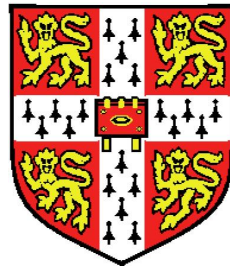


Structure, Properties and Treatments of Carbon Nanotube Fibres



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A thesis submitted for the degree of

Doctor of Philosophy

Preface

This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and the Acknowledgments. The research was conducted at the Department of Materials Science and Metallurgy of the University of Cambridge between October 2005 and May 2009, under supervision of Professor A. H. Windle. This thesis has not been submitted in whole or in part as consideration for any other degree or qualification at this or any other University. In accordance with the Degree Committee of the Faculty of Physics and Chemistry, this dissertation does not exceed 60,000 words.

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*To my parents, whose support has been a continuous source of
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Abstract

Carbon nanotubes (CNTs) possess exceptional mechanical, thermal and electrical properties along their main axis, superior to those of most materials. These can be exploited on a macroscopic scale by assembling the CNTs into a fibre with the nanotubes preferentially oriented parallel to each other and to the fibre axis. CNT fibres can be produced continuously, directly from the gas phase during CNT synthesis by chemical vapour deposition (CVD), and spun at rates of up to 70 m/min. Their combination of outstanding mechanical, electrical and thermal properties and low density (1 g/cm^3) makes CNT fibres a potential candidate for high-performance applications. The fibre specific strength and stiffness are typically 1 GPa/SG and 50 GPa/SG, respectively; however, at small gauge lengths ($< 2\text{mm}$) they also show values of 6 - 9 GPa/SG strength and 180 - 390 GPa/SG stiffness. The electrical conductivity of the CNT fibres is approximately $8 \times 10^5 \text{ S/m}$ and their thermal conductivity of the order of 50 W/mK. These properties derive from the long length, high alignment and efficient packing of the nanotubes in the fibre. Further improvements to the fibre structure and properties at long gauge lengths are possible through removal of impurities from the fibre by annealing.

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Chapter 1

Introduction

A fibre of carbon nanotubes (CNTs) is a macroscopic material in which the mechanical, electrical and thermal properties of carbon nanotubes along their main axis are exploited. CNT-based fibres can be produced in several ways: they can be spun from liquid crystalline suspensions, drawn from an array of aligned CNTs on a substrate, spun as a CNT/polymer fibre via a coagulation route, or spun directly from the gas phase during CNT growth by chemical vapour deposition (CVD). Chapter 2 reviews the basic properties of nanotubes, the methods for spinning CNT fibres and their main properties.

The fibres studied in this work are produced continuously in a one-stage process that covers synthesis, spinning and assembly of the nanotubes into a fibre, although post-spin treatments are also available to improve the fibre's properties. The experimental techniques used to produce, treat and characterise the structure and properties of the CNT fibres and their composites are discussed in Chapter 3.

The nanotubes are synthesised by a floating catalyst chemical vapour deposition route such that nanotubes grow up to millimetres in seconds and form an aerogel of entangled tubes and bundles that can be drawn from the reactor into a semi-dense fibre. The parameters for growth of nanotubes that can be spun continuously into fibres with mechanical properties in the range of high-performance materials are discussed in Chapter 4, with a distinction between synthesis and spinning parameters which allows for a comparison with other more conventional

CVD methods on the one hand and with solution-spinning of polymer fibres on the other hand.

The transition from an aerogel of CNTs to a dense fibre starts as the aerogel is drawn from the reactor and is completed by interaction of the semi-dense fibre with a suitable liquid. Throughout the process, the fibre's density increases by several orders of magnitude and the nanotubes are assembled into the final fibre structure. Chapter 5 deals with fibre density and the degree of CNT orientation imparted by the drawing and liquid-densification stages. The latter stage is also discussed further in terms of the role of the properties of the liquid and the internal surface of the CNT fibres during the densification process.

The structure of a CNT fibre consists of highly aligned nanotube bundles and some impurities formed during the CVD reaction in the form of molecular adsorbates, residual catalyst particles and carbonaceous particulates. The fingerprints of the nanotubes and these impurities are observed by scanning and transmission electron microscopy (SEM and TEM, respectively), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Raman spectroscopy. The composition and architecture of the fibre, based on these techniques, is discussed in Chapter 6.

The strength and stiffness of an ideal CNT fibre consisting of perfectly packed and aligned CNTs can be estimated by employing concepts from composite shear-lag theory and by using experimentally-determined values of tensile strength and shear strength of individual CNTs. Chapter 7 shows that at small gauge lengths (100 fibre radii) the tensile properties of CNT fibres can approach those of the ideal assembly. At longer gauge lengths, however, the presence of randomly-dispersed, small residual catalyst and carbonaceous particles decrease the fibre's tensile properties and result in a fibre with elements that do not bear load cooperatively, similar to a rigid-rod polymer fibre prior to post-spin annealing.

Some electrical and thermal properties of CNT fibres spun from the gas phase are also discussed in Chapter 7. Their electrical and thermal conductivities are presented and compared with those of other CNT fibres, individual nanotubes and graphite.

Through post-spin low temperature ($< 500^{\circ}\text{C}$) annealing under an inert atmosphere, impurity adsorbates can be removed from the fibre's internal surface and the alignment of CNT bundles increased, resulting in changes in the tensile

behaviour of the fibre and with a marked impact on its stiffness. Annealing at higher temperatures ($> 900^{\circ}\text{C}$) removes carbonaceous and residual catalyst particulates from the fibres. The purified fibres show a generalised improvement in stiffness and strength compared to the original material. An alternative purification method consists of ablating the impurities by laser irradiation. This process shows similarities with annealing at high temperature and both processes suggest a similar impurity removal mechanism involving the migration of impurities to the fibre surface. These three post-spin treatments are discussed in Chapter 8.

Concluding remarks on spinning CNT fibres from the gas-phase, their structure and properties are presented in Chapter 9. This section also includes comments on future studies and strategies to produce a fibre with a structure that can further exploit the outstanding properties of nanotubes.

Finally, Appendices A and B present a theoretical determination of the interface for stress transfer in polygonised and collapsed double wall carbon nanotubes, and results on mechanical properties in tension and compression, thermal conductivity and coefficient of thermal expansion of CNT fibre/polymer composites, respectively.

Chapter 2

Carbon Nanotube Fibres

2.1 Introduction

Carbon nanotubes have been considered a fascinating material for the last eighteen years, since they were first identified as tubular graphite layers capped by one hemisphere of a fullerene molecule (1). Their axial properties suggest the possibility of using CNTs as building blocks to make new macroscopic high-performance materials. In particular, their outstanding tensile strength and stiffness and low density make them ideal candidates for applications where a combination of lightweight and high mechanical performance is required.

The assembly of nanotubes into a macroscopic fibre, with the tubes aligned parallel with respect both to each other and to the fibre axis, is a natural way of exploiting their axial properties. This strategy is consistent with basic principles for making high-performance fibres, the properties of which are derived from extended molecules oriented along their main axis and parallel to the fibre (2).

2.2 Carbon Nanotubes

2.2.1 Structure

A carbon nanotube can be visualised as a hollow cylinder formed by rolling a graphite layer (graphene) and joining its edges along the cylinder axis. In the same way as a graphite layer, the tube is composed of carbon atoms each joined to

2.2 Carbon Nanotubes

three neighbours by strong sp^2 -hybridised σ bonds forming a honeycomb lattice, with the ends of the cylinder often capped. CNTs can consist of several concentric graphene layers, usually with no registry and separated by a distance of typically 0.34 nm, similar to the interlayer separation in turbostratic graphite. Depending on their number of layers, the tubes are termed single, double, triple, or multi wall (SWNT, DWNT, TWNT and MWNT, respectively).

The structure of a tube can be geometrically related to a graphene sheet by the chiral vector $C_n = na_1 + ma_2$, which defines the direction of rolling a sheet relative to the origin (0,0) to form a specific nanotube (3), as shown schematically in Figure 2.1.

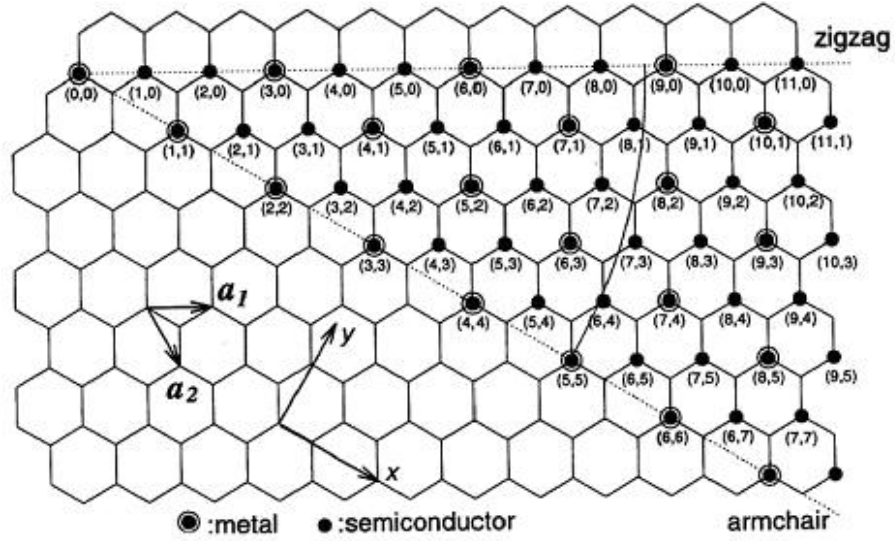


Figure 2.1: Schematic of a graphene sheet with unitary vectors a_1 and a_2 . A nanotube is equivalent to rolling a graphene sheet from the origin to a point (n,m) in the lattice (3).

The orientation of the six-membered carbon ring in the honeycomb lattice relative to the tube axis defines the nanotube's chiral angle (θ) through its (n, m) indices by

$$\theta = \arctan \left(-\frac{\sqrt{3}m}{2n + m} \right) \quad (2.1)$$

The chiral angle of SWNTs gives rise to three types of tube structures termed armchair, zig-zag and chiral, corresponding to chiral angles of $\pm 30^\circ$ (when $(n, m) = (2p, -p)$, for p an integer), 0° ($(n, m) = (p, 0)$) and others, respectively. The diameter (Φ) of any of these tubes is related to its indices and the lattice constant in graphene ($a = 1.42 \times \sqrt{3} \text{ \AA}$) by

$$\Phi = \frac{a\sqrt{m^2 + mn + n^2}}{\pi} \quad (2.2)$$

In reality, the structure of CNTs differs from a perfect graphene layer and contains defects in the hexagonal lattice such as vacancies, functionalities and topological defects (4). The presence of structural defects in nanotubes is equivalent to a low degree of graphitisation and can be determined experimentally using techniques such as Raman spectroscopy.

Typical nanotube diameters range from 0.7 nm to 15 nm for SWNTs and 10 to 100 nm for MWNTs. Recent improvement in nanotube synthesis have led to CNTs with lengths of the order of centimetres (5) and, in general, CNTs with aspect ratios of $10 - 10^7$ are routinely produced.

The properties of individual nanotubes are, ultimately, reminiscent of those of a single graphene sheet, however, with an increasing number of layers the properties of the tube change as the interaction between layers becomes more pronounced. A brief survey of mechanical, electrical and thermal properties of CNTs is presented below.

2.2.2 Mechanical Properties

Carbon nanotubes owe their strength and stiffness to their strong C-C bonds and their hexagonal array in the tube. Theoretically, their tensile properties are similar to those of graphite in the basal plane or of a single graphene sheet (6). However, their shape implies that their cross-section, at least in terms of tensile stress transfer, is not univocally defined. While it could be argued that the load-bearing area corresponds to the ‘thickness’ of the graphene layer (6), the nanotube in reality occupies a much larger space and, effectively, has a much larger cross-sectional area. A simple way to avoid determining the cross-section of a nanotube arbitrarily is to normalise its tensile properties with respect to the mass per unit

length of the nanotube, which is equivalent to using specific properties; that is, properties divided by the material's volumetric density, usually expressed as its specific gravity (SG).

Table 2.1 presents experimental values of specific strength and specific stiffness for an individual MWNT, a bundle of SWNTs and single-layer graphene, with their specific properties calculated using the areal density of graphene (0.75 mg/m^2). It can be seen that the measured properties of both the MWNT and the bundle of SWNTs are short of those of a single graphene layer. This, however, is not an indication of the presence of defects in the nanotubes used in these experiments, but rather due to the limited stress transfer between graphene layers, of adjacent tubes in the case of the SWNT bundle and between concentric layers of the individual MWNT. Thus, although the intrinsic strength and stiffness of nanotubes is approximately equivalent to those of a graphene layer they effectively, depend on the interaction between graphene layers (7). The more uniformly the graphene layers are stressed, the closer the values of strength and stiffness of a SWNT bundle or a MWNT will be to those of a graphene layer.

Table 2.1: Specific strength and stiffness of CNTs and graphene

Material	Strength (GPa/SG)	Stiffness (GPa/SG)	Reference
SWNT bundle	5.0	170	(8)
MWNT	20	300	(7)
Graphene	56	453	(9)

2.2.3 Comparison with Tensile Properties of High-Performance Fibres

A comparison of the tensile properties of nanotubes with those of current high-performance fibres is presented in Figure 2.2. The plot presents experimental values of specific strength and stiffness of individual carbon nanotubes and reported values for ultra-high molecular weight polyethylene (UHMWPE) fibre (10; 11), poly-(*p*-phenylene-2,6-benzobisoxazole) (PBO) fibre (12; 13), poly-paraphenylene terephthalamide (PPTA) fibre (14), S2 glass fibre (15), steel fibre (16), ultra-high

modulus (UHM) carbon fibre (15) and high-strength (HS) carbon fibre (15). The graph shows that the strength of individual CNTs is considerably superior to that of the fibres. The value of specific stiffness of individual MWNTs, as determined experimentally, is at the high end of the plot, with a value similar to that of PBO fibre although lower than that of UHM carbon fibre. The comparison gives an indication of the potential of using CNTs to make new high-performance fibres and in other applications, such as reinforcement in composites. Moreover, the values of specific strength and stiffness of nanotubes could, in principle, approximate those of a single graphene layer, which have been experimentally determined as 56 GPa/SG and 453 GPa/SG (9). For reference, such value of strength exceeds that of the strongest fibre in the graph (PBO fibre) by a factor of eight.

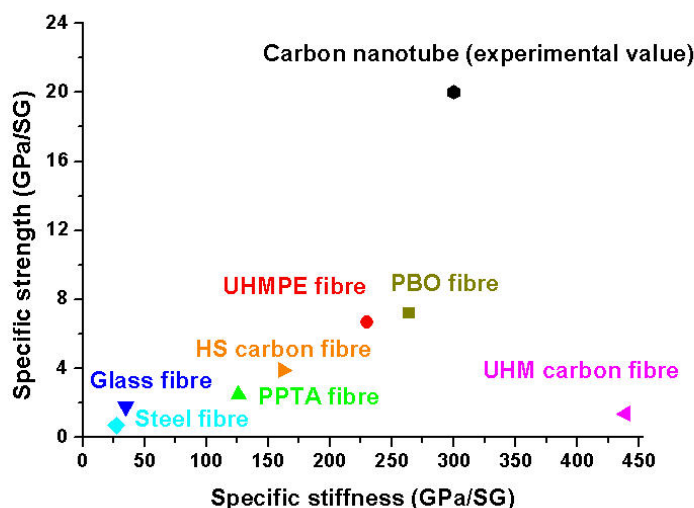


Figure 2.2: Comparison of experimental values of specific strength and stiffness of carbon nanotubes and reported values for high-performance fibres.

2.2.4 Electrical Properties

The unidimensional character of SWNTs makes them similar to quantum wires in which conduction occurs through discrete electron states and with the possibility of ‘ballistic transport’ (17), particularly when the diameter of the tubes is small.

The electronic properties of SWNTs depend on their molecular structure and can be related to their (n,m) indices. While all armchair tubes are metallic, only a fraction of the zig-zag type corresponding to those fulfilling the condition $(2n + m)/3 = \text{integer}$, are metallic. The remaining zig-zag tubes and all of the chiral type are semiconducting.

There are no equivalent relations for MWNTs, the electronic properties of which depend not only on the chiral angle of their layers but upon their separation (18). The electrical conductivity of a multilayered nanotube is also affected by electron hopping between graphene sheets, as occurs in graphite. Thus, while the conductivity of individual metallic SWNTs has been calculated theoretically and measured to be $\sim 10^8$ S/m (19; 20), for individual MWNTs it is only $\sim 10^6$ S/m (20). Similarly, the conductivity of an ideal graphene sheet has been estimated theoretically as 10^8 S/m (21), compared to 2.6×10^6 S/m for un-doped graphite (22). These values, summarised in Table 2.2, suggest that electron hopping between adjacent graphene layers can, potentially, limit the electrical conductivity of any macroscopic assembly of nanotubes. Note, however, that in nanoscale systems transport is naturally expressed as conductance, and that in practice, electrical conductivity of nanotubes or single graphene layers is a representative quantity only when the length of the tubes or the area of the graphene layers is on the scale of tens of microns or higher.

Table 2.2: Electrical conductivity of CNTs and related materials

Material	Electrical conductivity (10^6 S/m)	Reference
Metallic SWNT	100	(19; 20)
Individual MWNT	1	(20)
Single graphene sheet	100	(21)
Un-doped graphite	1	(22)

2.2.5 Thermal Properties

As with their mechanical and electrical properties, the thermal properties of carbon nanotubes are similar to those of graphite in the basal plane. In the direction of the basal plane, graphite has a thermal conductivity that peaks at near room

2.2 Carbon Nanotubes

temperature, with a value of $3000 - 4000$ W/mK (23). More recent experiments on the thermal conductivity of a single graphene layer give values of ~ 5000 W/mK (24), which in principle suggests that the theoretical estimate of 6000 W/mK (25) for individual nanotubes is reasonably accurate.

Experimental results from measurements on individual tubes and bundles indicate that thermal conduction in CNTs is dominated by phonons and that it peaks near room temperature, similar to graphite. However, there is great spread in the experimentally-determined values of thermal conductivity, ranging from 700 W/mK (26) to 3000 W/mK (27) for MWNTs and from $120 - 680$ W/mK (28) to $1750 - 5800$ W/mK (29) for bundles of SWNTs. Thermal conductivity values for CNTs, single-layer graphene and graphite parallel and perpendicular to the basal plane are presented in Table 2.3 below.

Table 2.3: Thermal conductivity of CNTs and related materials

Material	Thermal conductivity (W/mK)	Reference
SWNT bundle	120-5800	(28; 29)
Individual MWNT	700-3000	(26; 27)
Single graphene sheet	~ 5000	(24)
Graphite (parallel)	3000-4000	(23)
Graphite (perpendicular)	100	(23)

The wide range of values of thermal conductivity reported in the literature suggest that this property is highly dependent on the structure of the nanotubes. Although there is evidence of some dependence on nanotube length (30), it is unlikely that this is the cause of the variation in the data. Interestingly, the number of layers in the tube does not appear to have the same effect on thermal conductivity as it does on electrical conductivity or in tensile properties; nevertheless, the thermal conductivity between layers is still expected to be comparable to that in graphite perpendicular to the basal plane and approximately an order of magnitude lower than in the perpendicular direction.

2.3 Production of Carbon Nanotube Fibres

2.3.1 The Polymer/CNT Coagulation Route

The first method developed for spinning CNT-based fibres involves injecting a dispersion of nanotubes in an aqueous solution containing a surfactant, into the stream of a polymer solution, which results in the formation of a CNT/polymer gel fibre through coagulation. Excess solvent is subsequently removed and the material wound in its final form as a dense CNT/polymer fibre with typically 60 wt.% nanotubes (31; 32; 33). The process, shown schematically in Figure 2.3, allows continuous spinning of fibres with diameters of 10 – 100 μm at rates of ~ 1 m/min.

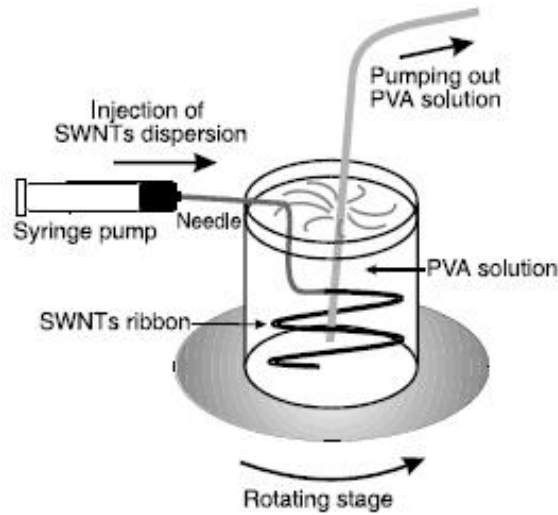


Figure 2.3: Schematic of the process for making CNT/polymer fibres by coagulation spinning. Schematic from reference (31)

The properties of the CNT/polymer fibres made by this method depend strongly upon the formation of semi-crystalline polymer domains during fibre spinning or as a consequence of post-spin treatments. When the polymer is mainly amorphous, the fibres exhibit outstanding values of toughness in tension

2.3 Production of Carbon Nanotube Fibres

through the combined effect of the nanotubes' strength and the tensile elongation of the amorphous polymer domains (32). If, on the other hand, the fibre is hot-stretched after spinning, semi-crystalline polymer domains parallel to the fibre axis are formed, increasing the fibre's strength and stiffness, although reducing its toughness (34).

While the CNT/polymer fibres produced by the coagulation-spinning route show high values of toughness, their strength and stiffness are lower than those of highly-drawn pure polymer fibres and of CNT fibres spun by different methods and made of longer nanotubes. Thus, it remains to be investigated if the high strength and stiffness of CNTs can be further exploited in fibres spun by this technique.

2.3.2 Liquid-Crystalline Spinning

In adequate concentrations, CNTs form lyotropic liquid crystalline dispersions in superacids (35) and in ethylene glycol (36), which can be injected into a coagulation bath and continuously spun as a CNT fibre (37), similarly to the spinning process in conventional rodlike polymer fibres such as poly-(p-phenylene benzo-bisthiazole) (PBO) fibres. A schematic of the process is presented in Figure 2.4, which shows the essential similarity with coagulation-spinning of CNT/polymer fibres.

In this method, the alignment of nanotubes in the lyotropic liquid crystal phase enables spinning the dispersion as a pure CNT fibre without the use of surfactants or a polymer. The process results in fibres with diameters of 50 – 100 μm with a high degree of orientation of nanotubes in the fibres, reminiscent of the alignment in the liquid crystal phase. However, the formation of a lyotropic nematic liquid crystal phase limits the length of the nanotubes that can be spun into a fibre to 1 – 100 μm . The combination of short tubes and high degree of alignment give the fibre spun by the liquid crystal route low tensile strengths of only ~ 0.2 GPa/SG, but with high stiffness of 110 – 140 GPa/SG (35; 36). Their electrical conductivity is in the range of $3 \times 10^4 - 4 \times 10^5$ S/m (36; 38) and their thermal conductivity is 20 W/mK along the fibre axis (38). Future

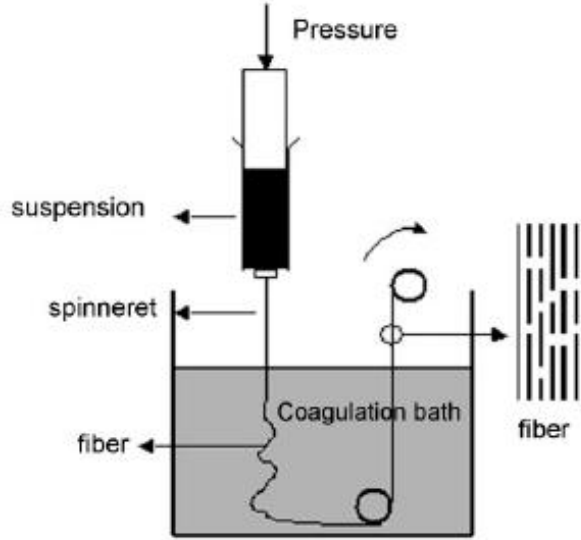


Figure 2.4: Schematic of the process for spinning CNT fibres from a lyotropic liquid crystal dispersion of nanotubes. Schematic from reference (36)

developments of this spinning method are likely to focus on spinning fibres made of longer nanotubes.

2.3.3 Spinning From Arrays of Aligned CNTs

Adjacent nanotubes in highly-aligned arrays grown on a substrate can be drawn to form a CNT fibre due to van der Waals forces between them (39). This process usually involves imparting a high level of twist on the material as it is drawn from the array to increase its density and improve the interaction between its elements, somewhat analogous to the process for spinning staple fibre. Typical fibre diameters range from 1 to 10 μm . A SEM image showing a fibre being drawn from a CNT array and twisted is presented in Figure 2.5

The tensile properties of the fibres made by this method have improved considerably since the process was first developed (39), most notably through the synthesis of longer nanotubes (40). However, the type of nanotube also appears to play a role in the mechanical properties of the fibre, with CNTs having fewer

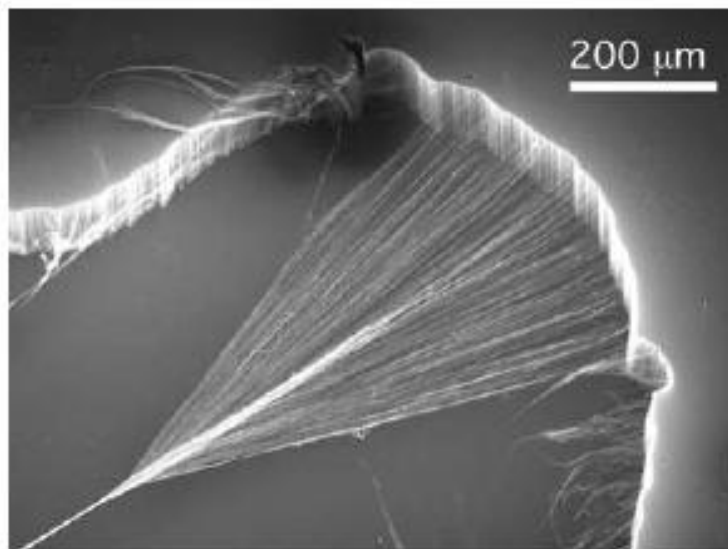


Figure 2.5: SEM image showing the process of spinning and twisting a CNT fibre from an array of aligned MWNTs grown on a substrate. Schematic from reference (39).

layers and larger diameters resulting in higher values of strength and stiffness and thus being favoured so far (40). Comparison of CNT fibres spun from arrays of nanotubes with the same length but different number of layers indicates strengths and stiffnesses of 0.2 – 0.5 GPa and 6 – 38 GPa, respectively, for 1 mm-long MWNTs fibres (41), while for fibres of 1 mm-long DWNTs probably collapsed, these values are 1.3 – 3.3 GPa and 100 – 263 GPa (40). The comparison is not made in specific units, as the density of the fibres is not reported, but nevertheless, the differences are expected to hold in specific units on account of the larger linear density of MWNTs.

The electrical conductivity of fibres drawn from arrays of aligned nanotubes has also benefited from recent process improvements, increasing from 3×10^4 S/m (39) to 8×10^5 S/m (41; 42), with no indication of a dependence on the number of layers within the nanotubes. Their thermal conductivity has been measured as 50 W/mK (43).

This route for CNT fibre spinning puts special requirements on the aligned

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CNT arrays from which the fibre is spun, in terms of the density of nanotubes in the substrate, the spacing between them and their degree of interaction and often implies that the window of synthesis conditions is narrow. If future developments lead to higher flexibility in the synthesis stage that allow growth of even longer CNTs of the double or single wall type, further improvements in tensile properties can be expected.

2.3.4 Direct Spinning from the Gas Phase

Carbon nanotubes can be directly spun from the gas phase during CVD. The process is based on synthesis conditions different from conventional CVD through the addition of sulphur and hydrogen and the high temperature ($> 1000^{\circ}\text{C}$) in the reactor. This produces exceptionally fast growth of long (length of millimetres) nanotubes in the gas phase which associate into larger objects through entanglements (44; 45) and can be spun continuously as a CNT fibre (46) at rates of 10 – 70 m/min. The assembly of nanotubes starts by drawing the mass of entangled CNTs, termed ‘aerogel’, from the reactor and is completed on-line via interaction of the fibrous material with liquid (47), which produces a dense fibre that can be wound on a reel. A schematic of the complete fibre spinning process is shown in Figure 2.6.

One of the main differences between this and other methods for making CNT fibres is that by spinning nanotubes directly from the gas phase, the process for making a CNT fibre can be completed in one stage. This does not mean that the nanotubes do not have to fulfill additional requirements for fibre spinning, as occurs in the other methods; however, it does not put a limit on the length of the nanotubes, one of the factors which determines the tensile properties of the fibre (Section 7.1).

The structure, properties and treatments of CNT fibres made by this method are the main subject of this thesis.

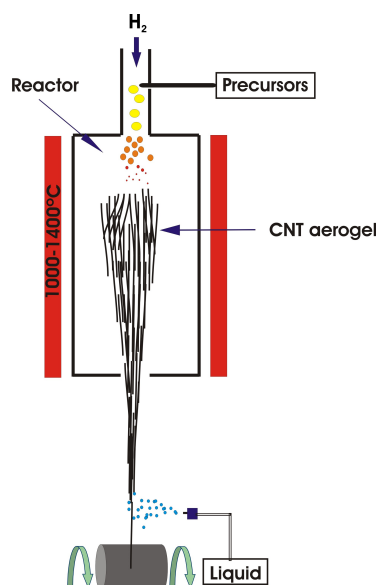


Figure 2.6: Schematic of the process for spinning CNT fibres directly from the gas phase during CVD.

2.4 Summary

Carbon nanotubes possess properties in close relation to those of graphite. Their outstanding axial strength, stiffness, and electrical and thermal properties are similar to those of graphite in the basal plane; however, the weak interaction between layers in adjacent nanotubes and in multilayered CNTs, also similar to that between layers in graphite, suggests that the properties of nanotubes can be exploited in macroscopic materials by maximising the contribution of the axial component of the physical properties of the tubes.

Their predominantly one-dimensional shape and anisotropic properties suggest that the assembly of CNTs into fibres is an optimal route for exploiting their properties. Currently existing strategies for spinning CNT-based fibres consists of wet-spinning of CNT/polymer fibres (31), wet-spinning from lyotropic suspensions (37), spinning from highly aligned CNT arrays (39) and by direct spinning of a CNT aerogel from the gas phase during CVD (46). The fibres produced by these methods have properties that take advantage of those of their CNT building blocks, however, they require further development to better exploit the axial

properties of nanotubes, particularly through the use of longer CNTs.

Chapter 3

Experimental Techniques

Specific details of the instruments, experimental parameters and techniques used in the empirical results referred to in this thesis, are discussed here.

3.1 Synthesis and Spinning Parameters

The fibre samples discussed in this report were produced from a liquid feedstock of 1.8/0.25/97.95 wt.% ferrocene/thiophene/ethanol, injected into the reactor at rates of typically 6ml/h with a Gibson liquid-chromatography pump, except where the actual synthesis of CNT fibres was the subject of study. In most cases, a hydrogen flow rate of ~ 2.5 L/min and a reactor temperature of 1300°C were used. The CNT aerogel was drawn initially from the reactor using a metal rod as a cold finger and subsequently attached to a winder. Winding rates ranged from 5 to 70 m/min. The fibres were produced under conditions that ensured continuous fibre spinning and uniformity of the product. A team of two people was required to complete the fibre spinning process. The fibre samples in this work were produced with the individual assistance of K. Koziol, A. Moisala, M. Motta and M. Pick.

3.2 Linear Density and Other Gravimetric Measurements

Gravimetric measurements of fibres were carried out with a Sartorius sub-micro balance with weight resolution of $0.1 \mu\text{g}$. The linear density of a sample was determined by taking several sections of fibre from a reel, typically 30 – 50 cm, measuring their length and separately weighing them on the balance. The average of individual linear density values was taken as an estimate of the nominal linear density of the fibre batch sample on the reel.

Prior to tensile tests, the linear density of each 20 mm sample was determined with a Textechno Favimat instrument by measuring the resonance frequency of oscillation of the fibre under tension, which can be related to its linear density ρ_l by

$$\rho_l = \frac{T}{4l^2 f^2} \quad (3.1)$$

where T is the tension applied to the fibre, l , its length and f its frequency of oscillation under tension (48). The linear density of lengths of fibre shorter than 10 mm was out of the range of the instrument and was therefore assumed to be equal to the nominal density from gravimetric measurements, although it was still compared with acoustic measurements in order to rule out the possibility of large variations over short lengths.

3.3 Thermogravimetric Analysis

The thermal stability of CNTs and their impurities has been under study for several years (49; 50; 51). Being composed mostly of carbon, the material lends itself to thermogravimetric analysis (TGA). Typically, the measurements are carried out in air or in an oxygen-rich atmosphere, so as to identify the different carbonaceous species in the sample by recording the mass-loss associated with the temperature at which they oxidise. In most cases, several decomposition peaks are readily separable and the fraction of CNTs, amorphous carbon and catalyst can therefore be determined.

The thermogravimetric measurements in this thesis were carried out using a TA Instruments Q500 TGA by recording the weight of a sample as its temperature was raised according to a predefined protocol. A minimum of approximately 5 mg was used in most experiments which, in the case of pure CNT fibres, consisted of a skein with approximately 100 m of fibre. Constant heating ramps of 1 – 10°C were used for all of the experiments. The position and mass loss associated to different decomposition peaks was obtained from fitting a curve of the derivative of mass with respect to temperature.

3.4 Electron Microscopy

Electron microscopy permits imaging of a material's microstructure at very high magnifications through the use of an electron beam focused with magnetic lenses and shone at the surface of the specimen. In scanning mode, the interaction of the electron beam with the sample produces scattering of secondary electrons from atoms in the sample and also causes electrons in the beam to be back-scattered from the sample after collision with atoms in the material, both events occurring mostly on the surface of the sample. These electrons can be detected separately and transformed into magnified images of the sample in secondary (SE) and backscattering (BS) modes, respectively. In SE mode, a detailed representation of the surface of a sample can be obtained; therefore, most scanning electron microscopy (SEM) images showing the morphology of a material are taken in this mode. In BS mode, the intensity of back-scattered electrons is proportional to the atomic number of the element involved in the electron collision, therefore, this mode is usually employed to image compositional differences in a sample, observed as intensity variations in the image of the material. Further elemental analysis can be carried out using energy-dispersive X-ray spectroscopy (EDS) by measuring the energy of photons emitted after scattering off atoms in the sample, which corresponds to energy transitions in the atoms in the material.

In transmission mode, electron beam energies 10 – 100 times higher than in scanning mode are used, which, in combination with the use of a thin specimen results in electrons being transmitted through the material. After interacting with the sample, the electron beam is magnified and focused to provide an image

of the structure of the material, in a manner which is conceptually similar to the acquisition of an optical image with an optical microscope in transmission mode.

For this thesis, CNT fibres were imaged using JEOL 6340F FEGSEM, 5800 SEM and 820 SEM microscopes, using typical acceleration voltages of 5 kV and 15 kV in SE and BS, respectively. Composite specimens were coated with platinum for 30 s in a sputter coater prior to SEM examination. The transmission electron microscope (TEM) instruments used were JEOL 200 CX and 2000 FX and Tecnai F20 FEGTEM.

Fibre diameter was determined by image analysis of SEM micrographs using Image J software application. Photoshop software was used to correct brightness and contrast in most SEM and TEM images.

3.5 Raman Spectroscopy

Raman spectroscopy is a characterisation technique based on inelastic scattering of light from materials and related to different vibrational modes of their atoms. Since it involves light in the visible range, only atoms on or near the surface of the material are excited and therefore, in most cases, Raman spectroscopy is only a surface characterisation technique. As Raman modes originate from scattering from atomic vibrational modes of oscillation, they are susceptible to frequency changes due to thermal variations, pressure and stress in the molecule, all of which translate as shifts in the position of the Raman peaks. A detailed discussion of the principles of this technique can be found in reference (52).

The main Raman-active vibrational modes in CNTs give rise to peaks at $\sim 1320\text{ cm}^{-1}$, 1580 cm^{-1} and $\sim 2635\text{ cm}^{-1}$, labelled D, G and 2D, respectively; although each effectively consists of a superposition of several peaks related to specific characteristics of the material (53). The first peak is associated with impurities in the form of sp^3 bonds and poor graphitisation and is referred to as the ‘disorder’ peak (D). The G peak originates from the tangential vibration of C atoms in a hexagonal lattice and is indicative of the degree of graphitisation in the material. It is common practice to evaluate the purity of a graphitic material as the ratio of the intensities of these peaks (I_D/I_G). The 2D peak, sometimes also referred to as G’, is a second order peak related to the D peak, although

not directly related to poor graphitisation in the material in the same way. It is, however, affected by the interaction between stacked graphene layers and by the termination of the layers (54; 55).

SWNTs and tubes with few walls show an additional Raman active mode associated with the radial expansion/contraction of the nanotube, referred to as radial breathing mode (RBM) and, typically, found in the range $70 - 400 \text{ cm}^{-1}$. It holds a special relation with the electronic band structure of the tubes, which allows estimation of the tube diameter from the Raman shift of the RBM peak (ω) (56). For nanotubes with diameters greater than 1 nm the diameter is obtained as

$$\Phi = \frac{234}{\omega - 10} \quad (3.2)$$

The interaction of carbon nanotubes with light in the visible range, as generally used in Raman spectroscopy, is highly susceptible to polarisation effects (57). Carbon nanotubes can behave as antennas due to their high aspect ratio, suppressing absorption and emission of light polarised perpendicular to the tube axis and giving the highest intensity for polarisation along the tube axis (58). For a system of preferentially-oriented nanotubes, as could be in a CNT fibre, polarisation effects are of great importance and can be used to measure the degree of orientation of the nanotubes in the sample. Typically, a measure of orientation is obtained from the distribution of intensities of the G band at different angles between the sample and the polarisation direction of the laser source (59), although often only intensities parallel and perpendicular to the laser polarisation direction are measured for the purposes of efficiency.

Axial strain in nanotubes and similar materials can be related to the resulting shift in Raman frequencies according to experimentally-determined coefficients. Reported values of Raman frequency change with applied strain for SWNTs, vapour-grown carbon fibres (VGCFs) and high-modulus carbon fibres are presented in Table 3.1. These values are specific to the materials shown in the table and not all of them are necessarily representative of the nanotubes in the CNT fibres used in this study. Of the values in the table, those in rows 4 and 5 are not representative of the CNT fibres, the first on account of the fact that most

3.5 Raman Spectroscopy

Raman active tubes detected experimentally are parallel to the polarisation direction and the second because the stiffness of the tubes is closer to that of the stiffer carbon fibre (row 6). Additionally, since the fibre is composed of both metallic and semiconducting tubes, a weighted average is calculated from rows 1 and 2. As a first approximation, the ratio of metallic to semiconducting tubes is assumed to be 1:2, although their proportion in the fibre and their contribution to the G band might be possibly different from this ratio. Furthermore, because the G^- peak is not as well defined as the G^+ in CNT fibres, only the values corresponding to the latter values are considered.

Table 3.1: Raman frequency shift with applied strain($\text{cm}^{-1}/\%$)

Material	D	G^-	G^+	2D	Reference
Semiconducting SWNT	20.5	11.7	16.7	37.3	(60)
Metallic SWNT	10.7	4.1	-0.4	25	(60)
VGCF (parallel)	-	-	30	-	(61)
VGCF (perpendicular)	-	-	8	-	(61)
CF ($E = 500\text{GPa}$)	-	-	7.5	-	(62)
CF ($E = 750\text{GPa}$)	-	-	12	-	(62)

Thus, in the context of CNT fibres, three possibilities of coefficients relating shift in Raman frequency to nanotube strain are proposed: the first assuming that all tubes are SWNTs, the second that they behave as a VGCF and the third as a high-modulus carbon fibre. These values of Raman shift per nanotube strain are presented in Table 3.2 and are used later in the present study to calculate nanotube strain from Raman measurements on CNT fibres.

Table 3.2: Reference values of Raman shift/nanotube strain for CNTs in fibres ($\text{cm}^{-1}/\%$)

Assumption	D	G	2D
SWNT	17.6	11.6	33.6
VGCF (parallel)	-	30	-
CF ($E = 750\text{GPa}$)	-	12	-

Raman spectroscopy measurements were performed with Renishaw Raman-scopes, using laser lines of 584 nm, 633 nm and 785 nm. Unless otherwise stated, the fibre was oriented parallel to the polarisation direction of the laser. Raman spectra were processed using the Renishaw WIRE 2.0 software application, using a multi-peak Gaussian fit.

3.6 X-ray Diffraction

X-ray diffraction (XRD) is a characterisation technique based on the interaction of light of wavelength λ comparable to the size of atoms, with the crystallographic planes of a material in accordance with Bragg's law,

$$n\lambda = 2d\sin\theta \quad (3.3)$$

where n is an integer, d the spacing between planes in the atomic lattice and θ the scattering vector. This allows for determination of the composition of a material through its crystal structure and provides information on the orientation of the crystals in the sample. In wide angle X-ray scattering (WAXS) mode, diffraction occurs from interatomic planes separated by distances of the order of angstroms and thus it is related to the crystal structure of the material in terms of atomic positions. Small-angle X-ray scattering (SAXS) occurs when larger entities diffract the X-rays and is associated with the degree of order in the structure typically in the range of 5 – 50 nm.

The crystallographic structure of nanotubes is similar to that of graphite. The stack of graphene layers in a nanotube and between layers of adjacent tubes give rise to the 002 reflection, corresponding to a d-spacing of around 0.34 nm similar to that observed between basal planes in turbostratic graphite and which can be used to measure the orientation of nanotubes in a sample. Other, lower intensity reflections from nanotubes correspond to the 100 and 101 planes, also reminiscent of their graphitic structure.

In the context of CNT fibres, X-ray diffraction provides valuable information on the structure of fibres not available with other techniques. Unlike Raman spectroscopy, XRD is not a surface analysis technique and can cover the whole

volume of a fibre, provided it has a high degree of order. The main characteristics that can be observed by XRD are the orientation and separation of CNTs and the composition of the residual catalyst particles. Moreover, the use of synchrotron radiation and a micro-beam diameter makes it possible to analyse the homogeneity across and along single fibre filaments in terms of their composition and CNT orientation.

XRD can be combined with X-ray fluorescence (XF) measurements. This technique is based on X-rays causing electronic transitions between inner and higher orbitals of atoms in the sample, which result in photons with energy characteristic of the atom being emitted from the sample, thus enabling the identification of particular elements in the material.

The XRD results presented in this thesis correspond to measurements in transmission mode. The majority were performed at the ID13 beamline of the European Synchrotron Research Facility (ESRF). The beamline was configured with a monochromatic beam, focused using a pair of KB-mirrors at a wavelength of 0.098 nm. A pre-calibrated on-axis Olympus microscope was used to position the sample at the focal spot and supported on a magnetic stage which allowed orthogonal x/y/z scans with sub-micron resolution. Individual measurements corresponded to exposure times of 1 – 20 s. Identical measurements were performed beside the fibres for background correction. The sample-to-detector distance was calibrated with corundum powder. A small number of measurements were made with a Bruker Nanostar diffractometer with a CuK_α radiation source (0.154 nm), at 40 kV and 40 mA with fibre exposure times of 3 – 8 hrs. Silver behenate was used for calibration of these measurements.

Data were analysed using the FIT2D and Bruker software applications in combination with conventional mathematical packages (Matlab, Origin, and Microsoft Excel).

3.7 Mechanical Tests

Tensile tests were performed using a Texttechno Favimat tensile tester with a 2N induction load cell. Samples were mounted vertically between two pairs of rubber grips closed by an adjustable-force spring. Grip-induced breakages were

prevented by polishing the grip faces with fine-grade silicon carbide paper and adjusting the alignment and force between grips. A strain rate of 10 %/min and a small pretension of ~ 6 MPa/SG to avoid fibre slack were used for all the tests. Except otherwise indicated, fibre length of 20 mm was used for all tensile tests. For tests of short gauge lengths (< 5 mm), fibre strain was corrected for grip strain. The stress-strain measurements on twisted fibres were performed by K. S. C. Heritage as part of an undergraduate research project.

Specific stress was calculated from force and linear density measurements and expressed in GPa/SG. This unit is numerically equivalent to N/tex, a unit preferred in the fibre industry, with tex being the fibre linear density in grams per kilometre. Stiffness was calculated from the steepest part of the stress-strain curve, typically in the range of 0.2 – 0.7 % fibre elongation.

The mechanical properties of composites in tension and compression were measured with an ESH servo-hydraulic machine and a Hounsfield single-column tester. The cross-sectional area of the specimens was determined with a Vernier calliper and their volume obtained by the archimedian principle.

3.8 Liquid Densification

Optical micrographs during the interaction of CNT fibres with liquids were collected with a KSV CAM200 system at a frame rate of 80 ms^{-1} as a drop of liquid at the end of a syringe was brought in contact with the fibre.

On-line fibre densification with liquid was carried out with acetone atomised with stainless steel Spray System nozzles. The acetone spray was directed to the fibre before it was wound on a reel and allowed to evaporate before fibre collection.

3.9 Electrical Measurements

Contacts for electrical measurements on CNT fibres were carried out by two methods. The first involved spreading silver paint on the fibre surface and letting the solvent evaporate for approximately one hour. The second consisted of soldering metal around the fibre surface by forcing the contact of low-temperature molten

solder with the fibre, followed by rapid cooling of the metal/fibre interface. Virtually identical values of electrical resistance were obtained by two- and four-point measurements. A number of experiments were carried out to evaluate the interaction between different solders and CNT fibres. These experiments were performed with a MUST Wilhelmy balance, at The Welding Institute (TWI) .

3.10 Thermal Measurements

The thermal conductivity of an array of CNT fibres and of CNT fibre/epoxy composites were determined using the Angstrom method (63). In this technique, a periodic temperature wave is induced in the specimen through a periodic heat flow source. The amplitude and phase of the temperature wave along the sample can be related to its thermal conductivity (K) by

$$K = \rho C_P \frac{(x_1 - x_2)^2}{2\delta \ln(T_1/T_2)} \quad (3.4)$$

where ρ is the volumetric density of the sample, C_P its specific heat capacity, $x_i - x_j$ the distance between measuring points i and j along the specimen, δ the phase lag between i and j and T_i the temperature wave amplitude.

Thermal measurements were performed with a FLIR SC 3000 thermal imager, which allowed continuous temperature recording and accurate determination of the distance between measurement points. The heat source used was a resistor attached to a variable DC/AC power supply, which was operated in the frequency range 1 – 100 mHz.

The coefficient of thermal expansion (CTE) of composites was measured with a Netzsch dilatometer in cooling and heating modes from -10°C to 60°C . The CTE of the fibres in the composites was determined using equation

$$\alpha_c = \frac{E_f \alpha_f V_f + E_m \alpha_m (1 - V_f)}{E_f V_f + E_m (1 - V_f)} \quad (3.5)$$

where the subscripts f , m and c refer to fibre, matrix and composite, respectively; E_x is the elastic modulus, V_f the fibre volume fraction and α_c the coefficient of thermal expansion (64). Volume fractions and elastic moduli were determined experimentally from TGA and tensile measurements, respectively.

3.11 Post-Spin Treatments

CNT fibres were annealed at low temperatures ($< 500^{\circ}\text{C}$) in a quartz tube in a furnace, using argon as a carrier gas. Prior to the treatment, the samples were mounted on alumina substrates and attached at both ends using a ceramic adhesive, cured at 100°C in an oven for 2 – 4 hrs.

For high temperature ($> 1000^{\circ}\text{C}$) annealing, the samples were also fixed to ceramic substrates following the same procedure. In this case, however, the heat treatment was carried out in a graphite furnace with an argon atmosphere. A heating ramp of 25°C was used for all of these experiments.

Laser experiments were conducted using a Gaussian CO laser with wavelength of $1\text{ }\mu\text{m}$. During irradiation, the samples were enclosed in a chamber with constant argon flow to avoid oxidation of the material. Temperature was recorded with a dual-wavelength pyrometer with spot size of $\sim 100\text{ }\mu\text{m}$ and a temperature measuring range from 300 – 2000°C . The laser was operated by Dr. A. Khan.

Chapter 4

Synthesis and Spinning of CNT Fibres

4.1 Introduction

In the first stage of CNT fibre spinning, nanotubes are synthesised by floating-catalyst chemical vapour deposition of a mixture containing iron, sulphur and a carbon source in a hydrogen atmosphere. The parameters of the reaction are somewhat similar to those used in common CVD nanotube growth and in the synthesis of vapour grown carbon fibres (65), the difference being that the combination of parameters used in the present study produce a very high nanotube growth rate and nanotube lengths in the range of millimetres (44; 45). This results in nanotubes associating and forming an aerogel that can be drawn from the reactor as a fibre (46). A schematic of the process is presented in Figure 2.6, showing the synthesis and drawing stages.

The parameters in the CVD reaction play a second fundamental role in fibre spinning, by determining the degree of entanglement of nanotubes in the aerogel and thus, the rate at which the fibres can be spun, similar to the role of polymer concentration in liquid-spinning of polymer fibres (66). This means that the quality of the product of the reaction is often compromised in order to achieve conditions under which a CNT fibre can be spun continuously.

4.2 The Chemical Vapour Deposition Reaction

In CNT fibre spinning, nanotubes are synthesised by CVD using iron as a catalyst, sulphur as an agent for growth enhancement, a source of carbon to form the nanotubes, and hydrogen as a carrier gas. The process is typically carried out by injecting a solution of ferrocene (iron source) and thiophene (sulphur source) in ethanol (carbon source) into a hydrogen-filled reactor at $1000 - 1350^{\circ}\text{C}$, although different choices of precursors and routes for introducing them in the reactor are also available.

The precise concentration of precursors in the reactor is fundamental for growing the maximum number of long nanotubes and to avoid the formation of other unwanted carbonaceous species. The proportions of carbon, iron, sulphur and hydrogen in the reactor are interlinked and finely tuned to synthesise nanotubes for continuous fibre spinning (67).

4.2.1 Iron Catalyst

Iron plays the role of the catalyst in the reaction and must be present in the correct concentration and particle size to enable nanotube nucleation. If the ratio of catalyst particles is too high, they tend to coalesce and catalyse the growth of poorly-graphitised tubules of large diameter, an example of which is shown in Figure 4.1. If, however, the ratio of iron to carbon atoms is too low, a fraction of the carbon species do not reach catalyst sites and form carbon particles instead of nanotubes and, even though enough nanotubes may still grow to form an aerogel, the ability to draw it is limited and the properties of the fibre poor. This implies that the concentration of iron is not dictated solely by the purity of the nanotubes synthesised, but also by the degree to which the resulting material can be drawn continuously as a fibre.

4.2.2 Sulphur

The addition of sulphur to the CVD reaction represents the most significant difference between the synthesis process used in the present study and more conventional CVD CNT growth processes. In adequate proportion relative to

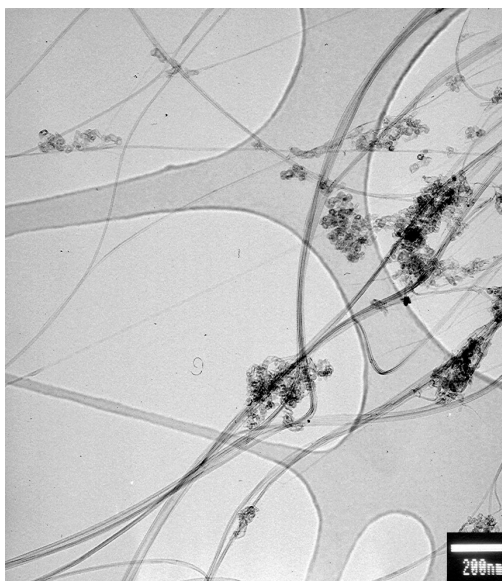


Figure 4.1: TEM image showing aggregates of particulates grown from large catalyst particles during CVD in CNT fibre spinning.

iron and carbon, sulphur enhances the catalytic activity of the iron particles and the carbon on their surface (68), which results in CNT growth rates of $0.1 - 1$ mm/s and CNT lengths of ~ 1.5 mm (69), whereas in standard CVD growth of millimetre-long nanotubes requires tens of minutes. At high temperatures, the presence of sulphur on the surface of catalyst particles also results in nanotubes with a few layers and with unusually large diameters, which autocollapse (70) and maximise their interface with adjacent nanotubes, with beneficial implications for stress transfer in the fibre (Section 7.1).

Sulphur is essential to this CNT fibre spinning process as it promotes the growth of long nanotubes at very fast rates relative to other methods, characteristics which cause them to entangle in the gas phase and form an aerogel which can then be drawn as a fibre; however, this occurs only if the amount of sulphur is balanced relative to the iron and carbon in the reaction (69). As the concentration of sulphur is decreased, CNT growth also decreases, making fibre spinning increasingly difficult and eventually impossible. Similarly, excess sulphur in the reaction decreases nanotube growth by poisoning the catalyst particles.

4.2.3 Carbon Source

The choice of a carbon source precursor for continuous spinning of a CNT fibre is relatively flexible, although the properties of the fibre do vary for different sources. Adjustments in other reaction parameters must be made for different carbon sources, to couple the decomposition route of the carbon source with the formation of iron particles of the right size to produce nanotube growth. Additionally, when the precursors are injected into the reactor as a liquid, the solubility of thiophene and ferrocene in the carbon source must be taken into account.

Table 4.1: Properties and synthesis conditions of CNT fibres

	Hexane	Ethanol
I_D/I_G	0.08	0.07
Strength (GPa/SG)	0.2	1.0
Stiffness (GPa/SG)	10	50
Ferrocene, thiophene, C-source (wt.%)	3.5, 1.8, 94.7	1.3, 0.25, 98.45
Temperature (°C)	1150	1350

The formation of a CNT aerogel that can be spun as a fibre is only part of the requirements on the carbon source. The precursor must also enable synthesis of nanotubes that form a fibre with desired physical properties, such as high strength and stiffness. Thus, while it is possible to spin CNT fibres from different hydrocarbon or alcohol precursors, for example, the properties of the resulting fibre will usually differ. Table 4.1 presents a comparison of properties of fibres made from hexane and ethanol, wound at the same rate and synthesised under conditions optimised for fibre strength in both cases. The Raman spectra of both fibres are very similar and do not suggest that they are made of a different type of nanotubes. Furthermore, the ratio of the D relative to G bands is almost identical, suggesting that the presence of carbonaceous impurities is comparable in both materials. However, the strength and stiffness of the fibre made from ethanol is greater by a factor of 5, which indicates that the fibres have important structural differences, which may be related to the length of the nanotubes.

4.2.4 Hydrogen

The carrier gas in the reaction not only provides an inert atmosphere to avoid carbon oxidation, but also plays an active role in the synthesis of nanotubes. Throughout the decomposition route of the carbon source, hydrogen facilitates the formation of intermediate carbon-containing species that subsequently take part in the catalysed growth of nanotubes. If, for example, the CNT fibre synthesis process is carried out in argon, which is not expected to play an active role in CNT growth, only soot consisting of large carbon particles is formed, rather than nanotubes. Figure 4.2 presents SEM micrographs of fibres made under identical synthesis conditions except for the composition of the carrier gas, in one case hydrogen (A) and a mixture of 20/80 vol. argon/hydrogen in the other (B). The images show the presence of large particles in the fibre made under the gas mixture.

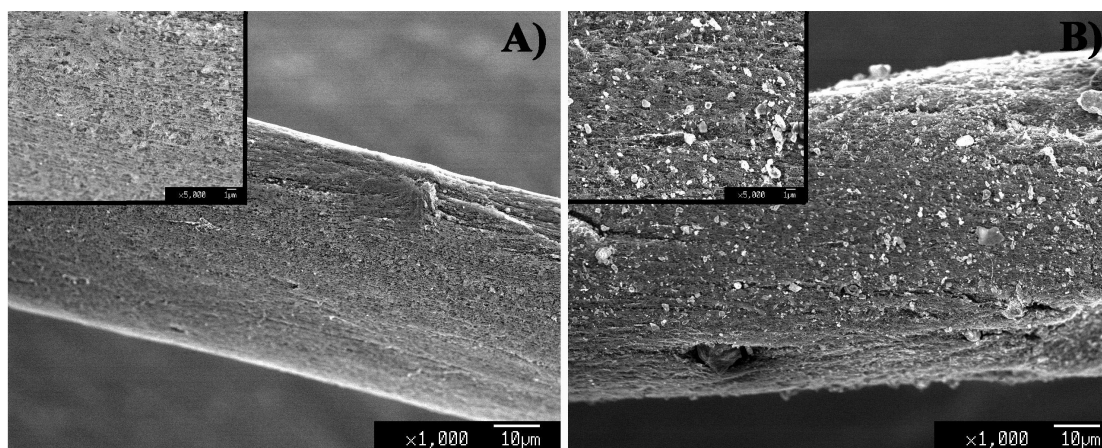


Figure 4.2: SEM micrographs of CNT fibres produced in hydrogen (A) and in a mixture of 20/80 vol. argon/hydrogen (B). Large carbon impurity particles are produced in the presence of argon instead of hydrogen.

4.3 Secondary Parameters Affecting Drawing of the CNT Aerogel

The ability to spin a CNT fibre from the gas phase relies upon the mechanical properties of the aerogel which in turn, are based on the parameters selected for the CVD reaction. As a first approximation, this dependence can be analysed by measuring the maximum rate at which the aerogel can be drawn from the reactor as the reaction parameters are varied. Note that in the fibre spinning process discussed in this work, the drawing rate is equivalent to the rate at which the material is wound as a fibre, and therefore, these terms are used interchangeably.

4.3.1 Gas Flow Rate

Figure 4.3 presents a plot of maximum drawing rate as a function of gas flow rate in the reactor for two different precursor mixtures, one containing ethanol and the other hexane as the carbon source. This shows that for both mixtures, maximum aerogel drawing rate increases with gas flow rate and that the hexane mixture results in higher drawing rates, under the synthesis conditions used in these experiments. However, it is uncertain if the differences between the two curves are indicative of differences in nanotube concentration or of the length of the nanotubes.

A similar plot is presented in Figure 4.4, showing the effect of gas flow rate upon an aerogel formed from the same precursor mixture, but this time using two different feed rates. For both throughputs, the maximum aerogel drawing rate increases monotonically with gas flow rate, although for the higher feed rate, the degree to which the aerogel can be drawn is significantly lower.

4.3.2 Precursors Feed Rate

The rate at which the precursors are injected into the reactor also affects the properties of the CNT aerogel and hence the ability to draw it into a fibre. A plot of maximum drawing rate against precursor feed rate is presented in Figure 4.5, for a gas flow rate of 1 L/min (with a precursor mixture different from that in Figure 4.4). It can be seen that the maximum drawing rate initially increases

4.3 Secondary Parameters Affecting Drawing of the CNT Aerogel

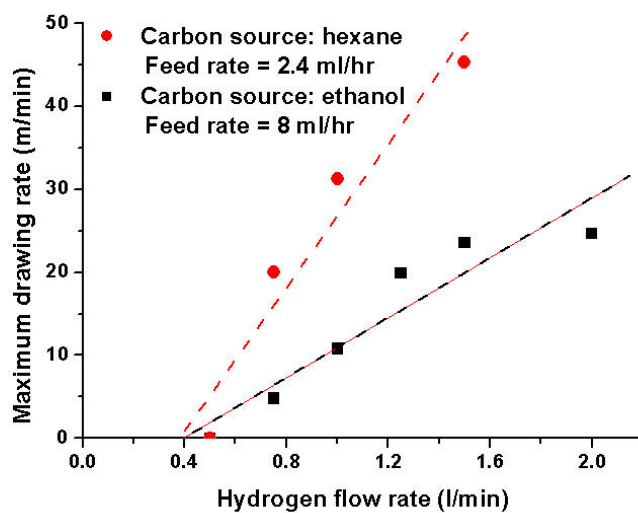


Figure 4.3: Maximum drawing rate of the CNT aerogel as a function of gas flow rate in the reactor, for ethanol and hexane carbon sources.

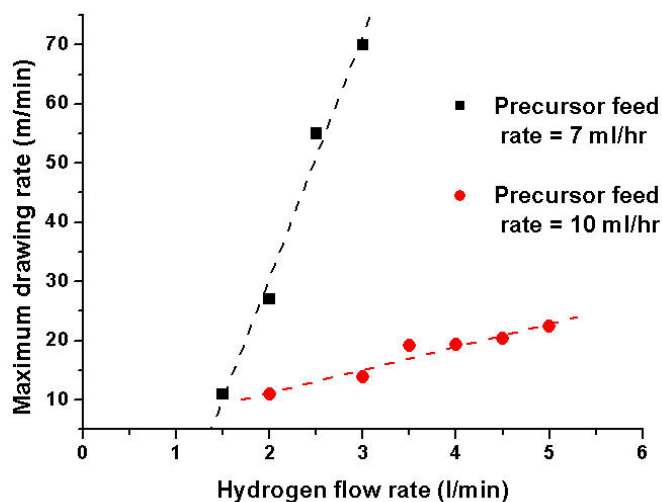


Figure 4.4: Maximum drawing rate of CNT aerogel as a function of gas flow rate in the reactor for two different feedstock injection rates.

4.3 Secondary Parameters Affecting Drawing of the CNT Aerogel

with feed rate but eventually peaks at a value dependent on the complete set of parameters in the reactor; and decreases for higher feed rates until continuous drawing of the aerogel is no longer possible.

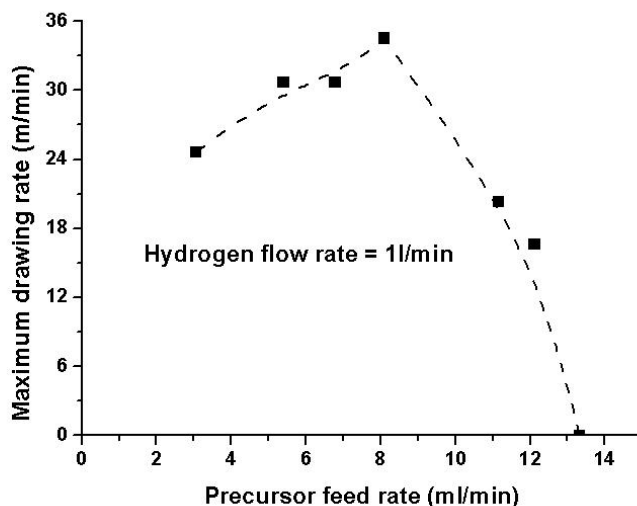


Figure 4.5: Maximum drawing rate of CNT aerogel as a function of the rate of injection of the feedstock into the reactor.

This suggests that at low feed rates, the main limitation on aerogel drawing is the concentration of nanotubes. As the feed rate increases, so does the concentration of nanotubes and, therefore, higher drawing rates are attainable. However, with increasing nanotube concentration the number of CNT entanglements in the aerogel also increases. Thus, as the feed-rate is increased, there is a point at which it reduces the maximum aerogel drawing rate. In this sense, increasing the gas flow rate appears to cause some form of dilution of nanotubes in the reactor, meaning that as higher volumes of gas are injected in the reactor, the entanglement of CNTs enables higher drawing rates of the aerogel.

The effects of the gas flow rate and precursor injection rate on the maximum fibre speed suggest that the degree to which the CNT aerogel can be drawn into a fibre depends critically on the concentration of nanotubes and their entanglement. In this respect, the process resembles liquid-spinning of polymer fibres,

in which the concentration and molecular weight of polymer in the solution are important parameters determining the entanglement of polymer chains and hence the spinning process and the ultimate properties of the resulting material (66).

4.4 Summary

In order to produce CNT fibres, CNT nanotubes are synthesised at high temperature ($> 1000^{\circ}\text{C}$) from a mixture of iron, sulphur and carbon in a hydrogen atmosphere. These synthesis conditions produce exceptionally long nanotubes at fast growth rates, causing them to entangle in the gas phase and to form an aerogel that can be drawn continuously from the reactor.

The parameters in the reaction determine not only the quality of the nanotubes but also their degree of entanglement and, thus, the ability to draw the aerogel and form a fibre. The carrier gas flow rate and the precursors feed rate are observed to affect the ability to draw the aerogel, suggesting that the concentration of nanotubes in the reactor determines the degree to which the aerogel can be drawn. Thus, it appears that there is some optimum level of entanglement in the aerogel for achieving the highest fibre winding rate, which is determined by the complete set of reaction parameters.

Overall, the synthesis of carbon nanotubes suitable for direct fibre spinning involves the precise tuning of several interlinked parameters such as the carrier gas flow, catalyst composition and concentration, precursor feed rate and hydrocarbon choice, amongst others. Clearly, in order to grow long and crystalline nanotubes, reduce the amount of impurities and form an aerogel suitable for continuous fibre spinning, a large number of parameters must be optimised. Unfortunately, the requirement of continuous spinning often means that excess catalyst is used in the synthesis reaction in order to provide sufficient aerogel strength to withstand continuous drawing at high rates. These conditions result in a fraction of the catalyst being redundant and thus becoming incorporated into the fibre as small particles (Chapter 6).

Finally, it is worth noting that the action of drawing the aerogel from the reactor is the first part of the process through which the nanotubes are assembled into a fibre. In the next chapter, the effect of the drawing rate on the orientation

and packing of nanotubes is discussed, as well as strategies for subsequently completing the CNT fibre assembly process.

Chapter 5

Fibre Assembly: Densification Treatments

The building blocks generated by the CVD reaction are assembled into a fibre, first by drawing the aerogel from the reactor, which brings nantoubes closer together and results in a semi-densified fibre. The semi-densified fibre requires further densification, which is achieved through interaction of the drawn fibre with liquid. Throughout the complete process of assembling nantoubes into a fibre by drawing and liquid-driven densification, the volumetric density of the material increases by several orders of magnitude.

Density is sometimes taken as an indirect measure of the physical properties of high-performance fibrous materials. Higher volumetric density indicates, for example, higher tensile strength and stiffness in polymer fibres due to a higher fraction of semi-crystalline domains (71) and higher thermal conductivity in carbon fibres (72) as stress transfer and the average phonon mean free path, respectively, increase with closer packing of fibre elements. This chapter considers the effects of drawing rate and liquid-densification on CNT fibre density. Throughout this thesis the terms densification and condensation are used interchangeably.

5.1 The Stages of Densification, Drawing Rate and Orientation

The first form of effective densification applied to the CNT aerogel is the drawing action itself. Drawing imparts a high degree of bundle alignment in the fibre by the resistance of the aerogel to flow against the gas, which is likely to be high because of the aerogel's high surface area and because the gas velocity in the reactor is of the order of 0.2 m/min, whilst a typical winding rate is 20 m/min. The drawing rate thus increases the fibre density from a SG of $10^{-6} - 10^{-8}$ in the aerogel form to $\sim 10^{-3}$ for the fibre immediately post-drawing.

This semi-densified diaphanous fibre is further condensed by interaction with liquid, typically acetone, resulting in a more compact fibre with specific gravity of around 1. Figure 5.1 shows a schematic of the densification process, with estimated fibre SG at different stages. Note, however, that the winding rate also affects the volumetric density of the fibre measured after liquid densification, as illustrated in Figure 5.2. With a higher drawing rate higher fibre density is obtained (47).

Fibre condensation with liquids can bring nanotubes and bundles of nanotubes within the fibre closer together, such that the interface between them is effectively increased. This association of nanotubes can be observed using XRD by inspection of the oriented component of the 002 reflection from graphene layers of neighbouring nanotubes in contact (for a discussion of XRD from CNT fibres refer to Chapter 6). Figure 5.4 shows typical diffraction patterns and the azimuthal profile from the 002 reflection for uncondensed (blue) and on-line condensed (black) fibres produced using a similar winding rate. An increase of 002 peak intensity relative to the base line for the condensed fibre is evident, which is indicative of an increase in the parallel association of nanotubes in bundles as a result of the liquid-stage densification, producing stacked graphene layers separated by a distance close to the d -spacing in turbostratic graphite. A similar increase in X-ray scattering from arrays of aligned SWNTs has been reported (73). In addition to enhanced scattering, the condensed fibre shows better alignment of nanotubes than in the uncondensed form, manifested by a smaller full-width-at-half-maximum (FWHM) of the azimuthal distribution of intensities. A higher

5.1 The Stages of Densification, Drawing Rate and Orientation

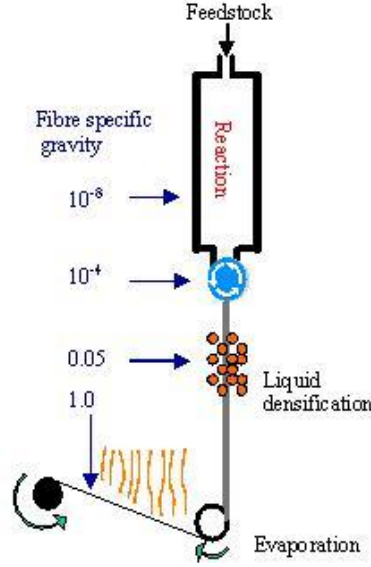


Figure 5.1: Schematic showing the specific gravity of a CNT fibre throughout the drawing process and on-line densification with liquid.

degree of nanotube alignment in CNT fibre densified by interaction with acetone is also observed by comparison of Raman spectroscopy measurements with the fibre oriented parallel and perpendicular to the laser polarisation direction, which show an increase in the ratio of the G band in parallel over perpendicular configuration of 10 – 50%, depending upon the initial orientation of the fibre. (A discussion of polarised Raman spectroscopy measurements on CNT fibres is presented in Chapter 6).

The process of drawing the aerogel affects the linear density of the resulting CNT fibre. As shown in Figure 5.2, linear density decreases with winding rate. A power fit to the data gives

$$\rho_l = 1.2 \times w^{-1.24} \quad (5.1)$$

where ρ_l is the linear density and w the winding rate. The exponent in the power law indicates that the linear density and winding rate are close to an inverse proportionality, although a larger number of data points for different winding rates are required to determine this more accurately. Assuming a constant mass

5.1 The Stages of Densification, Drawing Rate and Orientation

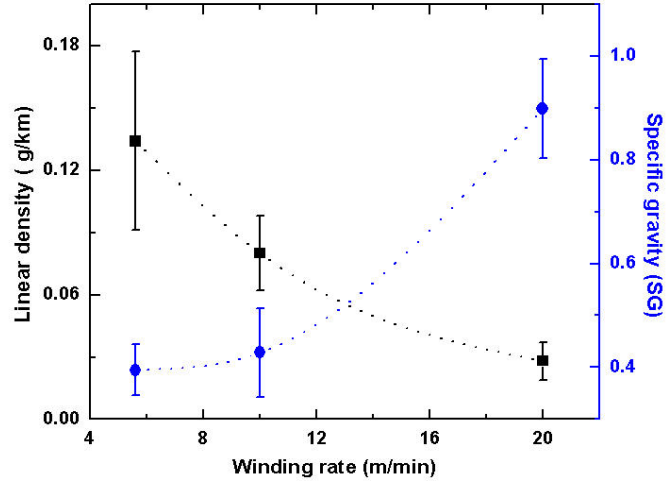


Figure 5.2: Linear and volumetric density of CNT fibres produced at different winding rates. Higher winding rates improve packing of bundles and other materials in the fibres, resulting in higher specific gravity values (Redrwan from reference (47)).

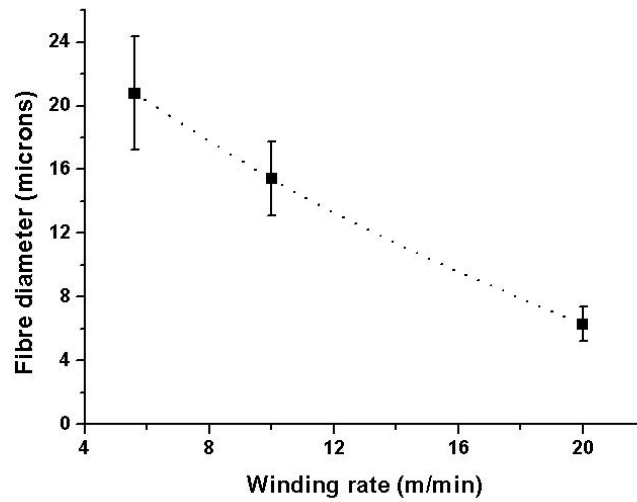


Figure 5.3: Diameter of CNT fibres produced at different winding rates.

5.1 The Stages of Densification, Drawing Rate and Orientation

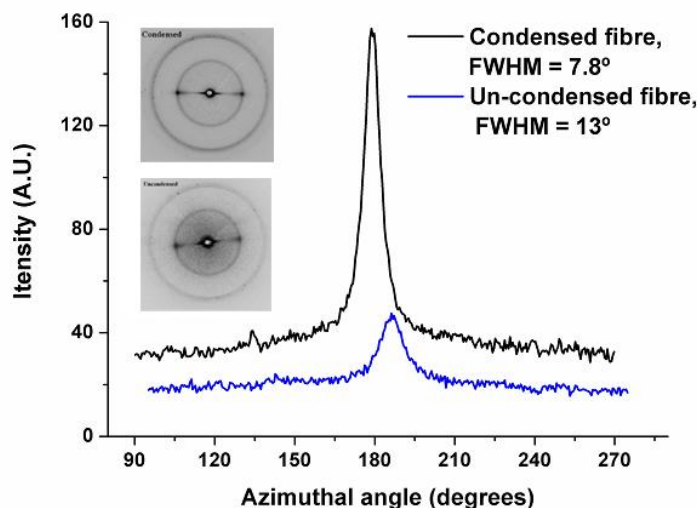


Figure 5.4: Comparison of XRD patterns of uncondensed (blue) and condensed (black) fibres and their azimuthal profiles from the 002 reflection.

flow rate in the system (corresponding to an exponent of -1), the values of linear density multiplied by the winding rate provide a measure of the yield in the conversion of the precursors to a fibre. For the data in Figure 5.2, the mass flow rate comes out as 0.7 mg/min and the yield as 2% conversion of carbon in the precursors to CNT fibre.

With increasing winding rate there is an increase in specific gravity for higher winding rates, approaching 1 for a rate of 20 m/min and indicating that higher packing efficiency is achieved at faster winding rates, however, no further significant increase in SG is observed above 20 m/min. In addition to this, as the winding rate is increased fibre diameter decreases, as shown in Figure 5.3.

The specific gravity of 0.9 for the fast winding speed (20 m/min) compares with the density of CNT fibres produced by other methods. Fibres spun from liquid crystalline suspensions of SWNTS have been shown to have specific gravity of 1.2 (37). Similarly, most reports of fibres spun from arrays of aligned arrays of MWNTs and twisted into condensed fibres give a SG of 0.8 (39).

The increase in volumetric density is the direct result of higher packing effi-

5.1 The Stages of Densification, Drawing Rate and Orientation

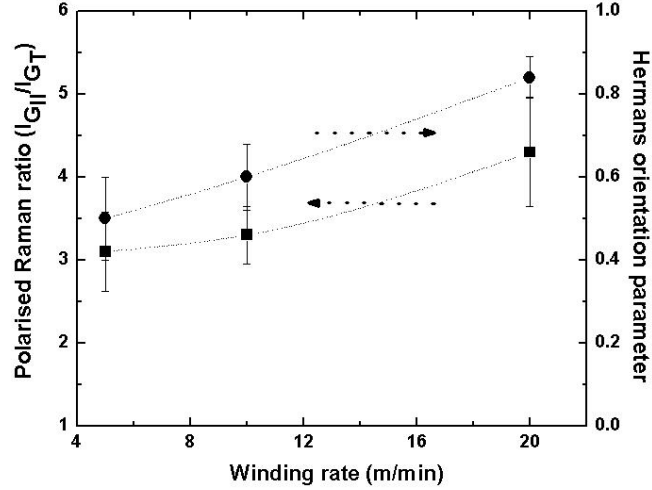


Figure 5.5: Plot of nanotube orientation with increasing winding rate, taken as the values of Hermans parameter (P_2) from SAXS and I_{Gpar}/I_{Gper} from polarised Raman spectroscopy (47).

ciency, as the degree of alignment of CNT bundles along the fibre axis increases with faster winding rates. Figure 5.5 shows a plot of the change in CNT orientation with winding rate, measured by Raman spectroscopy and small-angle XRD, again measured on the fibre after the liquid densification stage. The plot shows the change in Herman's orientation function, which takes values of 0 for no orientation and 1 for perfect orientation of the normal to the crystallographic plane perpendicular to the fibre axis (or -0.5 for perfect parallel orientation) (74), and which is equal to the second coefficient of the orientation distribution function expressed as a sum of Legendre polynomials, therefore referred to as P_2 ; as a function of winding rate. Also shown is the ratio of intensities of the Raman G band parallel and perpendicular to the polarisation direction of the laser (I_{Gpar}/I_{Gper}) as a function of winding rate. These results leave little doubt about the role of the winding rate in aligning CNT bundles; however, it should be added that CNT alignment should converge to a limit as even higher winding rates are used. However, the evidence thus far suggests that winding is disrupted by break-

age of the aerogel before this level of orientation is achieved, most likely due to the presence of impurities which limit both aerogel drawing and the alignment of CNTs.

5.2 Liquid Densification

Early studies showed that upon interaction with liquids, forests of aligned CNTs on substrates collapse into mechanically stable ‘foams’, ‘micro-needles’ and other morphologies depending on their initial structure (73; 75). A similar phenomenon has been observed for fibres based on CNTs (31; 41), which experience radial densification due to capillary forces when in contact with a liquid. Of the several methods for increasing the density of CNT assemblies, densification via liquid interaction is particularly attractive because it provides a simple way of obtaining highly packed materials. Additionally, because the time scale involved in the densification process is of the order of seconds, it can be used to densify CNT fibres continuously as they are drawn from the CVD reactor, without compromising the fibre spinning rate (76).

5.2.1 Experimental Observations of Fibre Densification

The dynamics of liquid densification of CNT fibres play an important role in CNT fibre spinning, as they enable densified fibres to be wound at fast rates as well as subsequent unwinding from the reel. In the experiments described here, the densification process is studied by forcing contact between an uncondensed fibre and a liquid droplet.

Figure 5.6 shows a series of photographic stills taken as a liquid drop of acetone on a small needle first approaches and then is brought into contact with an uncondensed fibre. Upon contact, instantaneous spreading of the liquid along the fibre occurs (Figure 5.6 (A-B)), forming a contact angle of approximately 35° between the fibre surface and the liquid meniscus. Simultaneously, as the liquid engulfs the fibre, the fibre condenses radially and its diameter decreases by a factor of 2 within a fraction of a second. After this initial violent densification,

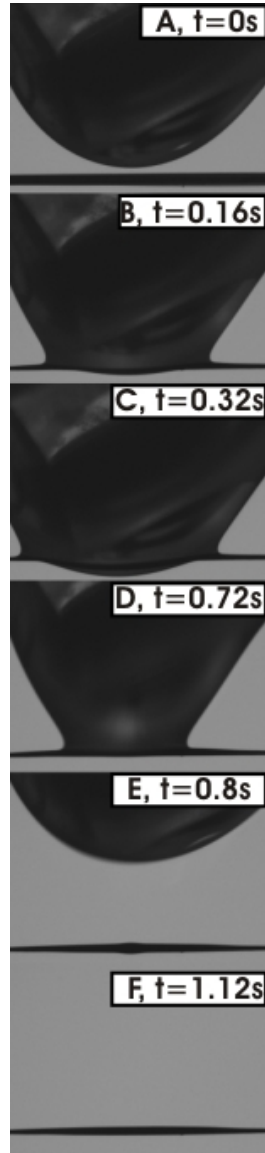


Figure 5.6: Sequence of photographic stills as a drop of acetone is brought in contact with (A-B) and removed from an uncondensed fibre (C-F).

no further diameter changes are observed (Figure 5.6 (B-C)) on a very short time frame even if the liquid is withdrawn (Figure 5.6 (D-F)).

However, a further decrease in fibre diameter is observed after a longer interval (~ 2 s) following removal of the liquid from the fibre surface. A series of optical images (Figure 5.7 (F-I)) shows a further more gradual reduction of cross-sectional area, with this second process resulting in a further diameter reduction by a factor of 4. The time delay between the drop removal and this secondary densification suggests that the process is driven by the evaporation of the absorbed acetone.



Figure 5.7: Secondary densification of a CNT fibre. Upon liquid evaporation, the fibre exhibits further radial condensation.

Further examination of Figures 5.6 and 5.7 reveals that the regions of the fibre closer to the liquid meniscus are condensed differently from those in contact with the main liquid phase, resulting in temporary variations in diameter along the fibre. As the fibre shrinks upon contact with the liquid front, liquid molecules infiltrate the porous material ('wick') along the fibre. However, the shape of the liquid meniscus along the fibre causes the regions at the edge of the meniscus to experience a higher radial compression. The effect of this densification gradient can be observed in Figure 5.8, as a graph of fibre diameter over time for the

middle- and edge-regions of the same fibre shown in Figures 5.6 and 5.7. This diameter change over time also supports the idea that the process of densification occurs in two stages, a rapid initial event upon contact of the solid and liquid, driven by the surface energy of the interfaces between solid, liquid and air, and a second, slower condensation due to liquid evaporation.

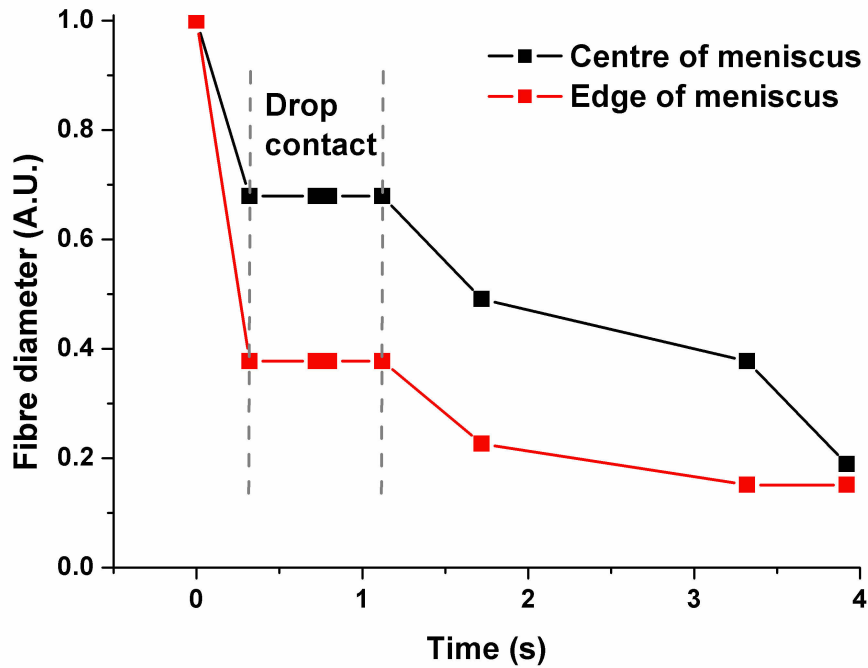


Figure 5.8: Fibre diameter change during fibre densification at the centre and edge of the liquid meniscus formed along the CNT fibre. The data correspond to the images shown in Figures 5.6 and 5.7.

Gravimetric and acoustic measurements indicate that the linear density of this particular fibre after condensation was 0.07g/km. This value, together with the diameter of the fibre in Figures 5.6 and 5.7 indicates that volumetric density increases from 0.07 to 0.3 during the first stage of densification and from 0.3 to 0.9 g/cm³ as the liquid subsequently evaporates. The density obtained after liquid evaporation is within the range of SG values (0.6 – 1.2) reported in the literature

for CNT fibres and other CNT arrays densified by a similar method (37; 73).

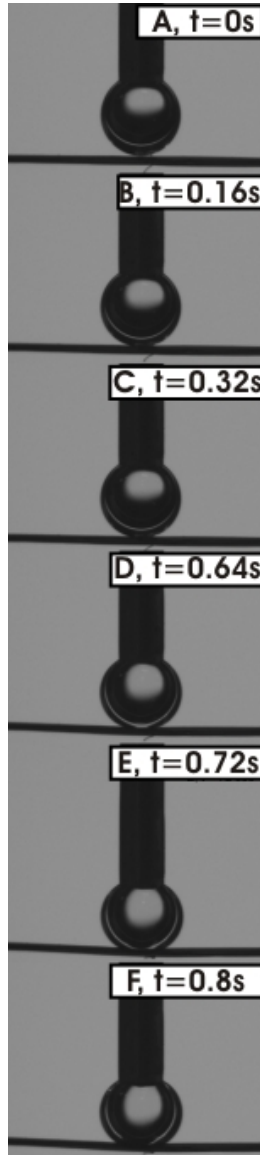


Figure 5.9: Sequence of photographic stills as a drop of water is brought in contact with an uncondensed fibre (A-B) and further forced against its surface (C-F).

Figure 5.9 presents a sequence of images showing radically different behaviour when a similar test is done using a drop of water instead of acetone. Upon contact of the solid and liquid phases, no engulfing of the fibre occurs and, moreover, a

contact angle of $\sim 180^\circ$ is established between the two. As the drop is further displaced onto the fibre surface, it exerts a force on the fibre perpendicular to the solid-liquid contact plane (Figure 5.9 (A-C)) and, eventually, moves the fibre behind the liquid drop.

5.2.2 Analysis of Liquid Densification

The process of liquid densification of CNT fibres is driven by wicking in the material due to its high internal surface area. In the same way that filaments tend to aggregate in wet hair, or when a brush is covered with paint (77; 78; 79), the elements in the fibre, probably as bundles, aggregate and condense through minimisation of the surface energy of the liquid/fibre/air system. This process can be described by taking the difference in total surface free energy (ΔE) between the system before and after wicking:

$$\Delta E = \gamma_{LV}S_F + (\gamma_{SL} - \gamma_{SV})S_B \quad (5.2)$$

where γ represents the surface energy of the liquid/vapour (LV), solid/liquid (SL) and solid/vapour (SV) interfaces; S_F to the increase in the area of the liquid phase after wicking and S_B to the internal area of the fibre covered by liquid. Thus, according to equation 5.2, wicking occurs when ΔE is negative. There are several important aspects liquid densification implicitly captured in equation 5.2. One is that the internal area of the fibre, S_B , is of the order of the total surface area of the nanotube bundles, while the much smaller S_F is comparable to the outer surface of the fibre only. This means that the fibre has a strong tendency to wick since it has abundant space for minimising its solid/air energy relative to the enlargement of the liquid/vapour interface. Nevertheless, while the liquid phase wets the fibre, it still adopts a geometry that minimises the surface energy of the liquid/air interface ($\gamma_{LV}S_F$) and, in doing so, forces the filaments together. Eventually, the aggregation of filaments stops as the capillary forces cannot compete with mechanical ones arising from the deformation of filaments and the system reaches equilibrium (77; 78). This corresponds to the first stage of densification, as illustrated in Figure 5.10.

5.2 Liquid Densification

The second stage of densification occurs as molecules between bundles evaporate and create pressure on the bundles forcing them closer to each other (Figure 5.10 (2)). Once sufficiently close in contact, the molecular interaction between nanotubes dominates any restoring forces that might emerge as the liquid phase retreats and therefore the nanotubes remain in a compact assembly. In a macroscopic assembly of filaments, the same pressure arises between the components during liquid evaporation, but in the absence of attractive forces between filaments, they do not necessarily remain in a dense assembly.

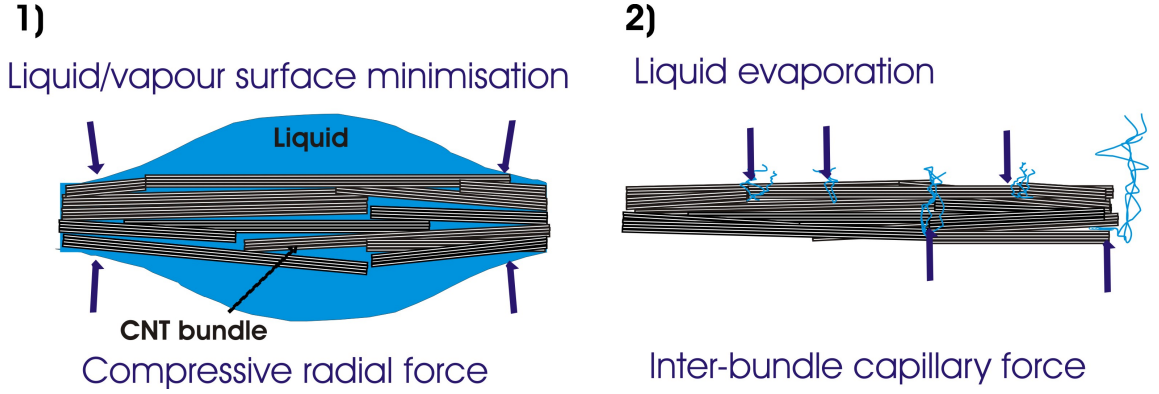


Figure 5.10: Schematic illustrating the interaction of nanotube bundles with liquid. On contact with the liquid the bundles are forced together (1), yet separated by liquid molecules. When the latter evaporate, further aggregation occurs (2).

The discussion above highlights two key properties of the liquid used for fibre densification, its surface tension and vapour pressure. The role of the first can be explored using equation 5.2 and taking the surface energy of individual phases as the sum of polar (γ_p) and dispersive (γ_d) components. The surface energy of the solid/liquid interface can be approximated as (80)

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_L^d \gamma_S^d} - 2\sqrt{\gamma_L^p \gamma_S^p} \quad (5.3)$$

Substituting in 5.2 and rearranging,

$$\Delta E = \gamma_{LV} (S_B + S_F) - \left(2\sqrt{\gamma_L^d \gamma_S^d} + 2\sqrt{\gamma_L^p \gamma_S^p} \right) S_B \quad (5.4)$$

Furthermore, assuming S_F is much smaller than S_B and taking the change in surface free energy normalised by the internal surface, this yields

$$\frac{\Delta E}{S_B} = \gamma_L^d + \gamma_L^p - 2\sqrt{\gamma_L^d \gamma_S^d} - 2\sqrt{\gamma_L^p \gamma_S^p} \quad (5.5)$$

Equation 5.5 now allows for a rough comparison of the ability of different liquids to wick in CNT fibres and thus, for example, taking $\gamma_S^d = 130\text{mJ/m}^2$ and $\gamma_S^p = 0$ (reported values of γ_S are discussed in section 7.1), it is observed that due to its lower surface tension and higher affinity to nanotubes, acetone gives a more negative value of $\Delta E/S_B$ than water. Although wicking may take place with a variety of liquids that could potentially access smaller spaces between CNTs than acetone (due to a higher affinity and a relatively low surface tension (81)), in the context of CNT fibre densification, the liquid must also have a vapour pressure that is low enough to allow densification at fast fibre spinning rates of tens of metres per minute, a feature of acetone.

In summary, densification occurs as a two-stage process due to capillary forces and evaporation of the liquid phase. This process relies on the ability of the liquid used to wick into the fibre as a means of eliminating the high energy nanotube-air surface and is dependent upon the dispersive and polar nature of the liquid. As minimisation of the surface area of the wicking liquid occurs, the liquid compresses the fibre radially and brings filaments closer together until equilibrium between the ‘capillary’ and ‘elastic’ energies of the system is established (77; 78). The second stage of the process is driven by liquid evaporation between neighbouring components (e.g. bundles) in the fibre.

5.3 Summary

In the transition from a nanotube aerogel to a fully densified fibre, orientation of bundles in the fibre and the volumetric density of the fibre are increased using faster winding rates, which occurs due to the resistance of the CNT aerogel to flow against the gas in the reactor. The semi-dense fibre is fully densified by interaction with liquid, usually acetone, in a two-stage process. The nanotubes are first brought together by capillary forces arising when the liquid wicks in

the fibre due to the high internal area of the CNT fibre. As the liquid phase reduces its surface area, it compresses elements in the fibre radially within a fraction of a second of contact between liquid and solid. At the second stage, the liquid evaporates, bringing bundles closer together and giving the fibre its final volumetric density. Higher densification of the fibre through both drawing and liquid condensation results in improved packing and orientation of bundles along the fibre, both of which have important effects on the physical properties of the material.

The composition of the densified fibre is discussed in the next chapter. It deals with the the identity of the elements that form the fibre structure and their relation to the synthesis and assembly processes, showing the degree of nanotube orientation and the detrimental effect of particulate impurities on bundle alignment.

Chapter 6

Fibre Structure

In this chapter, a description of the structure of CNT fibres is presented, without attempting to build a bridge between fibre structure and physical properties, a discussion that is left for the next chapter. A first glimpse of the species in the CNT fibre material is obtained by SEM and TEM. Thermogravimetric analysis is employed to reveal the nature and proportion of nanotubes, catalyst particles and impurities in the fibre. Microbeam X-ray diffraction is used to expose the structure and location of nanotubes, catalyst particles and other particulates. Further insight into the material's composition is obtained by Raman spectroscopy. These two techniques are also used to evaluate the orientation of bundles in the fibre. Throughout the characterisation, special emphasis is put on the homogeneity of the fibre.

6.1 Electron Micrographs of CNT Fibres

Perhaps the most basic and simplest indication of the structure of CNT fibres is obtained by electron microscopy. Scanning microscopy has the advantage that there is minimum sample preparation and that large areas of fibres can be observed. The secondary electron mode (SE) can be combined with the backscattering (BS) mode to provide more information on the location and nature of the elements present in the sample.

Figure 6.1 shows secondary electron scanning electron micrographs of condensed and uncondensed CNT fibres, exhibiting the main components in the ma-

6.1 Electron Micrographs of CNT Fibres

terial. The ribbed surface structure is indicative of long fibrils, which at higher magnification are identified as consisting of bundles of CNTs with diameter ~ 20 nm extending along the fibre axis. There is also evidence of particulates in aggregates of a few tens of nanometres randomly oriented in the nanotube network.

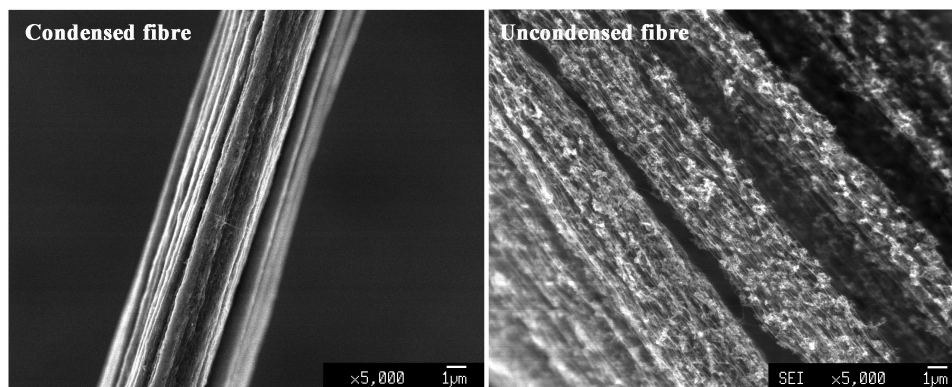


Figure 6.1: SEM micrographs of typical CNT fibres. When condensed (A), the fibres show the presence of elongated domains resembling fibrils of a few hundred nanometres. The micrograph of the uncondensed (B) material helps identify the nanotube network and impurities trapped there.

Further insight into these impurity aggregates is gained from backscattering mode, in which materials with large atomic number predominate. Figure 6.2 shows SEM micrographs in secondary mode (A) and backscattering mode (B) of a CNT fibre. The micrograph in BS mode shows weak scattering from nanotubes and carbonaceous impurities and bright spots due to residual iron catalyst particles of different sizes spread throughout the fibre. These particles are much longer than those actually responsible for nanotube growth and represent aggregates associated with redundant catalyst randomly distributed along the fibre.

Particulates consisting of both residual catalyst and carbonaceous impurities can be partially extracted from the fibre by a sonication procedure in an appropriate liquid, allowing for a more detailed inspection of their structure by different techniques. Under SEM, they appear in large clusters of aggregated particles of a few tens of nanometres. An example of this material is presented in Figure 6.3, for an extract obtained from some 100 m of CNT fibre as in Figure 6.1A. The

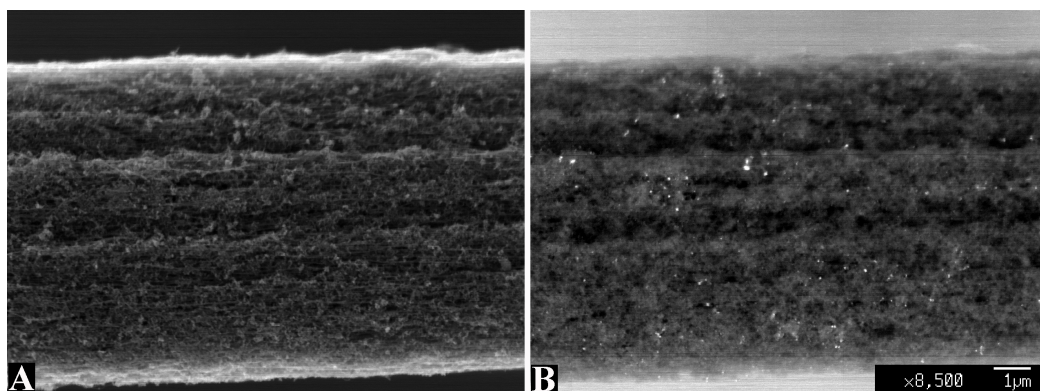


Figure 6.2: SEM micrographs of a typical CNT fibre using secondary electron (A) and back-scattering (B) modes. The bright spots in the BS image are due to aggregates of catalyst particles that do not participate in CNT growth but get trapped in the nanotube network between bundles and are distributed randomly within the fibre.

low magnification image (A) shows the impurity aggregates and some evidence of bundles of nanotubes, although greatly outnumbered by the particulates. At higher magnification (B), the irregular morphology of the particulates becomes more evident, confirming that they are not remains of nanotubes cut during sonication. The majority of the objects appear to be thick tubules of very low aspect ratio although particles are also present.

More characteristics of the elements making up the fibre can be observed in transmission microscopy (Figure 6.4). The majority of the nanotubes are of comparatively large diameter ($> 5\text{nm}$) but few walls (typically 2) and therefore collapse into ribbons (70). Most of the impurities consist of short fragments of poorly graphitised MWNTs and residual catalyst particles. Both of these impurity materials are routinely observed in CVD processes for CNT growth as reported in the literature (82), although sometimes with differences in their exact nature.

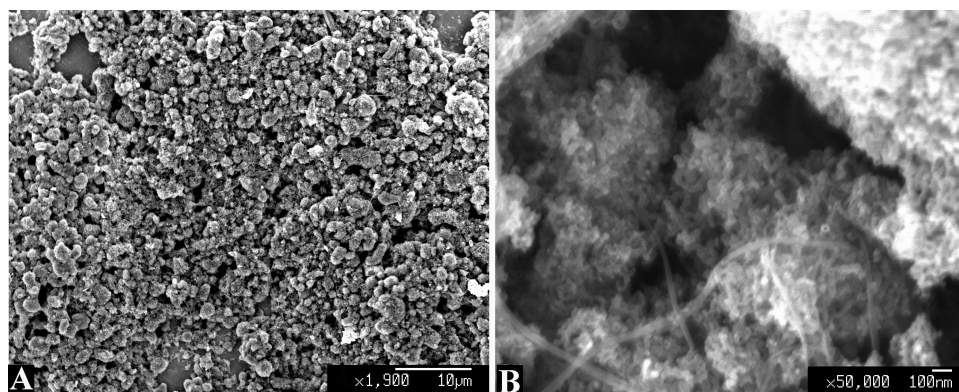


Figure 6.3: SEM micrographs of impurities extracted from CNT fibres by sonication in acetone. The extract consists almost entirely of large aggregates of particulates, although nanotube bundles are also observed (A). At high magnification (B) short tubules and particles of the order of tens of nanometres in diameter are identified.

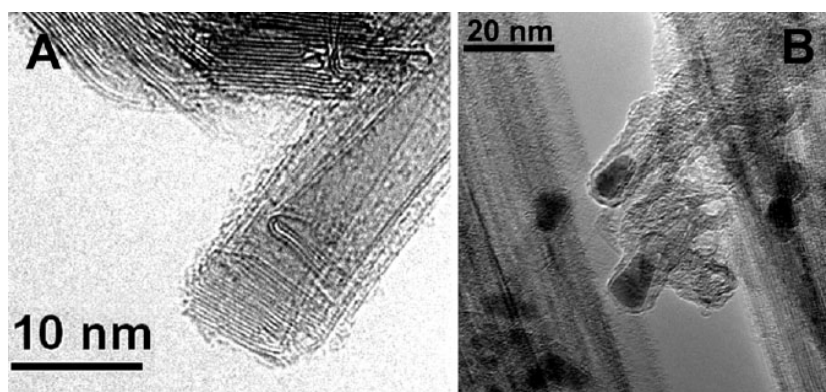


Figure 6.4: High-resolution transmission electron microscopy (HRTEM) images of typical collapsed nanotubes (A) and impurities (B) found in CNT fibres (47).

6.2 Structural Composition by Thermal Analysis

The composition of CNT fibres can be investigated by thermogravimetric analysis of samples of CNT fibre in the form of skeins, with typically 100 m of fibre and a weight of 5 mg. A first indication of the different species found in CNT fibres is presented in Figure 6.5 as a combined thermogravimetric analysis (TGA) plot of mass against temperature and the negative of the derivative of mass with respect to temperature ($-\partial m/\partial T$), each against temperature, obtained at a constant heating rate of 1°C/min in air and in argon, respectively. The thermogram in air has the distinctive fingerprints of nanotubes: a severe mass loss at $\sim 500^\circ\text{C}$ associated with oxidation of the tubes and a remanent weight corresponding to catalyst-related particles. In addition to these, the graph shows a third feature at lower temperature in the form of small decomposition peaks in the differential plot accounting for $\sim 12\%$ of the mass of this sample.

The overall shape of the thermogram is mostly in agreement with other thermogravimetric studies on CNTs (49; 83). The only discrepancy lies in the differential plot below 450°C , from which it can be observed that mass loss starts at 100°C and extends over a range of temperatures that are too low to correspond to oxidation of amorphous carbon (84). The implication is that $\sim 12\%$ of the weight of the CNT fibre consists of readily oxidisable or vapourisable species, $\sim 68\%$ is attributable to CNTs and other graphitic material and the remaining $\sim 20\text{ wt.}\%$ of the sample is related to catalyst particles, mostly as oxidised iron and therefore with $\sim 25\%$ additional mass. The nature of the species involved in each region of the thermogram is discussed separately below in more detail.

A more detailed representation of $-\partial m/\partial T$ against temperature up to 450°C is presented in Figure 6.6, showing four main decomposition peaks. The approximate temperature and total mass loss associated to each peak are obtained by integration of the Gaussian fit curves and included in Table 6.1.

The curve fit allows to relate the decomposition curve to potential oxidation or desorption processes occurring in the fibre and to determine the temperatures at which a marked mass loss takes place; although in reality, the exact combination and shape of decomposition peaks potentially differs from this simple fit. The

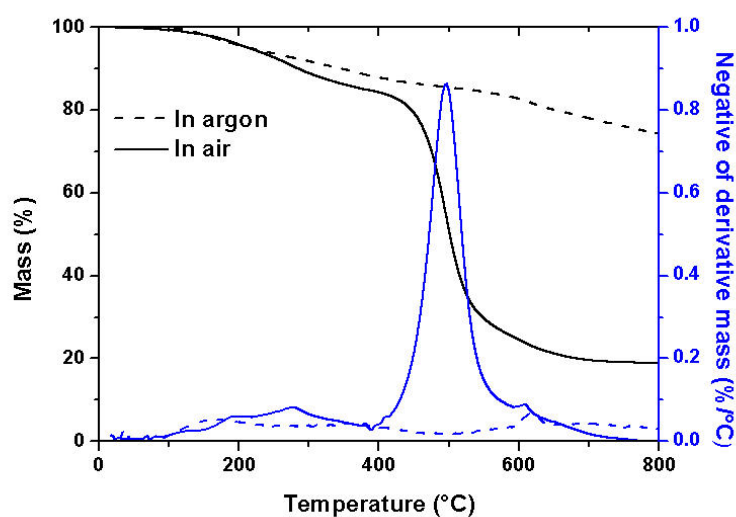


Figure 6.5: Thermograms of a mass of CNT fibre subjected to a constant heating rate of $1^{\circ}\text{C}/\text{min}$ in air and inert atmosphere (argon), respectively. Of the CNT fibre mass, $\sim 68\%$ consists of nanotubes and graphitic species, ~ 20 wt.% of residual catalyst (after oxidation) and $\sim 12\%$ of species removable below $\sim 400^{\circ}\text{C}$.

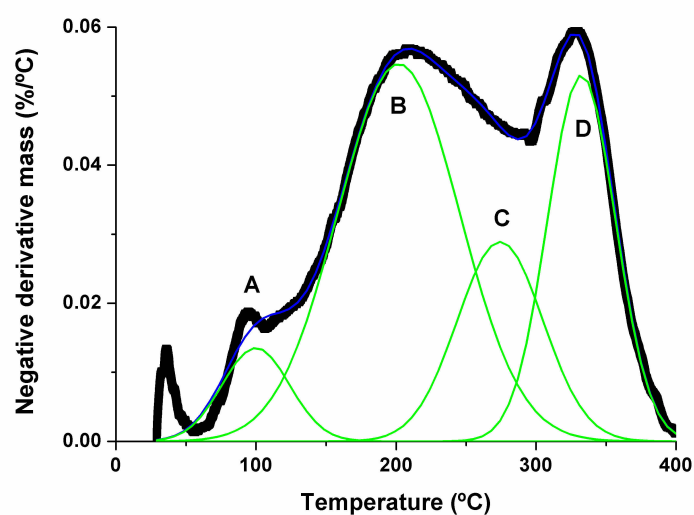


Figure 6.6: Plot of mass loss change per unit temperature increase up to 400°C, from a thermogravimetric analysis of a CNT fibre skein in air. The data are fitted by four Gaussian peaks centred approximately at (A) 100°C, (B) 200°C, (C) 270°C and (D) 330°C.

6.2 Structural Composition by Thermal Analysis

Table 6.1: Decomposition peaks obtained from thermogravimetric measurement in air

Peak	Peak temperature (°C)	Mass loss (wt %)
A	100	0.8
B	202	5.6
C	274	2.2
D	332	3.2
Total	-	11.8

first peak at 30°C is probably due to stabilisation of the instrument and not analysed further here. The middle of decomposition peak (A) is located at 100°C and suggests that it is due to water evaporation, representing 0.8% of the fibre mass. Less obvious is the origin of the two mass loss peaks at 202°C (B) and 274°C (C), which account for 5.6 wt.% and 2.2 wt.% of the sample, respectively. It is possible that the peak at 332°C (D), which constitutes 3.2% of the mass loss, is partially related to oxidation of amorphous carbon, reported to occur in a similar temperature range for other CNT systems (50; 51; 83).

Figure 6.7 presents a thermogram of a CNT fibre skein in argon and a curve fit consisting of three Gaussian peaks. This simple curve fit allows for a comparison of the decomposition curves from measurements in different atmospheres, however, its accuracy in reflecting all the mass loss processes that occur during the measurement is probably limited. The graph shows the three main decomposition peaks observed in the measurement in air atmosphere below 500°C (Figure 6.5). The small differences in peak position in inert atmosphere and total mass loss are partially attributed to variations between samples. The temperature and mass loss associated to each peak are given in Table 6.2.

The thermal removal of impurities from CNT fibres can be further confirmed from changes in their linear density. Figure 6.8 depicts a plot of linear density decrease of fibres annealed at different temperatures in air and inert atmospheres, respectively, determined acoustically (3). The plots shows a constant and similar mass loss in both atmospheres up to 360°C, with the differences identified as typical variations between samples. However, above 400°C, oxidation of amorphous carbon and, potentially nanotubes, makes the two curves diverge markedly.

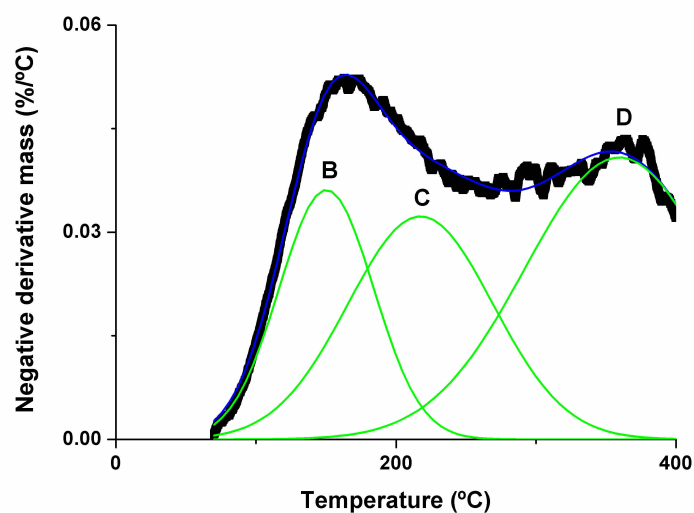


Figure 6.7: Plot of mass loss change per unit temperature increase up to 400°C, from a thermogravimetric analysis of a CNT fibre skein in argon. The data are fitted by three Gaussian peaks centred approximately at (B) 150°C, (C) 216°C and (D) 350°C.

6.2 Structural Composition by Thermal Analysis

Table 6.2: Decomposition peaks obtained from thermogravimetric measurement in argon

Peak	Peak temperature (°C)	Mass loss (wt %)
A	-	0
B	150	3
C	216	4.2
D	350	5
Total	-	12.2

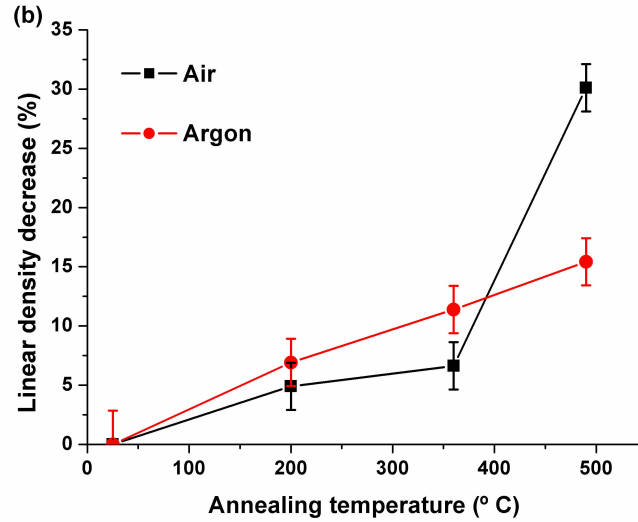


Figure 6.8: Plot showing relative decrease in linear density of samples annealed in air and argon atmospheres.

The results so far presented indicate that the thermal removal of material from the fibres below $\sim 450^{\circ}\text{C}$ does not require the presence of oxygen, suggesting that the mass loss detected is caused by thermal desorption of species from the fibre rather than from their oxidation. To some extent, this is not surprising; with a specific surface area of $100\text{--}400\text{ m}^2/\text{g}$, CNT fibres are readily prone to adsorption of gas, moisture and heavy organic molecules formed during the CVD process. To illustrate the point, let us consider that a 0.1 nm -thick layer of a material

6.2 Structural Composition by Thermal Analysis

with $SG = 1$ is adsorbed on the CNT fibre surface. A simple calculation indicates that such material would account for nearly 4% of the total mass of the fibre. Furthermore, the removal of adsorbates from the fibre has a considerable impact on both its structure and mechanical properties, as will be discussed later in Chapter 8.

The final region of the thermogram in Figure 6.5, corresponding to temperatures above 800°C, gives an indication of the amount of catalyst-related material in the sample. Typically a 10 – 20 wt.% of material is left after TGA up to 900°C in air. Interestingly, SEM reveals that during the TGA measurement the catalyst particles coalesce to form short tubular structures with diameters comparable to the original fibres, suggesting that catalyst aggregates template around the fibres, partially adopting their geometry. An example of a back-scattered electron micrograph of a CNT fibre skein heated to 900°C in air is shown in Figure 6.9. It shows a sea of fibrils with diameter ~ 30 nm and length ~ 50 μ m. Further insight into their composition is obtained by energy dispersive X-ray spectroscopy (EDS), which indicates that they consist mostly of iron and oxygen, although a small proportion of carbon was also detected, suggesting the presence of iron carbide with the iron oxide species. The proportion of iron, oxygen and carbon varies in the samples, as shown by two examples of EDS spectra in Figure 6.9.

An important reflection on the thermograms of CNT fibres is that the proportion of catalyst relative the fibre mass is strikingly high, some 10% – 20%. Some of the effects, all negative, of the catalyst particles on the fibre structure and properties are addressed later in this thesis (Chapter 7). Aside from those effects, the presence of such a great amount of catalyst is expected to decrease the thermal stability of the fibre by catalysing the decomposition of nanotubes and other graphitic species (85). This explains why nanotube oxidation occurs at a relatively low temperature of $\sim 500^\circ\text{C}$. Similarly low temperature for the decomposition of CNTs has been observed in other systems (49; 83).

In summary, thermogravimetric analysis on CNT fibres indicates that the fibre's composition is comprised of ~ 10 wt.% of adsorbed species, possibly ~ 2 wt.% amorphous carbon, ~ 70 wt.% graphitic materials and ~ 18 wt.% residual catalyst.

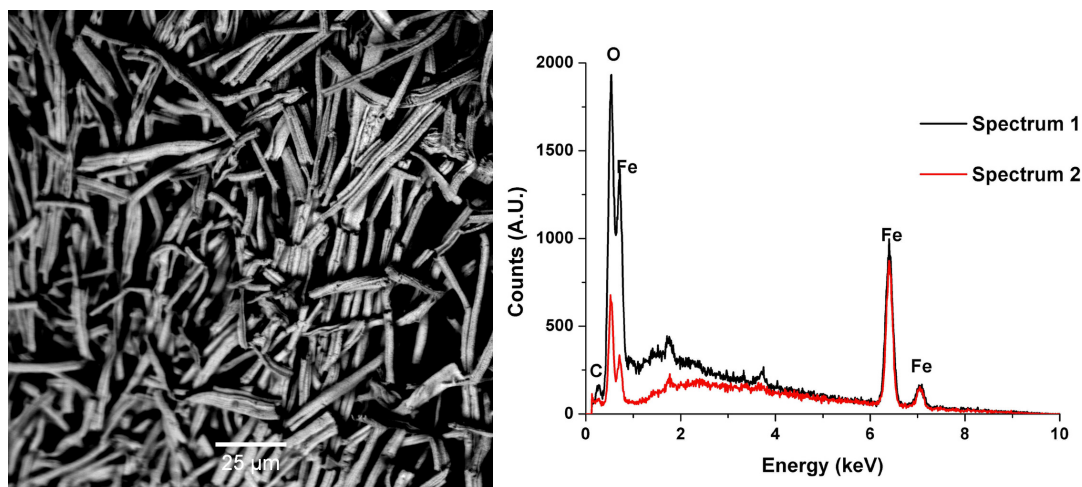


Figure 6.9: Back-scattered electron micrograph (left) and EDS spectra (right) of a CNT fibre skein after oxidation up to 900°C. Abundant carcasses with tube-like shape are present in the sample. EDS spectra indicate that the material is composed almost entirely of iron oxide, although the weak carbon signal suggests that iron carbide may also be present.

6.3 X-ray Diffraction From CNT Fibres

X-ray diffraction provides valuable additional information on the structure of CNT fibres not available with other techniques. Also, unlike Raman spectroscopy which is effectively a surface analysis technique, XRD covers the whole volume of fibre as long as the material is crystalline. The main characteristics that can be observed by XRD are the orientation and separation of CNTs and the composition of the residual catalyst particles. Moreover, the use of synchrotron radiation with a small beam diameter makes it possible to analyse the homogeneity of single fibre filaments across their diameter and along their length.

6.3.1 Compositional Analysis

A typical 2-D diffraction pattern from a CNT fibre wound at 20 m/min, with the fibre axis vertical relative to the pattern, is presented in Figure 6.10. The overall shape of the pattern falls in line with previous measurements on CNT fibres using

6.3 X-ray Diffraction From CNT Fibres

synchrotron radiation (86). It reveals a broad outer powder ring associated to residual catalyst particles and weak reflections from CNTs, the discrete spots being due to catalyst particle crystallites. The 002 reflection from graphene layer stacking is observed as a highly oriented reflection at the equator due to preferential orientation of CNT bundles parallel to the fibre axis, overlapping with an isotropic ring of lower intensity. In the small-angle (SA) region, a strong fibre streak associated to highly aligned bundles of CNTs is noticeable.

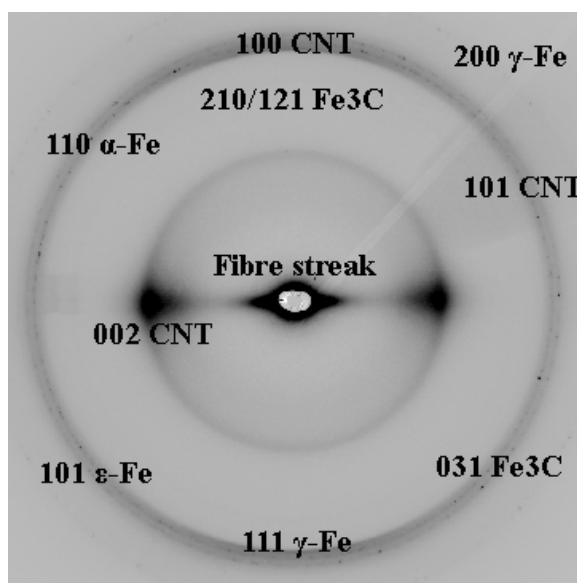


Figure 6.10: Typical diffraction pattern from a CNT fibre oriented vertically. A highly oriented 002 reflection from CNTs and a sharp fibre streak from bundles are observed. Residual catalyst-related reflections from α -, γ - and ϵ -iron and iron carbide (Fe_3C) are also identified.

A selected-range radial profile obtained by 360° azimuthal integration is presented in Figure 6.11, showing more clearly the various contributions to the fibre pattern. The individual peaks are obtained from a Gaussian fit and subtracting a 0-order polynomial. A complete list of the identified reflections is presented in Table 6.3.

The 002 reflection from adjacent graphene layers gives rise to a superposition of two Gaussian peaks, depicted in the radial profile in Figure 6.11. The position

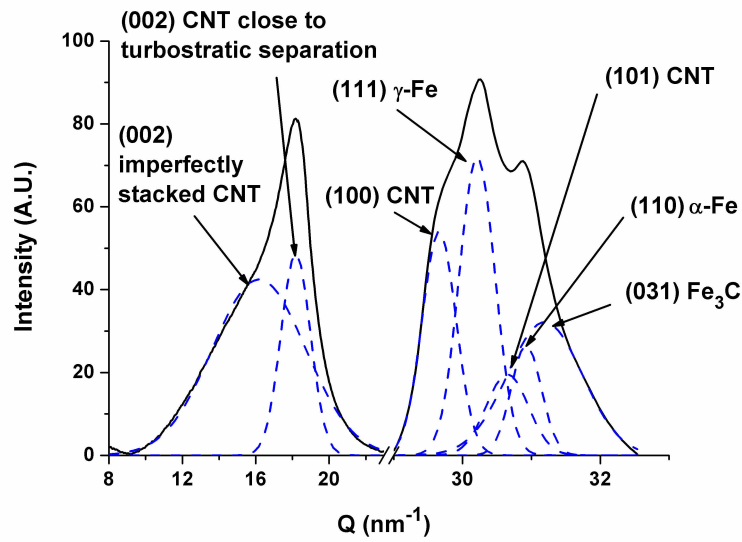


Figure 6.11: Selected-range radial profile from azimuthal integration of the pattern in Figure 6.10, showing the contribution to the 002 reflection from imperfectly stacked CNTs and tubes close to the turbostratic separation and the superposition of reflections from α - and γ -iron, iron carbide (Fe_3C) and the 100 and 101 reflections from CNTs at higher Q numbers.

6.3 X-ray Diffraction From CNT Fibres

of the first peak at 0.388 nm d -spacing and its broad distribution is indicative of nanotubes in proximity to each other but that do not quite reach the turbostratic separation (70; 86). The spread in separations between graphene layers is probably due to the interface between collapsed nanotubes with bundles. The second peak, on the other hand, is much narrower and centred at 0.345 nm. This d -spacing is close to the interlayer separation in turbostratic graphite, which suggests that this reflection arises from graphene layers closely packed, both from layers in nanotubes and from tubes in well organised bundles. As a first step, if it is assumed that the half-width of this peak is wholly representative of the number of graphene layers stacked, this numbers comes out to be 14.

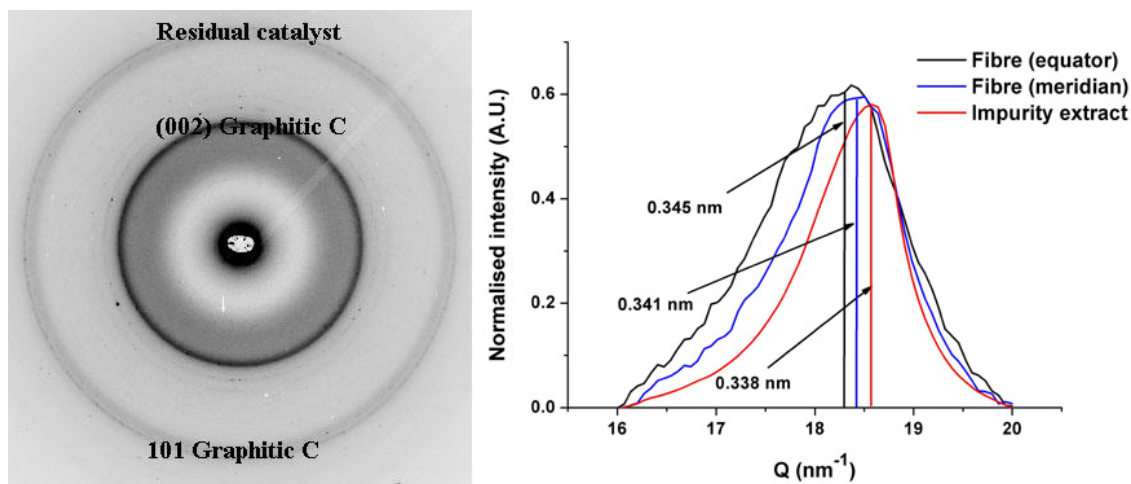


Figure 6.12: Typical diffraction pattern from a sample of impurities extracted from CNT fibres and a comparison of radial profiles from the impurities and from CNT fibres along the equator (black) and meridian (blue).

In the analysis of the reflections from graphene layers in CNT fibres it is imperative to consider that CNT fibres contain not only nanotubes but also impurities with some degree of graphitisation and therefore, the patterns are in reality a superposition of different graphitic materials. To illustrate the point, a diffraction pattern from a sample with mostly graphitic impurities is presented in Figure 6.12. The material consists mostly of carbon tubules and particles removed from the fibre by ultrasonication (as in Figure 6.3). On inspection of the pattern, the

6.3 X-ray Diffraction From CNT Fibres

main features observed in the fibres are noticeable: powder rings associated to catalyst particles and CNTs and a strong 002 reflection from graphene layers that shows no sign of orientation, as expected. After further analysis the peaks attributed to catalyst particles and the 100 and 101 from CNTs can be identified, with little difference found in comparison with the intensity profile in Figure 6.11. Similarly, the 002 reflection shows a broad peak at around ~ 0.382 nm d-spacing, as observed in the fibre pattern, and a sharper peak which for this material is centred in the vicinity of 0.338 nm and indicates a smaller separation between graphene layers.

Table 6.3: Measured d-spacing and assignation of fitted peaks

Number	d-spacing (nm)	Assignment
1	0.388	002 CNT (imperfect stack)
2	0.341-0.345	002 CNT (close to turbostratic graphite)
3	0.237	210/121 Fe ₃ C iron carbide
4	0.212	100 CNT
5	0.208	111 γ -iron
6	0.205	101 CNT
7	0.203	110 α -iron
8	0.201	031 Fe ₃ C iron carbide
9	0.189	101 ϵ -iron
10	0.179	200 γ -iron

The contribution from impurities to the fibre's diffraction pattern can be readily observed in Figure 6.12 by comparison of the radial profile from impurities with the radial profiles from the CNT fibre on the meridian and on the equator, respectively. The graph shows that at right angles to the fibre (equator), where the contribution from CNTs predominates over that from impurities, larger values of separation between graphene layers of the order of 0.345 nm are observed. At the meridian the opposite occurs, and due to the larger contribution of graphitic impurities with turbostratic structure relative to nanotubes at this orientation, the distribution has a lower average d-spacing of around 0.341 nm.

6.3 X-ray Diffraction From CNT Fibres

In the range of $29 - 33 \text{ nm}^{-1}$ Figure 6.11 shows the 101 and 100 reflections from CNTs, the latter being slightly more intense at the meridian in Figure 6.10 due to the preferential orientation of CNTs parallel to the fibre axis. The fitted profile also shows different iron phases related to residual catalyst mostly, with γ -iron being the most abundant, followed by α and with an almost unnoticeable presence of ϵ (not in this range). Interestingly, the pattern shows no significant sign of iron oxide, and in general only negligible traces are found. In addition to iron, iron carbide (Fe_3C) is also found in the sample as manifested by the strong 031 reflection and the lower intensity combination of 121 and 210 reflections.

The 002 (Figure 6.11) reflection from adjacent graphene layers in the fibre indicates that nanotubes are in close contact but that some of them, or parts of them, are separated by distances larger than the d-spacing in turbostratic graphite. The constraints of maximising contact area between nanotubes mean that closest approach is not possible between every part of every nanotube and result in imperfect stacking of some collapsed tubes. Moreover, the presence of nanotubes with different diameters, particularly those un-collapsed, is also likely to contribute to the imperfect stacking of graphene layers from adjacent tubes. However, it is noteworthy that part of the 002 reflection from the fibre originates from graphitic impurities (Figure 6.12), which unlike nanotubes, show no evidence of assembling with any crystallographic order, but contribute to the 002 reflection due to their multilayered structure.

As well as nanotubes and graphitic impurities, XRD shows the presence of residual catalyst in the fibre, in the form of α -, γ - and ϵ - iron and iron carbide (Fe_3C). Evidence of γ -iron in CNTs and in graphitic tubules is not surprising. The catalytic role of γ iron in nanotube formation is well known. Reports indicate that γ -iron particles at elevated temperatures are prevented from transforming into the α phase due to the high Young's modulus of graphite (87; 88) and a similar coefficient of thermal expansion between the two materials (89). The presence of ϵ -iron in CNT samples is possibly related to the high pressure that CNTs can induce on particles inside them (90). Iron carbide has also been observed to act as a catalyst in CNT growth by conventional CVD (91). What remains to be identified is which type of iron-containing particles are responsible for the synthesis of graphitic impurities such as tubules and nanoparticles. This

identification, beyond the reach of this work, will facilitate the removal of impurities by chemical treatments that preferentially target the particles, and perhaps most importantly, it will provide information that can lead to improvements in the synthesis process that can diminish the production of impurities.

6.3.2 Fibre Orientation and Uniformity

The superposition of oriented and unoriented components in the 002 reflection and in the small-angle (SAXS) region reveal more about the fibre structure in terms of the alignment of CNTs relative to the fibre axis. Figure 6.13 shows examples of azimuthal profiles obtained by integration of the pattern in Figure 6.10 in the range of the 002 reflection in the wide angle (WAXS) region, and in the range of $Q \sim 3 \text{ nm}^{-1}$ (d -spacing $\sim 2 \text{ nm}$) in the small angle region. Each profile is fitted by a 0-order polynomial and two Gaussian peaks. The shape of the profile and the curve fit suggest a superposition of three orientation populations: unoriented, poorly oriented and highly oriented; although not necessarily indicative of three different populations of elements in the fibre.

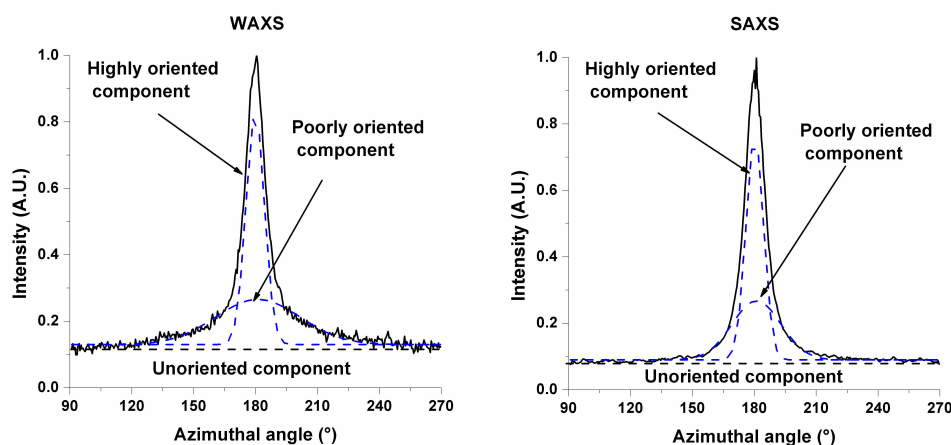


Figure 6.13: Azimuthal profile from the 002 reflection from nanotubes (left) and from small-angle diffraction from bundles (right), fitted by 0-order polynomial and two Gaussian peaks, suggesting the contribution from an unoriented, poorly oriented and highly oriented components in both wide and small angle.

6.3 X-ray Diffraction From CNT Fibres

A comparison of the populations is presented in Table 6.4, including their relative contribution to the pattern, obtained by integration over the whole azimuthal range, and two measures of orientation: the full-width-at-half-maximum (FWHM), which indicates the orientation spread in degrees, and Herman's orientation factor (P_2).

Table 6.4: Components of the azimuthal profile in Figure 6.13

Wide-angle			
Component	FWHM ($^\circ$)	P_2	Relative intensity
Highly oriented	12	0.98	0.21
Poorly oriented	57	0.68	0.18
Unoriented	-	0	0.61
Small-angle			
Component	FWHM ($^\circ$)	P_2	Relative intensity
Highly oriented	12	0.98	0.25
Poorly oriented	33	0.88	0.18
Unoriented	-	0	0.57

The table shows that the relative contribution of unoriented, poorly oriented and highly oriented components to their total integrated intensity of the azimuthal profile is very similar in WAXS and SAXS, with the unoriented component being more intense than the sum of the other two. In WAXS and SAXS, the highly oriented component has identical values of P_2 and FWHM of 0.98 and 12, respectively; while for the poorly oriented component the values are 0.68 and 57 in WAXS and 0.88 and 33 in SAXS. In spite of this small difference, the overall similarity between wide and small angle in the ranges selected indicates that the orientation of nanotubes and bundles is approximately equivalent.

The uniformity in orientation along and across fibres was investigated by varying the diameter of the X-ray beam used, thus being able to perform measurements at different scales. An example of the orientation variations in a fibre is presented in Figure 6.14, corresponding to a set of measurements along a millimetre of fibre obtained from a scan using an X-ray beam diameter of $\sim 10 \mu\text{m}$, and another set scanning an area $3 \mu\text{m}$ along and $3 \mu\text{m}$ across the fibre using a

6.3 X-ray Diffraction From CNT Fibres

beam diameter of ~ 300 nm. The uniformity of CNT orientation is plotted as histograms of the FWHM of the azimuthal profiles from WAXS only, although no differences are observed in SAXS. The FWHM is obtained by fitting each azimuthal profile with a 0-order polynomial and a single Lorentzian distribution for simplicity.

The histograms in Figure 6.14 show little variation in orientation along and across the fibre, both at the scale of tens of microns and at hundredths of nanometres. Additionally, comparison of the relative intensity of the oriented and un-oriented components also indicates a high degree of uniformity, with the relative contribution of each component not varying more than 8% from the mean.

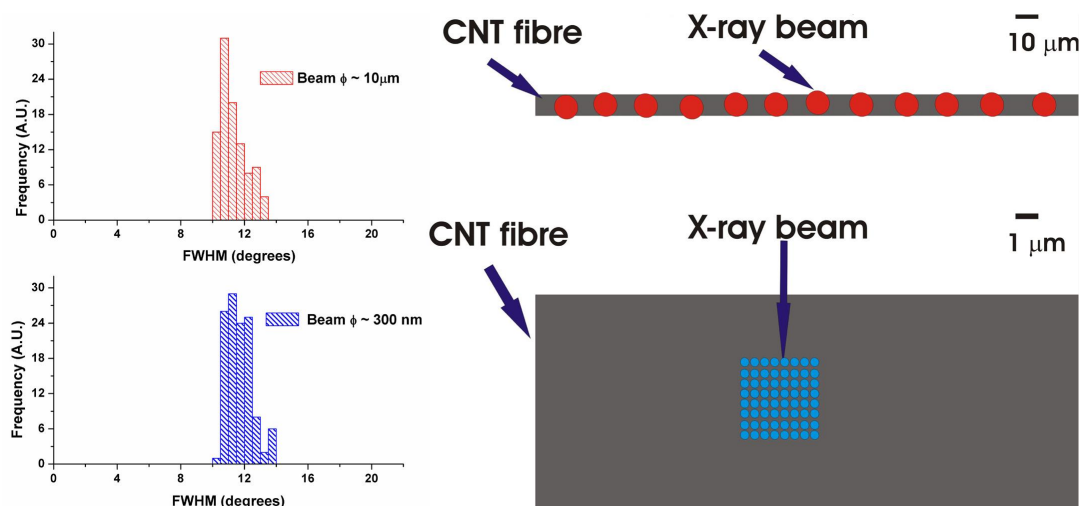


Figure 6.14: Statistical plots of orientation (FWHM) from a scan along 1 mm of fibre using a $10 \mu\text{m}$ -diameter X-ray beam, and a scan over an area $3 \mu\text{m}$ along and $3 \mu\text{m}$ across the fibre using a 300 nm-diameter beam.

The homogeneity of CNT fibres over lengths greater than 1mm is difficult to analyse by X-ray radiation. Due to the weak scattering from the $10 \mu\text{m}$ -diameter filament, it is necessary to employ a dedicated high intensity X-ray source (e.g synchrotron radiation) for a considerable period. This work provides the basis for further studies.

In summary, XRD measurements indicate that the orientation of nanotubes and impurities in the fibre give rise to an unoriented, semi-oriented and highly-

oriented components of the 002 reflection and the fibre streak. The unoriented component is associated predominantly to multilayered graphitic impurities randomly dispersed in the fibre. The oriented components, rather than suggesting that there are two populations of oriented elements in the fibre, are likely to correspond to different degrees of alignment of the same CNTs (or bundles) along their length. The presence of small randomly located impurity particulates, both as graphitic particulates and residual catalyst particles are likely to play a role in limiting CNT alignment.

Measurements with micro- and submicro-beam XRD show that there are no significant orientation variations across the fibre and along a length equivalent to ~ 100 diameters, and no evidence of localised defects in a scale < 100 nm can be found. These observations suggest that defects in the fibre structure are manifested as a generalised shortfall in alignment of its long elements throughout the fibre volume, rather than as large localised faults.

6.4 Raman Spectroscopy of CNT Fibres

Raman spectroscopy allows characterisation of nanotubes at a molecular level (92); however, because the length of the fibre extends continuously for kilometres, a conflict of scales arises, presenting one with the complexity of addressing issues of uniformity at a molecular level over great lengths. In this work the strategy adopted is to focus initially on fibre composition and homogeneity at a micron-scale. Subsequently, CNT orientation and long range variations over macroscopic lengths are investigated. The measurements are performed directly on CNT fibres and therefore correspond essentially to the fibre surface and not to the bulk. In this work, the term Raman frequency is used rather than Raman shift to avoid confusion with the shift in Raman frequencies.

6.4.1 Micro-Raman Analysis

Fibre structure, particularly its composition, is analysed from Raman spectra of fibres in small areas of a fibre typically $\sim 15 \mu\text{m}$ across and $\sim 50 \mu\text{m}$. The fibre surface was scanned using a 785 nm-wavelength laser with diameter $< 1 \mu\text{m}$ and

6.4 Raman Spectroscopy of CNT Fibres

taking consecutive measurements separated by $1\text{ }\mu\text{m}$ along and across samples which defines a rectangular mesh with a Raman spectrum corresponding to each point of coordinates on the fibre surface. For micro-Raman scans, the polarisation direction of laser did not match the fibre axis.

An example of an optical micrograph of a CNT fibre is shown in Figure 6.15. The frame encompasses the area where micro-Raman spectra maps were collected, with the axis in the direction across (X) and along (Y) the fibre for reference. The fibre is significantly irregular, which makes it difficult to hold all the image in focus at once. The image shows, amongst other features, a set of bright fringes on the right hand side and an isolated one on the left, with a depression in the middle of the sample.

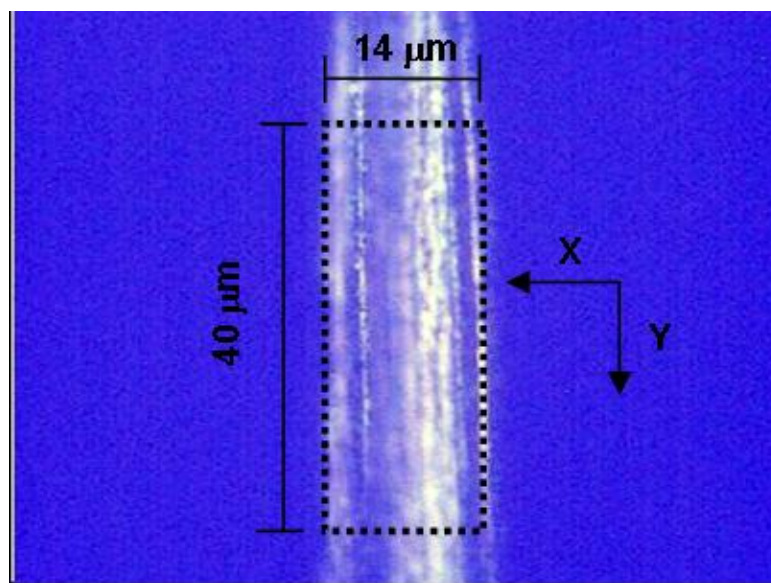


Figure 6.15: Optical micrograph of an area of a CNT fibre over which micro-Raman spectra scans were taken. The irregular topography of the fibre results in different focal planes. Note the presence of bright fringes parallel to the fibre axis.

An example of a typical map of intensities of the RBM between 150 cm^{-1} and 170 cm^{-1} , corresponding roughly to nanotubes with diameter $\sim 1.6\text{ nm}$, is presented in Figure 6.16, where the coordinates correspond to the coordinates on

the fibre surface defined in Figure 6.15. A considerable variation of intensity is observed on the map, particularly pronounced across the fibre in the X direction. In the Y direction, domains of similar RBM intensity can be identified, such as the stripe at $X = 5 \mu\text{m}$ (B) parallel to the fibre axis which is probably indicative of a bundle of SWNTs of diameter $1.5 - 1.8 \text{ nm}$ and length of at least $40 \mu\text{m}$. Other features are also present, such as an isolated sharp peak (A) and areas with no detectable RBMs (e. g. C).

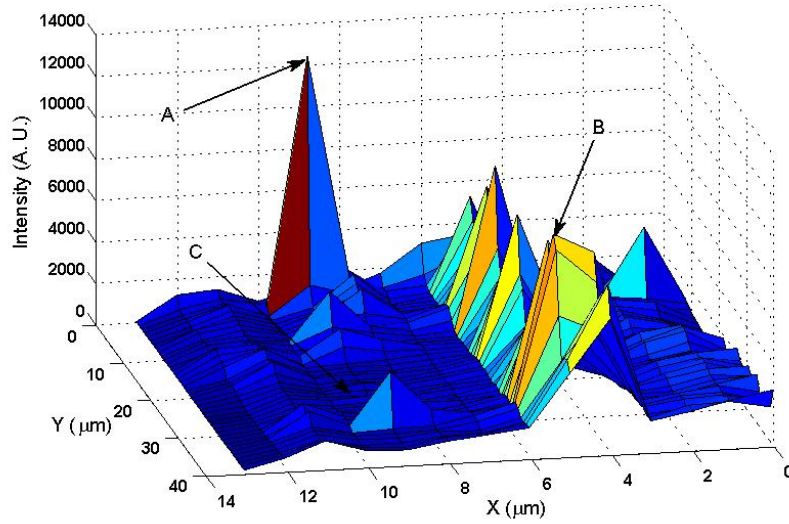


Figure 6.16: Intensity map of RBM in the vicinity of 165 cm^{-1} , corresponding to nanotubes with diameter of $\sim 1.5 \text{ nm}$. More uniformity is observed in the Y direction (fibre axis) than in the X direction. Points corresponding to a sharp and intense isolated peak (A), a high intensity domain (B) and large areas of negligible intensity (C) are analysed further below.

The spectra at points A , B and C on the map, corresponding to the highest intensity observed, a point on the high intensity stripe, and a point of negligible RBM intensity, respectively, are analysed further in Figure 6.17. The figure shows that both RBM active areas A and B exhibit a similar superposition of individual peaks in the spectra, with only a small offset of 3 cm^{-1} . The nanotube diameter (Φ) is obtained using $\Phi = 234/(\omega - 10)$ (56), and indicates that the majority of

6.4 Raman Spectroscopy of CNT Fibres

the nanotubes in resonance have a diameter of 1.4 nm. Of lower Raman intensity, the rest of the identifiable tubes have a diameter of ~ 1.7 nm and ~ 2.1 nm. Additionally, a few weak peaks at higher Raman frequency are observed. Their combination of low intensity and their asignation to small diameter tubes suggest that they could be inner tubes of nanotubes with few layers, with the outer layers damping the breathing mode of oscillation of the inner ones. Additional strong SWNT peaks at 200 cm^{-1} , 240 cm^{-1} and 260 cm^{-1} , corresponding to nanotubes with diameters of approximately 1.2 nm, 1 nm and 0.9 nm, respectively, are typically observed along CNT fibre samples.

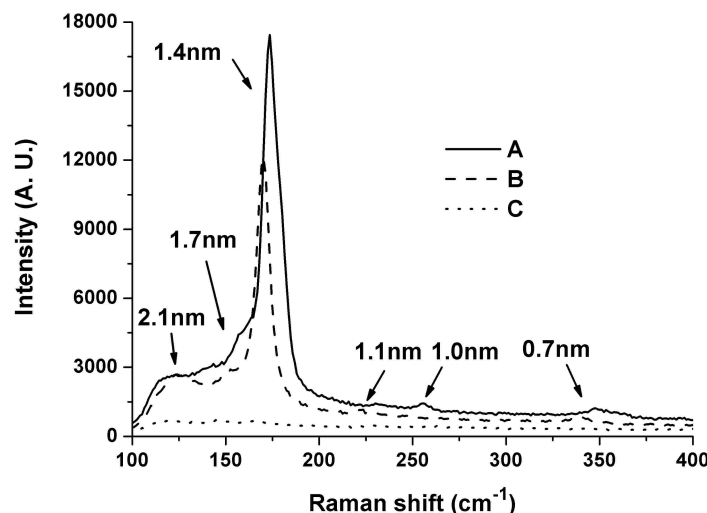


Figure 6.17: Raman spectra of RBM at different locations on a fibre, corresponding to points *A*, *B* and *C* in Figure 6.16. The high RBM intensity points (*A* and *B*) show predominance of 1.4 nm-diameter tubes and weaker peaks 1.7 nm and 2.1 nm SWNTs. Low intensity peaks from thin tubes are also observed in spectra *A* and *B*, suggesting that they are inner tubes in few-walled nanotubes.

G band intensities from the same area (Figure 6.15) are plotted in Figure 6.18. In general, the shape of the G peak can be accurately fitted by a single Gaussian distribution including the largely unresolved G^+ and G^- components and therefore, treated for the purposes of the map plot as a single peak. The G

band intensity distribution appears to reflect the surface topography of the fibre, dominating any more subtle effects of peak intensities.

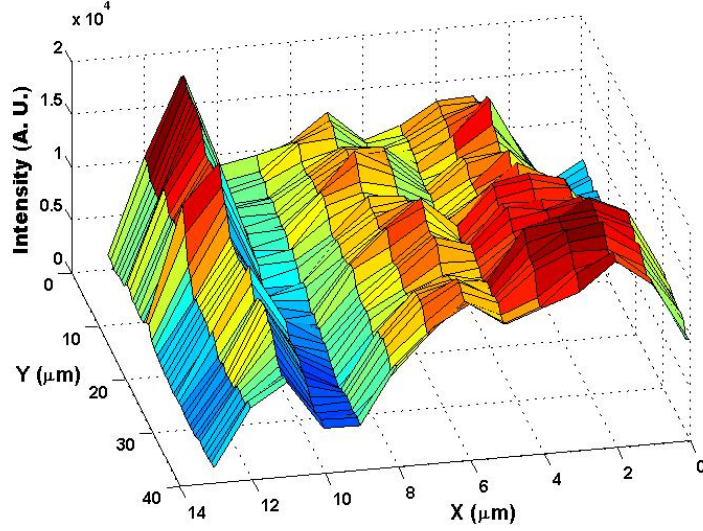


Figure 6.18: Intensity map of the G band. The intensity profile matches approximately the fibre's topography as differences in focal position give rise to different Raman peak intensities.

A second map of the G band is presented in Figure 6.19, where the surface consists of a plot of the band's frequency at the different measuring points. On inspection of the plot, the surface reveals significant variations in Raman frequency, particularly across the fibre (X direction), with values ranging from 1580 cm^{-1} to 1573 cm^{-1} . Less variation is observed along the fibre axis, with domains of similar Raman frequency extending through the whole length of fibre scanned. Amongst other features of the plot, one can distinguish a wide valley in green on the map, at 1576 cm^{-1} , two deep depressions of low Raman shifts of $\sim 1574\text{ cm}^{-1}$ positioned at $X = 9\text{ }\mu\text{m}$ and $X = 12\text{ }\mu\text{m}$, in the middle of which a high crest of values close to $\sim 1580\text{ cm}^{-1}$ runs parallel to the fibre axis.

The variation in position of the G band is extremely revealing because it is not attributable to the topography of the fibre. Spectra corresponding to locations of high (H), medium (I) and low (J) Raman frequency numbers are analysed

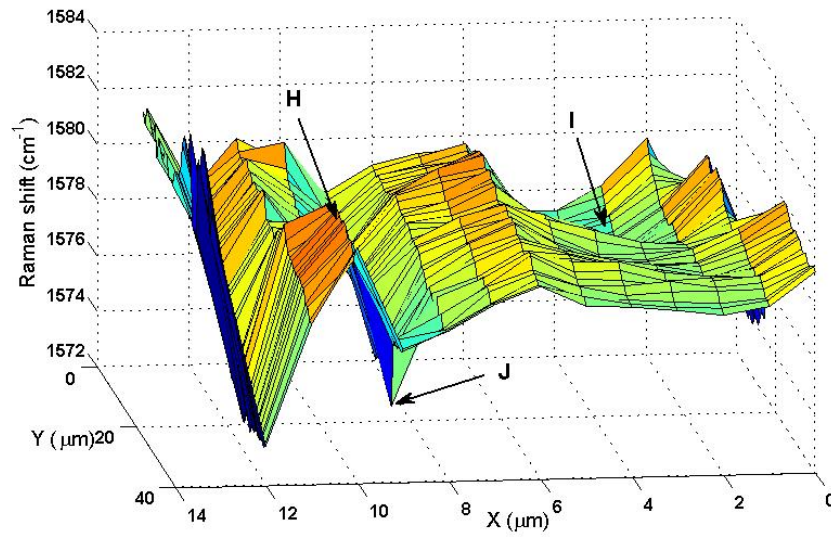


Figure 6.19: Map of Raman frequency of the G band. A clear variation across the fibre is observed, with well defined domains of high and low Raman shift extending along the fibre axis. Points *H*, *I* and *J*, of high, medium and low Raman frequency, respectively, are selected for further analysis.

6.4 Raman Spectroscopy of CNT Fibres

in more detail and presented in Figure 6.20. The spectra show a consistent shift in Raman frequencies, particularly pronounced for the first component of the 2D band, with no indication of the compositional differences at the three locations based on the shape of the peaks.

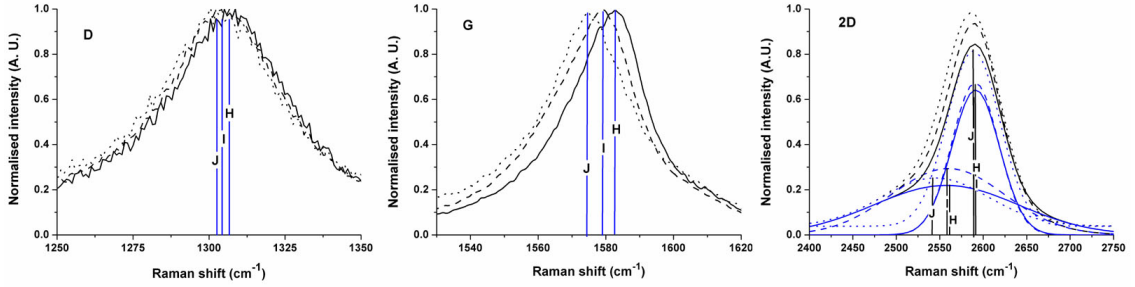


Figure 6.20: Normalised intensity of the D, G, $2D_1$ ($\sim 2570 \text{ cm}^{-1}$) and $2D_2$ ($\sim 2600 \text{ cm}^{-1}$) bands at different locations on the fibre, corresponding to points *H*, *I* and *J* on the map in fig 6.19. The shape of the peaks is very similar and does not reveal major differences in their origin, however, their position show a consistent shift.

The differences in Raman frequency of the D, G, $2D_1$ and $2D_2$ at points *H*, *I* and *J* is more appreciable in Figure 6.21, which shows the frequency difference of the three bands relative to their value at point *I*. The arbitrary choice of *I* as a reference value is a suggestion that a downshift and upshift in Raman frequencies are in principle equally probable.

A final map is presented in Figure 6.22, consisting of the ratio of intensities of the D over G peaks (I_D/I_G) in the same area of fibre as shown in Figure 6.15. The graph exhibits an irregular contour, with similar variations across and along the fibre axis. For reference, the calculated average gives a ratio of 0.29 and a standard deviation of ± 0.06 , or 20% of the mean.

A comparison of the spectra at points of high (*E*) and low (*F*) I_D/I_G ratios shows that they differ mainly in their G bands, rather than the D bands which although of different intensity exhibit a similar shape when normalised. Spectrum *E*, of higher I_D/I_G , comprises a symmetrical G peak with no clear evidence of specific tangential modes. In contrast, in spectrum *F* a clear asymmetry in the G

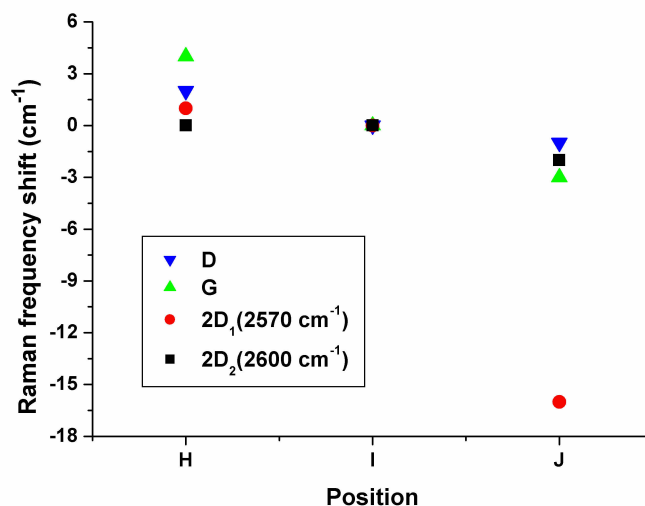


Figure 6.21: Graph of shift in Raman frequency of the D, G, $2D_1$ and $2D_2$ peaks at points *H*, *I* and *J*. The frequency shift is taken relative to the value at point *I*.

band is readily observable and the superposition of the G^+ and G^- modes clearly identified, suggesting the presence of metallic tubes. The spectra in this example show that a simple correlation between I_D/I_G and the presence of impurities in the fibre is not straightforward, as the contribution to the G pack arises from several species in the sample with different Raman scattering intensities.

The results from micro-Raman spectroscopy of CNT fibres show that their structure has homogeneous long domains along the fibre axis with significantly more variations across the fibre axis, suggesting that most structural differences in the fibre are found between neighboring bundles or other elements such as microfibrils rather than along them. Amongst the compositional differences is the presence of SWNTs, which appear to be highly localised in bundle according to their diameter. The diameter of SWNTs observed with a 785 nm laser line ranges from 0.9 nm to 2.1 nm, with the majority at ~ 1.4 nm. However, it must be emphasised that RBMs are a feature where significant intensity is observed from a small number of tubes fulfilling the resonance condition, the data are therefore not

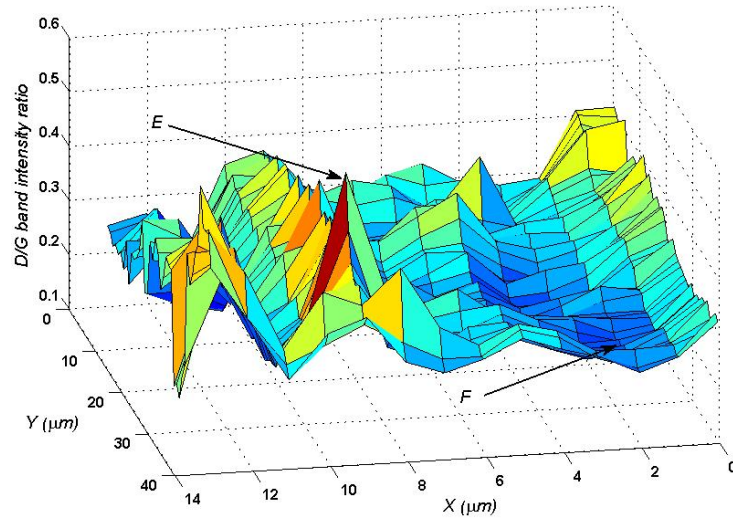


Figure 6.22: Ratio of intensities of the D over G bands. Locations E and F of high and low intensity ratios, respectively, are indicated as examples of structural variations in the material.

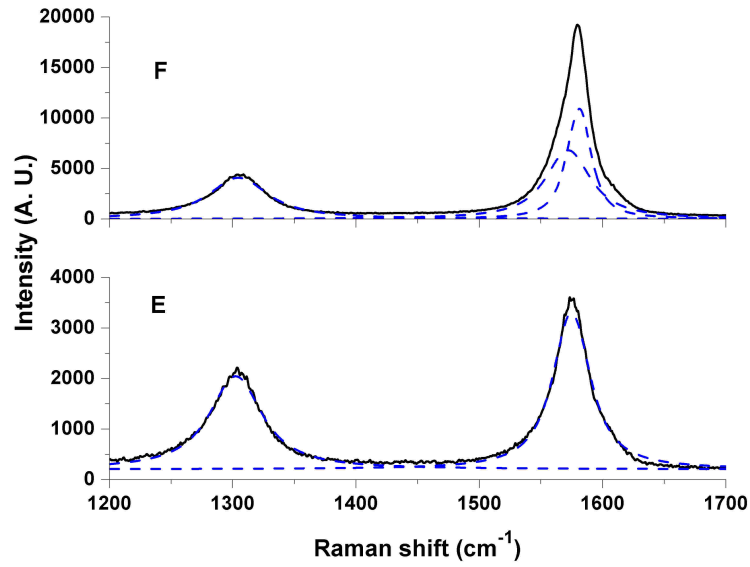


Figure 6.23: Comparative spectra at points of low (F) and high (E) I_D/I_G . The shape of the D peak is very similar in both spectra, unlike the G peak.

necessarily in conflict with XRD and electron microscopy measurements, which suggest that SWNTs and tubes of diameter ~ 1.4 nm are not the dominant CNTs present, and are likely to be a minority species amongst larger diameter collapsed tubes of a few layers.

Scans along and across the fibres using a submicro-laser do not show strong evidence of highly localised impurities larger than a few hundred nanometres on the fibre surface. This observations is in agreement with XRD measurements, and further supports the view the graphitic impurities in the fibre are small and randomly dispersed in the CNT bundle network. The scans also show Raman frequency variations on the fibre surface as a shift in Raman frequency between regions across the fibre, but not so marked along the fibre axis, suggesting that large elements such as bundles or microfibrils, tend to be composed of nanotubes with similar Raman frequencies, but shifted when compared to other neighbouring elements. There is no indication that this shift is due to compositional differences in the sample, but rather due to local variations in the modes of oscillation of the tubes probably associated to residual stress in the tubes reminiscent of their assembly into a fibre by mechanical drawing of the aerogel and densification by interaction with liquid.

6.4.2 Fibre Orientation and Uniformity

The analysis of the structure and homogeneity of CNT fibres based on Raman spectroscopy would be incomplete without considering the orientation of the nanotubes. To illustrate the point, a comparison of Raman spectra using a 633 nm laser with polarisation direction parallel and perpendicular to the fibre axis taken on the same spot on a fibre is presented in Figure 6.24. The figure shows that the intensity of the D peak is nearly identical in both configurations, in contrast with the G peak, the intensity of which is ~ 4 times higher when the laser polarisation direction is parallel to the fibre axis. The 2D peak is again sensitive to the sample orientation but the parallel/perpendicular intensity ratio is only ~ 2 in this case.

It is important to realise that the spectra from CNT fibres originates from scattering not only from nanotubes but also from other graphitic impurity species, such as poorly graphitised tubules, and that it is only by taking all into account

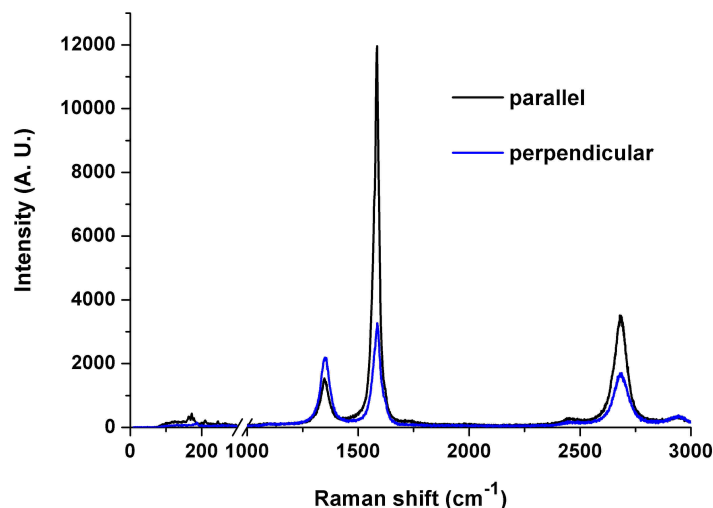


Figure 6.24: Spectra of a fibre parallel (black) and perpendicular (blue) to the polarisation direction of the laser. While the D peak shows little difference, the G and 2D show considerable dependence on the laser/sample configuration.

that the Raman spectra can be accurately analysed. A typical Raman spectrum of impurities extracted from fibres (as in Figure 6.3) is presented in Figure 6.25. Their defective structure is manifested as a high intensity ratio of the D over G peaks, with a value of 1.5. Additionally, the position of both the D and 2D peaks, at $\sim 1332 \text{ cm}^{-1}$ and $\sim 2650 \text{ cm}^{-1}$ respectively, is higher than for the fibre and indicates that the tubules are made of several graphene layers (55), also confirmed by the presence of the shoulder on the right-hand side of the G peak, in this case at 1611 cm^{-1} , typical of defective graphitic carbons. Due to their size and random orientation in the fibre, these impurities are not sensitive to polarisation effects.

Effectively, the Raman spectrum of CNT fibres depends both on their composition in terms of the relative amount of CNTs and carbonaceous impurities, and on the orientation of the nanotubes relative to the laser polarisation. However, because only nanotubes are sensitive to polarisation effects, their contribution to the Raman spectrum of the fibre can be separated from that of the graphitic

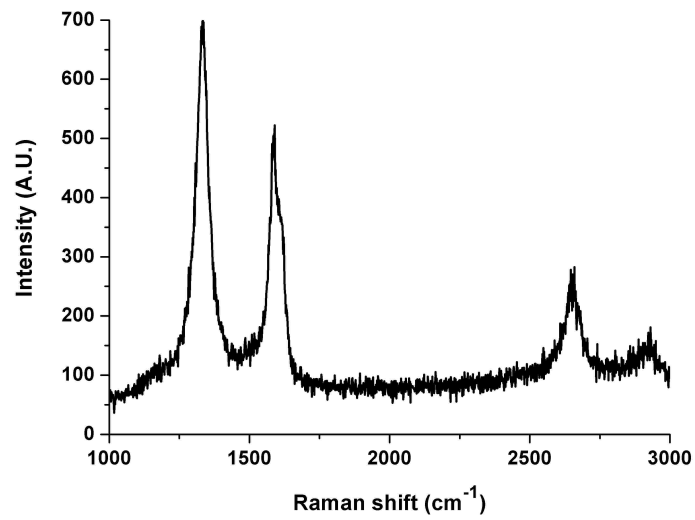


Figure 6.25: Raman spectrum of poorly graphitised impurities extracted from CNT fibres. Their defective nature is evidenced by the position of the D and G peaks at relatively high Raman frequency numbers and the high ratio of their intensities.

6.4 Raman Spectroscopy of CNT Fibres

impurities and to a first approximation can be determined as follows.

Take the measured value of intensity of the X Raman peak from the CNT fibre, I_x , to be the sum of the intensities arising from the carbonaceous impurities and the fraction of nanotubes oriented parallel to the polarisation direction, denoted I_x^i and I_x^n , respectively. Thus, for example, the equations for the G and D peaks read

$$I_G(\varphi) = I_G^i + I_G^n(\varphi) \quad (6.1)$$

$$I_D(\varphi) = I_D^i + I_D^n(\varphi) \quad (6.2)$$

where φ is the angle between the fibre axis and polarisation direction.

Additionally, from the spectrum of the carbonaceous impurities (e.g. Figure 6.25) the ratio of intensities between different peaks can be obtained, for example

$$I_G^i = 0.67 I_D^i \quad (6.3)$$

Furthermore, because the concentration of defects in the nanotubes, that is defects in their graphitic structure, is not likely to depend on their orientation relative to the fibre axis, the ratio of intensities of the D over G peaks from nanotubes is independent of the polarisation direction and therefore

$$\frac{I_D^n(\varphi_1)}{I_G^n(\varphi_1)} = \frac{I_D^n(\varphi_2)}{I_G^n(\varphi_2)} \quad (6.4)$$

For clarity, let us denote $I_G(\varphi = 0)$, the experimentally measured Raman intensity of the G peak from the fibre parallel to the polarisation direction, as α . Similarly, $I_D(\varphi = 0)$ as β , $I_G(\varphi = 90)$ as γ and $I_D(\varphi = 90)$ as ϵ .

After algebraic manipulation of equations 6.1-6.4, an expression for I_G^i in terms of experimentally measured parameters is obtained as

$$I_G^i = \frac{\alpha\delta - \gamma\beta}{\delta + 1.6\alpha - \beta - 1.6\gamma} \quad (6.5)$$

The intensity of the rest of the peaks can be calculated similarly.

6.4 Raman Spectroscopy of CNT Fibres

The graph in Figure 6.26 shows averaged values of Raman intensity obtained from 36 measurements at random locations along ~ 20 m of fibre, each measurement performed in parallel and perpendicular configurations. From the plot one observes that the intensity of the D peak is virtually the same in both configurations, while the intensity of the G peak is greater by a factor of ~ 3.5 in parallel. Similarly, the 2D peak shows roughly twice more intensity parallel than perpendicular to the polarisation direction.

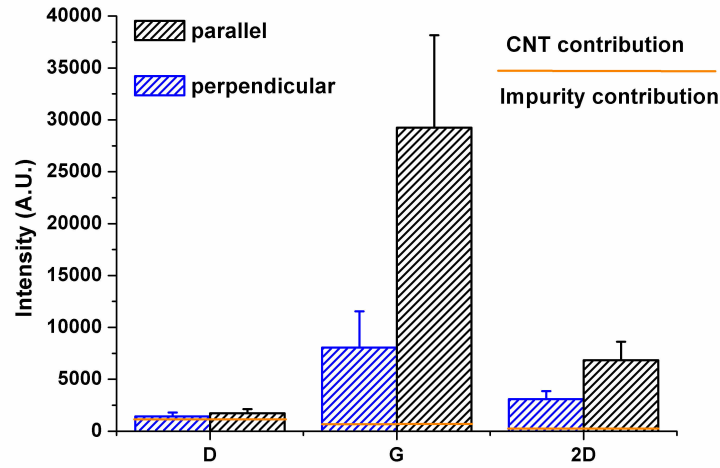


Figure 6.26: Comparison of averaged Raman intensities of the D, G and 2D peaks with the fibre parallel (black) and perpendicular (blue) to the polarisation direction of the laser, showing the anisotropy of the G and 2D bands. The orange line divides the contribution from impurities (below) and nantoubes (above).

The statistical values of Raman intensity in Figure 6.26 are effectively α, β, γ and ϵ . These values are used to calculate the individual contribution from the carbonaceous impurities and the nantoubes to the fibre spectrum, indicated in Figure 6.26 as an orange line separating their contributions. Thus, for example, the G band from the carbonaceous impurities accounts for a $\sim 3\%$ and $\sim 11\%$ of the total intensity of the fibre's G peak in the parallel and perpendicular configurations, respectively. In contrast, they contribute to the D band with

6.4 Raman Spectroscopy of CNT Fibres

$\sim 76\%$ (parallel) and $\sim 92\%$ (perpendicular) of the intensity, on account of their highly defective structure.

The data in Figure 6.26 are further used to calculate the ratio of intensities of the D over G and 2D over G bands, respectively, which are common parameters that reflect characteristics of nanotubes and other graphitic materials. In the case of CNT fibres, these quantities are polarisation dependent, however, the ratios can be determined for the nanotubes alone in the fibre, which gives values of $I_D^n/I_G^n = 0.015$ and $I_{2D}^n/I_G^n = 0.3$. Table 6.5 presents a comparison of the ratios for the nanotubes, impurities and of the whole CNT fibre parallel and perpendicular to the polarisation direction.

Table 6.5: Ratio of D over G and 2D over G Raman intensities

Material	I_D/I_G	I_{2D}/I_G
Nanotubes	0.015	0.3
Impurities	1.5	0.68
Fibre (parallel)	0.2	0.4
Fibre (perpendicular)	0.07	0.25

A final plot is presented in Figure 6.27, showing statistical data of the ratios of the D over G and 2D over G bands for fibres from different batches produced using the same synthesis conditions and winding rate. The distribution of D over G ratio intensities has a mean value of 0.12 ± 0.07 , however, the higher values spread up to ratios of 0.35. The 2D over G ratio has a mean of 0.31 ± 0.07 and is in remarkable agreement with the calculated value of 0.3 for nanotubes alone, presented in Table 6.5, showing that in parallel configuration the contribution to both peaks is dominated by nanotubes.

The results presented above show that the preferential alignment of nanotubes in CNT fibres and the presence of carbonaceous impurities have to be taken into account when interpreting their Raman spectra. The ratio I_D/I_G , for example, usually taken as a measure of the quality of CNTs in powder, is dependant on nanotube orientation in the case of CNT fibres and is therefore not single-valued. However, because unlike CNTs, the impurities in the fibre are not polarisation dependant, it is possible to determine the ratio I_D^n/I_G^n of the nanotubes alone, which is approximately 0.015 and indicative of a highly graphitised structure.

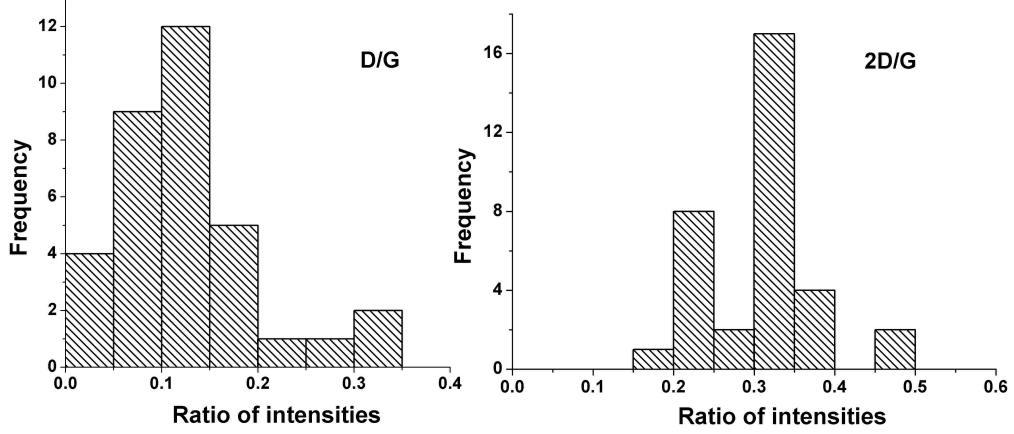


Figure 6.27: Distributions of the D over G and 2D over G ratios of Raman intensities of fibre from different batches.

Similarly, the effective degree of alignment of nanotubes on the fibre surface can also be determined as $I_G^n(\varphi = 0) / I_G^n(\varphi = 90) = 3.9$, which suggests that the nanotubes on the surface of the fibre are highly aligned parallel to the fibre axis, in agreement with XRD measurements for the whole of the volume of stacked CNTs in the fibre. This value compares with the ratio of ~ 6.5 observed in liquid crystalline spinning of SWNT fibres. Further comparisons are difficult because the CNT fibres in this study contain a variety of nanotubes with different number of layers and therefore with different susceptibilities to polarisation effects. While in MWNTs forests $I_G^n(\varphi = 0) / I_G^n(\varphi = 90)$ is of the order of 3.5 (93), measurements on individual SWNTs show virtually no intensity in perpendicular configuration (58).

Raman spectroscopy results also show that the highly aligned crystalline CNTs coexist with multilayered carbonaceous impurities with a very defective structure ($I_D^i / I_G^i = 1.5$). The combination of CNTs and impurities make the surface of the fibre have a value of the D over G bands of 0.12 on average, which is typical of nanotubes made by CVD, however, the spread in values for different

fibre batches indicate that there is space for improving the uniformity of samples.

6.5 Summary

This chapter has established the basic composition of the fibre, identifying and quantifying the mass fraction of several impurities reminiscent of the CVD reaction, such as adsorbates, amorphous carbon and residual catalyst particles, which represent approximately 8%, 3% and 18%, respectively, of the fibre mass, according to TGA measurements. The residual catalyst particles consist mostly of the γ and α phases of iron and Fe_3C iron carbide. Together with multilayered carbonaceous impurities, they are randomly dispersed throughout the fibre as small particulates, as determined by XRD and Raman spectroscopy.

The nanotubes in the fibre are highly graphitic and preferentially aligned parallel to the fibre axis, forming a network with uniform orientation across and along the fibre axis. Although spatially uniform, the orientation of nanotubes in this network indicates the presence of a misoriented component reflecting a generalised fault in the assembly of CNTs probably associated to impurity particulates preventing CNT elements from having a higher degree of alignment.

An observed shift in Raman frequencies across the fibre diameter is likely to be due to residual stress in CNT bundles, probably related to the assembly of nanotubes by mechanical drawing and interaction with liquid. The existence of residual stress in the fibre is analysed further in the next chapter.

The detailed discussion of the structure of CNT fibres in this chapter prepares the ground for the discussion on their physical properties in Chapter 7, particularly, the way in which the presence of aligned CNTs, residual catalyst and carbonaceous impurities coexisting together in the fibre determines the tensile properties of the material.

Chapter 7

Physical Properties of CNT Fibres

7.1 Mechanical

CNTs exhibit mechanical properties in close relation to those of graphite. Their strong and stiff in-plane bonds give nanotubes a specific stiffness ~ 300 GPa/SG and strength of ~ 20 GPa/SG, as determined experimentally (7); they could in principle reach 450GPa/SG and 60 GPa/SG, corresponding to the values obtained for a single graphene sheet (9). However, the interaction between layers in nanotubes and between the tubes themselves is mostly governed by van der Waals forces and the fact that nanotubes slide easily past each other (94). In the context of CNT fibres, the challenge is to make a material that exploits the axial properties of CNTs in spite of their ‘slipperiness’. The effect of poor transfer of stress between CNTs by shear is, in part, mitigated by using long CNTs in parallel assembly (37; 39; 41; 42; 47).

First, a theoretical analysis of the mechanical properties of CNT fibres that reconciles the tribological properties of graphite and the reported values of strength and stiffness for CNTs fibres is presented. Following this, a link is made between fibre structure and mechanical properties, which lays the foundations for a model describing the tensile properties of CNT fibres, and their comparison with rigid-rod-polymer fibres.

7.1.1 Theoretical Aspects

Stress Transfer in a Perfect CNT Assembly

The following model provides a link between the properties of a macroassembly of carbon nanotubes and those of the individual tubes, using the concept of shear-lag developed for fibre composite materials (95).

Consider an ideal fibre consisting of finite carbon nanotubes perfectly aligned along the fibre axis and separated from each other by the interlayer spacing typical of graphite crystal. Taking the length, l , and the outer radius, R , to be identical for all the tubes, it is assumed that in terms of stress transfer, each tube can be considered to be surrounded by a continuum, as schematically illustrated in Figure 7.1.

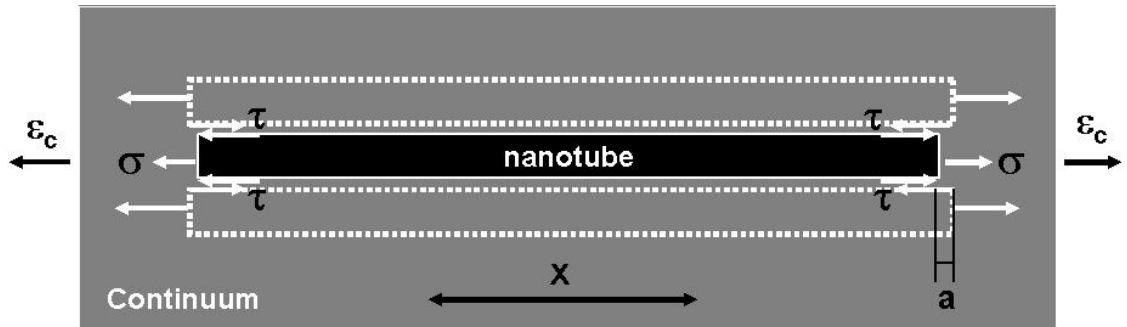


Figure 7.1: Schematic of a nanotube surrounded by a continuum. When the continuum is strain, stress is transferred to the nanotube by shear ($\tau(x)$), which results in axial stress build-up in the nanotube ($\sigma_n(x)$).

As the continuum is strained uniformly by ϵ_c , it will be locally perturbed by the presence of the nanotube and the transfer of load to it. Stress is transferred at the interface by shear due to the ‘friction’ stress between the nanotube and adjacent graphene layers surrounding it (Figure 7.1). From symmetry considerations, the shear stress in the ends of the nanotube must act in opposite directions and equal zero in the middle.

The shear stress distribution $\tau(x)$ translates into axial stress build up in the tube, such that the increment in axial stress $d\sigma_n$ in a length of nanotube dx is related to $\tau(x)$ by

$$Ad\sigma_n = S\tau(x)dx \quad (7.1)$$

Where A is the cross section of the tube and S the perimeter around the nanotube in shear (i. e. where a tube is in contact with its neighbours).

Shear stress between nanotubes arises from two distinct phenomena. The first is related to the surface energy of the newly exposed area created when nanotubes are displaced relative to each other. The second is the result of the resistance of one graphene layer to slide over the other, similar to the friction between surfaces of macroscopic materials.

It can be shown (e.g. reference (96)) that the first component of shear stress, τ_1 , is given by the surface energy of graphene, γ , and the length of newly exposed area of the nanotube, a , by

$$\tau_1 = \frac{\gamma}{a} \quad (7.2)$$

γ , has been measured for nanotubes (81; 94; 97; 98), graphite (99; 100; 101), graphene (102) and highly graphitised carbon fibres (103) using a wide variety of methods. These experimental values differ by an order of magnitude, probably due to differences in the exact composition of the materials used for the tests. Throughout this work, the average from these measurements, 0.13 J/m^2 , is used.

The second component of shear stress between nanotubes is due to ‘friction’ between adjacent graphene layers of nanotubes or similar graphitic materials. The maximum value it can take, τ_2 , is equal to the shear strength in graphite in the basal plane, which is equivalent to the shear strength between nanotubes and between graphene layers in MWNTs, which has been determined experimentally by atomic force microscopy (94; 104; 105; 106; 107). However, the reported values of shear strength between graphitic materials vary by more than three orders of magnitude. The scattering in values is unlikely to be only due to conditions in the experimental environment, such as pressure or the presence of particular gas molecules in the atmosphere, which are known to affect the tribological properties of graphitic materials (108). Even measurements on nanotubes performed in vacuum and ambient conditions give values that range from .04 MPa (94) to 69

MPa (104). It is likely that these large spread in values arises partially from differences in the order of the CNT surface and presence of impurities on the surface, as suggested by recent experiments (104), although the issue remains unclear. In this thesis, a conservative value of 29 kPa is used, corresponding to the average shear strength measured on macroscopic samples of single-crystal graphite (109) and in agreement with the low ‘friction’ observed between adjacent graphene layers in MWNTs (94). Note that taking this number, the shear component from the ‘friction’ between layers is some 15000 lower in magnitude than that due to graphene’s surface energy.

Stress Distributions in a Nanotube

In a composite with uniaxially aligned short fibres strained in a direction parallel to the fibres, stress is transferred to the fibres by shear and results in axial stress build-up from their ends. Analytic expressions for the shear and axial stress distributions in the fibres as a function of the stiffness and shear modulus of the matrix and the stiffness, radius and volume fraction of the fibres can be obtained using a shear-lag model (for a discussion on the shear-lag model in fibre composites refer to (110; 111)). However, with increasing strain in the composite the stresses at the interface eventually exceed the shear strength of the interface. In the case of a fibre/thermoset composite this leads to fibre ‘debonding’ and in the case of a metal matrix it leads to the matrix yielding at the interface. In both scenarios, after the interface fails, stress is still transferred to the fibre. As a result, the axial stress distribution in the fibres increases linearly from the ends of the fibre and reach a maximum value that remains constant along the rest of the fibre length. This maximum value of axial stress is dependant on the tensile yield stress and Young’s modulus of the matrix in the case of a fibre/metal matrix composite and on the coefficient of sliding friction between fibre and matrix in a fibre/thermoset composite.

A similar scenario is assumed for the nanotube/nanotube interface in the ideal CNT assembly, where the nanotubes take the place of the short fibres in the composite. With increasing ϵ_c , shear stress at the interface between nanotubes also increases, until the shear strength of the interface is exceeded and nanotubes

slide past each other. However, before nanotube sliding occurs, the maximum stress at the interface is considered approximately equal to the shear strength between graphene layer (τ_2), although excluding the ~ 0.2 nm at the ends of the tube susceptible to exposure of the high energy graphite surface. Thus, the shear stress distribution along a nanotube is divided in two regions, as shown in Figure 7.2. At the edges of the nanotube there is a small area (effectively close to a layer of atoms) where $\tau = \tau_1$ for $x \in (0, a)$ and the rest of the tube surface where the maximum shear stress is constant and equal to τ_2 .

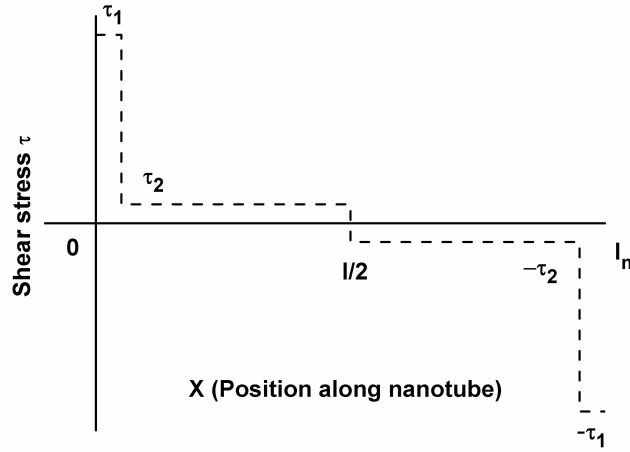


Figure 7.2: Shear stress distribution in a nanotube before nanotube sliding occurs. A high shear stress τ_1 arising from the material's surface energy acts on its ends. The rest of the nanotube's surface has a low shear strength τ_2 of ~ 30 kPa; but of course, extends over a very much greater length.

Having determined the shear stress distribution, the axial stress distribution in the nanotube can be obtained by integration of equation 7.1

$$\sigma_n(x) = \int_0^{l/2} \frac{S}{A} \tau(x) dx = \frac{S}{A} \left(\int_0^a \tau_1 dx + \int_a^{l/2} \tau_2 dx \right) \quad (7.3)$$

$$\sigma_n(x) = \frac{S}{A} (\gamma + \tau_2 x), \quad a \leq x \leq \frac{l}{2} \quad (7.4)$$

For the case of a perfectly round nanotube with its whole circumference ($2\pi R$) in contact with the continuum, the maximum axial stress in the tube can be obtained by taking $x = l/2$, which yields

$$\sigma_n^{max} = \frac{2\gamma}{R} + 2\tau_2\zeta \quad (7.5)$$

With ζ the nanotube's aspect ratio.

Note that the first term in equation 7.5 is independent from nanotube length and that for tubes with very low aspect ratio it would dominate, but only correspond to an axial stress of the order of 260 MPa. Equation 7.5 also captures the fact that due to their low shear strength, nanotubes would need to very long to reach their ultimate tensile strength, σ_n^u , and that therefore, there is a critical length (l_c) below which the nanotube would theoretically be pulled out of the continuum and above which it would fracture. For a round tube, l_c is given by

$$l_c = \frac{R\sigma_n^u}{\tau} \quad (7.6)$$

In order to appreciate the implications of equation 7.5 in more detail Figure 7.3 presents a comparative plot of the axial stress distributions at maximum shear stress, for round nanotubes with diameter of 1 nm and 5 nm and length of 1 μ m and 1 mm, respectively. For clarity, the position along the fibre is normalised relative to its length. The curves show the predominant role of the nanotube length, although they also evidence the decrease in tensile stress with increasing nanotube diameter. Taking a value of nanotube strength of 15 GPa and making use of equation 7.5, the critical aspect ratio, $\zeta_c = 2l_c/R$, comes out as $\zeta_c = 1 \times 10^6$.

Interface Between Nanotubes

Equation 7.4 was derived assuming the case of a perfectly round nanotube with its whole perimeter taking part in stress transfer. In reality, nanotubes are not perfectly round and tend to polygonise (112) or collapse into flat ribbons (113). Moreover, the stress transfer between a nanotube and its neighbours is likely to be restricted to a fraction of the nanotube's total surface area in contact with the surrounding tubes and which depends on the shape of the tubes. The ratio of the circumference of a nanotube in contact with the surrounding ones, over

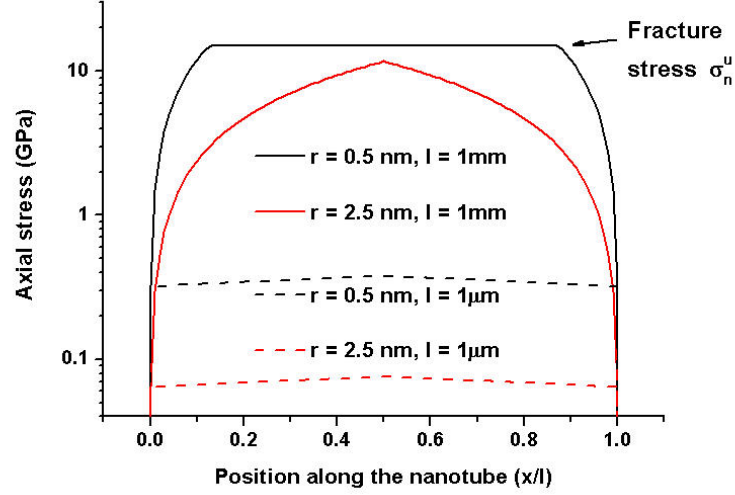


Figure 7.3: Axial stress distribution for nanotubes of different length and diameter, with the position along the nanotube (x) normalised to its length (l). The ultimate tensile strength of the nanotubes is arbitrarily taken as 15 GPa.

the complete circumference of the tube, is denoted Ω and determined below for polygonised and collapsed nanotubes.

First, in order to avoid defining the cross-sectional area of each nanotube with a particular geometry, stress is taken in specific units, thus, equation 7.4 is reexpressed as

$$\sigma'_n(x) = \frac{S\Omega}{\rho_l} (\gamma + \tau_2 x), \quad x \leq \frac{l}{2} \quad (7.7)$$

Equation 7.7 has the advantage that ρ_l , the linear density of a tube, is independent of the geometry of the nanotube and can be related to the areal density of graphene $\nu_g = 7.7 \text{ g/cm}^2$ and the radius of the equivalent round tube R by

$$\rho_l = 2\pi n R \nu_g \quad (7.8)$$

where n is the number of layers in the tube.

Take a hexagonal array of polygonised SWNTs (or DWNTs) separated by a distance d close to the turbostratic separation in graphite, with each tube defined

by the radius r of the curved sections between flat faces b , as schematised in Figure 7.4.

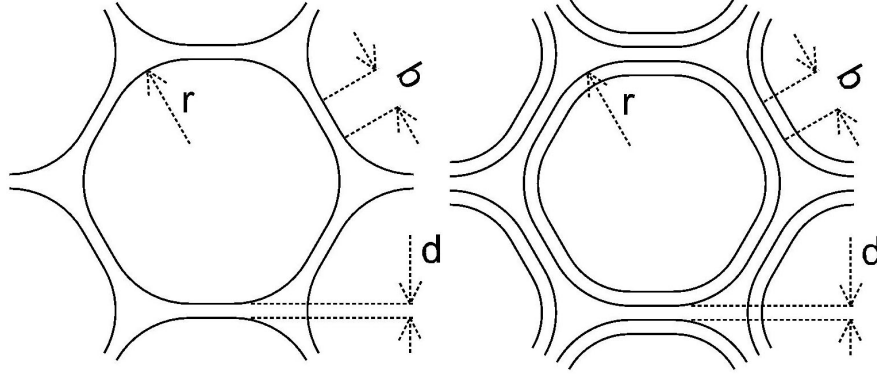


Figure 7.4: Schematic of bundles of polygonised SWNTs and DWNTs

For a polygonised tube in a bundle, the perimeter of the tube in contact with neighbouring nanotubes is taken as the sum of the straight sections b and Ω is given by

$$\Omega = \frac{6b}{2\pi R} = 1 - \frac{r}{R} \quad (7.9)$$

The energy of a SWNT in the bundle has a component from the cohesive energy between neighbouring layers, related to the surface energy of graphene, and a second component, of opposite sign, from the curvature of the tube, which can be estimated from classical theory of elasticity (114). The total energy per unit length of the tubes is thus expressed as

$$E = -\frac{\gamma}{2} \times 2\pi R\Omega + \frac{E_b}{2r^2} \times 2\pi R(1 - \Omega) \quad (7.10)$$

where E_b is the flexural rigidity of graphene and has units of energy and γ is the surface energy of the nanotube.

Substituting for r from equation 7.9

$$E = \pi\gamma R\Omega + \frac{\pi E_b}{R(1 - \Omega)} \quad (7.11)$$

The minimum energy configuration in terms of Ω can be obtained by differentiation of equation 7.11 with respect to Ω and setting equal to zero, which yields

$$\Omega = 1 - \frac{1}{R} \sqrt{\frac{E_b}{\gamma}} \quad (7.12)$$

This expression relates the equivalent round tube's radius (R) to Ω via two known parameters, E_b and γ . Interestingly, it also shows that the radius of the curved section (r) is not geometrically related to R . However, combining equations 7.9 and 7.12 gives,

$$r = \sqrt{\frac{E_b}{\gamma}} \quad (7.13)$$

For a bundle of DWNTs (see Appendix A), where each tube has an equivalent round tube's inner and outer radii R_1 and R_2 , respectively, and assuming that both tubes have the same Ω , equation 7.12 takes the form

$$\Omega = 1 - \frac{1}{R_1} \sqrt{\left(1 + \frac{R_1}{R_2}\right) \frac{E_b}{\gamma}} \quad (7.14)$$

Note that for large diameter double-wall tubes, where $R_1 - R_2 \ll R_1$, then,

$$\Omega \approx 1 - \frac{1}{R_1} \sqrt{\frac{2E_b}{\gamma}} \quad (7.15)$$

which corresponds to the expression for Ω for a SWNT taking twice the curvature energy ($2E_b$). This highlights the fact that while both walls of the the DWNT contribute to the curvature energy, the inner wall of a polygonised tube gains no energy through interaction with neighbours.

In the case where the nanotubes are collapsed due to their large diameter, the perimeter of interaction between adjacent nanotubes can be determined similarly to the case of polygonised tubes.

For a bundle of collapsed SWNTs, as schematised in Figure 7.5, Ω is taken as the length of the flatter segments of the tube over the total circumference of

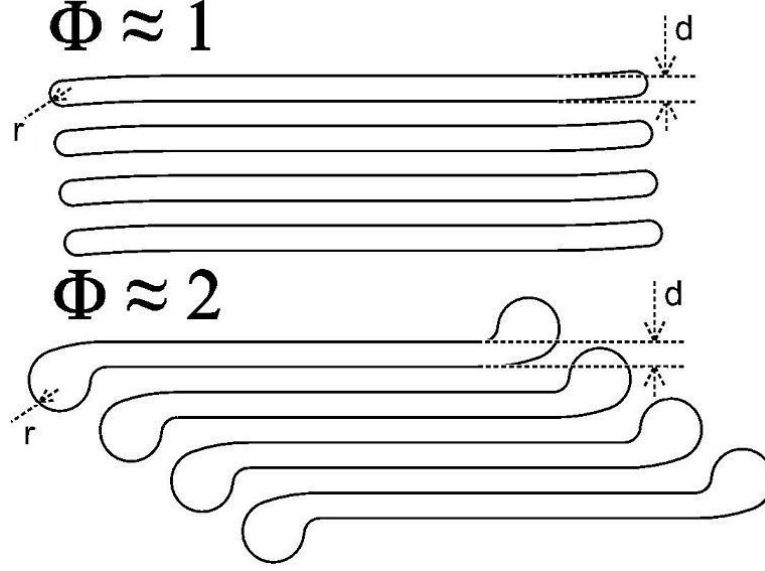


Figure 7.5: Schematic of collapsed SWNTs with different shape at the hair-pin edges.

the CNT. Ω can be geometrically defined by the curvature radius of the hair pin ends r and the equivalent round tube radius R according to,

$$\Omega = \frac{2\pi R - 2\pi r\Phi}{2\pi R} = 1 - \frac{\Phi r}{R} \quad (7.16)$$

where Φ is a constant related to the shape of the hair pin ends of the tube (Figure 7.5), that can take values in the range (1, 2).

Using the definitions of Ω and Φ the energy of the tube can be expressed as

$$E = -\gamma \times 2\pi R\Omega + \frac{E_b}{2r^2} \times 2\pi R(1 - \Omega) \quad (7.17)$$

The first term is twice that of equation 7.11, reflecting that the collapsed tubes benefit from internal bonding.

Substituting for r from equation 7.16

$$E = -2\pi\gamma R\Omega + \frac{\pi\Phi^2 E_b}{R(1 - \Omega)} \quad (7.18)$$

Differentiating with respect to Ω and setting equal to zero to get the minimum energy configuration in terms of Ω ,

$$\Omega = 1 - \frac{\Phi}{R} \sqrt{\frac{E_b}{2\gamma}} \quad (7.19)$$

Combining equations 7.16 and 7.19

$$r = \sqrt{\frac{E_b \Phi}{2\gamma}} \quad (7.20)$$

And although strictly Φ is a function of r , it is bounded in the range $(1, 2)$ and can be seen as a correction factor to account for the shape of the curved sections of the collapsed tube. Thus, for example, when Φ approaches 1, the tube is predominantly flat and Ω is higher than for an equivalent polygonised tube. This is due to the fact that the collapse of a tube brings an additional graphene layer in contact and therefore the tube can tolerate an increase in curvature energy thanks to the increase in cohesive energy.

The treatment for a bundle of collapsed DWNTs is straightforward and gives a solution of r identical to equation 7.20 taking $2E_b$, as discussed in Appendix A.

From the equations presented above it is evident that the geometry of the nanotube in a bundle is dictated by two quantities, the surface energy γ and the flexural rigidity E_b of graphene. γ is taken as 0.13 J/m^2 , as discussed previously and the flexural rigidity is taken as $2.21 \times 10^{-19} \text{ J}$ (1.47 eV), the average from reported estimates obtained by classical elasticity theory (113), molecular dynamics (115) and *ab initio* calculations (114; 116).

The expressions obtained for Ω for the different bundles are compared in Figure 7.6 as plots of Ω against the equivalent round tube's diameter (assuming $\Phi = 1$ for the collapsed tube based on experimental observation). Also on the plot are experimental data from image analysis of the HRTEM micrograph of collapsed tubes in Figure 2 of reference (70). The collapse transition diameter may be inferred as $\sim 4 \text{ nm}$ for SWNTs (117) and $\sim 5 \text{ nm}$ for DWNTs. The theoretical curves and experimental data evidence that a higher number of layers reduces Ω , on account of the increase in curvature energy as more layers are bent by polygonisation and collapse. It is also evident that on collapsing, CNTs

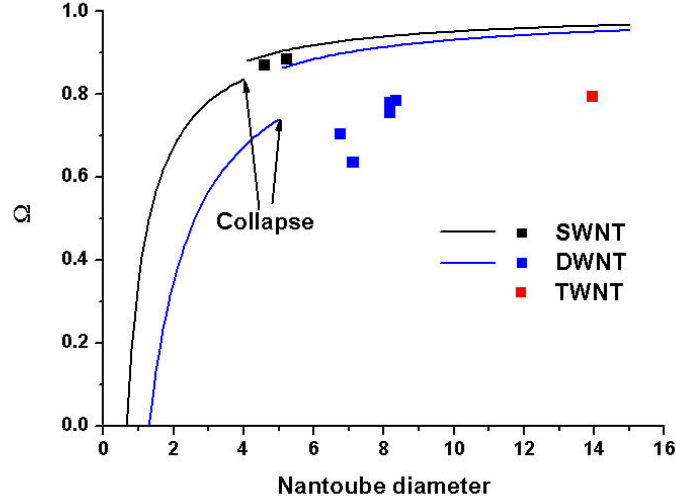


Figure 7.6: Plot of the fraction of a nanotube's perimeter available for stress transfer (Ω). Experimental data (squares) from image analysis of HRTEM micrographs of collapsed bundles in Figure 2 of reference (70).

maximise their contact with neighbouring tubes, which of course, is one of the driving forces of the geometrical transition itself. The experimental data are in line with the essential behaviour predicted by the model, the difference in the exact values possibly being due to the fact that the bundles analysed from HRTEM contain nanotubes of different diameters and therefore their contact is less efficient.

Theoretical Strength and Stiffness of the Ideal CNT Assembly

Having calculated the value of Ω it is possible to substitute for S (the circumference in contact with the tube) in equation 7.7 to give a refined relation for the axial stress in the nanotubes. For a polygonised SWNT, the axial stress distribution is given by

$$\sigma'_n(x) = \frac{1}{2\pi R\nu_g} \times 2\pi R \times \left(1 - \frac{1}{R} \sqrt{\frac{E_b}{\gamma}}\right) \times (\gamma + \tau_2 x) \quad (7.21)$$

$$\sigma'_n(x) = \frac{1}{\nu_g} \times \left(1 - \frac{1}{R} \sqrt{\frac{E_b}{\gamma}} \right) \times (\gamma + \tau_2 x) \quad (7.22)$$

whereas for a collapsed SWNT

$$\sigma'_n(x) = \frac{1}{\nu_g} \times \left(1 - \frac{\Phi}{R} \sqrt{\frac{E_b}{2\gamma}} \right) \times (\gamma + \tau_2 x) \quad (7.23)$$

These equations are expressions for the axial stress distribution in polygonised and collapsed tubes at the point of maximum stress transfer between the tubes and their neighbours and before nanotubes begin to slide past each other and the assembly fails. The assumption that all the tubes in the assembly are identical implies that the average stress in a single nanotube is equal to the average stress in the assembly. Thus, the tensile strength of a perfect assembly of polygonised tubes is given by

$$\bar{\sigma}'_n = \frac{1}{\nu_g} \times \left(1 - \frac{1}{R} \sqrt{\frac{E_b}{\gamma}} \right) \times \left(\gamma + \frac{\tau_2 l}{4} \right) \quad (7.24)$$

and for an assembly of collapsed tubes by

$$\bar{\sigma}'_n = \frac{1}{\nu_g} \times \left(1 - \frac{\Phi}{R} \sqrt{\frac{E_b}{2\gamma}} \right) \times \left(\gamma + \frac{\tau_2 l}{4} \right) \quad (7.25)$$

A plot of fibre specific strength, taken as the tensile strength of the ideal SWNT assembly, against nanotube diameter is presented in Figure 7.7, for nanotubes lengths of 2 mm, 1 mm, 0.1 mm and 0.01 mm, considering $\Phi = 1$ for collapsed tubes. The curves show the predominant role of nanotube length and the rapid decline in fibre strength as the tube length decreases to $\sim 50 \mu\text{m}$, at which point most of the tensile strength in the material comes from the surface energy component of the shear stress (τ_1). They also show that large nanotube diameter will be preferred in optimum mechanical properties. Note that for a nanotube length of 1 mm, which is readily attainable with current CVD techniques, values of strength in excess of current high-performance fibres are predicted. However, this assumes perfect assembly in line with the model in Figures 7.4 and 7.5 and

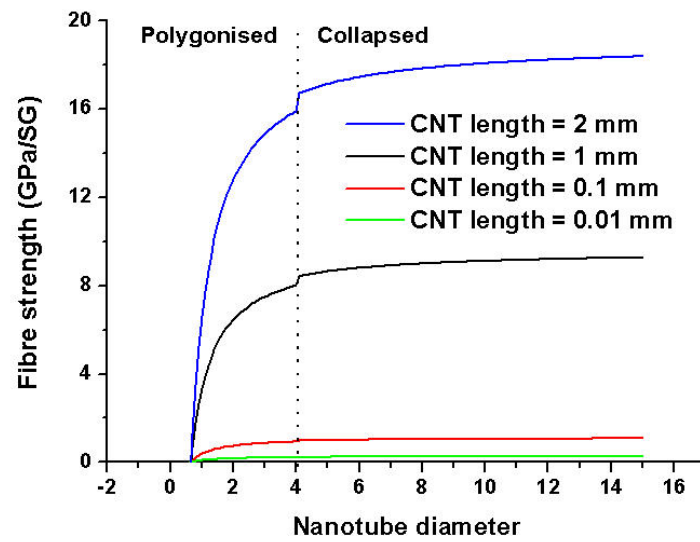


Figure 7.7: Specific strength of a perfect assembly of SWNTs with length of 2 mm, 1 mm, 0.1 mm and 0.01 mm, respectively. With decreasing CNT length, fibre strength decreases rapidly.

that effective stress transfer occurs between all nanotubes in the fibre, which are in fact not mean requirements in practice.

In principle, the stiffness of the assembly can also be determined from equations 7.24 or 7.25, depending on the type of nanotube. In a composite with discontinuous fibres oriented parallel to the sample main axis, the composite stiffness is related to the average stress in the fibres $\bar{\sigma}_f$ and the stiffness of the matrix Y_m by a rule of mixtures

$$Y_c = \frac{\bar{\sigma}_f}{\epsilon_c} V_f + Y_m (1 - V_f), \quad V_f > V_{min} \quad (7.26)$$

where V_f is the fibre volume fraction. In the case of the ideal CNT assembly $V_f = 1$ and the strain in the continuum ϵ_c corresponds to axial strain in the nanotubes and is therefore proportional to their stiffness. Effectively, the stiffness of the ideal CNT assembly Y_c in this simple model is equal to the stiffness of the individual nanotubes.

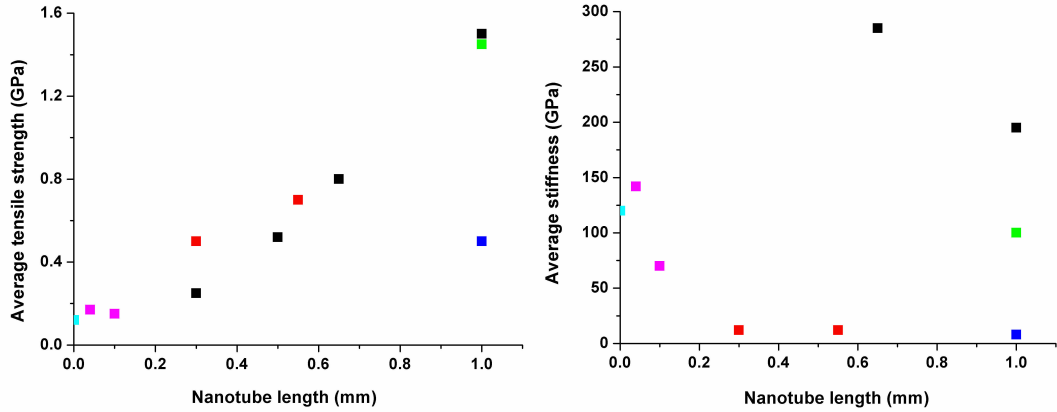


Figure 7.8: Reported values of fibre strength and stiffness of fibres made of nanotubes of different lengths and number of layers. The data are for fibres spun from arrays of aligned CNTs (black: DWNTs and MWNTs (40), red: MWNTs (118) and blue: MWNTs (41)), directly from the gas phase (green: mostly DWNTs (47)) and from a liquid crystal dispersion (pink: MWNTs (36) and light blue: SWNTs (37)).

For comparison with the theoretical prediction in Figure 7.7 a summary of the values of fibre strength reported in the literature for various CNT fibres, where the average length of the nanotubes is also reported, is presented in Figure 7.8 as a plot of fibre strength against CNT length. Values of fibre strength in units of GPa rather than GPa/SG are plotted because not all values of fibre SG are reported.

In spite of the fact that the type of nanotubes vary (covering the range SWNT to MWNT), the plot shows a clear correlation between fibre strength and nanotube length. However, encouraging as some of these experimental values may be, they still fall short of what would be expected from the simple model (Figure 7.7).

Note that the same correlation is not present for the fibre stiffness. This suggests that the stiffness of the CNT fibres reflects mostly differences in the orientation of CNTs in the fibres (119), in some cases due to specific processing parameters such as the application of twist.

Based on the model discussed above, it is clear that the first requirement for high values of fibre strength and stiffness is having long nanotubes of ideally as few layers as possible and large diameter so as to promote their collapse; and although an alternative to long nanotubes may be increasing the shear strength between nanotube interfaces, for example via introduction of covalent bonds, it remains to investigate if this can be done in sufficient quantity to increase shear strength per unit length while maintaining the tensile properties of the tube relatively intact. Implicit in the model is the importance of assembling nanotubes close together and parallel to each other with minimum disruption from entanglements or impurities so as to maximise their interfacial area and therefore stress transfer.

A further point regarding the stress transfer in nanotubes is that tensile stress in a CNT assembly will result in nanotube sliding before sliding of graphene layers within the tubes occurs, for at least two reasons. First, the interlayer separation within a tube is usually less than the separation between the tubes themselves, and secondly, because the area of interaction (through Ω) between concentric layers of each CNT is greater than between neighbouring nanotubes in a bundle. Thus, when an assembly of multilayered tubes reaches its maximum tensile stress before deforming plastically, the inner layers of nanotubes will effectively be in

the elastic regime. In this regime, the distribution of stresses in the layers can be related to their shear stiffness using a shear lag approach (120). A significant improvement to the present model would be made by taking into account the transfer of stress between graphene layers within a nanotube, which would allow to estimate the tensile strength of an ideal assembly of multilayered nanotubes; this development will be addressed in a subsequent study.

7.1.2 CNT Packing in Fibres and Tensile Properties

As shown in Chapter 5, the rate at which the aerogel is drawn out of the reactor affects the orientation and packing of nanotubes, which directly influence the CNT contact interface for stress transfer. Figure 7.9 shows average stiffness and strength of densified samples drawn out of the reactor at 5.6, 10 and 20 m/min, and tested at a gauge length of 2 mm (sample length/diameter ratio of 200/1). The plot indicates that both strength and stiffness increase significantly as the winding rate is increased. However, the width of the distribution (note error bars) also increases at faster winding rates.

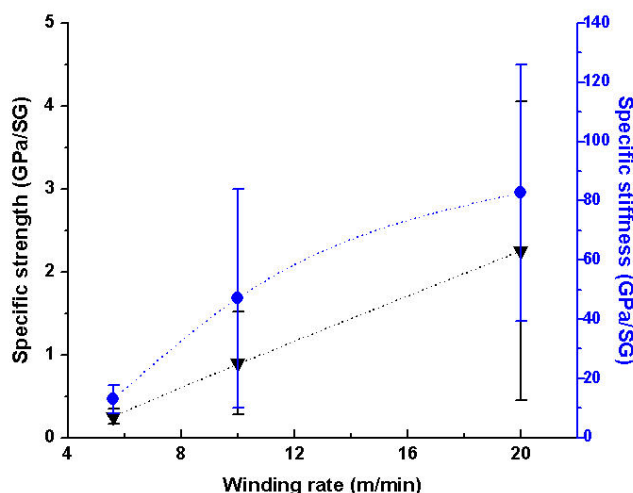


Figure 7.9: Tensile strength and stiffness in specific units, of fibres produced at different rates of wind up, tested at 2 mm gauge length (Replotted from (47)).

The increase in tensile properties with wind up speed in Figure 7.9 (which has been published in (47)) is an expected consequence of the corresponding increase in orientation and packing of CNTs (Section 5.1). Stiffness improves with orientation at higher drawing rates, as would be predicted (119), while strength increases due to the formation of longer domains of CNTs organised in oriented bundles.

The second fundamental factor in the assembly of CNT fibres is the densification through interaction with liquid. In order to have a qualitative measure of the effect of densification, the following samples are compared: an undensified fibre collected solely by drawing the aerogel; a second one collected in the same way, but with only a third of its length densified by contact with a small acetone drop (semi-densified); and a fibre densified on-line.

Figure 7.10 shows typical stress/strain curves of the undensified, semi-densified and on-line densified fibres. Overall, the shape of the curves differs in that the as-made and partially densified exhibit a tail at low strains, presumably due to the nanotube network being reshaped as nanotubes come in contact, followed by a steeper section of the curve up to what appears as a yield point, and after which further elongation is observed. In contrast, the densified sample shows a steep slope from the beginning of the test up to the yield point, which occurs at lower strain and higher stress than for the other samples.

Table 7.1: Mechanical properties of fibres with different degrees of densification

Fibre	σ^u (GPa)	σ^y (GPa)	δ (%)	E (GPa)	T (J/g)
Undensified	0.89	0.53	9.7	25	4.4
Semi-densified	0.95	0.73	6.3	35	2.8
Densified on-line	1.37	0.9	3.2	61	2.7

Table 7.1 contains the values of ultimate strength (σ^u), yield stress (σ^y), stiffness (E), strain-to-break (δ), and toughness (T) for these three fibres. It shows that σ^u , σ^y and E increase while δ and T decrease with greater densification.

These results show that the fracture stress is only moderately higher for the densified fibre than for the undensified and semi-densified ones, which indicates

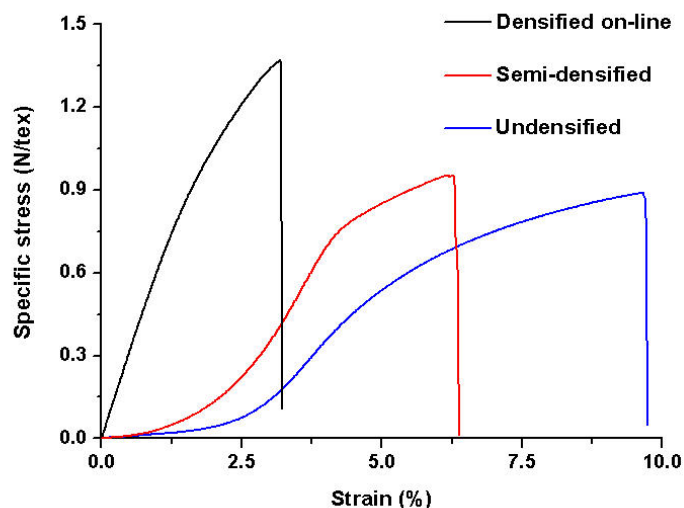


Figure 7.10: Stress-strain curves of fibres with different degrees of densification. Fibre strength and modulus increase with densification as the tube-tube interfacial area is increased.

that strength is dominated by defects which are not mitigated by increasing contact between nanotubes. The increase in CNT contact produces a more marked increase in stiffness, although it also results in a lower strain-to-break and a reduction in toughness. The plastic part of the curve, identified as the part of the region after the yield point (see Section 7.1.4), appears to be indicative of elements in the fibre sliding past each other and it is not surprising that this occurs more readily when the fibre is not densified.

The application of twist to CNT fibres is another common method for increasing their volumetric density (39). Figure 7.11 shows a comparison of stress-strain curves of a fibre after liquid-densification and fibres subsequently subjected to different levels of twist. With increasing level of twist the curves show a flatter initial region, followed by a steeper section which, nevertheless, evidences a lower stiffness than for the fibre without twist. Fibre strength also decreases with increasing twist and no indication of an improvement in toughness is observed either.

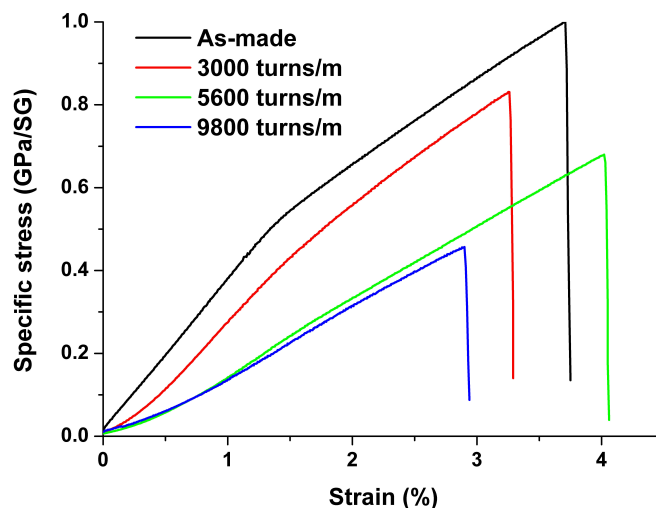


Figure 7.11: Stress-strain curves of fibres with different levels of twist applied after liquid-densification.

A likely interpretation of Figure 7.11 is that with the application of twist the load-bearing interface between bundles remains mostly unaffected, therefore not resulting in an improvement of strength or stiffness. Furthermore, because of bundle misalignment relative to the fibre axis induced by twisting, the axis of load-bearing elements is at an angle relative to the axial deformation of the fibre and thus, the tensile properties of the material are lower than those of the fibre without twist (119). In relation to the role of applying twist to CNT fibres produced by other methods, it appears that twist leads to an improvement in fibre properties only when it acts as a primary densification method (41). For fibres spun from the gas phase during CVD, that densification role is taken by the liquid.

7.1.3 Evidence of Intrinsic and Extrinsic Properties

From the discussion in the previous section it is evident that poor orientation of nanotubes or lack of densification of a fibre can be responsible for the tensile properties of a CNT fibre being considerably lower than those theoretically attainable.

Further insight into the role of defects can be gained by evaluating mechanical properties of fibres at different gauge lengths. Figure 7.12 presents a distribution of specific strength at 20 mm, 2 mm and 1 mm fibre gauge lengths (reproduced from (47)). The plot shows a peak at ~ 1 GPa/SG, present for the three lengths tested, and a second one at ~ 6 GPa/SG emerging at 2 mm and very clear at 1 mm gauge length and which occurs in the absence of the structural defects that give rise to the low-strength peak. The plot reflects the large spread in the high wind up speed data of Figure 7.9.

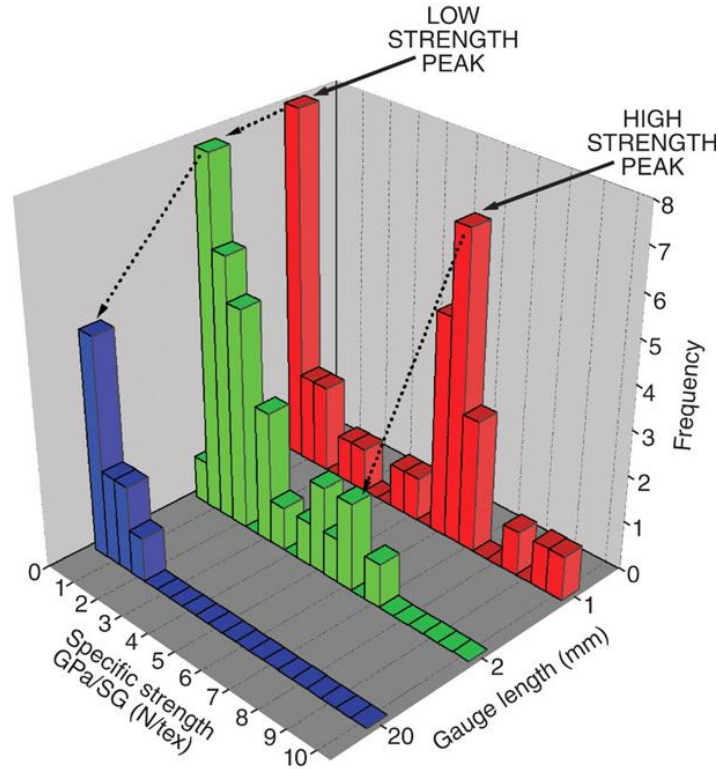


Figure 7.12: Distribution of specific strength for different gauge lengths. The bimodal distribution at 1 mm gauge length shows strength peaks ~ 1 GPa/SG and ~ 6 GPa/SG (47).

The bi-modal distribution at short gauge lengths suggests that there is a particular type of defect randomly located along the fibres, and typically found every few millimetres. In a 20 mm-long sample it is much more likely that a

defect will be present, hence the relatively low values of strength; however, as the gauge length is reduced the chance of testing a section of fibre with no presence of these defects increases. The importance of the high strength peak of the bi-modal distribution is that it is an indication of the properties of the material attainable if the fibre can be produced without the particular type of defects observed in longer sections of fibre, and which are likely to be induced during the spinning process but which are not intrinsic of the material.

A valuable indication of the nature of the defects in the fibre is obtained by comparison of the strength and stiffness of the same samples tested at the different gauge lengths, as presented in Figure 7.13. The plot reveals a strong correlation between strength and stiffness, with the implication that the defects found in the sample are not localised stress raisers, since this type of defects would affect fibre strength but not stiffness. Instead, the defects are present as collective failures in the assembly of elements throughout the bundle network structure, causing a decrease in both strength and stiffness.

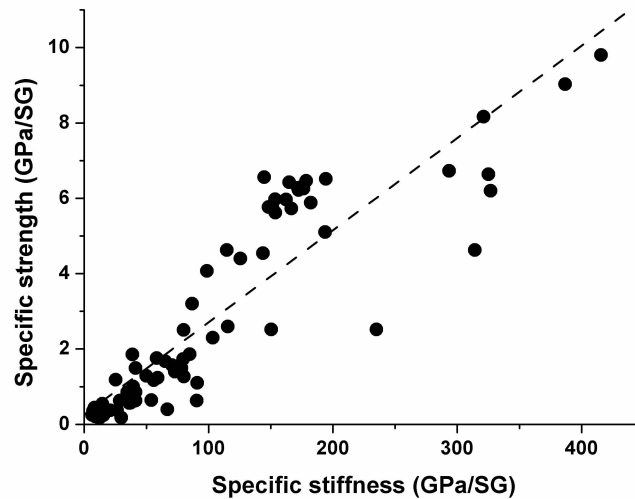


Figure 7.13: Plot of specific strength against specific stiffness of fibres tested at different gauge lengths, showing a clear correlation between the two tensile properties (Replotted from reference (47)).

The deficient assembly of CNTs in the fibre is partly due to impurities produced during CVD that become trapped in the bundle network, preventing the parallel packing of nanotubes and bundle (Figure 6.4B). Although of the order of tens of nanometres, the effect of impurities can propagate for much longer lengths as disruptions between bundles, with catastrophic effects for stress transfer. Additionally, by impeding the natural packing of bundles parallel to each other, they can result in residual stresses in bundles, with a detrimental effect on the cooperative loading of elements in the fibre and thus on its mechanical properties. Details of the most successful methods developed thus far for removing these impurities from CNT fibres are discussed in Chapter 8.

The nanotube ends are also defects in the CNT fibre structure. The ends limit the transfer of shear stress between nanotubes and cause the tubes to slide past each other before they reach their fracture stress. As a consequence, the fibre fracture stress is much lower than that of the nanotubes.

7.1.4 Tensile Deformation of CNT Fibres

Detailed information on the mechanical behaviour of a fibre in tension can be obtained by cyclic load tests, in which a sample undergoes a series of steps in which it is loaded to a given strain (or stress) and unloaded back to a recovery position typically corresponding to a small restoring pre-tension.

A typical load-unload sequence applied to a CNT fibre is depicted in Figure 7.14. The fibre, of 20 mm for this test, undergoes the following deformation sequence: it is strained to 1%, then unstrained down to a small pretension, strained to 2% of its original length, unstrained down to a small value of pretension and finally strained to rupture. The shape of the curve indicates that strain hardening takes place during the cycles, such that when the fibre is strained past its initial yield point (σ_{Y0}) to a stress σ_e , the latter becomes the new yield stress. The curve also shows that the loading cycles are accompanied by hysteresis and that the fibre does not recover entirely from deformations above the yield point.

Further insight into the tensile deformation of CNT fibres is presented in Figure 7.15, corresponding to a test in which a fibre is repeatedly strained to 3% of its original length and unloaded to a small pretension (A). The evolution of

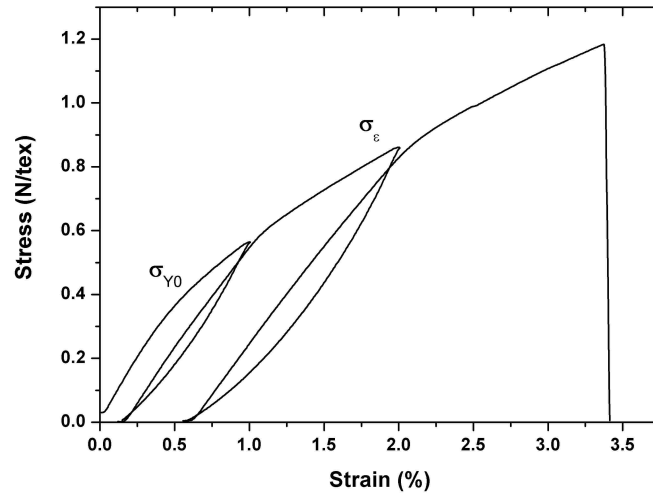


Figure 7.14: Stress-strain curve during a load-unload sequence of a CNT fibre at 20mm gauge length showing strain-hardening and hysteresis during loading cycles.

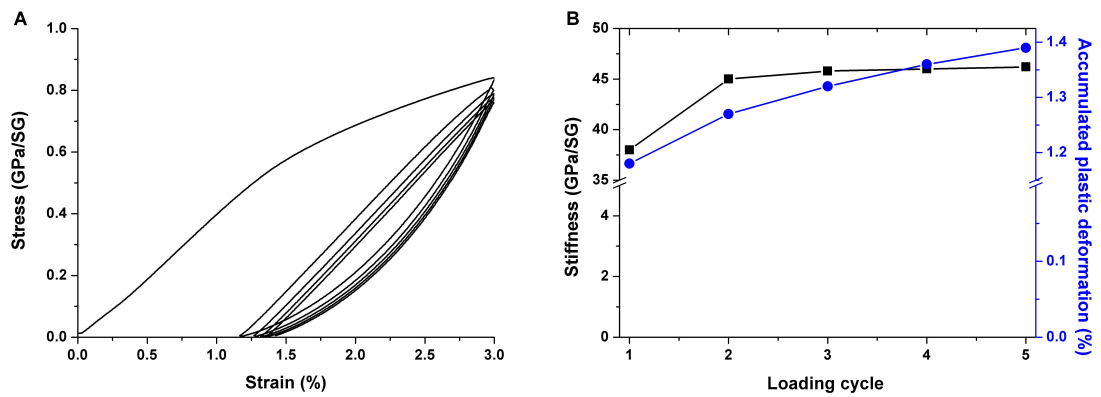


Figure 7.15: (A) Stress-strain curve during repeated load/unload cycles. (B) Stiffness and accumulated plastic deformation during the loading sequence.

the fibre's stiffness throughout the test (Figure 7.15B) occurs mainly as a result of the first cycle, suggesting that structural rearrangement with repercussions on stress transfer occurs on loading for the first time. The accumulated plastic deformation, on the other hand, appears to increase continuously as the fibre is strained, although there is an indication that it stabilises after a large number of loading repetitions. These results suggest that the initial large plastic deformation is responsible for the increase in stiffness.

Although load/unload cycles tests shows progressive inelastic deformation of the fibre with consecutive cycles, there is evidence that CNT fibres show a low level of creep. Figure 7.16A shows an example of a creep test in which a fibre is loaded up to a stress corresponding to 1% elongation, most likely past the fibre's yield point, and held under tension for several hours. From the curve, the strain as a function of time ($\epsilon(t)$) is found to be given by

$$\epsilon(t) = \epsilon_0 + \alpha \ln(t) \quad (7.27)$$

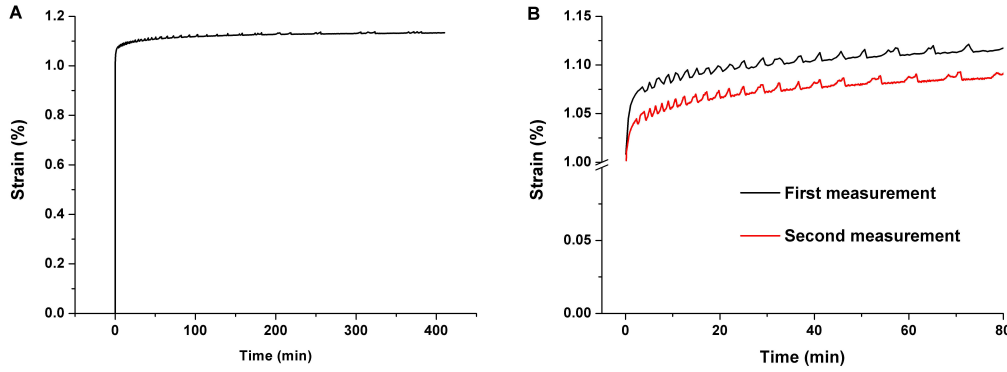


Figure 7.16: Fibre strain against time during creep test (A). Strain increases with the natural logarithm of time and therefore decays rapidly. Successive tests (B) evidence fibre stiffening through plastic deformation.

where ϵ_0 is an initial instant strain after loading and α a factor related to the strain increase with time. The logarithmic dependance on time implies that the curve decays very rapidly with time and that no appreciable strain occurs soon

after initial loading. Interestingly, consecutive identical tests in which a sample is strained to the same elongation (Figure 7.16B) show a progressive decrease in ϵ_0 , presumably due to fibre stiffening through plastic deformation in the first loading event.

The changes in fibre structure during loading cycles can be monitored by XRD. Figure 7.17 depicts a plot of the SAXS azimuthal spread (FWHM) from fibres strained five times to 1 %, 2 % and 2.5 % of their original length, respectively, and unloaded. The error bars based on the variations measured along each sample. The graph shows a small but constant decrease in the FWHM with increasing strain, showing that as the fibre is stretched the alignment of elements parallel to the its axis increases.

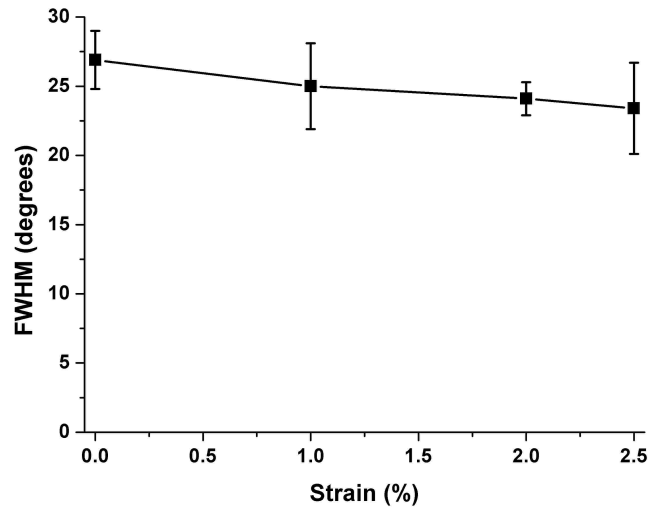


Figure 7.17: FWHM from the SAXS azimuthal profile from CNT fibres strained repeatedly to 1%, 2% and 2.5% of their original length. An increase in orientation of bundles is observed with fibre straining.

Further insight into the evolution of the fibre structure, effectively only of its surface, can be obtained from Raman spectroscopy measurements. From *in situ* measurements the tensile deformation of a fibre can be directly correlated to the deformation of the bundle network during fibre loading/unloading. Figure 7.18 is

a plot of the change in Raman frequency of the 2D₁ peak as a fibre is strained to 2.5 % of its original length and unloaded, with this particular peak being chosen as it shows the highest sensitivity to strain (60). Each point corresponds to 19 measurements along 70 μm of the 10 mm of the sample ¹. The sequence in the plot, indicated by arrows, starts with a small deformation, enough to hold the fibre under a minimum tension, that decreases the spread in Raman frequency values but does not change their average position. As the fibre is strained, a severe downshift in frequencies occurs up to 1.5 % fibre strain, probably close to the yield point of the fibre. The Raman frequency remains fairly constant from 1.5 % to 2.5 % fibre strain, although with a hint of an increase in the deviation from the mean. At the final stage of the test the fibre is unstrained to 1.5 % of its original length, which causes the Raman frequency to return almost to its original value.

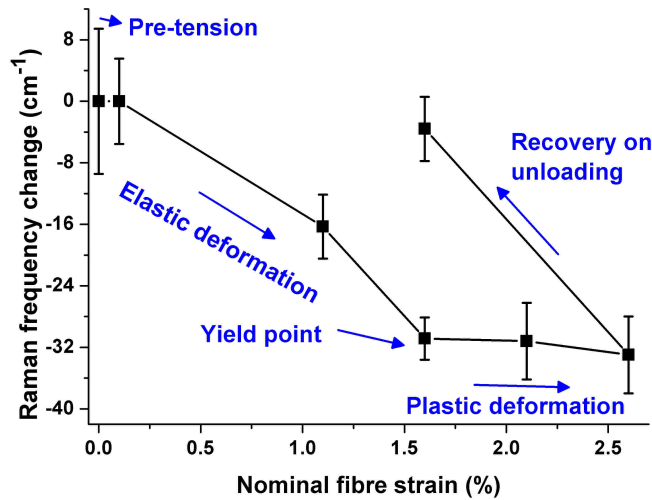


Figure 7.18: Raman frequency change of the 2D₁ band against fibre strain during a loading/unloading sequence.

Raman frequency values can be converted to nanotube strain (Section 3.5) during fibre deformation. Figure 7.19 shows a plot of nanotube strain calculated

¹The measurements were performed by R. Meenakshi under supervision of the author.

from the downshift of the D, G and $2D_1$ bands during fibre elongation. The curves of nanotube strain against fibre strain from the G and $2D_1$ bands show very similar behaviour throughout the test and similar values of nanotube strain at almost every point. Both bands indicate that elastic strain is very similar for the fibre and nanotubes. It is interesting to see that the D band gives much lower nanotube strains, possibly a consequence of this band having a large contribution from graphitic impurities and amorphous carbon.

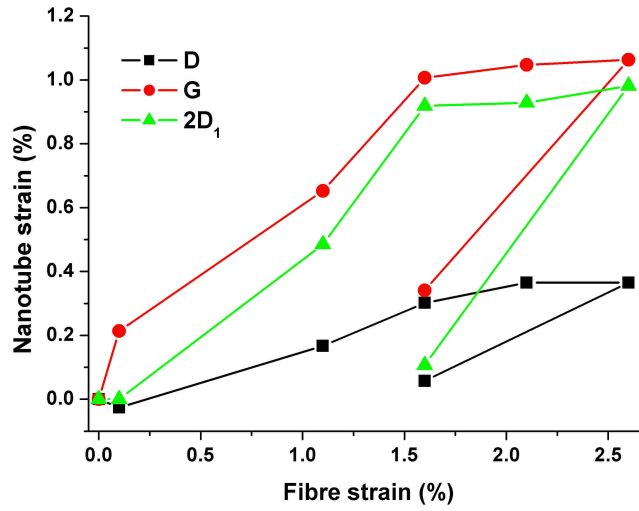


Figure 7.19: Nanotube strain calculated from Raman frequency downshift of the D, G, and $2D_1$ bands, against fibre strain. The G and $2D_1$ bands give similar values of strain close to that of the fibre, unlike the D which is likely to have a major contribution from impurities.

In terms of the deformation of nanotubes during fibre tensile deformation, these results indicate that the small initial load on the fibre decreases the scattering in Raman frequency. The tubes then are strained and make the fibre elongate $\sim 1.5\%$, but on further straining of the fibre no elastic deformation of the nanotubes occurs; finally, if the fibre is unstrained by 1% the tubes appear to return to their original state. With reference to the cyclic load in Figure 7.14, the experimental results support the view that σ_{Y0} is a genuine yield point.

For reference, the range of Raman frequencies in the fibre prior to tensile deformation, as discussed in the previous chapter (Section 6.4), can also be converted to values of nanotube strain. The values come out as 0.1 – 0.3% strain in the nanotubes and which must be equally present in compression and tension in the fibre structure. This level of residual strain (stress) in the tubes is significant compared to the stress in the tubes during tensile loading of the fibre.

7.1.5 A Model for the Tensile Deformation of CNT Fibres

The tensile behaviour of CNT fibres shows similarities to that of as-spun rigid-rod polymer fibres: both exhibit a stress-strain curve with elastic and plastic regions separated by a smooth yield area, the possibility to undergo strain hardening, and hysteresis under loading cycles (121). Furthermore, the correlation between fibre strength and stiffness in CNT fibres (Figure 7.13) is also typical of rigid-rod polymer fibres (122); and in general of materials where stress is transferred between oriented elements by shear.

Thus, based on the experimental results presented so far and borrowing ideas from rigid-rod polymer science, it is proposed that CNT fibres behave as a network or preferentially oriented elements which on fibre loading do not take stress cooperatively, partially due to differences in their initial strain as a consequence of residual stress in the nanotubes induced during the fibre assembly stages. Through successive fibre straining, the orientation of the network can be slightly corrected and the elastic deformation of the fibre increased; however, with little effect on the strain offset between elements and therefore on fibre strength.

To discuss the axial deformation of a CNT fibre a schematic illustrating the evolution of load-bearing elements in the fibre throughout a loading cycle is introduced in Figure 7.20. The image comprises a stress-strain plot during fibre loading/unloading, and the corresponding deformation of bundles preferentially oriented along the fibre axis (vertical), one group of bundles (*A*) being highly aligned before the test and the other (*M*) with crimp, and therefore with some initial degree of misalignment.

As the fibre is strained, aligned bundles are pulled and deformed elastically, while some crimped bundles are straightened, producing a steep section in the

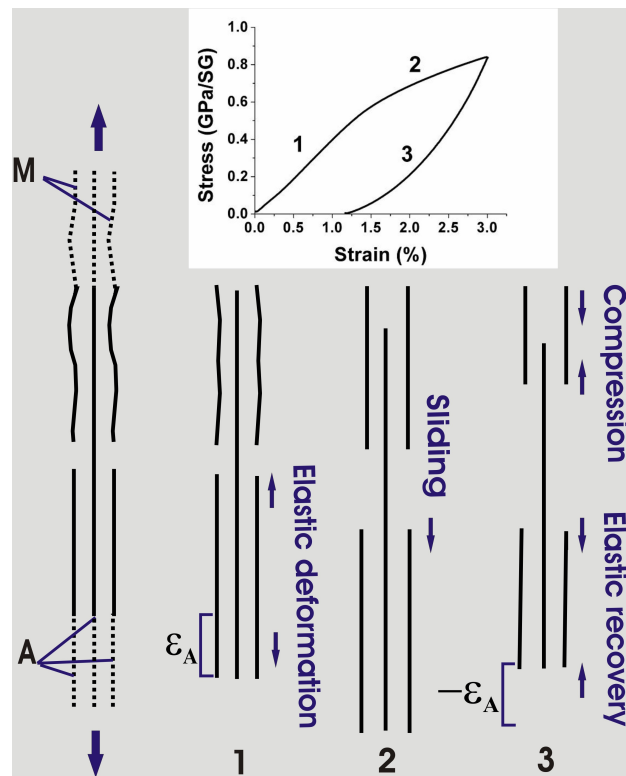


Figure 7.20: Model for the deformation of aligned (*A*) and crimped (*M*) bundles during fibre straining (inset). On loading, aligned bundles elongate (1) and stretch misoriented bundles (2), which contributes to the plastic deformation associated with sliding of elements. During unloading (3) a strain mismatch between the two types of bundles prevails.

stress-strain curve of the fibre (1) as a combination of the two contributions. When the aligned bundles reach a limit of elastic strain (ϵ_A) they slide, which contributes to further straighten and reorient the initially misoriented bundles (2). As the fibre is unloaded, the elastically deformed tubes tend to return to their original length, however, because they are in contact with newly straightened bundles, the restoring force competes with the resistance of bundles to be compressed (3), resulting in a strain mismatch between the bundles during and after unloading.

The stress in aligned (A) and misaligned (M) bundles during a sequence of fibre loading, unloading and reloading is shown schematically in Figure 7.21, with the fibre's stress-strain curve for reference in the background. The unloading curves emphasise the fact that the stress on the bundles during fibre unloading is uncertain. As the fibre is reloaded not only bundles A deform elastically, but also the newly straightened ones (M); however, because of their initial strain mismatch, their contribution to stress is only additive once bundles A have reached their elastic deformation limit (ϵ_A). The elastic contribution from bundles M terminates at the point where the stress equals the barrier for further sliding and straightening of elements, identified as the new fibre's yield point. Because the load-bearing elements act at different stages of the fibre strain, no cooperative build-up of stress occurs at any strain and, therefore, the fibre's fracture stress is not affected in spite of the improved bundle orientation after cyclic loading.

Strain mismatch of elements in as-spun fibres made of rigid-rod polymers, such as poly-(p -phenylene benzobisthiazole) (PBZT) for example, is manifested as surface undulations on the fibre, readily observed by SEM (122). Similar domains are not so clearly identifiable in CNT fibres, first because rather than a well defined solid fibre, as is the case for the polymer one, the nanotube bundles form a network of thousands of elements, in which any misorientation could be interpreted as arising from residual stress. Secondly, because the axial and bending stiffnesses and aspect ratio of CNT bundles is very different from those of polymer fibrils and, therefore, residual stress in bundles may lead to different structural features in a CNT fibre.

The model discussed above is a first approximation to reconcile several observations on the tensile deformation of CNT fibres, such as their elastic-plastic be-

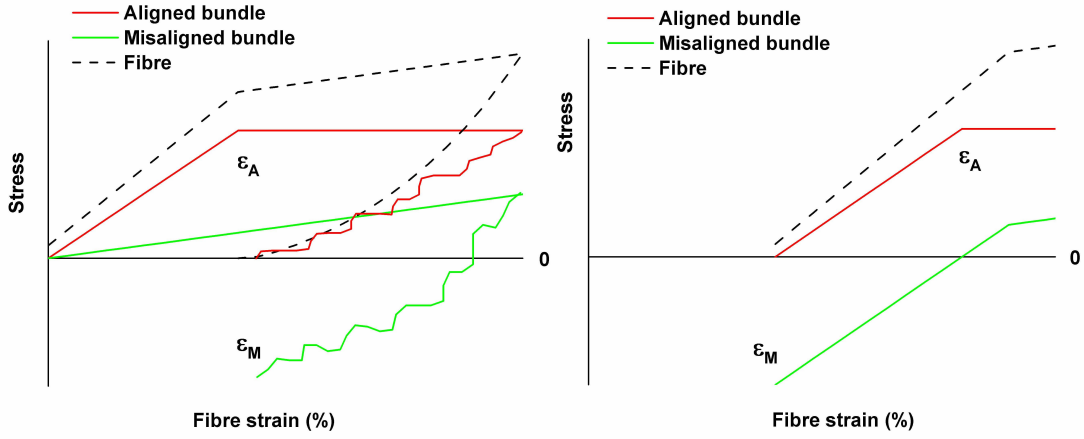


Figure 7.21: Schematic stress-strain curve of CNT bundles during fibre loading, unloading (left) and reloading (right). When aligned bundles are strained and reach their elastic limit (ϵ_A) only straightening of misaligned bundles occurs. On unloading a strain mismatch between bundles prevails, such that they do not take load co-operatively on reloading.

haviour, the occurrence of strain-hardening, and the hysteresis unloading loops; with direct measurements of strain and orientation of the bundles in the fibre structure. Further application of the model is made in the next chapter, which explores annealing as a means for rearranging load-bearing elements in the bundle network and its effect on the fibre's tensile properties.

7.2 Electrical

Although theoretically, individual CNTs can have electrical conductivity close to that of copper (19), it is likely that a macroscopic assembly of CNT will show significantly lower values due to the requirement of electron hopping between graphene layers (123), the presence of semiconducting as well as conducting nanotubes and the difficulties in forming an assembly of perfectly aligned and packed nanotubes. Nevertheless, CNT fibres and other macroscopic CNT-based materials have the advantage over metals, for example, of a low density and high

specific strength and stiffness, which makes them ideal candidates for a number of electrical applications, such as power transmission lines, given the achievement of sufficiently high electrical conductivity (124).

7.2.1 Electrical Conductivity of CNT Fibres Spun From the Gas Phase

The first step in measuring electrical properties of CNT fibres is establishing a good electrical contact between the material and the measuring devices. A simple strategy for doing this consists in forming a permanent metal contact on the fibre surface by forcing mechanical interaction between the single fibre filament (or a yarn with several fibre filaments) and molten solder, followed by rapid cooling of the metal adhered to the fibre (125). An example of a yarn of CNT filaments with SnSb contacts is shown in Figure 7.22. The electrical resistance of the fibre/contact interface using this method is very low, of the order $\sim 1 \Omega$ (Inset in Figure 7.22).

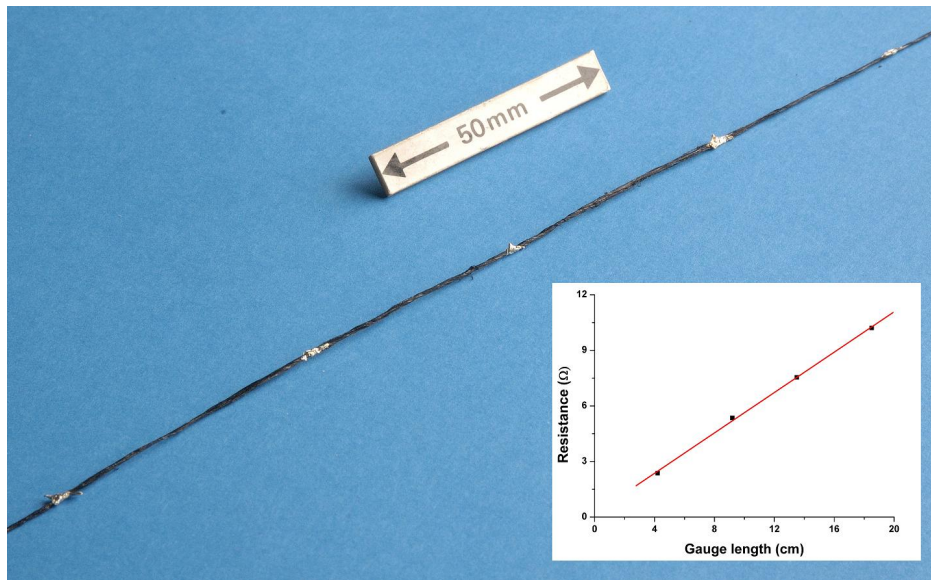


Figure 7.22: Photograph of a CNT yarn with SnSb contacts used for 4-point measurements. The interface has a very low electrical resistance of $\sim 1 \Omega$ (inset).

Soldered metal contacts on a CNT fibre can be used to perform 4-point electrical conductivity tests. The examples of voltage-current plots in Figure 7.23 show that both a single CNT fibre filament (left) and a yarn of ~ 1000 individual fibre filaments show ohmic behaviour, in agreement with the behaviour generally observed for CNT fibres (36; 38; 39; 41; 42). The electrical conductivity of the CNT fibres can be calculated from the voltage-current curves and the cross-sectional area of the fibre from SEM observation.

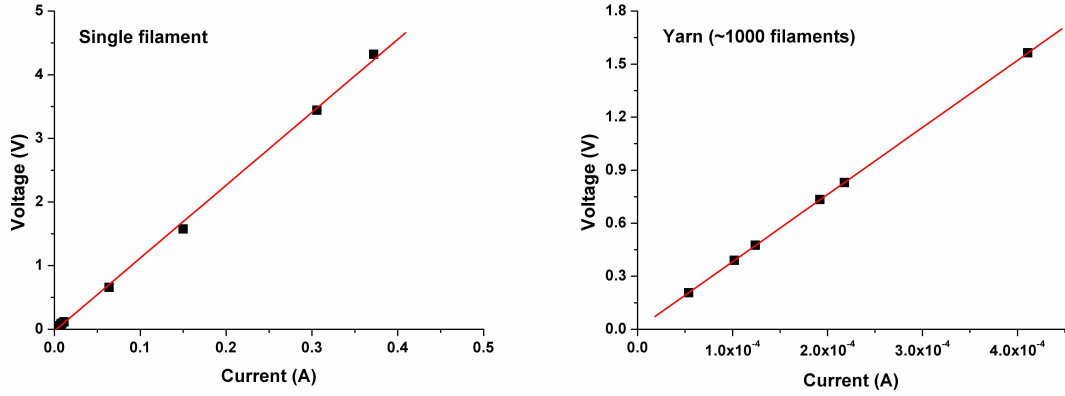


Figure 7.23: Voltage-current curves for a single CNT filament and a yarn of ~ 1000 fibre filaments. The curves show that the materials exhibit ohmic behaviour.

Table 7.2 presents an average value of electrical conductivity of the fibres in this work and a summary of the values reported in the literature for CNT fibres produced by different methods. The comparison shows that the CNT fibre spun from the gas phase has an electrical conductivity at the high end of the values, comparable to those of fibres drawn from arrays of aligned MWNTs and fibres spun from liquid crystalline dispersions of SWNTs. For reference, their conductivity of 8×10^5 S/m, is short of the value of 59×10^6 S/m for copper (126), however, only by a factor of ~ 8 when normalised by their volumetric density.

It is interesting that the values at the high end of the table converge, in spite of the fibre being made up of nanotubes with different number of layers, length and which are collapsed for the fibres spun from the gas phase, but probably round

Table 7.2: Electrical conductivity of CNT fibres at 300K

Spinning Method	CNT type and length (mm)	Conductivity (S/m)	Reference
Drawn from array	MWNT, 0.5 - 1.0	$0.3 - 8 \times 10^5$	(39; 41; 42)
From liquid crystal dispersion	MWNT, 0.1	8×10^3	(36)
From liquid crystal dispersion	N-MWNT, 0.05	3×10^4	(36)
From liquid crystal dispersion	SWNT, 0.001	4×10^5	(38)
Drawn from gas phase	mostly DWNT, 1.0	8×10^5	(124)

for the others. This convergence suggests that the electrical resistance between tubes plays a more dominant role than the resistance of the tubes themselves in determining the electrical conductivity of the fibre.

7.2.2 Fibre Structure and Electrical Properties

Similarly to their mechanical properties, the electrical conductivity of CNT fibres is affected by the processing parameters employed during fibre spinning. With increasing winding rate, for example, higher fibre electrical conductivity values are obtained, as shown in Figure 7.24. However, such an increase in conductivity is not entirely due to an improvement in bundle orientation and the formation of a larger interface between nanotubes with increasing winding rate. If the conductivity values are taken in specific units, that is, conductivity over specific gravity, then the increase in conductivity with winding rates is less marked. This suggests that part of the apparent increase in conductivity is partially geometrical, due to the decrease in cross-sectional area per unit linear density as higher winding rates are used.

Further insight into the role of density in the fibre's electrical conductivity can be gained by measuring electrical resistance of a CNT fibre as it is densified

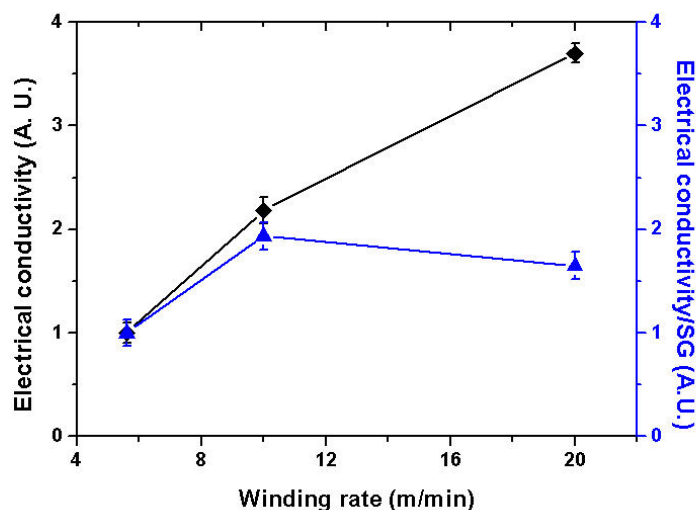


Figure 7.24: Electrical conductivity and electrical conductivity/SG of CNT fibres produced at different winding rates.

by interaction with liquid. Figure 7.25 shows a graph of electrical resistance and fibre diameter throughout the liquid-densification process, with indications of the points where the liquid is in contact with the fibre and when evaporation takes place. The curve shows that there are changes in resistance of only $\sim 10\%$ of the initial value during the condensation process, but that there is virtually no change before and after the treatment; this, in spite of a decrease in diameter by a factor of ~ 10 .

As shown in Chapter 5, densification of a CNT fibre increases the interface between nanotubes, however, according to Figure 7.25, with a negligible effect on the electrical conductivity of the fibre. The implication is that it is likely that electrical resistance in the CNT fibres is dominated by the end of the tubes, and that therefore, increasing the packing of tubes, for example through densification, does not reduce the total electrical resistance as the number of tube ends per unit length remains unchanged.

The effect of liquids on CNT fibres can be further studied by measuring electrical resistance of fibres on immersion in and extraction from liquids. Figure 7.26

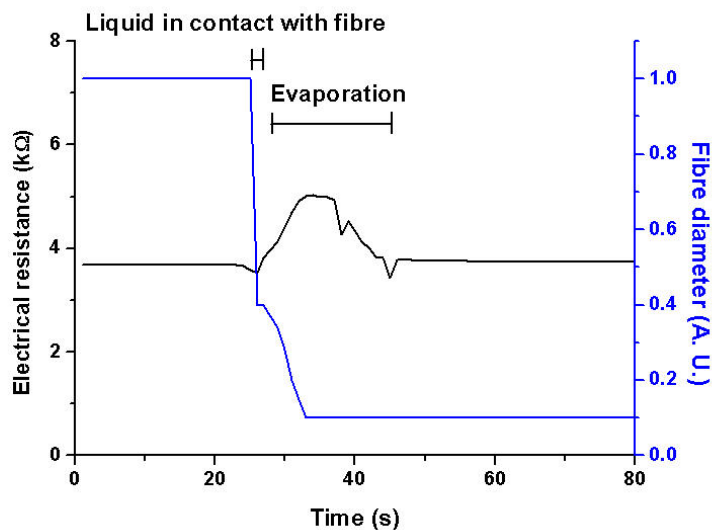


Figure 7.25: Electrical resistance and diameter change during fibre densification. In spite of a diameter decrease by a factor of ~ 10 , electrical resistance before and after liquid-densification is unaltered.

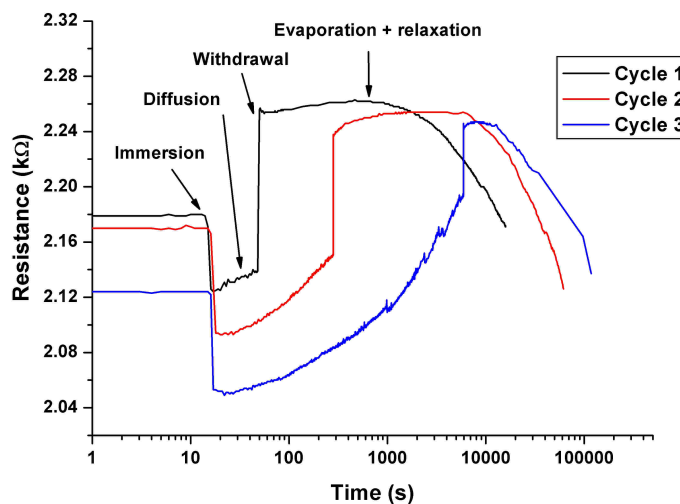


Figure 7.26: Electrical resistance of a CNT fibre during cycles of immersion in and extraction from a liquid bath.

shows a plot of electrical resistance against time for three consecutive immersion cycles of different duration in acetone. The curves show a clear drop in resistance upon immersion in the liquid, followed by a gradual increase in resistance up to the point when the fibre is removed from the liquid bath, which results in a sharp resistance increase and subsequently a slow decrease that brings the resistance back to its original value.

A similar experiment in which a CNT fibre is immersed in de-ionised water is presented in Figure 7.27, with an equivalent measurement in acetone shown for comparison. The curve indicates that immersion in water does not affect fibre resistance significantly, although a small increase is observed on extraction from the liquid bath followed by a gradual decrease to its original resistance value.

The shape of the curve corresponding to the measurement in acetone suggests that the initial drop in resistance is due to the first contact between liquid and fibre when the liquid wicks instantly in the fibre and establishes a liquid/solid interface. This process is not likely to occur when the fibre is immersed in water, in which case a small layer of air is probably present between the liquid and most of the internal surface of the solid. The gradual increase in resistance after immersion in acetone is associated to liquid molecules wicking in the relatively porous fibre structure, although it is uncertain if the liquid adsorbed on the internal surface of the fibre affects the conduction in the nanotubes themselves, or the resistance between them. After removal of the fibre from the bath, the curve of resistance is believed to be due to an overlap between liquid evaporation and the resulting structural relaxation. As the liquid molecules diffuse out of the fibre structural rearrangement of elements in the fibre occurs due to locally induced stress on the bundles as liquid molecules force their way out of the fibre. In the case of water, this effect is less pronounced due to its low affinity to graphitic surfaces.

The effects of bringing CNT fibres in contact with liquids are interesting from the point of view of the information they provide about the bundle network structure and the current conduction mechanism. Further experiments to investigate structural alterations of the bundle network during fibre wicking, ideally by micro-beam XRD, would clarify the extent to which variations in resistance are a consequence of structural rearrangements in the fibre rather than due to effects on the conduction mechanism in the fibre itself.

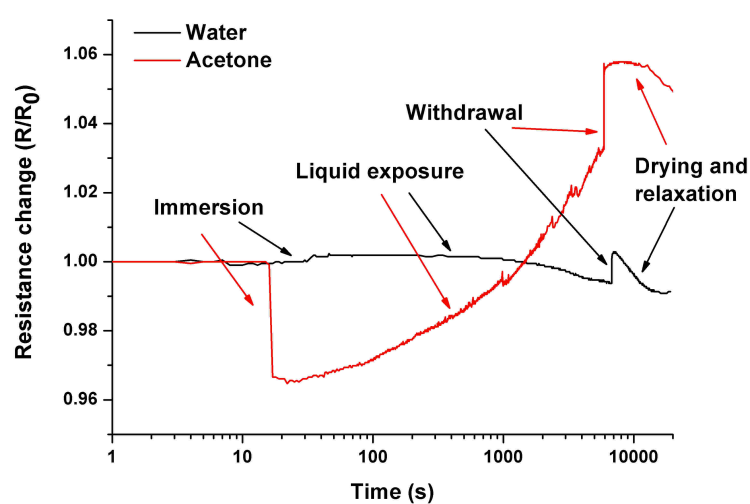


Figure 7.27: Electrical resistance of fibres during cycles of immersion in different liquids. In acetone (red) a clear increase in resistance on immersion suggest that diffusion is taking place, whereas in water (black) the fibre's resistance remains less affected.

7.3 Thermal

Thermal conductivity of CNT fibres was determined using the Angstrom technique (63), by measuring temperature variations along a CNT fibre specimen subject to a sinusoidal heat input. Thermal conductivity (K) was determined according to equation

$$K = \rho C_P \frac{(x_1 - x_2)^2}{2\delta \ln(T_1/T_2)} \quad (7.28)$$

where ρ is the volumetric density of the sample, C_P its specific heat capacity, $x_i - x_j$ the distance between measuring points i and j along the specimen, δ the phase lag between them, and T_i the temperature wave amplitude.

The measurements were carried out on an array of ~ 1000 single CNT fibre filaments parallel to each other and compacted into a yarn, similar to that shown in Figure 7.28, attached to a resistive heater as a source of a sinusoidal heat input.

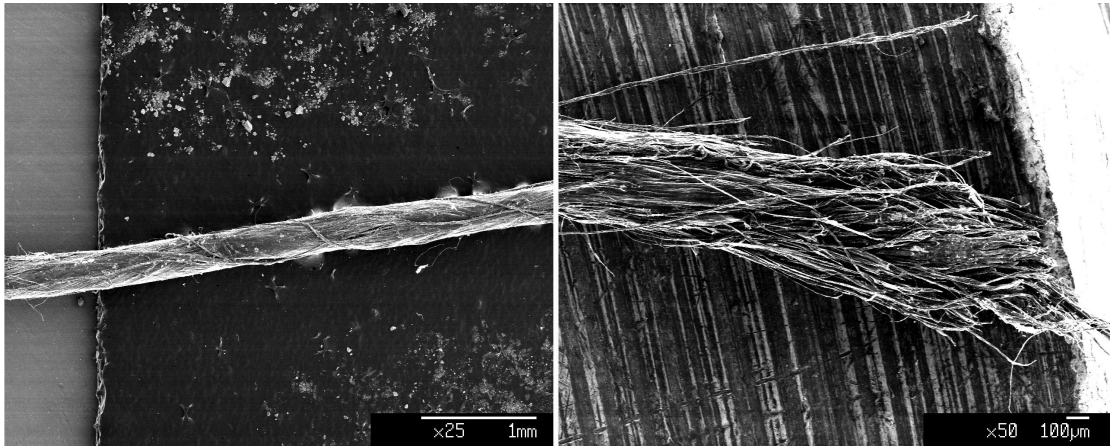


Figure 7.28: SEM micrographs of ~ 1000 CNT fibre filaments forming a yarn. A similar sample was used to determine the thermal conductivity of CNT fibres.

Figure 7.29 shows examples of thermal images of a CNT yarn at the points in time when the heat flow from the source was minimum (I), at mid value (II) and highest (III). The figure also presents a plot of temperature over time at different measuring points on the sample, evidencing a very small temperature phase lag but a significant temperature wave amplitude decrease along the fibre.

Thermal diffusivity was calculated using the first harmonic of the temperature wave at different positions along the yarn. A density of 1 g/cm^3 and a specific heat capacity of 0.68 J/gK corresponding to that of SWNTs (127), were used to calculate thermal conductivity values.

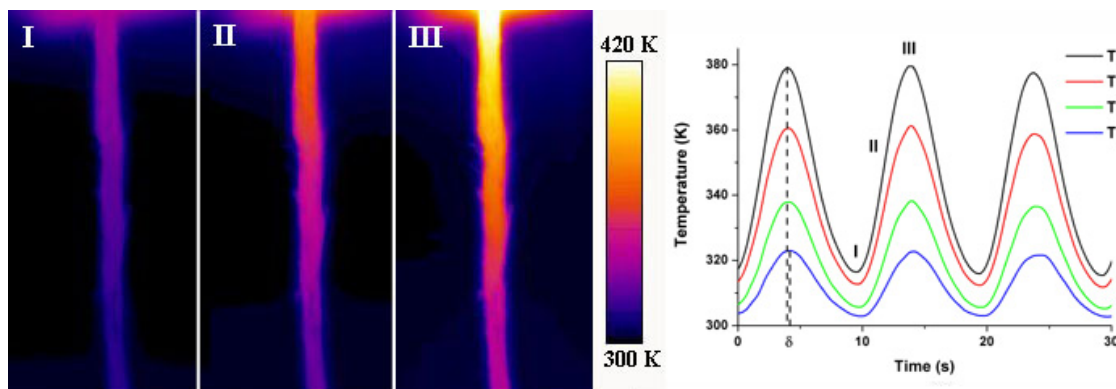


Figure 7.29: Left: thermal images of a yarn of CNT fibres subjected to a sinusoidal heat input. The images correspond to the lowest (I), mid-point (II) and highest temperature (III) of the temperature wave. Right: temperature waves at different locations along the sample, showing a small phase lag and a decrease in temperature amplitude with increasing distance from the heat source.

A value of diffusivity of $70 \text{ mm}^2/\text{s}$ (conductivity of 50 W/mK) is obtained for the sample shown in Figure 7.29. It compares with values reported for other CNT fibres and films of $19 - 26 \text{ W/mK}$ (43; 128) and $48 - 50$ (38; 43), respectively; however, it is very far from theoretical estimates of the conductivity of individual nanotubes (25) and of the thermal conductivity of highly graphitised carbon fibres with K of $\sim 1000 \text{ W/mK}$ (129). This short fall in thermal conductivity is, in part, due to the inefficient assembly of CNT fibres in the multi-filament bulk yarn due to the large separation between them, as observed in Figure 7.28. It is likely that the interface between adjacent nanotubes and bundles plays a determinant role in the thermal conductivity of any assembly of nanotubes. Note that in spite of the high values thermal conductivity of $\sim 1800 \text{ W/mK}$ measured on individual nanotubes (26; 27), for bundles of SWNTs, values as low as 120 W/mK have been reported (28).

The thermal conductivity of 50 W/mK of the yarn of ~ 1000 fibre filaments is likely to be highly affected by the inefficient assembly of the filaments and the resulting poor thermal interface, thus representing a low estimate of the thermal conductivity of the individual CNT fibre filaments. Preliminary results from measurements on short lengths of individual filaments suggest that the effective conductivity of the CNT fibre material is significantly higher.

7.4 Summary of Properties

The theoretical strength of an ideal fibre consisting of perfectly aligned nanotubes can, as a first approximation, be estimated using a shear-lag model in which axial stress in individual nanotubes builds up from shear stress transfer by neighbouring nanotubes. The low shear strength between graphene layers means that nanotube lengths of the order of millimetres are required to result in a fibre with tensile strength in the range of high-performance materials. According to the model, the specific strength of an ideal CNT fibre made up of 2 mm-long nanotubes is of the order of 15 GPa/SG.

In reality, CNT fibres show defects in the form of flaws in nanotube orientation and packing, with a detrimental effect on tensile properties. However, there is evidence of a bi-modal distribution of fibre strength at short gauge lengths (1 – 2 mm), with a low strength peak at 1 GPa/SG and a high strength one at 6 GPa/SG, indicative of randomly dispersed defects in the fibre structure. The correlation between fibre strength and stiffness implies that these defects are not localised stress raisers, but rather generalised faults dispersed in the CNT bundle network. These defects are nanotube and bundle packing faults due to impurity particles and entanglements, and the ends of the nanotubes themselves, which limit the transfer of shear stress between elements in the fibre.

At long gauge lengths (20 mm), the tensile deformation and room temperature creep behaviour of CNT fibres can be related to a bundle network of highly aligned elements that do not take load cooperatively. The relations between fibre structure and tensile properties are found to have similarities to those of rigid-rod-polymer fibres.

Experimental results show values of electrical conductivity of CNT fibres close to those of individual MWNTs, although two orders of magnitude below those of a single graphene sheet or a of an armchair SWNT. The results also indicate that the electrical resistance of the fibres is ohmic and that nanotube length and orientation appear to play an important in determining the electrical resistance of the CNT fibres.

The interaction of CNT fibres with liquids results in changes in the electrical conductivity of the fibres. The process is related to the possibility of liquids to wick into the material due to high internal area of the CNT fibres and suggests the possibility of using them as sensors.

Measurements of the thermal conductivity of an array of ~ 1000 CNT fibre filaments aligned and compacted together into a yarn, gave a value of 50 W/mK, in agreement with those of other CNT fibres and films. For reference, this value is a factor of 2.4 and 116 lower than the highest and lowest thermal conductivities reported for bundles of SWNTs, respectively. The packing and orientation of the fibre filaments in the yarn is far from efficient and is likely to result in a poor thermal interface between CNT fibres, therefore, the value of 50 W/mK is considered a lower estimate of the thermal conductivity of individual CNT fibres.

Chapter 8

Post-Spin Treatments of CNT Fibres

Post-spin heat treatment of high-performance fibres is a common means of promoting the formation of long highly crystalline domains along the fibre axis that in most circumstances, translate into superior stiffness and strength (72; 121; 130). CNT fibres are not an exception in this regard, however, rather than thermal activation of the components, the role of temperature in this case is targeted at the removal of impurities, which results in a more efficient association of CNT bundles in the fibre. This chapter presents examples of low ($< 500^{\circ}\text{C}$) and high ($> 1000^{\circ}\text{C}$) temperature post-spin treatments; the first type related to the desorption of heavy molecules between bundles and the second to the removal of residual catalyst particles and carbonaceous particulates by thermal annealing or laser ablation. The low temperature treatment was investigated with the assistance of N. Ibarra, under supervision of the author.

8.1 Low Temperature Annealing: Adsorbate Removal

Approximately 8 % of the mass of a CNT fibre spun from the gas phase consists of adsorbates in the CNT bundle network, which can be removed from the fibre by annealing in argon (Section 6.2). Furthermore, Figure 8.1 shows that the removal

8.1 Low Temperature Annealing: Adsorbate Removal

of these adsorbates, measured as the decrease in linear density, also produces and increase in bundle orientation in the fibre, as indicated by the decrease in the azimuthal spread of the fibre streak from SAXS.

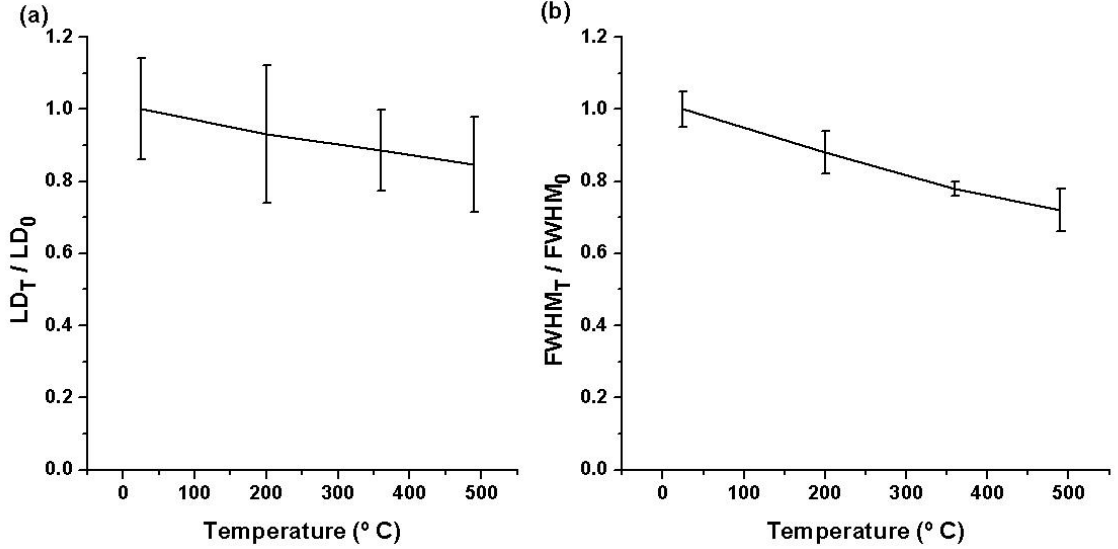


Figure 8.1: Ratio of linear density (a) and azimuthal spread (b) after annealing at different temperatures, over their original values (LD_T/LD_0 and $FWHM_T/FWHM_0$, respectively), showing the decrease in linear density and orientation improvement, both proportional to temperature of annealing.

The increase in bundle orientation with annealing temperature affects the tensile properties of CNT fibre. Plots of strain-to-break, stiffness, strength and yield stress against temperature of annealing are presented in Figure 8.2. These data are from tests using a gauge length of 20 mm and a treatment time of 10 min in Ar. Figure 8.2a shows that with increasing temperature of anneal, strain-to-break decreases, dropping to a third of its original value after treatment at 490°C. Fibre stiffness increases with higher annealing temperatures, reaching values close to 100 GPa/SG, compared to 50 GPa/SG for the as-made sample (Fig 8.2b). Fibre tensile strength (Figure 8.2c) appears almost unchanged after anneal for all the temperatures tested, with perhaps a marginal decrease at the highest. Additionally, Figure 8.2d shows a linear increase in yield stress with annealing

8.1 Low Temperature Annealing: Adsorbate Removal

temperature. It is noteworthy that, for all the tensile properties examined, the deviation from the mean is decreased as a consequence of heat treatment (yield stress is not an exception; for 490°C it is taken as the breaking stress, which is expected to have a larger inherent variance), indicating that with increasing temperature of anneal, more uniformity in tensile properties is observed.

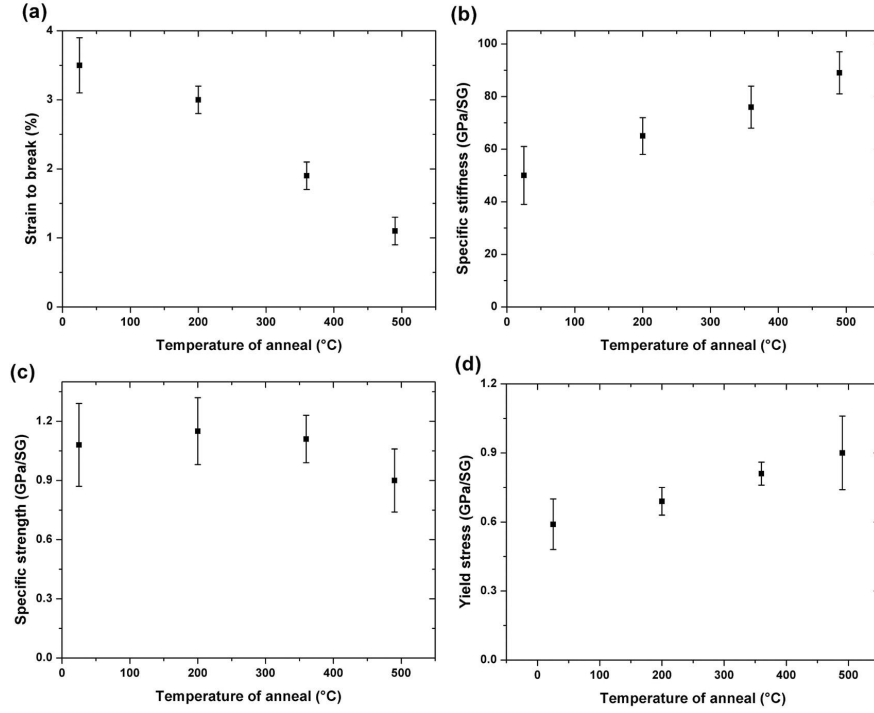


Figure 8.2: Effect of annealing temperature on strain-to-break (a), specific stiffness (b), specific strength (c), and yield stress (d) of CNT fibres.

Annealing affects not only the tensile properties of the samples, but also their tensile deformation mechanism. Figure 8.3a shows stress-strain curves for as-made and annealed fibres loaded to 1% strain and then unloaded to a small tension enough to evaluate the recovery of the material. The curves show that the hysteresis loops observed during the loading cycles applied to as-made fibres are significantly diminished after the 200°C treatment, greatly reduced for 360°C and are negligible for the 490°C annealing.

8.1 Low Temperature Annealing: Adsorbate Removal

It is also evident from the stress-strain curves that fibre strain recovery increases with annealing temperature. A plot of the plastic deformation in Figure 8.3b, taken as the permanent strain after unloading for different annealing temperatures, shows progressively smaller plastic deformation for higher annealing temperatures, with the fibre treated at 490°C evidencing no observable plastic deformation.

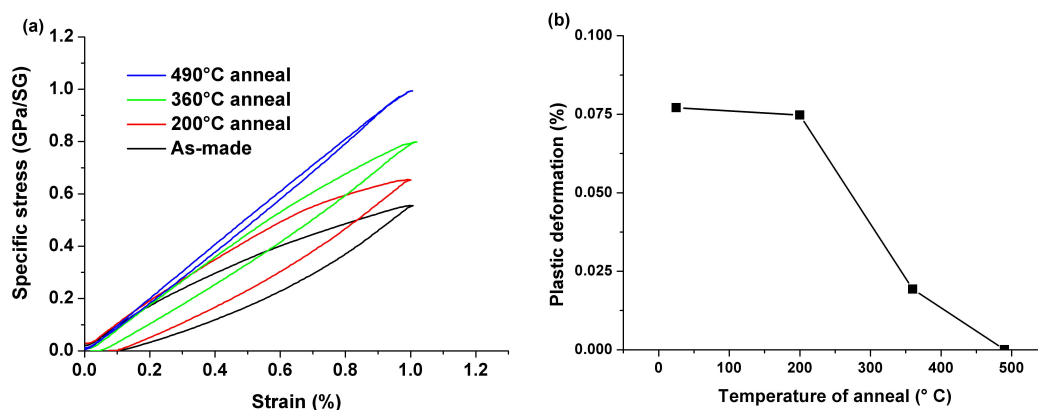


Figure 8.3: (a) Load-unload curves for as-made and annealed fibres strained to 1%. With higher temperature of annealing, the fibres behave more elastically, with no plastic deformation (b) observed after treatment at 490°C. Note from the shape of the curves that hysteresis is greatly decreased with heat treatment.

Hence it appears that the embrittlement of the fibre and the predominance of elastic deformation are a consequence of the improvement in bundle orientation and increased cooperative load-bearing of nanotubes in the fibre due to low-temperature annealing. These observations are in line with the effects of annealing on the structure and properties of rigid-rod polymer fibres (122). As-made PBZT fibres show increases in yield stress and stiffness and a decrease in strain-to-break, all proportional to annealing temperature (131). Furthermore, Raman spectra measurements on CNT fibres before and after treatment are virtually identical, ruling out for example, the change in tensile properties being due to the formation of cross links between nanotubes by carbyne chains, as has been observed to occur for uncollapsed DWNTs (132).

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

While for a polymer fibre, the role of annealing is to lower the local stress barrier for reorganisation of elements in the structure, for the CNT fibre the rearrangement of elements occurs as a result of the removal of impurities between bundles, which facilitates interaction between neighbouring bundles. As a consequence of the newly formed interface between bundles, the elements in the CNT fibre deform together when stressed, resulting in higher stiffness and yield stress and lower strain to break. Additionally, since the interaction between parallel bundles is increased, the material deforms more elastically, up the point (at 490°C annealing) that virtually no plasticity is observed and full recovery occurs after loading. That no significant change in strength is observed with annealing is due to strength being determined by defects in the fibre structure such as nanotube ends and the presence of particulates associated to residual catalyst.

The effect of annealing on the tensile properties of CNT fibres is essentially similar as for rigid-rod polymer fibres, in that the process aguments alignment and cooperative load-bearing between elements. However, the two types of materials have very different thermal stabilities and, while for rigid-rod polymer fibres the application of tension during annealing results in even higher orientation -increasing strength and stiffness from 1.6 GPa and 150 GPa for the original as-made fibres (121), to 4.2 GPa and 330 GPa (133)- the same effect has not been observed here to apply to CNT fibres.

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

Residual catalyst particles and small carbonaceous impurities in CNT fibres limit the assembly of bundles into a highly oriented and efficiently packed fibrillar structure. As a consequence, the properties of the fibres fall short of those of a perfect assembly of CNTs. Of the several techniques explored so far to remove particulate impurities from CNT fibres, the most promising involve high temperature treatments ($> 1000^{\circ}\text{C}$) as a means to vapourise these impurities. In this section, two high-temperature methods are discussed: annealing and laser ablation.

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

8.2.1 High-Temperature Annealing

Impurity Removal

The method for removing particulate impurities by annealing consists of heating CNT fibre samples at temperatures of 1000 – 1400°C in an inert atmosphere for a relatively short period of time (typically 10 minutes), so as to avoid potential nanotube graphitisation and thus enabling identification of the effects of impurities on fibre properties.

Figure 8.4 shows a comparison of SEM images of an as-made uncondensed fibre (A) and a similar sample after annealing at 1250°C. Note that the treated sample has a diameter of $\sim 25\ \mu\text{m}$, compared to $\sim 500\ \mu\text{m}$ in its original state, indicating that bundles are brought significantly closer together during the annealing process. More importantly, these micrographs show a bundle structure which has been substantially cleaned of impurities after annealing and appear to indicate that, besides residual catalyst, carbonaceous impurities are also removed in the annealing process.

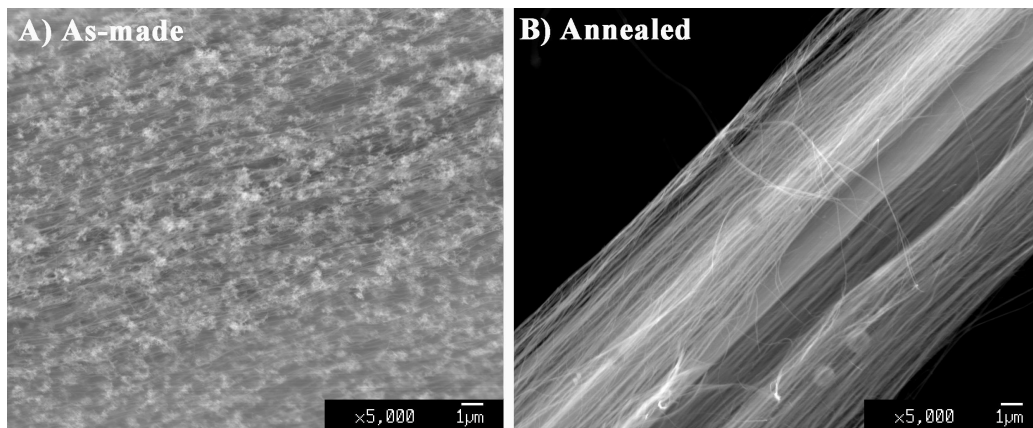


Figure 8.4: Comparative SEM micrographs of uncondensed fibres as-made (A) and after annealing (B) in an inert atmosphere at 1250°C.

The absence of residual catalyst particle in the annealed fibre is confirmed by XRD and X-ray fluorescence (XF) measurements, as shown in Figure 8.5. After annealing, the XRD powder rings associated to catalyst particles are not

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

observed in the fibre and the radial intensity profiles (Figure 8.5A) show only the 100 and 101 reflections associated to CNTs. X-ray fluorescence further confirms the removal of catalyst from the fibre. A comparison of two examples of XF spectra for as-made and annealed fibres (Figure 8.5B), normalised relative to the background signal, evidences the removal of iron-based impurities after the high temperature treatment.

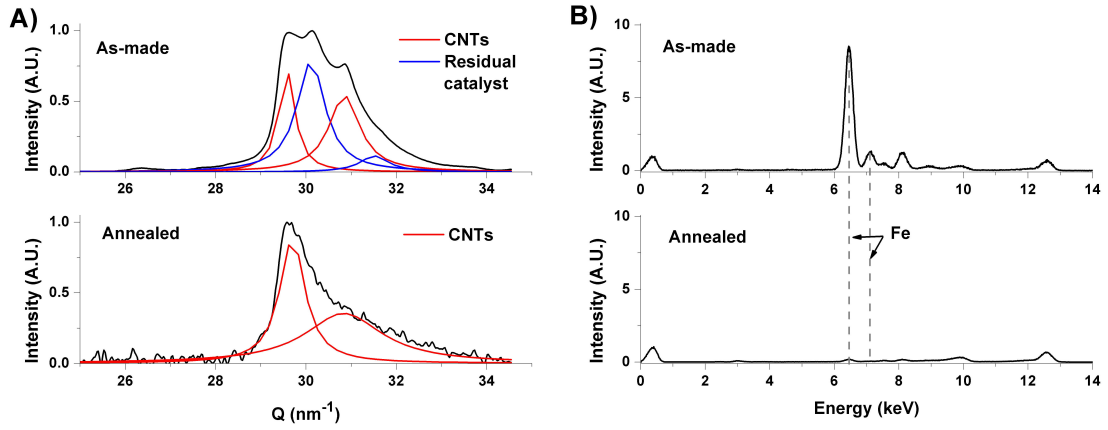


Figure 8.5: Selected-range XRD intensity profile (A) and X-ray fluorescence spectra (B) for as-made and annealed fibres, exhibiting the absence of iron in the fibre after the treatment.

The significant reduction of carbon particulates in the fibre after high-temperature annealing observed by electron microscopy matches observations from Raman spectroscopy measurements. A comparison of Raman spectra in Figure 8.6 shows a significant decrease of the D band for the annealed fibre relative to the as-made fibres, indicative of a material with fewer carbonaceous impurities. The treatment also appears to cause the emergence of intermediate frequency modes (IFM) (134), which is taken as a further indication that the annealed fibre is of higher purity.

It has been observed that high-temperature annealing can result in the formation of spherical particles in the fibre, some of which can be seen in Figure 8.4. They may be reasonably abundant depending on processing parameters and initial fibre composition. Such particles are typically made of carbon and have a large d-spacing of ~ 0.4 nm between graphene layers, as determined by XRD.

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

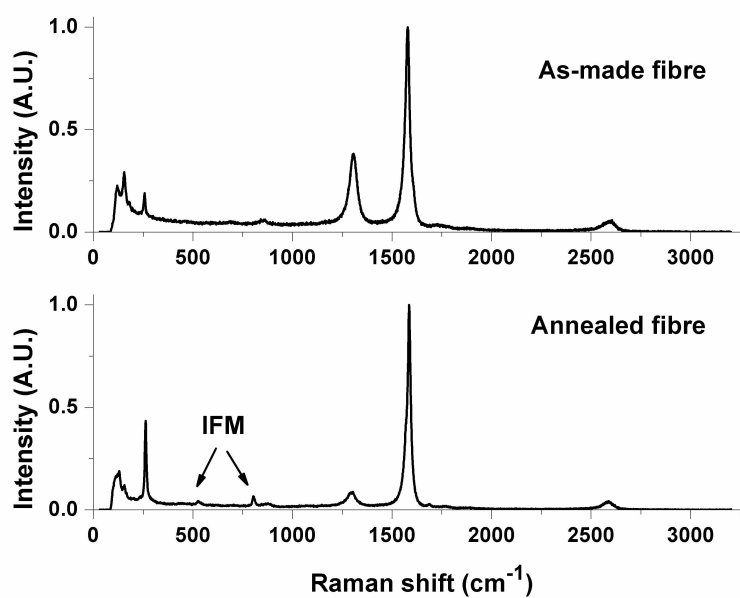


Figure 8.6: Normalised Raman spectra of a CNT fibre as made and after annealing at 1350°C. The removal of carbonaceous impurities results in a significant decrease of the D band and the emergence of IFM.

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

Figure 8.7 shows examples of fibres with carbon spheres. In the first example (Figure 8.7A), they very much predominate over nanotubes, suggesting that during formation of the spheres they can not only uptake carbon from carbonaceous impurities, but also from nanotubes. In general, however, these spheres tend to be located on the fibre surface, as shown in Figure 8.7B. This observation, supported by further microscopy analysis, suggests that during annealing the carbonaceous impurities tend to migrate as smaller entities from the inside of the fibre to its surface and then combine into larger objects before interacting with nanotubes.

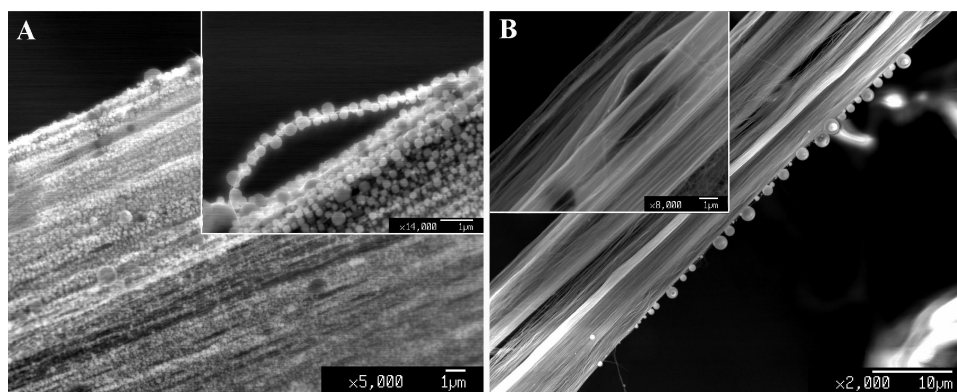


Figure 8.7: SEM micrographs of annealed fibres with evidence of carbon spheres. The particles are found predominantly on the fibre surface.

The formation of graphitic spheres, similar to these, has been extensively studied. It is well established that carbon spheres can be produced at temperatures above 900°C by various techniques, including direct pyrolysis of carbon-containing species (135; 136), iron-catalysed pyrolysis of hydrocarbons (137; 138), arc-discharge (139) and also by passing high current through CNT fibres (140). Thus it is not surprising to find that they also form after annealing CNT fibres. However, their behaviour at high temperatures has not been explored sufficiently to be able to predict their mutual interaction or their interaction with CNTs.

It appears that these carbon spheres are dominated by their surface energy and therefore exhibit liquid-like behaviour, despite the SEM analysis having been carried out on samples after cooling down to room temperature. SEM evidence suggests that they form from poorly-graphitised carbon into small entities that

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

can wick through the bundle network and emerge on the fibre surface, where they can combine into larger spherical objects. It remains unclear whether the carbonaceous impurities that are removed from the fibre structure follow a similar path as these carbon spheres, or if they are removed by association with iron particles. In any case, it is evident that the process is dominated by the small size of the particles which implies that they have different properties from the bulk.

The formation of carbon spheres during fibre annealing and their interaction with the bundle network remains under investigation. Further experiments are required to understand the mechanism by which residual catalyst and carbon impurities are removed from the CNT fibre and the exact experimental parameters that promote this over the formation of large carbon spheres.

Tensile Properties of High-Temperature Annealed Fibres

The effects of high-temperature annealing on the tensile properties of CNT fibres depend strongly upon the extent to which the fibre is clean of impurity particulates, be it residual catalyst, tubules or carbon spheres. When large carbon spheres are formed, fibre strength is decreased considerably, however, when this is avoided the treatment results in a fibre consisting of well aligned bundles that preserve a high degree of orientation (as shown in Figure 8.4), with a significant improvement in tensile properties.

Figure 8.8 presents distributions of strength (A) and stiffness (B) at different gauge lengths for fibres as-made and annealed at 1250°C. The strength comparison shows that the as-made sample, centred at 0.9 GPa/SG strength and with no evidence of a bi-modal distribution, shows no change at 20 mm gauge length after annealing. However, at 1 mm, the treated fibre exhibits a distribution centred at 1.9 GPa/SG and extending up to 2.5 GPa/SG, but importantly, with no indication of values of low strength. Fibre stiffness at both gauge lengths, at 40 GPa/SG for the as-made sample, increases to an average of 210 GPa/SG after annealing, up to a maximum of 250 GPa/SG.

The removal of particulate impurities through high-temperature annealing also notably affects the tensile behaviour of the fibres. Figure 8.9 shows examples

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

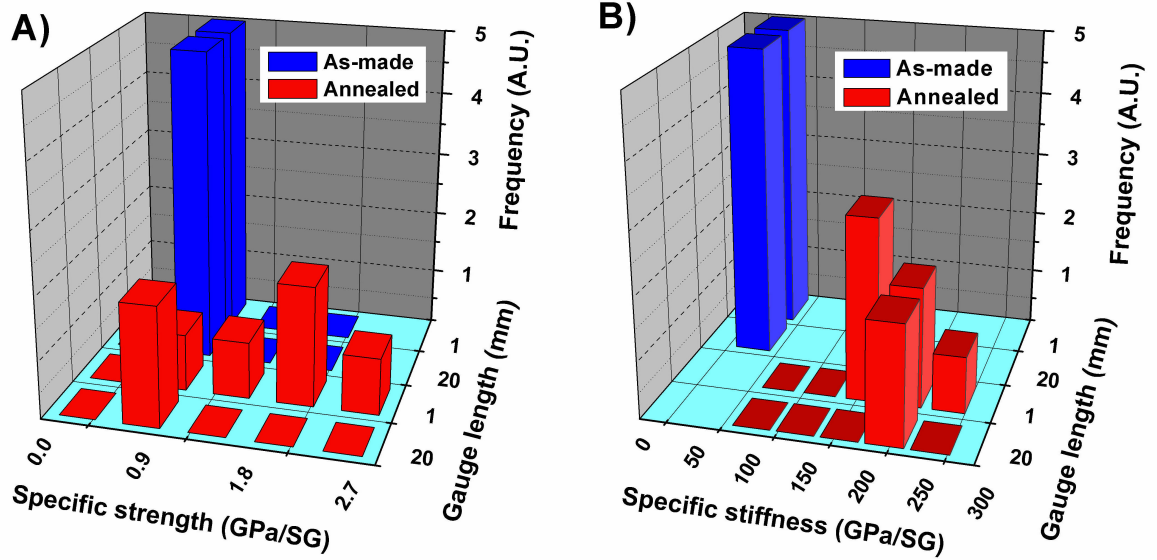


Figure 8.8: Fibre strength (A) and stiffness (B) distributions at 20 mm and 1 mm gauge length, for as-made and annealed CNT fibres.

of stress-strain curves of as-made and annealed fibres, for 20 mm and 1 mm gauge lengths. Brittler behaviour is observed for the treated fibres, with no identifiable evidence of a yield point. Furthermore, comparison of the treated fibres at both gauge lengths suggests that the relatively low strength of the annealed fibre at 20 mm appears to be due to premature fracture. The curves also show that the structural improvements in the fibre that increase its stiffness and strength have a detrimental effect on toughness, which for the 1 mm-gauge length goes from 2.55 J/g to 1.4 J/g after annealing.

The combination of the strength and stiffness distributions indicate that, as a consequence of annealing, stress transfer between bundles is significantly increased over a long length of fibre, evidenced by the high modulus observed even at the longer fibre gauge length and by the generalised increase in fibre strength at 1 mm. And although the results also show that localised defects can be formed during annealing, probably in the form of a large carbon sphere trapped between bundles (inset in Figure 8.7B), the overall bundle network structure after the treatment is a step closer to an ideal assembly of aligned nanotubes.

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

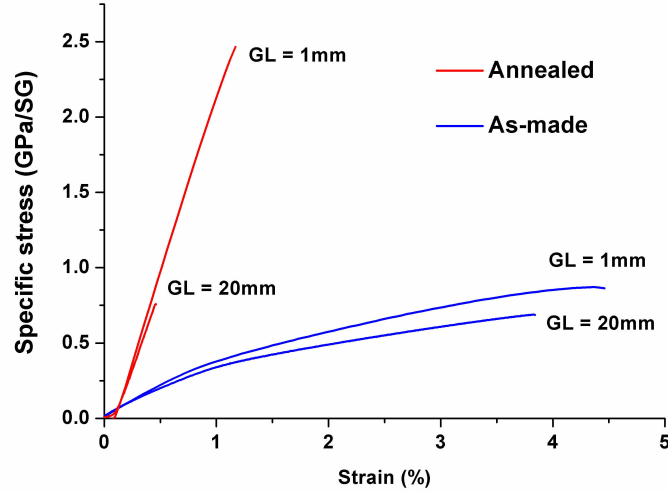


Figure 8.9: Stress-strain curves for different gauge lengths of as-made fibres and samples annealed at 1250°C

The results support a strategy for removing impurities from the fibre while preserving the bundle structure mostly intact and such that the tensile properties of the fibre are increased over long gauge lengths. They suggest that further understanding of the reactions taking place during the treatment and more exhaustive control of the relevant parameters during annealing will prevent the formation of localised defects, therefore increasing tensile strength and stiffness of CNT fibres at long gauge lengths to at least ~ 2.5 GPa/SG and ~ 250 GPa/SG, respectively.

8.2.2 Laser Ablation

Another technique for removing residual catalyst particle impurities in CNT fibres is laser ablation under an inert atmosphere. In the process, a CNT fibre is irradiated with a laser source and due to the high optical absorption of CNTs, a rapid increase in the local temperature of the fibre occurs, which can cause preferential ablation of impurities from the sample.

Comparison of an irradiated area on a CNT fibre after laser ablation and a typical area of an as-made material is shown in Figure 8.10. In this example of

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

ablation, the sample was subjected to five pulses of approximately 50 W/mm^2 for 100 ms each, using a $1 \mu\text{m}$ -wavelength Gaussian laser. The comparison shows the CNT fibre material mostly cleaned of residual catalyst and carbonaceous impurities after irradiation, with bundles forming a more compact network of aligned elements.

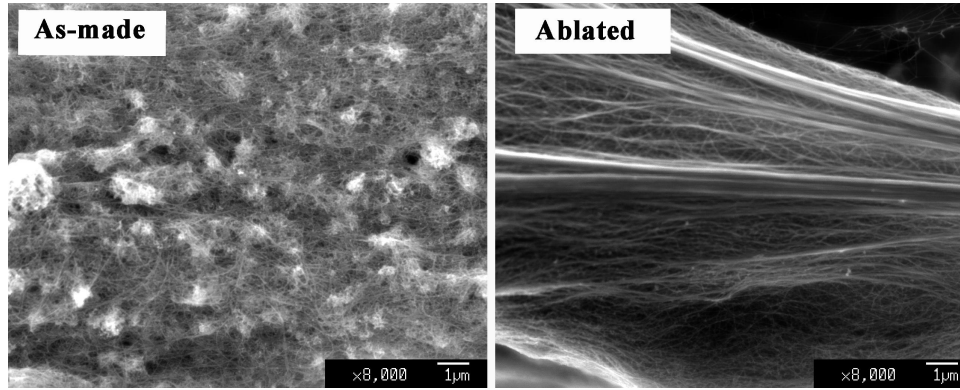


Figure 8.10: SEM micrographs of CNT fibres as made (A) and after laser irradiation (B), showing preferential ablation of impurities.

The degree to which carbonaceous impurities have been removed from CNT fibres can be observed by direct comparison of the Raman spectra of as-made and ablated fibres, such as those in Figure 8.11, corresponding to the original material and a CNT fibre after nine pulse events of 100 ms and $\sim 10 \text{ W/mm}^2$ irradiance each. A marked decrease of the D band is observable after ablation, taken as an indication that a large proportion of poorly graphitised impurities are effectively removed from the material. Furthermore, the spectrum after the treatment shows no major change in the G band, indicating that nanotubes were not significantly affected by the ablation process.

However, although impurities can be removed from the fibre by laser ablation, it is difficult to ensure that that ablation of nanotubes does not occur. This difficulty is partially due to the large number of parameters involved in the ablation process, including laser irradiance, pulse duration and number of pulses; and properties of the fibre such as its thermal conductivity, optical absorption and surface area per unit mass. In general, it has been observed that the window

8.2 High Temperature Treatments: Residual Catalyst and Carbon Particulate Removal

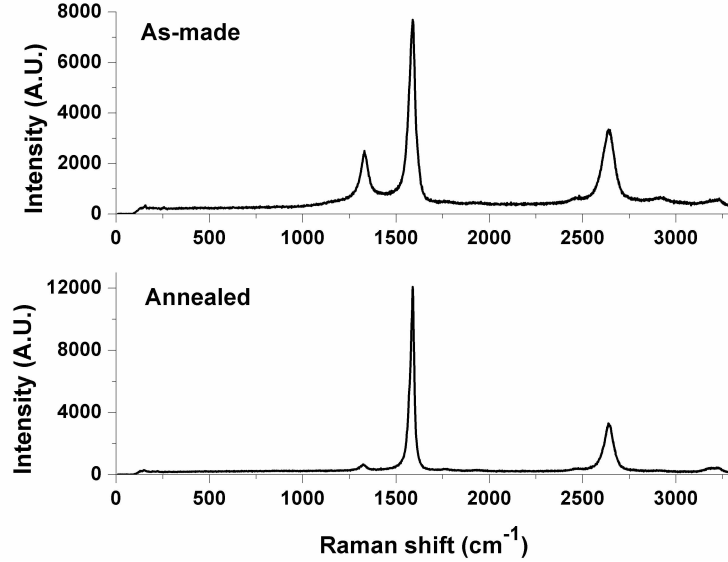


Figure 8.11: Raman spectra of fibres as-made (top) and after ablation of carbonaceous and residual catalyst impurities (bottom), showing a marked decrease in the D band after the treatment, but otherwise no major changes in the peaks.

for impurity removal involves an irradiance of $\sim 1 - 100 \text{ W/mm}^2$ and pulses of $\sim 10 - 100 \text{ ms}$. The effects of irradiance and laser pulse duration are shown qualitatively in Figure 8.12 as SEM micrographs of fibres after ablation, with the approximate maximum surface temperature as measured by a pyrometer included for reference. Thus, an irradiance of $\sim 1 \text{ W/mm}^2$ for $\sim 10 \text{ ms}$ promotes the formation of spherical particles preferentially formed from impurities. However, a longer pulse results in the formation of pits on the fibre surface, probably associated with the spheres uptaking carbon from nanotubes. The use of higher irradiance doses leaves less trace of impurities and spheres, although frequently causing ablation of nanotubes. Thus, so far, the results suggest that the laser parameters must be such that the energy downloaded into the fibre causes migration of particulate impurities to the fibre surface and their vaporisation before they form large spherical entities that can degrade CNTs.

Under the experimental parameters used here, the mechanism whereby particulate impurities dissociate from the CNT fibre appears to be somewhat similar

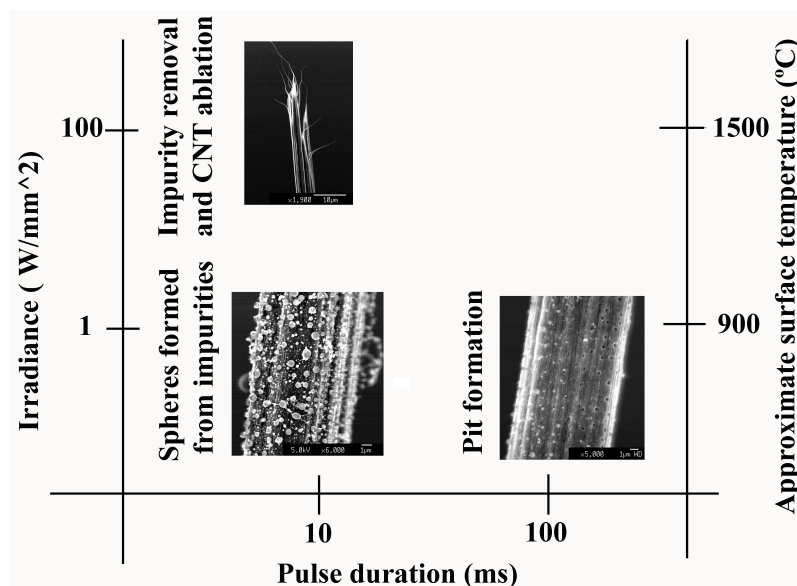


Figure 8.12: Qualitative map of the structural effects of irradiance dose and pulse duration during laser irradiation of CNT fibres, showing SEM evidence of the formation of carbon spheres and ablation of impurities.

under laser ablation and high temperature annealing. In both processes, there is evidence of impurities migrating to the fibre surface and clustering into carbon-based spheres. And, although the temperature evolution and distribution in the two treatments is radically different, the onset of impurity removal appears to be in the range of $900 - 1400^{\circ}\text{C}$ in both cases.

A key advantage of this process over high temperature annealing, is the ability to remove impurities within a fraction of a second. However, during laser ablation, several complex processes occur simultaneously over very short time scales and over a very localised area. These characteristics make the impurity removal process by ablation difficult to control and to apply along large gauge lengths.

8.3 Summary

Low temperature ($< 500^{\circ}\text{C}$) annealing in an inert atmosphere increases bundle orientation in the fibre through the removal of adsorbates produced during the

CVD reaction. The increase in orientation and improvement in the interaction between elements produce a fibre with higher stiffness and yield stress and a more elastic behaviour during tensile deformation, however, at the expense of lower strain-to-break and toughness; in line with studies on annealing rigid-rod polymer fibres. However, no improvement in strength is observed when particulate impurities remain between bundles.

The removal of particulate impurities, both carbonaceous and residual catalyst, can be achieved by high temperature ($> 900^{\circ}\text{C}$) annealing in an inert atmosphere. The removal mechanism appears to involve migration of impurities as small entities to the fibre surface. Further optimisation of the treatment is required to avoid the aggregation of migrating impurities into large carbon spheres that remain anchored to the fibre surface. However, samples with reduced impurities show a strength of ~ 2 GPa/SG and stiffness of ~ 250 GPa/SG at 1 mm gauge length. More importantly, their stiffness at 20 mm gauge length is also ~ 250 GPa/SG and their strength ~ 1 GPa/SG only due to premature fibre fracture, which indicates that the treatment succeeds in improving the whole structure of the fibre except for the formation of a few localised defects as large carbon spheres.

A second strategy for removing particulate impurities from the fibre involves laser ablation. The results from using this technique also suggest a model of impurities migrating to the fibre surface and either being vaporised or aggregating into carbon-based spheres depending on experimental parameters, similar to the process observed after high temperature annealing.

The treatments discussed in this chapter show some degree of mitigation of the detrimental role of impurities in the fibre's tensile properties. However, it remains a challenge to achieve complete removal of impurities from the fibre while preserving the network of nanotubes intact. The difficulty in doing so points to the importance of avoiding the formation of impurities at the synthesis stage.

Chapter 9

Conclusions and Future Directions

One of the unique aspects of CNT fibres spun from the gas phase during CVD is that they are produced in a continuous process that incorporates both the synthesis of the CNT building blocks and their assembly into a dense fibre. The synthesis conditions used, particularly through the role of sulphur, produce exceptionally rapid growth of nanotubes with lengths of millimetres, resulting in their entanglement and the formation of an aerogel that can be then drawn into a fibre, provided that the right concentration of nanotubes is present in the reactor. However, a large fraction of the catalyst used does not take direct part in CNT growth, some of it becoming incorporated into the fibre structure. Optimisation of synthesis conditions to minimise the amount of residual catalyst, without affecting either the ability to spin the CNT fibre continuously or its physical properties, remains an open task. A possible step in this direction would be to investigate whether particular types of catalyst particles found in the fibre do not take part in nanotube growth. This would enable the modification of the synthesis conditions during CVD so as to prevent the formation of such catalyst particles.

In gas-phase CNT fibre spinning, the parameters used for the CVD reaction, most notably gas flow rate and precursor feed rate, affect the concentration of CNTs in the gas phase and thus the ability to draw the aerogel into a fibre. The

effect of the concentration of nanotubes is somewhat similar to that of the concentration of polymer chains in liquid-spinning of polymeric fibres, which determines the density of entanglements in the polymer solution and hence the ability to spin and draw a fibre.

As the aerogel is drawn from the reactor, its resistance to flow against the gas phase causes nanotubes to align in the direction of drawing, with this process providing most of the nanotube preferential orientation in the fibre. With increasing drawing rates, a higher degree of orientation of nanotubes is obtained, until the drawing rate eventually exceeds the rate at which the aerogel is formed and the drawing process is disrupted. The increase in nanotube alignment augments the packing efficiency of the CNT building blocks, the volumetric density of the fibre and its tensile strength and stiffness. However, it is likely that higher degrees of CNT orientation can be obtained by decreasing the number of entanglements in the aerogel through optimisation of synthesis parameters in the CVD reaction.

Through interaction with liquid, the drawn fibre undergoes a transition that increases its volumetric density by several orders of magnitude. This process occurs in two stages, the first is driven by the liquid wicking into the fibre and compressing it radially as its interface with air is minimised and the second by forces arising due to evaporation of liquid molecules between bundles. The parameters of the liquid that directly affect the densification process are its surface tension, affinity to nanotubes and vapour pressure.

Through the process of liquid-densification, nanotubes are brought closer and reach a separation similar to the inter-layer separation in turbostratic graphite. As a result, more nanotubes contribute to stress transfer, increasing fibre strength and stiffness and causing the material to deform more elastically, which, however, produces a decrease in toughness. Further studies are required to evaluate the degree of infiltration of different liquids into the fibre and whether they can produce different degrees of densification after their evaporation.

An ideal assembly of CNT fibres would be formed of only perfectly aligned nanotubes. The theoretical strength and stiffness of this perfect assembly can be approximated using a shear-lag model where tensile stress in nanotubes builds up linearly from the ends due to constant shear stress between tubes and has the shear strength of graphite as maximum. The interfacial area between adjacent

CNTs available for stress transfer can be related to the cohesive energy density and flexural rigidity of graphene and determined for polygonised and collapsed nanotubes. The theoretical estimate indicates that values of specific strength superior to those of existing high-performance fibres can be attained if the nanotubes have a length of the order of millimetres, provided that they are perfectly assembled.

Further additions to the proposed model are required to make it more representative of real CNT fibres. Stress transfer between layers within nanotubes could be taken into consideration, which would enable determination of the theoretical strength and stiffness of fibres made of multilayered nanotubes. A further addition could be to account for a CNT assembly made up of nanotubes with a range of lengths rather than assuming identical length for all the nanotubes.

The structure of the CNT fibres consists of a network of aligned bundles of nanotubes that coexist with impurities formed during the CVD reaction. These impurities are mainly molecular adsorbates and residual catalyst particulates, accounting for approximately 7% and $\sim 15\%$ of fibre mass, respectively and an undetermined fraction of carbonaceous particulates of nanometric dimensions. Rather than being highly localised, the particulate impurities are randomly distributed along and across the fibre, causing a generalised shortfall in the orientation of the CNT bundle network and a disruption in nanotube packing. The defective structure of the fibre gives rise to a bi-modal distribution of strengths at small gauge lengths (~ 1 mm), with the lower strength, centred at ~ 1 GPa/SG, corresponding to the properties of the defective structure and the higher strength, centred at ~ 6 GPa/SG, being that of a less defective structure closer to the ideal assembly of CNTs. A correlation between strength and stiffness further indicates that the defects are not localised entities but rather generalised faults in the assembly of the CNT network.

At 20 mm or longer gauge lengths, the tensile behaviour of the fibres shows a combination of elastic and plastic deformation and the occurrence of strain hardening. Structural analysis using Raman spectroscopy and SAXS shows elastic deformation of nanotubes and suggests that plastic deformation occurs through bundles sliding past each other and the straightening of neighbouring elements.

The mechanical behaviour of the CNT fibre under tension is indicative of a structure in which the elements do not take load cooperatively and closely resembles the behaviour of as-spun rigid-rod polymer fibres. Nevertheless, further study is required to clarify the deformation mechanism in CNT fibres. The evolution of the fibre structure during simple tensile tests, load/unload cycles and creep-type tests could be monitored by Raman spectroscopy to determine the stresses in the CNT network, at least on its surface and by micro-XRD, which would show changes in orientation and separation between nanotubes.

Post-spin treatments can be used to remove impurities from CNT fibres. Annealing at temperatures below 500°C produces desorption of adsorbates from the fibre structure and an increase in bundle orientation, leading to a stiffer, though less tough fibre, which deforms almost exclusively elastically. The effects of annealing on the mechanical properties of CNT fibres fall in line with similar treatments on rigid-rod polymer fibres and also show that with increasing purity and orientation, CNT fibres tend to deform purely elastically.

The most significant impurities in CNT fibres consist of randomly-dispersed carbonaceous and residual catalyst particulates. Thus far, the most effective strategy for removing these impurities while preserving the nanotube network involves annealing the fibre under an inert atmosphere at temperatures around 1200°C. This process can produce a fibre virtually free of particulates, translating to a fibre strength of ~ 2 GPa/SG at 1 mm-gauge length and stiffness of ~ 250 GPa/SG at both short and long gauge lengths. However, although the treatment succeeds in improving the structure of the fibre over long lengths, it can lead to impurities aggregating into larger spherical entities that remain in the fibre structure and which cause premature fracture of the fibre at longer gauge lengths. Further understanding of the removal mechanism is required in order to optimise the annealing parameters to produce a fibre exclusively composed of oriented nanotubes.

The electrical resistance of CNT fibres spun from the gas-phase is ohmic and of the order of 8×10^5 S/m, in line with that observed for CNT fibres spun by other techniques. CNT orientation and packing have an influence on the electrical properties of the fibre, although far less than on its mechanical properties and due mostly to the increase in the volumetric density of the fibre rather than on

the actual conduction mechanism. Overall, more experimentation is required to relate fibre structure to its electrical conductivity. Additional measurements of electrical properties at different temperatures and at high voltages would provide valuable information on the potential of CNT fibres for a number of applications.

The electrical conductivity of the fibres produced in the present study is sensitive to the presence of liquid molecules on the fibre surface. The high internal surface area of the CNT fibre, unusual for a high performance fibre, means that liquid molecules can wick into the fibre and thus have a direct effect on its electrical resistance. This suggests the possibility of using CNT fibres as sensors; again, further experiments are required to clarify the cause of the changes in resistance and to evaluate the performance of the material compared to existing sensors.

The thermal conductivity of CNT fibres spun from the gas phase, measured on an array of around 1000 single fibre filaments, is of the order of 50 W/mK. This value is similar to those observed for other CNT fibres and films, although significantly lower than the thermal conductivity of individual nanotubes. An increase in fibre thermal conductivity is expected after removal of impurities, however, it is still necessary to identify other routes for increasing thermal conductivity and whether they involve a fibre with longer nanotubes, tubes with different number of layers, or higher bundle alignment. Interestingly, a comparison of the thermal conductivity of CNT fibres with that of bundles of CNTs (the basic structure into which nanotubes assemble) indicates that the fibre have lower thermal conductivity by a factor of 2 and 116 of the lowest and the highest values reported in the literature, respectively. Overall, further investigation of the thermal transfer between nanotubes is required to better evaluate the thermal conductivity of larger assemblies of nanotubes such as CNT fibres.

The gas-phase spinning method for making CNT fibres covers from the synthesis of the nanotubes to winding a fully dense fibre in one process. It enable continuous fibre spinning at relatively high rates. The structure of the fibre takes advantage of outstanding mechanical, electrical and thermal properties of individual nanotubes and situate the fibre in the range of high-performance materials. However, there are indications that the material can have significantly superior properties if its structure is improved by decreasing the amount of impurity particulates trapped within the CNT bundle network. This can be achieved

by post-spin treatments, but future efforts to improve the material must also contemplate optimisation of the spinning process at the synthesis stage.

Appendix A

Stress Transfer Interface Between DWNTs (Ω)

A.1 Polygonised DWNTs

Take a bundle of polygonised DWNTs as schematised in Figure 7.4, with the outer and inner radii of the equivalent round tubes denoted R_1 and R_2 , respectively. Ω can be defined as

$$\Omega = 1 - \frac{r}{R_1} \quad (\text{A.1})$$

The total energy per unit length of a DWNT in the bundle is expressed as

$$E = -\frac{\gamma}{2} \times 2\pi R_1 \Omega + \frac{E_b}{2r^2} \times 2\pi (R_1 + R_2) (1 - \Omega) \quad (\text{A.2})$$

Substituting for r from equation A.1

$$= -\pi\gamma R_1 \Omega + \frac{E_b\pi}{1 - \Omega} \frac{1}{R_1} \left(1 + \frac{R_2}{R_1}\right) \quad (\text{A.3})$$

The minimum energy configuration in terms of Ω can be obtained by differentiation of equation A.3 with respect to Ω and setting equal to zero, which yields

$$\Omega = 1 - \frac{1}{R_1} \sqrt{\left(1 + \frac{R_2}{R_1}\right) \frac{E_b}{\gamma}} \quad (\text{A.4})$$

Combining equations A.1 and A.4 gives,

$$r = \sqrt{\left(1 + \frac{R_2}{R_1}\right) \frac{E_b}{\gamma}} \quad (\text{A.5})$$

For $R_1 - R_2 \ll R_1$,

$$r \approx \sqrt{\frac{2E_b}{\gamma}} \quad (\text{A.6})$$

A.2 Collapsed DWNTs

For a bundle of collapsed DWNTs, with the outer and inner tube having equivalent round tube's radii R_1 and R_2 , respectively, Ω is taken as

$$\Omega = 1 - \frac{\Phi r}{R_1} \quad (\text{A.7})$$

where Φ is a constant related to the shape of the hair pin ends of the tube, that can take values in the range $(1, 2)$, as described in Section 7.1.

Using the definitions of Ω and Φ the energy of the tube can be expressed as

$$E = -\frac{\gamma}{2} \times 2\pi R_1 \Omega - \frac{\gamma}{2} \times 2\pi R_2 \Omega + \frac{E_b}{2r^2} \times 2\pi (R_1 + R_2) (1 - \Omega) \quad (\text{A.8})$$

Substituting for r from equation A.7

$$E = -\pi\gamma\Omega (R_1 + R_2) + \frac{\pi\Phi^2 E_b}{R_1 (1 - \Omega)} \left(1 - \frac{R_2}{R_1}\right) \quad (\text{A.9})$$

Differentiating with respect to Ω and setting equal to zero to get the minimum energy configuration in terms of Ω ,

$$\Omega = 1 - \frac{\Phi}{R_1} \sqrt{\frac{E_b}{\gamma}} \quad (\text{A.10})$$

Combining equations A.7 and A.10

$$r = \sqrt{\frac{E_b}{\gamma}} \quad (\text{A.11})$$

Appendix B

CNT Fibre Composites

B.1 Introduction

CNT fibres are ideal candidates for unidirectional composites. Their high thermal and electrical conductivities, tensile strength, stiffness and work to fracture (Chapter 7) suggest that their incorporation into matrices could lead to a wide variety of new composite materials with properties rivalling those of current high-performance fibre composites. A brief description of a method for manufacturing high volume fraction ($> 25\%$) macroscopic CNT fibre/polymer composites and a discussion on their tensile properties, coefficient of thermal expansion and thermal conductivity is presented below.

Most samples subjected to mechanical tests were produced and the tests themselves were carried out by R. J. Mora as part of a Master in Philosophy research project under the supervision of the author. Details of the work can be found in references (141; 142).

B.2 Composite Sample Manufacturing

CNT fibre/polystyrene specimens were made by casting a solution of 5 wt.% polymer ($M_w = 280000$) in degassed toluene into a mould containing an array of ~ 1000 aligned individual fibres, followed by evaporation of the solvent in an oven at 60°C for 12 hrs. Thermoset/fibre composite samples were produced by

B.2 Composite Sample Manufacturing

direct infiltration of a mixture of epoxy resin and hardener into a similar array of fibres placed in a mould. After allowing for the resin to diffuse through the fibres, the mould was left in an oven at 140 °C for 16 hours to cure the resin. The specimens for compression test were cylindrical while those for tensile tests had dog-bone shape, as illustrated in Figure B.1.

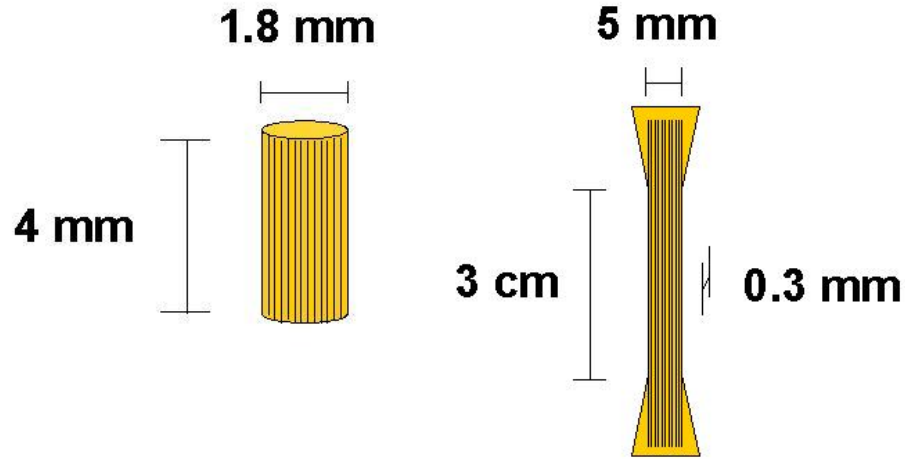


Figure B.1: Schematic of specimens used for compression (left) and tensile (right) tests.

The strategy for establishing the effective fibre volume fraction in the composites consisted of measuring the mass fraction of carbon nanotubes in the composite by TGA, measuring the density of the pure polymer sample and of the composite and then calculating fibre volume as the volume not occupied by the polymer. The values of the fibre volume fraction, V_f , and the effective fibre density, ρ_f , are shown in Table B.1 for specimens which were subsequently subjected to mechanical measurements and fractographic analysis.

The data of Table B.1 are particularly interesting in that the density of the fibre is much greater than that of the as-spun material determined from the mass per unit length measured on a balance and the cross sectional area obtained by SEM. The implication is that the fibre was not completely condensed when taken off line, so that it included air, which was then displaced by the polymer matrix during the formation of the composite. The fact that the fibre density

B.3 Mechanical Properties

Table B.1: Nominal and measured fibre density in epoxy and polystyrene matrices

Matrix	Fibre mass frac. (%)	Fibre vol. frac. (%)	Nominal fibre density (g/cm ³)	Measured fibre density (g/cm ³)
Epoxy	22	27	0.42	0.91
Epoxy	17	18	0.59	1.04
Epoxy	26	30	0.49	0.97
Polystyrene	24	30	0.5	0.7

nearly doubles in the epoxy composite but reaches a values of only 0.7 g/cm³ for polystyrene probably reflects the greater difficulty in filling all the voids in the fibre on account of the higher molecular weight of the polymer ($M_w \sim 280000$) compared with the uncured epoxy.

B.3 Mechanical Properties

Data for stiffness, fracture stress and energy absorption at fracture in tension are given in Table B.2 for CNT fibre/PS and CNT fibre/epoxy composites, and the pure polymer specimens.

Table B.2: Mechanical properties of composites in tension

Material	Stiffness (GPa)	Strength (MPa)	Energy to break (J/g)	Fibre volume fraction (%)	Density (g/cm ³)
CNT fibre/ PS	2.0	63	0.27	24	1.05
PS	1.3	23	0.1	0	0.97
CNT fibre/ epoxy	18.8	253	1.9	27	1.1
Epoxy	1.2	43	0.8	0	1.2

Comparison of pure and reinforced PS shows a noticeable increase in strength, stiffness and energy to break on addition of CNT fibres. Interestingly, the strain to break for both materials is very similar, although significantly greater than the

B.4 Analysis of Reinforcement

value of $\sim 3.5\%$ for CNT fibres. Overall, the pure PS and the CNT fibre/PS composites showed evidence of residual solvent in the specimens, which is responsible for their relatively low values of strength and stiffness.

The CNT fibre/epoxy reinforced composites also showed an increment in strength and stiffness as compared with pure thermoset. In spite of the reduced strain to break, the higher strength levels of the reinforced epoxy meant that the material showed an increase in toughness as indicated by energy absorbed before fracture. An increase in compressive properties was also observed, as summarised in table B.3

Table B.3: Mechanical properties of composites in compression

Material	Stiffness (GPa)	Yield stress (MPa)	Energy absorbed at yield stress (J/g)	Fibre volume fraction (%)	Density (g/cm ³)
CNT fibre/ epoxy	10	130	1.7	14	1.1
Epoxy	1.2	40	0.6	0	1.2

B.4 Analysis of Reinforcement

The results from tensile and compression tests with pure matrix and CNT-fibre reinforced composites were analysed in terms of the mechanical properties measured experimentally and those obtained theoretically. Un-sized carbon fibre (CF) composites were also manufactured following the same procedure to act as comparators. A summary is presented in table B.4, containing values for the ratio of the experimental value of stiffness (E_{test}/E_{theory}) and strength ($\sigma_{test}/\sigma_{theory}$) over the theoretical one based on a simple rule of mixtures.

The data reveal that CNT fibre composites make excellent use of the fibre stiffness and strength both in tension and compression. Although in tension, a value greater than one is observed for CNT fibre composites, this might be the consequence of an underestimation of the fibre stiffness through uncertainties in

B.4 Analysis of Reinforcement

Table B.4: Theoretical and measured mechanical properties of CNT fibre and carbon fibre composites

	Tension $E_{\text{test}}/E_{\text{theory}}$	Tension $\sigma_{\text{test}}/\sigma_{\text{theory}}$	Compression $E_{\text{test}}/E_{\text{theory}}$
CNT fibre/PS	0.67	0.85	-
Carbon fibre/PS	.06	0.12	-
CNT fibre/epoxy	1.4	0.9	0.92
Carbon fibre/epoxy	0.6	0.8	0.4

determining the density of CNT fibres. Moreover, the relevance of the results summarised in Table B.4 is that they imply that further improvements in stiffness or strength of CNT-fibres should be directly manifested in an improvement of the mechanical properties of CNT-fibre composites, particularly with epoxy as matrix.

The level of reinforcement of the thermoset achieved with the CNT fibres used in this study is evaluated as the increase in modulus (∂E) or strength ($\partial \sigma$) of the composite upon addition of a (volume fraction V_f , or) mass fraction M_f , of fibre. For compression $\partial \sigma$ refers to the increase in yield stress. The data are presented in Table B.5 in the same form as that reported for composite systems with high mass/volume fractions of nanotubes (143; 144).

Table B.5: Reinforcement in CNT fibre composites

Reinforcement factor	Tension	Compression
$\partial E/\partial M_f(\text{GPa})$	49	45
$\partial \sigma/\partial M_f(\text{MPa})$	840	600

The results from mechanical tests manifest good coupling between the polymer matrix and the CNT fibre due to the strong adhesion of the polymer to the fibre at a sub-micron scale. This not only provides excellent stress transfer between the two, but also increases the surface area of interaction by diffusion of polymer into voids within the fibre structure. Figure B.2 shows an SEM micrograph of a CNT fibre at the fracture surface of a polystyrene composite. A higher magnification (Figure B.2b) micrograph depicting a nanotube bundle covered by

polymer further supports the view that there is considerable adhesion between both materials.

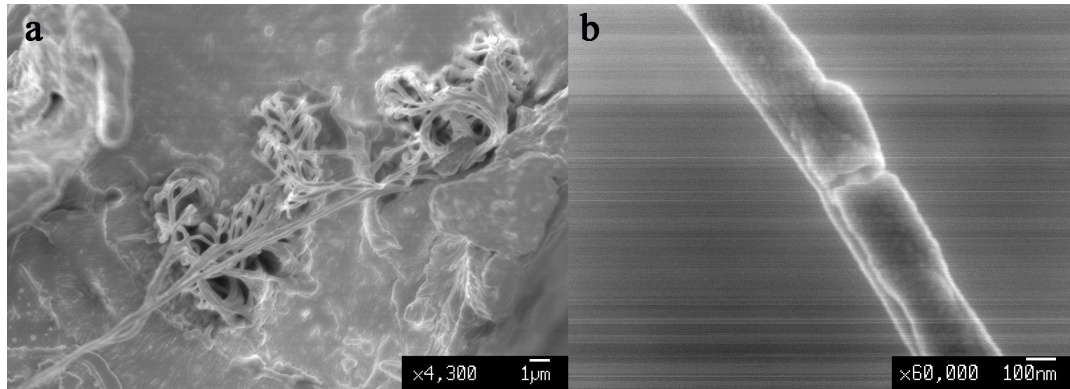


Figure B.2: Scanning electron micrographs of a CNT-fibre/PS composite after mechanical test.

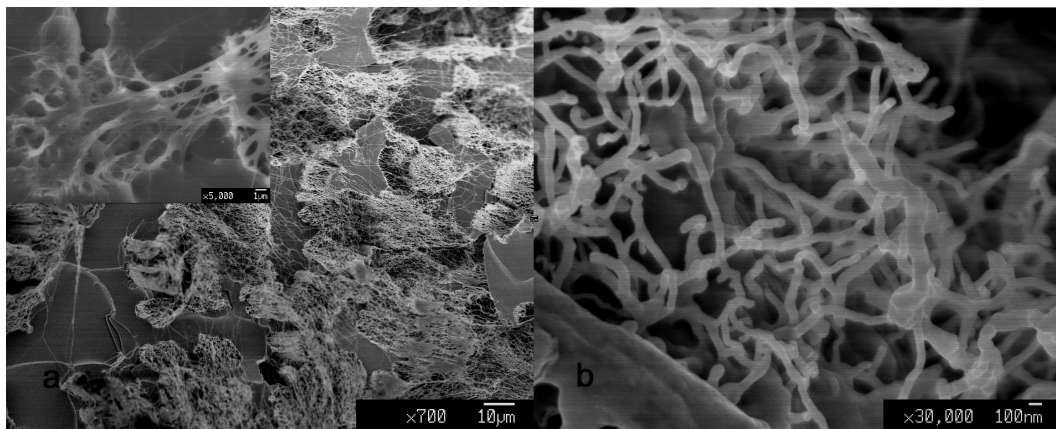


Figure B.3: Scanning electron micrographs of CNT fibre/epoxy composites after mechanical tests. Good matrix-fibre adhesion is observed in bundles of nanotubes covered with polymer exposed after tension (a), and compression tests (b).

Similarly, Figure B.3 shows SEM images of typical fracture surfaces of epoxy composite specimens tested in tension (a) and compression (b). A very clean fracture surface is appreciated, with no evidence of fibre pull-out. Fractography analysis shows that failure of the specimen in tension occurs with a measure of

B.5 Coefficient of Thermal Expansion of CNT Fibres and Their Composites

nanotube pull-out within the individual fibres (inset Fig B.3 a). The scale of the pulled-out entities is of the order of 0.1 microns, which corresponds to CNT bundles rather than individual nanotubes.

The results indicate that CNT fibres are particularly suitable for polymer matrix reinforcement and that their high surface area results in good adhesion between fibre and matrix without need for any additional treatments.

B.5 Coefficient of Thermal Expansion of CNT Fibres and Their Composites

The coefficient of thermal expansion (CTE) of a material is of fundamental importance in applications where it is required to perform in a broad range of temperatures and specially when materials with different CTE converge at an interface.

At present, no value for the coefficient of thermal expansion of CNT fibres has been reported in the literature and it remains an open question whether fibres and other macro-assemblies of nanotubes have a similar CTE to their individual constituents. As a reference, there are a number of studies of the CTE at different temperatures of individual CNTs; theoretically, it has been suggested that SWNTs exhibit a volume contraction for temperatures between $\sim -170^\circ\text{C}$ and $\sim 230^\circ\text{C}$ (145; 146; 147), with a longitudinal thermal expansion at room temperature as low as $-6 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ (145). Although there is some discrepancy in the values of CTE for the same nanotubes, negative values for the longitudinal CTE are predicted for SWNTs of different diameters and helicities according to all the studies. Experimentally, a negative volume expansivity between 30°C - 1330°C has been measured for bundled SWNTs using X-ray diffraction (148), supporting the theoretical predictions.

The strategy for estimating the CTE of CNT fibres was to measure the coefficient of thermal expansion of CNT-reinforced composites, and from this, back calculate the value for the individual filaments using equation

$$\alpha_c = \frac{E_f \alpha_f V_f + E_m \alpha_m (1 - V_f)}{E_f V_f + E_m (1 - V_f)} \quad (\text{B.1})$$

B.5 Coefficient of Thermal Expansion of CNT Fibres and Their Composites

Where the subscripts f , m and c refer to fibre, matrix and composite, respectively. E_x is the elastic modulus, V_f the fibre volume fraction and α_c the coefficient of thermal expansion (64). Although the CTE of epoxy resin can be found in the literature, it was measured experimentally to ensure that it corresponded to the value of CTE of the matrix as prepared by the particular manufacturing process used. The accuracy of the measurement was evaluated by measuring the CTE of T300 carbon fibre/epoxy composite samples made by the same process and comparing experimental with literature values. The samples used consisted of small cylindrical specimens similar to those shown in Figure B.1, with fibre volume fractions between 10% and 40%.

A plot of the longitudinal thermal expansion of CF/epoxy (red) and CNT fibre/epoxy (black) composites against temperature is presented in Figure B.4. For this samples, the experiments were carried out by first cooling the specimen gradually to -20°C , then heating up steadily to 60°C and finally cooling down back to room temperature, as indicated by the arrows. Both curves show a predominantly linear behaviour, except for periods in which the instrument is in the transition from heating to cooling mode (and viceversa). The CTE was determined as the slope of the linear part of the curves in fig B.4, which did not vary significantly with temperature.

Table B.6: CTE at room temperature of cured epoxy, CNT fibre and T300 carbon fibre

Material	CTE ($\times 10^{-6} \text{ }^\circ\text{C}^{-1}$)	
	Experimental	Reported
Epoxy	85	65 (149)
CNT fibre	-1.45	-1.3* -10**
Carbon fibre	-0.27	-0.41 (150)

*CTE of in-plane graphite (151) and ** of a (10, 10) SWNT (145).

A summary of results is presented in Table B.6, which also includes reported values of CTE at room temperature for a similar epoxy, T300 CF, in-plane graphite and a (10, 10) SWNT. For the epoxy sample, the coefficient of thermal expansion of $85 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ obtained experimentally is in very good agreement

B.6 Thermal Conductivity of CNT Fibre Composites

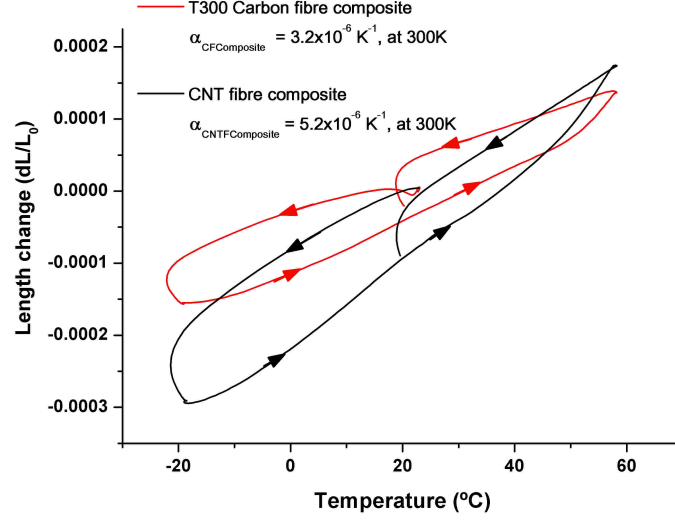


Figure B.4: Plot of the longitudinal thermal expansion (dL/L_0) of CNT fibre/epoxy and T300 carbon fibre/epoxy composites against temperature.

with a value of $65 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ found in the literature (149). For T300 carbon fibres, an experimental value of $-0.27 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ is calculated from the measurements, which compared to $-0.41 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ reported by the manufacturer (150) shows good agreement and provides further confidence of experimental accuracy. The measurements on the CNT fibre composite gave a CTE of CNT fibres of $-1.45 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, comparable to the in-plane thermal expansion of graphite of $-1.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (151) at the same temperature, although greater than theoretical estimates for SWNTs of $\sim -10^{-5} \text{ }^\circ\text{C}^{-1}$ (145).

B.6 Thermal Conductivity of CNT Fibre Composites

The use of CNT fibres in composites is an interesting route for exploiting the thermal conductivity (K) of CNTs. This technique avoids problems with methods in which nanotubes are used in powder form and which have the inherent difficulty

B.6 Thermal Conductivity of CNT Fibre Composites

of achieving simultaneously a uniform dispersion of nanotubes in the matrix and high CNT loadings.

The CNT fibre/thermoset composite specimens studied were produced as described above, with K1100 carbon fibre/epoxy specimens were made for comparison. In the experimental set-up, a composite sample was attached to a heater connected to a power source with variable amplitude and frequency, which produced a temperature wave in the specimens and from which the thermal conductivity of the composite could be calculated according to Angstrom's technique (63). An example of temperature measurements on a specimen is presented in fig B.5, for a sample subjected to a heat wave with period of 50s. Inspection of the temperature wave curves along the specimen show the same frequency as the heat source and a progressively smaller amplitude (A_i) and larger time lag ($t_2 - t_1$) with increasing distance from the heat source.

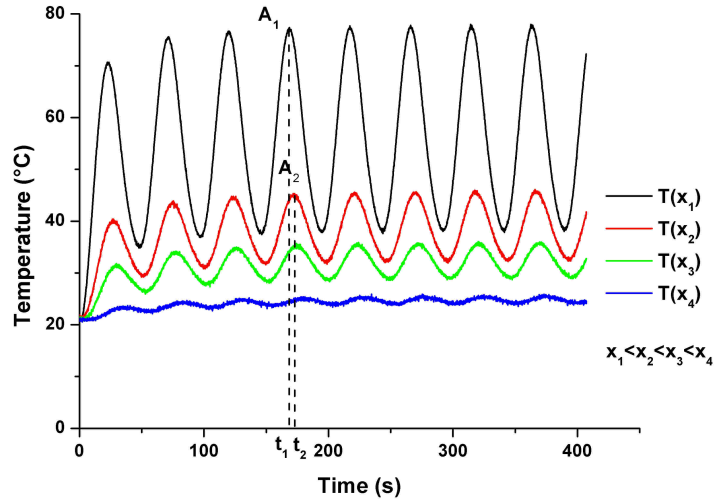


Figure B.5: Temperature of a CNT fibre/epoxy sample at progressively longer distances ($x_i < x_{i+1}$) from the heat source.

For reference, typical thermal images during equivalent tests are presented in Figures B.6 and B.7 for a sample of pure thermoset and a CNT fibre composite, respectively. The images are taken at times corresponding to the minimum (I),

B.6 Thermal Conductivity of CNT Fibre Composites

half (II) and maximum (III) values of the heat supplied to the sample. The frequency and amplitude of the heat source were kept identical for both systems to obtain a direct visual indication of the different diffusivities. Although the heat delivered to each sample might differ due to differences in the contact with the heat source, comparison of the images of the two materials shows qualitatively the marked difference in heat conduction between the pure thermoset and the CNT fibre composite.

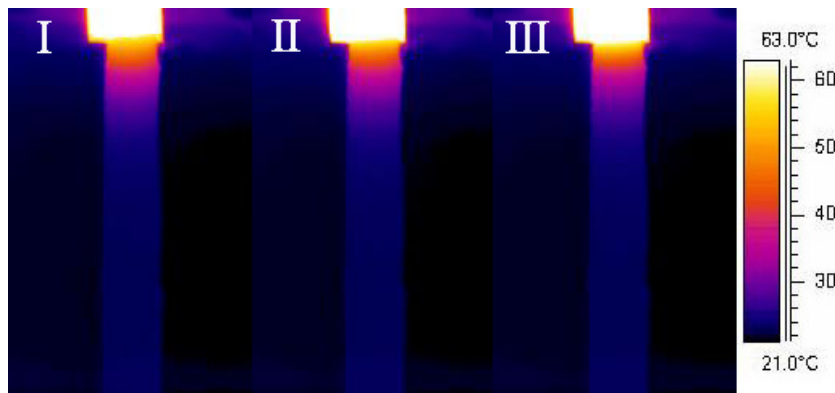


Figure B.6: Thermal image of an epoxy specimen subjected to a sinusoidal heat wave, corresponding to valley (I) mid-point (II) and crest (III) of the heat wave.

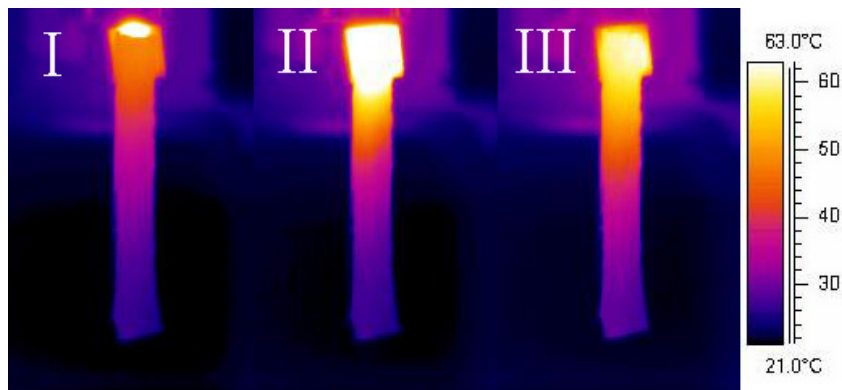


Figure B.7: Thermal image of a CNT fibre/epoxy specimen subjected to a sinusoidal heat wave, corresponding to valley (I) mid-point (II) and crest (III) of the heat wave.

B.6 Thermal Conductivity of CNT Fibre Composites

Results for the neat epoxy and the CNT and CF composites are presented in Table B.7, containing the fibre volume fraction, the composite thermal diffusivity and the fibre thermal conductivity derived from that of the composites. Inspection of the table indicates values for epoxy and K1100 in agreement with the literature (129; 149), confirming the accuracy of the experimental technique used. It is encouraging that the thermal diffusivity of the matrix is raised by a factor ~ 30 with addition of 17% mass of CNT fibre, which gives this composite the highest thermal conductivity compared to other CNT/polymer composite systems.

Although the addition of CNT fibres produces a notable increase in the thermal conductivity of the matrix, the increase in K per increase per unit mass of CNTs is only 48 W/mK, in contrast with a value of 142 W/mK for a somewhat comparable system consisting of 3 wt% SWNTs magnetically aligned in epoxy (152), or a value of 928 W/mK for the carbon fibre.

Table B.7: Data for thermal diffusivity of composites and comparison of experimental and nominal thermal conductivity of fibres

Specimen	Fibre Vol. frac. (%)	Diffusivity (mm^2s^{-1})	Experimental fibre K (WmK^{-1})	Nominal fibre K (WmK^{-1})
Epoxy	0	0.2	-	-
CNT fibre composite	17	7.8	48	50 (Section 7.3)
K1100 CF composite	11	123	1000	927.6 (129)

It is plausible that the relatively low values of K of the CNT fibre composites are due to misorientation of the fibres, a heterogeneous distribution of fibres in the matrix and the presence of voids induced during the manufacturing process. However, the values are far from the conductivity of individual CNTs of ~ 1000 W/mK and suggest that the CNT-CNT and CNT-epoxy interfaces play a dominant role in heat transfer and can therefore limit the extent to which the axial conductivity of nanotubes can be exploited. Further experiments are required to clarify the matter.

B.7 Summary

CNT fibre composite specimens with high fibre volume fraction were produced by infiltration of the polymer into an array of aligned fibre filaments. Tensile and compression tests suggest that the composite stiffness and fibre volume fraction are related *pro rata* and that the ultimate tensile strength of CNT fibre composites is $\sim 90\%$ of the value predicted by a simple rule of mixtures. Surprisingly, the results show that CNT-fibres provide good reinforcement in compression as well as in tension. The coefficient of thermal expansion of the composites was measured and from these, the CTE of the fibres was calculated as $-1.45 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, which is comparable to that of graphite in the basal plane. The thermal conductivity of the CNT fibre/epoxy composites, determined using the Angstrom's technique, is ~ 30 higher than that of the matrix, however, a factor of ~ 20 lower than that of an equivalent specimen made with K1100 carbon fibre.

References

- [1] S. Iijima, “Helical Microtubules of Graphitic Carbon,” *Nature*, vol. 354, pp. 56–58, 1991. 4
- [2] H. Staudinger, *Die Hochmolekularen Organischen Verbindungen. Kautschuk und Cellulose*. Berlin: Springer Verlag, 1932. 4
- [3] M. S. Dresselhaus, G. Dresselhaus, and P. C. Ekland, *Science of Fullerenes and Carbon Nanotubes*. San Diego: Academic Press, 1996. 5
- [4] A. L. Mackay and H. Terrones, “Diamond from Graphite,” *Nature*, vol. 352, p. 762, 1991. 6
- [5] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, “Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes,” *Science*, vol. 306, pp. 1362 – 1364, 2004. 6
- [6] B. I. Yakobson, C. J. Brabec, and J. Bernholc, “Nanomechanics of Carbon Nanotubes: Instabilities Beyond Linear Range,” *Phys. Rev. Lett.*, vol. 79, pp. 1297–1300, 1996. 6
- [7] B. Peng, M. Locascio, P. Zapol, S. Li, S. L. Mielke, G. C. Schatz, and H. D. Espinosa, “Measurements of Near-Ultimate Strength for Multiwalled Carbon Nanotubes and Irradiation-Induced Crosslinking Improvements,” *Nature*, vol. 3, pp. 626–631, 2008. 7, 91
- [8] M. Yu, B. S. Files, S. Arepalli, and R. S. Ruoff, “Tensile Loading of Ropes of Single Wall Carbon Nanotubes and their Mechanical Properties,” *Phys. Rev. Lett.*, vol. 84, pp. 5552–5555, 2000. 7

REFERENCES

- [9] C. Leev, X. Wei, J. W. Kysar, and J. Hone, “Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene,” *Science*, vol. 321, pp. 385–388, 2008. 7, 8, 91
- [10] H. van der Werff and A. J. Pennings, “Tensile Deformation of High Strength and High Modulus Polyethylene Fibers,” *Colloid Polym. Sci.*, vol. 269, pp. 747–763, 1991. 7
- [11] A. J. Pennings, M. Roukema, and A. van der Veen, “Further Studies on the High-Speed Gel-Spinning of Ultra-High Molecular Weight Polyethylene,” *Polym. Bull.*, vol. 23, pp. 353–359, 1990. 7
- [12] W. W. Adams, “Private communication,” *The Richard Smalley Institute, Rice University, Houston, Texas*, 2007. 7
- [13] W. W. Adams and R. K. Eby, “High-Performance Polymer Fibers,” *MRS Bull.*, pp. 22–26, 1987. 7
- [14] K. Steel, Ltd., and Japan, “Advancing Composites in Aerospace,” *E.I. duPont de Nemours and Co.*, 1987. 7
- [15] P. Morgan, *Carbon Fibres and Their Composites*. Boca Raton, Fla.: Taylor and Francis, 2005. 7, 8
- [16] K. Steel, Ltd., and Japan *Kobelco Technology Review*, vol. 8, 1990. 7
- [17] S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, “Carbon Nanotube Quantum Resistors,” *Science*, vol. 280, pp. 1744–1746, 1998. 8
- [18] P. Lambin, L. Philippe, J. C. Charlier, and J. P. Michenaud, “Electronic Band Structure of Multilayered Carbon Tubules,” *Comp. Mat. Sci.*, vol. 2, pp. 350–356, 1994. 9
- [19] L. X. Benedict, V. H. Crespi, S. G. Louie, and M. L. Cohen, “Static Conductivity and Superconductivity of Carbon Nanotubes: Relations Between Tubes and Sheets,” *Phys. Rev. B*, vol. 52, no. 14, pp. 935–940, 1995. 9, 122

REFERENCES

- [20] A. Bachtold, M. S. Fuhrer, S. Plyasunov, M. Forero, E. H. Anderson, A. Zettl, and P. L. McEuen, “Scanned Probe Microscopy of Electronic Transport in Carbon Nanotubes,” *Phys. Rev. Lett.*, vol. 84, no. 26, pp. 6082–6085, 2000. 9
- [21] L. Pietronero, R. Strassler, H. R. Zeller, and M. J. Rice, “Electrical Conductivity of a Graphite Layer,” *Phys. Rev. B*, vol. 22, p. 904, 1980. 9
- [22] W. Primark and L. H. Fuchs, “Radiation Damage to the Electrical Conductivities of Natural Graphite Crystals,” *Phys. Rev.*, vol. 103, p. 541, 1956. 9
- [23] C. N. Hooker and A. R. Ubbelohde, “Thermal Conductance of Graphite in Relation to its Defect Structure,” *Proc. Roy. Soc. A*, vol. 284, p. 17, 1965. 10
- [24] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, “Superior Thermal Conductivity of Single-Layer Graphene,” *Nano Lett.*, vol. 8, pp. 902–907, 2008. 10
- [25] S. Berber, Y. Kwon, and D. Tomanek, “Unusually High Thermal Conductivity of Carbon Nanotubes,” *Phys. Rev. Lett.*, vol. 84, pp. 4613–4616, 2000. 10, 131
- [26] P. Kim, L. Shi, A. Majumdar, , and P. L. McEuen, “Measurement of Thermal Conductivity of Individual Multiwalled Carbon Nanotubes by the 3ω Method,” *App. Phys. Lett.*, vol. 87, p. 013108, 2005. 10, 131
- [27] P. Kim, L. Shi, A. Majumdar, , and P. L. McEuen, “Thermal Transport Measurements of Individual Multiwalled Nanotubes,” *Phys. Rev. Lett.*, vol. 87, p. 215502, 2001. 10, 131
- [28] I. Hsu, M. T. Pettes, A. Bushmaker, M. Aykol, L. Shi, and S. B. Cronin, “Optical Absorption and Thermal Transport of Individual Suspended Carbon Nanotube Bundles,” *Nano Lett.*, vol. 9, pp. 590–594, 2009. 10, 131

REFERENCES

- [29] J. Hone, M. Whitney, C. Piskoti, and A. Zettl, “Thermal Conductivity of Single-Walled Carbon Nanotubes,” *Phys. Rev. B*, vol. 59, p. R2514, 1999. 10
- [30] Z. L. Wang, D. W. Tang, X. B. Li, X. H. Zheng, W. G. Zhang, L. X. Zheng, Y. T. Zhu, A. Z. Jin, H. F. Yang, and C. Z. Gu, “Length-dependent Thermal Conductivity of an Individual Single-Wall Carbon Nanotube,” *App. Phys. Lett.*, vol. 91, p. 123119, 2007. 10
- [31] B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, and P. Poulin, “Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes,” *Science*, vol. 290, pp. 1331–1334, 2000. 11, 16, 45
- [32] A. B. Dalton, S. Collins, J. Razal, E. Munoz, V. H. Ebron, B. G. Kim, J. N. Coleman, J. P. Ferraris, and R. H. Baughman, “Super-Tough Carbon-Nanotube Fibers,” *Nature*, vol. 423, p. 703, 2003. 11, 12
- [33] A. B. Dalton, S. Collins, J. Razal, E. Munoz, V. H. Ebron, B. G. Kim, J. N. Coleman, J. P. Ferraris, and R. H. Baughman, “Continuous Carbon Nanotube Composite Fibers: Properties, Potential Applications, and Problems,” *J. Mater. Chem.*, vol. 14, pp. 1–3, 2004. 11
- [34] P. Miaudet, S. Badaire, M. Maugey, A. Derre, V. Pichot, P. Launois, P. Poulin, and C. Zakri, “Hot-drawing of Single and Multiwall Carbon Nanotube Fibers for High Toughness and Alignment,” *Nano Lett.*, vol. 5, pp. 2212–2215, 2005. 12
- [35] V. A. Davis, L. M. Ericson, A. N. G. Parra-Vasquez, H. Fan, Y. Wang, V. Prieto, J. A. Longoria, S. Ramesh, R. K. Saini, C. Kittrell, W. E. Billups, W. W. Adams, R. H. Hauge, R. E. Smalley, and M. Pasquali, “Phase Behavior and Rheology of SWNTs in Superacids,” *Macromolecules*, vol. 37, pp. 154–160, 2004. 12
- [36] S. Zhang, K. K. K. Koziol, I. A. Kinloch, and A. H. Windle, “Macroscopic Fibers of Well-Aligned Carbon Nanotubes by Wet Spinning,” *Small*, vol. 4, no. 8, pp. 1217–1222, 2008. 12, 13, 105, 124, 125

REFERENCES

- [37] L. M. Ericson, H. Fan, H. Peng, V. A. Davis, J. S. W. Zhou, Y. Wang, R. Booker, J. Vavro, C. Guthy, A. N. G. Parra-Vasquez, M. J. Kim, S. Ramesh, R. K. Saini, C. Kittrell, G. Lavin, H. Schmidt, W. W. Adams, W. E. Billups, M. Pasquali, W. Hwang, R. H. Hauge, J. E. Fischer, and R. E. Smalley, “Macroscopic, Neat, Single-Walled Carbon Nanotube Fibers,” *Science*, vol. 305, pp. 1457–1450, 2004. 12, 16, 43, 49, 91, 105
- [38] W. Zhou, J. Vavro, C. Guthy, K. I. Winey, J. E. Fischer, L. M. Ericson, S. Ramesh, R. Saini, V. A. Davis, C. Kittrell, M. Pasquali, R. H. Hauge, and R. E. Smalley, “Single Wall Carbon Nanotube Fibers Extruded from Super-Acid Suspensions: Preferred Orientation, Electrical, and Thermal Transport,” *J. Appl. Phys.*, vol. 95, no. 2, pp. 649–655, 2007. 12, 124, 125, 131
- [39] M. Zhang, K. R. Atkinson, and R. H. Baughman, “Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology,” *Science*, vol. 306, pp. 1358–1361, 2004. 13, 14, 16, 43, 91, 109, 124, 125
- [40] X. Zhang, Q. Li, T. G. Holesinger, P. N. Arendt, J. Huang, P. D. Kirven, T. G. Clapp, R. F. DePaula, X. Liao, Y. Zhao, L. Zheng, D. E. Peterson, and Y. Zhu, “Ultrastrong, Stiff, and Lightweight Carbon-Nanotube Fibers,” *Adv. Mater.*, vol. 19, pp. 4198–4201, 2007. 13, 14, 105
- [41] S. Zhang, L. Zhu, M. L. Minus, H. G. Chae, S. Jagannathan, C. Wong, J. Kowalik, L. B. Roberson, and S. Kumar, “Solid-State Spun Fibers and Yarns from 1-mm Long Carbon Nanotube Forests Synthesized by Water-Assisted Chemical Vapor Deposition,” *J. Mater. Sci.*, vol. 43, pp. 4356–4362, 2008. 14, 45, 91, 105, 110, 124, 125
- [42] Q. Li, Y. Li, X. Zhang, S. B. Chikkannanavar, Y. Zhao, A. M. Dangelewicz, L. Zheng, S. K. Doorn, Q. Jia, D. E. Peterson, P. N. Arendt, and Y. Zhu, “Structure-Dependent Electrical Properties of Carbon Nanotube Fibers,” *Adv. Mater.*, vol. 19, pp. 3358–3363, 2007. 14, 91, 124, 125

REFERENCES

- [43] A. E. Aliev, C. Guthy, M. Zhang, S. Fang, A. A. Zakhidov, J. E. Fischer, and R. H. Baughman, “Thermal Transport in MWCNT Sheets and Yarns,” *Carbon*, vol. 45, pp. 2880–2888, 2007. 14, 131
- [44] H. M. Cheng, F. Li, X. Sun, S. D. M. Brown, M. A. Pimenta, A. Marucci, G. Dresselhaus, and M. S. Dresselhaus, “Bulk Morphology and Diameter Distribution of Single-Walled Carbon Nanotubes Synthesized by Catalytic Decomposition of Hydrocarbons,” *Chem. Phys. Lett.*, vol. 289, pp. 602–610, 1998. 15, 29
- [45] H. W. Zhu, D. H. Wu, B. Q. Wei, R. Vajtai, and P. M. Ajayan, “Direct Synthesis of Long Single-Walled Carbon Nanotube Strands,” *Science*, vol. 296, pp. 884–886, 2002. 15, 29
- [46] Y. Li, I. A. Kinloch, and A. H. Windle, “Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis,” *Science*, vol. 304, pp. 276–278, 2004. 15, 16, 29
- [47] K. Koziol, J. Vilatela, A. Moisala, M. Motta, P. Cunniff, and M. S. A. Windle, “High-Performance Carbon Nanotube Fiber,” *Science*, vol. 318, pp. 1892–1895, 2007. 15, 40, 42, 44, 57, 91, 105, 107, 108, 111, 112
- [48] V. Gonsalves, “Determination of Denier and Strength of Single Filaments by Vibroscope and Heim Tensile Tester,” *Tex. Res. J.*, vol. 17, pp. 369–375, 1947. 19
- [49] B. Kitiyaman, W. E. Alvarez, J. H. Harwell, and D. E. Resasco, “Controlled Production of Single-Walled Carbon Nanotubes by Catalytic Decomposition of CO on Bimetallic Co-Mo Catalyst,” *Chem. Phys. Lett.*, vol. 317, pp. 497–503, 2000. 19, 58, 64
- [50] T. Zhao, Y. Lui, and J. Zhu, “Gas and Pressure Effects on the Synthesis of Amorphous Carbon Nanotubes,” *Chinese Sci. Bull.*, vol. 49, pp. 2569–2571, 2004. 19, 61

REFERENCES

- [51] A. R. Harutyunyan, B. K. Pradhan, J. Chang, G. Chen, and P. C. Eklund, “Purification of Single-Wall Carbon Nanotubes by Selective Microwave Heating of Catalyst Particles,” *J. Phys. Chem. B*, vol. 106, pp. 8671–8675, 2002. 19, 61
- [52] E. Smith and G. Dent, *Modern Raman Spectroscopy: a Practical Approach*. Chichester: John Wiley and Sons, 2005. 21
- [53] M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, “Raman Spectroscopy of Carbon Nanotubes,” *Physics Reports-Reviews Section of Phys. Lett.*, vol. 409, pp. 47–99, 2005. 21
- [54] H. Wilhelm, M. Lelausian, E. McRae, and B. Humbert, “Raman Spectroscopic Studies on Well-Defined Carbonaceous Materials of Strong Two-Dimensional Character,” *J. Appl. Phys.*, vol. 84, pp. 6552–6558, 1998. 22
- [55] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim., “The Raman Fingerprint of Graphene,” *App. Phys. Lett.*, vol. 91, p. 233108, 2007. 22, 84
- [56] M. Milnera, J. Kürti, M. Hulman, and H. Kuzmany, “Periodic Resonance Excitation and Intertube Interaction from Quasi-Continuous Distributed Helicities in Single-Walled Carbon Nanotubes,” *Phys. Rev. Lett.*, vol. 84, pp. 1324–1327, 2000. 22, 76
- [57] A. Jorio, M. A. Pimenta, A. G. S. Filho, G. G. Samsonidzea, A. K. Swan, M. S. Unlu, B. B. Goldberg, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, “Raman Spectra of Carbon Nanotubes by Cross-Polarized Light,” *Phys. Rev. Lett.*, vol. 90, p. 107403, 2003. 22
- [58] A. Jorio, A. G. Souza, V. W. Brar, A. K. Swan, M. S. Unlu, B. B. Goldberg, A. Righi, J. H. Hafner, C. M. Lieber, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, “Polarized Resonant Raman Study of Isolated Single-Wall Carbon Nanotubes: Symmetry Selection Rules, Dipolar and Multipolar Antenna Effects,” *Phys. Rev. B*, vol. 65, p. 121402, 2002. 22, 89

REFERENCES

- [59] T. Liu and S. Kumar, “Quantitative Characterization of SWNT Orientation by Polarized Raman Spectroscopy,” *Chem. Phys. Lett.*, vol. 378, pp. 257–262, 2003. 22
- [60] S. B. Cronin, A. K. Swan, M. S. Unlu, B. B. Goldberg, M. S. Dresselhaus, and M. Tinkham., “Resonant Raman Spectroscopy of Individual Metallic and Semiconducting Single-Wall Carbon Nanotubes Under Uniaxial Strain,” *Phys. Rev. B*, vol. 72, p. 035425, 2005. 23, 117
- [61] H. Sakata, G. Dresselhaus, M. S. Dresselhaus, and M. Endo, “Effect of Uniaxial Stress on the Raman Spectra of Carbon Fibers,” *J. Appl. Phys.*, vol. 63, no. 8, pp. 2769–2772, 1988. 23
- [62] R. J. Y. Y. Huang, “Microstructure and Mechanical Properties of Pitch-Based Carbon Fibres,” *J. Mater. Sci.*, vol. 29, pp. 4027–4036, 1994. 23
- [63] A. J. Angstrom *Ann. Phys. Chemie*, vol. 144, p. 513, 1861. 27, 130, 167
- [64] J. Schapery, “Thermal Expansion Coefficients of Composite Materials Based on Energy Principles,” *J. Comp. Mater.*, vol. 2, pp. 380–404, 1968. 27, 165
- [65] R. Barker and P. Harris, *Chemistry and Physics of Carbon*, vol. 14. New York: Marcel Dekker, 1978. 29
- [66] W. Hoogsteen, H. Kormelink, G. Eshuis, G. ten Brinke, and A. J. Pennings, “Gel-spun Polyethylene Fibres: Part 2 Influence of Polymer Concentration and Molecular Weight Distribution on Morphology and Properties,” *J. Mater. Sci.*, vol. 23, pp. 3467–3474, 1988. 29, 37
- [67] M. S. Motta, I. Kinloch, A. Moisala, M. Pick, and A. Windle, “The Parameter Space for the Direct Spinning of Fibres and Films of Carbon Nanotubes,” *Physica E*, vol. 37, pp. 40–43, 2006. 30
- [68] G. Tibbets and M. Balogh, “Increase in Yield of Carbon Fibres Grown Above the Iron/Carbon Eutectic,” *Carbon*, vol. 37, p. 241, 1999. 31

REFERENCES

- [69] M. S. Motta, A. Moisala, I. A. Kinloch, and A. H. Windle, “The Role of Sulphur in the Synthesis of Carbon Nanotubes by Chemical Vapour Deposition at High Temperatures,” *J. Nanosci. Nanotechnol.*, vol. 8, pp. 1–8, 2008. 31
- [70] M. Motta, A. Moisala, I. A. Kinloch, and A. H. Windle, “High Performance Fibres from ‘Dog Bone’ Carbon Nanotubes,” *Adv. Mater.*, vol. 19, pp. 3721–3726, 2007. 31, 56, 68, 101, 102
- [71] R. E. Robertson, “Polymer Order and Polymer Density,” *J. Phys. Chem.*, vol. 69, pp. 1575–1578, 1965. 39
- [72] J. B. Donnet and R. C. Bansal, *Carbon Fibers 2nd edition*. New York: Oxford University Press, 1990. 39, 134
- [73] D. N. Futaba, K. Hata, T. Yamada, T. Hiraoaka, Y. Hayamizu, Y. Kadukate, O. Takanike, H. Hatori, M. Yumura, and S. Iijima, “Shape-engineerable and Highly Densely Packed Single-Walled Carbon Nanotubes and Their Applications as Super-Capacitor Electrodes,” *Nat. Mat.*, vol. 5, pp. 987–993, 2006. 40, 45, 49
- [74] J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger *Rec. Trav. Chim. Pays Bas*, vol. 65, p. 427, 1946. 44
- [75] N. Chakrapani, B. Wei, A. Carrillo, P. Ajayan, and R. S. Kane, “Capillary-driven Assembly of Two-Dimensional Cellular Carbon Nanotube Foams,” *Proc. Natl. Acad. Sci.*, vol. 101, pp. 4009–4013, 2004. 45
- [76] K. K. Koziol, M. Pick, J. J. Vilatela, and A. H. Windle, “Enhancement of the Structure and Properties of Carbon Nanotube fibre.” Patent application GB0708293.6, 2007. 45
- [77] D. Py, R. Bastien, J. Bico, B. Roman, and A. Boudaoud, “3D Aggregation of Wet fibers,” *Eur. Phys. Lett.*, vol. 77, p. 44005, 2007. 50, 52
- [78] J. Bico, B. Roman, L. Moulin, and A. Boudaoud, “Elastocapillary Coalescence in Wet Hair,” *Nature*, vol. 432, p. 690, 2004. 50, 52

REFERENCES

- [79] E.Kissa, *Handbook of Fiber Science and Technology IIB*. New York.: M. Lewin, S. B. Sello Eds., 1984. 50
- [80] D. K. Owens and R. C. Wendt, "Estimation of the Surface Free Energy of Polymers," *J. Appl. Poly. Sci.*, vol. 13, pp. 1741–1747, 1969. 51
- [81] S. D. Bergin, V. Nicolosi, P. V. Streich, S. Giordani, Z. Sun, A. H. Windle, P. Ryan, N. P. P. Niraj, Z. T. Wang, L. Carpenter, W. J. Blau, J. J. Boland, J. P. Hamilton, and J. N. Coleman, "Towards Solutions of Single-Walled Carbon Nanotubes in Common Solvents," *Adv. Mat.*, vol. 20, pp. 1876–1881, 2008. 52, 93
- [82] M. L. Terranova, V. Sessa, and M. Rossi, "The World of Carbon Nanotubes: An Overview of CVD Growth Methodologies," *Chem. Vap. Deposition*, vol. 12, pp. 315–325, 2006. 56
- [83] Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, and S. Iijima, "Purification of Single-Wall Carbon Nanotubes," *Solid State Commun.*, vol. 112, pp. 35–37, 1999. 58, 61, 64
- [84] R. Robertson, "Amorphous Carbon," *Adv. in Phys.*, vol. 35, no. 4, pp. 317–374, 1986. 58
- [85] B. C. Gates, J. R. Katzer, and G. C. Schuit, *Chemistry of Catalytic Processes*. U.S.: McGraw-Hill, 1979. 64
- [86] R. J. Davies, C. Riekkel, K. K. Koziol, J. J. Vilatela, and A. H. Windle, "Structural Studies on Carbon Nanotube Fibers by Synchrotron Radiation Microdiffraction," *Submitted*. 66, 68
- [87] V. Pichot, P. Launois, M. Pinault, M. Mayne, and C. Reynaud, "Evidence of Strong Nanotube Alignment and for Iron Preferential Growth Axis in Multiwalled Carbon Nanotube Carpets," *Appl. Phys. Lett.*, vol. 85, p. 473, 2004. 70
- [88] H. Kim and W. Sigmund, "Effect of Graphitic Structure on the Stability of FCC Iron," *J. Cryst. Gro.*, vol. 267, p. 738, 2004. 70

REFERENCES

- [89] H. Kim and W. Sigmund, “Iron nanoparticles in Carbon nanotubes at various temperatures,” *J. Cryst. Gro.*, vol. 276, pp. 594–605, 2005. 70
- [90] L. Sun, F. Banhart, A. V. Krashenninnikov, J. A. Rodriguez-Manzo, M. Terrones, and P. M. Ajayan, “Carbon Nanotubes as High-Pressure Cylinders and Nanoextruders,” *Science*, vol. 312, pp. 1199–1202, 2006. 70
- [91] M. Mayne, N. Grobert, M. Terrones, R. Kamalakaran, M. Rühle, H. W. Kroto, and D. R. M. Dalton, “Pyrolytic Production of Aligned Carbon Nanotubes From Homogeneously Dispersed Benzene-Based Aerosols,” *Chem. Phys. Lett.*, vol. 338, p. 101, 2001. 70
- [92] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, “Structural (n, m) Determination of Isolated Single-Wall Carbon Nanotubes by Resonant Raman Scattering,” *Phys. Rev. Lett.*, vol. 86, p. 1118, 2001. 74
- [93] A. M. Rao, A. Jorio, M. A. Pimenta, M. S. S. Dantas, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, “Polarized Raman Study of Aligned Multiwalled Carbon Nanotubes,” *Phys. Rev. Lett.*, vol. 84, pp. 1820–1823, 2000. 89
- [94] A. Kis, K. Jensen, S. Aloni, W. Mickelson, and A. Zettl, “Interlayer Forces and Ultralow Sliding Friction in Multiwalled Carbon Nanotubes,” *Phys. Rev. Lett.*, vol. 97, p. 025501, 2006. 91, 93, 94
- [95] H. L. Cox, “The Elasticity and Strength of Paper and Other Fibrous Materials,” *Brit. J. Appl. Phys.*, vol. 3, pp. 72–79, 1952. 92
- [96] A. Kis and A. Zettl, “Nanomechanics of Carbon nanotubes,” *Phil. Trans. R. Soc. A*, vol. 366, pp. 1591–1611, 2008. 93
- [97] L. X. Benedict, N. G. Chopra, M. L. Cohen, A. Zettl, S. G. Louie, and V. H. Crespi, “Microscopic Determination of the Interlayer Binding Energy in Graphite,” *Chem. Phys. Lett.*, vol. 286, pp. 490–496, 1998. 93

REFERENCES

- [98] A. H. Barber, S. R. Cohen, and H. D. Wagner, “Static and dynamic wetting measurements of single Carbon nanotubes,” *Phys. Rev. Lett.*, vol. 92, no. 18, p. 186103, 2004. 93
- [99] R. Zacharia, H. Ulbricht, and T. Hertel, “The Interlayer Cohesive Energy of Graphite from Thermal Desorption of Polyaromatic Hydrocarbons,” *Phys. Rev. B*, vol. 69, p. 155406, 2004. 93
- [100] L. A. Girifalco and L. A. Lad, “Energy of Cohesion, Compressibility and the Potential Energy Functions of the Graphite System,” *J. Chem. Phys.*, vol. 25, no. 4, pp. 693–697, 1956. 93
- [101] J. V. Larsen, T. Smith, and P. W. Erickson, “Naval Ordnance Laboratory Technical Report,” pp. 71–165, 1971. 93
- [102] Y. Hernandez, V. Nicolosi, M. Lotza, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun’ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurty, R. Goodhue, J. Hutchinson, V. Scardaci, A. C. Ferrari, and J. N. Coleman, “High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite,” *Nat. Nanotechnol.*, vol. 3, no. 9, pp. 563–568, 2008. 93
- [103] I. C. Roselmant and D. Tabor, “The Friction of Carbon Fibres,” *J. Phys. D: Appl. Phys.*, vol. 9, pp. 2517–2532, 1976. 93
- [104] O. Suekane, A. Nagataki, H. Mori, and Y. Nakayama, “Static Friction Force of Carbon Nanotube Surfaces,” *App. Phys. Exp.*, vol. 1, p. 064001, 2008. 93, 94
- [105] M. R. Falvo, R. M. Taylor, A. Helser, V. Chi, F. P. Brooks, S. Washburn, and R. Superfine, “Nanometre-Scale Rolling and Sliding of Carbon Nanotubes,” *Nature*, vol. 397, pp. 236–238, 1999. 93
- [106] M. Yu, B. I. Yakobson, and R. S. Ruoff, “Controlled Sliding and Pullout of Nested Shells in Individual Multiwalled Carbon Nanotubes,” *J. Phys. Chem.*, vol. 104, pp. 8764–8767, 2000. 93

REFERENCES

- [107] B. Bhushan, X. ling, A. Jungen, and C. Hierold, “Adhesion and Friction of a Multiwalled Carbon Nanotube Sliding Against Single-Walled Carbon Nanotube,” *Phys. Rev. B*, vol. 77, p. 165428, 2008. 93
- [108] J. K. Lancaster and J. R. Pritchard, “The Influence of Environment and Pressure on the Transition to Dusting Wear of Graphite,” *J. Phys. D: Appl. Phys*, vol. 14, pp. 747–762, 1981. 93
- [109] D. E. Soule and C. W. Nezbeda, “Direct Basal-Plane Shear in Single-Crystal Graphite,” *J. App. Phys.*, vol. 39, pp. 5122–5139, 1968. 94
- [110] A. Kelly and N. H. Macmillan, *Strong Solids 3rd edition*. Oxford: Oxford University Press, 1986. 94
- [111] D. Hull and T. W. Clyne, *An Introduction to Composite Materials 2nd edition*. Cambridge: Cambridge University Press, 1996. 94
- [112] R. S. Ruoff, J. Tersoff, D. C. Lorents, S. Subramoney, and B. Chan, “Radial Deformation of Carbon Nanotubes by van der Waals Forces,” *Nature*, vol. 364, pp. 514–516, 1993. 96
- [113] N. G. Chopra, L. X. Benedict, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, “Fully collapsed Carbon nanotubes,” *Nature*, vol. 377, p. 135, 1995. 96, 101
- [114] K. Kudin, G. Scuseria, and B. Yakobson, “C₂F, BN, and C Nanoshell Elasticity from *ab initio* Computations,” *Phys. Rev. B*, vol. 64, p. 235406, 2001. 98, 101
- [115] Q. Lu, M. Arroyo, and R. Huang, “Elastic Bending Modulus of Monolayer Graphene,” (*cond – mat.mtrl – sci*), vol. *arXiv* : 0901.4370v1, 1996. 101
- [116] O. Gulseren, T. Yildirim, and S. Ciraci, “Systematic *ab initio* Study of Curvature Effects in Carbon Nanotubes,” *Phys. Rev. B*, vol. 65, p. 153405, 2002. 101

REFERENCES

- [117] J. A. Elliott, J. K. W. Sandler, A. H. Windle, R. J. Young, and M. S. P. Shaffer, "Collapse of Single-Wall Carbon Nanotubes is Diameter Dependent," *Phys. Rev. Lett.*, vol. 92, no. 9, p. 095501, 2004. 101
- [118] K. R. Atkinson, S. C. Hawkins, C. Huynh, C. Skourtis, J. Dai, M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, and R. H. Baughman, "Multifunctional Carbon Nanotube Yarns and Transparent Sheets: Fabrication, Properties, and Applications," *Physica B*, vol. 394, pp. 339–343, 2007. 105
- [119] T. Liu and S. Kumar, "Effect of Orientation on the Modulus of SWNT Films and Fibers," *Nano Lett.*, vol. 3, pp. 647–650, 2003. 106, 108, 110
- [120] L. Zalamea, H. Kim, and R. B. Pipes, "Stress Transfer in Multi-Walled Carbon Nanotubes," *Comp. Sci. Tech.*, vol. 67, pp. 3425–3433, 2007. 107
- [121] S. Allen, A. G. Filipov, R. J. Farris, and E. L. Thomas, "Macrostructure and Mechanical Behavior of Fibers of Poly-p-phenylene Benzobisthiazole," *J. Appl. Polym. Sci.*, vol. 26, p. 291, 1981. 119, 134, 138
- [122] S. R. Allen, R. J. Farris, and E. L. Thomas, "High Modulus/High Strength Poly-(p-phenylene benzobisthiazole) Fibres, Part 2 Structure-property Investigations," *J. Mater. Sci.*, vol. 20, pp. 4583–4592, 1985. 119, 121, 137
- [123] M. Dresselhaus, G. Dresselhaus, and J. E. Fischer, "Graphite Intercalation Compounds: Electronic Properties in the Dilute Limit," *Phys. Rev. B*, vol. 15, p. 3180, 1977. 122
- [124] K. L. Stano, K. Koziol, M. Pick, M. S. Motta, A. Moisala, J. J. Vilatela, S. Frasier, and A. H. Windle, "Direct Spinning of Carbon Nanotube Fibres from Liquid Feedstock," *Int. J. Mater. Form.*, vol. 1, pp. 59–62, 2008. 123, 125
- [125] J. J. Vilatela, A. Bahrami, and A. H. Windle, "*Manuscript in preparation*," 123
- [126] E. G. West, *Copper and its Alloys*. Chichester: Wiley, 1982. 124

REFERENCES

- [127] J. Hone, B. Batlogg, Z. Benes, A. Johnson, and J. Fischer, “Quantised Phonon Spectrum of Single-Wall Carbon Nanotubes,” *Science*, vol. 289, p. 1730, 2000. 131
- [128] J. E. Fischer, W. Zhou, J. Vavro, M. C. Llaguno, C. Guthy, R. Haggemueller, K. I. Winey, M. J. Casavant, and R. E. Smalley, “Thermal Transport in MWCNT Sheets and Yarns,” *J. Appl. Phys.*, vol. 93, p. 2157, 2003. 131
- [129] “Thornel K-1100 Carbon Fiber Data Sheet,” *Cytec Industries Inc.*, 2009. 131, 169
- [130] P. Smith, P. J. Lemstra, B. Kalb, and A. J. Pennings, “Ultrahigh-Strength Polyethylene Filaments by Solution Spinning and Hot Drawing,” *Pol. Bull.*, vol. 1, pp. 733–736, 1979. 134
- [131] S. R. Allen, R. J. Farris, and E. L. Thomas, “High Modulus/High Strength Poly-(p-phenylene benzobisthiazole) Fibres, Part 1 Structure-property Investigations,” *J. Mater. Sci.*, vol. 20, pp. 2727–2734, 1985. 137
- [132] H. Muramatsu, Y. A. Kim, T. Hayashi, M. Endo, M. Terrones, and M. S. Dresselhaus, “Oxidation and Thermal Stability of Linear Carbon Chains Contained in Thermally Treated Double-Walled Carbon Nanotubes,” *Small*, vol. 3, pp. 788–792, 2007. 137
- [133] W. W. Adams and R. K. Eby, “High-Performance Polymer Fibers,” *MRS Bull.*, pp. 22–26, 1987. 138
- [134] L. Alvarez, A. Righi, T. Guillard, S. Rols, E. Anglaret, D. Laplaze, and J. L. Sauvajol, “Resonant Raman study of the structure and electronic properties of SWNTs,” *Chem. Phys. Lett.*, vol. 316, pp. 186–190, 2000. 140
- [135] Y. Z. Jin, C. Gao, W. K. Hsu, Y. Zhu, A. Huczko, M. Bystrzejewski, M. Roe, C. Y. Lee, S. Acquah, H. Kroto, and D. R. M. Walton, “Large-scale Synthesis and Characterization of Carbon Spheres Prepared by Direct Pyrolysis of HydroCarbons,” *Small*, vol. 43, pp. 1944–1953, 2005. 142

REFERENCES

- [136] X. Yan, T. Xu, S. Xu, G. Chen, H. Liu, and S. Yang, "Fabrication of Carbon Spheres on a-C:H Films by Heat-Treatment of a Polymer Precursor," *Small*, vol. 42, pp. 2735–2777, 2004. 142
- [137] X. Liu, B. Huang, and N. J. Coville, "The $\text{Fe}(\text{CO})_5$ Catalyzed Pyrolysis of Pentane: Carbon Nanotube and Carbon Nanoball Formation," *Small*, vol. 40, pp. 2791–2799, 2002. 142
- [138] P. Serp, R. Feurer, P. Kalck, Y. Kihn, J. Faria, and J. Figueiredo, "A Chemical Vapour Deposition Process for the Production of Carbon Nanospheres," *Small*, vol. 39, pp. 615–628, 2001. 142
- [139] W. A. de Heer, P. Poncharal, C. Berger, J. Gezo, Z. Song, J. Bettini, and D. Ugarte, "Liquid Carbon, Carbon-Glass Beads, and the Crystallization of Carbon Nanotubes," *Science*, vol. 307, pp. 907–910, 2005. 142
- [140] Y. Li, X. Zhong, and A. H. Windle, "Structural Changes of Carbon Nanotubes in Their Macroscopic Films and Fibers by Electric Sparking Processing," *Carbon*, vol. 46, pp. 1751–1756, 2008. 142
- [141] R. J. Mora, J. J. Vilatela, and A. H. Windle, "Properties of Composites of Carbon Nanotubes Fibres," *Compos. Sci. Technol.*, vol. in press, 2009. 158
- [142] R. J. Mora, "Manufacturing of High Strength Carbon Nanotube Fibre Composites," *MPhil Thesis, Department of Materials Science and Metallurgy, University of Cambridge*, 2007. 158
- [143] J. N. Coleman, W. J. Blau, A. B. Dalton, E. Muoz, S. Collins, B. G. Kim, J. Razal, M. Selvidge, G. Viegro, and R. H. Baughman., "Improving the Mechanical Properties of Single-Walled Carbon Nanotube Sheets by Intercalation of Polymeric Adhesives," *App. Phys. Lett.*, vol. 82, p. 1682, 2003. 162
- [144] Z. Wang, Z. Liang, B. Wang, C. Zhang, and L. Kramer, "Processing and Property Investigation of Single-Walled Carbon Nanotube (SWNT) Bucky-paper/Epoxy Resin Matrix Nanocomposites," *Composites: Part A*, vol. 35, p. 1225, 2004. 162

REFERENCES

- [145] D. T. Y.-K. Kwon, S. Berber, “Thermal Contraction of Carbon Fullerenes and Nanotubes,” *Phys. Rev. Lett.*, vol. 92, p. 015901, 2004. 164, 165, 166
- [146] N. Parkash, “Determination of Coefficient of Thermal Expansion of Single-Walled Carbon Nantoubes Using Molecular Dynamics Simulation,” *M. Sc. Thesis, Florida State University*, 2005. 164
- [147] Y. H. K. C. H. H. Jiang, B. Liu, “Thermal expansion of single wall Carbon nanotube,” *J. Eng.Mater. Technol.*, vol. 126, p. 265, 2004. 164
- [148] Y. Yosida., “High-temperature Shrinkage of Single-Walled Carbon Nanotube Bundles up to 1600 K,” *J. App. Phys.*, vol. 87, pp. 3338–334, 2000. 164
- [149] *Guide to Plastics*. New York: Mc Graw-Hill, 1979. 165, 166, 169
- [150] “Torayca T300 Carbon Fiber Data Sheet,” *Torayca Carbon Fibers America Inc.* 165, 166
- [151] W. C. Morgan, “Thermal Expansion Coefficients of Graphite Crystals,” *Carbon*, vol. 10, pp. 73–79, 1972. 165, 166
- [152] E. S. Choi, J. S. Brooks, D. L. Eaton, M. S. Al-Haik, M. Y. Hussaini, H. Garmestani, D. Li, and K. J. Dahmen, “Enhancement of Thermal and Electrical Properties of Carbon Nanotube Polymer Composites by Magnetic Field Processing,” *Appl. Phys.*, vol. 94, pp. 6034–6039, 2003. 169