomly on the rig or its housing, as opposed to being solely within the nano-fibres. This effect was assumed to be the result of the negatively charged electrode/polymer jet repelling the negatively charged ionic head of the surfactant which coated the CNT surfaces. This ejection mechanism was also found to completely destroy the electrospinning process, causing the polymer jet to disintegrate and electro-spray.

Exploring the surfactants ionic response to the electrospinning electrode polarity has not yielded any benefits which would result in the production of higher quality nano-fibres. However, it has revealed that, despite the previous reports in literature, electrode polarity choice does make a difference to the resultant nano-fibres during electrospinning. These findings can not only be used in the event of changing the surfactant which disperses the CNTs, but for any electrospinning solution that contains ionic materials. Using a combination of these findings and the previous chapters, the next chapter investigates the possibility of both fully recovering and purifying the aligned CNTs arrays using a steam treatment method.

6.4 Carbon Nanotube Recovery

6.4.1 Introduction

One of the biggest aspects of this project was solving the issue of recovering the carbon nanotubes (CNTs), without impairing the high-quality and the alignment of the material. The surfactants used to non-covalently functionalise the CNTs can be extremely hard to remove from the CNT’s surface, once manipulation has finished (Ausman et al. 2000). Almost all published work which aims to manipulate CNTs for an application, involves functionalising them, and then either uses acids for CNT recovery, which could damage the CNTs (Zhang et al. 2005), or simply leaves them functionalised. Within this project, leaving the CNTs coated in surfactant molecules will continue to interrupt the van der Waals forces which give rise to their remarkable mechanical properties. Furthermore, this residual surface coating prevents CNT-to-CNT contact necessary for electron transport, significantly reducing the conductivity of any potential material these CNTs are used in. Being able to fully recover the aligned CNTs and restore their extreme properties would allow for their use in applications in advanced electronics, charge storage and next generation composite materials.
Figure 6-10 – A schematic diagram of the steam purification process on the aligned CNT loaded nano-fibres, showing the aligned array of CNTs in the nano-fibres, the steam purification process and the purified CNTs.

Thermal evaporation in an inert atmosphere was explored as a potential method for removing the surfactant and polymer to recover the aligned CNTs. However, this process resulted in an introduction of residual amorphous carbon as well as other contaminants, which coated the surface of the CNTs, maintaining the disruption of the needed van der Waals forces [see Chapter 6.2.4]. As previously explained in Chapter 2.3.3, Tobias et al. (2006) published a method for removal of these amorphous carbons, while simultaneously evaporating other materials through the introduction of steam to the baking chamber. The steam was found to only remove the less ordered carbon and defective graphitic structures, leaving just purified CNTs. For the first time in literature, this process for targeted removal of polymeric and amorphous carbons was applied to the aligned arrays of CNTs, in a bid to fully recover and purify the aligned sheet, for high performance applications [see Figure 6-10].

6.4.2 Experimental Procedure

For this investigation, two surfactants were used as the CNT dispersant, an anionic and non-ionic: sodium dodecyl benzene sulfate (SDBS) and Brij 58. This was to allow for the direct comparison between the final steam purified materials, looking for potential contaminants caused by the metal content within SDBS, (as was discovered in Figure 6-5). The CNTs were dispersed using 0.1% weight fraction of each surfactant into an aqueous solution, with the surfactants at a ratio of 1:10. The dispersing was conducted using an ultrasonic tip probe using the parameter discovered in Chapter 6.2.3. Once sonicated, the solution was centrifuged at 5000G for 30 minutes, removing any remaining undispersed material from the solution. Polyethylene oxide (2,000,000 Mₐ) was blended with each of the final solutions, rendering the solutions ready for electrospinning.
Each solution was electrospun at an accelerating voltage of +12 kV, using a single needle spinneret, set at a distance of 22 cm from a high speed collection drum (rotating at 8.1 m/s). The temperature and relative humidity of the atmosphere during electrospinning was recorded as 21°C and 41% respectively. The drum was wrapped in a silicone coated paper, to allow easy removal of the produced fibres before thermal treatment. Each of the nano-fibre samples were removed from the paper and folded several times into a coupon, ensuring that the fibre alignment is maintained. This produced a significantly thicker sample, both enabling easier handling and ensuring more material was available for analysis after the treatment. This was because only 3.9% weight fraction of the sample was CNT, so a significant mass loss and reduction in material size is to be expected.

![Figure 6-11 – A schematic diagram of the experimental equipment set up used to steam treat the nano-fibre samples, where the simple valve system allows manual control over when the steam is allowed to enter the furnace, preventing issues such as steam condensation during cooling.](image)

In order to allow easy loading/unloading of the sample during the baking process, the thick aligned CNT loaded nano-fibre coupons were mounted onto a silicon wafer substrate, and inserted into the centre of a Carbolite quartz tube furnace (as demonstrated in Figure 6-11). The quartz tube was then purged with nitrogen for 30 minutes before elevating the temperature, minimising the risk of any residual oxygen burning the CNTs within the sample. With the nitrogen gas fixed at a flow rate of 0.5 L/min, the tube furnace was heated at a rate of 20°C per minute, up to the set target temperature. Once this temperature was reached, it was maintained for 3 hours, before being left to cool naturally back to room temperature. Once the temperature had fallen to that of the room, the nitrogen could be stopped and the sample unloaded. In order to allow direct comparison of the effects steam has on the samples, this process was repeated both with and without steam. For samples that were to be steam treated the process was identical with these added steps. During the nitrogen purge
of the furnace, it was also important to ensure the de-ionised water vessel was also purged, ensuring any dissolved oxygen was also removed. To generate the steam, the water vessel was heated close to boiling point as the furnace heated up, where once the target temperature was reached, the valves were adjusted to allow nitrogen to bubble through it, carrying water vapour in to the reaction chamber. Steam was only allowed into the furnace during the 3 hour period that it was heated to the target temperature, preventing condensation during cooling, and reciprocating the volume of steam from sample to sample. Each baking process, conducted both without steam and with steam, was conducted on all SDBS samples at temperatures ranging from 500°C to 1000°C, at 100°C intervals. The investigation was not repeated on all Brij 58 samples due to the time requirements it placed on this project. However, Brij 58 samples were steam treated at 900°C to allow the direct comparison with the SDBS samples.

Thermogravimetric analysis (TGA) was used several times in this study, allowing confirmation of the CNT content, and insight into how and at what temperatures the different constituent materials within the nano-fibres thermally breakdown. For each analysis, tests were conducted in both air and nitrogen, from room temperature to 900°C, at a heating rate of 10°C/minute. Although steam purification is conducted in nitrogen, TGA analysis conducted in air will provide some insight into any oxidation reactions that could take place, which could reveal if the steam is facilitating them also. This need was increased further, as a thorough analysis of the thermal degradation of materials such as SDBS has not been found elsewhere in literature, and so was required for this investigation to help identify any residual chemicals. This was followed with Raman spectroscopy, which was used extensively in order to assess the CNT quality, as well as to give an indication as to the level of amorphous carbon remaining in each sample. All Raman analysis conducted in this investigation was done so with a 782 nm (red) laser, at a power of 1%, ensuring that none of the samples were damaged or altered in any way during the analysis. Electron microscopy techniques such as energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) were also used to provide visual and chemical analysis of the samples.
6.4.3 Thermogravimetric Analysis of Composite Components

In order to fully characterise the effects that steam purification has on the nano-fibre materials, it is first essential to appreciate how each of the constituent materials within the nano-fibres thermally degrade, in both air and nitrogen atmospheres. Figure 6-12 reveals the TGA curves taken of each material component of the composite: PEO, SDBS, and CNT.

PEO is the electrospinnable polymer used across all samples, and can be observed to be almost completely removed in either atmosphere [Figure 6-12 (A)]. In nitrogen the majority is removed at 385°C, leaving only a small residual of 2.5%, whereas in air, the majority oxidises at a significantly lower 220°C, leaving no residual by 650°C. CNTs however will begin to oxidise at a temperature this high, requiring thermal baking in a nitrogen atmosphere. The overall conclusion from these results is that we expect that the PEO will leave a coating of residual amorphous carbon on the CNTs; this is some of the targeted material that should be removed during the steam purification process.

![Figure 6-12](image)

Figure 6-12 - TGA results, carried out in both air and nitrogen, are plotted from 150°C for each chemical in order to eliminate any water content that make comparisons difficult. These curves show the thermal decomposition of all materials used in the production of SDBS/CNT loaded nano-fibres. A) PEO decomposes in air at 220°C and is not removed in N₂ until 385°C. B) SDBS shows two distinct mass losses in N₂ and has a more complex decomposition due to an oxidation in air. C) CNT wetcake is not removed in N₂ and oxidises in air at 590°C. D) The electrospun nano-fibres show the mass losses associated with a combination of the three materials and indicate how the fibres will decompose during the thermal treatment processes.
The CNTs within the wetcake material behave as explained previously in Chapter 4.2.4, where no material is removed in nitrogen, as no oxidation processes can occur. However, in air, the CNTs oxidise at 590°C, leaving a residual of 9.5%, which the majority is the metal catalyst, iron. This residual iron would oxidise at high temperatures in the presence of air, forming iron oxide (Fe$_2$O$_3$). Any other materials that remain would be contaminants found within the wetcake as a result of the manufacturing processes; see Chapter 4 for more information regarding this.

![Figure 6-13](image)

**Figure 6-13** – These two TGA curve identify the parts of the SDBS molecule that thermally degrade (or oxidise) with increasing temperature. The colour areas marked on the SDBS molecule indicate the coloured arrows of the curve at which this part of the molecule is affected.

The thermal decomposition of SDBS is significantly more complex compared to all the other materials within the nano-fibres and, to further complicate things, its decomposition differs depending on whether oxygen is present. This is due to various aspects of the molecule oxidising and
adding mass, while other parts are simultaneously evaporating. So, in order to try and simplify the decomposition routes, each will be explained separately, starting with the nitrogen atmosphere.

When heated in nitrogen, the chemical degradation steps of SDBS are slightly easier to follow, where each region of the curve is assignable to a section of the molecule: the alkyl chain, the phenyl ring and the ionic head [see Figure 6-13]. Each of the mass loss peaks were identified by calculating the relative atomic mass of the fragments, with respect to the total mass of the molecule. At each stage of the molecule’s decomposition, a hydrogen atom is left on the end of the termination, where a previous part of the molecule once was bound. The residual remaining product after the analysis is the ionic head of the surfactant, which again is terminated by a hydrogen atom, to balance the charge of the anion. This was calculated to be most likely in the form of sodium bisulfite (NaHSO₃). Comparisons between the relative atomic mass and the recorded residual suggest that there should be zero amorphous carbon left as a result of the decomposition of SDBS, although the ionic head of the molecule would remain on the CNT surface regardless of steam purification. This should not be the case for Brij 58 however [see Figure 6-5].

When SDBS is heated in air, the results are significantly more complex, due to the presence of the oxygen, which means that mass can be gained as well as lost [see Figure 6-13]. While some parts of the SDBS molecule may still evaporate as before, oxygen can now react with a decomposition products or residuals, simultaneously adding mass while it is being lost. In the event of this happening, it can be almost impossible to detect directly from the TGA data, as the two weight changes can cancel each other out.

In order to decipher the decomposition route of SDBS in air, the previous result when in nitrogen can be used as a good indication of the order that the molecule is likely to degrade in. It can be a fairly safe assumption that, when heated in air, the alkyl chain will again be the first section of the molecule to breakdown. However, when comparing to the nitrogen result, it is noticed that the mass loss associated with this part of the molecule is slightly lower, 39.2% compared to the 48.6% before. It is unlikely that only part of the chain would decompose, however it is far more likely that there may have been another reaction such as an oxidation. Evidence for this is shown in the TGA curve, where instead of one smooth drop, there is a series of them. By assuming that the alkyl chain has fully decomposed, and by again measuring the relative atomic mass difference, it is suggested that an oxidation reaction has occurred. The relative atomic mass change equates to 33, which suggests the addition of two oxygen atoms (+16 each) and a hydrogen atom (+1). The obvious reaction is the addition of a hydroxyl group to the phenyl ring, where the alkyl chain has been removed. It is unlikely that the oxygen would react with the ring itself due to the higher energy sp² bonding between the
carbon atoms. It is suggested that the other oxygen atom is attributed to a change in the oxidation state of the sulphur, from sulfite (+4) to sulfate (+6), which can be expected at high temperatures. This leads to the suggestion that the new molecule produced during these reactions is sodium 4-hydroxybenzenesulfonate [see Figure 6-14].

![Image](image.png)

Figure 6-14 – The proposed thermal-oxidation of SDBS producing the peaks seen in the TGA data. The arrow colours relate to the coloured areas marked in Figure 6-13, with the final molecule being the residue remaining after the TGA had reached 900°C.

The final mass loss is seen at approximately 780°C, and is far less complex. This peak can easily be attributed to the decomposition of the new hydroxyphenyl group and a hydrogen atom from the ionic head. Giving the final residue from the thermal/oxidation degradation to be sodium hydrogen sulfate (NaHSO₄), containing an extra oxygen atom compared to the nitrogen residual, which is confirmed in the residual mass difference. Figure 6-14 reveals each step of the oxidation of SDBS when heated in air.

The final TGA curve in Figure 6-12, D, is a result of CNT loaded nano-fibres containing all of the previously discussed materials. Although each of the individual material TGA curves will provide insight as to the mass loss peaks and residuals, a combined TGA was also acquired to both confirm the CNT content of the nano-fibres, and ensure that none of the materials within the nano-fibres react at elevated temperatures. For example, by one material acting as a catalyst for the decomposition of another, or for the formation of a different compound compared to the straight forward decompositions displayed in Figure 6-12 (A, B and C). The CNT content was again confirmed to be approximately 3.9%, as was expected for the original CNT mass fraction of the solution used to produce it, and from the TGA results in Chapter 5.4. Furthermore, comparing each of the mass losses to the calculated material constituents reveals no adverse and or unwanted reactions between materials at higher temperatures. Each material thermally degrades independently and the ratios of the mass loss peaks follow those expected for the individual materials. This observation of independent thermal degradation, also bares significance in revealing how the different materials within the nano-fibres, are chemically bonded. In Chapter 5.6, small angled X-ray scattering found that
there was a structured bond between the CNT and the surfactant, but it was not clear on the type or structure of the bond. This independent thermal degradation observation, clarifies that the surfactant and CNTs, are only bonded by a weak van der Waals interaction. Should there have been any other form of higher energy bonding, such as a covalent or ionic bond. Then it would be expected that the degradation temperatures observed in the TGA would be higher, with energy being required to break the bond. It would also be expected that the degradation steps would not independent, where the thermal breakdown of both items would occur once the bond is broken at the higher temperature. With this result, the steam purification of the nano-fibres could now be conducted and analysed.

6.4.4 Thermogravimetric Analysis of Steam Purified Materials

Once each sample that had its CNTs dispersed with SDBS was successfully electrospun, the nano-fibres were then baked both with and without steam at a range of temperatures. This was because the steam purification conditions within the tube furnace could not be directly mimicked within a TGA. So, in order to assess and understand the purification process, TGA was employed once again in order to try and quantify the mass fraction of both the CNTs and the amorphous carbons (if any) remaining in the material after the either of the two processes. It was expected that the samples baked without steam should contain the same mass of residual carbon, as no processes were in place to remove it. It was also hypothesised that, for the samples that were baked with steam, there would be a significant reduction in the amorphous carbon content, compared to those baked without it (Tobias et al. 2006). What wasn’t clear was how the process would vary with increasing temperature.

Figure 6-15 displays each of the TGA curves obtained in air from the samples containing SDBS that were baked at a range of temperatures in either a pure nitrogen filled furnace, or subjected to steam purification. For all the samples baked in just a pure nitrogen atmosphere, the results show that there is minimal difference to the carbon content with increasing temperature, as was expected [see Figure 6-15, A]. However, interestingly the temperature at which the mass is lost does slightly increase with increased baking temperatures, which we attribute to an increase of annealing of defects in carbonaceous materials. Furthermore, there is no CNT peak at the expected 590°C, as seen from the wetcake TGA in Figure 6-12. It is not clear why this is the case, as CNTs were confirmed present by Raman spectroscopy [see appendix item E for the Raman spectrum]. However, it is thought that this is the result of the presence of the large amounts of amorphous carbons promoting CNT oxidation. This oxidation promotion effect was only seen in samples that were baked without steam treatment.
Figure 6-15 – TGA curves acquired from the SDBS/CNT/PEO nano-fibres that were both baked in a nitrogen atmosphere either without steam (A) or with steam (B). All of these TGA assessments were carried out in air at an equipment recommended heating rate of 10°C/min. Comparing the results it can be seen how the introduction of steam not only removes amorphous carbons from the samples, but also that the process is increasingly more efficient with increasing temperatures.

The TGA data obtained from the samples that were steam purified was, as expected, quite a different story [see Figure 6-15, B]. Initial comparative observations of the curves identify that, with increasing steam treatment temperature, the mass of carbon removed in the TGA is decreased. Meaning that, after steam purification, most volatile carbon species have been removed effectively, and re-heating the residue will not result in any further mass loss. What is also striking about these results is that, although with steam treatment we expect less amorphous carbon content, we also see that there is no CNT oxidation peak. Where, because the TGA analysis was conducted in air, there should be a CNT oxidation peak. Raman spectroscopic analysis later confirmed that the presence of the CNTs within the sample remains (with more detail presented in the next section), which signifies that they were surviving temperatures in excess of 900°C in an oxidative atmosphere, an achievement never before reported in literature!

Assessing each TGA result in Figure 6-15 (B) individually also demonstrates some other interesting discoveries. The sample steam treated at 500°C shows a mass loss similar to that expected from the raw material, insinuating that no additional material has been removed, despite the presence of steam. This suggests that not only is the steam purification technique ineffective at these temperatures, but also that the polymer and surfactants are being carbonised, as opposed to being removed. Similarly, the results for the sample baked at 600°C display a large mass drop which is almost identical to that observed when baking without steam. This result again confirms that the steam molecules do not oxidise samples at these temperatures and that the process is therefore ineffective, in agreement with the results published by Tobias et al. (2006). The mass difference of approximately
46%, between samples baked at 500°C and 600°C, is not a result of the steam's presence, but rather the increased baking temperature thermally evaporating more materials.

Tobias et al. (2006) claimed that the steam used for the purification of CNTs, is only active for carbonaceous oxidation at temperatures above 750°C. However, our TGA curves reveal that there is a clear difference from 700°C, suggesting that the steam is active at a slightly lower temperature. Additionally, the CNT mass loss peak from samples baked at 700°C, while small, isn't found at 450°C like the other samples, but rather at 650°C. Further increasing the steam treatment temperature to 800°C also saw a small increase in this mass loss temperature again to 700°C, while also seeing it reduce in size.

Figure 6-16 – The percentage mass of the samples remaining after TGA in air up to 900°C, plotted against the temperature at which they were baked in a nitrogen atmosphere either with or without steam. These results reveal how the steam purification process is active at temperatures of 700°C and above.

This discovery suggested that there may be a relationship between steam purification temperature and the residual remaining in the TGA pan after heating in air, i.e. the mass of amorphous material found within the sample after the initial treatment. Figure 6-16 plots the residual mass (as a percentage) found remaining in the TGA after each analysis was conducted, whereby any mass removed is the residual amorphous carbon and CNTs that failed to survive the high temperatures in oxygen. Displaying the data in this manner provides easy demonstration of both how the steam purification process is active at temperatures of 700°C and above, and how the steam purification process is increasingly more effective with increasing temperatures. It can also be seen how 100% of the material, including the CNTs, has survived being heated in oxygen at temperatures above 900°C, when steam treated at 900°C and above. To clarify, all samples were analysed using Raman spectroscopy to confirm the presence of CNTs within the sample. Only the samples that were steam
treated at temperatures above 700°C revealed features that confirmed the CNTs survival when heating in air to 900°C.

As mentioned previously in Chapter 3, the oxidation temperature of CNTs can be directly related to their quality. Although the CNTs were found to have survived the TGA process for the steam treated samples, there were still some that did oxidise, giving clues as to why the others were surviving. CNTs were seen to oxidise at 650°C and 700°C, for samples steam treated at 700°C and 800°C respectively. This suggests that the CNTs are increasing in quality with increasing steam purification temperature, where the reduction in the number of defects in the crystal structure is providing greater resistance to oxidation. When steam treated at 900°C there were no obvious CNT oxidation peaks found, suggesting that all the CNTs within the material now have an oxidation temperature closer to the 1200°C of pure graphene. However, when steam treating the CNTs at the increased temperatures, there was a reduction in the material which was remaining after the process. When performing the treatment at a temperature of 900°C, only approximately 40% of the expected CNT content was remaining.

6.4.5 Raman Spectroscopic Analysis

Raman spectroscopy was used mainly in order to confirm whether or not a sample had CNTs remaining within it. However, upon comparing the spectra between each of the steam-purified samples, a number of distinct differences could be seen that reveal information as to how the quality of the samples changed as a function of treatment temperature. At this stage, the only indication that the quality of the samples and the CNTs within was improving was through the increase in oxidation temperatures found using TGA. By comparing Raman features, such as background intensity levels and peak width, a relative measurement of the amorphous carbon content can be obtained. All Raman spectroscopic analysis in this chapter, was conducted using a 782 nm (red) laser. This was because using any other wavelength of laser would not be in resonance with the CNTs within the sample, and would cause analytical features such as the D to G peak ratio to be a poor representation. For example, using a 514 nm (green) laser, will result in a poor signal in the CNTs D-band, making it appear that the CNTs are of a higher quality than is the case.

One of the most simplistic ways to assess the amorphous carbon content within the samples was to compare the background levels of their Raman spectra. It has been previously reported how the presence of amorphous carbons and other such impurities increases photon/phonon scattering,
resulting in both broadening of the signal peaks and an increase in the level of background scattering (fluorescence) (Ferrari & Robertson 2000). In most cases, it is good practice to remove any background signals from a spectrum as to ensure a constant baseline for sample to sample comparison, such as the intensity ratios of the D and the G-peaks. However, in Figure 6-17 (A), this has not been done, and the spectra have only been normalised to the G-peak, allowing the background levels of the spectra to be compared. As a general rule, it is assumed that the lower the background level, the lower the amorphous carbon content within the material being analysed. The average background level between the ranges of 1400 cm\(^{-1}\) to 1475 cm\(^{-1}\) was measured and plotted in Figure 6-17 (B). This was chosen because there were no peaks associated with this area that could affect the results. These measurements revealed, how the background levels are reduced on the samples which were steam treated. Furthermore, they were found to significantly reduce as the treatment temperature is increased, causing a need to plot the data with a logarithmic scale. This demonstrates graphically how the steam purification process is more effective at higher treatment temperatures. This result supports the proposals of increasing steam treatment effectiveness with temperature, as suggested from the TGA data previously. It also proves that CNTs were contained within all of our samples after treatment. It could be that this rapid increase in the steam treatment effectiveness with higher temperatures, is the result of something as simple as increased reaction rates (Myers 2003). However, there was insufficient time on this project as to investigate the effects of steam treatment duration, and this could possibly be of interest for future work.

Figure 6-17 – The Raman spectra of each of the steam purified samples treated at different temperatures (A), where each spectra has not been adjusted other than a normalisation to the G-peak, revealing the gradual reduction in the background level intensity with increasing treatment temperature. The average background intensity has also been measured between the ranges of 1400 cm\(^{-1}\) to 1475 cm\(^{-1}\) and plotted as a function of treatment temperature (B), revealing the effect temperature has on the efficiency of the steam purification process.
As well as the reduction in the background signal intensities of the spectra, the reduction in amorphous carbon content also reduces the scattering of the Raman signals, subsequently narrowing the signal peaks (Kim et al. 2005; Stobinski et al. 2010). Narrowing in this manner allows some signal splitting to be revealed (two peaks originally only appeared to be one), where in some cases, this has allowed weaker vibration/excitation signals to become well defined in the spectrum. Examples of this can be found in the G band, with the G-peak becoming more distinct with higher treatment temperatures [see Figure 6-17 for evidence of this, and for a reminder of the different G-peaks see Chapter 3.3]. The spectra in Figure 6-17 illustrate how this ‘narrowing’ process has evolved with the increasing sample purity, as a direct result of the increase in steam treatment temperature. This was observed for all the key CNT Raman signals, as well as the D peak and the 2D peak (where the 2D peak is not shown in Figure 6-17, see appendix item E for an example of this peak). By using data analysis software ‘Origin 9.1’, a deeper detailed analysis of the D and 2D peaks was performed, revealing how the peak positions increasingly blue shift as the steam treatment temperature was increased (where the difference in wavelength becomes smaller). This suggests that the vibrational energy loss through defect scattering (from defective amorphous carbons) has been reduced, presenting yet more evidence that the samples have been increasingly purified with increasing steam baking temperature [see Figure 6-18].

Figure 6-18 – The results from the D and 2D peak analysis. Where increasing the steam treatment temperature can be seen to reduce the amorphous carbon content, through the peak narrowing which can be seen as a reduction in full width half maximum (FWHM), and the blue shift can be seen as a reduction in the peak wavenumber location.

The reduction in amorphous carbon content seen across the samples would only attribute to the increasingly defined Raman spectra. It would not account for the increasing oxidation temperature of the CNTs, especially to the temperatures found beyond the limit of our TGA equipment. As previously explained, the increase in oxidation temperature is a result of the CNTs possessing fewer
defects and a more perfect crystalline structure. Raman spectroscopy can again be used to assess the level of defects through the ratio of intensities between the D-band and G-band signals [see Figure 6-17]. Figure 6-19 plots the ratio between these two peaks as a function of steam treatment temperature. The quality of the CNTs (i.e. number of defective sites) can be seen to increase by almost a factor of 5 as the treatment temperature increased from 500°C to 1000°C. No evidence was seen to suggest that this improvement is a result of the CNTs ‘healing’ their defective sites with increasing temperature, but rather the steam removing defective nanotubes and defective sections of the tube, such as kinks, lattice exclusions and the tube end caps (Kim et al. 2005; Shao et al. 2007). For the sample treated at 500°C, the quality of the material appeared to decrease from that of the original wetcake. This result was attributed to the heavy inclusion of amorphous carbons in to the sample from the partial removal of the polymer and surfactant, as opposed to the CNTs now being of a lower quality.

The confirmation that the samples contained CNTs as opposed to any other kind of graphitic carbon, arises from the presence of the radial breathing mode (RBM). A signal unique to CNTs, that corresponds to the radial expansion and contraction of the tubes themselves. This Raman spectroscopic feature can be used to calculate the diameter of the CNT that is responsible for the signal using Equation 3-8. Knowing the diameter of the CNT and the laser energy that it was excited by (giving rise to the Raman response seen in the spectra), allows the use of the Kataura plot to identify

![Figure 6-19 – The measured ratio between the intensity of the D-band and the G-band Raman peaks, across the steam treated samples as a function of the treatment temperature, revealing how the quality of the CNTs increases with treatment temperature. The blue dotted line indicates the D to G ratio of the original wetcake material.](image-url)
whether that nanotube possesses metallic or semi-conducting properties (Kataura et al. 1999). Performing this form of analysis on various samples enables the speculation as to if any specific type or diameter of CNT is removed by the steam purification process.

Figure 6-20 – The RBM measured from CNTs before they were steam treated, after they were steam treated and after they had been re-baked in an oxidative atmosphere. Each of the sets of data were corrected for background and then normalised so that they each have an area of 1. This reveals how the ratio of metallic to semi-conducting tubes changes with treatments, suggesting that metallic CNTs are preferably oxidised. Each of the calculated CNT diameters have been located on the Kataura plot, where semi-conducting CNTs are black dots and metallic CNTs are red dots. The energy of the laser has also been marked on the plot as a red dotted line. The number areas of the Kataura plot correspond to the peaks in the spectra, which are also numbered.

Figure 6-20 shows exactly this, where careful measurements of the RBM has been taken of CNT samples: before they were steam treated (when in wetcake form), after they were steam treated and after they had been re-baked in an oxidative atmosphere at 900°C, and survived. In each case, the corresponding nanotube diameter has been calculated and referred to the Kataura plot to identify whether it possesses metallic or semi-conducting properties. In order to try and distinguish if a particular diameter or type of nanotube is being preferentially oxidised, each of the RBM measurements were background corrected and normalised so that the total area under the curve is equal to 1. Doing this allowed for a direct ratio between the different peaks to be measured after each treatment. After each treatment, the marked ratios demonstrate how the ratio of metallic nanotubes to semi-conducting falls, indicating that these could be preferentially oxidising over other CNTs, although it is not clear why this would be the case. However, an alternative speculation, based on the
observation of the results, is that the larger nanotubes are being oxidised preferentially. This theory is more sensible, as larger tubes would have a greater chance for defects to develop during their growth (being a larger crystal). It is also possible that the larger diameter nanotubes could be the outer wall of a double-walled CNT. Multiple walled CNTs typically have a wall separation distance of 0.334 nm, corresponding to 0.668 nm across both sides of the tube (Dresselhaus et al. 1995). This then means that the 1.60 nm tube could be the outer wall of the 0.92 nm nanotube, and that it is burning before the inner wall, purely as it is covering it. In order to find a definitive result and to accurately conclude if any type of CNT is oxidising preferentially, further Raman spectroscopic analysis will need to be conducted using other laser energies.

6.4.6 Comparison between Anionic and Non-Ionic Samples

Figure 6-21 – Electron micrographs of the SDBS steam treated nano-fibres (A) and the Brij 58 steam treated nano-fibres (B). Where large contaminants can be identified in the SDBS steam treated sample as the white blobs on top of the nanotubes.

While assessing the various thermal properties of numerous surfactants in chapter 6.2.4 (page 120), potential contaminants caused by the metal content within SDBS were identified. SEM imagery of the aligned mat of CNTs after the steam purification process revealed these contaminants were a reality. Figure 6-21 (A) displays the acquired micrographs of the electrospun nano-fibres produced with the CNTs dispersed with SDBS. The contaminants can be observed as the white particles, 0.2 to
1 μm, all over the nanotubes. EDX was used on these contaminants in order to reveal their chemical composition, and aid identification of their source. This form of analysis found that the particles were (as predicted from the SDBS TGA data in Figure 6-13) containing a high concentration of oxygen sodium and sulphur, indicating that they were a result of the use of the anionic SDBS surfactant. In order to avoid these inclusions, there were two options: use an acid wash to remove the residuals, or use an alternative surfactant. Although the acid washing technique proved effective when attempted, the easiest solution, that would also minimise manufacturing costs, would be to use another surfactant.

Brij 58 was employed as a direct alternative to the SDBS, as it was demonstrated in Chapter 6.2 to be both an effective CNT dispersant and being easy to remove thermally. The nano-fibres produced were steam treated much the same as the SDBS containing ones at a temperature of 900°C, and imaged for comparison. Figure 6-21 (B) displays the obtained micrograph revealing both the aligned CNTs and the lack of contaminants, demonstrating both that other surfactants can be used in this process, and that the inclusions found before were from the SDBS. This result signifies that, for the first time in literature, the alignment of CNTs over an area and then be fully recovered without damaging their high-quality, can be claimed. Furthermore, it allows for these materials to be used in a broad spectrum of applications, depending on the necessary material attributes.

6.4.7 Steam Treatment of As-grown Nanotubes and the Wetcake Material

Once the potential for this steam treatment process was realised, other opportunities to explore its potentials were presented. As a result, the steam treatment process was applied to an as-grown multi-walled nanotube (MWNT) forest, which was mounted on a silicon wafer. This sample was grown by J. S. Chen at the University of Surrey, using a cold wall photo-thermal chemical vapour deposition (PT-CVD) process, where the heat needed was supplied by halogen lamps (Chen et al. 2011; Shang et al. 2010; Ahmad et al. 2013). It was noticed, after growth had finished and the sample had been analysed in an SEM, that there was a large amorphous carbon cap at the top of the CNTs [see arrowed area of Figure 6-22]. The steam treatment process was employed using identical methods as outlined previously, in an attempt to try and remove this top and free the ends of the CNTs, in order to allow their characterisation. The CNT forest was grown as part of a project to develop carbon interconnects for electronics packaging and an amorphous cap, common when stopping the CVD growth process, would be a significant barrier to electrical connectivity.
Figure 6-22 (B) reveals an electron micrograph of the MWNT forest after the steam purification treatment was applied. Here, the amorphous carbon top can no longer be as straightforwardly distinguished from the rest of the CNT forest, providing a strong indication that it is either no longer present or substantially reduced in size. In order to quickly assess the outcomes of the treatment we again resort to Raman spectroscopy. Figure 6-23 displays the acquired spectra before and after the steam treatment process. As with the other comparative spectra in this investigation, the data has only been normalised to the G-peak, no background data has been removed, to allow a measure of amorphous carbon content within the sample. Comparing the two results illustrates a similar result to as before, displaying how before the treatment the spectra contains a very high background signal (fluorescence), which obscures the Raman features of the CNTs. However, once the amorphous carbon has been removed by the steam treatment process, the spectra is revealed to have almost no background, and the distinguishable Raman signals to be expected. This result demonstrates that the steam treatment method can be applied to other forms of CNT sample.

Figure 6-22 – Electron micrographs of an as grown MWNT forest, grown on a silicon substrate. Where the samples were imaged before (A) and after (B) steam treatment, showing that the arrowed amorphous carbon head on the forest has been removed, cleaning the tops of the MWNTs. These micrographs were acquired by J. C. Chen.
In order to further demonstrate the diversity of the steam treatment technique, the original Thomas Swan CNT wetcake product was loaded into a ceramic boat and purified through the same methods outlined previously. The improvements in quality were as expected, and identical in trend to those previously presented. However, in the earlier TGA data it was shown that, when purified at 900°C, the CNTs became super-resilient and survived an oxidative atmosphere at temperatures above 900°C [see Figure 6-15]. As the TGA residuals could not be recovered for analysis, to prove this result and demonstrate that it was not an effect caused by a contaminant or any other additive, the steam treated wetcake was re-baked in air at 900°C. Raman spectroscopy was then conducted on the residual which remained at the end of the process.

![Raman spectra](image)

**Figure 6-23** – The Raman spectra of the as-grown CNT forest taken before and after the steam treatment process had been applied. As with some previous Raman spectra in this chapter, to allow direct comparison the data has only been normalised to the G-peak. Comparing the two spectra it can be observed how the spectrum taken before the steam treatment has a significant background (fluorescence), obscuring almost all of the peaks. Where the spectrum taken after steam treatment displays a background signal which is mainly flat, allowing all of the predominant CNT features to be seen.

Figure 6-24 confirms, without doubt, the CNTs presence by displaying the typical spectra of a single or double walled CNT, including indicative features to nanotubes, such as the RBM. This result proves that some of the CNTs within a steam purified sample will resist oxidation at temperatures above 900°C, a considerable improvement on the original wetcake material which saw the CNTs oxidise at 590°C. Although the mass of material remaining after both thermal treatments was minimal (approximately 10% of the original CNT content), this result is still significant. The D to G ratio of the CNTs found remaining was measured at 0.033, considerably lower than anything measured previously.
Pristine CNTs of this nature combined with the ability to withstand extreme temperatures, could bring realisation to organic electronics that would otherwise be unsuitable for harsh high temperature environments.

The most striking feature of this result is in the intensity of the RBM. In all other previously seen cases, the RBM has always been small compared to the G-band (about a third in comparative intensity). With this spectra however, the RBM was found to be of a greater intensity than the G-band. While acquiring the Raman data, in some places on the sample spectra needed to be retaken as the RBM signal was so large it saturated the detector, preventing the collection of results. It is not clear why these RBM peaks are so large, however it was suggested that perhaps that CNT walls are so pristine and free of other materials that they can ‘breathe’ far easier than ever before. The same could be said for the Raman spectroscopic signal itself, where the RBM is usually considered a weak response and easily disrupted by other materials. Without those other materials the full signal would be received by the analytical equipment, and hence give rise to an increased signal strength.

Figure 6-24 – The Raman spectra obtained using a red laser, from the CNT wetcake (before any treatment is applied), and the CNT wetcake after it has been steam purified at 900°C and then re-baked in an oxidative atmosphere at 900°C. The presence of the CNTs unique RBM mode on the treated sample, provides compelling evidence of their survival in oxidative atmospheres, at temperatures considerably higher than they would have done prior to steam treatment. The RBM has been noted to be unusually high compared to the G peak. The data has been normalised to the highest peak, with the silicon reference peak labelled. Furthermore, the D to G ratio shows an order of magnitude improvement on the original wetcake material.
When analysing these RBM peaks of the steam treated wetcake as before (in Figure 6-20), they correspond to nanotubes with diameters of 1.73 nm and 0.96 nm ± 0.02 nm. Nanotubes of these diameters would not normally be considered the inner and outer wall of a double-walled CNTs, as their difference in size is larger than the reported wall separation distance of 0.668 nm. This then suggests that these are two separate single-walled CNTs, as opposed to a double-walled nanotube. Referring these calculated diameters to the Kataura plot as done before, reveals that these signals correspond to a semi-conducting tube (1.73 nm) and a metallic tube (0.96 nm). Further evidence of the presence of single-walled nanotubes can be found when analysing the G-peaks, in particularly when comparing the intensity of the G+ and G- peaks. The ratio between the G+ and G- peaks was found to be approximately 0.23, which is known to be indicative of single-walled carbon nanotubes (Jorio et al. 2002). The presence of single walled nanotubes, as opposed to double walled, could account for the significantly increased intensity in the RBM signal, where double-walled nanotubes should have a restricted RBM as the two walls will interfere with one another.

Although a full understanding of these results was not achieved, further investigation work could identify the processes behind both the CNT oxidative resistance and the extreme RBM Raman signals found. Further work should focus on either understanding what makes the CNTs oxygen resistant, or securing a higher mass of CNTs that can be treated in order to make them oxygen resistant, enabling the commercial use in applications that involve extreme temperatures, such as high temperature electronics for use in reactors and the space industry.

6.4.8 Electrical Conductivity Analysis of Steam Purified Carbon Nanotubes

After the successful recovery of the aligned CNT arrays, the increased purity of the material after steam treatment led to question of how this affects conductivity. In order to investigate this, an area of aligned CNTs was electrospun and rolled into a rope, as outlined in Chapter 5.5. This rope was then subjected to steam purification where, although it reduced in size by almost two thirds, the structure of the rope was maintained. To reduce any contact resistance between the CNTs and the probes used to measure the conductivity, silver dag solution was applied to the rope at specific distances. The dimensions of the rope were measured in a scanning electron microscope, allowing the resistivity of the rope be calculated.

Figure 6-25 reveals the results from the resistivity measurements of the steam purified carbon nanotube rope. Measuring the gradient of the data, using a linear fitting, we found a resistivity of 72 ±
$8 \times 10^{-4} \ \Omega m$ (approximately $140 \ S/m$), which is a two orders of magnitude improvement on the original non-treated sample resistivity of $0.28 \pm 0.02 \ \Omega m$, measured in Chapter 5.5. More interestingly, this value of resistivity it almost identical to parallel plane resistivity of graphite, which would account for the tube-to-tube conductance, with each nanotube acting as a graphitic plane [see Figure 6-25] (Pierson 1993). This result implies that, in order to achieve greater conductivities from these CNT ropes, some form of junction and doping is required to reduce tube-to-tube resistance. Although this was not further explored, literature has demonstrated that this can be achieved by doping the CNTs with some form of dopant, which effectively promotes CNT interconnections (Nirmalraj et al. 2009; Kulesza et al. 2006). It is important at this stage to note that, as before in Chapter 5.5, the same error in the rope diameter measurement, from the inclusion of voids, could result in measured conductivity being better than suggested.

![Graph of resistances](image)

**Figure 6-25** – The graph (A) displays the measured resistances of the steam purified CNT rope. By extrapolating the data, the resistivity of the material was measured to be $72 \pm 8 \times 10^{-4} \ \Omega m$. Interestingly, the contact resistance was measured to be negative, also the error calculated from the fitting suggest that this may not be the case. The schematic diagram (B) demonstrates the electrical currents path, from one graphitic plane to the next, giving rise to the parallel plane resistance of graphite.

### 6.4.9 Conclusions

Thermal evaporation in an inert atmosphere was explored as a potential method for removing the surfactant and polymer from the surface of the carbon nanotubes (CNTs). However, this process resulted in a considerable amount of residual amorphous carbon which coated the surface of the CNTs, disrupting the van der Waals forces which give CNT materials their extreme properties. This investigation built on the published work of Tobias *et al.* (2006), where a steam purification method
for removal of amorphous carbons, while simultaneously evaporating other materials, was added to the furnace previously used to evaporate materials.

This integration of methods meant that, for the first time in literature, this process was reproduced on electrospun aligned CNT loaded nano-fibres, where the targeted removal of the polymeric and amorphous carbon materials resulted in sheets of highly aligned pure nanotubes. Confirmed using thermogravimetric analysis and Raman spectroscopy, the aligned CNTs once treated were found to have a significantly lower amorphous carbon content and be of a considerably higher quality (possessing a significantly lower defect density). This lower defect density also meant that the steam treated CNTs were increasingly resistive to oxidation, and could survive much higher temperatures, in excess of 900°C in air. However, in addition to this, by investigating the treatment as a function of temperature we also found that this purification process can be scaled, with regards to the temperature that it is baked at. The results found that higher treatment temperatures produced ever purer samples.

While the surfactant sodium dodecylbenzenesulfonate (SDBS) was found to introduce sodium-containing contaminants (present as an oxide or sulfate) into the aligned CNT samples, replacing it with Brij 58 ensured that this issue was avoided. This meant that again in this chapter, the ability to take premade CNTs, align them, and finally fully recover them (maintaining their original high-quality and alignment), can also be claimed as a first in literature. This was further developed to apply this technique to a rolled rope of nanotubes, allowing the resistivity to be measured after the steam treatment process. This revealed a resistivity of $72 \pm 8 \times 10^{-4}$ Ωm (approximately 140 S/m), which was a two order to magnitude improvement on the sample measured in Chapter 5.5. This was found to be identical to the perpendicular planar resistivity of graphite, suggesting that in order to further improve the conductivity, some form of tube-to-tube interconnects would be needed.

This chapter was then brought to a close by demonstrating how this steam treatment process can be applied to other types of carbon-nanotube-containing sample, other than aligned nano-fibres. An as-grown multi-walled CNT forest, and a sample of the original raw wetcake material were also subjected to the same purification process. The CNT forest was found to almost completely lose its amorphous carbon top, enabling sharper Raman features to be observed. The wetcake material, once steam purified was re-baked at 900°C in air to demonstrate how CNTs are now resistive to oxidation, and can now survive extreme temperatures. Raman spectroscopic analysis of the surviving CNTs found it to possess a remarkable spectrum, where the radial breathing mode had an intensity stronger than the G-band.
6.5 Conclusions

This chapter has thoroughly explored the aspects of the project which now allow for the maximum loading of carbon nanotubes (CNTs) within the electrospun polymer solution. Gaining this necessary detailed knowledge has allowed for the CNTs to be aligned at a maximum rate, which in turn maximises the overall processing rate of the various steps taken to produce highly aligned arrays of CNT loaded nano-fibres.

In order to accomplish this goal, various ionic and non-ionic surfactants were benchmarked against one another, identifying their maximum CNT loading and ideal sonication power that should be used to ensure maximum dispersion efficiency. Sodium dodecyl sulfate (SDS) and Brij 58 demonstrated to be the most efficient at dispersing CNTs, with both leaving almost zero residual undispersed material remaining after centrifuging. By using a novel micro-centrifuge technique, SDS and Brij 58 were found to produce the best dispersion when tip sonicated at an intensity of 17.2 W/ml and 18.5 W/ml, respectively. This investigation was continued further to analyse each surfactant with thermogravimetric analysis. This allowed for the thermal degradation of each surfactant (both in air and nitrogen) to be probed, identifying any potential contaminants left which if used in a CNT/polymer composite could have detrimental effects on its properties. SDS was found to leave a large amount of residue after thermal breakdown, owing to its sodium and sulphur content. Brij 58 however was found to leave virtually zero residual after thermal breakdown, with only a small carbon residual of less than 1% of the original material mass, making this surfactant ideal. The residuals left on the CNTs between these two fibres were further compared in the CNT recovery section of this chapter.

While exploring the various surfactants in the first part of this chapter, it was noticed how surfactants vary with regards to the ions they contain (if any), leading to the question of how surfactant ionicity influences electrospinning with either a positive or negative electrode. Benzalkonium chloride (ADBAC) as the cationic surfactant, SDS as the anionic surfactant, and Brij 58 as the non-ionic surfactant, were all used to disperse CNTs at a weight fraction of 0.1% and electrospun with polyethylene oxide (PEO), using both a negative electrode and a positive electrode. The results revealed how solution systems dispersed with a non-ionic surfactant saw no preference between electrode polarities, however the same could not be said of the ionic surfactants. The anionic surfactant SDS found that it only electrospun with a positive electrode, and that with a negative electrode the electrostatic repulsion would expel the anionic surfactant coated CNTs from the electrospinning jet, disintegrating it. On the contrary, the cationic surfactant ADBAC was the opposite, where it only produced good fibres with the negative electrode. Electrospinning the ADBAC solution with a positive electrode saw the jet fail to hold as much charge and whipping was reduced such that fibres were sticking together in flight and landing wet (unlike the repulsion like for like charged fibres
would be expected). This electrode polarity preference depending on the solution being used is a significant result, with all journal papers to date claiming that there is no difference between electrospinning with either electrode polarities. The work reported here, has demonstrated that this is not the case, and that electrode polarity should be carefully considered when electrospinning ionic solutions.

The final section of this chapter investigated the prospects of CNT recovery by thermal evaporation; this however led to amorphous carbon deposits forming on the surface of the CNTs. Steam purification was employed to successfully selectively remove the polymeric and amorphous carbon deposits from the aligned arrays and as a result fully recover the CNTs. This was found to return the CNTs to a quality significantly better than there were originally supplied in. The steam purification technique uses a simple nitrogen oven but with the addition of steam. The steam molecules will react with less ordered amorphous carbon at temperatures over 700°C, to purify and clean the surface of the CNTs. The steam does not oxidise any highly crystalline CNTs, due to the high energy sp² bonding. The mechanics of the steam purification process were explored as a function of temperature, revealing how increasing treatment temperatures increase the level of purification. It was eventually found that, when steam purifying CNTs at temperatures of 900°C, they were purified to such an extent that their resistance to oxidation was increased such that they could now survive an oxidative atmosphere at temperatures over 900°C, something never before claimed in literature.

With the investigations in this chapter leading to viable solutions as to allow for the high-weight fraction loading of CNTs into solution, and their undamaged purified recovery after alignment. All that remains in this project is to re-engineer the electrospinning technique for high through-put nano-fibre production. The next chapter in this thesis explores some of the designs and results for large area industrially scalable production of aligned CNT nano-fibre sheets. This chapter will explore the prospects of achieving this goal, and the project’s main objects by reviewing the possibility of both needle and needleless electrospinning systems.
7 Novel Designs for Large-Area Electrospinning

7.1 Introduction

Previously, Chapters 5 and 6, developed and optimised methods for the dispersing and alignment of single walled carbon nanotubes, in a manner which then allowed their full recovery as an aligned purified sheet. However, one final project objective, which remains unaddressed, is the adaptation of the electrospinning technique to allow commercial scale-up of the nano-fibre production process. By using the knowledge and experience already acquired on electrospinning, here we justify the re-engineering of the technique for the production of large-area aligned carbon nanotubes.

Typical electrospinning with a single needle spinneret, is a slow process, with solution consumption rates at a maximum of 700 µl per hour. Repeating this style of electrospinning in a series of multiple operations over an area would, over time, produce large areas of aligned carbon nanotubes. However, this is extremely time consuming, and not commercially viable, leading to the necessity to design a scalable alternative. Designing and building a commercially viable scaled-up electrospinning system, involves careful consideration of numerous aspects; these include: the collector design, the electrical and physical shielding requirements, the motor requirements, the power supply requirements, the safety features, the design of the spinneret/electrode, and the solution delivery method. In this chapter, each of these aspects will be outlined, explaining their purpose and necessary requirements, with a justification as to their final design and implementation. The chapter will then compare each of the developed techniques to one another, leading to a purposed solution which will meet the projects outlined objectives.

Based on the reviewed developments in the field of scaled up electrospinning systems in Chapter 2.4.2, it was decided to engineer both needle and needleless systems. This allows for the full consideration and exposure of the potential pros and cons of both options. Although needleless electrospinning systems have been demonstrated to be capable of delivering the required production rates, they also have demonstrated a possible necessity for higher voltages, potentially making alignment unobtainable through increase fibre velocities. This led to the need to explore needle-based
systems simultaneously, exploring all options to guarantee this project meets its objectives, by one way or another. However, before introducing the different spinnerets developed, this chapter begins by outlining the design and implementation of the large nano-fibre collector, and its housing.

7.2 Large Scale Collection Drum and Housing Design

7.2.1 Introduction

Before any scaled-up electrospinning assembly can be developed, a large-area collection drum (and a suitable housing for it), must first be built to accommodate the large-area substrates. This chapter outlines all of the relevant steps taken in ensuring that the final built system was both suitable for purpose, and safe to operate.

This was achieved by first designing and building the collection drum, and its relevant aspects, including the motor and mounting. Once this has been accomplished, the next stage detailed in this chapter, is explain how we achieved the application of some form of shielding, allowing the rig to be safely used within a secure environment. This then leads this chapter to its final stage, where vigorous health and safety consideration has led to the addition of various health and safety features which allow for safe operation within a laboratory environment.

7.2.2 Collector Design

As can be observed in Appendix item A, there are many electrospinning collector designs which are capable of producing areas of highly aligned nano-fibres. However, due to the design logistics and Taylor cone production limitations, most of these designs cannot be scaled-up to produce the large areas of nano-fibre, which are required for this project. After reviewing literature and experimental data in Chapters 2.4.2 and 5.3, it was concluded that the cheapest and simplest solution was to use a large high speed drum as the collector. The simple motive behind this decision was that any further scale-up of this style of collector purely involves increasing either the length or diameter of the drum, as this will be least disruptive to the strength and distribution of the of the electrostatic field. The initial design is displayed in Figure 7-1, where a simple suspended drum over some form of spinneret would meet the necessary criteria for alignment and scalability.
Figure 7-1 depicts an example of the general electrospinning set up chosen for further development in this project. In this instance, the first striking change from the set-up used before, is that the collection drum is now located above the electrode/spinneret [Figure 7-1, arrow 3], as opposed to being below like before [Figure 2-5 – The schematic diagram is a basic set up to an electrospinning apparatus for collection of aligned fibre, where the introduction of a high voltage to a spinneret causes a solution fed from a syringe pump to form a Taylor cone (1 & A), which subsequently produces a jet of material which accelerates towards a collector at a known velocity, whipping and drawing into a nano-fibre (2 & B). Once the fibre has reached the collector it should have dried, where it is collected on a rotating drum at the velocity of the fibre, producing an aligned mat (3 & C). A typical scanning electron micrograph of aligned polyethylene oxide (PEO) nano-fibres produced from this typical equipment set-up is also shown (C)]. This alteration was necessary to avoid any unwanted solution spits and drips that were previously a common occurrence. This avoids simple gravitational drips onto the collection drum during experimental preparation, wetting the substrate and damaging fibres.

Although the large collection drum itself is simple in design, due to its size, its positioning and mounting, much consideration was needed for its design for successful operation. This was because the surface speed of the drum can reach velocities as high as 30 m/s, and we need to consider the energy stored in the drum, which could be hazardous if not secured. This was also as incorrect position,
which could affect the spinning, may be challenging to alter after the drum has been secured. It was important to ensure that the drum was: an adequate distance from an adjustable shelf below it (where the spinneret would be located), in a position that allowed for the sheets of nano-fibres to be easily removed, and finally centralised so that it was the closest electrically ground object to the nano-fibre spinneret (ensuring that nano-fibres were not attracted to another other part of the rig). Figure 7-2 illustrates the final design of the collection drum and its mounting, as well as illustrating how the mounting can be used to store the other equipment such as the motor servo. In an attempt to keep weight minimised, the entire drum was made of a light-weight conductive aluminium alloy. This ensured maximum safety by minimising the momentum of the drum during operation. Using a metal drum also allowed for its surface to be easily kept at a zero potential (or electrically grounded), causing the charged nano-fibres to be attracted to the drum during spinning. In order to guarantee that the electrostatic field was uniform, it was critical that the drum was as smooth as possible, making sure it was of a uniform thickness of metal, in order to avoid local charge build up. Any inconsistencies on the drums surface or in its wall thickness, would give rise to an uneven electrostatic field, which could result in uneven fibre collection (Teo & Ramakrishna 2006).

Figure 7-2 – From design to reality: a schematic diagram of the collection drums position, within the simple electrospinning rig housing, designed for building in this project (A). This set-up design, was accepted as final for this project, and later built as shown the in the photograph (B).
In order to decrease the risk of a drum jamming incident, a magnetic coupling was designed to be installed between the motor and the drum [see Figure 7-1 arrow 2]. Initially, this magnetic coupling was designed to provide the driving link between the motor and the drum, maximising safety by preventing the motor from overheating in the event of the collector drum jamming. It was also designed to prevent any subsequent electrostatic charge created by the electric motor from being passed through the drive shaft to the ground collector drum. This was ordered from Carter Bearings Ltd., however it was not until installation that it was discovered that the drum was too heavy for the magnets to hold the rotation. Instead, an insulating plastic static coupling was used. Although the static coupling still provides the electrostatic insulation required between the drum and motor, it does not offer the same safety protection in the event of a drum jam. This meant that the motor used to drive the drum had to have some form of safety cut-off, in the event of a drum jam.

![Figure 7-3 – The collection drum’s electric motor power supply and servo drive wiring set-up, including the custom cable design. All items were secured within a ground rack mountable case for safe housing (as shown). The various aspects of the wiring which were manually added to allow for custom integration, are also shown and labelled; this includes the optional 10 \(\Omega\) 100 W breaking resistor (7).](image)

The drum itself is rotated by a high-speed, high-torque electric motor [Figure 7-1, arrow 1]. This motor provides the driving force needed for high rotational speeds needed for the efficient collection of nano-fibres, as defined in Chapter 5.3. The motor chosen was a Parker SMB60 (electric motor with internal brake), which was controlled by the Parker ViX250IE servo drive, where both of which were purchased from www.micromech.co.uk. The motor and servo drive (motor control unit),
were chosen based on: the motor’s high specification performances, the servo’s programmable precision, and past successes with these models, and prior to this project. This motor was also selected because of various safety features which allow for safer working; this included the now required jam detection as mentioned in the previous paragraph.

To prevent any fire risk as a result of the drum jamming, the motor was programmed to abort operation at any point when a specified rotational tolerance was exceeded. This meant that, when a very low resistance to rotation was detected, such as the beginning of a jam or accidental contact, the motor would abort operation and raise an alarm. This program for the motor can be found in the appendix, item F. In order to utilise all of the desired safety features of the motor, both the motor’s power supply unit (PSU), and servo drive had to be manually wired [see Figure 7-3]. Due to the volume of wiring involved, and various customisation, both PSU and servo for the motor were mounted within an electrically grounded rack mountable case for safe implementation. During the motor installation, it was suggested by the manufacturer to add in an additional large 10Ω 100W breaking resistor (with a suitable heat sink), to minimise the risk of the motor over heating in the event of a motor failure or drum jam; this was implemented to maximise the safety of this build.

The final collection drum and suitable housing unit design were built by Carter Bearings Ltd. to our specification, where the design was altered to include lockable wheels on the bottom, to allow easy transport, should the equipment need to be moved. Figure 7-2 (B) displays a photograph of the finished rig, where the drum can be seen secured in electrically insulating plastic bearings (green mounting), just above the height-adjustable shelf. As the rig was too big for anything other than a custom built fume cabinet in which to contain it, it was decided to apply shielding to the rig mounting directly. This is significantly more cost effective, as well as being far easier and cheaper to both ventilate and control the atmospheric properties (as well as providing the physical and electrical protection required).

7.2.3 Shielding Design

One of the biggest challenges faced in building this large scale rig was how to apply some form of shielding. The challenge was to design shielding (whether it be in the form of a walk-in cabinet or directly applied), which was both cost effective as well as meeting the necessary requirements. The requirements that shielding needed to fulfil, included: providing adequate electrical protection, providing physical protection (from moving parts), preventing nano-fibres from exiting the rig (which could be harmful if inhaled), reducing air-flow for energy efficient fume extraction, and providing an atmospheric seal (allowing temperature and humidity to be independent from the laboratory).
Figure 7-4 – These two images show the final shielding design concept (A), and a photograph of the final completed product (B). The technical drawings for the Perspex cuts can be found in the appendix item G. Image B also displays the black rubber seals used to ensure an enclosed environment, as well as a wooden shelf, which houses the rig’s electrical equipment.

As it was decided to apply the shielding directly to the electrospinning rig’s mounting frame, Perspex sheets were designed so that they could be easily bolted to the sides of the rig itself, allowing it to be easily removed should the need arise (whether it be for further adaptations, relocation or cleaning). It was confirmed by the University of Surrey’s health and safety department that 4 mm thick Perspex would meet necessary protection requirements, with the doors being 6 mm thick as to withstand the extra stresses introduced through constant opening/closing [see appendix G, for the shielding technical drawings]. These Perspex cuts were made to order from Aquarius Plastics Ltd. based in Guildford. The Perspex cuts where bolted to the frame, with an airtight rubber seal around every fixing, ensuring an enclosed environment within the electrospinning rig. For any areas of isolated metal, that could potentially hold residual charge and cause injury, best efforts were made to use non-conducting fixings (for example nylon bolts etc.). However, this was not always possible due to strength requirements, and items such as door hinges had to be metallic in composition. Such items then required electrically grounding, as to prevent charge build-up and comply with health and safety regulators. The rig doors themselves had wooden handles added for ease of access, and were secured with magnetic strips. Figure 7-4 (image A), shows the final shielding concept, as well as a photograph of the finished product (image B). This image also shows the addition of a wooden shelf, which provides housing for both the motor servo and the high-voltage power supply.
The final aspect of the shielding design was to implement a suitable extraction system to the roof of the equipment. This enabled the use of the rig to include other, solvent based polymers. This enabled safe working during electrospinning, preventing potentially hazardous nano-fibres from being released into the laboratory atmosphere and inhaled, while also preventing the build-up of any solvent vapours which could become hazardous to health, or a fire hazard (should flammable solvents be used). Figure 7-5 reveals the final extraction system, which was fitted to the roof of the large-area electrospinning equipment. Within the extractor housing resides a series of filters, which will remove all hazardous materials from the air, before releasing this air out of the building. The filters contained (in order of closest to the collection drum) include: a coarse, non-woven filter to remove large particles and any airborne nano-fibres, a high-efficiency particulate air (HEPA) filter for removing any residual nano-particles that could be airborne, and finally a carbon filter to remove any hazardous solvents (should they be used). The implementation of this extraction system enabled the use of nano-materials (such as carbon nanotubes), and expanded the equipment’s capability to include any solvent system. All aspects of the building and development of this equipment since Figure 7-2, were done solely by myself. For this reason it was incredibly important to ensure that this equipment was safe to use, as I was responsible for any injuries caused by unsafe aspects.

![Figure 7-5](image)

Figure 7-5 – A photograph of the custom built extraction system that was installed on the roof of the collection drum housing, with the three filters contained within it labelled.

7.2.4 Health and Safety

Through-out the design and development of the large area electrospinning rig, safety concerns and considerations have been constantly referred to, adapting the designs to eliminate all possible points of danger and ensure maximum safety. Both during construction and after, a review
of the safety features was undertaken. This diligence towards safety led to various changes to the design, including: drum balancing, power supply selection, redundant electrical interlocks, emergency stop systems, door locks, and radiation testing.

As the collection drum was custom built, rather than being manufactured, it was not appropriately balanced for high-speed rotation. This then resulted in the drum producing violent vibrations when spun, which exerted unsafe stresses on the bearings and could have led to catastrophic failure. Due to the lack of available professional equipment, the collection drum had to be balanced manually. To do this, an arm of known weight was added the drum at 45º points around the drum’s circumference, starting at the point which was known to be heaviest (along the drum weld). High precision scales were then used to accurately measure the weight at each point of the drum, revealing the side of the drum that was unbalanced. Counter weights were then cemented to the drum on the lighter sides, balancing the drum. Repeat measurements were then taken at all the same points on the drum surface confirming that the drum was now balanced. This allowed safe, high-speed drum rotation, without the major vibrations seen initially.

Various power supply units (PSU) were considered for use on this equipment and for each model the specifications were compared and scrutinised. It was decided that the most cost-effective solution was to limit the output of the PSU to 60 kV. This kept the costs to a minimum and ensured that unsafe voltages cannot be accidentally applied to any system. The PSU chosen was a reversible polarity Glassman ‘FJ60R2-22’, which was selected not only for its remote control functionality, but also due to the various additional safety features. These features included: arc quenching (which removes the high-voltage supply for a short period to prevent further arcing, before reapplying it again), arc counting (which fully disables the high-voltage after a threshold of arcing) and thermal overload protection.

An electrical interlock system is essential when using a high voltage, and allows for the hazardous potential to be turned off safely in the event of an entry to the electrospinning rig during operation. For this reason, the interlock system was carefully designed before being installed, and fully tested by a professional before any power supply was implemented on the equipment. The interlock system comprises of a simple low voltage circuit (+3 V), consisting of numerous different switches. The circuit design for this system can be found in the appendix, item H. When a switch is tripped and the circuit broken, the system is considered ‘breached’. As such the high voltage is removed, rendering the equipment safe. This interlock system was kept separate from the collection drum and syringe pump, this was to allow the rig enclosure to be entered to perform maintenance, such as spinneret cleaning or solution resupplying.
The first interlock installed is a key switch, which prevents any use of the rig without the key holder’s knowledge, where without the key the high voltage cannot be switched on. This key switch is then followed by four interlock switches: two ‘rocker’ switches [see Figure 7-6, image A], and two kinetic blade switches [see Figure 7-6, image B] (one of each on each door). The kinetic blade switches were installed as an afterthought, as it was considered that if the rocker switch became jammed, the system could be breached without breaking the interlock system, whereas the kinetic switches are physically broken upon opening the door. Where possible, all electrically isolated metal bolts where replaced with nylon bolts; this removed any risk of charging. In addition to the interlocks, a suitable emergency stop button was also added to the rig. This was wired directly to the mains input, killing the power to the entire rig should it be used (this includes the power supply, motor and syringe pump). This also disables the motor and applies the motors built-in brake, stopping the drum promptly.

Figure 7-6 – These three images show the ‘rocker’ (A) and kinetic (B) interlock safety switches used on the electrospinning rig, as well as the wooden door lock (C), preventing accidental access. The metal bolts seen in image B were replaced with nylon bolts shortly after this photograph was taken.

As well as the recommendations made on the interlocks, the electrical professional also advised on installing a suitable door lock, preventing any accidental access. The easiest solution would have been to install a metal bolt; however this could have potentially interfered with the electro-static field. The alternative solution was to design a lock out of wood, which fits over the door handles [see Figure 7-6, image C]. The design successfully locked over the door handles, securing the door and the preventing accidental access.

Once the system was signed off as being safe to use by the University of Surrey’s health and safety officer, the system was tested for radiation. Breaking radiation, or ‘Bremsstrahlung’, is an electromagnetic radiation produced when particles accelerated by high voltages rapidly decelerate. Typically, in order for hazardous radiation levels to be produced, the equipment requires a high-vacuum, which this rig is not. However, in the interest of safety, it was considered appropriate to
ensure this was the case. To conduct the test, mock electrospinning experiments (both needle and needleless) were set up without any polymer solution, using existing electrode/spinneret systems. Each system was then slowly charged-up from 0 to 75 kV (positive and negative polarity), while continuously taking radiation measurements with a scintillation tube. Throughout the whole range of potentials, there were no changes to the background radiation levels observed. This radiation test was then repeated with a polymer solution, producing nano-fibres by electrospinning, which also did not increase any levels radiation, confirming that the system was safe to use.

7.2.5 Conclusions

This chapter has outlined all of the steps taken and careful considerations, in designing and building the large area collection drum assembly and its housing. This was initially was approached by developing the large collection drum (with an electrospinnable surface of 1.2 x 0.8 m), and its mounting, outlining all of the necessary design components which were needed for its successful implementation. The mounting was further adapted to not only secure the high speed rotating collector, but also to include adjustable shelves to house the other electrospinning equipment, such as power supply and motor control unit.

Following the completion of this, safety shielding was applied directly to the outside of the housing structure. This not only significantly reduced development costs (when compared to building a walk-in fume cabinet), but also allowed for the rig to be repositioned, should the need arise. This shielding was also designed to isolate the apparatus inside the rig, for electrospinning parameter control (such as temperature and humidity), and personal protection. To fully diversify the electrospinning rigs capability, an air filtration system was added to the top of the assembly, allowing any hazardous materials to used safety.

This chapter then moved on to detailing all of the various health and safety features, which were included to ensure that any electrospinning could be conducted without risk. This included items such as electrical interlocks and door locking devices. After applying numerous safety features which maximised user safety, this assembly was commissioned and ready for electrospinning. However, before any electrospinning could be conducted, the next stage in the project was to design and build working electrospinning assemblies, using the traditional needle-based spinnerets. This was so that any produced nano-fibres on the new system, could be compared to those produced previously in Chapter 5.
7.3 Needle-based Spinneret Electrospinning Designs

7.3.1 Introduction

With the completion of the large area collection drum housing in the last chapter, it became necessary to begin designing and building the electrospinning spinneret systems that generate the nano-fibres. This chapter introduces and explains the design implications of the needle-based systems built for use with the large area collector, including a single needle system and a multi-needle system. The implementation of these systems both demonstrates the successful design and implementation of the large area collector and its housing [see Figure 7-7], as well as giving rise to the production of potentially the first large areas of aligned carbon nanotubes (CNTs) produced by electrospinning.

Figure 7-7 – A photograph of the large area electrospinning equipment, designed and built for this project. In this photo the collection drum can be seen to be primed with silicone-coated release paper, with the single needle spinneret system underneath, ready to produce nano-fibres.
7.3.2 Single Needle Spinneret

This project’s main objective is high-throughput large-area electrospinning, which cannot be achieved with a single needle system, due to the slow solution processing rates involved. It was beneficial to design and build a single needle spinneret, for reasons such as smaller sample size (for new solution testing), ease of application in simple experiments, and proof of concept. This also allowed a direct comparison between the nano-fibres produced on previous rigs [see Chapter 5], and on the new larger rig outlined in Chapter 7.2.

Figure 7-8 – The simple single-needle electrospinning platform, showing how the needle can be repositioned to point in any direction to accommodate for any requirements that the new rig may have (A). Later, the design was slightly altered in order to balance the electro-static field (B), as it was noticed that the fibres were drawing away from the copper track seen at the top of image A.

Originally, the previously used electrospinning rigs were designed to be permanent systems made of TUFNOL, a heavy highly-insulating composite material. However, this would not have been suitable on the designed larger rig, as it was unclear how the electrospinning set-up would need to be designed to be best suitable. For example, it was unclear how the metal frame would affect the electrostatic field, and as such the spinneret would need to be moved into an optimum position before fibres could be produced. With this in mind, a simple system was designed to be light-weight and completely adaptable to any situation that is required [see Figure 7-8]. Due to its low cost (compared to TUFNOL), its availability, reported chemical resistivity, and its reported high breakdown voltage of 40 MV/m (Babrauskas 2005; Xu & Xu 2002), it was constructed using push-fit polyvinyl chloride (PVC) waste water pipes. PVC was chosen over TUFNOL, as this electrospinning assembly would by operating at lower voltages, and therefore TUFNOL was not necessary. This allowed for the design to be altered...
in any way, as the pipe could be simply be pulled apart and rebuilt, allowing the reposition of the needle in any direction [see Figure 7-8, image A]. This design was later altered to ensure that the electrostatic field was symmetrical; as it was noticed during testing that the fibres were drawn towards the right, away from the copper track in which the spinneret was seated [see Figure 7-8, image B, spinneret position].

With any needle-based electrospinning system, a syringe pump is required to deliver the solution to the spinneret(s). After a review of numerous different syringe pump systems, a ‘Chemyx OEM’ syringe pump was ordered from KR Analytical Limited. This was selected because of its low cost, simple PC control functionality, and proven reliability in previous experiments. These pumps consistently demonstrated that they could produce high pressures and withstand high electrical potentials in all of the previous experiments. Figure 7-8 displays the Chemyx syringe pump next to the electrospinning rig.

The first nano-fibres were produced on the new large rig outlined in the previous chapter, using this designed adaptable single needle spinneret. They were produced using an aqueous solution consisting of 2% weight fraction polyethylene oxide (PEO) (with an average molecular chain length of 2,000,000 M\textsubscript{v}), 1% weight fraction of Brij 58 surfactant, and 0.1% carbon nanotubes (CNTs), which had previously proved successful in Chapter 6.2. In order to reveal if the previous electrospinning parameters defined in Chapter 5, were suitable for use on the newly built assemblies, the parameters were set to those previously found to be optimum. Where: the high speed collection drum (covered in silicone paper) was rotated with a surface velocity of 8.1 m/s, the atmosphere before this spin was
dehumidified and measured as 23°C and 41% relative humidity, a total of 8 ml of solution was fed at a pump rate of 700 µl per hour, and the spinneret was charged at +12 kV while being positioned approximately 20 cm from the collection drum. If these parameters remain the optimum ones (despite the rig change), then the nano-fibres produced would be highly-aligned and of a uniform consistency.

Figure 7-9 reveals the first aligned CNT-loaded nano-fibre arrays, produced on both the newly built large-area electrospinning rig, and the new single needle spinneret. The results demonstrate that not only can the new set-ups suitably generate aligned nano-fibre arrays, but also that the optimum parameters outlined in Chapter 5 are transferable between equipment. This similarity in electrospinning parameters across equipment was expected, as the parameters are mainly governed by the solution properties, such as viscoelasticity, as previously explained in Chapter 2.4.4. Comparing the nano-fibres produced this time around, to those made before, revealed no obvious differences or issues. This result confirmed that the new process and equipment are as efficient as before at generating arrays of aligned nano-fibres, but this time on a significantly larger scale. In order to further progress this project, the electrospinning process must now be developed to increase throughput, decreasing processing times.

7.3.3 Multi-Needle Spinneret

One of the primary concerns when considering needleless electrospinning as a scaled-up solution, was that extreme voltages are typically needed (as was discussed in Chapter 2.4.2). As a result, it was decided to explore other scale-up solutions, such as a multi-needle array. Work began on designing a suitable multi-needle electrospinning rig which could increase the fibre production rates.

Just like with all other aspects of this large-area scale-up development, careful design consideration was required to ensure that the electrospinning process runs smoothly and evenly, producing uniformly and consistently aligned arrays of CNT-loaded nano-fibres. When designing a multi-needle system, there are four key requirements that the design must follow in order to achieve the desired output. The first of these requirements is that the needle spinnerets must be at least a distance of twice their length apart, in order to avoid the electrostatic shielding of one another (Nilsson et al. 2000). The second requirement is that all the spinnerets must be an identical distance from the collection drum, in order to ensure that the electrostatic field strength applied to each polymer jet is equal. Any slight variation in each spinnerets distance to the collection drum will significantly alter the electrostatic field strength that is applied to the Taylor cone, obeying Coulomb’s
law (also known as the inverse square law) (Resnick et al. 2007). Variances in the electrostatic field strength will alter the acceleration of the polymer jet, which ultimately leads to variance in both nano-fibre diameter and overall alignment (as explained in Chapter 2.4.5). The third requirement is that each spinneret must have an equal length of tubing to the syringe pump. This is purely to ensure that each spinneret is supplied with solution at the same rate, in order to produce a uniform array of nano-fibres evenly across an area. The final requirement is that the multi-needle array must be fully adjustable, i.e. be able to bend into different positions depending on the desired outcome, much in the same way as with the single needle system introduced in the previous chapter. This was to allow the assembly to be adjustable for any electrospinning position, as well as allowing the deposition area to be adapted by simple changing the rotation of the needle array. Approaching these requirements were somewhat more complex than encountered previously with the single needle system, this is purely due to the necessary consideration of four spinnerets as opposed to the single before.

Figure 7-10 – (A) A schematic diagram of the multi-needle electrospinning rig, showing all of the design features, including needle/spinneret locations. (B) A photograph of the finished built rig during an electrospinning run, revealing the aligned nano-fibres on the collection drum.
With these specifications defined, the rig in Figure 7-10 (A) was designed and built. This rig was built out of PVC waste pipe, for the same reasons as outlined in the previous chapter. The design was intended to meet each of the requirements, where each needle is positioned in such a way that it will be exactly 20 cm from the collector drum, while being separated at equal distances from each other. Because the only PVC pipe ‘bends’ available were at either 45° or 90° angles, the design had to allow for a 45° bend. Using trigonometry, it was calculated that, in order to meet the separation and drum distance requirements, the spinnerets needed to be approximately 15 cm apart. The needle spinnerets were each fed through small holes at each calculated location and secured with electrical insulating tape. The PTFE tubing coming from each needle was cut to equal lengths (ensuring equal solution pressure), and passed through tubing splitters in pairs until into one tube which was fed from the syringe pump. The splitter attached to the feed from the syringe pump was also attached to the high voltage (HV) supply; this allowed for the solution to be charged, which in turn equally charged all the needles. This meant that no needle needed to be attached directly to the HV supply, or that any high voltage tracks between each needle were needed, which could have possibly unbalanced the electrostatic field across all needles, as seen with the single needle rig.

![Image](image.jpg)

**Figure 7-11** – A scanning electron micrograph of the nano-fibres produced with the multi-needle system (A). Further samples were produced with the multi-needle system with an increased volume of solution, which led to larger areas of aligned CNT-loaded nano-fibres being produced (B).

The photograph in Figure 7-10 (B) displays the multi-needle rig built to the shown design, operating without any issues (the resultant fibres can also be seen on the drum). All needles appeared to be electrospinning nano-fibres equally, with no obvious problems with solution delivery or electrostatic field unbalances. The fibre sample seen in Figure 7-10 (B) was spun with the same
parameters as with the single needle system outlined in the previous chapter [see Figure 7-11 (A) for an electron micrograph of the resulting nano-fibres produced]. However, the only difference between the single and multi-needle systems was that the solution delivery was 4 times faster. In this case, 8 ml of solution was delivered in 3 hours, instead of the usual 12 hours. Although in theory this system is significantly slower than a needleless system, which has the potential to generate hundreds of jets simultaneously, these results demonstrate that multi-needle systems are a possible alternative. If required, this system can be further scaled to include more needles across numerous rows along the collection drum, and then repeated on the other side of the drum, further increasing the potential throughput of this system.

Further nano-fibre samples were electrospun using the multi-needle rig, but this time with a much larger volume of solution (28 ml), and allowed to electrospin over a longer period (10 hours). This produced the projects first, and potentially the World’s first large areas of aligned CNTs, as demonstrated in Figure 7-11 (B). This achievement was a huge step forward, leaving us on the doorstep to achieving the project goal, of obtaining, consistent large areas of highly-aligned CNTs! Despite reaching this key milestone of the project, investigations were continued in the next chapter to explore the prospects of needleless electrospinning, as an increased throughput alternative.

7.4 Needleless Spinneret Electrospinning Design

7.4.1 Introduction

The next stage of the scaling-up process within this project, is to explore and investigate the potential of further increased nano-fibre throughput, through the process of needleless electrospinning. Needleless systems can have numerous benefits over needle-based systems, such as a significantly higher density of electrospinning jets, substantial nano-fibre throughput, and a zero chance of spinneret blockages. However, when striving for the large area alignment of CNTs, the importance of the controlled environment and the stability of the Taylor cones are essential. This led to a number of key design implications, which produced a patentable needleless system, which will be introduced in this chapter.

Typically, needleless electrospinning involves some form of large electrode spinneret, which is submerged within a reservoir of electrospinnable polymer solution. During the spinning process, the electrode is rotated, while being subjected to a large electrical potential (30 – 120 kV) (Petrik & Maly
2009). As the electrode rotates, the polymer solution forms a thin layer on the drum surface, which is then charged, forming Taylor cones, and subsequent polymer jets, that are electrostatically attracted to the collector drum located above. The main variation in this form of electrospinning is in the electrode design; this design is the subject of several patents [see Chapter 2.5]. As previously mentioned (Chapter 2.4.2), one of the largest nano-fibre throughputs commercially quoted to date has been achieved using a smooth, uniform drum-electrode. However, this has been known to produce nano-fibres of inconsistent widths, due to a non-uniform electrostatic field (Petrik & Maly 2009). A non-uniform electrostatic field causes the polymer jets created from different areas of the electrode to have a different velocity, and therefore alignment will vary as the collection drum can only be rotated at one speed [see Chapter 5.3, for details of nano-fibre alignment]. This also means that the density of Taylor cones will vary across the electrode and a uniform deposition will not be obtained. With this in mind, this chapter will begin by explaining how the electrospinnable solution will be controlled to only produce Taylor cones from specified, controlled locations, as well as limiting their size. This chapter will then move on from this to explain how the electrostatic field can be manipulated into uniformity across the length of the electrode, ultimately giving rise to our needleless electrospinning solution for the large area alignment of carbon nanotubes.

We will then conclude by refining the various needleless electrospinning parameters, such as electrode rotational velocity and spinning potential. This led to the optimization of the needleless process, achieving significant improvements of over 18x the electrospinning solution processing rates, when compared to that have been previously achieved with the multi-needle system.

### 7.4.2 Solution Manipulation with Hydrophobicity

Possibly more important than the collection drum housing design, the needleless electrospinning electrode needs to be designed and developed to a critical standard, ensuring not only a maximum fibre throughput, but more importantly nano-fibres which are produced consistently and uniformly across the length of the electrode. To achieve this, we need to develop a mechanism which controls both the size and positions of the generated Taylor cones. By controlling Taylor cone formation, the essential nano-fibre parameters needed for the alignment of the loaded carbon nanotubes (CNTs) can be consistently regulated.

As one of the project’s principal constraints is that the solution must be aqueous-based, it was considered to utilise hydrophobicity in order to gain control over the needleless electrospinning process. Tailored hydrophobic and hydrophilic areas across the surface of the electrode should
provide the necessary control for manipulating size and locations of Taylor cone formations. The alternative to this was to adapt the electrode’s structure in order to manipulate the electrostatic field, in a manner that there were areas of focused electrostatic field strengths that electrospinning could only occur in. An example of this is the inclusion of ‘spikes’ or raised areas, where a point charge is introduced and as such the electric field is concentrated. These point charge sites will promote Taylor cone growth in these areas as opposed to others (Theron et al. 2001), as well as limiting to size of the cone to the spike tip.

Figure 7-12 - These three photographs illustrate the step by step process taken to test the hydrophobic/hydrophilic effects on the polymer solution, when using a silicon wafer as the substrate. Showing A: The application of the hydrophilic areas, B: the results of a direct test on deionised water, and C: the little effect either surface had on the polymer aqueous solution.

To decipher whether the solution can be manipulated by surface properties or whether a point charge system would be required, a simple test was conducted to investigate how a PEO loaded aqueous based solution would behave when applied both hydrophobic and hydrophilic surfaces. This was achieved by constructing a ‘dipstick’, which was prepared with a simple pattern, consisting of a hydrophobic surface with hydrophilic areas. To achieve this, a silicon wafer was used as the hydrophobic surface (Ou et al. 2004). Figure 7-12 (image A), displays the slice of wafer which was used to form the dipstick. Hydrophilic regions were applied to the silicon in the form of PVC adhesive tape. However, the tape was to remain on the surface to act as the hydrophilic surface for the solution to bind to. Before submerging the wafer into the solution, the theory was first tested using de-ionised water [see Figure 7-12, image B], which behaved as suggested, where the water collected only on the
tape-covered areas. However, once the wafer was submerged into the CNT/polymer aqueous solution [see Figure 7-12, image C], total wetting was observed, regardless of the surface hydrophobicity. This demonstrates that, despite being predominantly an aqueous solution, the presence of the polymer allows for wetting of hydrophobic surfaces.

This result confirmed that the use of hydrophobicity, to control the electrospinnable solutions behaviour on the electrode’s surface, is not applicable when using the PEO systems. This then confirms that, instead of controlling the application of the polymer solution to control nano-fibre production (as was attempted), the electrostatic field must be manipulated instead. This then means, as suggested earlier in this chapter, that the electrode must be designed to incorporate point charges, such as spikes, to limit Taylor cone size and location.

### 7.4.3 Manipulation of the Electrostatic Field

Manipulating the electric field through the addition of spikes introduces point charges, which dictate the Taylor cone formation. However, it is important when using features such as spikes to create point charges, to gain an understanding of how their structure parameters will affect the electrostatic field. Factors such as spike length, aspect ratio and density, could all be critical. For example, if the spikes are located too close to each other, their electrostatic field emitted from each one could interfere with one another, reducing the field strength at the tip, whereas if they were too long or too short, then they may not enhance the field intensity enough to control the Taylor cone formation. This led to the question of what is the minimum required electrostatic field strength required to produce a Taylor cone? Simply reducing the electrostatic potential until electrospinning stops on the single needle electrospinning rig provided a quick estimation of the minimum potential needed to be approximately 9 kV (when using a positive polarity) [displayed in Figure 7-8]. Using the basic principle of charge divided by separation distance, the electrostatic field can be crudely approximated to be $4.5 \times 10^4$ V/m. However, this approximation does not take into consideration, temperature or humidity, and more importantly the field enhancement as a result of the spinneret tip. In order to generate a more accurate estimation, computational modelling software ‘COMSOL Multiphysics’ (version 4.2), was employed to simulate the electrostatic field of a to-scale single needle electrospinning system, using finite element analysis. The COMSOL model was programmed to simulate a resulting electrostatic field at the minimum potential of 9 kV, allowing for the minimum electrostatic field strength to be estimated.
Figure 7-13 displays the resulting COMSOL simulation of the electrostatic field (displayed as both a heat map and an arrowed diagram), which was calculated for a scaled model of the large area collection drum and a single needle spinneret. The permittivity of air was set to 1.0008, which correlates to approximately a temperature of 25°C and relative humidity of 45% [see Chapter 2.4.3 for air permittivity relationships]. The simulation calculated that the electric field strength at the tip of the needle spinneret was approximately $5.52 \times 10^5$ V/m. This calculated minimum electrostatic field strength required for the Taylor cone to produce a jet is closely related to the size of the Taylor cone, and as such could be considerably lower with smaller spinnerets. Furthermore, this value is over an order of magnitude higher than estimated previously. While the introduction of temperature and humidity will change the value slightly, this is primarily a result of the field enhancement from the single spinneret tip.

![Figure 7-13](image)

Figure 7-13 – A to-scale COMSOL simulated model of the resulting electrostatic field (including both a heat map and arrowed plot), when a single needle spinneret is charged at 9 kV within the large area collection rig built for this project. The electrostatic field strength at the tip was found to be $5.52 \times 10^5$ V/m.
The value for the minimum electrostatic field strength can then be used as an approximation when designing a needleless electrode. With each purposed design, COMSOL will again be used to simulate the resultant electrostatic field, allowing the identification of any undesirable aspects, such as unbalanced tip-to-tip field-distribution or unwanted ‘hotspots’. In order to keep simulation and prototype building simple, it was decided that a spiked drum would be the starting point for electrode design. Each spike would enhance the electrostatic field and effectively act as a single spinneret, in a way similar to the single needle system in Figure 7-8. Each spike of an equal size, positioned uniformly across a drum’s surface, would subsequently control where and at what size the Taylor cone is formed, controlling the fibre diameter and ensuring uniform fibre delivery. The presence of the spikes would enhance the field at the tip only, lowering the field on the drum’s surface and preventing Taylor cones from forming anywhere else. It was important to design a spiked drum that distributes the charge evenly across the array of spikes, in order to control the fibre deposition. It has already been reported how a smooth drum has been seen to have an uneven charge distribution, and subsequently produces more nano-fibres at the ends of the drum than in the middle (Niu et al. 2009). This was briefly explored with another COMSOL simulations. Figure 7-14 displays the resulting electrostatic field produced from an electrode of equal size but with no spikes. In order to try and prevent this field unbalance, a number of different drum designs were modelled to scale (within the large collector rig as with Figure 7-13), and simulated in COMSOL, as before. In order to access the electrostatic field uniformity, the resulting field strengths were calculated for both the outside spikes and the middle spikes when the electrode was charged at +60 kV. Any substantial difference between the two field strengths will indicate an electrostatic field unbalance.

![Figure 7-14](image-url) – A COMSOL simulation of the electrode (to-scale), where in this case it has no features, and is purely a flat drum. The model was simulated with a potential of +60 kV applied, revealing an electrostatic field strength of approximately $8.35 \times 10^5$ V/m on the ends of the drum, and $3.35 \times 10^5$ V/m in the centre. The simulations corresponding colour scale can be found in Figure 7-15.
Figure 7-15 – A small selection of the various different electrode ideas simulated in COMSOL when a potential of +60 kV is applied, in an attempt to even electrostatic field distribution across the electrode’s surface. Each of the designs are as follows: A) A generic spiked electrode (where charge is observed to concentrate at the end spikes), B) With shortened spikes (which reduced the field unbalance but also reduced the field as a whole), C) Shortened End Spikes (which increase field balance but passed field onto the next spike), D) Every other spike removed (which failed to aid in any case other increasing the field as a whole), E) Every other spike removed with curved ends (which aided field balance but only slightly), F) Every other spike removed with outside features (further balanced the field but with a reduced nano-fibre output with fewer spikes), and G) The original spiked electrode from ‘A’ with larger outside features (which had maximum output and a balanced field).
Figure 7-15 displays a selection of some of the designs simulated with the COMSOL modelling software. Simulation ‘A’ is a model of a simple spiked electrode, where each spike was set at 4.5 mm high, and 5 mm apart. This was chosen because of a spiked/pinned drum product that was already readily available (more information on this will be provided in Chapter, 7.4.4). With this design, electrostatic field enhancement can be observed to be significantly higher on the outside spikes, as expected. It was thought that shortening of the spikes (in simulation ‘B’) would reduce the ‘shielding effect’ caused by each spike’s emitted field, and even the field across the spike array. This was found to be not as significant as hoped, and it generally reduced the overall strength of the electrostatic field across the whole array of spikes. However, further developing this result, it was then considered that only reducing the height of the outside spikes would lower their field and even the field distribution (giving rise to simulation ‘C’). This unfortunately resulted in a ‘knock-on’ effect, increasing the electrostatic field strength on the spike next to the reduced height outside spike. We thus returned to the original electrode design, and considered increasing spike separation distance to at least twice that of the spike height, so as to reduce shielding effects (as previously mentioned in Chapter 7.3.3), leading to simulation ‘D’ (Bonard et al. 1999). This had a significant effect of increasing the strength of the electrostatic field on each spike (where shielding was now minimised). However, this was rejected as an option, as with half the number of spikes (spinnerets), electrospinning rates will be halved, and the uniformity of the electrostatic field was still relatively poor, with the measured field strength difference between the outside and the centre spikes being almost no different to the original design (A). To further reduce this difference in the field strength across the array of spikes, the end corners of the electrode were rounded, in an attempt to exploit Coulomb’s law (inverse square law) and further concentrate the field on the spikes in the centre (simulation ‘E’). This was found to result in the strongest electrostatic field measurements of all designs, however the field was still far from uniform across the array of spikes.

It was noticed, during all of these simulations that after the outside spikes, the electrostatic field distribution is generally even. As a result it was thought that adding additional spikes or electrodes, to the outside of the design, that are not used for electrospinning, would have the same effect. Simulation ‘F’ reveals the effect that these new outside features have on the electrostatic field distribution. In this case, although overall field strength is slightly reduced across all of the spikes, the overall field distribution is significantly more uniform. In order to try and increase this effect caused by the outside features, they were increased in size, which resulted in again an evening of the field distribution. Lastly, due to the results seen in simulation D, where the number of spinnerets was halved too little effect (when compared to the sacrifice to the electrospinning rate), the spikes were returned to the original (simulation A) formation. This resulted in our final model in simulation ‘G’,
which was found to produce the best results with regards to the field strength on the spikes, and the overall field distribution across the spikes. Although the field strength was significantly reduced across all of the spikes, it was measured to still be greater than the minimum that was measured on the single needle system earlier in this chapter. This design was then taken forward for implementation in the next chapter.

### 7.4.4 Fibre Electrode Rig Design (Prototype 1)

It was shown in the previous section that, the only way to manipulate the water-soluble polymer solution successfully, was to use point charges on the electrodes surface, in this case by adding spikes. With this in mind, a pinned (spiked) drum was purchased from William R Stewart and Sons [see Figure 7-16, B], which was constructed of an aluminium drum with carbon steel pins (approx. 1140 pins of length 4.5 mm, spaced 5mm apart). The design of the electrode was identical to the one modelled in Figure 7-15, simulation ‘A’, which revealed how the spikes create point charges on the tips, limiting Taylor cone formation to only these areas.

![Figure 7-16](image)

*Figure 7-16 – A schematic diagram (A) of the needleless rig and a photograph of the final build (B), showing how the spiked drum will be charged and rotated within the gutter of solution.*

As well as the attention to detail in the electrode, careful design was also needed for the implementation of a suitable assembly as to house it. The concept of the design was simple, to have the electrode submerged within a reservoir of polymer solution, that when slower rotated produces a thin film of solution over the spinnerets to produce the polymer jets, and as such the nano-fibres
However, several design factors had to be included into the build, in order to ensure consistent nano-fibre production, uniform nano-fibre production, easy cleaning, and safe running, especially due to the high voltages involved. Within this project, attempting to meet all of these requirements resulted in a prototype device, which after initial tests, led to an optimised second device.

Figure 7-16 reveals the first prototype device, which was designed so that the electrode (with a diameter of 100 mm pin-to-pin and a length of 100 mm), was secured and rotated within a PVC gutter section (112 mm in diameter). This was chosen for two reasons, the first being as before in Chapter 7.3.2 that it is cheap and easy to acquire, and the second being that it was of a similar size to the electrode, which minimises the volume of fluid needed in the bath to coat the pins. The electrode itself was required to be rotated slowly via an electric motor, at a speeds typically around 3-10 rpm, depending on the solution thickness (Tang et al. 2010; Cengiz et al. 2010). The motor was connected by a plastic gear and rubber drive belt; insulating the motor from the high potential stored within the drum. Further to this, the motor is powered by an isolated 6 V battery, preventing any additional charge leakage through the motor. This battery also allowed for the speed of the motor to be altered using a variable resistor, preventing the drum from rotating too fast as to disrupt electrospinning or too slow as to lead to solution depletion from the spikes before a complete electrode rotation.

The entire rig design was mounted using nylon nuts and bolts onto a 10 mm thick TUFNOL support, which was thick enough to be electrically insulated for potentials up to 90 kV. As a last precautionary method, the whole platform was mounted on several 10 mm² rubber feet, which combined with the TUFNOL and the rubber drive belts, provide more than the necessary electrical protection required to safely operate this electrospinning equipment at the required high potentials. To remove the risk of accident in the event of the electrode jamming, the tension of the belt and pulleys was adjusted to allow slip, should the electrode become stuck. This reduced the possibility of the motor overheating in the unlikely event of a jam. As well as safety, usability was also considered during the design and building of this rig; in a bid to reduce cleaning and maintenance, the entire drum and solution gutter was installed so that it was easily unclipped and removed from the main structure.

At this stage, it is important to note that the large external features used to promote uniformity in the simulations were not added to the design [see Figure 7-15, simulation G]. This was because they were not available at the time of this set-up’s construction completion, and testing was decided to continue without. These were added to the second prototype, in the next chapter.
Before any live testing was conducted, the electrode and its assembly were subjected to an electrical breakdown test, within the safety of an electrically-secured chamber. During this test, the potential of the rig was increased from 0 V to 60 kV slowly, looking for any electrical breakdown. Simultaneously while charging the rig, a Geiger counter was employed to measure the radiation levels, ensuring that there was no bremsstrahlung emission as a result of the high potentials. The rig was successfully charged to 60 kV, with no evidence of electrical breakdown, and only a negligible raise to the radiation levels detected of 0.2 µSv/h (when fully charged at 60 kV), which is well within safe working limits.

7.4.5 Initial Nano-fibre Samples and Resulting Design Adaptations

The initial tests that were conducted on the prototype introduced in the previous section [see Figure 7-16, image B], were done so using a PEO (2,000,000 M,) aqueous based solution, mixed at a weight fraction of 2% PEO, which has been successfully used with single needle spinneret systems throughout this thesis. The fluid reservoir was filled with 50 ml of polymer solution, opposite to the large rotating collection drum which was coated in a silicon release paper. The needleless spinneret was set at distance of 15 cm from the collection drum, as this had been previously reported as being the optimum for nano-fibre collection (Wu et al. 2010; Niu et al. 2011; Elmarco 2010). The atmospheric conditions were noted on the day of testing to be at a temperature of 21ºC, and relative humidity of 52%.

Figure 7-17 – The first PEO (nano-)fibres produced on the spiked electrode needleless electrospinning system. This micrograph reveals that the thicker fibres were landing wet (seen as the large splodges), and that the fibre diameters as a whole, vary substantially from a few micrometres to tens of nanometres.
Before enabling the high-voltage, the spiked electrode’s drive motor was connected to the battery, powering its rotation. It was immediately observable that the polymer solution was predominantly adhering to only one side of the drum, where the solution’s high-viscosity was preventing flow across the surface of the electrode, leading to an uneven solution coating. Upon enabling the high-voltage supply, and increasing it to 40 kV, this uneven coating was causing any polymer jets to be primarily be produced on the one coated side of the electrode. Furthermore, it was also observed that these jets were extremely thick, resulting in the fibres failing to dry before collection, saturating the collector drum and preventing further nano-fibre collection [see Figure 7-17]. Although this first test failed to produce fibres correctly, it demonstrated that either: the solution needed to be less viscous, as to allow flow for an even electrode covering, or some form of solution applicator is required.

With this previous result in mind, another aqueous solution was mixed, but this time comprising of 1% weight fraction PEO instead (of the same polymer chain length). However, although this solution allowed for flow across the electrode’s surface (solving the issue of an uneven drum coating), it failed to produce any polymer jets, even up to the power supply’s maximum of 60 kV. There were however, drips/spits of solution ejected from the drum. This observation implied that the viscoelasticity of the solution was insufficient to allow the formation of the polymer jets needed to produce nano-fibres. With the failure of this suggested solution for achieving an even fluid coating on the electrode’s surface, the only other alternative was to introduce some form of applicator that would distribute the polymer solution across the electrode surface.

Figure 7-18 – The addition of a brush to the top of the fluid reservoir (A), provided the necessary solution application control to ensure a thin, even coating, over the electrode. This allowed the electrode to produce the high quality nano-fibres, as seen in the scanning electron micrograph (B).
The requirement for a solution applicator, whether it be a brush or a scraper, was found to be the only viable solution in achieving a thin uniform layer of polymer across the drum, for the efficient production of nano-fibres. Wu et al. (2010) documented how a flat flexible plastic scraper was required in order to use the more viscous polymeric solutions. However, a scraper of this form would not be suitable for use on the spiked electrode due to the inhomogeneity of the surface. With this in mind, the most simplistic solution, was to install a wooden brush, with polypropylene (PP) bristles (in this case a simple draft excluder), to the top of the needleless rig’s vertical support [see Figure 7-18, image A]. As with the installation of the shielding in chapter 7.2, careful consideration was taken not to use any metallic parts (if possible), to prevent distorting the electrostatic field.

![Figure 7-19 – A histogram of the nano-fibre diameters, produced on both the needleless and single needle electrospinning systems (A), where the single needle system produces more consistent nano-fibres. This was attributed to the unbalance in the electrostatic field at the ends of the electrode, where a photograph (B) during spinning demonstrates that jets predominantly originate from either of the two ends (arrowed).](image)

This addition of a brush-style applicator, provided the necessary solution control which ensured an even, thin film of polymer fluid across the electrode surface. The thinner film of solution resulted in a more controlled and significantly more uniform application of polymeric fluid to each spinneret (spike) on the electrode. This in turn reduced the size of each Taylor cone generated on the tip of each spike, resulting in the polymer jets produced to be considerably smaller. This subsequently reduced the diameter of each of the produced fibres, meaning that the solvent fully evaporated before collection, avoiding the thick, wet fibres observed before. This produced the significantly higher quality fibres seen in Figure 7-18, image B. However, a closer look at the micrographs of the nano-fibres revealed that their diameter distribution is still significantly broader than those produced with a single needle spinneret system [see Figure 7-19, A]. A closer look visually at the electrospinning process of this electrode confirmed that, as predicted in Chapter 7.4.3 (in Figure 7-15, A), a concentration of the electrostatic field is at the ends of the electrode. As such, this stronger field,
located at either end, will produce significantly thicker fibres due to the larger Taylor cones formed [see Figure 7-19, B]. Despite this, Figure 7-18 (B) is still a promising step in to the right direction, especially when compared with the initial attempted nano-fibre sample, in Figure 7-17.

While producing the nano-fibres in Figure 7-19, the motor driving the rotation of electrode experienced its batteries running low, causing the rotation to slow considerably. It was noticed that, during this period, a significant additional number of jets were produced from the electrode. This could have been because it allowed the brush to produce an even thinner film, or maybe because it provided the Taylor cones additional time to form. In order investigate this further, and to explore the mechanisms behind it, a variable resistor was used to alter the speed of the electrode’s rotation. The results of this investigation will be detailed in the next section of this thesis.

7.4.6 Reducing Drum Rotation Speed

It has already been mentioned in Chapter 7.4.4 how the rotational speed of the electrode is important to nano-fibre production rates. During the initial testing in the previous chapter, the effects of this were witnessed, where a slowing of the drum saw increased fibre production. It is theorised that if the speed of electrode rotation is too slow, then the solution on each spinneret will deplete before a complete rotation, lowering throughput. On the contrary, if rotating too fast, it could fail to provide the Taylor cones with sufficient time to form, again reducing nano-fibre throughput.

However, as simple as this investigation sounds, it is extremely difficult to measure the nano-fibre production rate with the needleless electrospinning system as, unlike with a syringe fed system, the depleted solution cannot be easily quantified. It was decided that the best way to investigate for the ideal electrode rotation speed was visual, using high definition photography equipment. For this investigation, the electrospinning parameters were kept identical to the previous chapters: the fluid reservoir filled with 50 ml of aqueous based 2% weight fraction PEO (2,000,000 Mv) solution, an electrode distance of 15 cm from the collector, and an electrode potential of +40 kV. In order to control the electrode’s rotational speed, a variable resistor (1 – 10 Ω) was applied the electrode’s motor battery, allowing direct control while the motor is running. This allowed the rotation speed of the electrode to be varied between 0 and 25 rpm, while monitoring the fibre production. Note: special care was taken to power down the high voltage supply and ground any residual charging before handling the variable resistor, as to avoid electric shock.
Despite the difficulty and ambiguity in assessing the effects of electrode spinning speed, using only photography equipment, it became clear that, the slower that the drum was spun, the more jets that were observed. However, during the testing, it was also noticed that for resistances above 9 Ω, the motor did not have enough power to rotate the electrode (when combined with a reservoir full of solution). This means that, in order to investigate this further, the motor needs to be re-geared (or replaced), to provide the high torque at low rotational speeds. Despite this, the density of polymer jets observed to be generated from the electrode was significantly increased when the speed was set at 6 rpm, as seen from the photograph in Figure 7-20. The jets were observed to initiate as soon as that row of spikes/spinnerets were raised from the bath. Furthermore, they were also seen to be sustained across the majority of the electrode, up until the point of resubmission into the reservoir, i.e. the solution coating each spinneret did not deplete. This suggests that the electrode’s rotational velocity could be further reduced, possibly allowing more jets to be produced, while reducing solvent evaporation from the unused solution. However, due to this projects time constraints, this mechanism was not studied further, and time was invested in further improving nano-fibre alignment and consistency, when using a needleless system.
Despite this significant step forward in understanding needleless electrospinning, there still remained the issue with the produced nano-fibre inconsistencies, as a result of the unbalanced electrostatic field. In addition to this, the usage of this prototype also exposed a number of design flaws, which ultimately led to difficulties in its efficient implementation during nano-fibre production. These difficulties all concerned the polymeric fluid, in particular the storing of it, manipulation of it and the monitoring of it. During electrode rotation, a large volume of fluid would spill over the sides of the guttering, usually around the brush, depositing on the support structure below. In the event of using a conductive solution, such as one containing carbon nanotubes, this spill could lead to a dangerous current leak, resulting in damage to equipment or personal injury. Also, during the electrodes rotation, the solution was sometimes seen to foam, which was caused by the brush used to maintain a thin coating [see Figure 7-21]. While foaming was only a minor occurrence, in the event of it happening, the spinnerets would be smothered and no Taylor cones would form. Furthermore, this meant it was also extremely difficult to monitor the volume of remaining solution in reservoir during electrospinning, leading to the requirement for some form of transparent window. In the next section, we explain how we redesigned, and remade the needleless electrospinning system, in order to overcome these challenges. This redesign also includes the introduction of the large external electrode features, which were unable to be included in the initial prototype [see Figure 7-15, simulation G, for a reminder].
7.4.7 Fibre Electrode Rig Redesign (Prototype 2)

The previous chapter concluded that the needleless electrode electrospinning rig had three design flaws that needed to be overcome, in order to both produce nano-fibres as intended and to allow for easier/safer operation. These issues were identified as: solution spillage during operation (from the reservoir), foaming of the brush (which hindered the electrospinning process), and a difficulty assessing the remaining solution with the reservoir. In order to overcome these challenges, it was decided to redesign the assembly, and build a second prototype, as opposed to adapting the original.

Figure 7-22 – Photographs of the second prototype of the needleless electrospinning system, designed with the aim to overcome the design flaws associated with the first. The labelled changes are: 1) a redesigned clip system holding the drum in position far more accurately and securely; 2) lip-edges, to reduce solvent loss from the solution reservoir; 3) an adjustable brush allowing for position to be changed to avoid foaming; 4) a transparent window to allow easy monitoring of the solution levels and 5) the external electrodes for balancing the electrostatic field.

Figure 7-22 displays the photographs of the final design of the second prototype, where each key change has been labelled. The design was focused on eliminating the previously mentioned issues, while maintaining the project’s objectives of producing large-area uniform arrays of aligned carbon nanotubes. The first change (seen at label 1), was to redesign the clips that secure the electrode in place. While the clips on the previous prototype were adequate, there was slight electrode movement when the reservoir was full, which could affect the electrospinning process. The new clip design is significantly tighter and prevents any movement. The second alteration (seen in label 2), was to reduce the area between the platform and the electrode, this change intended to reduce solvent loss from the reservoir, while simultaneously avoiding the potentiially hazardous spills seen before. The first prototype’s platform had on average a gap of 1 cm around the electrode, which potentiually caused a
premature solvent loss from the reservoir. This second prototype however was engineered to have almost no gaps, with the final outcome having an average gap of just a few millimetres at most. The third change (which is not visible in Figure 7-22 as it is covered by the brush, at label 3), focused on the redesign of how the brush is supported, where the addition of tracks were added to the brushes bolt locations, as to allow complete movement for fine adjustment. By adjusting the pressure the brush applies to the electrode, it now allows for the thickness of the polymer coating applied to be adjusted. This also means that more viscous solutions can be used to the same effect. More importantly, this alteration to the original design, was to try and minimise foaming of the solution that was seen during operation. The fourth alteration (seen at label 4), was the inclusion of a transparent window. This enables the study of the fluid within the reservoir, as well as allowing the easy monitoring of the solution levels. The final addition to this design was the inclusion of the large electrodes which balance the electrostatic field (which was simulated in Figure 7-15, G, and displayed in Figure 7-22, label 5). Despite what is shown in Figure 7-22, the addition of the large outside electrodes does not completely obscure the view of the solution through the transparent windows, as a suitable gap was left to maintain viewing. While rebuilding all of the aspects of this second prototype, special consideration was constantly given to reducing the metal content of the construction, in a bid to further even out the electrostatic field. Where previously metal brackets and screws were a necessity, epoxy and nylon bolts were used as a replacement, further balancing the electrostatic field.

![Figure 7-23](image)

**Figure 7-23** – A histogram of the nano-fibre diameters produced using the second prototype needleless system (A), where the histograms for single needle and the first needleless prototype have been included for comparison. The addition of the large electrode features displayed in Figure 7-22 (5), was attributed to this significant improvement in the consistency of fibre diameters. A photograph taken during operation reveals how jets of similar sizes can be seen all over the electrode, as opposed to a preference to either end.

Initial testing did see some noticeable improvements in the produced nano-fibres. However, it was observed when studying the fibres that there was still a significant frequency of jet disintegration (owing to the strong electrostatic field at the higher potentials of +40 kV), resulting in spitting, which
damaged the rest of the sample. Wu et al. (2010) reported how increasing the polymer content reduces this issue, but at the same time the polymer chain length must be reduced to ensure that the viscosity is within electrospinnable limits [see Chapter 5.2.2]. With this in mind, the PEO within the electrospinnable solution, was changed from a molecular weight of 2,000,000 M\textsubscript{v} to 1,000,000 M\textsubscript{v}. This allowed the polymer content within the solution to be increased to 5%, while remaining at a viscosity that it could be electrospun. Electrospinning with this new polymer saw a substantial improvement, and eliminated the jet disintegration issue.

Electrospinning with the new prototype demonstrated significant improvements over the first, with each of the outlined issues with the previous prototype being eliminated. During operation, there was zero solution spillage observed, and significantly reduced signs of premature solvent loss. Sessions left to spin until solution depletion saw very little residual dried polymer remaining in the reservoir (compared to the previous prototype). As with the previous systems (single needle and first prototype needleless), identical electrospinning conditions were repeated to allow a direct comparison. The results from this found notable improvements on the diameter consistency of the nano-fibres, with a measured fibre diameter distribution of half of what was seen with the first prototype [see Figure 7-23]! The electrospinning process on this new rig proved to produce cleaner, more consistent sheets of nano-fibres [see Figure 7-24, image E]. Furthermore, the area, over which nano-fibres were observed to be deposited, was significantly more controlled, where the jets were observed to travel straight up rather than flay out, [see Figure 7-24, image A]. This improvement on nano-fibre deposition control further increases the throughput of the electrospinning apparatus, by purely preventing nano-fibres from depositing elsewhere on the rig. This significant improvement to the fibre quality and deposition is owed to a combination of the redesigned solution management assembly, and due to the introduction of the large electrode electrostatic field balancers into the rig design. Figure 7-25 displays COMSOL simulations, where the electrostatic field has had its magnitude and direction represented with proportional arrows. This reveals how the introduction of the large external electrodes on the second prototype, both straighten and even out the electrostatic field across the entire electrode electrospinning surface. A closer image of the electrode revealed how the polymer was now forming small droplets of a similar size on each spinneret, where from these droplets the polymer jets were originating [see Figure 7-24, image D]. This new observation was again the result of the improved application of solution to the electrode, and further demonstrates why the nano-fibres produced were of a significantly greater uniformity.
Figure 7-24 – These four photographs and one scanning electron micrograph, reveal the significant improvements to the needleless electrospinning process that was achieved with the second prototype. The addition of the large electrode confirmed the modelling simulations and proved effective in balancing the electrostatic field (A). This field balancing promoted uniform electrospinning across the entire electrode surface (B + C). A closer look at the electrode demonstrated how small droplets of polymer solution were forming on the spinneret tips, producing the polymer jets (D) which resulted in the nano-fibres collected (E).
As it is extremely difficult to estimate the remaining solution in the reservoir, and hence measure the electrospinning rates, the process was left to run until complete solution depletion. The entire reservoir of solution took approximately 1 hour to deplete of its 50 ml contents, which is a factor of 72 increase on the single needle system, which processes 700 µl per hour. With this result, the next step of the project is to apply these optimised techniques to carbon-nanotube-loaded solutions, in order to reach the project’s goal of large-area alignment of nanotubes.

7.4.8 Needleless Electrospinning of Carbon Nanotubes

In order for the designed and built needleless electrospinning system to be a viable solution to this project, it is required that it must be able to electrospin carbon nanotube (CNT) loaded solutions. As with the single and multi-needle electrospinning systems, loading the electrospinnable solution with CNTs for the needleless rig was simple, and introduced no complications to the operation of the electrode.

To prepare the electrospinnable solutions, 5% weight fraction of PEO (1,000,000 Mₐ) was blended with an aqueous-based solution consisting of a 0.1% weight fraction CNT dispersion, where the CNTs were dispersed by ultrasonic irradiation (using the optimised parameters from Chapter 6.2.3), with 1% weight fraction of Brij 58. Once the polymer had successfully blended within the
solution, 50 ml was added to the fluid reservoir. As before, the electrode was positioned at a distance of 15 cm from a silicone coated collection drum.

During operation, the electrostatic potential was slowly ramped up until polymer jets were observed. However, unlike with the PEO only solution systems, polymer jets were observed at a considerably lower potential of +30 kV. This result was extremely advantageous to the project, as it meant that the polymer jets would be accelerating to a significantly lower velocity than before, promoting improvements to alignment. It is suggested that this promotion of polymer jets is caused by an electrostatic field enhancement generated by the CNTs within the solution (Smith & Silva 2009).

In order to further probe this phenomena, it was thought that perhaps utilising the ionic surfactant polarity preferences seen in Chapter 6.3, this minimum electrospinning potential could be reduced further, allowing greater improvements in the nano-fibre alignment to be achieved.

The ionic surfactant chosen for this investigation was sodium dodecyl sulfonate (SDS), as it was demonstrated to be the best during the surfactant investigation in Chapter 6.2. The CNTs were dispersed with the SDS in deionised water at a concentration on 0.1% weight fraction CNT and 1% weight fraction SDS. However, unlike with the previous needleless solution, PEO with a molecular weight of 2,000,000 was again used, at the original weight fraction of 2%, as was used with the needle spinnerets. With all the previous needleless investigations, a shorter PEO chain length at a higher concentration was required to prevent the polymer jets disintegrating, in the intense electrostatic field. It was thought that as electrospinning was occurring at a significantly lower potential, compared to before, that this would no longer be a problem. Furthermore, increasing the polymer content in the previous samples also meant that the final nano-fibres had a lower relative CNT weight fraction (with the increased mass of polymer), effectively lowering CNT processing rates. By returning to the original weight fractions, processing rates have been maximised.

Initially, when electrospinning this new SDS loaded solution using the same parameters as before, a positive electrode was used as this was previously found to be the surfactants preferential polarity. This produced a few jets but only at potentials above +50 kV, meaning that any jets produced were rapidly accelerated towards the collector and potentially destroyed. Overall, the jet output was very low and any jets that were produced varied largely in width, with some being large blobs rather than fibres. However, when the electrode was switched to a negative polarity, the effect was much the opposite. Jet production was high, with a high density of jets seen across the entire drum surface, even at potentials as low as -12 kV. Needleless electrospinning with potentials as low as -12 kV has been previously unreported, with most publications reporting minimum potentials ranging from 60 to 120 kV in any case (Petrik & Maly 2009). Replacing the solution with 100% PEO found that no jets were
produced at potentials this low, meaning the ability to electrospin at a lower potential, is a result of both the SDS and CNT loading. More interestingly still, unlike with the single needle spinnerets, no spitting or CNT ejection from the fibre was observed, although it was not clear why this was the case [see Chapter 6.3, for a reminder]. It is suggested that perhaps this response is due to the negative polarity of the electrode, repelling the anionic surfactant coated nanotubes towards the collection drum, and in doing so causing the promotion of electrospinning jets. The basis of this suggestion, is that unlike with the single needle spinneret, where CNT ejection from the jet was observed, the electrostatic field from the needleless system is straight and uniform, meaning material will only travel in one direction. In order to clarify this result, further investigations must be conducted on this mechanism, this includes using a cationic surfactant to see if the response is the same with a positively charged electrode. Despite the significance of this discovery, large-area electrospinning of CNTs was achieved with Brij 58 as the surfactant to meet the project objectives, just not at this significantly lower potential now found. With tight project time limitations at the end of this project, this work was considered future refinement of the needleless process, and no further investigations were conducted.

Being able to conduct electrospinning with a needleless system at potentials as low as -12 kV, is not only safer with regards to electrical hazards, but also allows for far easier nano-fibre alignment, as the polymer jets will have a much lower initial acceleration. The results from these experiments demonstrated that not only can CNTs be electrospun using a needleless electrode, but more so that they enhance the process to allow for lower potential operation. These achievements lead to the final investigation of this thesis, whereby each of the developed electrospinning systems are compared to one another.

7.4.9 Conclusions

Chapter 7.4 has outlined and justified each step that was taken in this project, in order to scale-up the electrospinning process, using a needleless electrode spinneret. These investigations ultimately led to the production of a prototype which was capable of electrospinning 50 ml of solution per hour, which is a substantial improvement of nearly two orders of magnitude on the previous rate of the traditional single needle system. This achievement leads this thesis to a commercially viable scale-up solution to the large are alignment of carbon nanotube loaded nano-fibres.
The investigations conducted in reaching our goal included: solution manipulation, electrode electrostatic simulations, the development of two needleless electrospinning prototypes, and the electrospinning of carbon nanotubes. The solution manipulation investigation, found that the polymeric fluid could not be controlled using a patterned hydrophobic/hydrophilic surface. Instead, a textured electrode surface in the form of an array of spikes had to be applied to the electrode in order to manipulate the electrostatic field. This conclusion ultimately led to various electrode designs, which were simulated in the COMSOL Multiphysics software, allowing for each design’s generated electrostatic field to be critically analysed. The results from these simulations led us to a novel external electrode design which fully balanced the electrostatic field across the electrode. Enabling both the size and position of the Taylor cones to be controlled across the electrode’s surface led to a greater uniformity in the resulting nano-fibres produced.

Applying a carbon nanotube loaded polymer solution to the final needleless assembly design, saw a reduction in the required electrospinning parameters, specifically the minimum needed voltage in order to produce jets. It was found that the presence of the nanotubes caused a field enhancement at the spinneret tips, allowing needleless electrospinning to be conducted at potentials as low as -12 kV, despite not altering the electrospinning assembly or parameters. Needleless electrospinning has not previously been reported to be possible at potentials this low. This result has a significant benefit in both the safety of the process and with further testing could improve the alignment of the nano-fibres, as the polymer jets accelerate to a significantly lower velocity, lessening the requirement for high-speeds on the rotating drum collector.

Chapter 7 will be concluded in the next section, where each of the electrospinning assembly designs will be compared. These comparisons include: nano-fibre throughputs (electrospinning rates), resulting nano-fibre consistencies, and resulting nano-fibre alignment. Leading this thesis to present its designed, developed and optimised electrospinning solution, for the large area alignment of carbon nanotubes.
7.5 Comparison between Needle and Needleless Designs

7.5.1 Introduction

With the completion of each of the designed, built and optimised electrospinning assemblies, this thesis can enter its final chapter, in comparing each designs capabilities to one another. This project prioritises the alignment of carbon nanotubes above any other objective. With that in mind, each assembly will be assessed based on its observed nano-fibre throughputs, nano-fibre consistencies, and overall nano-fibre alignment. This will then allow the thesis to present its justified solution, in order to fulfil the original project objectives, which were outlined in Chapter 1.1, leading us to the concluding chapter.

7.5.2 Comparison of Fibre Throughputs

The immediate question when assessing the electrospinning assemblies, is how do they compare with regards to nano-fibre throughput (or spinning rates)? With the project objective being to achieve a commercially-scalable electrospinning solution, each of the built assemblies will be compared, not only on their measured throughputs, but also on their realistically achievable scaled-up deposition rates.

With each rig in question, the measured throughputs were achieved by measuring the depleted solution, after electrospinning over the course of an hour. This method is not usually the preferred method of assessment, as it fails to take into consideration mechanisms such as deposition control. For example, this method of assessment will not take into consideration any fibres that are deposited elsewhere on the rig, as opposed to the collection drum, or any solution that drips/spills. Typically, the preferred method of assessment is in weighing the collected material after a known operation time. However, it was not possible to accomplish this on our electrospinning set-up due to the inability to swap the collection drum for a wire frame, which would normally be used for easy nano-fibre removal. Although attempts were made, it was not possible for this method to be done using the silicone release paper as an alternative. This was because the paper held a considerable level of moisture, which gave rise to substantial errors in the final weighed material. Furthermore, PEO also retains a considerable amount of moisture, which makes comparisons on samples collected on different dates difficult to conduct fairly. This method would require a full study of drying and weight loss and may not, ultimately prove feasible, once environmental fluctuations are taken into consideration. Regardless, using the depleted solution method as an alternative, the comparison of electrospinning rates can be seen in Table 7-1.
Table 7-1 – This table tabulates the different electrospinning rates of each of our optimised electrospinning systems, where the substantial rates of the needleless system can be realised.

<table>
<thead>
<tr>
<th>ELECTROSPINNING ASSEMBLY</th>
<th>MEASURED FIBRE THROUGHPUT</th>
<th>POTENTIAL FIBRE 1 m² THROUGHPUT (SCALE-UP ESTIMATE BASIS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SINGLE-NEEDLE</td>
<td>0.7 ml/hour</td>
<td>(Not scalable)</td>
</tr>
<tr>
<td>MULTI-NEEDLE</td>
<td>2.8 ml/hour</td>
<td>16.8 ml/hour (6x 4 needle arrays, 3 on each side)</td>
</tr>
<tr>
<td>NEEDLELESS (V2)</td>
<td>50 ml/hour</td>
<td>500 ml/hour (1 m long electrode, originally 10 cm)</td>
</tr>
</tbody>
</table>

Table 7-1 reveals the significant advantage that our needleless electrospinning system has over conventional designs, when comparing electrospinning rates. This is a substantial achievement when comparing the rates to commercial available systems such as the Elmarco Nanospider™, which boasts nano-fibre production rates of 160 g per hour (for its 6.4 m long electrode system) (Elmarco 2010). When using a polymeric solution consisting of 5% weight fraction polymer, our needleless electrospinning assembly is predicted to also demonstrate similar nano-fibre production rates, of 25 g per hour per metre of electrode, equating to 160 g per hour for a comparable 6.4 m electrode length. Our needleless system, while demonstrating similar processing rates to that of the Elmarco system, also has several added advantages over the Nanospider™, including: greater nano-fibre consistencies (through the balancing of the electrostatic field), the ability to align the nano-fibres, and the ability to use aqueous-based solutions, at significantly lower potentials. Although the needleless system’s nano-fibre consistencies were improved with the addition of the large external electrode, it still remains important to compare them to those of the single and multi-needle assemblies.

7.5.3 Comparison of Fibre Consistencies

The next assessment is to compare the diameter distributions of the nano-fibres, from one electrospinning assembly to another. Within this project it is important to obtain a narrow distribution of nano-fibre diameters, as this minimises the variation in polymer jet velocity (during spinning), and as such increases the alignment of the fibres, and the CNTs within them. Furthermore the production of significantly thicker fibres could provide the CNTs with room to twist during the spinning process, worsening the final alignment.
This can be achieved by measuring the diameter of a sample of nano-fibre (in this case a sample size of 60 fibres), which are produced on each electrospinning assembly. Collecting data in this manner allows for direct comparison, through the plotting of a histogram. The histogram then provides visual indication of both the nano-fibre diameter distributions, as well as an indication of the general sizes.

Table 7-2 – A table of comparative histograms, revealing the nano-fibre diameters produced on each of the electrospinning assemblies, where it can be revealed that the needleless assembly produces the thinnest fibres, as well as having a diameter distribution comparable to the single needle set-up.

<table>
<thead>
<tr>
<th>ELECTROSPINNING ASSEMBLY</th>
<th>NANO-FIBRE DIAMETER HISTOGRAM</th>
<th>AVERAGE DIAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>SINGLE-NEEDLE</td>
<td><img src="image1" alt="Single Needle Histogram" /></td>
<td>200 ± 30 nm</td>
</tr>
<tr>
<td>MULTI-NEEDLE</td>
<td><img src="image2" alt="Multi Needle Histogram" /></td>
<td>220 ± 50 nm</td>
</tr>
<tr>
<td>NEEDLELESS (V2)</td>
<td><img src="image3" alt="Needleless V2 Histogram" /></td>
<td>110 ± 30 nm</td>
</tr>
</tbody>
</table>
Table 7-2 contains each of the histograms generated from the analysis of the nano-fibres produced on each electrospinning assembly. Comparing the graphs reveal how the multi-needle electrospinning assembly generates both the largest nano-fibres, as well as the biggest distribution in diameters. It is thought that it is possibly due to a slight variation in the electrostatic field strength on the outside spinnerets. However, as the needleless electrospinning assembly is found to have a comparable distribution to that of the single needle set-up, as well as producing the smallest nano-fibres, it was deemed unnecessary to investigate the multi-needle rig any further.

The needleless assembly proves to be the best choice for nano-fibre throughput and is the better assembly for the production of smaller, consistent nano-fibres. The remaining comparison between these electrospinning rigs is to assess their ability to produce aligned nano-fibres.

7.5.4 Comparison of Fibre Alignment

With the projects primary goal being carbon nanotube alignment, the comparison of each assembly’s ability to align nano-fibres is perhaps the more crucial. Regardless of the quality of the nano-fibres, or the rate at which they can be produced, if an electrospinning assembly is unable to produce aligned arrays it is unsuitable as a solution to meet this projects goals.

Figure 7-26 – The nano-fibre alignment distribution, for each of the three assemblies built. Although the single needle assembly can be seen to have the highest alignment (through the narrowest distribution of orientations), the needleless system can be observed to be comparable to the multi-needle system.
As before with the previous assessment for consistency, nano-fibre samples were produced on each assembly and analysed. In order to assess the alignment the fast-Fourier transformation technique was used, as outlined in Chapter 5.3. By repeating this process, a distribution curve is obtained for each assembly, revealing their nano-fibre orientation distribution to a normal. Where before in Chapter 5.3 we compared the full width half maximum (FWHM) of each curve, in this case the curves were compared directly [see Figure 7-26].

Figure 7-26 displays the distributions of the nano-fibres orientation to a normal, revealing how the traditional single needle design produces the highest degree of alignment. However, the multi-needle and needleless systems, can be seen to have almost identical distributions, illustrating the performances of the needleless system once again. Although the single needle system produces nano-fibres which are approximately 33% more aligned (when comparing the difference in FWHM of each curve), the process is not commercially scalable and unsuitable for this project. As such, this demonstrates that the needleless assembly is the only viable option to meet this project’s objectives. Furthermore, it is considered, that with further refinement of the electrospinning parameters, such as collection drum speed etc., alignment can be further improved on the needleless system.

7.5.5 Conclusions

The comparative analysis of each electrospinning system has revealed how the needleless assembly is the ideal solution to meet this project’s goals. Although the system was found to not quite align nano-fibres to the extent of the original single needle system, it was demonstrated to be significantly more efficient at fibre production, as well as producing them with smaller diameters, across a narrower distribution. With further work, increased alignment on the needleless system could be obtainable, through the optimisation of the spinning parameters.

The assessment of the nano-fibre throughput illustrated how our needleless system can produce nano-fibres at a comparable rate to commercially-available solutions, while doing so with the added advantages of needing lower electrospinning potential, allowing the use of aqueous solutions and achieving nano-fibre alignment. It is for these reasons that this electrospinning design is claimed to be the World’s first large area set-up for the alignment of carbon nanotubes.

This result concludes the experimental sections of this thesis and leads us to the concluding chapter, summarising how this project has re-engineered the electrospinning process for the large area alignment of carbon nanotubes, using a method that is commercially scalable.
7.6 Conclusions

This final experimental chapter, has detailed of the steps taken in designing and building the World’s first large-area electrospinning rig for the alignment of carbon nanotubes (CNTs). Using all of the previously conducted investigations explained in past chapters, a needleless electrospinning device has been successfully designed, built, and optimised to produce sheets of aligned CNTs, at a solution processing rate of 50 ml per hour (for a 10 cm long electrode), with the easily obtainable potential to increase this to 500 ml an hour, with a 1 metre long electrode.

This chapter began by justifying all of the design implications that went into the building of the large area collection drum, and its housing. This includes the installation of the motor and motor controls, the safety shielding applied to the outside of the housing, the fume extraction system, and numerous health and safety features that ensure safe operation. Once the collection drum and its housing were completed, work began on building the various electrospinning apparatus, stating with the single and multi-needle spinneret systems. Using simple design innovation, with readily available materials, both single and multi-needle systems were built to be completely adaptable to any electrospinning system. While both assemblies demonstrated the ability to produce arrays of nano-fibres, only the multi-needle set-up produced the World’s first large area array of aligned CNTs.

Despite this success, this project continued on from this to develop a needleless electrospinning alternative. Through a series of computational models and the development of two prototypes, a novel needleless electrospinning electrode was built. The final design included the addition of two innovative external electrode features, which balanced the electrostatic field. The balancing of the electrostatic field overcame the common issue associated with large area needleless electrospinning, of a broad distribution of produced nano-fibre diameters. However, this design still maintained the added ability of it being aqueous solution compatible, uniform in fibre deposition, and able to produce aligned fibres, leading to a patent of the design. Further testing with this design using CNT loaded solutions led to the discovery of lower voltage electrospinning, through the electrostatic field enhancement caused by the nanotubes. This resulted in needleless electrospinning being able to be accomplished at potentials as low as -12 kV, an achievement not previously reported. This discovery not only rendered the process significantly safer, but also led to increased nano-fibre alignment.

This chapter, and as such this thesis, were brought to conclusion through the comparison of the three difference designed electrospinning systems. The needleless system was repeatedly revealed to be the ideal solution to meet all of this project’s objectives, paving way for the commercial alignment of CNTs, for the development of next generation composites.
8 Concluding Remarks & Future Work

8.1 Summary of Objectives and Achievements

After recognising the demands modern societies have today for materials which can deliver both increased performance and efficiency, science and industry set out to develop the next generation of functional advanced composite materials. As these composite materials were developed, it was realised that stronger, more conductive reinforcements were required to further enhance the properties of the resulting composites. Selected because of their outstanding mechanical and electrical properties, cylindrical tubes of graphitic carbon, known as carbon nanotubes, were proposed as an ideal candidate as a composite’s reinforcement. This was providing that a method could be developed to produce large areas of aligned arrays of them, in order to harness their properties on a macroscopic scale. With this premise, this project was instituted in collaboration with Thomas Swan & Co. Ltd., with the primary objective of investigating, and engineering, a cost-effective manufacturing process for the production of large, aligned areas of their single-walled carbon nanotube product. Secondary to this objective, it was outlined that any production processes of the nanotube alignment must involve only water, and include the use of no other solvent systems, in order to ensure ease of commercial compatibility.

This thesis has detailed all of the science and innovation that has led to the successful development, of a commercially-viable electrospinning device, which has rendered it possible to achieve large-area alignment of carbon nanotubes, using aqueous-based systems. The development of this technology has allowed for composite materials research to reach new potentials that are required for today’s demanding applications, with the aligned nanotubes providing the increased strength and conductivity needed for multi-functional materials. Furthermore, the investigations within this thesis have provided a better understanding of underlying principles, such as: controlling the electrospinning jet parameters for higher quality nano-fibres [Chapter 5.2], optimisation for aligned nano-fibre collection [Chapter 5.3], assessing carbon nanotube alignment within polymer nano-fibres [Chapter 5.4], the performance effects of carbon nanotube loading within nano-fibres [Chapter 5.5], surfactant utilisation for efficient carbon nanotube dispersion [Chapter 6.2], and
needed electrospinning designs [Chapter 7.3]. As well as expanding the understanding of known concepts, these investigations have also led to fresh discoveries, shedding new light on items such as: the crystalline interface between carbon nanotubes and the polymer within nano-fibres [Chapter 5.6], introducing a novel method for nanotube dispersion assessment [Chapter 6.2.3], exposing the effects of solution ionicity when electrospinning [Chapter 6.3], the discovery of oxygen-resistant carbon nanotubes as a result of steam purification [Chapter 6.4], the development of a novel needleless electrospinning design that balances the electrostatic field to produce high volumes of aligned nano-fibres [Chapter 7.4], and the discovery of the field-enhancement that carbon nanotubes provide to allow lower voltage needleless electrospinning [Chapter 7.4.8].

The successes of this project are owed to the careful planning and execution of various investigations, leading to an evolution of each of the project’s steps detailed in this thesis. This project began in Chapter 4, with the assessment of Thomas Swan’s single-walled carbon nanotube material (known as ‘wetcake’). Using various analytical techniques, the material was assessed for both quality and its chemical content. The results from this characterisation, found that the carbon nanotubes within the ‘wetcake’ product were of a high quality, displaying indications of high linearity, and with a low frequency of crystalline defects. This enabled us to conclude that the nanotubes within this product were ideal for producing highly-aligned arrays within polymer nano-fibres. Furthermore, due to the higher quality, they also displayed the potential to exhibit improved mechanical properties over what previously reported less linear materials had achieved.

The promising assessment of the carbon nanotubes granted the project’s continuation into Chapter 5. This involved developing a deeper understanding of the electrospinning processes, ultimately allowing for the carbon nanotubes to be introduced and aligned, demonstrating the project’s proof-of-concept. Achieving this involved various investigative steps, which first aimed to consistently produce high-quality nano-fibres. This included the exploration of parameters such as the effects of the electrospinnable solutions viscosity and the effects of atmospheric temperature and humidity. Once this was accomplished, the project evolved into further developing our understanding of electrospinning, in order to achieve highly-aligned arrays of nano-fibres. This involved a thorough investigation and mathematical modelling of the polymer jet’s velocity during the electrospinning process. The results from this produced an accurate approximation of the polymer jet’s final velocity to be 9.2 ± 1.2 m/s, allowing for the rotating-drum-style collector to collect nano-fibres as highly aligned arrays. At this point in the project, introducing carbon nanotubes into the electrospinnable polymer system produced arrays of aligned nanotube-loaded nano-fibres. Raman spectroscopy and thermogravimetric analysis revealed that the carbon nanotubes where not only manipulated into
highly-aligned arrays, but also undamaged as a result of the process. Further analysis of the fibre’s mechanical properties, demonstrated that a nanotube loading of just 3.9% weight fraction increased the ultimate tensile strength by up to 320%, the ductility by up to 315%, and the Young’s modulus by up to 430%, when compared to the original properties of the polymer nano-fibres. Electrical analysis found an improvement of 8 orders of magnitude, when compared to the original polymer, with a measured resistivity of $0.28 \pm 0.02 \, \Omega m$. This chapter then continued to better understand these enhancements to the materials properties, where small angled X-ray scattering was employed to probe the molecular interface between the carbon nanotubes and the polymer. Evidence was found of a lamella two-layer nano-structure, as well as a previously unreported structure of 3.04 nm in size, which was attributed to a restructuring at the nanotube interface, as a direct result of the nanotubes introduction. It was this exposed restructuring of the polymers crystalline structure which may have provided the polymer chains a ‘rigid’ scaffold to bind to, giving rise to the significant increase in mechanical performance witnessed in the resultant material.

With the confirmed alignment of carbon nanotubes by electrospinning, and strong evidence to propose their outstanding improvements to composites, this project’s next steps were in optimising the chemistry of the electrospinnable solution. Chapter 6 began addressing this stage in the project, by investigating the efficiency of numerous surfactants in their ability to disperse carbon nanotubes. To achieve this, a novel micro-centrifuge technique was introduced, revealing how the effectiveness of the surfactants varies with the power density of ultra-sonication. This produced an ideal sonication power density for achieving the highest nanotube loading, when using each individual surfactant. The best surfactants for dispersing nanotubes were found to be sodium dodecyl sulfate (SDS) and Brij 58, which left virtually zero residual undispersed material, when sonicated at power densities of 17.2 W/ml and 18.5 W/ml respectively. However, as this project aimed for aligned arrays of carbon nanotubes, it was important to be able to remove the surfactant after alignment. Thermogravimetric analysis was used once again to assess how each surfactant thermally degraded and at what temperature. It was found that the SDS left large metallic residuals, which would be unwanted in the final material. Whereas Brij 58 left only a small amorphous carbon residual, making it the ideal surfactant to use in this project. However, while exploring these surfactants, it was noticed how some surfactants vary with regards to their ionic content, and it led to the question of how this would affect the electrospinning process across electrode polarities? By simply electrospinning solutions loaded with either a non-ionic (Brij 58), cationic (benzalkonium chloride) or anionic (SDS) surfactant, with both a negatively and positively charged spinneret, this question was answered. Literature has previously stated that there is no difference to the resulting nano-fibres between electrospinning polarities, however we found this not to be the case. While the non-ionic system saw no difference
between spinneret polarities, the same could not be said for the ionic solutions. The anionic surfactant was found to preferentially electrospin with the positive electrode, whereas the cationic surfactant was opposite, and preferentially span with the negative electrode. In either case, electrospinning with the non-preferred electrode produced poor quality nano-fibres, and in some cases even led to jet disintegration. This result made a substantial improvement to the understanding and implementation of electrospinning ionic systems, and ensured higher-quality nano-fibres, regardless of the solution’s ionic content. This chapter was then brought to a conclusion, with the exploration of a steam purification method, for the complete removal of polymeric and amorphous carbons, allowing for the full recovery of the aligned carbon nanotubes. In this process, the steam molecules react with the less ordered amorphous carbons in the sample, provided they are treated at temperatures of over 700°C. This led to the discovery that, employing this method on the aligned nanotubes, recovered them to a quality significantly higher than that they were originally supplied in. Furthermore, it was found that, as the treatment temperature was increased, so did the resulting material’s quality, where nanotubes treated at a temperature of 900°C were found to be purified to such as extent that they were able to survive an oxidative atmosphere at temperatures above 900°C. This oxidation temperature was significantly higher than the original maximum of 590°C, observed before any treatment, and something never before claimed in the literature.

With the optimisation of the electrospinnable solution, and the demonstrated full recovery of the aligned carbon nanotubes, this project entered the final stage. Chapter 7 explained how the electrospinning process was re-engineered to design, develop and commission a fully scalable system, which enabled the full commercialisation of carbon nanotube alignment. This was achieved by first designing and building a large-area collection drum, within a suitable housing. This included the implementation of many aspects, such as: the motor choice and installation, the design and installation of the safety shielding, the design and installation of the fume extraction system, and the inclusion of many safety features. Once this was completed, the design and building of the electrospinning assemblies began. Initially, using simple innovation, both a single-needle and multi-needled assembly were designed and built, where each design was engineered to be completely adaptable to any electrospinning system. Both of these systems demonstrated to successfully produce aligned nano-fibres, with the multi-needle system producing the World’s first large-areas of aligned carbon nanotubes. Despite this success, this project strived to develop a system with significantly increased fibre production rates. Through a series of computational models and the development of two prototypes, a final novel needleless electrospinning system was created, which boasted a balanced electrostatic field. Unlike most modern needleless assemblies, this design was capable of electrospinning aqueous based solutions, across a uniform area, while maintaining nano-fibre
diameter consistency, and still achieving similar processing rates of 25 g per hour per metre of electrode, compared to those already commercially available. The successes of this device’s development led to a patentable design, which met the projects objectives. Further testing with this device using carbon nanotubes led to the discovery of significantly lower voltage operations, through an electrostatic field enhancement, provided by the nanotubes. This resulted in needleless electrospinning being performed at potentials as low as -12 kV, an achievement previously unimaginable.

With the development and engineering of all of the aspects of this project, including: the electrospinnable solution, the steam purification technique, and a high-throughput electrospinning system, capable of processing aqueous based solutions. It is concluded that the objectives outlined at the beginning of this project, have be accomplished, and that all project requirements have been met. This successful project, has generated the required technology, in order to pave the way for the development of the next generation, of advanced materials and multi-functional composites.

8.2 Future Work

Throughout each of the many investigations conducted in this project, there were many examples of further research that could be of scientific interest, providing the answers to clarify unexplained results. In each case, pursuing the clarification was outside the scope and/or means of this project, and with the appreciation of time constraints, efforts were kept focused on the main tasks at hand. However, there are several areas that could be of interest for further work, specifically in the best interests of aligned carbon nanotube integration within a composite material.

8.2.1 Exploring New Surfactant/Polymer Systems

Chapter 5.6 introduced a new unreported small angled X-ray scattering peak, which was found to relate to the polymers crystalline restructuring upon the introduction of carbon nanotubes. Gaining a thorough insight into the implications of this and a greater model of the structures formed, could lead to a better application of polymer and surfactant. With a clear understanding of the structures forming, a more chemically-suited polymer and surfactant system could produce a stronger crystalline
response. This may increase the stress transfer from the polymer to the carbon nanotubes, enhancing the mechanical properties of the final composite. This research, could then also allow more efficient use of alternative polymer and surfactant systems, paving the way for this project to explore the prospects of applying the aligned nanotube loaded nano-fibres, directly to a composite. This would then negate the need to recover the carbon nanotubes, further decreasing processing times and production costs. As an example of this (although we found it unsuitable in Chapter 6.2), Triton X-100 has been reported to lead to property enhancements, when used to disperse carbon nanotubes into epoxy based composite systems (Geng et al. 2008). With better understanding, it is thought that other polymer/surfactant systems could result in similar benefits.

8.2.2 Further Exploring the Oxidative Resistant Carbon Nanotubes

In Chapter 6.4, carbon nanotubes were demonstrated to be resistant to oxidative attack at temperatures over 900°C, but only after they had been steam-treated at a temperature of 900°C (or above). However, it was not definitively identified how the steam purification process altered the carbon nanotubes to possess this remarkable ability. Further work in achieving an understanding of this should begin with the characterisation of the carbon nanotubes using a more comprehensive Raman spectroscopic analysis. This should involve using a variety of different laser energies, where performing this both before and after the steam purification technique would lead to a full quantisation of the nanotube types present in the sample. This should ultimately determine more definitively whether a specific type or size of nanotube is being attacked. Once the understanding of the process has been realised, it is thought that larger yields of the super-resilient carbon nanotubes should be achievable. Should this be successful, this will then lead to the development of nanotube-loaded composites, which are suitable for high-temperature applications.

8.2.3 Refinement of the Needleless Electrospinning Parameters

Chapter 7.4 introduced a novel needleless electrospinning assembly for the large area, high-throughput production of carbon nanotube loaded nano-fibres. Although aligned arrays of nano-fibres, with an acceptable narrow distribution of diameters were obtained, further work can be invested in refining the electrospinning parameters. Due to the project’s time constraints, electrospinning parameters were limited to known values that were found to be optimum on another
assembly. Further work with this final design introduced in this thesis should include optimisations such as: electrospinning voltage (including the lower voltages found in Chapter 7.4.8 when using carbon nanotubes), electrode rotational speed, operating distance from collector, and collector rotational speed. It is considered that with all of the optimum parameters found, better quality nano-fibres and higher throughputs can be achieved, when using the needleless assembly.

8.2.4 Maximising Carbon Nanotube Loading

One aspect of this project which was scarcely explored, is the maximisation of the carbon nanotube loading within the electrospinning solution. Although varying degrees of nanotube loadings were investigated in Chapter 5.5, nothing was included above 0.1% weight fraction. Further work with this project should include a brief investigation into the maximisation of the nanotube loading within the polymer solution. Achieving a maximum loading will, in turn, also achieve a maximum nanotube processing rate during electrospinning. It is thought that increasing the nanotube loading in the solution, could cause issues with regards to solution conductivity, possibly hindering the electrospinning process. Should this further work be conducted, special care needs to be given in making sure this is conducted safely.
References


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Gilbert, W., 1628. De Magnete, Magneticisque Corporibus, et de Magno Magnete Tellure (On the Magnet and Magnetic Bodies, and on That Great Magnet the Earth) 1st ed.,


Jirsak, O. et al., 2009. A method of nanofibres production from a polymer solution using electrostatic spinning and a device for carrying out the method.


### Appendix

A. This section was taken from pages 93-95 of “A review on electrospinning design and nanofibre assemblies”, W E Teo and S Ramakrishna 2006. Reprinted with permission from IOP. Copyright IOP Publishing Ltd.

#### Table 2. Schematic diagram of various electrospinning set-ups for multiple spinnerets and to obtain various fibrous assemblies. (Assuming spinneret is given a positive charge unless otherwise stated.)

<table>
<thead>
<tr>
<th>Assembly-aligned fibrous mesh</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Rotating drum</td>
<td>Simple set-up</td>
<td>Highly aligned fibrous assemblies are difficult to fabricate</td>
</tr>
<tr>
<td></td>
<td>Large area of aligned fibres can be fabricated</td>
<td>Fibre breakage may occur if rotating speed is too high (Matthews et al 2002, Kim et al 2004, Chew et al 2005, Wannatong et al 2004)</td>
</tr>
</tbody>
</table>

#### B. Parallel electrodes

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple set-up</td>
<td>Thicker layer of aligned fibres are not possible</td>
</tr>
<tr>
<td>Highly aligned fibres are easy to obtain</td>
<td>There is a limit in the length of the aligned fibres (Li et al 2003)</td>
</tr>
<tr>
<td>Aligned fibres are easily transferable to another substrate</td>
<td></td>
</tr>
</tbody>
</table>

#### C. Rotating wire drum collector

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple set-up</td>
<td>Thicker layer of aligned fibres are not possible</td>
</tr>
<tr>
<td>Highly aligned fibres are possible</td>
<td>Fibres may not be aligned throughout the whole assembly (Katta et al 2004)</td>
</tr>
</tbody>
</table>

#### D. Drum collector with wire wound on it

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple set-up</td>
<td>Aligned fibres are concentrated on the wire instead of the whole drum (Bhattarai et al 2005)</td>
</tr>
<tr>
<td>Highly aligned fibres are possible</td>
<td></td>
</tr>
<tr>
<td>Area of aligned fibres on the wire is adjustable by varying wire thickness</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. (Continued.)

<table>
<thead>
<tr>
<th>Nature</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
</table>
| E. Rotating tube collector with knife-edge electrodes below | Highly aligned fibres possible  
Aligned fibres covered the whole tube  
Thicker layer of aligned fibre deposition is possible | Setup requires a negative electrode to be effective  
Only possible for small diameter tube (Teo et al. 2005) |
| F. Controlling electrospinning jet using knife-edge electrodes | Highly aligned fibres possible  
Able to control the direction of fibre alignment on the tube  
Thicker layer of aligned fibre deposition is possible | Setup requires a negative electrode to be effective  
Only possible for small diameter tube (Teo et al. 2005) |
| G. Disc collector | Simple set-up  
Highly aligned fibres are possible  
Able to fabricate arrayed fibres by attaching a rotatable table on the edge of the disc | Unable to retain high fibre alignment at the same rotating speed when the deposited fibres are thicker  
| H. Array of counter-electrodes | Simple set-up | Fibre patterning is not consistent throughout the assembly  
Area of the assembly is limited  
Thicker fibrous assembly is not possible (Li et al. 2004) |
Table 2. (Continued.)

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Rotating drum with sharp pin inside</td>
<td>Large area of arrayed fibres can be fabricated</td>
<td>Set-up is complicated. Thicker area of arrayed fibre assembly may not be possible (Sundararay et al. 2004)</td>
</tr>
<tr>
<td>J.</td>
<td>Blade placed in line</td>
<td>Simple set-up. Yarn can be easily removed from the collector. Collected yarn is highly aligned.</td>
<td>Fabricated yarn is of limited length. Deposited fibres have to be dipped in water first before yarn is formed (Teo and Ramakrishna 2005)</td>
</tr>
<tr>
<td>K.</td>
<td>Ring collector placed in parallel</td>
<td>Simple set-up. Twisted yarn can be fabricated.</td>
<td>Fabricated yarn is of limited length. One of the rings has to be rotated to twist the fibres that are deposited into yarn (Dalton et al. 2005)</td>
</tr>
<tr>
<td>L.</td>
<td>Yarn collection using water bath</td>
<td>Simple set-up. Long continuous yarn can be fabricated. Fibres in the yarn are generally well aligned.</td>
<td>Yarn collection speed is relatively slow (Smit et al. 2005, Khil et al. 2005)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mass production</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Multiple spinnerets</td>
</tr>
</tbody>
</table>
B. Proof of derivation for the relativistic momentum of an electron in an electron microscope can be achieved easiest through reverse engineering the formula. This is due to numerous terms cancelling each other out:

\[ p = \sqrt{2m_0 eV \left( 1 + \frac{eV}{2m_0 c^2} \right)} \]  \hspace{1cm} \text{Equation A - 1} \\
\[ p = \sqrt{2m_0 eV + \frac{(eV)^2}{c^2}} \] \hspace{1cm} \text{Equation A - 2} \\
\[ p^2 c^2 = 2m_0 c^2 eV + (eV)^2 \] \hspace{1cm} \text{Equation A - 3}

At this stage it is relevant to recall Equation 3-6 and insert for \( \frac{eV}{c^2} \):

\[ p^2 c^2 = 2m_0 c^2 (E - E_0) + (E - E_0)^2 \] \hspace{1cm} \text{Equation A - 4}

Recalling Equation 3-5 and remembering that at \( E_0 \) momentum is zero and therefore energy equates to \( E_0 = m_0 c^2 \). If we substitute this into Equation A - 4 and simply, we can then prove this derivation:

\[ p^2 c^2 = 2m_0 c^2 E - 2m_0^2 c^4 + E^2 - 2m_0 c^2 E + m_0^2 c^4 \] \hspace{1cm} \text{Equation A - 5} \\
\[ p^2 c^2 = E^2 - m_0^2 c^4 \] \hspace{1cm} \text{Equation A - 6} \\
\[ E^2 = p^2 c^2 + m_0^2 c^4 \] \hspace{1cm} \text{Equation A - 7}

where Equation A - 7 is identical to the relativistic relationship between energy and momentum (Equation 3-5).
C. Derivation of jet solvent mass approximation, as a function of time, using a sigmoidal function.

<table>
<thead>
<tr>
<th>Basic sigmoid function, where $y$ is mass, and $x$ is arbitrary units of time:</th>
<th>[ y(x) = \frac{1}{1 + e^{-x}} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass is lost during spinning through evaporation, not gained, so function is flipped:</td>
<td>[ y(x) = 1 - \frac{1}{1 + e^{-x}} ]</td>
</tr>
<tr>
<td>Translate the function to start from 0, giving a function of solvent mass loss:</td>
<td>[ y(x) = 1 - \frac{1}{1 + e^{(6-x)}} ]</td>
</tr>
</tbody>
</table>
D. Using the function of solvent mass loss in Appendix C, to model an approximation of the jets mass as a whole:

<table>
<thead>
<tr>
<th>Measuring the approximate mass of the average polymer particle on the collection drum ( (P) ), while knowing the weight fraction of polymer in the solution ( (P%) ), provides an indication of the solvent mass ( (m_s) ):</th>
</tr>
</thead>
</table>
| \[
    m_s = \left( \frac{P}{P\%} \times 100 \right) - P
\] |

<table>
<thead>
<tr>
<th>If we combine this with the solvent mass loss approximation, we obtain a function of the solvents mass loss as a function of time:</th>
</tr>
</thead>
</table>
| \[
    m_s(t) = \left( \left( \frac{P}{P\%} \times 100 \right) - P \right) \left( 1 - \frac{1}{1 + e^{(6-t)}} \right)
\] |

<table>
<thead>
<tr>
<th>Finally, we add the final mass of the polymer, to complete the approximation for the total mass:</th>
</tr>
</thead>
</table>
| \[
    m(t) = \left( \left( \frac{P}{P\%} \times 100 \right) - P \right) \left( 1 - \frac{1}{1 + e^{(6-t)}} \right) + P
\] |

A graph demonstrating how the different parts of the expression contribute to the approximation:
E. Raman spectrum of the aligned carbon nanotubes that were baked in nitrogen at 900°C, without any steam treatment.
F. The motor program used which includes the safety jam detection.

```
START:
DECLARE(INIT)
DECLARE(REPT)
GOSUB(INIT)
ON
O(000)
PROFILE1(1.00,1.00,4096,5.000)
USE(1)
MC
STOP0
G
LOOP(REPT,0)
END
FAULT:
"FAULT"
END
INIT:
OFF
W(AO,0)
W(AB,0)
W(AM,0)
W(EX,3)
W(EQ,0)
W(BR,9600)
W(CL,100)
W(CQ,0)
W(IC,8160)
W(Ei,2)
W(EQ,2)
LIMITS(3,1,0,200.00)
W(EW,50)
W(IT,10)
GAINS(5.00,0.00,10.00,5.00,0)
W(IM,1)
W(IW,25)
W(ES,1)
MOTOR(39682,6.7,4096,4100,1680,1.30,3.60,0.191)
BRAKE0(M,50,50)
W(PC,300)
W(TL,4096)
W(IC,8160)
END
REPT:
IF(IN,=,0XXXX)
"IL-type 1GOTO(START)"
IF(IN,=,0XXXX)
S
END
```
G. The Perspex cut designs used for the implementation of shielding to the large-area collector.
H. The interlock circuit diagram which displays the general workings of the large-area electrospinning rigs safety systems.
Decoration of multiwalled carbon nanotubes with protected iron nanoparticles

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ABSTRACT

A method to simultaneously synthesize carbon-encapsulated magnetic iron nanoparticles (Fe-NPs) and attach these particles to multi-walled carbon nanotubes (MWCNT) is presented. Thermal decomposition of cyclopentadienyliron dicarbonyl dimer [(C5H5)2Fe2(CO)4], over a range of temperatures from 250 °C to 1200 °C, results in the formation of Fe-NPs attached to MWCNT. At the same time, a protective carbon shell is produced and surrounds the Fe-NPs, covalently attaching the particles to the MWCNT and leading to resistance to acid dissolution. The carbon coating varies in degree of graphitisation, with higher synthesis temperatures leading to a higher degree of graphitisation. The growth model of the nanoparticles and subsequent mechanism of MWCNT attachment is discussed. Adsorption potential of the hybrid material towards organic dyes (Rhodamine B) has been displayed, an indication of potential uses as a material for water treatment. The material has also been electrospun into aligned nanocomposite fibres to produce a soft magnetic composite (SMC) with future applications in sensors and fast switching solenoids.

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1. Introduction

Iron and iron oxide nanoparticles have received significant interest in recent years [1] for applications such as: anodes for lithium-ion batteries [2,3], magnetic resonance imaging [4], magnetic fluid hyperthermia [5] and cancer diagnosis [6]. The synthesis method should be simple, cheap and scalable, as well as being able to provide a means of protecting the nanoparticles.

A number of synthesis routes have been proposed for iron and iron oxide nanostructures [7]. Methods include: decomposition [8], microwave-hydrothermal [9], ultra-sonication assisted [10], hydrolysis of iron chloride [11], gas–liquid interfacial synthesis [12], the reverse micelle method [13], laser pyrolysis [14], laser ablation [15] and liquid–solid-solution [16]. They are also a result of high iron loading in carbon nanotube (CNT) synthesis [17] and similar results can be achieved by filling CNTs [18,19]. Here we demonstrate a one-step thermal synthesis method to simultaneously grow and encapsulate iron nanoparticles (FeNP) and attach them to preformed carbon nanotubes, to form a nanoparticle–multiwalled carbon nanotube (FeNP–MWCNT) hybrid material. The resultant composite is both magnetic and oleophilic, allowing for possible applications in oil recovery [20]. A carbon coating has been shown to encapsulate the nanoparticles, leading to stability in air and protection of the nanoparticles from dissolution in acidic media (hydrochloric and nitric acids have been tested). Effective encapsulation
results in the ability of the hybrid to be introduced into harsh environments and allow for chemical processing to occur. MWCNT and FeNP functionalisation can be carried out in the same manner owing to the graphitic coating [21]. Functionalisation has the potential to improve biocompatibility, improve selectivity [22] and enhance functionality [3]. The relatively low synthesis temperature (250 °C) to produce encapsulated nanoparticles has only been seen in a handful of journals [9,12,23–25] and none using a one-step synthesis route. The system introduced in this study avoids complex synthesis routes and provides a low cost, simple route for protecting iron rich nanoparticles.

Typically, coatings are used to protect the material from wear and oxidative damage [26] and to improve properties such as electronic conductivity [27] and biocompatibility in vivo [28]. Protective coatings have been produced using a variety of materials, such as alumina [25], silica [29], and a variety of polymers, such as polyethylene glycol (PEG) [22] and PEG-polyisoprene block copolymers [30]. Amorphous carbon coated magnetic iron nanoparticles have been synthesized using a polymer-templated method [31] and has been shown to be stable in air [32,33]. The same method has also produced graphitic carbon coatings [34], another method of producing graphitic carbon coatings include evaporation of metals with a hydrocarbon flow [35] and decomposition of iron nitrate in the presence of starch [36]. However, no resistance to acidic media is shown, where acid resistance is shown [37] multiple synthesis steps are required. Simultaneous nanoparticle growth and protection is beneficial, as it negates the need for further processing steps, which increase cost, and can lead to increased loss of product and contamination of the material. Graphitic carbon coatings are expected to exhibit beneficial properties over other coatings, such as electron conductivity and potential for biocompatibility.

Synthesizing a carbon coating around the iron nanostructures has benefits over other coatings, as the chemistry is well known and functionalisation can be used to attach useful moieties, such as anti-cancer drugs (e.g. doxorubicin) for targeted cancer treatment [38,39] or selective groups, such as those used for enzyme immobilization [40]. Nanoparticle formation and subsequent carbon coating in a one-step synthesis route can be achieved by the choice of precursor used.

The decomposition of iron pentacarbonyl in the presence of oleic acid is a well known method for Fe-NP formation [23]. Ferrocene has also been shown to decompose and form a carbon shell around the iron nanoparticles and has shown to exhibit novel structures [41]. Cyclopentadienyliron dicarbonyl dimer [(C5H5)Fe2(CO)4], was chosen in this work because, unlike other precursors, it can form free radicals during decomposition, due to the dimeric nature of the molecule [42]. Studies have shown it to be a useful radical initiator in free radical photo-polymerisation [43] and has been shown to act as a catalyst for MWCNT growth [44]. The presence of free radicals is likely to aid the attachment of the nanoparticles to carbon nanotubes during the nucleation process. The reaction mechanism for radical formation is shown in Fig. 1, where the μu-bonded carbonyl groups (CO bonded to both iron atoms) break a bond with one of the iron atoms, forming the intermediate species. This species can then break down into two identical radicals, as the iron–iron bond is broken and one electron from the sigma bond goes to each of the iron species.

Radicals are extremely reactive species and are short lived; these species could react with nearby MWCNT material and form chemical bonds. The iron-containing bonding sites will then act as fixed nucleation sites for nanoparticle formation. In this work a mechanism for nanoparticle formation on MWCNT samples is proposed and the properties of the resultant composite material are investigated.

2. Experimental

Cyclopentadienyl iron(II) dicarbonyl dimer [(C5H5)Fe2(CO)4] (99%, Sigma Aldrich) was combined with commercially available MWCNTs (Arkema Graphistrength) a ratio of 10:1. This was achieved by dispersing the nanotubes in chloroform (>99%, Sigma Aldrich) and adding the precursor before sonicing (225 W) for 1 h. The resultant homogenous solution was dried under air. The solid was collected and placed in a ceramic boat before being introduced into a tube furnace. All experiments were carried out at atmospheric pressure in nitrogen gas. The final temperature, temperature rate and holding time were varied across experiments in order to ascertain the optimum synthesis conditions. All experiments were left to cool to below 70 °C before the sample was removed from the tube furnace chamber.

Adsorption of rhodamine B dye (Sigma Aldrich) was demonstrated by diluting the dye solution to a concentration of 10 nmol dm−3 using de-ionised water. The solution was placed in a quartz cuvette and a small amount of the composite material was added. The solution was analyzed by UV/visible spectroscopy (Varian Cary 5000) before and 5 min after the addition of the composite material.

Electrospinning the material into aligned sheets was achieved by dispersing the magnetic hybrid material in water under ultra-sonication (300 W, for 30 min using a fine tip probe) using sodium dodecylbenzene sulfonate (SDBS) as a surfactant. Once dispersed, the solution was blended with polyethylene oxide (2,000,000 Mv) (PEO) to give it desired viscoelastic properties, allowing it to then be electrospun onto a high speed rotation surface (+15 kV, at a distance of 22 cm).

3. Results and discussion

The iron nanoparticle decorated MWCNT material was found to be magnetic both as a solid and in solution. In order to determine if the magnetic material was protected, it was soaked in a 2 M solution of hydrochloric acid (Sigma Aldrich) and tested with a magnet. The effect of synthesis temperature on the protective ability of carbon shell that encapsulates the nanoparticles was also investigated.

The carbon shell has the ability to protect the internal nanoparticle, provided that the carbon layer fully encapsulates the particle. Hydrochloric acid was chosen as, unlike other mineral acids (HNO3 and H2SO4), it is not expected to oxidise the carbon shell [37]. Resistance to an external environment is required for medical applications, such as cancer treatment [1]. A fraction of the hybrid material was added to 2 M HCl for 24 h and then filtered, before being washed.
with water and re-dispersed in methanol. To determine if the synthesis temperature had an effect on shielding ability, the acid test was carried out on samples produced at low (250 °C) and high (1000 °C) temperatures. Temperatures below 250 °C have not, so far, produced protected nanoparticles using a one-step synthesis method. nanoparticle formation is not expected much below 250 °C when using this precursor, which exhibits a decomposition point of 194 °C.

Higher synthesis temperatures are expected to produce larger nanoparticles due to increased coagulation and Ostwald ripening. Samples synthesised over a range of temperatures (250 °C, 550 °C, 1000 °C and 1200 °C) were analysed by STEM using a HAADF detector. From the images collected, the diameters of 100 nanoparticles were measured for each synthesis temperature, histograms showing the range of measured nanoparticle sizes and average size can be found in the Supplementary information. Results confirm that nanoparticles are larger with increased synthesis temperature.

Fig. 2a shows that the hybrid material is magnetic and remains so after acid soaking, indicating that a significant number of nanoparticles are well protected from acid dissolution. During the acid treatment process, the materials synthesized at low temperature gained a slight green colour, whilst the high temperature analogue remained clear. This indicates that high temperature synthesis conditions result in a more efficient protection for iron nanoparticles from HCl(aq). After acid soaking, materials synthesized at higher temperatures were removed from solution when in close proximity to a magnet more quickly than those synthesized at low temperature. This supports the observed colour change in proving that more nanoparticles synthesized at low temperature were dissolved after soaking in HCl(aq) as a result of less protection around the nanoparticles.

In Fig. 2c the majority of particles are between 10 and 40 nm with the smallest being less than 10 nm and the largest above 90 nm. The nanoparticles are anchored at specific sites, such as MWCNT defects or at crossover points. Particles have a uniform coating of carbon, suggesting that this step occurs after the nanoparticle has been synthesized, i.e. carbon coating occurs in the cooling process, confirming the mechanism proposed in Fig. 5. Using the internal carbon source provided by the iron precursor allows for a high iron to carbon ratio,
which is desired for many applications where protected magnetic particles are used. Overall there is a significant quantity of iron present in the sample, as can be seen in Fig. 2c.

The elemental profile in Fig. 3b across the nanostructure indicates that the nanoparticle is predominantly made of iron, comprising of an iron rich core of about 50 nm diameter. It can be deduced that as the iron precursor decomposes to form mainly metallic iron particles and that the nitrogen gas used in synthesis avoids significant oxidation. However, partial oxidation does occur. This leads to the presence of an iron oxide shell, approximately 5 nm in thickness. This is indicated in the EELS spectra by an increase in the oxygen content around the nanoparticle. The large peak of carbon at the periphery of the nanoparticle proves that it is coated in a carbon layer. The coating is mostly amorphous, determined by the low level of organization, compared to the highly ordered planes seen in the nanotube walls, as shown in Fig. 4c.

In Fig. 4a, the nanoparticle appears to be attached to the carbon nanotube using amorphous carbon as “molecular glue”. The initiation of the attachment is proposed to be a result from radical formation during the decomposition of the precursor (Fig. 1). The radicals formed could attack the MWCNTs and form a bond between an iron atom and a MWCNT before the radical further decomposes to form the beginning of a FeNP. The Fe-NP grows in size following the mechanism in Fig. 5 and subsequently exudes carbon from the nanoparticle upon cooling. In this case the carbon layer has remained amorphous; it encapsulates the iron-rich nanoparticle and supports the attachment of the nanoparticle to the MWCNT.

As the carbon shell is predominantly an amorphous coating (see Fig. 4a), it is hypothesised that the majority of the carbon present was not absorbed into the iron nanoparticles to form an iron carbide phase. However, a graphitic carbon coating can be resolved for the low (Fig. 4b) and the high (Fig. 4c) temperature synthesis routes, indicating that this can occur even at low synthesis temperatures. Many particles imaged by STEM show the same shell, it has been concluded that the carbon shell is a result of nanoparticle synthesis and not overlap of a near-by carbon nanotube. STEM has been used to characterise degree of graphitisation unambiguously, although Raman spectroscopy and XRD would assess a larger amount of sample the majority of signal obtained in both of these techniques would be due to the MWCNT material and not the graphitic shell surrounding the nanoparticles. To graphitize at relatively low temperature the nanoparticle must act as a catalyst for this transformation. Iron oxide nanoparticles have been shown to be catalytically active at temperatures as low as 110 °C [45], it is therefore feasible that the nanoparticles can act as a catalyst for graphitizing carbon.

Iron oxide has been shown to be present in the product at high (Fig. 3) and low (Fig. 4b) temperatures. The iron oxide shell is only present in some of the material, with less iron oxide seen at higher synthesis temperatures. The presence of iron oxide can be described with two competing explanations: as a result of oxygen from the precursor or oxidation in air after synthesis. There is appreciable oxygen content in the organometallic compound used, from the CO ligands, which could lead to the oxidation of synthesised nanoparticles, depending on the decomposition mechanism of these groups. The disproportionation reaction of carbon monoxide has been shown to form CNTs and onion-like particles [46], meaning that free carbon and free oxygen are present in the system. At high temperatures, these oxygen containing groups do not lead to as many nanoparticles containing iron oxide; this could be explained by the carbon present reducing iron oxide to iron during synthesis [3].

At low temperature, the system does not have enough energy to initiate this process and therefore the oxide remains. If this were the only mechanism of iron oxide formation, the carbon adsorbed by the particle would be exuded after oxidation had occurred. Subsequently, the carbon layer would remain as an amorphous coating. However, particles with graphitic shells and iron oxide surrounding the FeNP have been also observed at these low temperatures (Fig. 4b). Therefore, the oxidation of the FeNP by the oxygen contained in the precursor is not the only mechanism.

Another potential explanation is that oxidation occurs after nanoparticle formation. This could be explained by the FeNP exuding the carbon as a discontinuous layer that does not fully encapsulate and protect the internal nanoparticle.

![Fig. 3 – (a) A single nanoparticle attached to a MWCNT (synthesized at 1200 °C), showing the line across which Electron Energy-Loss spectra was acquired, to measure the carbon (C), oxygen (O) and iron (Fe) relative composition within the nanoparticle. (b) The relative intensity of the C, O and Fe signals across the nanoparticle shows that the core of the particle is iron rich, with an iron oxide shell which in turn is surrounded by a carbon coating. The small difference in peak maxima position for O and C confirm separate shells are present. The discontinuities in the spectra are related to errors in the spatial drift corrections during Electron Energy-Loss Spectroscopy (EELS) (indicated by the arrows). (A color version of this figure can be viewed online.)](image-url)
The nanoparticle is then subject to oxidative attack, leading to an iron oxide layer surrounding the iron rich centre. In this explanation, amorphous carbon with a thickness of 6 nm (Fig. 3) does not sufficiently protect the nanoparticle from oxidation. Similarly, the graphitized layer seen in Fig. 4b is not sufficient to protect the encapsulated nanoparticle from oxidation. This would require the carbon shell to expand, which seems unlikely. Although if many graphitic planes are seen, rather than one continuous sheet, this may be possible but would leave areas of the nanoparticle surface completely unprotected.

Graphitisation of the carbon layer is seen at both low and high temperature synthesis (Fig. 4b and c). Carbon will be absorbed and subsequently exuded from the nanoparticle as graphitic layers, if enough energy is present to overcome the energy barrier associated with the phase transformation. At the low synthesis temperatures seen in this study (250 °C), graphitic carbon is not expected to be formed from iron nanoparticles. It could be that the presence of an iron oxide layer provides an alternative low energy pathway for graphitisation and analysis of the produced graphitic layers appears to show a highly defective structure. This would support the argument for iron oxide being present before the synthesis, leading to an iron oxide layer surrounding the iron rich centre. In this explanation, amorphous carbon with a thickness of 6 nm (Fig. 3) does not sufficiently protect the nanoparticle from oxidation. Similarly, the graphitized layer seen in Fig. 4b is not sufficient to protect the encapsulated nanoparticle from oxidation. This would require the carbon shell to expand, which seems unlikely. Although if many graphitic planes are seen, rather than one continuous sheet, this may be possible but would leave areas of the nanoparticle surface completely unprotected.

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carbon encapsulated nanoparticles of cobalt and nickel [54] as well as iron [36]. This supports the proposed model in Fig. 5, that the carbon is exuded upon cooling.

The carbon shell has shown to produce both amorphous (Fig. 3) and graphitic (Fig. 4b and c) carbon phases. As described above, carbon is exuded from the nanoparticle upon cooling (Fig. 5, stage 7), which is true for graphitic carbon formation. When the energy present in the system is greater than the activation energy required to form an iron carbide phase, carbon will be dissolved into the iron nanoparticle, upon cooling this carbide phase is exuded from the nanoparticle as graphitic planes. The graphitic planes form uniformly over the surface of the nanoparticle, producing carbon shells that encapsulate the inner nanoparticle.

If amorphous carbon surrounds the nanoparticle, it can be concluded that insufficient energy was present to form an iron carbide phase. The process would therefore stop at stage 4 of Fig. 5, with carbonaceous groups being broken down at the surface of the nanoparticle but not absorbed. Amorphous carbon may still encapsulate the nanoparticles and even provide some degree of protection to the internal particle, however rigid bonding structure of graphitic sheets (see Fig. 4c) and increased resistance to oxidative attack is expected to provide improved protective ability to the internal nanoparticle.

A small amount (20 mg) of the magnetic nanohybrid was added to a weak solution of rhodamine dye (10 nmol dm$^{-3}$), and within 5 min the solution underwent a colour change from pink to clear. To demonstrate the adsorption of the dye on to the composite material, UV/visible spectroscopy was undertaken on a solution of the dye before and after the removal by the composite material (see Fig. 6). Five minutes after the composite was added, a magnet pulled the composite and adsorbed dye to the bottom of the cuvette, in order for the after removal measurement to be taken.

The rhodamine was adsorbed by MWCNT surfaces through a number of interactive forces, such as aromatic stacking of the sp$^2$ hybridised carbon. This is a result of electron orbital overlap between the nanotube and the aromatic ring of the dye molecule [55].

As carbon is adsorbed into the Fe-NP carbon-containing iron phases are produced, these are austenite ($\gamma$-Fe) and cementite (Fe$_3$C). An iron phase of ferrite ($\alpha$-Fe) and a separate carbon layer are thermodynamically favourable, when compared to $\gamma$-Fe and Fe$_3$C, at room temperature [53]. Yu et al. also propose a metal–carbon fused phase during the formation of the nanohybrid.

Fig. 5 – (1) Iron precursor ((C$_5$H$_5$)$_2$Fe$_2$(CO)$_4$) decomposes to form (2) iron vapour; agglomeration occurs, to form (3) iron nanoparticles. (4) Carbon-containing groups are broken down on surface leading to free carbon that (5) adsorbs into iron nanoparticle forming iron carbide species and (6) becomes saturated. Upon cooling (7) the trapped carbon diffuses to the surface forming separate iron and carbon phases, (8) as carbon deposits build up on the surface the nanoparticle is completely encapsulated. (A color version of this figure can be viewed online.)

Fig. 6 – UV/visible spectroscopy of rhodamine dye solutions before (black) and after (red) the removal by a small amount of magnetic composite material. Results show that rhodamine ($P_{\text{max}}$ at 550 nm) is adsorbed on to the surface of the composite material and can be removed from solution using a magnet. The presence of the composite in solution has increased the background signal measured. (A color version of this figure can be viewed online.)
there must be low levels of amorphous carbon contamination present. The material produced in this study is expected to be a superior candidate for adsorption of organic dyes because of the combination of high surface area MWCNT graphitic surfaces, with low amorphous carbon content, high iron to carbon ratio, and importantly magnetic nanoparticles that can draw the MWCNT material out of solution with a magnet (see Fig. 2a).

In order to further demonstrate the application versatility of this new magnetic CNT nano-hybrid, a soft magnetic composite (SMC) was also produced (see Fig. 7) revealing further applications for SMC items such as rotating machinery, fast switching solenoids [56] “intelligent fibres” for military clothing [57] and magnetic sensors [58]. SMC materials are commonly produced using iron powder and resin, using magnetic nanoparticle loaded CNTs as opposed to iron has the added benefit of improved mechanical performance [59]. Electrospinning this solution resulted in a large area of highly aligned nano-fibres loaded with magnetic CNTs. Magnetism in the SMC is demonstrated (despite the low CNT content), confirming that the magnetic nano-hybrid material can have further applications in advanced SMCs.

4. Conclusions

A one-step thermal synthesis method of producing carbon encapsulated magnetic iron nanoparticles attached to MWCNTs has been outlined. The relatively low temperatures used have only been reported in a handful of journals and none which encapsulate the nanoparticle in parallel. The choice of precursor, cyclopentadienyl iron dicarbonyl dimer, is paramount to the successful synthesis of the composite material by providing an iron and carbon source with a favourable decomposition route to produce nanoparticles, as has not previously been studied in this manner. A mechanism for nanoparticle formation has been outlined and the structures of the nanoparticles have been investigated. Higher synthesis temperatures increase the protective ability of the carbon coating.

By synthesizing protected magnetic nanoparticles on to carbon nanotubes the scope for functionalisation and the attachment of linking molecules opens up new possibilities of research in the fields of energy management, chemical processing and biotechnology. The hybrid material has also been electrospun to form a lightweight and aligned CNT composite that can be manipulated with a magnet, highlighting how the material may find applications as a soft magnetic composite. Producing high surface area solids like this could help to overcome the hurdles of nanoparticle contamination for future applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.11.042.

REFERENCES


Highly aligned arrays of super resilient carbon nanotubes by steam purification

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ABSTRACT

Steam treatment has been applied to our prefabricated highly aligned areas of electrospun carbon nanotube composite nano-fibres, leading to controlled and targeted removal of polymeric and amorphous carbon materials, resulting in areas of highly aligned, highly crystalline, pure nanotubes. Raman analysis shows how the $I_D$ to $I_G$ intensity ratio was reduced to 0.03, and the radial breathing mode peak intensity, used for nanotube diameter calculation, changes. Therefore, suggesting that some carbon nanotubes are more resistant to steam assisted oxidation, meaning that specific carbon nanotube diameters are preferentially oxidised. The remaining carbon nanotubes have displayed a significant improvement in both quality, with respect to defect density, and in crystallinity, resulting in an increased resistance to oxidation. These steam treated super resilient carbon nanotubes are shown to withstand temperatures of above 900 °C under ambient conditions. Applying this purification method to electrospun nano-fibres leads the way for the next generation of composite materials which can be used in high temperature extreme environments.

1. Introduction

Due to their remarkable mechanical, thermal and electrical properties, combined with their high aspect ratio, carbon nanotubes (CNTs) have received high levels of scientific interest [1–3]. Through previous research, we have already demonstrated how their remarkable properties can be implemented into composite materials and electronics [4–6]. However, these beneficial properties are only true for pristine CNTs. Using current growth processes, defects in the CNT structures and impurities such as amorphous carbon are unwanted by-products which limit the scope of these materials in future applications. However, steam treatment has been shown to purify CNTs, removing the unwanted by-products, which is expected to improve these beneficial properties.

In this work, previous research in to steam assisted purification of CNTs [7–9] has been advanced to also show selective oxidation of CNTs with high defect concentrations, which has shown selectivity towards certain CNT diameters, a previously unreported result. CNTs that survive this treatment are of extremely high quality/crystallinity, and as such display increased, and in some cases total resistance to oxidation under ambient conditions above 900 °C. This degree of improvement in oxidation temperatures has not been observed previously.

The customised steam treatment process has, for the first time, been applied to highly aligned electrospun CNT-polymer composite fibres and successfully removed polymer, surfactant, amorphous carbon and defective CNTs. This results in highly aligned CNT sheets of high CNT quality, over large areas suitable for technology integration.
Selectivity in the oxidation of carbon species arises from the lower energy required to break the chemical bonding, hence preferentially oxidising less ordered materials. CNTs are highly crystalline, tubular sp² carbon structures and are more difficult (require more energy) to oxidise than amorphous carbon and polymeric carbon contained in the composite fibres. Water molecules do not thermally dissociate into hydrogen and oxygen at temperatures below 2000 °C [10], but will oxidise carbon through two key reaction processes when elevated to temperatures of 700 °C and above, reacting with only defective or amorphous carbons [7]. Not only does this process have a large potential for upscale and commercialisation, it can be carried out at atmospheric pressure and only requires water as the reactant.

Applying this treatment process to electrospun CNT composite fibres allows for large scale production of highly aligned CNT buckypapers on a macroscopic scale [11]. This paves the way for applications in super-tough composite fibres [12], super capacitors and electronic textiles [13], to name a few. There are several successful routes to manipulate CNTs into uniform orientations, one being electrospinning in which large areas of aligned CNT fibres can be obtained at relatively high speed [14]. This process forms nano-fibres through exerting electrostatic forces on a viscoelastic solution, causing uniaxial stretching as it solidifies, before being collected [15]. Electrospinning a polymer solution or melt, loaded with CNTs, produces arrays of aligned fibres, in which the embedded CNTs are also aligned, which has been reported to improve many of the materials properties, including charge transport between CNTs [16–19]. However, embedding CNTs in a polymer could potentially have detrimental effects on the mechanical and electronic properties of the material, unless the polymer (and surfactant) is removed. In the work reported here we propose a method using steam treatment which supersedes traditional thermal processing when elevated to temperatures of 700–590 °C, after the CNTs were dispersed; this was in order to pre-treat the wetcake material, CNTs were oxidised in air at around 500 °C (3.9% weight, assuming all of the solvent is evaporated; this was confirmed by thermogravimetric analysis (TGA)).

The single-walled CNTs (SWCNTs) used in this study were purchased at 5000 g from Aldrich, with an average molecular weight of 2,000,000 M₀, after the CNTs were dispersed; this was in order to prevent the ultra-sonic irradiation cleaving the polymer chains, which would reduce viscoelasticity, rendering the solution unsuitable for electrospinning [22]. Once electrospun, this solution effectively produces PEO nano-fibres embedded with CNTs at 3.9% weight, assuming all of the solvent is evaporated; this was confirmed by thermogravimetric analysis (TGA).

The solutions were electrospun at +12 kV from a single needle spinneret at a distance of 20 cm from a high speed (10 m/s surface velocity), electrically ground, rotating drum. The drum itself was wrapped in a silicone coated paper, to allow easy removal of the produced fibres. The resultant electrospun fibres were folded several times (much like a sheet of paper), in a manner which maintains the fibre alignment, in order to produce a thicker sample (enabling easier handling and analysis after baking). In order to quantify the CNT alignment after electrospinning, a polarised Raman spectroscopy method, as outlined by Hwang et al. [23] was employed in this work. We found that circa 94 ± 2% of the CNTs to be aligned over large areas as described in the experimental details.

TGA was used to both confirm CNT content but also to confirm how and at what temperatures the different materials used in this investigation thermally breakdown. Fig. 1 shows individual TGA curves of the three chemicals that constitute the CNT loaded nano-fibres produced during electrospinning and then a fourth curve for the final nano-fibres themselves. For each material, the analysis was conducted in both air and nitrogen, from room temperature to 900 °C, at a heating rate of 10 °C/min.

The percentage mass losses of each of the TGA curves were assigned by calculating the relative atomic weight with respect to the total molecular weight of the sample. Detailed analysis of some of the TGA curves can be found in the Supplementary information item S1. Results confirm that, in both air and nitrogen, the majority of PEO is removed before 450 °C, with the PEO thermally degrading at a significantly lower temperature in air through an oxidation process. The thermal decomposition of SDBS takes very different routes depending on whether this is performed in nitrogen or in air. In nitrogen, the alkyl chain of the molecule is removed by 480 °C (48.5% of the total weight). The benzene ring is subsequently lost by 800 °C, leaving the head of the surfactant, now present in the form of sodium hydrogen sulphite (NaHSO₃). In air, the compound follows a different decomposition route due to the presence of oxygen, the head of the surfactant is still not removed but has been oxidised and as such the residue left above 800 °C is attributed to NaHSO₃. With regards to the wetcake material, CNTs were oxidised in air at around 590 °C and only the metal catalyst remains, whereas in nitrogen, the lack of oxygen prevents CNT oxidation and therefore the sample is unaffected. As previously mentioned, in order to align the CNTs into a sheet, all three of these materials need to be combined and electrospun. The final TGA curve in Fig. 1D is of the electrospun CNT loaded nano-fibres. This result is effectively the combination of all three of the other TGA curves, and provides an indication of what species are expected to be present after thermal treatment, with and without steam over a range of temperatures.

In preparation for the steam treatment process, the thick, aligned, CNT loaded fibre mats were mounted on a silicon wafer and loaded into the centre of a Carbolite quartz tube furnace (as shown in Fig. 2A). The quartz tube is purged with nitrogen at ambient pressure before elevating the temperature, minimising the risk of residual oxygen oxidising the
CNTs in the sample (Fig. 1C). The furnace is then heated at 20 °C/min up to a target temperature, where this temperature is held for 3 h, to ensure maximum beneficial effects, before being left to cool by air. As the furnace heats up, the water is heated close to boiling point; when ready, the nitrogen is then bubbled through it at a rate of 2 L/min, carrying water vapour in to the reaction chamber to selectively oxidise the fibrous material. Steam was introduced in to the furnace during the 3 h period that the furnace was at the target temperature, preventing condensation and controlling the volume of steam passed over the sample. Once the furnace had returned to room temperature, the samples were removed and analysed. Electron microscopy images of the CNTs at each stage of the process can be found in the Supplementary data (Fig. S4).

3. Results and analysis

3.1. Raman spectroscopy

Raman spectroscopy is a non-invasive analytical technique, which is well documented for the characterisation of CNTs,
owing to the ease and versatility of the technique and the significant amount of information that can be gathered from a single spectrum [24]. Pristine CNTs will produce a spectrum with well-defined narrow peaks and with low background intensity. The presence of amorphous carbons and other impurities will increase photon/phonon scattering, resulting in both broadening of the peaks and an increase in the level of background scattering [25]. Fig. 3A plots the spectra of samples that were steam treated over a range of temperatures. In some cases it is good practice to remove any background signals from the spectrum to allow a baseline for sample comparison; however in Fig. 3 we have not done so. This allows the background level of each spectrum to be compared. Generally speaking, the lower the background level, the lower the amorphous carbon content [25]. In Fig. 3B, the background level of samples baked at different temperatures can be seen to reduce as the steam treatment temperature is increased, demonstrating how the steam purification process is more effective at higher temperatures. Note: all Raman analysis conducted in this article was done so with a 782 nm (red) laser, with a power of 1%, this ensured that the sample was not burnt or altered during the analysis. Most other publications that claim high purity SWCNT materials analyse their samples with a 514 nm (green) laser, which will naturally produce a graphitic defect signal (D band) significantly lower in intensity. In these cases, it is not a fair assessment of the SWCNT material.

In addition to lowering the background level of the spectrum, reducing the amorphous carbon content minimises the signal scattering, subsequently narrowing the peaks [26]. This reveals the fine structure of the G band, with the G’ peak being more apparent at higher temperatures. The stacked spectra in Fig. 3A highlight how this ‘narrowing’ process evolves with increasing sample purity; as the steam treatment temperature is increased and the sample is further purified, peak splitting is more predominant, allowing weaker vibrations/excitations to be defined in the spectrum. Narrowing of the Raman peaks was also observed for the other key peaks, including the D and the 2D peaks. Further analysis of these peaks additionally revealed that the peak locations increasingly blue shift as steam treatment temperature increases, suggesting that vibrational energy loss through defect scattering has been reduced, providing further evidence that the samples have been increasingly purified with increasing steam baking temperature [see Supplementary item S2 for plots of FWHM and peak location against steam baking temperature for both the D and 2D peaks].

The CNTs used in this experiment are predominantly SWCNTs and DWCNTs; in such samples, radial breathing mode(s) (RBM) and the G-band are the strongest features seen in the spectra. The RBM region, unique to single/double walled CNTs, relates to a circumferential vibration of the nanotube and is directly proportional to the diameter of the nanotube. Nanotube diameters were determined using the formula proposed by Dresselhaus et al. for bundles of nanotubes [27] and is accurate for CNTs in the diameter range of 1–2 nm. RBM peaks of CNTs with diameters above 2 nm are not measureable with the Raman Spectrometer used. Additionally RBM peaks will only appear if they are in resonance with the laser energy used, as set out by the Kataura plot [28].

Differences in RBM peak intensities were realised for samples treated with and without steam at 1000 °C, Fig. 4A plots the RBM region of the Raman spectra for both samples. As already described, steam treatment can selectively remove amorphous and polymeric carbon (due to the lower energy required to break the carbon bonding), and as such does not oxidise the majority of CNTs. The presence of typical CNT peaks in Raman spectra (RBM, D and G) as shown in Fig. 3A after steam treatment, even at temperatures of up to 1000 °C, confirm that CNTs are still present in the sample. Closer analysis of the RBM peak positions show them to remain constant, which indicates that the diameter of the CNTs was not affected by the steam treatment process, as we expected. However, the relative peak intensities have changed, suggesting that some specific diameters of CNTs are preferentially removed during the steam treatment process. We expect that CNTs with a high number of defects will be removed, and as such CNTs of specific diameters may have a higher number of defects, allowing the steam to oxidise them. However, it could be that some CNT chiralities are more susceptible to oxidative attack by steam compared to others, but this could not be deduced from the laser energies.
available within the Raman instrument used. Further work would be needed to confirm this theory.

The RBM peak locations were found to correspond to CNT diameters of 0.92, 1.22 and 1.63 ± 0.02 nm, where the smallest and largest diameters are within error of being potentially the inner and outer wall of a double walled CNT (with a wall separation distance of 0.69 nm). While the 1.23 nm diameter walled tubes are only single walled, it is CNTs with this diameter which have seen the highest Raman peak increase after steam treatment. This could be due to either impurities being removed from their walls, allowing the weak Raman signal to be increasingly detected, or the result of outer walls being removed off of double/few walled CNTs, leaving only the centre wall. This result is supported in Fig. 4A by a small peak seen at a Raman shift of 132 cm⁻¹, which is visible when for the sample baked without steam but missing on the sample that was steam treated.

The intensity of the D peak and the G peak were compared, given as an \( I_D/I_G \) ratio, to assess the quality of the material with respect to the concentration of defects present in the sample. Doing this revealed that the steam treatment has been proven to reduce the level of disorder in the sample, indicated in Fig. 4B. Here the \( I_D/I_G \) ratio decreases with increasing steam treatment temperature, indicating both increasing purity and increasing crystallinity. This increase in the sample purity also resulted in an increase in the RBM signal intensity. This is an indication that a stronger RBM signal was coming from SWCNTs or DWCNTs over other CNT species in the treated samples, indicating that the other carbon species where removed during the purification process [9,26]. This yet again proves that the high temperature steam treatment process leaves only high quality, highly crystalline CNTs, which we later found to resist oxidation at temperatures above 900 °C.

3.2. Thermogravimetric analysis

TGA was further utilised in order to analyse both the steam and non-steam treated samples. Conditions seen in the tube furnace could not be mimicked using our TGA as we could not introduce steam to the furnace. However by analysing the samples in the TGA in air, the mass loss for the carbon content can be analysed, with higher crystallinity CNTs having a higher oxidation temperature than amorphous carbon. High levels of amorphous carbon were known to be present in the samples baked at lower temperatures and amorphous carbon content is decreased with increasing temperature of the bake (as shown by Raman spectroscopy results).

Samples baked without steam (in a nitrogen only atmosphere) were analysed by TGA in air (Fig. 5A). Results show that water content (present through adsorption of moisture in air) differs and is lost before 100 °C and as a result the TGA analysis had to be conducted from 150 °C for a fair comparison. Subsequent behaviour was found to be similar; all samples display a similar mass loss between 410 °C and 470 °C (increasing slightly with treatment temperature), corresponding to the oxidation of carbon materials (including the CNTs). However, there is no CNT decomposition at 550 °C (as seen in Fig. 1C), this suggests that the presence of large amounts of amorphous carbon is promoting CNT oxidation and oxidising them at a lower temperature, this is only seen in samples treated without steam.

Fig. 5B displays the TGA curves for samples baked with the steam treatment. Samples baked at 600 °C were found to be similar in relation to total mass lost and the temperatures at which those losses occur, compared to the non-steam treated samples. It can therefore be deduced that both samples contain the same ratios of materials and that steam has had no effect on the sample at this temperature, this is in agreement with Tobias et al. that the steam purification reaction starts at 700 °C.

Samples baked with steam above 700 °C do not exhibit the same behaviour as those without steam. The mass loss seen at approximately 450 °C is now not seen until 650 °C and considerably reduced (for higher temperatures removed entirely). This indicates that the addition of steam to the baking process oxidises and removes more carbonaceous materials than is otherwise removed in an inert (nitrogen) environment. The temperature at which steam starts to oxidise amorphous carbon can be probed further by comparing the residue left in the TGA pan (measured as a percentage of the starting weight). This was done for samples baked both in nitrogen and with
the addition of steam, over a range of temperatures (Fig. 6). Steam is oxidatively active above 700 °C, from which the residue is greater for steam treated samples when compared to those treated in nitrogen (where more CNTs which resist oxidation survive). This is a clear indication that more lower ordered carbonaceous material has been removed due to steam assisted oxidation.

As previously noted, the presence of unique CNT Raman peaks in the spectra when analysing samples baked above 700 °C in steam (Fig. 3), confirms that CNTs remain after the treatment process. Therefore, the carbonaceous material removed is predominantly polymeric and amorphous carbon, not the CNTs. TGA analysis revealed that samples that have been steam treated above 700 °C exhibit very small mass losses, this corresponds to either the oxidation of some remaining defective CNTs (but not the majority) or some amorphous material which may have survived in a dense agglomerate (that the steam could not penetrate). The oxidation temperature, during TGA, increases with the steam treatment temperature. For the sample steam treated at 800 °C, fewer still CNTs are oxidised between 600 °C and 750 °Ci n TGA. This is significantly higher than the corresponding TGA curve of the raw CNT product (Fig. 1), and demonstrates how steam treated CNTs are now more resistant to oxidation. This is because the CNTs now have fewer defective points for oxidation to initiate (as shown in Fig. 3). After steam treatment at 900 °C, very little mass loss (if any) is observed through TGA. This indicates that the oxidation temperature of CNTs is further increased, and is above 900 °C (the limit of our TGA). Raman spectroscopy confirmed that the residual from the TGA sample analysed in air, contained CNTs, proving that the CNTs in the highest temperature steam treated samples are resistant to oxidation. Even in air at temperatures above 900 °C. Furthermore the $I_D/I_G$ ratio was found to be as low as 0.03! This is a substantial improvement on the wetcake material which oxidised at 590 °C and had an $I_D/I_G$ ratio of 0.36. This demonstrates that the steam treated CNTs are of such purity and crystallinity, that their oxidation temperature is closer to that of pristine graphene (1200 °C). This degree of improvement in CNT oxidation temperature has never before been reported and allows the development of high temperature CNT devices, for applications in extreme environments.

### 3.3. Sodium contamination

Although steam treatment has successfully shown the selective removal of carbonaceous materials from the polymer and surfactant, it cannot remove the ionic groups present in the surfactant. We carried out X-ray analysis in a SEM to confirm that a compound containing sodium was the major contaminant present in the aligned CNT samples as residue from the surfactant (this supports TGA data seen in Fig. 1B). Other surfactants that do not contain sodium could be used and would
lead to lower contamination levels. However, SDBS has proved to be the best surfactant for obtaining high weight concentration dispersions of our carbon nanotubes (Thomas Swan, Elicarb wetcake), which remained stable when blended with PEO for the electrospinning alignment process.

The presence of large deposits of sodium oxide is a problem for future applications of the material, hindering both electron transport and reducing active surface area. An acid washing procedure was implemented to remove the contaminant material. A sample was immersed in concentrated hydrochloric acid (36%) and left for 10 min and stirred intermittently, and washed with deionised water in triplicate. The baked fibre had kept its shape throughout the acid washing process, indicating that this process could be feasible in an industrial setting. EDX analysis [see Supplementary item S3] proved that sodium deposits had been removed from the sample, leaving an aligned sheet of steam purified CNTs with minimal amorphous carbon.

4. Conclusion

Steam treatment of aligned electrospun carbon nanotube fibres has been demonstrated to selectively remove carbonaceous impurities and polymeric material, leaving highly aligned sheets of high quality, high purity carbon nanotubes. Raman spectroscopy and thermogravimetric analysis have shown that steam treatment can reduce both amorphous carbon content and remove areas of CNTs with a high concentration of defects, leading to extremely low D to G peak ratios. Raman results illustrate a change in RBM peak intensities, which suggests that the steam treatment can selectively oxidise different types/diameters of carbon nanotubes, which we attribute to these types/diameters having a higher degree of defects. However, no link between semiconducting or metallic CNTs being preferentially oxidised has been deduced.

CNTs in our steam treated composite samples were found to be substantially more resistant to oxidation, where the oxidation temperature of the CNTs increased with steam treatment temperature. Samples that were steam treated at temperatures above 900 °C were found to have totally resisted oxidation at temperatures above 900 °C, a substantial improvement on the original oxidation temperature of the material and previous unreported in literature.

The surfactant used to disperse CNTs, SDBS, has been shown to leave sodium-containing residue after the steam treatment process. The sodium can be removed from the resultant baked fibres by an acid washing procedure, which maintains aligned sheets of CNTs. Alternative surfactants have more recently been used to successfully obtain the same highly aligned carbon nanotube sheets without sodium contamination and will be reported in the future.

These processing steps have led to higher quality aligned carbon nanotube sheets that have the potential to be developed into high temperature CNT devices, for applications in extreme environments. The removal of polymer (and impurities from the CNTs) will increase both the conductivity and surface area. We envisage their future application in areas such as advanced electronics, charge storage and next generation composite materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.11.061.

REFERENCES


