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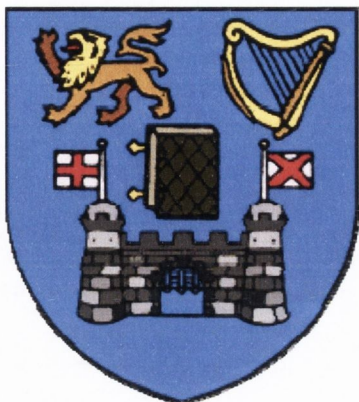
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# **Purification and Electrical Characterisation of Nanotube and Nanowire - Polymer Composites**

By

Robert Murphy

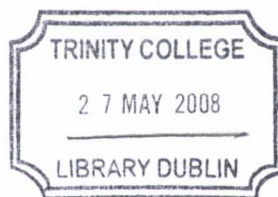
A thesis submitted for the degree of

Doctor of Philosophy  
in the  
University of Dublin

Department of Physics  
Trinity College Dublin

May 2006





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I declare that the work in this Thesis has not been previously submitted as an exercise for a degree to this or any other university.

The work described herein is entirely my own, except for the assistance mentioned in the acknowledgements and the collaborative work mentioned in the list of publications.

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A handwritten signature in blue ink that reads "Robert Murphy". The script is cursive and fluid, with the first letters of each word being capitalized and prominent.

Robert Murphy

May 2006

“Errors using inadequate data are much less than those using no data at all”

Charles Babbage

1791 – 1871

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I want to dedicate a very big and very special thank you to my family. To my parents for nurturing a desire to learn from day one and for their unconditional, priceless support and patience. To my brothers and sisters and extended family, a big thank you for everything as well.

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## Abstract

The yield and purity of multiwalled carbon nanotube (MWNT) soot was maximised by control of production parameters. The optimal production parameters were found to be  $J = 190 \text{ A/cm}^2$  and  $P = 500 \text{ Torr}$  achieving a yield of up to 24mg/min with an approximate MWNT purity of 55% as measured by electron spin resonance (ESR).

We have described a one step, high yield, non-destructive purification and processing method for MWNT-containing soot using a conjugated organic polymer host, PmPV. This host selectively suspends nanotubes relative to impurities. The fraction of available MWNTs suspended can be measured using electron spin resonance. This rises with increasing polymer mass before saturating at approximately 50% by mass for a soot to polymer mass ratio of 1:5. Thermogravimetric analysis can then be used to calculate the mass of nanotubes suspended and hence the purity of the original soot. Furthermore, this allows the calculation of numerical constants relating the ESR signal intensity to the nanotube mass allowing the routine calculation of nanotube content. Finally the host polymer was removed by filtration giving 91% pure nanotube material. In this case the yield of 17% pristine nanotubes were reclaimed from the soot. Full optimisation of this process could lead to yields of up to 40%.

It was also demonstrated that a second conjugated polymer host, PFO, can also suspend MWNTs effectively with an optimum settling time of 96 hrs. However, graphitic nanoparticles also remain suspended which can be attributed to the structure of the polymer itself.

A series of composite materials were produced using the insulating polymer PVP and MWNTs. Both DC and AC conductivities were measured at a range of temperatures and electric-field values. At room temperature, the zero-field values were observed to follow a percolation power law with percolation threshold  $p_c = 1.76$ , critical exponent  $t = 7.4 \times 10^{-4}$  and conductivity prefactor of  $\sigma_0 = 21 \text{ S/m}$ . A percolation model based upon the concept of *excluded volume* can relate  $p_c$  and  $t$  to the MWNT aspect-ratio. The measured

value for  $p_c$  suggests that a distribution of MWNT aspect-ratios exists and that the longest nanotubes dominate the overall electrical connectivity. The measured critical exponent  $t$  agrees with the predicted value using an average MWNT aspect-ratio of a  $\sim 117$ . Finally, the measured  $\sigma_0$  can be attributed to a thin coating of amorphous polymer surrounding each MWNT.

Temperature dependence of the conductivity data rules out any thermally activated conduction mechanism such as variable range hopping, instead suggesting a tunnelling mechanism. Fluctuation induced tunnelling as a possible conduction mechanism cannot be ruled out through temperature dependence results but appears to break down when electric field dependence is analysed. The exact nature of the tunnelling cannot be fully described using the available data.

A series of composite materials were produced using the insulating polymer PMMA and novel inorganic nanowires. We have shown that  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  nanowires are highly conducting and form a percolation network with very low threshold of  $p_c = 1.3 \times 10^{-5}$ . This appears to be the lowest threshold measured to date for any 1-d conductor/insulator composite system. This result can be explained by the debundling of the nanowires during sample fabrication at low nanowire concentrations. In addition the data shows the importance of the longer nanowires in the sample. The highest measured conductivity was  $4 \times 10^{-3} \text{ S/m}$  which is large enough for anti-static applications.



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## **Appendix A – Publication List**



# Chapter 1

## 1.1 Scientific Background

The 20<sup>th</sup> century saw an explosion in the interdisciplinary field of ‘materials science’ producing a wide variety of interesting materials. Prior to this, the traditional materials that served as the basic building blocks for millennia remained the same. These consisted mainly of naturally occurring elements or compounds such as metals, wood, stone, minerals, glass and natural fibres. In the last century, many new and interesting materials were discovered due to a number of reasons. These include the appearance of large-scale industry established during the industrial revolution; the development of chemistry as a formal science; the two world wars and the twentieth-century ‘space race’. This list is by no means exhaustive but the latter two examples demanded novel materials and the former two examples provided part of the solutions. Strong yet lightweight materials such as carbon-fibre reinforced epoxy composites are one such example. The National Aeronautics and Space Administration (NASA) sponsored many research programs in this field to produce materials for aerospace to compete with aluminium [Lubin]. It has taken over two decades of laboratory based research but these materials are now being incorporated commercially into aeroplanes and spacecraft.

Another important point to note is that while certain materials had been known to exist for many years, their properties were not fully understood. This was due to either the unavailability of the pristine material itself or because of the absence of a comprehensive scientific theory, such as Quantum Mechanics. This is particularly true in the case of semiconductors. A century ago, our knowledge of germanium and silicon was poor even though they had been identified in 1871 and 1787 respectively. Through a combination of understanding the fundamental properties of these materials and advances in material production and purification methods, these factors ultimately led to the invention of the transistor in 1948 [Bardeen]. This single invention has changed the face of the planet. This demonstrates that both an intimate material knowledge and also the availability of high quality materials are required in tandem. Without one or the other, the transistor may never have been invented!

A relatively new class of interesting materials are conjugated polymers which were discovered in 1977 by Heeger, MacDiarmid and Shirakawa [Shirakawa]. Traditional polymers are insulators but this discovery opened up a massive field of research into conductive polymers. Polymers could no longer be classified as passive materials and these materials can be used for applications such as organic light emitting diodes (OLEDs) and solar cells. Potentially, these can be produced at a fraction of the cost of their inorganic counterparts with the additional properties of flexibility and robustness. This discovery was rewarded with the Nobel Prize in Chemistry in 2000.

Four years earlier, this prize was awarded to Kroto, Curl and Smalley for their discovery of the Buckminsterfullerene molecule,  $C_{60}$  in 1985 [Kroto]. This was only the third stable form of carbon ever to be discovered after diamond and graphite. This paved the way to the discovery of the fourth allotrope of carbon in the form of nanotubes in 1991 [Iijima]. This exciting new material has been predicted to have many interesting and potentially unique properties. Theoretically, this is the only known material that is both strong enough and light enough to support its own weight in providing a cable hundreds of kilometres long into space for a 'space elevator'.

Electronically, a nanotube can exist either as a semiconductor or as a metal purely due to the wrapping of the carbon atoms. These molecular wires have been proposed as a solution to Moore's Law for integrated circuits [Moore]. This predicts the limits of current integrated circuit technology at around 2015 – 2020. In theory, an integrated circuit could be comprised of transistors made from semiconducting nanotubes which are connected using metallic nanotubes. These could also act as heat transfer channels.

There are however many great limitations to ever realising these futuristic ideas, none the least being nanotube purification and processability. In general, the current production methods for nanotubes also produce unwanted materials such as metal catalyst particles and/or other forms of extraneous carbon. Nanotube transistors [Tans] and ballistic conductors [Frank] have been demonstrated for individual nanotubes. These approaches,



while useful for understanding the fundamental properties of nanotubes, are not practical or useful for producing circuits containing  $10^9$  integrated devices.

A more realistic approach to addressing the issues of purification and processability is to combine nanotubes with a polymer. Through careful selection of the polymer host, purification of the as-produced nanotube material is possible. Furthermore, these composite materials can easily be handled and processed using standard techniques. By varying the nanotube dilution in the host, various effects can be observed from bulk properties to almost individual nanotube networks. The main focus of the work in this thesis is nanotube purification using complementary polymers along with electrical characterisation of novel composite materials. These include both carbon nanotube-polymer and inorganic nanowire-polymer systems.

## **1.2 Thesis Outline**

The main materials studied in this thesis are first introduced in Chapter 2: carbon nanotubes and polymers. The properties of carbon nanotubes are described in great detail and an overview of nanotube-polymer composite materials is presented. Finally, the theory of charge transport in composite systems is introduced with an emphasis on carbon nanotube-polymer composites.

The focus of Chapter 3 is on sample preparation and experimental methods. Production and purification of carbon nanotubes are discussed. The formation of carbon nanotube-polymer composite materials (which are the main interest of this work) is then outlined. Finally, the various characterisation techniques used in this thesis are presented.

Chapter 4 contains the first set of experimental results consisting mainly of electron spin resonance measurements of nanotube soot and nanotube-polymer composites. This technique allows us to monitor and quantify the nanotube content in various soots and therefore to optimise the production method. Measurements on composite materials then allow for a non-destructive purification scheme for multi-walled nanotubes. Finally, the relative merits of two conjugated polymers in purifying nanotubes are then compared.

A set of novel nanotube-polymer composites was produced and Chapter 5 deals with the electrical properties of these materials. The nature of nanotube network formation as a function of nanotube volume fraction is described by analysing the DC and AC conductivities. Temperature and electric-field dependence of these conductivities are then measured in order to attempt to determine the underlying charge transport mechanism. Various possible candidates are studied and these are discussed in detail in the second half of this chapter.

The third and final experimental chapter, Chapter 6, looks at the room temperature DC and AC properties of a very novel inorganic nanowire-polymer composite. These nanowires are metallic and of large aspect-ratio. This leads to composite materials with huge increases in conductivity at very low nanowire volume fractions. Debundling of nanowires in the polymer leads to the lowest recorded percolation threshold to date for a 1-d conductor/insulator system.

The main important results achieved in this body of work are then summarised in Chapter 7. A brief debate on possible future work leading from these results is then discussed.

## References

- Bardeen, J. and Brattain, W. H., *Physical Review*, **74**, 230-231, (1948)
- Frank, S., Poncharal, P., Wang, Z. L., *et al. Science*, **280**, 1744-1746, (1998)
- Iijima, S. *Nature*, **354**, 56-58, (1991)
- Kroto, H. W., Heath, J. R., O' Brien, S. C., *et al. Nature*, **318**, 162-163, (1985)
- Lubin, G, *Handbook of Composites* (Von Nostrand Reinhold, New York, 1982)
- Moore, G. *Electronics*, **38**, 114-117, (1965)
- Shirakawa, H, Louis, E. J., MacDiarmid, A. D., *et al. Journal of the Chemical Society – Chemical Communications*, **16**, 578-580, (1977)
- Tans, S. J., Verschueren, A. R. M. and Dekker, C. *Nature*, **393**, 49-52, (1998)



## Chapter 2

### 2.1 Introduction

This chapter will introduce the important properties of the materials used in the main body of work, namely carbon nanotubes and polymers. The physical and chemical properties of carbon nanotubes will be presented. In addition, a description of the polymer matrices used in this study will be given. A brief overview of carbon nanotube-polymer composites and their main applications is then provided. Finally, a specific overview of these composite materials for electrical applications will be presented along with a theoretical background into charge transport in nanotube-polymer composite materials.

### 2.2 Carbon Nanotubes

#### *Physical Structure of Carbon Nanotubes*

Carbon is one of the most abundant elements in nature and is considered unique amongst the elements due to the wide variety of diverse structures and forms that it can assume. This is partly due to the fact that three possible hybridisations occur:  $sp$ ,  $sp^2$  and  $sp^3$ ; and it is the only group IV element that can form stable double-bonds. Silicon and germanium, for example, exhibit primarily  $sp^3$  hybridisation.

For centuries, the only two stable allotropes of carbon known to exist were diamond and graphite. In diamond, carbon atoms exhibit  $sp^3$  hybridisation, in which four bonds are directed towards the corners of a regular tetrahedron. This results in an extended, rigid, three-dimensional network with a bond length of 1.56 Å between  $sp^3$  carbon atoms. For graphite,  $sp^2$  hybridisation is present within three carbon atoms, evenly distributed in the x-y plane ( $120^\circ$ ) forming planar graphene sheets with a carbon-carbon (C-C)  $sp^2$  bond length of  $a_{CC} = 1.42$  Å. Overlap of the unhybridised  $p_z$  orbitals results in the weak van der Waals interaction between graphene layers producing the extended graphite with interplanar spacing of 3.35 Å. Furthermore, the electrons in the  $p_z$  orbital form a cloud and are no longer localised to any particular, individual carbon atom. This explains why

graphite can conduct electricity. Diamond, on the contrary, behaves as an electrical insulator because all of the electrons are localised within the  $sp^3$  bonds.

In 1985 however, Kroto, Curl, and Smalley [Kroto] discovered the ‘football’ shaped molecule  $C_{60}$ , the first new member of the fullerene family. This spherical cage consists of twenty hexagons of carbon and importantly, twelve pentagons (as required by Euler’s Law), which provide the necessary curvature of the structure to close the sphere. The coordination at each carbon atom in  $C_{60}$  is not planar, as is the case in graphite, but is slightly pyramidal with some  $sp^3$  character present in essentially  $sp^2$  bonded carbon atoms. Other fullerenes of different radii and shape were subsequently discovered, such as  $C_{70}$  and  $C_{80}$ .

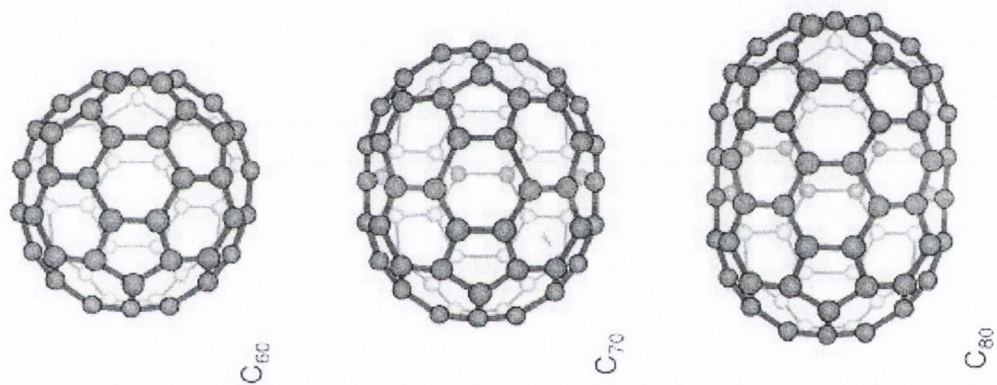


Figure 2.1: The  $C_{60}$  molecule and other members of the fullerene family.

Figure 2.1 shows that one can form  $C_{70}$  by inserting ten carbon atoms into a  $C_{60}$  molecule. Repeating this process produces the  $C_{80}$  fullerene and one can imagine repeating this process a large number of times, to produce a capped cylinder with a very large length-to-diameter aspect ratio.

An explosion of research into this new family of carbon nanostructures ultimately led to the very important discovery of multi-walled carbon nanotubes by Iijima at the NEC Laboratory in Japan in 1991 [Iijima<sup>1</sup>]. Two years later Iijima also discovered single-walled carbon nanotubes [Iijima<sup>2</sup>]. Carbon nanotubes have been predicted to have very

interesting electronic and mechanical properties and much experimental work has been done in an attempt to verify many of these predictions.

### *Structure of Carbon Nanotubes*

An ideal carbon nanotube can be considered as a single layer of a graphite sheet (graphene) rolled up to form a seamless cylinder which is closed at each end by the introduction of pentagons into the hexagonal networks. This structure is called a single-walled carbon nanotube (SWNT) and usually has a diameter in the range 0.7 – 2.0 nm. A multi-walled carbon nanotube (MWNT) is regarded as the composition of concentric SWNTs with an inter-shell spacing of 0.34 nm, a value that is slightly greater than the basal inter-plane separation of bulk graphite (0.335 nm). Iijima attributed this difference to a combination of the tubule curvature and van der Waals interactions between successive cylinders [Iijima<sup>1</sup>].

It is possible to construct many different SWNTs depending on the rolling orientation of the graphene hexagonal network. This property is known as the chirality (or helicity) of the nanotube. There are two special types of nanotube, known as ‘armchair’ and ‘zigzag’, which are achiral. In these configurations, two C-C bonds on opposite sides of each hexagon are perpendicular and parallel, respectively, to the nanotube axis. All other conformations, where the C-C bonds lie at angle to the tube axis are known as chiral structures.

Mathematically, the chirality of a nanotube can be defined in terms of a chiral vector,  $\vec{C}_h = n\hat{a}_1 + m\hat{a}_2$ , where  $\hat{a}_1$  and  $\hat{a}_2$  are the unit vectors in the two dimensional hexagonal lattice, and  $n$  and  $m$  are integers with  $0 \leq m \leq n$ . Figure 2.2(a) displays the specific chiral vector (OA) for the SWNT described by the parameters  $(n,m) = (4,2)$ . This particular nanotube can be constructed by rolling the graphene sheet so that the end points O and A coincide. The chiral vector determines the circumference (and hence diameter,  $d_t$ ) of a SWNT and in the general case, the lattice site  $(n,m)$  is superimposed with the origin  $(0,0)$ . Another important parameter is the chiral angle  $\theta$ , which is defined as the angle between  $\vec{C}_h$  and  $\hat{a}_1$ . The translation vector  $\vec{T}$  lies perpendicular to  $\vec{C}_h$  on the unrolled lattice and



points along the nanotube axis. Each different pair  $(n,m)$  describe a unique nanotube structure and these hexagonal lattice points which define the chiral vector are shown in Figure 2.2(b).

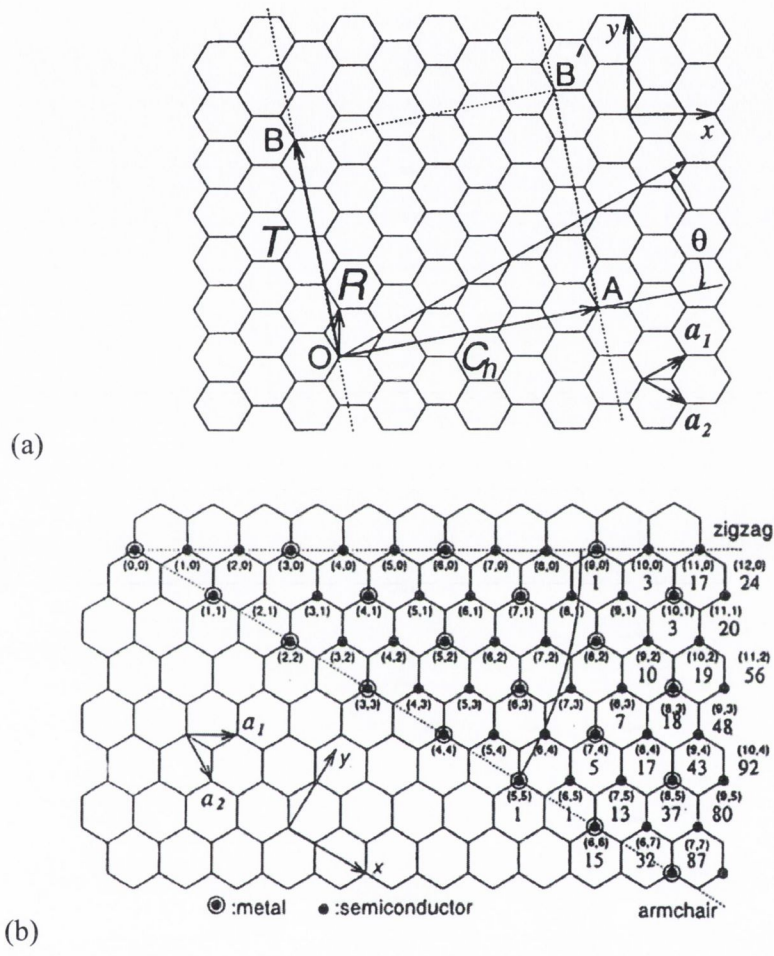


Figure 2.2: (a) The chiral vector  $\vec{C}_h$  for the  $(n,m) = (4,2)$  SWNT. (b) The 2D graphene sheet along with the  $(n,m)$  pairs that specify the chiral vector of the nanotube. The circled dots denote metallic nanotubes and the small dots represent semiconducting nanotubes.

As previously mentioned, SWNTs can be classified into three types. Armchair nanotubes are formed when  $n = m$  whereas zigzag nanotubes are formed when  $m = 0$ . All other nanotubes for which  $0 < m < n$  are called chiral. Typical examples of these three structures are illustrated in Figure 2.3.



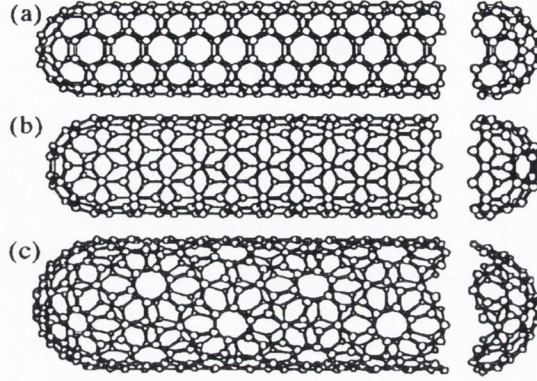


Figure 2.3: Three typical single-wall nanotube types: (a) (5,5) armchair, (b) (9,0) zigzag and (c) (10,5) chiral. Each end is capped by half of a fullerene molecule.

The diameter and the chiral angle ( $d_t, \theta$ ) also uniquely describe a particular nanotube and it can be verified that these values have the following relations with (n,m):

$$d_t = \frac{|\vec{C}_h|}{\pi} = \frac{a}{\pi} \sqrt{m^2 + n^2 + nm} \quad (2.1)$$

$$\theta = \tan^{-1} \frac{\sqrt{3}n}{2m + n} \quad (2.2)$$

where  $a = 2.46 \text{ \AA}$  is the lattice constant in the graphene sheet. Note that  $a = \sqrt{3}a_{cc}$ . Armchair nanotubes correspond to  $\theta = 30^\circ$  while zigzag nanotubes correspond to  $\theta = 0^\circ$ . All other nanotubes have chiral angles in the range  $0^\circ < \theta < 30^\circ$  as illustrated in Figure 2.2(b).

Multi-walled nanotubes (MWNTs) can be imagined as the ‘Russian doll’ extension of single-walled nanotubes. They can consist of up to 100 graphene sheets which are rolled up into concentric cylinders with an inter-shell spacing of 0.34 nm, similar to the interlayer spacing of graphite. Due to the multiple shells, multi-walled nanotubes are much stronger than single-walled nanotubes. Also, it is easier to isolate individual multi-walled nanotubes because of their size whereas single-walled nanotubes tend to aggregate in bundles.

Because of the remarkable strength and stability of the  $sp^2$  carbon-carbon bonds present in nanotubes, their current-carrying capability is outstanding. Both SWNTs and MWNTs have been observed to carry current densities of greater than  $10^9$  A/cm<sup>2</sup> before electrical breakdown by electromigration [Dekker, Wei]. These are more than 3 orders of magnitude greater than that for copper. The latter measurement was performed at a temperature of 250°C and the MWNT resistance remained constant for the lifetime of the experiment (334 hours) indicating the high stability of the device.

For a MWNT, each individual shell does not necessarily have the same chirality. There is no correlation between the concentric shells and they can be either metallic or semiconducting (depending on the (n,m) requirement (2.5) described in the next section). Although MWNTs can withstand remarkable current densities, eventually however at a certain high threshold power, the outermost shell can be destroyed through rapid oxidation in air [Collins<sup>1</sup>]. Collins et al [Collins<sup>2</sup>] consecutively destroyed 14 shells of a MWNT electrically and observed a random ordering of metallic and semiconducting shells by monitoring the conductance as a function of an applied gate bias.

Carbon-carbon covalent bonds are among the strongest bonds in nature with the in-plane C-C bond in graphite having an elastic constant of 1.060 TPa [Dresselhaus]. A nanotube which is a uniform structure based on a perfect arrangement of these bonds is expected to display very high strength along its axis. Theoretical and experimental studies have predicted the tensile strength of nanotubes to be up to 600GPa which is two orders of magnitude higher than that of current high-strength carbon fibres [Breuer]. The Young's modulus for an individual SWNT has been calculated to be 640GPa [Gao], which is consistent with experimental measurements [Yu<sup>1</sup>]. The density of SWNTs is approximately 1.3 g/cm<sup>3</sup> [Hadjiev] compared to a value of 1.8-1.9 g/cm<sup>3</sup> for commercial carbon fibres. This is an important factor in the production of light-weight materials for advanced applications such as in the aerospace industry. Composite materials fabricated from nanotubes incorporated into a polymer matrix for mechanical purposes will be discussed in section 2.4.



The thermal conductivity of a carbon nanotube is highly anisotropic, diamond-like along the length of the tube and insulating in the transverse direction [Breuer]. This is closely connected to the high strength of the atomic bonds in nanotubes along which vibrational energy can efficiently travel. Theory predicts a room-temperature thermal conductivity of  $6000 \text{ Wm}^{-1}\text{K}^{-1}$  for an isolated SWNT whereas experimental values of approximately  $200 \text{ Wm}^{-1}\text{K}^{-1}$  have been measured [Biercuk]. This property of nanotubes could be particularly useful for the extraction of heat in nanoscale electronic devices.

The most interesting property of carbon nanotubes however is the electronic structure because they can be either metallic or semiconducting purely due to their chirality. This characteristic will be discussed in further detail in the next section.

### *Electronic Properties of Carbon Nanotubes*

Even though the chemical composition of all perfect carbon nanotubes is fundamentally the same, the electronic structure of any particular SWNT can be either metallic or semiconducting depending on its diameter and chirality. This can be explained by looking at the band structure of a SWNT whose electronic properties are strongly related to the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The analogue for a solid-state material is the behaviour of the energy dispersion in the neighbourhood of the Fermi level.

Imagine the construction of a SWNT by taking individual  $sp^2$  hybridised carbon atoms and assembling them together one at a time. Initially, when there are only two atoms present, the discrete HOMO and LUMO states are the  $\pi$  and  $\pi^*$  molecular orbitals, produced by the overlap of the  $p_z$  atomic orbitals. As more atoms are added, these states split due to the Pauli Exclusion Principle. This ultimately leads to formation of HOMO and LUMO bands because of the extensive number of carbon atoms in a SWNT. These are the  $\pi$  and  $\pi^*$  bands, respectively, and are separated by the Fermi level. Thus a nanotube's electronic behaviour is essentially determined by the  $p_z$  orbitals. The  $\sigma$  and  $\sigma^*$  bands produced by the splitting of the  $sp^2$  molecular orbitals lie far above and below the



Fermi level and can be neglected in determining the nanotube's electronic behaviour. Similarly, mixing of the  $\sigma$  and  $\pi$  orbitals can be ignored.

The electronic band structure of a SWNT can be obtained from that of two-dimensional graphite (graphene). A tight-binding model which considers only nearest-neighbour interactions (and ignores those between planes) gives the 2-D energy dispersion in the vicinity of the Fermi level as [Wallace]:

$$E_{2D}(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)} \quad (2.3)$$

where  $\pm$  correspond to the unoccupied  $\pi^*$  band and fully occupied  $\pi$  band respectively;  $\gamma_0$  is the nearest-neighbour overlap integral and  $a = 2.46 \text{ \AA}$  is the lattice constant in the graphene sheet. A three-dimensional plot of the dispersion relations of these bands is shown in Figure 2.4(a) [Avouris]. The first Brillouin zone of graphene is hexagonal and this is also illustrated in Figure 2.4(a). The two bands are degenerate only at the six K points (the corners of the Brillouin zone) through which the Fermi energy passes and hence graphene is a zero-gap semiconductor or semimetal.

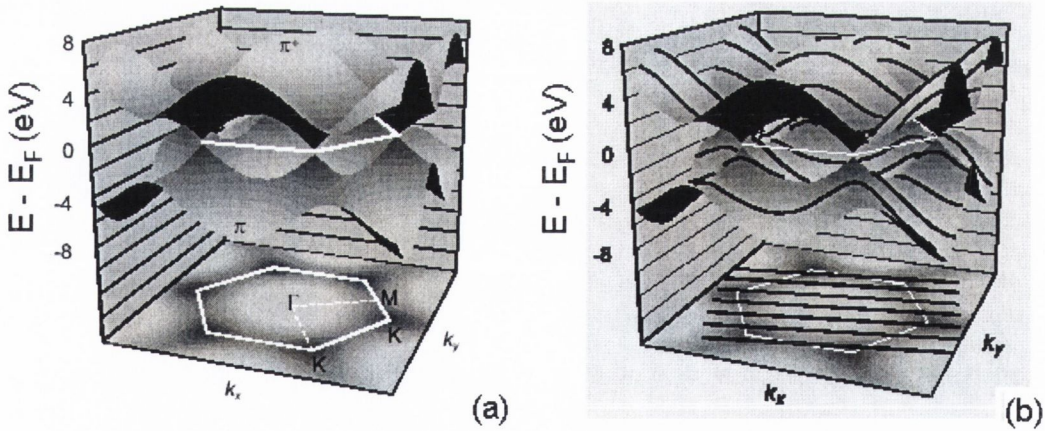


Figure 2.4: (a) The band structure of graphene in the neighbourhood of the Fermi level. The valence ( $\pi$ ) and conduction ( $\pi^*$ ) bands meet at the six corners (K points) of the first Brillouin zone. (b) The black lines represent the allowed  $k$ -states for a chiral SWNT as determined by the boundary condition (2.4).

Due to the small diameter of a SWNT the number of allowed electronic states in the circumferential direction is discrete, whereas the allowed wave-vectors along the nanotube axis form a continuum since the nanotube length is essentially infinite. Therefore, the band structure of a SWNT can be derived from that for graphene with the incorporation of the Born-Von Karmen periodic boundary condition required for quantisation of the wave-vectors,  $\vec{k}$ , in the circumferential direction:

$$\vec{k} \cdot \vec{C}_h = 2\pi j \quad (2.4)$$

where  $j$  is an integer and  $\vec{C}_h$  is the chiral vector.

This confinement condition means that the allowed states of a nanotube lie on parallel lines in the first Brillouin zone of graphene that are separated by a spacing of  $2\pi/|\vec{C}_h|$ .

Figure 2.4(b) displays sets of these lines for a chiral nanotube. The 1-D energy dispersion for the SWNT is obtained by restricting Eqn (2.3) to these quantised  $k$ -states. It can be seen from Figure 2.4 that there is a gap between the  $\pi$  and  $\pi^*$  bands of graphene everywhere except at the six K points of the Brillouin zone. Therefore a SWNT will have a bandgap unless one of these K points intersects with an allowed  $k$ -state line, in which case it will be metallic. The general criterion for a SWNT to be metallic is given by:

$$(n - m) \bmod 3 = 0 \quad (2.5)$$

Thus it is apparent that all armchair nanotubes ( $n = m$ ) are truly metallic whereas this is true for only one third of zigzag nanotubes ( $m = 0$ ). The 1-D dispersion relations for an armchair (5,5) nanotube, a zigzag (9,0) nanotube and a zigzag (10,0) nanotube are displayed in Figure 2.5 [Saito<sup>1</sup>].

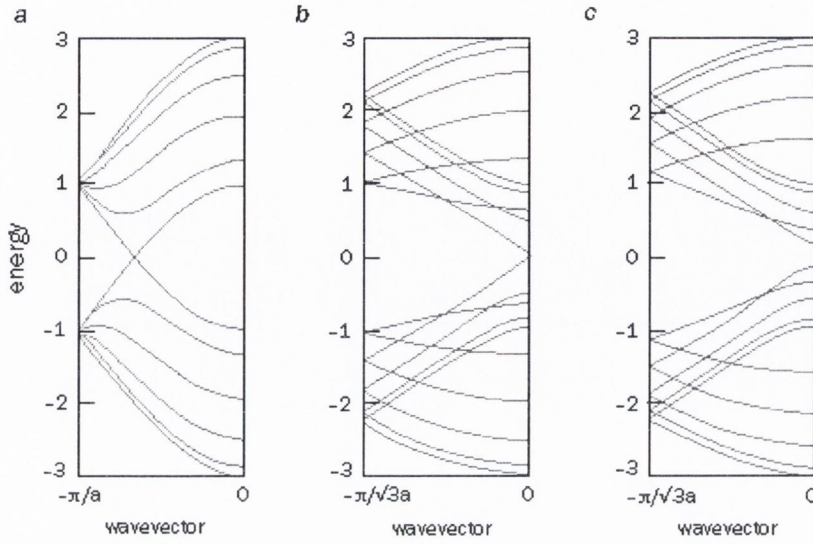


Figure 2.5: Dispersion relations for three nanotubes: (a) armchair (5,5) (b) zigzag (9,0) and (c) zigzag (10,0). The first two nanotubes are metallic whereas the third nanotube is semiconducting as governed by condition (2.5). Energy is in units of overlap integral  $\gamma_0$ .

By combining the dispersion relation with the number of available electronic states per wavevector ( $dN/dk$ ), the density of states (DOS) for any nanotube can be calculated. Figure 2.6 shows the DOS for both a semiconducting (10,0) and a metallic (9,0) zigzag SWNT [Saito<sup>2</sup>]. For each nanotube, the DOS contains sharp peaks known as van Hove singularities. It has been shown that SWNTs can be induced to fluoresce via the de-excitation of promoted electrons across the gap between singularities [Bachilo].



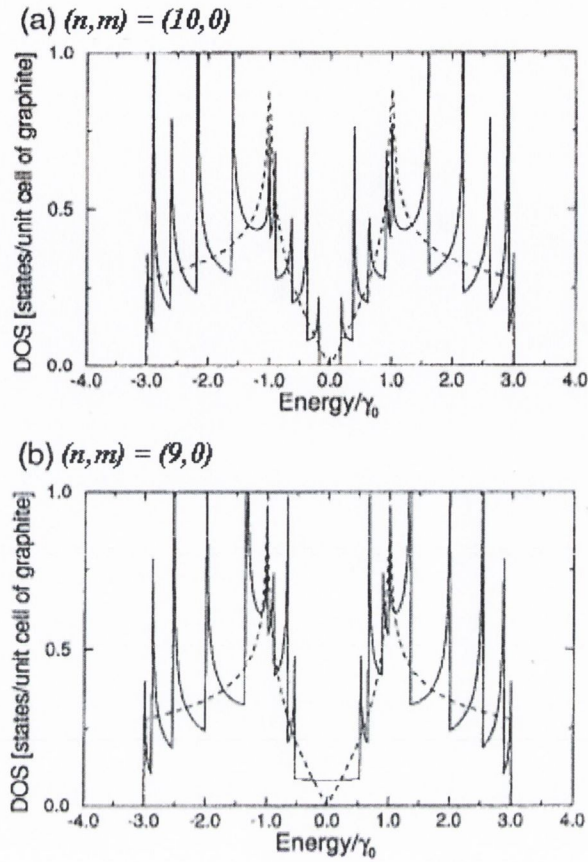


Figure 2.6: Electronic density of states for two zigzag SWNTs: (a) semiconducting  $(10,0)$  and (b) metallic  $(9,0)$  nanotubes. The corresponding DOS for semimetallic graphene is also plotted (dashed lines) for comparison.

For all metallic nanotubes, irrespective of their diameter and chirality, it can be shown that the density of states at the Fermi level, per unit length along the nanotube axis is a constant value given by [Saito<sup>1</sup>]:

$$N(E_F) = \frac{8}{\sqrt{3}\pi a \gamma_0} \quad (2.6)$$

The overlap energy has been predicted to be  $\gamma_0 = 2.5\text{eV}$  for a single graphene sheet [Dresselhaus, Mintmire]. Experimentally, a value of  $2.7\text{eV}$  has been estimated from scanning tunnelling spectroscopy DOS data for a SWNT [Wildoer].

The band-gap  $E_g$  of a semiconducting nanotube has been predicted to vary inversely with its diameter  $d_t$  and can be written as [White]:

$$E_g = \frac{\gamma_0 a}{\sqrt{3} d_t} \quad (2.7)$$

independent of chirality. The bandgap of semiconducting SWNTs can be varied continuously from 0eV to 1eV through diameter variation. Thermal energy at room temperature exceeds the band-gap for nanotube diameters  $\geq 14\text{nm}$ . Therefore, all MWNTs with  $d_t \geq 14\text{nm}$  are either metallic or semi-metallic. In the limit where the diameter becomes infinite we simply have a zero band-gap semiconductor: graphene.

One of the most important electrical properties of metallic nanotubes is the reduced probability for carrier scattering as a consequence of the limited number of allowed electronic states [White]. This leads to ballistic transport over distances of greater than  $1\text{ }\mu\text{m}$  [Frank]. Effectively the electrons encounter no resistance and dissipate no energy in the conductor. Room temperature conductivity values of  $3 \times 10^6\text{ S/m}$  have been measured for ropes of predominantly metallic (10,10) SWNTs (as determined using x-ray diffraction and transmission electron microscopy) [Thess, Fischer]. This value is twenty times smaller than that for silver indicating the true metallic behaviour of nanotubes. In studies of MWNTs with a metallic outer shell that are bonded to metal electrodes, it was concluded that the electrical transport at low energies is dominated by outer-shell conduction [Schoenenberger].

### ***Chemical Properties of Carbon Nanotubes***

In order to fully exploit the unique properties of nanotubes, it is necessary to be able to process and handle these materials on a macroscopic scale. Carbon nanotubes in their unmodified, pure form are highly unreactive due to the seamless arrangement of hexagonal rings without any dangling bonds. This makes them insoluble in all common solvents. This is a major barrier for further processing of raw nanotube soot and two main approaches have been taken to remedy this. These involve (1) covalent and (2) non-covalent interactions between nanotubes and various chemical species.

### ***Covalent Functionalisation***

Carbon nanotubes are not highly reactive but as they are subject to the rules of carbon chemistry, this means they can be covalently functionalised. Covalent modifications of nanotube tips and sidewalls include oxidation and fluorination. As one might expect, the more highly strained caps at the end of nanotubes contain the most reactive carbon atoms [Colbert] and hence the ends of nanotubes are more susceptible to functionalisation than the side-walls. It is known that real nanotubes are not completely defect-free. Several different structures other than the main hexagonal shape are incorporated along the tubule walls such as pentagons and heptagonal rings. These sites are potentially more reactive than the more stable, majority hexagonal lattice [Chang]. Also, smaller diameter single wall nanotubes are more reactive than larger nanotubes.

Nanotubes respond to strong acids and other chemical oxidisers which can attach functional groups (e.g. hydroxyl, carboxyl and ketone groups) directly to the ends and side walls [Dillon, Yu<sup>2</sup>, Hiura]. Other species such as small molecules or polymer chains can then be covalently attached to these functional groups through traditional chemical reactions [Sun]. After various modifications, the dissolution of SWNTs in common organic solvents such as tetrahydrofuran (THF), dichloromethane and chloroform has been demonstrated [Chen<sup>1</sup>, Hamon, Riggs, Czerw]. Water-soluble functionalised nanotubes have also been produced [Riggs, Czerw]. Direct fluorination of side-walls has also been achieved between 250°C and 400°C. [Nakajima]. Fluorination at a temperature above 400°C was found to cause decomposition of the nanotube structure indicating the harsh treatment involved.

The major drawback to all of these schemes however is that covalent modification dramatically alters the structure and intrinsic properties of the nanotubes themselves. The treatments involved generally destroy the ends of the nanotubes and damage the sidewalls. This leads to severe disruption of the nanotube band structure and unique electronic properties. For example, oxidation of nanotubes introduces scattering defects which reduce the mean free path and ultimately the loss of ballistic transport.



### *Non-covalent Chemistry*

Noncovalent chemistry involves self-assembly of molecules or macromolecules about nanotubes to form thermodynamically stable structures held together by weak non-covalent interactions. These include hydrogen bonding,  $\pi$ - $\pi$  stacking, van der Waals forces, electrostatic forces and hydrophobic and hydrophilic interactions [Chen<sup>2</sup>, Star<sup>1</sup>]. This approach offers an advantage in that the nanotube's structure is not changed and hence its electronic properties are largely retained.

A commonly employed approach to the stable dispersion of nanotubes is through the use of a surfactant in an aqueous suspension [Burghard]. This method relies on the hydrophobic nature of nanotubes which allows surfactant molecules to arrange into ordered micelles around the nanotubes. These solutions while stable are not particularly useful in producing nanotube films due to the presence of the surfactant which forms large crystalline regions when dried.

Nanotubes can be combined with various polymers to form stable composite dispersions. Coupling between MWNTs and the  $\pi$ -system for conjugated polymers such as poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV) has been reported [Curran, Star<sup>1</sup>]. It was originally assumed that the polymer wraps around the nanotube but through binding energy considerations [Coleman<sup>1</sup>], this seems unlikely. Dispersion of nanotubes via polymer wrapping has been suggested in non-conjugated polymers [O'Connell, Star<sup>2</sup>]. O'Connell [O'Connell] formed stable SWNT dispersions using polyvinylpyrrolidone (PVP). It was proposed that the wrapping is thermodynamically driven and leads to a screening of the hydrophobic interaction at the nanotube-solvent interface.

Another advantage of these weakly bonded composites is that unlike covalently bonded composites [Niyogi], the process is reversible and the polymer can be removed relatively easily. Alternatively, the nanotubes can remain in the matrix allowing easy processing.

## 2.3 Polymers

Many of the interesting properties of carbon nanotubes have been extolled in the previous sections. However, as was mentioned (and will be discussed further in the next chapter), the problems of nanotube purity and processability are critical issues. Complementary materials to nanotubes that address these issues are polymers.

### *PmPV*

One conjugated polymer used in this work was poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) (PmPV) which is a derivative of the more widely studied polyphenylenevinylene (PPV). The repeat unit is shown in Figure 2.7.

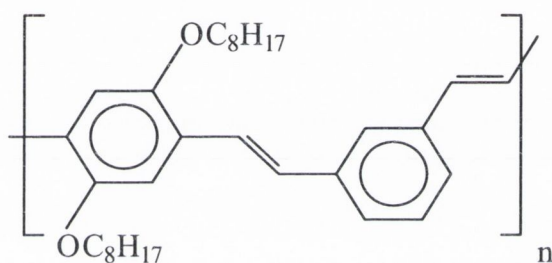


Figure 2.7: Repeat unit structure of the polymer poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene), PmPV.

PmPV is a light-emitting polymer [Davey, Drury] with a meta-linked phenyl which adds curvature to the otherwise planar para-monomer. This allows a slight helical twist to the planar backbone and this flexibility is believed to permit interactions with a nanotube over the whole length of the molecule (~5-10 repeat units) [in het Panhuis]. The polymer was synthesised in our laboratory in Trinity College and a detailed description of the production is presented in Chapter 3.

### *PFO*

Another conjugated polymer poly(9,9-di-*n*-octylfluorenyl-2,7'-diyl) (PFO) as shown in Figure 2.8 was obtained commercially from the American Dye Source, Inc. (product code ADS129BE).

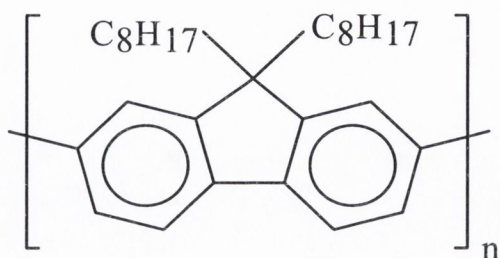


Figure 2.8: Repeat unit structure of the polymer poly(9,9-di-n-octylfluorenyl-2,7'-diyl), PFO.

PFO is a blue light-emitting polymer with a rigid backbone and octyl side chains that can facilitate interactions with nanotubes.

### PVP

A third polymer used to form composites was polyvinylpyrrolidone K25 (PVP) as shown in Figure 2.9. This was obtained commercially from Sigma-Aldrich (product code 81400 Fluka).

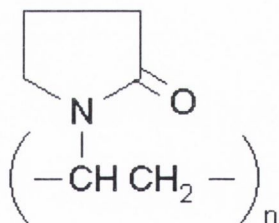


Figure 2.9: Repeat unit structure of the polymer polyvinylpyrrolidone, PVP.

PVP is soluble in water and other polar solvents. When dry it is a light flaky white powder, which readily absorbs up to 18% of its weight in atmospheric water. Therefore before usage it must be dried in an oven. Industrially it is used for a variety of applications including coatings for photo-quality ink-jet papers and transparencies, as well as in inks for inkjet printers. This is due to the fact that it binds to polar molecules



exceptionally well. PVP is completely amorphous and its glass transition temperature is approximately  $T_g = 168^\circ\text{C}$ .

## **2.4 Carbon Nanotube - Polymer Composite Materials**

Carbon nanotubes have attracted much interest since their discovery in 1991. Much of the early research focused on the intrinsic physics and chemistry of these materials without much consideration for large-scale applications. Due to the outstanding and interesting characteristics that were discovered in these early works, many diverse potential applications have been proposed and investigated [Baughmann]. These include mechanical reinforcement of materials [Cadek<sup>1</sup>], biological and chemical sensing [Wong], field emission [Teo], transistors [Tans<sup>1</sup>] and supercapacitors [An] to name a few. In order to realise their potential, a number of problems with nanotubes need to be addressed.

First, the issue of nanotube purity is a huge barrier to large-scale applications. This will be discussed in greater detail in section 3.2. Another issue is the production cost of nanotubes. Currently, commercial nanotubes cost \$375/g for soot containing up to 35% impurities and \$2000/g for oxidative-purified soot containing up to 5% impurities (Carbon Nanotechnologies Incorporated). One would expect these costs to decrease as applications are found and nanotubes are produced on a larger scale. A third problem with nanotubes is their utility. As-produced nanotube material is a soot and further processing and manipulation is required in order to produce useful devices. Pristine nanotubes have low solubility in organic solvents so direct dissolution is not possible.

A solution to some of these problems is to combine the nanotube material with a polymer to produce a composite. This approach is advantageous for a number of reasons. First, it will be shown that through the careful choice of polymer, nanotube purification is possible. This process also creates a composite material that can be easily handled and manipulated with standard solution techniques such as spin-coating. The bank of available polymers is enormous with wide and varied properties and this opens up a large field of novel materials. Polymers are generally cheap to produce and through the

addition of a small volume fraction of nanotubes, an economical composite can be produced combining favourable properties of both components. Useful examples include harnessing the mechanical strength and/or electrical conductivity of nanotubes to fabricate lightweight, mechanically tough, conductive plastics. Due to their large aspect ratios, only small quantities of nanotubes are generally needed to impart a particular property to the matrix without compromising any of the polymer's intrinsic properties (such as flexibility for example).

The critical challenges in composite production lie in uniformly dispersing the nanotubes in an appropriate matrix. Depending on the application, other questions are important such as achieving nanotube-matrix adhesion that provides effective stress transfer for mechanical reinforcement along with avoiding intra-nanotube sliding between individual nanotubes in bundles.

#### ***Carbon Nanotube - Polymer Composite Research in Trinity College***

While the study of carbon nanotubes is a relatively new field, the use of nanotubes as fillers for composite materials is even newer, being less than ten years old. One of the very first studies concerning carbon nanotube-polymer composites is that of Curran et al [Curran]. The very first stable composite solution (over 6 months stability) was produced with MWNTs dispersed in poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene (PmPV). An increase of up to eight orders of magnitude in conductivity was measured along with a fivefold increase in device lifetime for organic LEDs produced with the composite compared to the pristine polymer.

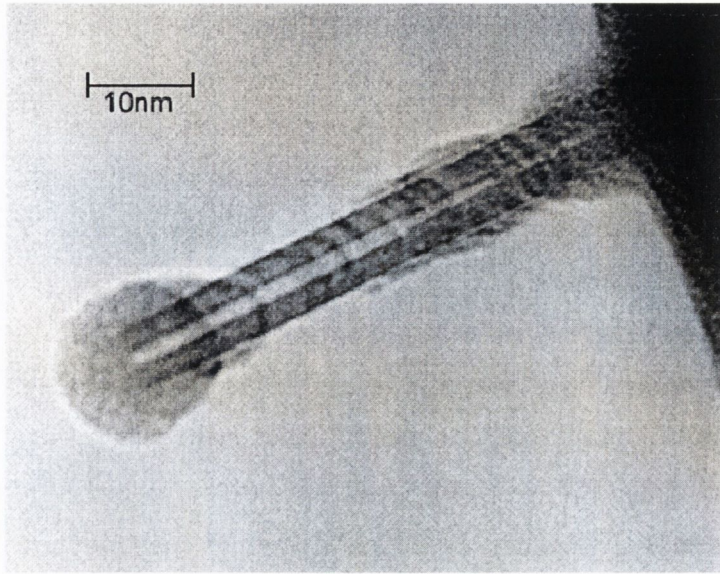
The preferential suspension of MWNTs relative to impurities in this same polymer was first reported by Coleman et al [Coleman<sup>2</sup>]. This purification effect was verified by electron spin resonance (ESR) and Raman spectroscopy. The former method is discussed in detail in chapter 4. The Raman studies involved the comparison of the peaks at  $1350\text{cm}^{-1}$  and  $1580\text{cm}^{-1}$  which are attributed to nanotubes and graphitic impurities respectively. Raman spectroscopy performed on low concentration SWNT-PmPV composites [Dalton<sup>1</sup>] also showed preferential selection of SWNTs plus diameter

selectivity. Fine features appear in the composite spectra that can be assigned to the radial breathing modes (RBM) of SWNTs (which are highly diameter dependent). The range of SWNT diameters in the soot were calculated to be  $d = 1.32 - 1.54$  nm while those that remained suspended in the polymer belonged to the narrower distribution of  $d = 1.45 - 1.54$  nm.

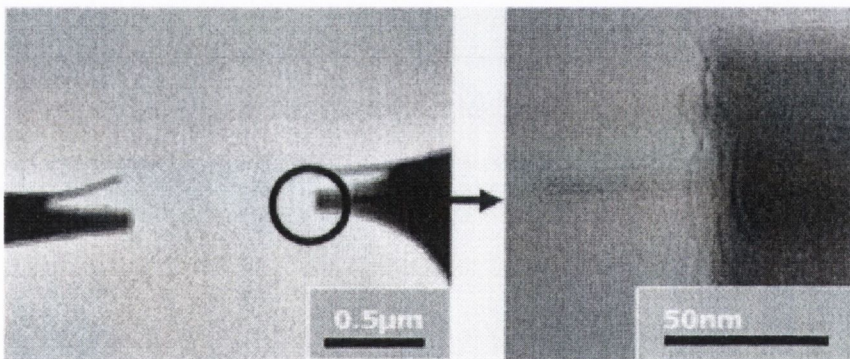
Electrical measurements involving this composite [Coleman<sup>3</sup>, Kilbride] have reported the formation of a percolating network of nanotubes. Further composites produced using the polymer polyvinyl alcohol (PVA) displayed similar behaviour and a percolation threshold as low as  $p_c = 2.9 \times 10^{-4}$  by volume was measured. Fluctuation induced tunnelling (FIT) and space charge limited conduction (SCLC) mechanisms are reported for composites with MWNT volume fractions  $p < 1\%$  and  $p > 1\%$  respectively. The SCLC behaviour was due to the presence of traps in PmPV and FIT occurred between nanotubes separated by very thin polymer layers.

These polymer layers surrounding individual MWNTs have been imaged using transmission electron microscopy for both PmPV [McCarthy] and PVA [Cadek<sup>2</sup>] as shown in Figures 2.10 and 2.11 respectively.





*Figure 2.10: TEM image of a MWNT coated with a thin layer of PmPV.*



*Figure 2.11: TEM image of a MWNT coated with a thin crystalline layer of PVA.*

These thin layers are of thicknesses  $< 5\text{nm}$ . In the case of PVA, it has been shown that the layer plays an important role in the mechanical properties of the composite. The nanotube-matrix stress transfer is enhanced by the layer [Cadek<sup>2</sup>]. Furthermore, differential scanning calorimetry (DSC) measurements [Ryan<sup>1</sup>, Ryan<sup>2</sup>] show that nanotubes act as nucleation centres for crystallinity in semi-crystalline polymers. An increase from 14% crystallinity for PVA itself to 28% was measured upon the addition of 1 wt% MWNTs. A model relating the thickness of the coating around the MWNT to the rate of increase of crystallinity with volume fraction was derived [Cadek<sup>1</sup>]. This predicts thickness values comparable to those observed by TEM.

A final result demonstrating the first generation of highly advanced carbon nanotube-polymer composites that can outperform conventional materials is that of Dalton and coworkers [Dalton<sup>2</sup>]. Using a coagulation technique, they produced a 100m long composite fibre of nanotubes embedded in PVA which is tougher than any natural or synthetic fibre. The energy required to break the fibre (toughness) at a strain of 30% was 570 Jg<sup>-1</sup>. This value is over 3 times greater than that for spider dragline silk and over 17 times greater than that for Kevlar fibre [Vollrath].

The area of composites for electrical applications was alluded to briefly. A small volume fraction of nanotubes added to polymers can drastically alter their electrical characteristics without compromising other properties. This is particularly useful in the production of lightweight, conductive plastics for use in applications for electrostatic dissipation, electromagnetic interference and flexible displays. Critical issues relating to the successful fabrication of composites for these purposes include uniform dispersion in the matrix, minimisation of the percolation threshold and maximisation of the overall composite conductivity. Insight into these questions can be gained by studying the electrical response as a function of nanotube volume fraction, temperature and electric field.

## 2.5 Carrier Transport in Composite Materials

The carrier transport mechanism in composites or other disordered media is a complicated function of a number of factors including temperature and electric field. A general expression for the conductivity of such a material can be written as:

$$\sigma(T, E) = \sigma_0 f_1(T) f_2(E) \quad (2.8)$$

where  $\sigma_0$  is an independent conductivity and  $f_i$  are unknown functions dependent on the particular system and regimes probed. The most likely candidates for conduction mechanisms that are expected in carbon nanotube – polymer composites are discussed in the following sections.



### ***Quantum Mechanical Tunnelling***

For composite systems where the conducting channels are interrupted by sufficiently thin barriers, a tunnelling process can occur. This could be either directly between the conduction bands of conducting particles (such as nanotubes) or through one or several intermediate states within the insulating bandgap. The probability of tunnelling is given by the square of the wavefunction  $|\Psi|^2$  which decays exponentially with thickness. This probability multiplied by the electron flux  $n(v_x)$  at the barrier (where  $v_x$  is the approaching electron velocity) gives the tunnelling current density and for electrons:

$$J = \int_0^{\epsilon_m} n(v_x) p(\epsilon_x) d\epsilon_x \quad (2.9)$$

where  $p(\epsilon_x)$  is the transition probability for electrons with energies  $\epsilon_x$  up to a maximum energy  $\epsilon_m$ .

The shape of the barrier is important in calculating the probability and hence current density. For non-trivial shapes the Wentzel-Kramers-Brillouin (WKB) approximation is employed which approximates an arbitrary barrier shape as a superposition of rectangular barriers. For a barrier with varying height  $V(x)$  across its thickness  $w$ , the transition probability for electrons with energies  $\epsilon_x$  can be estimated as:

$$p(\epsilon_x) = \exp \left\{ -2 \int_0^w \sqrt{\frac{2m}{\hbar^2} (V(x) - \epsilon_x)} dx \right\} \quad (2.10)$$

where  $m$  and  $\hbar = 2\pi\hbar$  are electron mass and Planck's constant respectively.

For a simple rectangular barrier of width  $w$  and height  $V_0$  (assumed to be large for pure tunnelling) it can be shown that the conductivity can be written as [Hurd]:

$$\sigma = \sigma_0 \exp \left( -\frac{\pi \chi w}{2} \right) \quad (2.11)$$

where  $\sigma_0$  is a constant and  $\chi = \sqrt{\frac{2mV_0}{\hbar^2}}$  equals the tunnelling constant. This tunnelling constant is a measure of wavefunction decay and can also be considered as an inverse tunnelling distance. In addition, it can be shown that for low voltages, this form of



conductivity also describes any arbitrarily shaped barrier when the WKB approximation is used [Simmons, Lamb].

The field-independent tunnelling current for a rectangular barrier decays exponentially with barrier width but for moderate electric fields  $E < E_0$ , the field-dependent current is given by [Celzard]:

$$j \approx j_0 \exp \left[ -\frac{\pi \chi w}{2} \left( \frac{E}{E_0} - 1 \right)^2 \right] \quad (2.12)$$

where  $E_0 = \frac{4V_0}{ew}$ .

Essentially, tunnelling is a temperature independent process because the crucial parameter is the width of the barrier. However, depending on the material and temperature scale under study, because tunnelling current is highly sensitive to barrier thickness, a small variation due to thermal expansion or contraction can play an important role in determining the overall current.

### ***Hopping Transport***

Hopping transport is a common conduction mechanism in disordered media such as amorphous semiconductors and conductor-insulator composites. The term hopping describes the phonon-assisted quantum mechanical tunnelling transfer of an electron between two localised electronic states centred at different locations in energy and space. This process differs substantially from conventional electronic band transport in solids, since localised states are not compatible with the translational symmetry of crystals.

### ***Nearest-Neighbour and Variable Range Hopping***

When the Fermi energy lies in a range of energies where states are localised in a highly disordered medium (Anderson localisation) then two conduction mechanisms are possible.

First, there can be direct excitation of an electron from a localised state at the Fermi level ( $E_F$ ) into the conduction band ( $E_C$ ) so that the electron now belongs to an extended state. This contributes to the conductivity in a way similar to that of a conduction electron in a metal. Unlike a metal however, the carrier density  $n(T)$  is generally small and quite temperature sensitive. This leads to a highly temperature dependent band transport conduction mechanism described by an Arrhenius activation law:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (2.13)$$

This form of conduction is normally predominant at high temperatures or when the activation energy  $\Delta E = E_C - E_F$  is small. This can be thought of as an expression that describes temperature dependent Ohmic conductivity with  $\sigma_0$  being a constant.

### *Mott Variable Range Hopping*

Second, thermally activated hopping conduction by electrons between localised states near the Fermi energy can occur. There can be a finite probability that an electron in a filled state below the Fermi level, upon the absorption of a phonon, can jump to an unfilled state above  $E_F$ . This probability of hopping from one state to another is the product of a number of factors including the Boltzmann factor (describing the distribution of energies) and a factor dependent on the overlap of the wavefunctions.

The wave function of a localised state decays according to  $\exp(-\alpha R)$  at a distance  $R$  from the localisation centre, where  $\alpha$  is the inverse localisation length. If the average nearest neighbour distance is  $R_{ij}$  then we can describe localisation as being very strong if  $1/\alpha \ll R_{ij}$ . In this case, overlap of wavefunctions is negligible and the most energetically favourable hop by an electron is to a state nearest in space. This is known as ‘Miller-Abrahams’ or ‘nearest-neighbour’ hopping [Miller]. In this case, a conductivity temperature dependence of the form given by Eqn (2.13) is also expected (with  $\Delta E = E_i - E_j$ )

If however the inverse localisation length is comparable to the average nearest neighbour distance ( $1/\alpha \geq R_{ij}$ ) then significant overlap of wavefunctions is to be expected and in this

instance the most energetically favourable transition need not necessarily be to the nearest empty state in space. Mott's argument is described as follows [Mott].

First, the probability of finding an electron a distance  $R$  from its initial site is proportional to the square of the wavefunction and is given by  $\exp(-2\alpha R)$ . Second, due to the electron's need for energy-conserving phonon assistance in overcoming the energy mismatch  $W$  between the final and initial state, we must multiply this by the Boltzmann factor (which determines the number of phonons of energy  $W$  available). Hence, at a given temperature, the probability  $p$  of an energy-upward transition from one state to another, separated in space and energy by  $R$  and  $W$  respectively, is proportional to the product of these two factors:

$$p \sim \exp\left(-2\alpha R - \frac{W}{k_B T}\right) \quad (2.14)$$

The essential point introduced by Mott's analysis is that there exists a trade-off between hopping distance  $R$  and mismatch energy  $W$  which implies that the nature of the most probable hops changes with temperature. For example, suppose two competing final states for an electronic transition exist with distance and energy separations  $(R_A, W_A)$  and  $(R_B, W_B)$  from the initial state. State A is closer in space ( $R_A < R_B$ ) but state B is closer in energy ( $W_B < W_A$ ). At a certain temperature, hops to A contribute to the conductivity more than hops to B due to smaller space separation. As the temperature is lowered, the hopping probability decreases for both transitions (because of the second term in Eqn (2.14)) but  $p(A)$  decreases more rapidly than  $p(B)$  because  $W_A > W_B$ . At some temperature,  $p(B)$  exceeds  $p(A)$  and it is now more energetically favourable to make the longer hop. This is because in spite of the smaller wavefunction overlap, the phonon contribution becomes appreciable and the more desirable it is for the electron to hop further in space to find a lower  $W$ .

This enhanced probability of encountering this smaller  $W$  is achieved by allowing the electron to choose among a larger selection of final state sites contained within a larger neighbourhood, namely a sphere of increased radius  $R$  surrounding the initial site. This restricts the range of available energies and  $W$  and  $R$  are related as follows:



$$W(R) = \frac{3}{4\pi R^3 N(E_F)} \quad (2.15)$$

where  $N(E_F)$  is the constant density of states at (and about) the Fermi level.

This expression can be substituted into Eqn (2.14) and the probability can be maximised with respect to  $R$  by setting  $dp/dR = 0$ , yielding the most probable hopping distance of:

$$R_{opt} \approx (\alpha N(E_F) k_B T)^{-1/4} \quad (2.16)$$

Assuming that these most probable hops dominate conductivity, by substituting this value into Eqn (2.14), an expression for the Mott 3-d variable range hopping (VRH) conductivity is given by:

$$\sigma = \sigma_0 \exp \left( - \left( \frac{T_{1/4}}{T} \right)^{1/4} \right) \quad (2.17)$$

where  $T_{1/4} \approx \frac{18\alpha^3}{k_B N(E_F)}$  and  $\sigma_0$  is dependent on  $N(E_F)$  and the average hopping distance,

and can be assumed to be temperature independent. It is easy to see that this argument can be extended to  $d$ -dimensions and in this more general case the conductivity exponent  $x = 1/4$  should be replaced by  $x = 1/(1+d)$ .

### ***Efros-Shklovskii Variable Range Hopping***

Mott derived his VRH exponent  $x = 1/4$  for a system of non-interacting carriers and for a constant density of states near the Fermi energy or a slowly varying function of energy. In disordered systems however (such as a MWNT-polymer composite) localised electrons cannot screen the Coulomb interaction as effectively as in metals. Coulomb interactions in a many-electron system deplete the density of states  $N(E)$  near the Fermi energy  $E_F$ , relative to the non-interacting case. Efros and Shklovskii [Shklovskii] argued that if Coulomb interactions are included, the ground state is stable with respect to a one-particle excitation only if  $N(E)$  has a quadratic dependence on energy  $E$  near  $E_F$ .

The Efros and Shklovskii (ES) argument may be summarised as follows. Consider the ground state of a disordered system of localised electrons. States below the Fermi energy

will be occupied, those above empty. Consider a filled state of energy  $E_i$  and an empty state of energy  $E_j$ . If there is a transition of the electron from  $i$  to  $j$  and Coulombic interactions are included, then the net energy change will be:

$$W = E_j - E_i - \frac{e^2}{4\pi\epsilon r_{ij}} \quad (2.18)$$

where  $\epsilon$  is the permittivity of the medium and  $r_{ij}$  is the spatial separation of the sites. This third term is the Coulombic potential between the negative charge added at  $j$  and the effective positive charge added at  $i$ . But for the stability of the original (ground) state we require  $W \geq 0$ . This limits the density of states at low energies. Efros and Shklovskii argue that the charges will adjust their configurations to form a ground state such that  $W = 0$  for all  $r_{ij}$ . This condition results in 3- and 2-dimensional density of states of the form:

$$\begin{aligned} N_{3D}(E) &= N_3(E - E_F)^2 \\ N_{2D}(E) &= N_2(E - E_F) \end{aligned} \quad (2.19)$$

where  $N_3$  and  $N_2$  are constant densities of states dependent on the dielectric constant of the material only. Obviously,  $N(E)$  cannot continue to rise indefinitely and it is assumed to level off when  $N(E)$  reaches that constant density of states which is obtained if Coulomb interactions are neglected. Since  $N(E)$  vanishes only at  $E_F$ , a “soft” Coulomb gap opens which is dependent only on the bulk dielectric constant. This independence from microscopic detail is a result of the densities of states being determined solely using Coulomb’s law.

Mott’s argument can be further modified to include a non-uniform density of states of the general form [Jana]:

$$N(E) = N_v(E - E_F)^v \quad (2.20)$$

where  $v$  is an integer and this produces a temperature dependent conductivity of the form:

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_x}{T}\right)^x\right) \quad (2.21)$$

where the exponent  $x$  depends on both dimension  $d$  and density of states index  $v$ :

$$x = \frac{v+1}{d+v+1} \quad (2.22)$$

Therefore for both  $d = 3$  and  $d = 2$  dimensions with  $v = 2$  and  $v = 1$  respectively, the ES-

$$\text{VRH exponent } x = \frac{1}{2} \text{ and } T_{1/2} \approx \frac{2.8\alpha e^2}{k_B \epsilon}.$$

If a constant density of states is assumed ( $v = 0$ ) one recovers the Mott exponent  $x = \frac{1}{4}$  in three dimensions.

For disordered materials, various models have been proposed to predict the electric field dependence of the current density when hopping between localised states is the dominant conduction mechanism [Hill, Apsley, Pollak]. The application of an electric field  $E$  has the effect of reducing the energy of the hop in the direction of the field and increasing the energy  $W_{ij}$  in the direction opposite to the field. This alters the probability of a hop (as given by Eqn (2.14)) and  $W_{ij}$  must be replaced by  $W_{ij} \pm eR_{ij}E$ . Small electric field values are assumed ( $eER_{\text{opt}} \ll W$ ) to ensure that there is little influence on the potential barrier width and that therefore hopping remains the dominant mechanism. Various non-trivial analyses have deduced field-dependent hopping current densities of the general form [Celzard]:

$$j(E) \propto \exp(cE^p) \quad (2.23)$$

so that an exponential dependence of the field raised to some power  $p$  is observed, where  $c$  is a constant [Celzard]. Predicted values for  $p$  include  $p = 1$  and  $2$ .

Analyses for strong electric fields [Jana] ( $eER_{\text{opt}} \gg W$ ) argue that since the field energy is greater than the hopping energy, hopping can occur without any energy transfer from phonons. By replacing  $W$  with  $eER$  and following a similar line of analysis as that for Mott-VRH, a high field dependent (and temperature independent) conductivity of the following form is derived:

$$\sigma = \sigma_0 \exp\left(-\left(\frac{E_x}{E}\right)^x\right) \quad (2.24)$$

where the exponent  $x$  is the same as given in Eqn (2.22). In 3-dimensional Mott systems,  $x = \frac{1}{4}$  as before.



### ***Fluctuation Induced Tunnelling***

Sheng and co-workers [Sheng<sup>1</sup>, Sichel, Sheng<sup>2</sup>] developed a thermally sensitive tunnelling model to describe conduction in disordered materials between large metallic islands separated by relatively small insulating barriers. Conduction occurs by tunnelling between the metallic conduction bands through an insulating bandgap, rather than by hopping between localised states in the bandgap. The conductive elements are mesoscopic and conductivity limited by Coulomb Blockade [Imry] is not a limiting factor. In that instance, the conducting islands are so small that the electrostatic charging energy involved in the transfer of a single electron from one region to the next is greater than thermal energy ( $e^2/C > k_B T$ ). This is not expected in carbon nanotube systems due to their size.

Sheng modelled each barrier or junction as a parallel-plate capacitor. It was shown that thermally activated voltage fluctuations across each insulating barrier (assumed to be parabolic) play an important role in determining the following overall temperature dependence of conductivity:

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T + T_0}\right) \quad (2.25)$$

$$T_1 = \frac{wAE_0^2}{8\pi k_B} \quad (2.26)$$

$$T_0 = \frac{2T_1}{\pi\chi w} \quad (2.27)$$

where the tunnelling constant  $\chi = \sqrt{\frac{2mV_0}{\hbar^2}}$  and  $E_0 = \frac{4V_0}{ew}$ .  $\sigma_0$  is a conductivity pre-factor with a slowly varying temperature dependence that can be neglected; A and w are the tunnel cross-sectional area and width respectively;  $V_0$  is the potential of the barrier; e and m are the electronic charge and mass respectively;  $\hbar = 2\pi\hbar$  is Planck's constant and  $k_B$  is Boltzmann's constant.

Physically,  $T_0$  represents the temperature at which the fluctuation effect becomes significant. It can be seen from Eqn (2.25) that for low temperatures such that  $T \ll T_0$ ,

the conductivity becomes temperature independent and reduces to the expected form for simple tunnelling through a parabolic barrier of thickness  $w$  (as given by Eqn (2.11)). Thus, the conductivity can be interpreted as a simple tunnelling conductivity in which the barrier height decreases with increasing temperature. At large temperatures such that  $T \gg T_0$ , Eqn (2.25) reduces to:

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T}\right) \quad (2.28)$$

and this represents a thermally activated hopping process with  $k_B T_1$  equal to the activation energy.

If the dispersion of conductive particles in the insulating matrix is homogeneous, then the composite conductivity at a given temperature can be described by the behaviour of a single tunnel junction. By geometric considerations the gap width ( $w$ ) can be assumed to vary with filler volume fraction  $p$  as [Boettger]:

$$w \propto p^{-1/3} \quad (2.29)$$

This model also predicts the temperature and electric field dependence of current density as follows:

$$j \approx j_0 \exp\left[-\left(\frac{T_1}{T + T_0}\right)\left(\frac{E}{E_0} - 1\right)^2\right] \quad (2.30)$$

where  $j_0$  is a constant current density independent of electric field and temperature. This expression is valid for  $E < E_0$  and for  $E > E_0$ , the current density is expected to have a slower, non-exponential dependence on  $E$  [Sheng<sup>1</sup>]. It can be shown that at low electric fields ( $E \ll E_0$ ), for a given temperature the FIT current density can be reduced and expressed using Eqn (2.23) with a power exponent  $p = 1$ .

## 2.6 Electrical Transport in Carbon Nanotube Systems

Electrical measurements on individual carbon nanotubes have been performed by a number of groups over the last decade. Exotic effects have been reported for these individual one-dimensional tubes such as Coulomb blockade [Tans<sup>2</sup>], Luttinger liquid

behaviour [Bockrath], the Kondo-effect [Nygard] and Aharonov-Bohm oscillations [Bachtold]. These effects arise from quantum transport in nanotubes but are generally only observed at extreme conditions such as very low temperatures and/or high electrical and magnetic fields. Another difficulty with this field of study is the sample preparation, which can be very time-consuming, expensive and ultimately very difficult to reproduce. These are all limitations to any potential real applications but the main barrier to applicability is the production of any useful number of integrated nano-devices.

A more realistic approach for the exploitation of the interesting properties of carbon nanotubes is to produce macroscopic networks of nanotubes. This strategy has been realised by making sheets of nanotubes themselves and also by their incorporation into polymer matrices. Both of these systems provide interesting systems to study the physical properties of charge transport in nanotube networks and also in individual nanotubes themselves. An added advantage to the production of nanotube-polymer composites is that the materials are actually functional as compared to brittle nanotube sheets.

There have been numerous studies on charge transport in extended carbon nanotube systems. Two categories dominate in the literature: (1) Bulk nanotube samples such as pellets or mats; and (2) nanotube-polymer composites. Various mechanisms such as Variable Range Hopping (VRH) and Fluctuation Induced Tunnelling (introduced in section 2.5) have been reported and a brief review of the important results to date follows.

### ***Transport in Carbon Nanotubes***

There has been extensive research on the area of charge transport in extended carbon nanotube systems such as mats or pellets. These mats or sheets are generally as-grown or prepared by micro-filtration (known as ‘buckypaper’). As with nanotube-polymer composites, which are discussed in the next section, temperature and electric field dependence of the current-voltage characteristics are very useful tools in determining the underlying charge transport mechanism.



Fischer et al [Fischer] first reported a metallic temperature dependence ( $d\sigma/dT < 0$ ) for the conductivity of mats of randomly oriented SWNTs. However, a reversal to non-metallic behaviour ( $d\sigma/dT > 0$ ) was observed at a crossover temperature in the range  $T^* = 35 - 210\text{K}$ . The variation in  $T^*$  was due to compression of the samples. A similar trend was also seen by several other groups [Grigorian, Fuhrer<sup>1</sup>]. A fibrillar model for conduction proposed by Kaiser et al [Kaiser], similar to that used for conducting polymers, was found to fit the data well:

$$\sigma(T) = \frac{\alpha}{T} + \sigma_0 \exp\left(\frac{-T_c}{T + T_s}\right) \quad (2.31)$$

where  $\alpha$ ,  $\sigma_0$ ,  $T_c$  and  $T_s$  are fitting constants (described in section 2.5). The first term is due to the metallic conductivity of the nanotubes themselves. The second term represents fluctuation induced tunnelling (FIT) through thin barriers at the contacts between the metallic regions.

Another well-reported conduction mechanism in nanotube mats is variable range hopping (VRH). Charge carriers are localised and hopping conductivity between localisation centres of varying separation dominates. This behaviour exhibits the following characteristic temperature dependence:

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_x}{T}\right)^x\right) \quad (2.32)$$

where the exponent  $x = 1/(1+d)$  in  $d$  dimensions,  $T_x$  is a fitting temperature (above which the hopping conductivity should become temperature independent) as defined in section 2.5. In the majority of bulk nanotube systems,  $d = 3$  and therefore  $x = 1/4$ . When Coulombic interactions are included, the theory of Efros and Shklovskii (ES-VRH) predicts  $x = 1/2$ .

Mott VRH ( $x = 1/4$ ) has been reported by numerous groups in a variety of samples. These include acid-treated [Fuhrer<sup>2</sup>, Gaal], annealed [Yosida<sup>1</sup>] and as-grown [Liu] SWNT mats; a pressed SWNT pellet [Benoit] and pressed arc-discharge MWNTs [Yosida<sup>2</sup>]. In the Mott model,  $T_x$  is related to the carrier localisation length  $\xi$  ( $= 1/\alpha$ ). This is effectively the coherence length of the electronic wavefunctions. By estimating a value for the density of

states at the Fermi level, some authors [Benoit, Fuhrer<sup>2</sup>] have used this expression to calculate very different lengths ranging from  $\xi = 8 - 700\text{nm}$ . These length scales are of the order of nanotube diameters and lengths respectively, from which varying interpretations as to the nature of the localisation are deduced. Possible origins range from intra-bundle electron confinement (transverse localisation) to wavefunction decay along the nanotube lengths (longitudinal localisation). The latter would support the notion that the network consists of metallic or semi-metallic nanotubes with extended electronic states localised along their lengths but which are separated by inter-tube barriers to conduction. A surprising result however is that this value was obtained using acid-treated nanotubes because this generally introduces defects which can disrupt the extended electronic nature.

The requirement of a Coulomb gap in the density of states (DOS) means that ES-VRH ( $x = 1/2$ ) is usually observed at much lower temperatures than Mott-VRH. This effect has been seen by Chauvet et al [Chauvet] in aligned MWNT films at  $T < 100\text{mK}$  suggesting strong screening of electron-electron interactions in MWNTs at normal temperatures.

### ***Transport in Carbon Nanotube - Polymer Composites***

There are various studies in the Literature pertaining to electrical properties of carbon nanotube-polymer composites. The majority of these reports only study the effect of varying the nanotube content on the room temperature ohmic conductivity. These percolation results are summarised in Table 5.1 in Chapter 5. Only a handful of groups have actually proposed conduction mechanisms for composites based on temperature and electric field dependence of their data.

An interesting case to note is that of Benoit et al [Benoit]. While Mott-VRH was observed for a SWNT pellet, this behaviour switched to ES-VRH once the same SWNTs were incorporated into a PMMA matrix. This demonstrates the opening of a soft Coulomb gap around the Fermi level and that electron-electron interactions became important. The addition of the polymer results in ineffective screening between neighbouring electronic sites. The gap was found to decrease with increasing SWNT

volume fraction,  $p$ , from  $\Delta_{CG} = 2.5\text{meV}$  to  $0.5\text{meV}$  as  $p$  increases from 1% to 8%. This follows the expected trend because for the SWNT pellet (effectively  $p = 100\%$ ), this gap disappears and Mott behaviour is re-established. The authors also found that the localisation of carriers in their composites is intrinsic to the SWNT system and that  $\xi \sim 28\text{nm}$  did not depend on the nanotube volume fraction.

Upon the application of an electric field  $E$ , a non-linear increase in conductivity was seen. This was attributed to a heating effect and could be incorporated into the ES-VRH temperature dependence through the concept of an *electric temperature*:

$$T_{elec} = \frac{e\xi E}{k_B} \quad (2.33)$$

where  $e$  and  $k_B$  are the electronic charge and Boltzmann constant respectively. This model is known as the hot electron model.

Variable range hopping has also been observed in a SWNT-epoxy composite [Choi] with a crossover from Mott type to ES type. Localisation lengths ranging from  $\xi = 7 - 26\text{nm}$  were calculated for non-aligned and aligned samples respectively, processed using a magnetic field. At low temperatures, the ES Coulomb gap ranges from  $\Delta_{CG} = 25 - 15\text{meV}$  for non-aligned and aligned samples respectively. The authors claim that an increased  $\xi$  for the aligned sample can be attributed to increased bundle size. This also explains the reduced Coulomb gap for the same sample since the Coulomb charging energy for larger bundles becomes smaller.

Tang et al [Tang] grew SWNTs in aligned channels in an insulating zeolite crystal. Although this is not a polymer, the material can still be considered as a nanotube-insulator composite system. The authors report a VRH exponent of  $x = \frac{1}{2}$  but do not attribute this to ES behaviour. Instead, it is claimed that the behaviour is actually Mott VRH in 1-dimension (such that  $x = 1/(1+d) = \frac{1}{2}$ ). This is quite probable as the nanotubes were grown in highly aligned nano-pores.



As briefly mentioned in section 2.4, Kilbride et al [Kilbride] suggested fluctuation induced tunnelling for MWNT composites produced using both PmPV and PVA polymers. A geometric argument related the nanotube separation (and hence tunnelling width) to the nanotube volume fraction. By transforming the conductivity versus volume fraction data, a straight line fit was obtained indicating a tunnelling process. The actual tunnelling was ascribed to fluctuation induced tunnelling because this has previously been reported in carbon-black polymer composites [Connor]. This was not fully verifiable however because temperature dependent data was not available.

Unsurprisingly, the metallic term in Eqn (2.31) has only been observed in mats of nanotubes and not for composites. These mats can be imagined as a series of touching metallic rods, both with and without barriers present at the contact regions. For well-dispersed, homogeneous composites, it is expected that barriers to conduction are present at every contact point between the metallic nanotubes in the form of a thin polymer layer coating. Figures 2.10 and 2.11 show TEM images of polymer layers around individual nanotubes. The crystalline polymer coating around the nanotube in Figure 2.11 actually formed within the bulk of a composite. Therefore, it is easy to understand why the aforementioned mechanisms tend to dominate the Literature when a composite is visualised as a series of conducting rods separated by small regions of thin insulating material.

## References

- An, K. H., Kim, W. S., Park, Y. S., *et al. Advanced Functional Materials*, **11**, 387-392, (2001)
- Apsley, N. and Hughes, H. P. *Philosophical Magazine*, **31**, 1327-1339, (1975)
- Avouris, P. *Chemical Physics*, **281**, 429-445, (2002)
- Bachilo, S. M., Strano, M. S., Kittrell, C., *et al. Science*, **298**, 2361-2366, (2002)
- Bachtold, A., Strunk, C., Salvetat, J. P., *et al. Nature*, **397**, 673-675, (1999)
- Baughman, R. H., Zakhidov, A. A. and de Heer, W. A. *Science*, **297**, 787-792, (2002)
- Benoit, J. M., Corraze, B. and Chauvet, O. *Physical Review B*, **65**, 241405, (2002)

Biercuk, M. J., Llaguno, M. C., Radosavljevic, M., *et al. Applied Physics Letters*, **80**, 2767-2769, (2002)

Bockrath, M., Cobden, D. H., Lu, J., *et al. Nature*, **397**, 598-601, (1999)

Boettger, H. and Bryskin, U. V., *Hopping Conduction in Solids*, (Berlin Verlag Akademie, Berlin, 1986)

Breuer, O. and Sundararaj, U. *Polymer Composites*, **25**, 630-645, (2004)

Burghard, M., Duesberg, G., Philipp, G., *et al. Advanced Materials*, **10**, 584, (1998)

Cadek<sup>1</sup>, M., Coleman, J. N., Ryan, K. P., *et al. Nano Letters*, **4**, 353-356, (2004)

Cadek<sup>2</sup>, M., Coleman, J. N., Barron, V., *et al. Applied Physics Letters*, **81**, 5123-5125, (2002)

Celzard, A., McRae, E., Furdin, G., *et al. Journal of Physics-Condensed Matter*, **9**, 2225-2237, (1997)

Chang, H. P. and Bard, A. J. *Journal of the American Chemical Society*, **113**, 5588-5596, (1991)

Chauvet, O., Forro, L., Zuppiroli, L., *et al. Synthetic Metals*, **86**, 2311-2312, (1997)

Chen<sup>1</sup>, J., Hamon, M. A., Hu, H., *et al. Science*, **282**, 95-98, (1998)

Chen<sup>2</sup>, R. J., Zhan, Y. G., Wang, D. W., *et al. Journal of the American Chemical Society*, **123**, 3838-3839, (2001)

Choi, E. S., Brooks, J. S., Eaton, D. L., *et al. Journal of Applied Physics*, **94**, 6034-6039, (2003)

Colbert, D. T., Zhang, J., McClure, S. M., *et al. Science*, **266**, 1218-1222, (1994)

Coleman<sup>1</sup>, J. N., Fleming, A., Maier, S., *et al. Journal of Physical Chemistry B*, **108**, 3446-3450, (2004)

Coleman<sup>2</sup>, J. N., Dalton, A. B., Curran, S., *et al. Advanced Materials*, **12**, 213, (2000)

Coleman<sup>3</sup>, J. N., Curran, S., Dalton, A. B., *et al. Physical Review B*, **58**, R7492-R7495, (1998)

Collins<sup>1</sup>, P. G., Hersam, M., Arnold, M., *et al. Physical Review Letters*, **86**, 3128-3131, (2001)

Collins<sup>2</sup>, P. C., Arnold, M. S. and Avouris, P. *Science*, **292**, 706-709, (2001)

Connor, M. T., Roy, S., Ezquerra, T. A., *et al. Physical Review B*, **57**, 2286-2294, (1998)

Curran, S. A., Ajayan, P. M., Blau, W. J., *et al. Advanced Materials*, **10**, 1091, (1998)

- Czerw, R., Guo, Z. X., Ajayan, P. M., *et al. Nano Letters*, **1**, 423-427, (2001)
- Dalton<sup>1</sup>, A. B., Stephan, C., Coleman, J. N., *et al. Journal of Physical Chemistry B*, **104**, 10012-10016, (2000)
- Dalton<sup>2</sup>, A. B., Collins, S., Munoz, E., *et al. Nature*, **423**, 703-703, (2003)
- Davey, A. P., Drury, A., Maier, S., *et al. Synthetic Metals*, **103**, 2478-2479, (1999)
- Dekker, C. *Physics Today*, **52**, 22-28, (1999)
- Dillon, A. C., Gennett, T., Jones, K. M., *et al. Advanced Materials*, **11**, 1354-1358, (1999)
- Dresselhaus M.S., Dresselhaus G. and Eklund P. C., *Science of Fullerenes and Carbon Nanotubes* (Academic Press Inc., San Diego, 1996)
- Drury, A., Maier, S., Ruther, M., *et al. Journal of Materials Chemistry*, **13**, 485-490, (2003)
- Fischer, J. E., Dai, H., Thess, A., *et al. Physical Review B*, **55**, R4921-R4924, (1997)
- Frank, S., Poncharal, P., Wang, Z. L., *et al. Science*, **280**, 1744-1746, (1998)
- Fuhrer<sup>1</sup>, M. S., Cohen, M. L., Zettl, A., *et al. Solid State Communications*, **109**, 105-109, (1999)
- Fuhrer<sup>2</sup>, M. S., Holmes, W., Richards, P. L., *et al. Synthetic Metals*, **103**, 2529-2532, (1999)
- Gaal, R., Salvetat, J. P. and Forro, L. *Physical Review B*, **61**, 7320-7323, (2000)
- Gao, G. H., Cagin, T. and Goddard, W. A. *Nanotechnology*, **9**, 184-191, (1998)
- Grigorian, L., Williams, K. A., Fang, S., *et al. Physical Review Letters*, **80**, 5560-5563, (1998)
- Hadjiev, V. G., Iliev, M. N., Arepalli, S., *et al. Applied Physics Letters*, **78**, 3193-3195, (2001)
- Hamon, M. A., Chen, J., Hu, H., *et al. Advanced Materials*, **11**, 834, (1999)
- Hill, R. M. *Philosophical Magazine*, **24**, 1307-1325, (1971)
- Hiura, H., Ebbesen, T. W. and Tanigaki, K. *Advanced Materials*, **7**, 275-276, (1995)
- Hurd, C. M. *Journal of Physics C-Solid State Physics*, **18**, 6487-6499, (1985)
- Iijima<sup>1</sup>, S. *Nature*, **354**, 56-58, (1991)
- Iijima<sup>2</sup>, S. and Ichihashi, T. *Nature*, **363**, 603-605, (1993)
- Imry, Y., *Introduction to Mesoscopic Physics*, (Oxford University Press, Oxford, 1997)



in het Panhuis, M. I., Munn, R. W. and Blau, W. J. *Synthetic Metals*, **121**, 1187-1188, (2001)

Jana, D. and Fort, J. *Physica B-Condensed Matter*, **344**, 62-65, (2004)

Kaiser, A. B., Flanagan, G. U., Stewart, D. M., *et al.* *Synthetic Metals*, **117**, 67-73, (2001)

Kilbride, B. E., Coleman, J. N., Fraysse, J., *et al.* *Journal of Applied Physics*, **92**, 4024-4030, (2002)

Kroto, H. W., Heath, J. R., O'Brien, S. C., *et al.* *Nature*, **318**, 162-163, (1985)

Lamb D. R., *Electrical Conduction Mechanisms in Thin Insulating Films*, (Methuen, London, 1967)

Liu, B. B., Sundqvist, B., Andersson, O., *et al.* *Solid State Communications*, **118**, 31-36, (2001)

McCarthy, B., Coleman, J. N., Czerw, R., *et al.* *Journal of Physical Chemistry B*, **106**, 2210-2216, (2002)

Miller, A. and Abrahams, E. *Physical Review*, **120**, 745-755, (1960)

Mintmire, J. W., Robertson, D. H. and White, C. T. *Journal of Physics and Chemistry of Solids*, **54**, 1835-1840, (1993)

Mott, N. F. and Davis, E. A., *Electronic Processes in Non-Crystalline Materials*, (2<sup>nd</sup> Ed., Clarendon Press, Oxford, 1979)

Nakajima, T., Kasamatsu, S. and Matsuo, Y. *European Journal of Solid State and Inorganic Chemistry*, **33**, 831-840, (1996)

Niyogi, S., Hamon, M. A., Perea, D. E., *et al.* *Journal of Physical Chemistry B*, **107**, 8799-8804, (2003)

Nygard, J., Cobden, D. H. and Lindelof, P. E. *Nature*, **408**, 342-346, (2000)

O'Connell, M. J., Boul, P., Ericson, L. M., *et al.* *Chemical Physics Letters*, **342**, 265-271, (2001)

Pollak, M. and Riess, I. *Journal of Physics C-Solid State Physics*, **9**, 2339-2352, (1976)

Riggs, J. E., Guo, Z. X., Carroll, D. L., *et al.* *Journal of the American Chemical Society*, **122**, 5879-5880, (2000)

Ryan<sup>1</sup>, K. P., Lipson, S. M., Drury, A., *et al.* *Chemical Physics Letters*, **391**, 329-333, (2004)

Ryan<sup>2</sup>, K. P., Cadek, M., Nicolosi, V., *et al.* *Synthetic Metals*, **156**, 332-335, (2006)

- Saito<sup>1</sup>, R., Dresselhaus, G. and Dresselhaus, M. S., *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998)
- Saito<sup>2</sup>, R., Fujita, M., Dresselhaus, G., *et al. Applied Physics Letters*, **60**, 2204-2206, (1992)
- Schonenberger, C., Bachtold, A., Strunk, C., *et al. Applied Physics A-Materials Science & Processing*, **69**, 283-295, (1999)
- Sheng<sup>1</sup>, P., Sichel, E. K. and Gittleman, J. I. *Physical Review Letters*, **40**, 1197-1200, (1978)
- Sheng<sup>2</sup>, P. *Physical Review B*, **21**, 2180-2195, (1980)
- Shklovskii, B. I. and Efros A. L., *Electronic Properties of Doped Semiconductors*, (Springer, Berlin, 1984)
- Sichel, E. K., Gittleman, J. I. and Sheng, P. *Physical Review B*, **18**, 5712-5716, (1978)
- Simmons, J. G. *Journal of Applied Physics*, **34**, 1793-1803, (1963)
- Star<sup>1</sup>, A., Stoddart, J. F., Steuerman, D., *et al. Angewandte Chemie-International Edition*, **40**, 1721-1725, (2001)
- Star<sup>2</sup>, A., Steuerman, D. W., Heath, J. R., *et al. Angewandte Chemie-International Edition*, **41**, 2508, (2002)
- Sun, Y., Wilson, S. R., MacMahon, S., *et al. Proceedings of the Electrochemical Society*, **2000**, 282-290, (2000)
- Tang, Z. K., Sun, H. D. and Wang, J. *Physica B*, **279**, 200-203, (2000)
- Tans<sup>1</sup>, S. J., Verschueren, A. R. M. and Dekker, C. *Nature*, **393**, 49-52, (1998)
- Tans<sup>2</sup>, S. J., Devoret, M. H., Dai, H. J., *et al. Nature*, **386**, 474-477, (1997)
- Teo, K. B. K., Minoux, E., Hudanski, L., *et al. Nature*, **437**, 968-968, (2005)
- Thess, A., Lee, R., Nikolaev, P., *et al. Science*, **273**, 483-487, (1996)
- Vollrath, F. and Knight, D. P. *Nature*, **410**, 541-548, (2001)
- Wallace, P. R. *Physical Review*, **71**, 622-634, (1947)
- Wei, B. Q., Vajtai, R. and Ajayan, P. M. *Applied Physics Letters*, **79**, 1172-1174, (2001)
- White, C. T., Robertson, D. H. and Mintmire, J. W. *Physical Review B*, **47**, 5485-5488, (1993)
- Wildoer, J. W. G., Venema, L. C., Rinzler, A. G., *et al. Nature*, **391**, 59-62, (1998)
- Wong, S. S., Joselevich, E., Woolley, A. T., *et al. Nature*, **394**, 52-55, (1998)

- Yosida<sup>1</sup>, Y. and Oguro, I. *Journal of Applied Physics*, **86**, 999-1003, (1999)
- Yosida<sup>2</sup>, Y. and Oguro, T. *Journal of Applied Physics*, **83**, 4985-4987, (1998)
- Yu<sup>1</sup>, M. F., Files, B. S., Arepalli, S., *et al.* *Physical Review Letters*, **84**, 5552-5555, (2000)
- Yu<sup>2</sup>, R. Q., Chen, L. W., Liu, Q. P., *et al.* *Chemistry of Materials*, **10**, 718-722, (1998)



## Chapter 3

### 3.1 Introduction

This chapter describes the material and sample production along with the experimental methods used to study the samples. An introduction to carbon nanotube production plus the issues pertaining to nanotube purification are addressed. The purification problem for arc-discharge MWNTs can be resolved through combination with a polymer to produce a composite material. The composite production and subsequent characterisation methods are described. Finally, the sample preparation and experimental set-up for electrical testing of composite materials are detailed.

### 3.2 Material Production and Purification

#### *Production of Carbon Nanotubes*

Carbon nanotubes can be synthesised by various different production methods. Nanotube properties vary radically according to the production method employed. These methods tend to belong to one of two main approaches to nanotube formation.

The first approach involves the condensation of carbon atoms, after the evaporation of an extremely pure graphitic source, in an inert atmosphere. The arc-discharge and laser ablation techniques fall into this category and nanotube formation occurs at high temperatures of between 3000 - 4000°C. These temperatures are necessary to melt the graphite source. Both multi-walled (MWNT) and single-walled (SWNT) nanotubes can be produced using these techniques, with a catalyst (such as Fe, Co, Ni) necessary for SWNT formation [Iijima, Bethune].

The second general approach is the chemical decomposition of a hydrocarbon gas, also in an inert atmosphere, over a transition metal catalyst (CVD). The catalyst is needed to initiate nanotube growth and the diameter of the nanotube is determined by the size of the metal particle. A nanotube can either grow from the tip or the base of the nanoparticle [Dai]. The general growth mechanism involves the decomposition of the hydrocarbon firstly into its constituent elements followed by carbon atoms desorbing onto the metallic

particle. These atoms then diffuse (either along the surface or through the bulk of the metal) to the growing wall of the nanotube. Various gases such as methane and benzene vapour have been used to grow nanotubes but the most commonly reported carbon source is acetylene [Rao]. It appears that acetylene is a better hydrocarbon than benzene for SWNT growth because it contains fewer carbon atoms per molecule. Nanotube growth has been demonstrated at temperatures from anywhere between 550 - 1200°C. Multi-walled nanotubes generally grow at temperatures below 850°C, whereas for SWNT formation, temperatures of above 900°C are necessary because of the larger energy of curvature involved.

Arc-discharge can be considered the most favourable technique for nanotube production for numerous reasons. Nanotubes produced by this method are highly graphitised whereas nanotubes produced by the other common methods tend to contain more defects as verified by TEM. Arc-discharge MWNTs appear long, rigid and kink-free which is advantageous for composite dispersion. Other types of nanotube can form tangled bundles. This method can produce MWNTs without the use of a catalyst, unlike CVD where impurities will always be present in the as-produced material. This method can be used to produce large quantities of nanotubes whereas laser ablation is limited to producing laboratory research samples of a few milligrams at a time.

#### ***Arc Discharge Method***

Multi-walled carbon nanotube soot was produced using the Krätschmer arc-discharge method. This was initially developed to produce fullerenes and can produce large quantities of nanotubes per run (up to 700mg in 30mins) [Cadek].

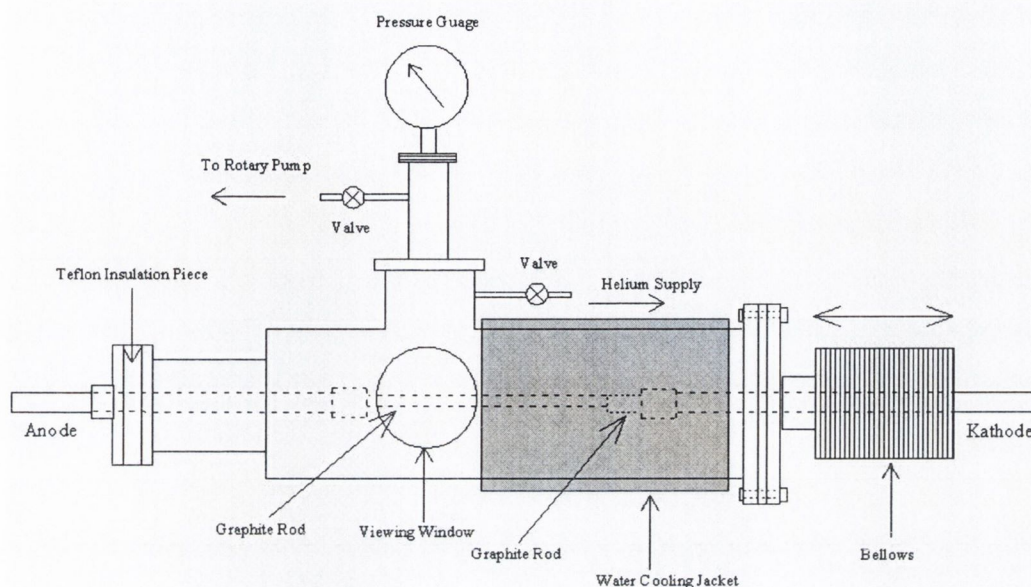


Figure 3.1: Schematic of the Krätschmer arc-discharge generator.

The Krätschmer generator, as shown in Figure 3.1, consists of a cylindrical steel chamber approximately 350 mm in length and 100 mm in internal diameter. Enclosed in the generator are two highly pure graphitic electrodes: a 99.5% pure stationary cathode and a 99.998% pure moveable anode. The purity of the anode is important, as this is the electrode that is consumed to produce the nanotubes. The rods are initially polished and aligned, as continuously parallel electrodes are necessary throughout the process to ensure uniform production of nanotubes.

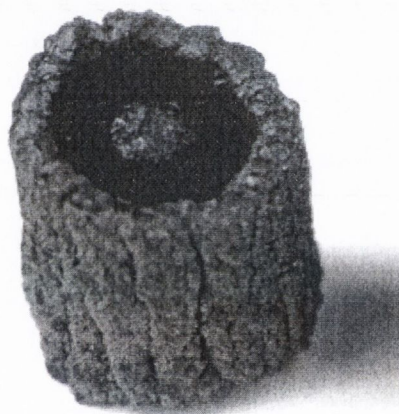
The chamber is continuously water cooled through the use of a water-cooling jacket around the exterior of the chamber. This is necessary because of the large temperatures involved in the production process (up to 4000°C). The chamber is evacuated and refilled with helium. This is repeated three times to ensure the removal of any contaminants, such as oxygen or water vapour, which could introduce defects in the nanotubes. The helium pressure is then fixed at 500 Torr.

A small DC power supply (which can deliver up to 3.2 kW) provides the constant current needed to maintain an arc across the two electrodes. These are initially in contact and



ignition of the plasma is achieved by slowly separating them. The rod separation is varied until a potential difference of 23 V is established between the electrodes.

Throughout the process, the anode is consumed and nanotube-containing soot is deposited on the cathode. Continuous adjustment of the anode position to maintain a constant potential difference of 23 V between the rods ensures a stable plasma and hence uniform nanotube production. Once the production parameters become unstable and the anode is consumed, the process is completed. After evacuation of the chamber with helium to remove unwanted vapours and nano-particles and to ensure sufficient cooling, a cylindrical deposit is found on the cathode, as shown in Figure 3.2.

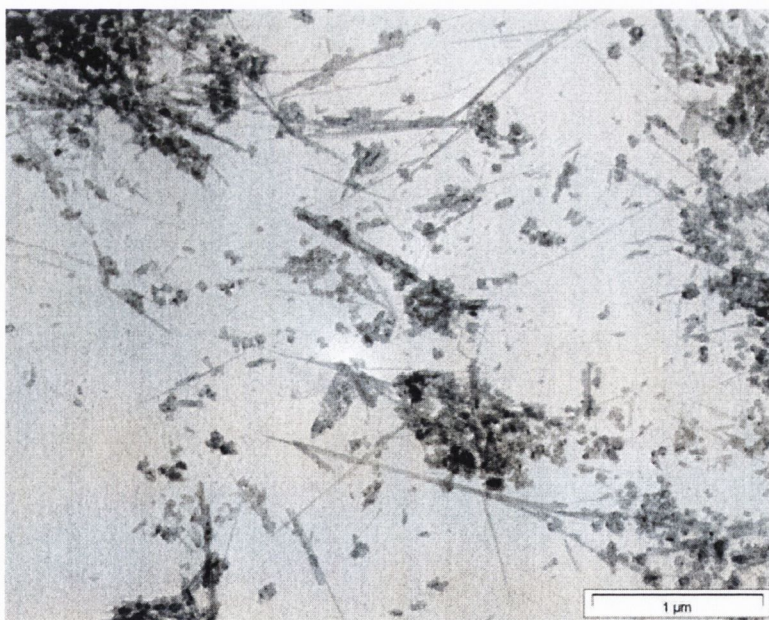


*Figure 3.2: Nanotube-containing cathodic deposit from the arc-discharge generator.*

This deposit consists of a hard, grey outer shell made up of mainly pyrolytic graphite and a soft, inner core of black soot which is rich in carbon nanotubes. The nanotube-containing soot is reclaimed manually by simply breaking open the hard shell and removing the soot with a spatula. This soot contains a mixture of MWNTs and graphitic impurities.

### *Purification of Carbon Nanotubes*

While carbon nanotubes have many interesting properties which could make them suitable for various applications, one major obstacle to their full exploitation is the problem of batch purity. As mentioned in the previous section concerning the arc-discharge production method, carbon nanotubes are not the only product and this is also true for nanotubes created using any other production method. A typical soot product from the arc-discharge chamber (see Figure 3.3) contains anywhere between 50-70% non-nanotube material such as amorphous carbon and graphitic nanoparticles (such as carbon “onions” which are multi-walled fullerene molecules). Residual metallic particles may also be present depending on whether a catalyst was employed. All of these non-nanotube species are unwanted impurities and pose a problem to both the study of intrinsic nanotube properties and any potential applications. Of critical importance to address this issue is a purification method that does not damage the nanotubes in order to retain their unique properties. Another important requirement for any real-world applications is a high yield of pristine nanotubes.



*Figure 3.3: TEM image of the original untreated MWNT soot produced by the arc-discharge method.*



A variety of methods for nanotube purification have been proposed. The most common treatments in the literature tend to be chemical oxidation or high temperature gas-phase oxidation (or a combination of both). These methods rely on the relatively small difference in the resistance to oxidising agents of the hexagons in nanotube sidewalls and the less stable structures in the impurities. Examples of oxidising agents used include nitric acid [Dillon], potassium permanganate in acid solution [Hiura], oxygen [Shi, Ebbesen] and carbon dioxide [Tsang]. These methods do remove impurities but also have the undesirable effect of damaging the nanotubes themselves. The caps of nanotubes contain five and seven membered carbon rings (similar to carbon onions) and are therefore more reactive and susceptible to damage than the sidewalls. If there are any defects in the walls themselves these areas are also points of attack during oxidation. Apart from the destructive nature of these purification methods, another major disadvantage is the low yields obtained. Ebbesen et al [Ebbesen] reported a loss of over 99% of the original nanotube product after oxygen treatment at 700°C.

Shelimov et al [Shelimov] developed a method for nanotube purification by ultrasonically assisted filtration. Nanotubes were dispersed in methanol by ultrasonic agitation. These dispersions are unstable and flocculation followed by precipitation occurs within a minute. To prevent this from happening, high power ultrasonication was required continuously during micro-filtration and this had the adverse effect of cutting the nanotubes and introducing sidewall defects. This process also failed to remove large aggregates consisting of amorphous carbon ( $\sim 1\mu\text{m}$ ). The authors propose that the only way to remove these impurities is further purification through chemical oxidation.

An alternative approach to nanotube purification that does not damage or destroy the nanotubes is size exclusion chromatography. This method was first demonstrated by Duesberg et al [Duesberg<sup>1</sup>, Duesberg<sup>2</sup>]. A MWNT-surfactant aqueous suspension was prepared by ultrasonication and was then filtered through a column containing controlled pore glass with an average pore size of 140nm. Various fractions were collected and by atomic force microscopy (AFM) and Raman spectroscopy it was found that this method



is successful in separating small quantities of nanotubes into fractions with small length and diameter distributions. A major disadvantage to the technique however is that it is not practical for large quantities of nanotubes. Generally only milligram scale quantities are obtained.

None of the aforementioned purification schemes can simultaneously fulfil the requirements of (1) a high-yield of (2) pristine nanotubes. An alternative purification method that satisfies both of these issues is presented in Chapter 4.

### ***Production of PmPV***

The polymer poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) (PmPV) was synthesised by Anna Drury in our laboratory in Trinity College and the monomer unit is shown in Figure 3.4. This is a derivative of the more widely studied polyphenylenevinylene (PPV) whereby aliphatic side groups are introduced to a phenyl ring to allow solubilisation in common solvents. PmPV is a co-polymer whereby approximately one third of the repeat units are altered by switching the phenyl linkage to a *meta* conformation rather than a *para* one.

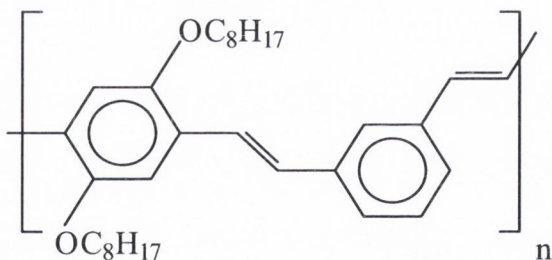


Figure 3.4: Repeat unit structure of the polymer poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene), PmPV.

A Horner-Emmons poly-condensation reaction in dry dimethyl formamide (DMF) was used as the synthetic route [Davey, Maier, Drury]. Hydroquinone is the starting material. This is reacted with potassium hydroxide and bromooctane in a solution of dimethyl sulphoxide (DMSO) to form 1,4 dioctoxybenzene. This material will eventually become

the substituted *meta* phenyl on the polymer backbone. A methyl bromination is performed on 1,4 dioctoxybenzene using potassium bromide and *para*-formaldehyde in the presence of acetic and sulphuric acids to produce 1,4-bis (2,5-di-n-octoxy) bromomethyl benzene. This is then heated with triethyl phosphite to form the Horner ester, 1,4-bis (2,5-di-n-octoxy) phenyl diethyl phosphonate. This material is the immediate precursor of the polymer.

The conversion of the precursor to polymer is done by the Emmons condensation reaction. For the polymer, the Horner ester is reacted with isophthalaldehyde. This molecule has two CHO groups in the *meta* position. This means that when it reacts with the Horner ester there is still a free CHO group to react with another ester molecule. This can continue until the reaction is quenched to produce a long chain polymer. It should be noted that if the precursor were reacted with *para*-phtaldehyde the result would be all *para*-PPV. In the case of the polymer a polycondensation reaction terminates the reaction.

The introduction of *meta* linkages introduces a steric effect. Energy minimisation calculations for a perfect PmPV chain in which all the vinylene double bonds are in the *trans* position have been carried out [in het Panhuis]. These show that a single PmPV strand tends to form a planar strand with a helical twist, whereas all *trans*-PPV is a planar molecule. This slight curvature should make the molecule much more flexible and this is believed to be one of the reasons why there is good interaction between the polymer and a nanotube. In reality however, there will always be some *cis* linkages but Horner PmPV has been characterised as having a very low *cis-trans* ratio [Drury].

### 3.3 Carbon Nanotube - Polymer Composite Preparation

The following general algorithm for nanotube-polymer composite formation was followed throughout this thesis. For each particular study, this recipe was adjusted accordingly to suit the particular system under investigation. Typical experimental parameters for a PmPV – nanotube composite are presented below. These include solvent

used, polymer concentration, sonication time etc. The actual values employed for other composites are specified in the relevant section relating to the individual experiments.

(1) A polymer solution of concentration 20 g/L was prepared by adding 100 mg PmPV to 5 mL of toluene (the preferred solvent in this case). This was then sonicated using a high-power sonic tip (120W) for 1 minute to ensure complete dissolution of the polymer.

(2) To produce a composite with MWNT to polymer mass ratio of 1:5, 20mg of MWNT soot were added to the polymer solution. This was further sonicated for 1 minute using the sonic tip to initially break up any large aggregates of nanotubes and/or impurities. The composite was then transferred to a low-power (60W) sonic bath for 2 hours to ensure uniform dispersal and homogeneity.

(3) The solution was then left to settle for 48 hours. This allowed for impurities in the MWNT soot to sediment out of solution. These include turbostratic graphite and carbon onions.

(4) The top two thirds of the settled solution (supernatant) was removed from the settled solids by decantation. In the case of PmPV, it was found that MWNTs remained highly dispersed and suspended in this top fraction but more importantly it appeared to be relatively impurity-free.

(5) This MWNT-polymer composite solution was then further processed accordingly. In the case of electrical measurements, composite films were created by spin-coating and baking the solution on glass substrates. For electron spin resonance (ESR) analysis, the solution was drop-cast and baked on spin-free quartz substrates. The residual solvent in the sediment was evaporated and this dry powdery material was also investigated by ESR in spin-free quartz tubes. For optical measurements, the solution was simply diluted to the required concentration and studied in a cuvette.



### 3.4 Carbon Nanotube - Polymer Composite Characterisation

The MWNT-polymer composites prepared according to the general recipe described in the previous section were characterised using a variety of destructive and non-destructive techniques, which will be described in the following subsections.

#### *ESR Sample Preparation*

Composites were produced according to the general methodology described in the previous section. The host polymers used in the ESR work were poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV) and poly(9,9-di-n-octylfluorenyl-2,7'-diyl) (PFO). Their structures are shown in Figures 2.7 and 2.8 respectively. The samples were prepared for ESR analysis as follows.

##### *(A) PmPV*

Various masses of PmPV (ranging from 20 mg to 160 mg) were added to toluene, with each solution having a concentration of 16.7 g/L. The solutions were sonicated for 1 min using a high power sonic tip and then 20 mg of MWNT soot from the same batch were added to each. The resulting composite solutions were further sonicated for 1 min using the sonic tip and then for 2 hours in a low power (60W) sonic bath to ensure good dispersal and homogeneity. They were then left to settle for 48 hours to allow impurities to sediment out. For each sample the resulting suspension was separated from the sediment by decantation. The sediments were dried and weighed. The masses are summarised in Table 3.1.

|   |                                 | Composite1 | Composite2 | Composite3 | Composite4 | Composite5 |
|---|---------------------------------|------------|------------|------------|------------|------------|
| 1 | Mass PmPV, $M_{poly}$ (mg)      | 20.4       | 79.9       | 100.0      | 130.9      | 160.7      |
| 2 | Mass MWNT Soot, $M_{soot}$ (mg) | 20.3       | 20.3       | 20.3       | 20.1       | 20.6       |
| 3 | Sediment Mass (mg)              | 18.8       | 18.8       | 18.3       | 16.6       | 18.5       |
| 4 | Solute Mass (mg)                | 21.9       | 81.4       | 102        | 134.4      | 162.8      |

Table 3.1: Summary of the data obtained in the PmPV work. Rows 1-2 contain the masses of the initial ingredients while rows 3-4 contain the masses of the sediment and solute after 48 hours settling, respectively.

(B) PFO

Six identical samples were prepared, each with 60 mg of PFO added to 3 mL of toluene (solution concentration of 20 g/L). These solutions were then placed in an oven at 50°C for 30 mins to dissolve the polymer. To each sample, 20 mg of nanotube soot were added and these composite mixtures were sonicated for 1 min with a high-power sonic tip. They were then sonicated for an additional 2 hours in a low-power (60 W) sonic bath to ensure complete and uniform dispersal. The composites were left to stand for different times varying from 0.5 to 96 hrs (in order to allow any impurities to fall out of solution). After this, each composite was decanted leaving two phases: a black sediment and a suspension with a blue-black appearance. These sediments were dried and weighed. The masses are summarised in Table 3.2.

|   |                                 | Composite1 | Composite2 | Composite3 | Composite4 | Composite5 | Compsite6 |
|---|---------------------------------|------------|------------|------------|------------|------------|-----------|
| 1 | Settling Time (hours)           | 0.5        | 2          | 8          | 24         | 48         | 96        |
| 2 | Mass PFO, $M_{poly}$ (mg)       | 60.5       | 60.4       | 60.3       | 60.5       | 60.1       | 60        |
| 3 | Mass MWNT Soot, $M_{soot}$ (mg) | 20.2       | 20.2       | 20         | 20.5       | 20.2       | 20.2      |
| 4 | Sediment Mass (mg)              | 11.5       | 15.3       | 13.6       | 13.1       | 15.2       | 18.1      |
| 5 | Solute Mass (mg)                | 69.2       | 65.3       | 66.7       | 67.9       | 65.1       | 62.1      |

Table 3.2: Summary of the masses in the PFO work for various settling times (row1). Rows 2-3 contain the masses of the initial ingredients while rows 4-5 contain the masses of the sediment and solute, respectively.

For each composite, ESR was performed on both the decanted solution and the sediment. Depending on the sample, between 0.5 mL to 1.5 mL of the solution were drop cast onto a spin free quartz plate and dried. This produced solute films in the mass range 10 – 15mg to ensure that an appreciable ESR signal was obtained. In addition, two samples of each sediment powder weighing approximately 4.5 mg each were prepared in spin free quartz tubes. This was due to the sediment powder not being completely homogenous.

### *Thermogravimetric Analysis*

Thermogravimetric analysis (TGA) involves measuring the mass of a material as a function of temperature increase. The instrument used in this work was a Perkin Elmer Thermogravimetric Analyser 7. Approximately 10 mg of the material being tested (e.g. nanotube soot, polymer or composite material) was placed into an aluminium crucible and then positioned onto a balance inside a temperature programmable furnace. The sample was heated at a rate of 10°C/min from 25°C to 1000°C and its mass was continuously monitored. In all cases the carrier gas was air (to ensure complete oxidation of the sample by 1000°C) with a flow rate of 20 L/min. For the polyvinylpyrrolidone (PVP) samples which absorb moisture from the environment, these were dried in an oven at  $T \sim 110^{\circ}\text{C}$  to remove any water content before performing TGA. This did not have any adverse effect on the composite structure since the glass transition temperature of PVP is  $T_g = 168^{\circ}\text{C}$ .

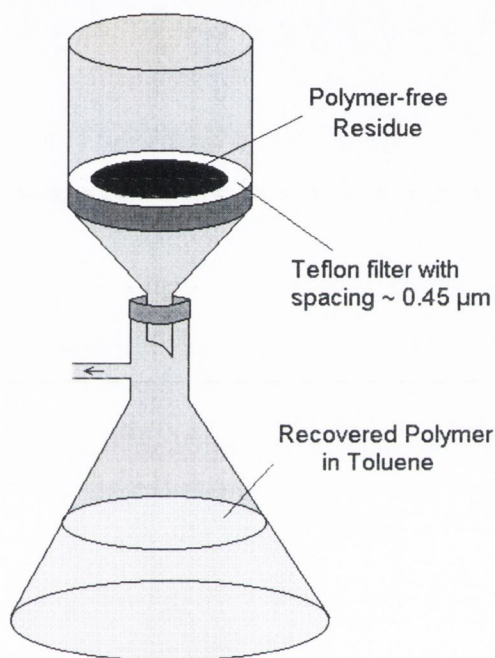
### *Transmission Electron Microscopy*

All transmission electron microscopy (TEM) measurements on samples (both raw MWNT soot and purified material) were performed using a Hitachi H7000 electron microscope which was capable of a magnification of x600,000. An accelerating voltage of 100 keV was used. The nanotube sample was dispersed in a solvent such as methanol using a high power sonic tip (120W) for 2 mins. A holey carbon TEM grid was dipped into the dispersion and then allowed to dry free-standing in air. The measurements were performed by Brendan McCarthy and Martin Cadek.



### ***Buchner Filtration***

Buchner filtration was performed, on both the PmPV and PFO composite solutions, to observe what forms of carbonaceous material(s) remained in both polymer suspensions. The apparatus is shown in Figure 3.5. A Teflon filter membrane with a pore size of 450nm (Millipore FHUP04700) was placed on a porous sintered glass substrate. This pore size is smaller than the average MWNT length ( $L \sim 2000\text{nm}$ ) yet larger than the diameter of spherical graphitic nanoparticles ( $d \sim 1\text{-}100\text{nm}$ ).



*Figure 3.5: Buchner filtration of polymer-nanotube suspensions.*

To ensure that the pores did not become easily clogged, the composite solutions were diluted before filtration. For both polymers, approximately 10 mL of decanted solution were mixed with 250 mL of toluene and this was sonicated for about 1 min in the low power sonic bath. The dark dispersion was filtered in 50mL stages (purely limited by the volume of the funnel) at an approximate flow rate of 5mL/s leaving a black residue on the filter paper. As more material became deposited on the filter the filtration rate slowed down. In both cases, the filtrate had the appearance of the original polymer only (bright yellow for PmPV and clear for PFO). This indicated both the presence of polymer and also the absence of MWNTs (and graphitic particles if any remained in solution).

Immediately after all of the diluted 260mL solution was filtered, another 250 mL of toluene were poured through the residue, washing away more residual polymer. This process was repeated a number of times until the filtrate emerged absent of any polymer as verified both visually and also from UV-VIS spectroscopy. The residue was retrieved by placing the filter paper in a bottle of toluene and this was agitated in a low power sonic bath for 5 mins. The residue easily detached from the filter and became dispersed in the toluene. This dispersion was then allowed to settle and over a period of hours, the dark material sedimented out of solution (also indicating the absence of any polymer). These fractions could be separated and the sediment dried. Alternatively, to speed up the process, the solution could be placed in a Teflon dish in an oven at 60°C to evaporate the toluene. Transmission electron microscopy (TEM) and ESR were performed on these residues and the results were then compared with those of the original MWNT soot (as detailed in Chapter 4).

### **3.5 Electrical Device Preparation**

According to the recipe detailed in section 3.3, a highly pure MWNT-polymer composite solution was separated from unwanted impurities. For electrical measurements, the polymer polyvinylpyrrolidone (PVP) was used. This is soluble in water along with a variety of polar solvents, and a preliminary investigation using optical microscopy was undertaken to determine the best solvent for MWNT dispersal. Under the same mixing conditions, no aggregates were observed for ethanol down to the resolution of the microscope ( $\sim 5\mu\text{m}$ ). This was unlike for water, in which case aggregates of diameter  $100\mu\text{m}$  were observed indicating the importance of the solvent as well as the polymer in nanotube dispersion.

A stock polymer solution was then prepared in ethanol at a concentration of 100g/L. This high concentration was chosen in order to produce films of a desired thickness after drop-casting of the solution. MWNTs were added to this stock in a ratio of 1:4 by mass relative to the polymer. The MWNTs were dispersed in the polymer using high power sonication (120W) for 2 minutes followed by 2 hours lower sonication (60W). These short sonication times ensured good dispersion without shortening of the nanotubes, as verified



by transmission electron microscopy (TEM). This suspension was allowed to settle for 24 hours to enable any large impurities to sediment out. Following this, the nanotube-rich, impurity free supernatant was separated from the sediment by decanting. This composite solution was labelled mfl and taken to be the composite stock. This was then diluted with the polymer stock to produce composite solutions of varying nanotube volume fraction. These were ready to be deposited by standard solution processing techniques to form solid-state films for electrical characterisation.

Glass substrates (12mm x 12mm) were firstly cleaned in an aqueous solution of Decon 90 and then rinsed with water. After this, they were rinsed with isopropanol (IPA) followed by spinning at 2000rpm to ensure rapid drying. These were then placed face down in a shadow mask for deposition of a common bottom electrode by non-reactive plasma sputtering of a highly pure gold target (99.99%). The chamber was evacuated to a low pressure of less than  $2 \times 10^{-5}$  mbar. This was then backfilled with argon and a plasma was formed. The argon ions possess sufficient kinetic energy to remove gold atoms from the target. A uniform layer of gold approximately 80nm in thickness was formed on the glass substrates at a constant deposition rate of  $0.5 \text{ \AA s}^{-1}$ . This would serve as a common bottom electrode for six test pads.

Immediately before spin-coating of the composite, the solution was agitated with the sonic tip (120W) for 1 minute to destroy any nanotube aggregates that may have formed. This also ensured a standard procedure for samples with different histories. In each case, a film layer was produced by spin-coating 0.1mL of solution at 1000rpm on top of the gold electrode on glass. The substrate was then placed in an oven for 1 hour at 60°C to ensure complete removal of any residual solvent. It was determined from Dektak profilometry that the thickness of this monolayer of composite was approximately 300nm for a polymer concentration of 100g/L at this spin speed. The process was repeated four more times to build up a film of sufficient thickness for testing (1-2  $\mu\text{m}$ ).

Film thickness measurements were performed by surface profilometry using a Dektak 3ST surface profiler. A channel was etched through the nanotube-polymer composite film



with a razor blade and a diamond stylus scanned the surface of the material measuring the depth of the trench. Measurements were performed in at least three positions in each film and average film thicknesses,  $L$ , were between 1-2  $\mu\text{m}$  for the PVP-MWNT composites (Table 3.3). It should be noted that the film thicknesses were determined at positions in the films (such as region D shown in Figure 3.6) far from the active areas used in electrical testing.

| Sample | MWNT volume fraction<br>p | Film Thickness, L<br>( $\mu\text{m}$ ) | $\Delta L$<br>( $\mu\text{m}$ ) |
|--------|---------------------------|----------------------------------------|---------------------------------|
| mf4    | $6.6 \times 10^{-3}$      | 1.62                                   | 0.01                            |
| mf4x   | $4.9 \times 10^{-3}$      | 1.30                                   | 0.03                            |
| mf6    | $1.7 \times 10^{-3}$      | 1.35                                   | 0.03                            |
| mf7    | $8.2 \times 10^{-4}$      | 1.37                                   | 0.01                            |
| mf9    | $2.1 \times 10^{-4}$      | 1.72                                   | 0.04                            |
| mf0    | 0                         | 1.68                                   | 0.01                            |

Table 3.3: MWNT/PVP film thickness measurements from Dektak surface profilometry.

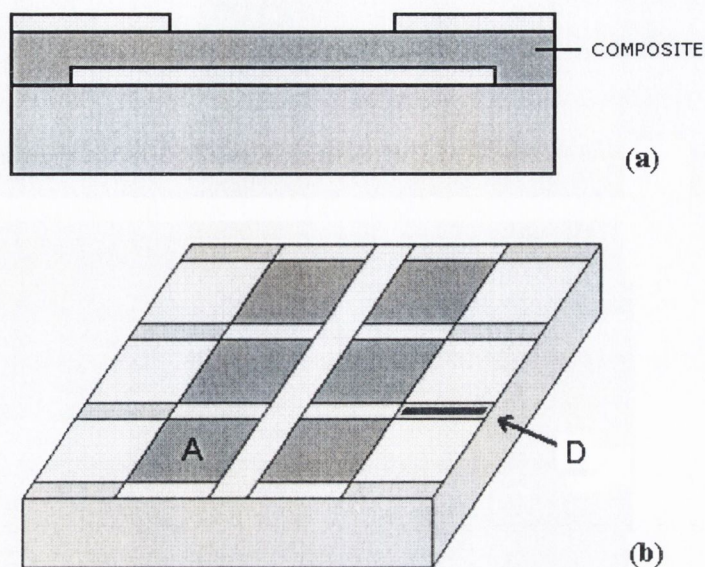


Figure 3.6: Schematic of (a) a cross-section and (b) a top view of the six-finger sandwich structure device produced for electrical testing. Region A represents the active area of  $6\text{mm}^2$ .

The final stage in the sample preparation was deposition of top gold contacts. Again, the substrates were placed face down in another shadow mask for thermal evaporation of six gold fingers. This deposition method was preferred to sputtering for the top electrodes to avoid the production of filaments through the polymer. Highly pure gold wire was obtained from Sigma-Aldrich (0.5mm diameter and 99.999% purity). Approximately 1cm of the wire was rolled into a ball and placed into a tungsten evaporation boat. Once the chamber was evacuated to a low pressure of less than  $2 \times 10^{-5}$  mbar, a current of 2A was passed through the boat. Once the gold wire was observed to become molten, the current was reduced slightly to control the deposition rate and this was monitored using a quartz crystal. After about 30 seconds, the baffle plate was opened and an 80nm layer of gold was deposited. Once the completed device was removed from the chamber, a small area of composite was removed by scratching to expose the bottom electrode and this was contacted using conductive silver paste.

### 3.6 Electrical Characterisation

Temperature dependent electrical measurements were performed using an Oxford Instruments CCC1104 liquid helium closed cycle cooler system. The closed cycle cooler system includes the cryostat built on an Edwards model CS2/9 cold head, a water-cooled compressor unit and integral control unit, a pair of flexible helium lines, and an intelligent temperature controller (Oxford ITC503).

Helium is compressed to 16.5 bar in the compressor (Edwards Cryodrive 1.5) and then expanded in a controlled manner in the cold head to produce the cooling. The ITC controls the heater power to achieve stable control of temperature set point and ramping. The cold stage of the cold head is attached to a copper block which contains a rhodium-iron thermocouple and two wire-wound resistor heaters to allow variable temperature measurement and operation respectively. A home-built sample holder to contain the (12mm x 12mm) sandwich samples (described in section 3.5) is attached directly to this cold stage and is grounded via a laser-table. The first stage of the cooler is connected to a copper radiation shield and an outer vacuum chamber then surrounds this to provide vacuum insulation for the cryostat. This space is pumped to high vacuum ( $10^{-4}$  to  $10^{-5}$  mbar) before the cryostat is cooled down. All electrical measurements were performed at temperatures between 20-300K.

Electrical measurements were performed on sandwich structure devices prepared by drop-casting as described previously. The sample was placed under high vacuum ( $\sim 10^{-5}$  mbar) in the sample holder in the cryostat. Contact was made with the electrodes using pressure probes. Conductive silver paint was applied to the electrodes to enhance the probe-electrode contact whilst also avoiding contact resistance between them. All wires were plaited to prevent movement and generation of stray emfs leading to electrical noise.

DC current-voltage (I-V) characteristics were measured using a Keithly Model 2400 sourcemeter. A home written Visual Basic programme was used to control the input parameters. The samples were subjected to the applied voltage range 0 to 2.5V in both



forward and reverse bias with a step voltage of 0.025V. This upper limit was chosen to ensure device stability and reproducibility (as discussed further in Chapter 5). The zero-field conductivity,  $\sigma_{DC}$ , was calculated for each pad (of thickness  $L$  and area  $A$ ) from the slope of the I-V curves about 0V as:

$$\sigma_{DC} = \left( \frac{I}{V} \right) \left( \frac{L}{A} \right) \quad (3.1)$$

Measurements were performed on all six electrodes and the average conductivity is reported.

### *Impedance Spectroscopy*

Impedance spectroscopy (or Dielectric spectroscopy) is an established non-destructive tool for analysing electrical properties of conductor-insulator composite materials [MacDonald]. The dynamics of bound or mobile charge in the bulk or interfacial regions of a material can be investigated. Dielectric relaxation as a whole is the result of the movement of dipoles (dipole relaxation) and electric charges due to an applied alternating field, and is usually observed in the frequency range  $10^2$ - $10^{10}$  Hz. Relaxation mechanisms are relatively slow compared to resonant electronic transitions or molecular vibrations, which usually have frequencies above  $10^{12}$  Hz. In particular, for nanotube-polymer composites, impedance spectroscopy is sensitive to boundaries.

A small sinusoidal excitation voltage at an angular frequency  $\omega = 2\pi f$  is applied to the sample:

$$V(t) = V_{AC} \cos(\omega t) = V_{AC} \text{Re}[e^{i\omega t}] \quad (3.2)$$

where  $\text{Re}[\ ]$  means the real part of a complex number. The corresponding current response is:

$$I(t) = I_{AC} \cos(\omega t - \varphi) = I_{AC} \text{Re}[e^{i\omega t} e^{-i\varphi}] \quad (3.3)$$

The phase difference  $\varphi$  is zero only if the sample exhibits purely resistive behaviour. If the sample is purely capacitive, the current leads the voltage and  $\varphi = 90^\circ$ . Analogous to the definition of resistance, impedance can be defined as the ratio of  $V(t)/I(t)$ . The magnitude or modulus is then  $V_{AC}/I_{AC}$  plus it has an associated phase of  $\varphi$ .

The total impedance of a material can be modelled by an equivalent electrical circuit. The total impedance can be calculated from various impedance elements added in series, in parallel or a combination of both. The impedance of a resistance R is simply equal to itself:

$$Z_R = R \quad (3.4)$$

whereas the impedance of a capacitance C is given by

$$Z_C = -i/\omega C \quad (3.5)$$

reflecting the phase difference of the current response to the applied voltage.

Because of the phase difference, the impedance of the sample is a complex function and can be defined as:

$$\begin{aligned} Z^* &= Z' - iZ'' \\ &= R - iX(\omega) \\ &= R - \frac{i}{\omega C} \end{aligned} \quad (3.6)$$

with the real part  $Z'$  equal to *resistance* R, and the imaginary part  $Z''$  equal to *reactance*  $X(\omega)$ . In this analysis, the equivalent circuit is a resistance and a capacitance added in series. The reactance is completely due to a capacitance C and no inductive element is present. By convention,  $Z^*$  is defined with a minus sign so that  $Z''$  can be considered a positive number. Physically, the minus sign indicates that the current response leads the voltage because of the capacitive elements present. The real and imaginary parts of impedance can be plotted on an Argand diagram known as a Cole-Cole plot. Alternatively, in polar form the impedance can also be written as:

$$Z^* = |Z^*| e^{i\phi} \quad (3.7)$$

where  $|Z^*| = \sqrt{Z'^2 + Z''^2}$  is the modulus of impedance and  $\phi = \arctan\left(\frac{Z''}{Z'}\right)$  is the phase.

A graph of  $|Z^*|$  and  $\phi$  both plotted versus frequency is known as a Bode plot and whilst containing the same information as a Cole-Cole plot, is easier to interpret because frequency is explicitly plotted.

Other functions exist that are transformations of the impedance such as the admittance of a material defined as:

$$Y^* = \frac{1}{Z^*} \quad (3.8)$$

$$= Y' + iY''$$

where the real and imaginary parts are known as *conductance* and *susceptance* respectively.

Physically, a conductor-insulator composite material is best modelled as a resistance and capacitance acting in parallel. In this instance, the total impedance is given by:

$$\frac{1}{Z^*} = \frac{1}{Z_R} + \frac{1}{Z_C} \quad (3.9)$$

$$= \frac{1}{R} + \frac{1}{(-i/\omega C)}$$

which corresponds to the more natural admittance representation for a parallel circuit:

$$Y^* = \frac{1}{R} + i\omega C \quad (3.10)$$

The modulus of admittance ( $|Y^*| = 1/|Z^*|$ ) can be calculated as a function of frequency. This represents the total contribution of conductive and capacitive elements to charge transport. The modulus of admittance can therefore be used to monitor the transition through the percolation threshold for a composite material composed of conducting nanotubes embedded in an insulating polymer.

AC measurements were performed using a Zahner IM6e Impedance analyser in the frequency range 1-10<sup>6</sup> Hz. The upper limit was fixed by the resolution of the instrument. The lower limit of the instrument was 10<sup>-2</sup> Hz but by including the lowest 2 decades of frequency, the scan-time would have increased twenty-fold without any real gain in information. A modulating bias of V<sub>AC</sub> = 50mV was applied (with zero DC bias). This value was large enough to ensure a relatively noise-free current response but also small enough to ensure a linear current response. Analogous to the slope of the I-V



characteristics, the modulus of admittance can be multiplied by a geometric factor to produce a frequency dependent AC conductivity called the *electric modulus*:

$$|\sigma^*(\omega)| = |Y^*(\omega)| \frac{L}{A} \quad (3.11)$$

For an equivalent circuit consisting of a resistance and a capacitance in parallel (see Eqn (3.10)), this becomes:

$$|\sigma^*(\omega)| = \sqrt{\frac{1}{R^2} + (\omega C)^2} \frac{L}{A} \quad (3.12)$$

At low frequencies, this approaches a constant value except for pure dielectric materials.

## References

- Bethune, D. S., Kiang, C. H., Devries, M. S., *et al. Nature*, **363**, 605-607, (1993)
- Cadek, M., PhD Thesis, Trinity College Dublin, (2003)
- Dai, H., *Nanotube Growth and Characterization in Carbon Nanotubes: Synthesis, Structure, Properties and Application* edited by M. S. Dresselhaus, G. Dresselhaus and P. Avouris, (Springer, Berlin, 2001)
- Davey, A. P., Drury, A., Maier, S., *et al. Synthetic Metals*, **103**, 2478-2479, (1999)
- Dillon, A. C., Gennett, T., Jones, K. M., *et al. Advanced Materials*, **11**, 1354-1358, (1999)
- Drury, A., Maier, S., Ruther, M., *et al. Journal of Materials Chemistry*, **13**, 485-490, (2003)
- Duesberg<sup>1</sup>, G. S., Burghard, M., Muster, J., *et al. Chemical Communications*, 435-436, (1998)
- Duesberg<sup>2</sup>, G. S., Blau, W., Byrne, H. J., *et al. Synthetic Metals*, **103**, 2484-2485, (1999)
- Ebbesen, T. W., Ajayan, P. M., Hiura, H., *et al. Nature*, **367**, 519-519, (1994)
- Hiura, H., Ebbesen, T. W. and Tanigaki, K. *Advanced Materials*, **7**, 275-276, (1995)
- Iijima, S. *Nature*, **354**, 56-58, (1991)
- in het Panhuis, M. I., Munn, R. W. and Blau, W. J. *Synthetic Metals*, **121**, 1187-1188, (2001)
- MacDonald, J. R., *Impedance Spectroscopy: Emphasizing solid materials and systems*, (Wiley, New York, 1987)

Maier, S, PhD Thesis, Trinity College Dublin, (2000)

Rao, C. N. R., Satishkumar, B. C., Govindaraj, A., *et al.* *ChemPhysChem*, **2**, 78-105, (2001)

Shelimov, K. B., Esenaliev, R. O., Rinzler, A. G., *et al.* *Chemical Physics Letters*, **282**, 429-434, (1998)

Shi, Z. J., Lian, Y. F., Liao, F. H., *et al.* *Solid State Communications*, **112**, 35-37, (1999)

Tsang, S. C., Harris, P. J. F. and Green, M. L. H. *Nature*, **362**, 520-522, (1993)

## Chapter 4

### 4.1 Introduction

A study of carbon nanotube soot and nanotube-polymer composites through electron spin resonance (ESR) will be presented in this chapter. The theory behind ESR and the experimental set-up is introduced. A brief review of the main nanotube ESR studies and results from the Scientific Literature is then discussed.

This chapter deals with quantification of the actual nanotube content in both as-produced soot and polymer composite samples. The results are presented in the following order. Firstly, the arc-discharge nanotube production technique was optimised to improve the purity of the as-produced nanotube soot and ESR was used to monitor the approximate purity of the samples. The technique was further developed allowing the exact purity of nanotube samples to be calculated whilst also eliminating the destructive element. The potential of two conjugated polymers to successfully purify nanotube soot samples is then compared and their relative merits are presented.

### 4.2 Electron Spin Resonance

Electron spin resonance (ESR) is a spectroscopic technique based upon the resonant absorption of microwave energy by flipping magnetic dipoles in the presence of a static magnetic field [Wertz]. Magnetic dipoles arise from net electronic angular momentum, primarily electron spin angular momentum. The presence of the magnetic field splits the otherwise degenerate levels into two allowed, quantised spin states. This is known as the Zeeman effect. If the sample is then irradiated with electromagnetic radiation of a suitable frequency, absorption due to magnetic dipole transitions may occur. This is the principle behind ESR.

When an unpaired electron (which has spin  $\frac{1}{2}$ ) is placed in a magnetic field ( $B_0$ ), there are only two possible energy states that it can occupy due to the Zeeman effect: highest energy when its magnetic moment ( $\mu$ ) lies antiparallel to the field and lowest energy when its magnetic moment lies parallel to the field. These two states are labelled by the spin quantum numbers  $m_s = \pm \frac{1}{2}$  respectively and the energy of each state is given by:



$$E = g\mu_B B_0 m_s \tag{4.1}$$

where  $g$  is the  $g$ -value which describes the local environment of the electron spin and  $\mu_B$  is the Bohr magneton which is the natural unit of electron magnetic moment. For an isolated free electron,  $g = 2.0023$ .

In order for transitions to occur, the quanta of the incident microwaves ( $h\nu$ ) must equal the energy splitting between these two levels and hence the condition for resonance is:

$$\Delta E = h\nu = g\mu_B B_0 \tag{4.2}$$

where  $h$  is Planck's constant and  $\nu$  is the microwave frequency. This is shown in Figure 4.1 and it is important to note that in the absence of a magnetic field there is no energy splitting and the spin states have the same degenerate energy. Also, the energy difference varies linearly with magnetic field. Unlike most spectroscopic techniques, it is more practical to use a fixed microwave radiation frequency and to vary the magnetic field by varying the current in an electromagnet.

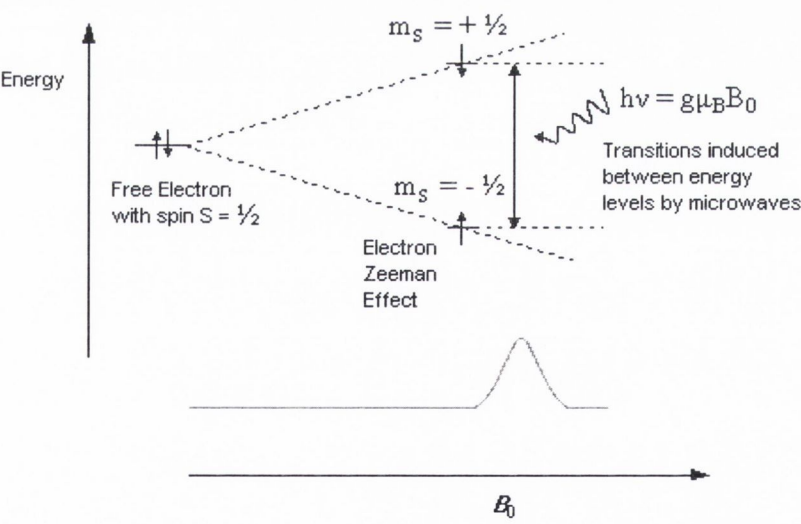


Figure 4.1: Microwave induced resonance between electron spin states in the presence of a magnetic field.

4.3 ESR Setup and Experimental

The spectrometer consists of a number of mains parts: the bridge, the magnet, the console and the cavity. Shown in Figure 4.2 are the parts of the bridge. The microwave source (A) is a klystron which operates on the principle of electron bunching. This is a vacuum tube well known for its low-noise characteristics. The spectrometer operates in the X-Band at a microwave frequency of approximately 9.75 GHz (which corresponds to a wavelength of about 32 mm). This must be tuned to the exact resonant frequency of the cavity before any measurements are performed to ensure that the cavity is an ideal absorber. The variable attenuator (B) varies the power level of the source microwaves. The circulator (C) ensures that the source microwaves only reach the sample in the cavity (D) and that only the reflected microwaves reach the detector diode (E). The detector operates at an optimum current of 150 mA and the reference arm (F) ensures that this level is maintained.

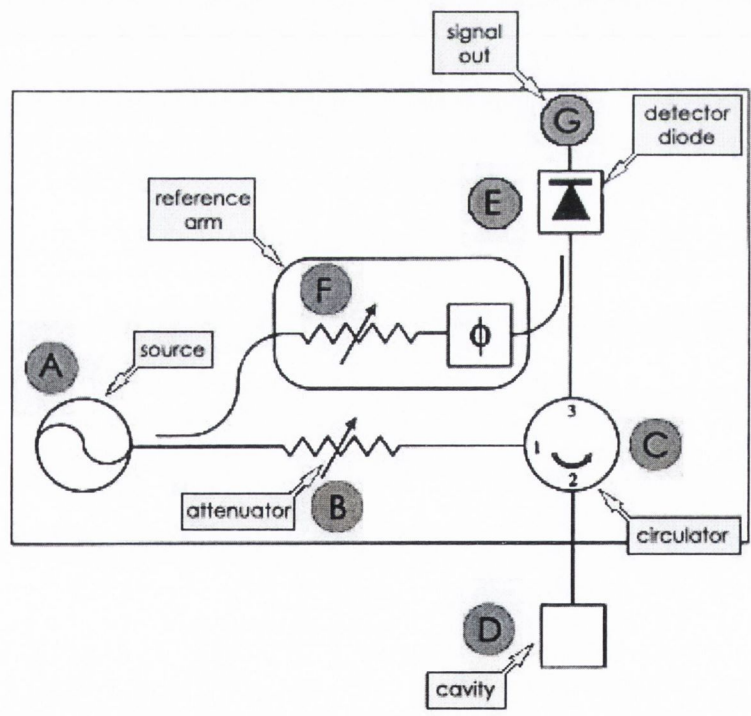


Figure 4.2: Block diagram of ESR bridge.

Field modulation is employed and so the first derivative of the spectrum is measured. Electron spin resonance measurements were made at room temperature using 100 kHz field modulation with a  $TM_{011}$  mode cavity. To avoid distortion of the spectrum, the modulation amplitude was kept at less than or equal to one third of the peak-to-peak linewidth. Calculation of g-values was carried out by comparison of the signal with that of a sample with known g-value, in this case, that of  $F^+$  centres in MgO with  $g = 2.0023$ . The field range was calibrated with a proton NMR probe that gave absolute field values. Changes in signal intensity related to changes in the Q factor, due to the presence of the (lossy) sample, were corrected for by using the measured attenuation of the MgO  $F^+$  signal in the presence of the sample. For a given paramagnetic species, the ESR signal intensity is proportional to the number of paramagnetic centres in the measured sample.

#### 4.4 Literature Review of ESR of Carbon Nanotube Systems

The most comprehensive ESR study on carbon nanotubes to date has been performed by Chauvet et al [Chauvet]. The samples consisted of aligned, ultrasonically filtered thin films of multi-walled nanotubes with diameters in the range  $10 \pm 5$  nm and average lengths of  $1\mu\text{m}$  similar to the MWNTs produced in Trinity. The ESR response of the nanotube samples displayed different behaviour above and below 40K.

All spectra consisted of a single Lorentzian line-shape above 40K. The spin susceptibility  $\chi_s$  was derived from the ESR signal strength and this remained temperature independent, signifying Pauli behaviour attributed to conduction electrons. This indicates that the nanotubes are either metallic or semi-metallic, as is expected for nanotubes with these diameters. From the Pauli susceptibility, the density of states at the Fermi level was calculated to be  $N(E_F) = 2.5 \times 10^{-3}$  states/eV/atom which is comparable to that of graphite [Yafet]. A crude estimate of the carrier density was then calculated using the Fermi energy of graphite (at 200K) to give  $n \sim 4 \times 10^{18} \text{ cm}^{-3}$ . This low density of carriers indicates that the nanotubes are more semi-metallic in nature than metallic. Below 40K, the signal line shape became progressively asymmetric. The spin susceptibility was measured to be inversely proportional to temperature indicating Curie behaviour. This is a signature of localised spins and hence localised carriers. This provided an estimate of



$1.3 \times 10^{18}$  localised spins  $\text{cm}^{-3}$ , similar to the Pauli value for free carriers in the semi-metallic nanotubes.

The  $g$ -values were measured for the nanotubes aligned both parallel and perpendicular to the magnetic field and were found to be  $g_{\parallel} = 2.0137$  and  $g_{\perp} = 2.0103$  respectively. This anisotropy originates from that of planar graphite where  $g_{ab} = 2.0026$  and  $g_c = 2.050$  [Wagoner]. Unlike their graphitic analogues however (where  $g_{ab} < g_c$ ), for nanotubes  $g_{\parallel} > g_{\perp}$  and this is attributed to the possibility of ring currents around the nanotube axis. Another point of note is that the  $g$ -value anisotropy for nanotubes  $\Delta g$  is much smaller than for graphite and this can be understood by considering the respective geometries. For a sample consisting of randomly oriented nanotubes, an average  $g$ -value can be calculated. The angular dependence of the  $g$ -value for one nanotube oriented at an angle  $\theta$  relative to the magnetic field can be written as:

$$g = \sqrt{(g_{\parallel} \cos \theta)^2 + (g_{\perp} \sin \theta)^2} \quad (4.3)$$

$$\approx g_{\parallel} + (g_{\perp} - g_{\parallel}) \sin^2 \theta$$

Therefore averaging over all possible angular orientations by substituting the average  $\langle \sin^2 \theta \rangle = \frac{1}{2}$  gives an average nanotube  $g$ -value of  $g_{\text{NT}} = 2.012$ . A similar analysis for graphite (or graphitic particles) produces an average  $g$ -value of  $g_{\text{GP}} = 2.018$ .

Likodimos et al [Likodimos] reported similar behaviour to Chauvet for MWNTs produced using the arc-discharge method. A transition from Pauli-like to Curie-like spin susceptibility was observed but at the lower temperature of 15K. The measured average room temperature  $g$ -value was  $g_{\text{NT}} = 2.0130(5)$  in good agreement with the previous study.

Zhang et al [Zhang] employed ESR to compare the quality of MWNTs produced by the arc-discharge technique with two different inert gases: helium and argon. The measured  $g$ -values for helium- and argon-produced nanotubes (at a pressure of 150 Torr) were  $g_{\text{HE}} = 2.0123$  and  $g_{\text{AR}} = 2.0206$  respectively. In conjunction with transmission electron

microscopy (TEM), the authors suggest that the He-nanotubes are well-graphitised and ordered unlike the disordered Ar-nanotubes. These reported g-values concur with those average values for MWNTs and graphitic particles of Chauvet.

A theoretical study on ESR in 1-D interacting metals with primary emphasis on carbon nanotubes was undertaken by De Martino and coworkers [De Martino]. By deriving the spin-orbit coupling, the resulting ESR spectrum was analysed. Major differences in the spectra for SWNTs and MWNTs were found. For SWNTs, spin-charge separation should not be affected by spin-orbit coupling and hence a double peak spectrum is expected. The peak splitting depends on the strength of the spin-orbit coupling. The prediction is limited however because no estimate for the expected splitting is provided. This could turn out to be negligible when compared to the resolution of a spectrometer.

For MWNTs, it was assumed that all conduction electrons contributing to the ESR signal reside on the outermost shells only. A single asymmetric spectrum is predicted at low temperatures ( $T < 20\text{K}$ ) which is in agreement with the measurements of Chauvet mentioned previously. As the temperature increases, the degree of symmetry increases and more structure appears. While the authors have not performed calculations for  $T > 40\text{K}$ , if this trend continues then one would expect to observe a single symmetric peak (such as a Lorentzian) at a finite temperature.

Coleman et al [Coleman<sup>1</sup>-Coleman<sup>4</sup>] performed the first ESR studies on both nanotube soot and also nanotube-polymer composite materials. Multi-walled nanotubes produced using the arc-discharge method in Trinity College were used. Measurements on the various components of the cathodic deposit from the generator revealed that integrated spectra for the inner-core soot consisted of two distinct Lorentzian curves. These were centred around g-values of  $g = 2.011$  and  $g = 2.020$  in close agreement with the average values for nanotubes and graphitic particles (GP) respectively, as calculated by Chauvet. The area under each Lorentzian curve is proportional to the number of spins present for each particular species. This allowed an estimate of the soot purity ( $I_{\text{ESR}}$ ) to be calculated

by taking the ratio of the normalised signal intensity (NSI) for the nanotube curve to that of the total signal. This can be written as:

$$I_{ESR} = \frac{NSI_{NT}}{NSI_{NT} + NSI_{GP}} \quad (4.4)$$

It is important to note that this ratio is representative of, but not exactly equal to the actual nanotube purity. This is due to the difference in magnetic spin susceptibility of nanotubes and graphitic particles.

Composites were produced using the same soot mixed into various polymer solutions such as polystyrene, dioctyl naphthalene and poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV). Stable suspensions were only obtained using PmPV. These suspensions were then allowed to settle for defined periods of time after which the supernatant was separated from the sediment by decantation. ESR was performed on both fractions (the sediment and the supernatant) and in each case the relative area of the nanotube and GP curves were compared (similar to the raw soot itself). This technique allows a quantitative estimate of the nanotube content in the supernatant and the sediment. It was discovered that the polymer PmPV preferentially suspends MWNTs in solution while GP tend to sediment out of solution. An optimum settling time of 48hours was found at which the majority of the GP had fallen out of solution while the MWNT fraction remained constant.

#### 4.5 Optimisation of the Arc Discharge Method

A general outline for the production of MWNTs using the arc-discharge method was described in Chapter 3. The particular parameters such as helium pressure and current density were originally discovered by trial and error to produce nanotube-containing soot. The actual quality of the product was not initially studied systematically and therefore not optimised.

The aim of this study was to optimise the nanotube production before addressing the issues of purification and composite production. The quality of the product was studied by TEM. The ESR method developed by Coleman et al [Coleman<sup>1</sup>-Coleman<sup>4</sup>] described



in the previous section allowed a quantitative estimate for the MWNT content of as-produced soot to be calculated.

The nanotube production was carried out by Martin Cadek according to the method detailed in Chapter 3. The potential difference was maintained at 23V while the current density was varied between  $J = 165\text{--}195\text{ A/cm}^2$  and the helium pressure was varied between  $P = 300\text{--}500\text{ Torr}$ . The yield for each run was defined as the mass of nanotube soot separated from the hard shell material divided by the production time. This is plotted in Figure 4.3 as a function of production parameters. Clearly, the yield increases as both current density and pressure increase with the largest value of 24 mg/min obtained for  $J = 190\text{ A/cm}^2$  and  $P = 500\text{ Torr}$ . At the other end of the scale, the lowest yield of 2.6 mg/min was produced with  $J = 165\text{ A/cm}^2$  and  $P = 300\text{ Torr}$ . While this suggests that nanotube production can be increased by increasing current density and pressure, no information about the actual microstructure of the nanotube soot can be obtained from this result alone.

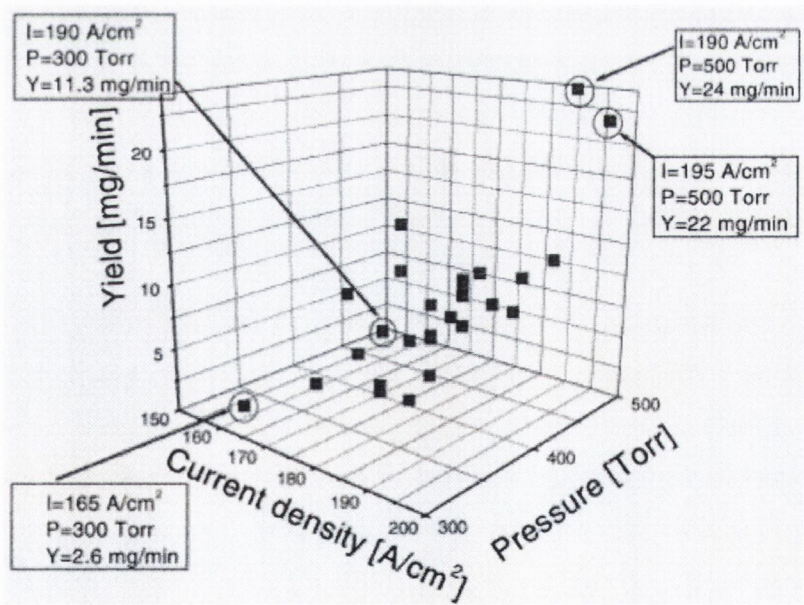


Figure 4.3: Nanotube yield as a function of the production parameters of current density and helium pressure.

TEM analysis was then performed on various soot samples representative of different yields (low, mid and high). Shown in Figures 4.4(a) and (b) are TEM images for the lowest (2.6 mg/min) and highest yield (24mg/min) samples respectively. It can be seen that there are relatively much fewer nanotubes in the low yield sample. It also appears that the few nanotubes present in Figure 4.4(a) are much shorter ( $L < 500\text{nm}$ ) than those in Figure 4.4(b). A similar trend was seen for the mid yield sample. This suggests that not only do increased current density and pressure lead to increased yields but also produce a higher purity product. One must be careful in drawing absolute quantitative conclusions from TEM images however as these pictures represent an area of only  $\sim 5 \mu\text{m}^2$ .

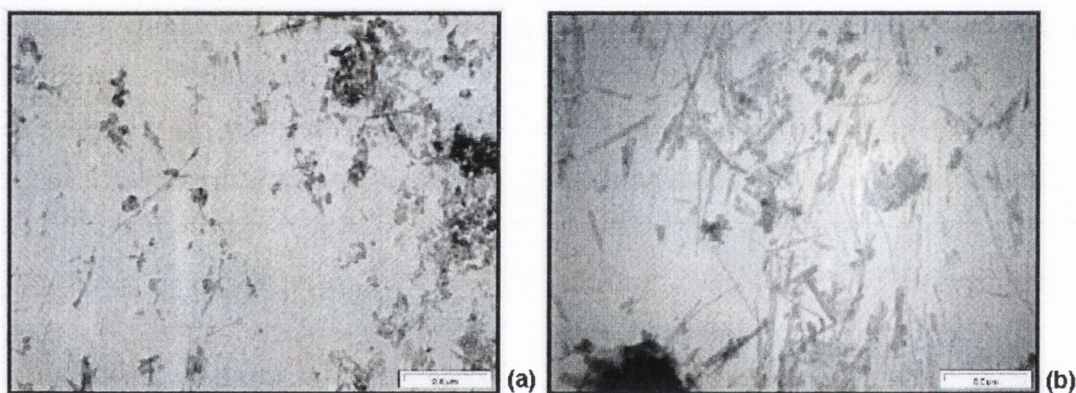


Figure 4.4: TEM images of the MWNT soot product produced using different production parameters: (a)  $J = 165 \text{ A/cm}^2$  and  $P = 300 \text{ Torr}$  with a low yield of  $2.6 \text{ mg/min}$  and (b)  $J = 190 \text{ A/cm}^2$  and  $P = 500 \text{ Torr}$  with a high yield of  $24 \text{ mg/min}$ . Scalebars are  $0.5\mu\text{m}$ .

ESR measurements were then performed on different soots representative of low, mid and high yields (see Figure 4.5). The spectra were integrated and two Lorentzian curves could be fitted in the manner of Coleman et al. These were centred around the g-values for nanotubes ( $g_{\text{NT}} = 2.012$ ) and graphitic particles ( $g_{\text{GP}} = 2.018$ ) corresponding to field strengths of approximately 3480G and 3465G respectively. The shoulder at the higher field value is indicative of the nanotube content in the soot. The area under the each Lorentzian curve is proportional to the number of spins present for that particular species. An estimate of the purity ( $I_{\text{ESR}}$ ) can be calculated by taking the ratio of the of the



normalised signal intensity (NSI) for nanotubes to that of the total signal. This can be written as:

$$I_{ESR} = \frac{NSI_{NT}}{NSI_{NT} + NSI_{GP}} \tag{4.4}$$

It is important to note that this ratio is representative of, but not exactly equal to the actual nanotube purity. This is due to the difference in magnetic spin susceptibility of nanotubes and graphitic particles. Using this number as an indicator of approximate nanotube purity, values of 35% and 55% were calculated for low ( $Y = 8.7\text{mg/min}$ ) and high ( $Y = 22\text{mg/min}$ ) yield samples respectively.

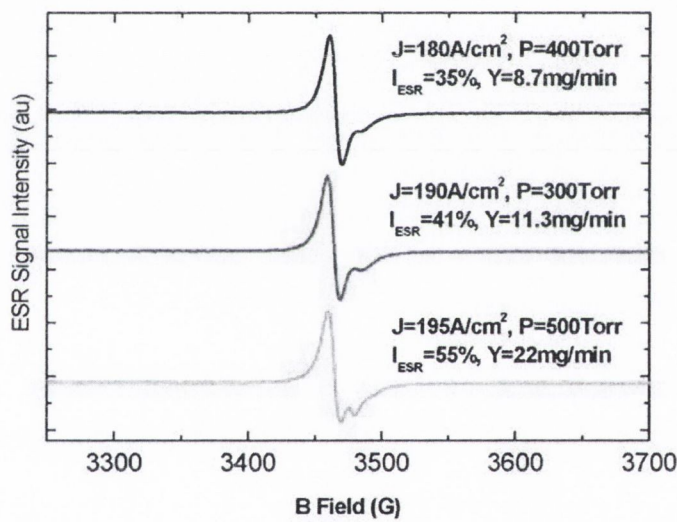


Figure 4.5: ESR derivative spectra for MWNT soot products produced using different production parameters. The shoulder at 3480G is indicative of nanotubes.

While the  $I_{ESR}$  values over-estimate purity, they can be compared directly with one another as they follow the same trend as the actual purity. It will be shown in the next section that by calculating the actual purity, these  $I_{ESR}$  estimates generally agree within 15%. It can clearly be seen from Figure 4.5, that the purity increases with increasing current density and pressure in production (as was suggested by TEM analysis). The optimal production parameters were found to be  $J = 190 \text{ A/cm}^2$  and  $P = 500 \text{ Torr}$ . A yield



of up to 24mg/min has been achieved with an approximate MWNT purity of 55%. Refinement of this value in the next section reduces this value to an actual purity of 48% but this is still the highest known figure for any as-produced arc-discharge MWNT soot to date.

The next issue to address is purification of the soot to increase this value further. A purification method is developed in the next section. This involves using a conjugated polymer to selectively suspend MWNTs and through a combination of ESR and Thermogravimetric analysis (TGA), an actual purity of nanotube soot can be calculated.

#### **4.6 PmPV Results and Discussion**

In order to purify MWNT soot and also to determine the actual nanotube purity, a range of PmPV composites were prepared for ESR study. Details of the sample preparation are given in section 3.4. By varying the polymer to MWNT soot ratio, an optimum value could be obtained for nanotube purification. All of the relevant numerical values used or calculated in this work are given in Table 4.1.

A typical set of derivative spectra for a composite material is shown in Figure 4.6. The MWNT soot curve (A) clearly consists of two components. In contrast, the sediment (B) and solute (C) curves appear to be dominated by one component each as was previously observed by Coleman et al [Coleman<sup>1</sup>]. Curve (D) will be discussed later on. For each sample, these spectra were integrated and in all cases could be deconvoluted into two Lorentzian curves centred about g values associated with MWNTs and GP. The area under each curve is a measure of the total number of spins present in each species and is referred to simply as the ESR signal.

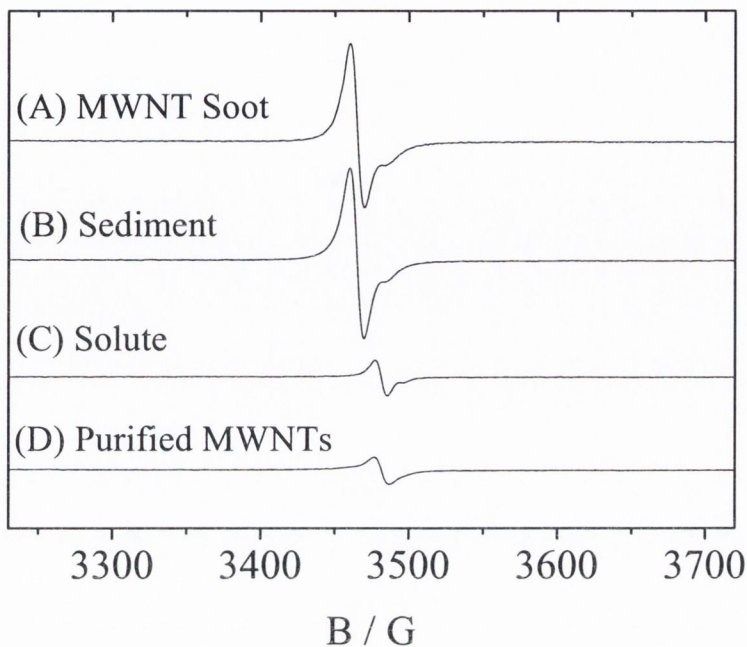


Figure 4.6: ESR derivative spectra of (A) original MWNT Krätschmer generated soot, (B) the sediment from a typical PmPV composite formed after 48 hours settling time, (C) a drop cast film made from the solute of a typical PmPV composite formed after 48 hours settling time and (D) the polymer-free, 91% pure MWNTs. In the first two spectra two components, MWNT and GP, are present. The last two spectra consist almost solely of the MWNT component.

|    |                                                    | Composite1            | Composite2             | Composite3             | Composite4             | Composite5             |
|----|----------------------------------------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| 1  | Mass PmPV, $M_{poly}$ (mg)                         | 20.4                  | 79.9                   | 100.0                  | 130.9                  | 160.7                  |
| 2  | Mass MWNT Soot, $M_{SOOT}$ (mg)                    | 20.3                  | 20.3                   | 20.3                   | 20.1                   | 20.6                   |
| 3  | Sediment Mass (mg)                                 | 18.8                  | 18.8                   | 18.3                   | 16.6                   | 18.5                   |
| 4  | Solute Mass (mg)                                   | 21.9                  | 81.4                   | 102                    | 134.4                  | 162.8                  |
| 5  | Percentage of MWNTs in Solution, $P_{NTsol}$ (%)   | 19                    | 40                     | 50                     | 47                     | 50                     |
| 6  | Percentage of GP in Solution,, $P_{GP sol}$ (%)    | 1.9                   | 2.0                    | 3.2                    | 2.8                    | 5.0                    |
| 7  | Percentage of Solute by mass due to MWNTs & GP (%) | 6.4                   | 3.6                    | 3.6                    | 3.2                    | 2.7                    |
| 8  | Mass MWNTs in Solution (mg)                        | 1.1                   | 2.6                    | 3.2                    | 4.0                    | 3.7                    |
| 9  | Mass GP in Solution (mg)                           | 0.27                  | 0.28                   | 0.44                   | 0.32                   | 0.66                   |
| 10 | Mass MWNTs in Soot (mg)                            | 5.9                   | 6.4                    | 6.5                    | 8.6                    | 7.5                    |
| 11 | $k_{NT}$ (mg)                                      | $8.4 \times 10^{-12}$ | $11.0 \times 10^{-12}$ | $12.0 \times 10^{-12}$ | $16.4 \times 10^{-12}$ | $12.8 \times 10^{-12}$ |
| 12 | $k_{GP}$ (mg)                                      | $8.4 \times 10^{-12}$ | $7.6 \times 10^{-12}$  | $8.3 \times 10^{-12}$  | $6.4 \times 10^{-12}$  | $6.4 \times 10^{-12}$  |
| 13 | Purity (%)                                         | 29                    | 32                     | 32                     | 43                     | 36                     |

Table 4.1: Summary of the data obtained in the PmPV work. Rows 1-2 contain the masses of the initial ingredients while rows 3-4 contain the masses of the sediment and solute after 48 hours settling, respectively. Rows 5-6 contain the percentage of MWNTs and GP held in solution calculated using ESR and row 7 contains the percentage of the solute by mass due to carbonaceous materials calculated from TGA. Rows 8-10 contain the mass of MWNTs, GP held in solution and the mass of MWNTs in the soot calculated by combining ESR results with TGA. The last three rows contain the ESR/Mass proportionality constants for MWNTs and GP, and the purity of the soot used in each sample, respectively.

For each solute film, the ESR signal obtained was initially normalised to represent 1 mg of that solute. This signal was then multiplied by the total mass of the solute to give the normalised signal intensity (NSI) that one would obtain from a measurement of the whole solute. Similarly, for each composite, the two sediment signals were averaged and the



NSI for the entire sediment was calculated. Because the solute and sediment signals were normalised, the sum of their MWNT (and GP) components must represent 100% of the MWNTs (and GP) available. Hence, by direct comparison of the solute and sediment NSIs for MWNTs (and GP), the percentage of MWNTs (and GP) held in solution (and in sediment) were calculated using Eqn (4.5) (or similar for GP).

$$P_{NTsol} = 100 \times \frac{NSI_{NTsol}}{(NSI_{NTsol} + NSI_{GPsol})} \quad (4.5)$$

It was previously shown [Coleman<sup>5</sup>] that the intensity of each normalised Lorentzian (NSI<sub>i</sub>) is proportional to the mass of the species present (M<sub>i</sub>) allowing us to write an equation of the form:

$$M_i = k_i (NSI_i) \quad (4.6)$$

where  $k_i$  is a proportionality constant related to the magnetic spin susceptibility. It should be noted that the  $k$  values for MWNTs and GP are expected to be different from one another.

The percentage of MWNTs held in solution ( $P_{NTsol}$ ) was calculated for each composite and is shown in Figure 4.7 as a function of increasing polymer mass. For equal parts polymer and MWNT soot, only about 20% of the available MWNTs remain suspended in solution. As the amount of polymer is increased so too does the percentage of MWNTs held in solution. This appears to saturate however, above approximately 80 mg of PmPV used. The saturation occurs at approximately 50% of the available MWNTs being held in solution. This could indicate that the PmPV has a preference for certain types or sizes of MWNT and not for others e.g. certain outer shell diameters, lengths etc. Raman spectroscopy performed on low concentration SWNT-PmPV composites [Dalton] has shown preferential selection of SWNTs according to their diameters. Previous results on PmPV holding 63% of available MWNTs show that this figure is batch dependent [Coleman<sup>1</sup>]. Similarly, the percentage of GP held in solution ( $P_{GPsol}$ ) was calculated for each composite and is relatively small with a maximum value of 5% being calculated for the 160 mg polymer sample.

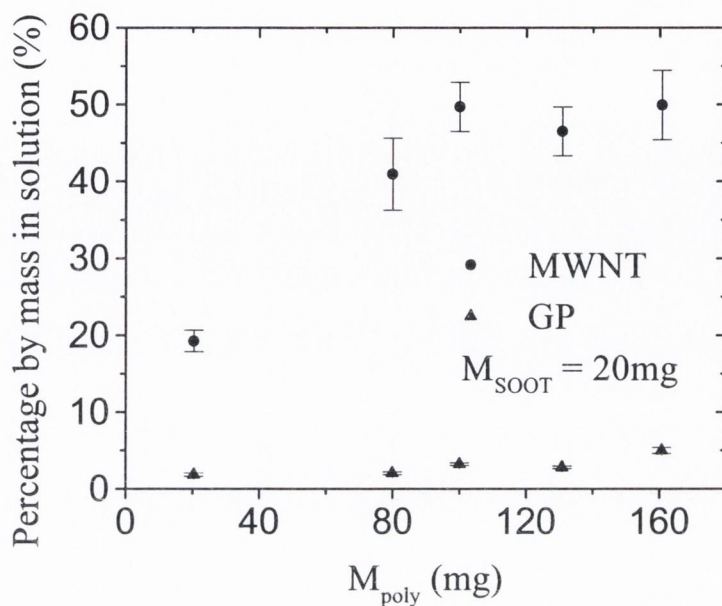


Figure 4.7: Percentage of MWNTs and GP held in solution versus mass of PmPV, calculated using ESR.

To calculate the total mass of MWNTs ( $M_{\text{NT}}$ ) and GP ( $M_{\text{GP}}$ ) in the MWNT soot, Thermogravimetric analysis (TGA) was performed on a dried film of each decanted composite solute. The curve for PmPV alone, as shown in Figure 4.8, shows that virtually the entire polymer is oxidised by 650°C.

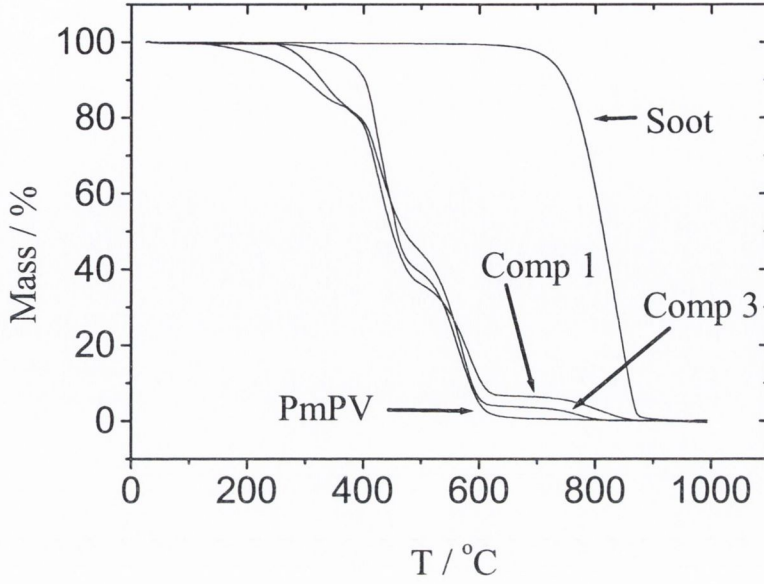


Figure 4.8: TGA curves for PmPV, the original MWNT soot and two typical composite films of different mass fractions. The PmPV oxidises completely before 650°C whereas the carbon soot only begins to burn at 700°C. For the composite films there is no oxidisation between these temperatures which allows the mass of MWNTs in the samples to be calculated.

However, for composite solutes, the films clearly have a shoulder above 650°C which is due to the MWNTs and GP in the film. From this shoulder the percentage by mass of the solute which is carbonaceous material (mostly MWNTs with a small amount of GP) is known. Since the total mass of the solute is known then the total mass of carbonaceous materials in solution ( $M_{\text{CARBONsol}}$ ) can be found. From ESR the percentages of MWNT and GP in solution can be calculated (using Eqn (4.5)). Therefore the masses of carbonaceous materials in solution from the ESR and TGA results can be equated to give:

$$\left(\frac{P_{\text{NTsol}}}{100}\right)(M_{\text{NT}}) + \left(\frac{P_{\text{GPsol}}}{100}\right)(M_{\text{GP}}) = M_{\text{CARBONsol}} \quad (4.7)$$

The initial mass of the MWNT soot in each sample is also known ( $M_{\text{SOOT}}$ ):

$$M_{\text{NT}} + M_{\text{GP}} = M_{\text{SOOT}} \quad (4.8)$$



Hence the two unknowns  $M_{NT}$  and  $M_{GP}$  could be calculated for each sample allowing an average purity of the MWNT soot used in this experiment to be calculated as 34% in good agreement with previous measurements [Wildöer]. This value is supported by a TEM image of the raw MWNT soot as shown in Figure 4.9 demonstrating large amounts of GP present. While an average purity has been stated, the purity of soot used in each composite varied from 29% to 43% (Table 4.1), suggesting significant soot inhomogeneity on a macroscopic scale.

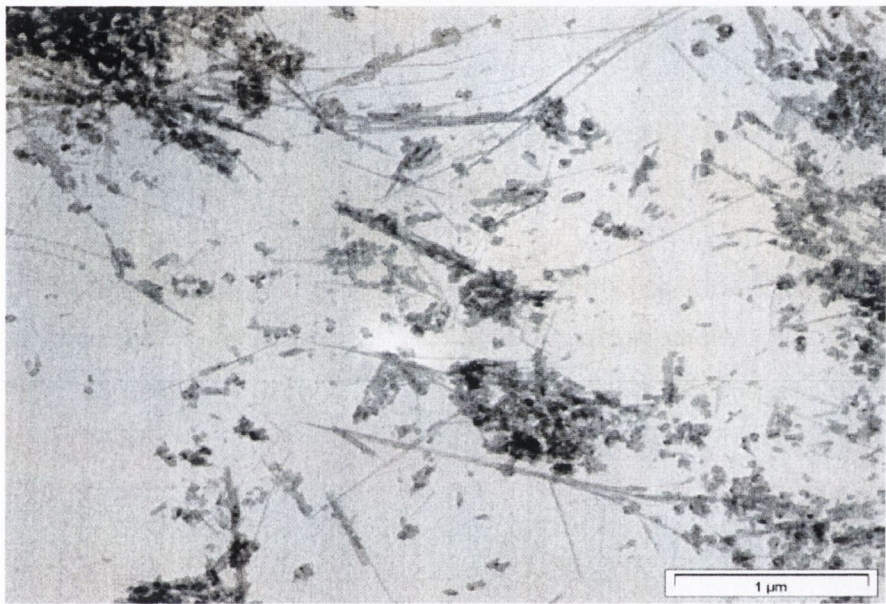


Figure 4.9: TEM image of the original untreated MWNT soot.

Knowing  $M_{NT}$  and  $M_{GP}$  for each sample, the masses of MWNTs and GP held in each solution,  $M_{NTsol}$  and  $M_{GPsol}$  respectively, were calculated for each sample, simply as the first two terms in Eqn (4.7). These masses are both shown in Figure 4.10 versus increasing polymer mass. The trend of Figure 4.7 appears evident with the mass of MWNTs held in solution increasing until it saturates at approximately 4 mg of nanotubes being held in solution. As previously mentioned, the soot was quite inhomogeneous which would account for the fact that the saturation in mass is not as level as that shown in Figure 4.7. The mass of GP held in solution is quite small compared to the MWNTs. In fact, the smallest mass ratio of MWNT:GP in a purified solution is still a factor of ten greater than that for the crude soot.

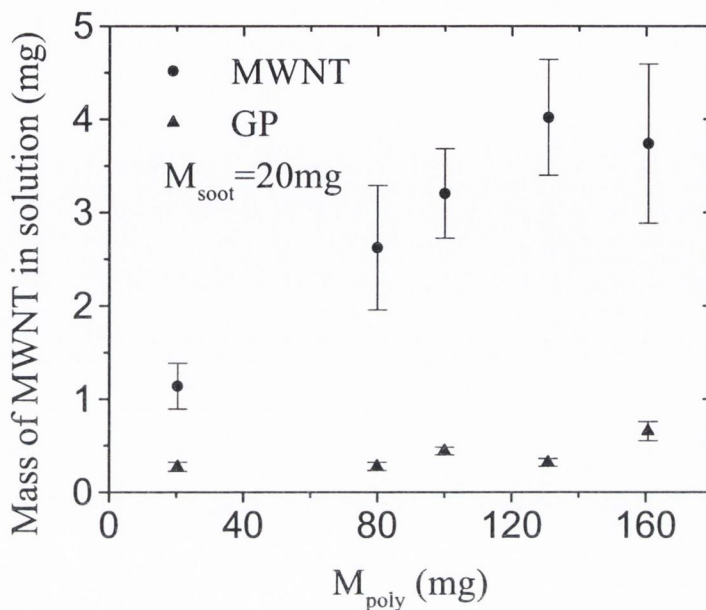


Figure 4.10: Mass of MWNTs and GP held in solution versus mass of PmPV, calculated by combining ESR with TGA.

These results also allowed us to calculate the normalised ESR signal intensity to mass proportionality constants ( $k_i$ ) for MWNTs and GP. For each solute both  $NSI_{NTsol}$  and  $NSI_{GPsol}$  are known. Combining these with the calculated masses of MWNTs and GP in a given solute ( $M_{NTsol}$  and  $M_{GPsol}$  respectively), the proportionality constants could be calculated using Eqn (4.6). These were found to be  $k_{NT} = (12.1 \pm 2.8) \times 10^{-12}$  mg and  $k_{GP} = (7.4 \pm 0.9) \times 10^{-12}$  mg. These constants allow us to calculate the mass of MWNTs and GP in a sample solely from an ESR spectrum and hence the purity of the sample. This removes the need to perform TGA and so is a completely non-destructive quantification process. These numbers were also calculated using a different PmPV/MWNT composite made from different batches of both PmPV and MWNT soot and are as follows:  $k_{NT} = (13.5 \pm 2.3) \times 10^{-12}$  mg,  $k_{GP} = (8.8 \pm 1.5) \times 10^{-12}$  mg. These results show that these numbers are constant within experimental error and so are due to fundamental properties of MWNTs and GP respectively, rather than being batch dependent. Hence, in future the MWNT content, by mass, of MWNT soot or of any



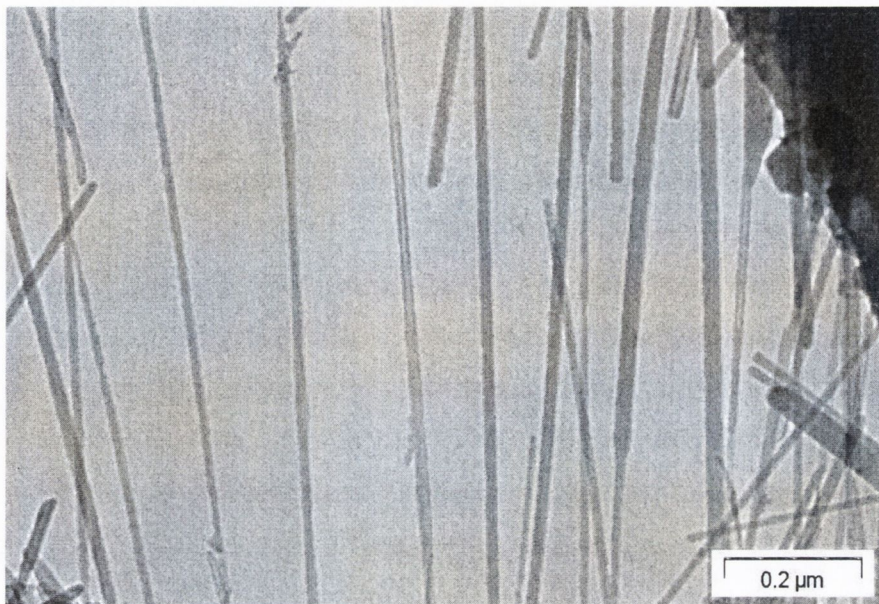
composite can be calculated solely from ESR measurements (a non-destructive process) without having to perform TGA (a destructive process) on the sample. However, it should be noted that these constants are spectrometer dependent, but once calculated for a particular machine, eliminate the need for TGA.

As described in section 3.4, the polymer was removed from the purified composites by Buchner filtration. ESR was then performed on the purified residue from the Teflon filter. The signal obtained is the curve (D) shown in Figure 4.6 and was dominated by a single Lorentzian due to MWNTs. This is quite unlike the original MWNT soot signal where the GP component was dominant. The mass of GP present in this residue was calculated with Eqn (4.6) using the calculated  $k_{GP}$  and the normalised ESR signal intensity for the measured GP Lorentzian. Hence, the total mass of MWNT present in the residue was calculated giving a purity of  $91 \pm 2\%$ , in good agreement with the calculated masses of MWNT and GP in solution given in Table 4.1.

It should be noted that the purified solution was separated from the sediment by decantation in order to facilitate the numerical analysis. However, the final purity of the reclaimed MWNT residue can be further increased by carefully pipetting the required volume of solution from the top of the sample bottle. This is because no definite interface between sediment and solute exists in real systems, but rather a continuous distribution, with sediment concentration decreasing exponentially with the distance from the bottom of the sample container [Hunter]. Sacrificing the bottom part of the solution avoids the tail of this distribution and also any disturbance of the settled sediment, resulting in GP levels below the level of detection of the ESR spectrometer.

This purified residue was further investigated using transmission electron microscopy (TEM). Shown in Figure 4.11 is a TEM image that was representative of this residue. A large number of clean, polymer-free MWNTs can be seen with hardly any trace of GP. This can be compared with Figure 4.9 of the initial soot showing large quantities of graphitic impurities in addition to the MWNTs.





*Figure 4.11: TEM image of the PmPV-free MWNTs.*

It has been shown that for MWNT soot with an average purity of 34%, when mixed with PmPV, up to half of the available nanotubes are suspended in solution. These results show that for every 100 mg of soot treated in this way, approximately 17 mg of highly pure, pristine nanotubes can be extracted. However, this process is far from optimised. The results presented in the previous section show that soot containing up to 50% MWNT by mass, can be routinely produced by the arc-discharge method [Cadek]. In addition, previous results have demonstrated that 63% of available MWNTs can be extracted for a different batch of PmPV. This suggests the possibility of tailoring the polymer to disperse seventy or even eighty percent of the MWNTs present. In this event, it would be possible to extract up to 40 mg of high quality MWNTs from every 100 mg of soot. This extremely high yield is complemented by the possibility of re-use of both polymer and solvent and the non-destructive nature of the technique. Thus this process paves the way for the large-scale production of highly pure, untainted carbon nanotubes for ‘real world’ applications.

#### 4.7 PFO results and Discussion

As described in the previous section, the polymer PmPV selectively suspends MWNTs in solution while allowing non-nanotube impurities to sediment over time. This procedure has a very useful and practical application in nanotube purification. It also produces novel composite materials that have been studied for electrical [Coleman<sup>6</sup>, Kilbride], optoelectronic [Fournet] and optical applications [O' Flaherty].

There are some drawbacks however with this polymer. First, the material was produced in small quantities in Trinity College only (as described in section 3.2). These batches are much smaller than required for large-scale applications such as MWNT purification and hence availability is an issue. Second, as was seen in the previous section, the polymer only suspended a maximum of 50% of the available nanotubes present. In order to try and increase this figure and also to address the problem of availability and economy, an alternative commercially available polymer could act as a solution.

It was believed that the conjugation in PmPV is important in the formation of a stable suspension with MWNTs due to  $\pi$ - $\pi$  interactions and therefore another conjugated polymer was selected. Initial results demonstrated that the polymer poly(9,9-di-n-octylfluorenyl-2,7'-diyl) (PFO) (monomer structure shown in Figure 2.8) could produce such stable suspensions and was therefore chosen for further study. A settling study to determine the optimum sedimentation time was performed (similar to that performed for PmPV by Coleman et al [Coleman<sup>1</sup>]) and the sample preparation is described in section 3.4. The experimental data are presented in Table 3.2. ESR was then performed in the same manner as for PmPV and the spectra for a typical soot, sediment and dried solute are shown in Figure 4.12. The main features are the same as for the PmPV composites (see Figure 4.6). Two phases are present in the MWNT soot and the sediment and solute appear to contain predominantly one or the other of these. A broad shoulder appears in the sediment curve at the high field value of approximately 3480G indicating the sedimentation of a sizeable fraction of the MWNTs in the original soot.

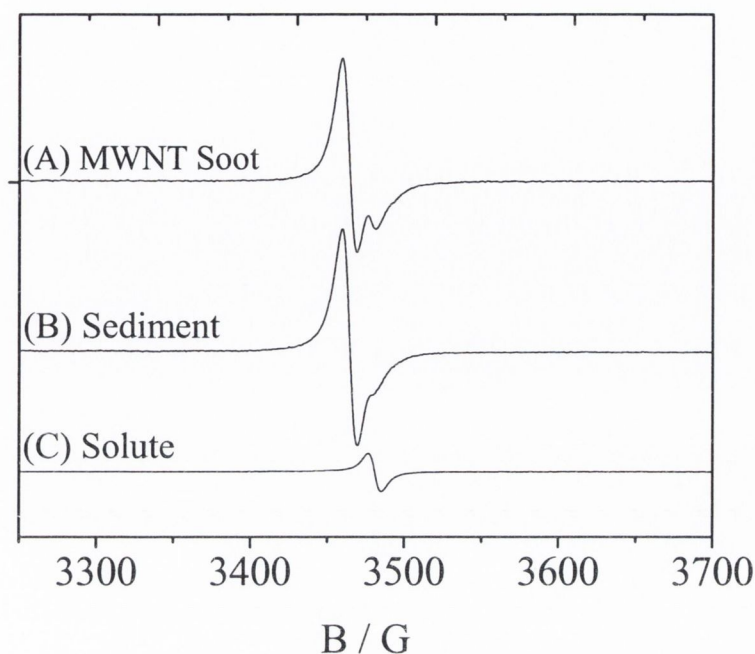


Figure 4.12: ESR derivative spectra of (A) original MWNT Krätschmer generated soot, (B) the sediment from a typical PFO composite formed after 96 hours settling time, (C) a drop cast film made from the solute of a typical PFO composite formed after 96 hours settling time.

The numerical analysis was similar to that for PmPV and the results for the various PFO composites are shown in Figure 4.13 as a function of settling time. It is quite apparent that the amount of graphitic particles (GP) held in solution falls dramatically over time, from 27% after 0.5 hours to under 4% after 96 hours. The nanotubes however appear much more stable in solution falling from 55% after 0.5 hours to just 35% after 96 hours. In fact the 96 hour solution remained stable over a period of months with no additional sediment forming. These settled solutions are quite rich in nanotubes similar to PmPV but contain more graphitic impurities than the latter.



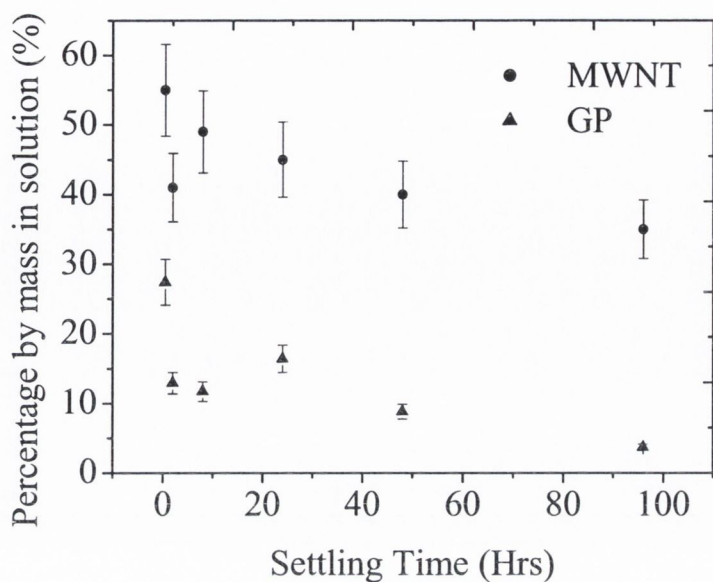


Figure 4.13: Percentage of MWNTs and GP held in PFO solution versus sedimentation time.

The supernatant decanted from the 96-hour settled sample was diluted and filtered using a Buchner funnel to remove the polymer as described in section 3.4. The residue was recovered and was further investigated by microscopy. Figure 4.14(a) shows a TEM image of the PFO-free residue obtained using Buchner filtration. This differs from the PmPV-free nanotube residue because of the presence of large quantities of nanoparticles along with nanotubes. Nanoparticles attached to an individual nanotube are also shown in an atomic force microscopy (AFM) image (Figure 4.14(b)) of the residue. These particles appear to be approximately spherical and their maximum diameter as estimated from TEM images is approximately 100 nm.

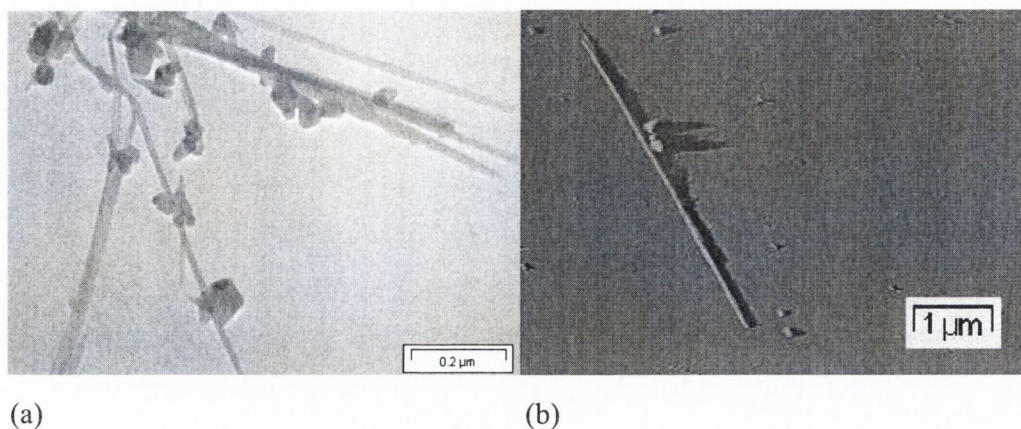


Figure 4.14: (a) TEM image and (b) AFM image of PFO-free residue showing nanotube(s) along with other nanoparticles.

By combining ESR and TGA and using Eqns (4.7) and (4.8), the solute was determined to consist of 90% by mass of nanotubes and 10% by mass of impurities. This figure is similar to that obtained for PmPV but the main difference lies in the nature of the impurities in each case. From TEM, the PFO impurities consist mainly of small spherical nanoparticles. Assuming an average MWNT diameter and length of 17nm and 2μm respectively, and that the average diameter of impurity nanoparticles is similar to that of the nanotubes (as estimated from TEM), then it can be calculated that there are approximately 13 nanoparticles per nanotube. Therefore, while the mass of the composite solute is mainly due to nanotubes, the number density of nanoparticles far exceeds that of the nanotubes.

The difference between the PFO residue and that for PmPV can possibly be explained by the structure of the polymers themselves. It has been conjectured previously that PmPV can map onto the chiral structure of nanotubes [McCarthy]. There is no tendency however to attach to nanoparticles. The backbone of the PFO monomer consists of two six membered rings connected by a pentagon. This is exactly the type of structure expected to provide the curvature needed for closure of graphitic nanoparticles. It is therefore likely that the PFO backbone can bind efficiently to the graphitic nanoparticles present in the crude soot. Both polymers disperse nanotubes well but the additional

presence of nanoparticles in the PFO composites means that this polymer is not ideal for the purification of crude MWNT soot.

These PFO composites are fundamentally interesting in their own right and have other potential applications in electronic and/or optical engineering. O’Flaherty et al [O’Flaherty] produced MWNT composites using both PmPV and PFO which acted as efficient optical limiters and the magnitude of the light pulse dissipation is comparable with the most efficient phthalocyanine compounds. Furthermore, angular dependent scattering studies of these composites could clearly differentiate between the contributions of nanotubes and graphitic nanoparticles. Theoretically, Mie scattering is expected for particles with one or more dimensions greater than or equal to the wavelength of the incident light (such as nanotubes with length  $\sim 2000\text{nm}$ ). Alternatively, Rayleigh scattering is expected for particles with dimensions smaller than the wavelength of the incident light (such as spherical nanoparticles with diameter  $< 100\text{nm}$ ). In the case of PmPV, an almost exclusive Mie behaviour was observed whereas for PFO composites a considerable Rayleigh component was also observed. This confirms the composition of the two polymer composites and that the scattering technique can provide further information about the shape and size of the inclusions than is possible by ESR.

#### 4.8 Conclusions

In summary, the arc-discharge method for producing MWNT soot was optimised and the approximate purity of the soot was monitored using ESR. It has been shown that multi-walled carbon nanotubes can be effectively purified using a conjugated organic polymer (PmPV) to selectively suspend MWNTs relative to graphitic impurities. The fraction of available MWNTs (or GP) suspended can be measured using ESR. This rises with increasing polymer mass before saturating at approximately 50% by mass with only trace amounts of GP remaining in solution. The actual mass of MWNTs and GP in solution can be measured using TGA. In conjunction with ESR this allows the total mass of MWNTs and GP in the original soot to be calculated giving its purity. Furthermore we can use this data to define and determine proportionality constants relating species mass (MWNT or GP) to ESR signal intensities, eliminating the destructive element (TGA) from the



characterisation process. Finally the polymer was removed from the purified composite solutions by Buchner filtration, resulting in a 91% pure nanotube product. Optimisation of this technique could ultimately lead to a yield of up to 40 mg of pristine MWNTs from every 100 mg of soot.

It has also been demonstrated that a second polymer, PFO, can suspend MWNTs effectively with an optimum settling time of 96 hrs. However, PFO also suspends graphitic nanoparticles with a maximum diameter of approximately 100 nm which can be attributed to the structure of the polymer itself.

## References

- Cadek, M., Murphy, R., McCarthy, B., *et al. Carbon*, **40**, 923-928, (2002)
- Chauvet, O., Forro, L., Bacsá, W., *et al. Physical Review B*, **52**, R6963-R6966, (1995)
- Coleman<sup>1</sup>, J. N., O'Brien, D. F., Dalton, A. B., *et al. Chemical Communications*, 2001-2002, (2000)
- Coleman<sup>2</sup>, J. N., Dalton, A. B., Curran, S., *et al. Advanced Materials*, **12**, 213, (2000)
- Coleman<sup>3</sup>, J. N., O'Brien, D. F., Dalton, A. B., *et al. Journal of Chemical Physics*, **113**, 9788-9793, (2000)
- Coleman<sup>4</sup>, J. N., O'Brien, D. F., Panhuis, M. I. H., *et al. Synthetic Metals*, **121**, 1229-1230, (2001)
- Coleman<sup>5</sup>, J. N., Dalton, A. B., McCarthy, B., *et al. Proceedings of the MRS Fall Meeting*, Boston, USA, (2001)
- Coleman<sup>6</sup>, J. N., Curran, S., Dalton, A. B., *et al. Physical Review B*, **58**, R7492-R7495, (1998)
- Dalton, A. B., Stephan, C., Coleman, J. N., *et al. Journal of Physical Chemistry B*, **104**, 10012-10016, (2000)
- De Martino, A., Egger, R., Murphy-Armando, F., *et al. Journal of Physics-Condensed Matter*, **16**, S1437-S1452, (2004)
- Fournet, P., Coleman, J. N., Lahr, B., *et al. Journal of Applied Physics*, **90**, 969-975, (2001)

- Hunter, R. J. *Introduction to Modern Colloid Science*, (Oxford University Press, Oxford, 1993)
- Kilbride, B. E., Coleman, J. N., Fraysse, J., *et al. Journal of Applied Physics*, **92**, 4024-4030, (2002)
- Likodimos, V., Glenis, S., Guskos, N., *et al. Physical Review B*, **68**, 045417, (2003)
- McCarthy, B., Coleman, J. N., Czerw, R., *et al. Journal of Physical Chemistry B*, **106**, 2210-2216, (2002)
- O'Flaherty, S. A., Murphy, R., Hold, S. V., *et al. Journal of Physical Chemistry B*, **107**, 958-964, (2003)
- Wagoner, G. *Physical Review*, **118**, 647, (1960)
- Wertz, J. E. and Bolton J. R., *Electron Paramagnetic Resonance* (Chapman and Hall, New York 1986)
- Wildoer, J. W. G., Venema, L. C., Rinzler, A. G., *et al. Nature*, **391**, 59-62, (1998)
- Yafet, Y in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic, New York, 1963)
- Zhang, H. Y., Liu, S. H., Wei, A. X., *et al. Journal of Physics and Chemistry of Solids*, **61**, 1123-1125, (2000)

## Chapter 5

### 5.1 Introduction

In this chapter, the electrical properties of various composites of carbon nanotubes dispersed in an insulating polymeric matrix are studied. The effect of varying the nanotube volume fraction and the formation of a percolating network will be discussed. The conductivity percolation parameters themselves will be discussed and a model based upon the concept of *excluded volume* will be presented to predict these. Temperature and electric field dependent conductivity measurements are presented and based upon these results, possible charge transport conduction mechanisms are considered.

### 5.2 Percolation Theory

#### *Introduction to Percolation*

Percolation theory provides a satisfying model to describe spatially random processes in a wide range of physical phenomena. The most important aspect of the traditional model is the presence of a well-defined, sharp phase transition at which long-range connectivity first appears. Examples of these transitions range dramatically from the propagation of star formation in supernovae as a function of interstellar gas density; the containment to outbreak of disease in a population; the liquid-gel transition in polymer gelation; and the glass transition in amorphous materials as a function of temperature [Zallen].

The main transition that concerns the present study is that of the insulator-conductor transition in composite materials which occurs at critical conducting filler volume fraction known as the percolation threshold,  $p_c$ . At this volume fraction, a spanning cluster appears for the first time and many physical properties (e.g. electrical and thermal conductivity) become critical. This is illustrated in Figure 5.1 for the conductivity of a composite containing conductive rods. At filler volume fractions  $p \ll p_c$ , no extended connectivity exists and the conductivity is that of the insulating matrix itself (region (A)). The addition of an extra rod in this regime will increase the spanning size of a cluster of rods but no continuous network will yet occur and no increase in conductivity is measured. For large  $p \gg p_c$  a fully connected network of conductive pathways exists and



macroscopically measurable conduction can take place (region (C)). The addition of an extra rod does not increase the conductivity dramatically since a large number of pathways exist already. The interesting region is that labelled (B) for volume fractions  $p \sim p_c$ . In this regime, the addition of an extra rod has a large effect on the macroscopic response because previously isolated large clusters of rods now become connected and continuous networks first appear allowing a large conductivity to occur.

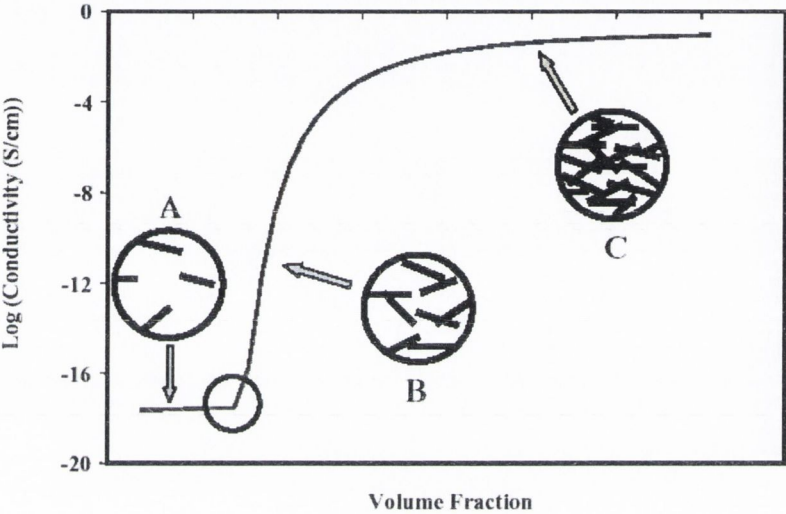


Figure 5.1: Typical conductivity versus volume fraction curve displaying the onset of percolation for a system of conducting sticks. A completely unconnected network exists at (A) while a fully extended network exists at (C). A drastic increase in conductivity occurs around the percolation threshold  $p_c$  where long range connectivity first begins to appear as illustrated at (B).

Because the growth in conductivity is rapid just above the percolation threshold a variety of expressions have been proposed to model the response such as power laws and exponential functions [Stauffer, Shklovskii]. It has been found empirically that this response can be well described by the following power law (for  $|p-p_c| \ll 1$ ):

$$\sigma = \sigma_0 (p - p_c)^t \tag{5.1}$$

where  $\sigma_0$  is a conductivity prefactor and  $t$  is a critical exponent. The physical significance of these fitting parameters is not very well understood. Experiments involving insulating and conductive spheres on regular lattices have reported constant values of  $t = 1.3$  and  $t =$

2.0 in 2 and 3 dimensions respectively [Sahimi]. These values hold for these regular systems but their universality does not transfer to more complicated systems as will be discussed in the following section. The significance of  $\sigma_0$  is not fully understood either. It has been suggested that  $\sigma_0$  equals the intrinsic conductivity of the filler since mathematically,  $\sigma = \sigma_0$  when  $p = 1$  (since  $p_c \ll 1$ ). Physically this does not make sense as the system would no longer be a composite and also the criterion for Eqn (5.1) ( $|p - p_c| \ll 1$ ) would not be obeyed. Setting these complications aside for now however,  $\sigma_0$  and  $t$  could simply be accepted as fitting parameters with no physical significance but the same cannot be said of the percolation threshold  $p_c$ . As explained above, this does have a very real and important meaning.

One of the less well established points of classical percolation theory concerns the ability to accurately predict the threshold  $p_c$  of conducting fillers in an insulating matrix in real systems for other than the most simply shaped objects (e.g. spherical inclusions). In general,  $p_c$  becomes smaller as the connectivity of the system increases. It will be shown that the concept of *excluded volume* is particularly efficient in treating the problem of percolating systems in which the inclusions possess a large aspect-ratio, such as cylinders.

### ***Classical Geometric Percolation***

In classic percolation theory, Scher and Zallen firstly demonstrated that the fractional volume  $p_c$  associated with the onset of percolation is, to a reasonable accuracy, a dimensional invariant for all lattices [Scher, Zallen]. By multiplying the site-percolation critical occupation probability by the filling factor of the lattice, they found in three dimensions that  $p_c = 0.16$  within an accuracy of a few percent in all cases. This value of 16% is known as the SZ invariant and has been frequently misapplied when discussing ‘real-life’ percolating networks such as carbon-black/polymer composites [Robertson]. This is because the SZ invariant was derived for lattices composed of a disordered mixture of metallic spheres and insulating (or missing) spheres of equal radii. This is a very specific criterion and the SZ analysis cannot be simply applied to other non-regular

systems. An example of one such system is a composite material consisting of conducting particles (spherical or otherwise) embedded in a *continuous* insulating matrix [Balberg<sup>1</sup>].

The percolation properties of real composites are, in general, complicated functions of a variety of parameters. These include the filler particle shape and size, the spatial arrangement of the distribution, the dispersion of the filler particles and the nature of the connectivity between the filler particles [Balberg<sup>1</sup>]. A theory that incorporates the main difficulties with non-trivial systems was derived by Balberg [Balberg<sup>2</sup>]. Based upon the concept of *excluded volume* he was first able to predict  $p_c$ . This was further expanded by Foygel et al [Foygel] to predict the percolation exponent  $t$  and this is outlined in the following sections.

### ***Excluded Volume Percolation***

The excluded volume of an object,  $V_{EX}$ , is defined as the volume around the object into which the centre of a similar object is not allowed to enter if overlapping of the two objects is to be avoided [Onsager]. The total excluded volume,  $V_{EXTOT}$ , is this volume multiplied by  $N_c$ , the critical number of objects required to form a percolation pathway:

$$V_{EXTOT} = N_c V_{EX} \tag{5.2}$$

It is straightforward to show that the excluded volume of a sphere is simply 8 times the volume of the sphere itself and that the shape is also a sphere. This “universality” applies to systems of other regular objects (e.g. cubes and ellipsoids). This does not however apply to irregular objects, such as cylinders for example, and the relative orientation of the objects plays an important role. As an illustration, the two-dimensional excluded volume for two cylinders is displayed in Figure 5.2 and it can be seen that an angular dependence exists for  $V_{EX}$ .



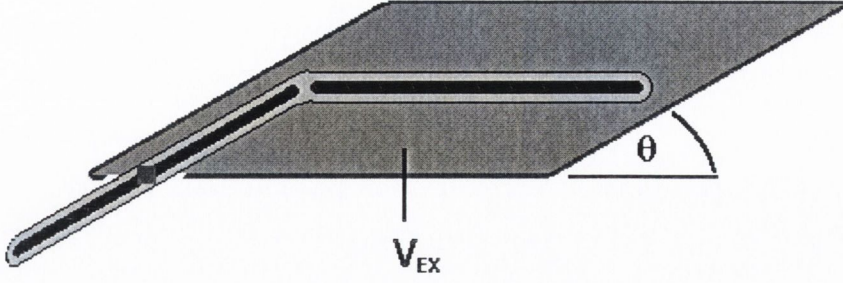


Figure 5.2: Two-dimensional excluded volume of two cylinders oriented at an angle  $\theta$  relative to one another.

For the sake of analytical simplicity, it is assumed that the filler particles can be considered as interpenetrating (or soft core). This is obviously not the case for MWNTs but through Monte Carlo simulations [Foygel] it has been shown that this assumption is valid for objects with large aspect-ratios. This holds for nanotubes and the assumption does not significantly alter the results.

Assuming a total volume of unity, if  $V$  equals the volume of a nanotube, then the probability that a randomly chosen point in the composite belongs to the polymer is  $1-V$ . At the percolation threshold  $p_c$  there are a critical number of nanotubes,  $N_c$ . Therefore, assuming soft core nanotubes, at the percolation threshold the probability that a randomly chosen point belongs to the matrix (polymer) is given by:

$$1 - p_c = (1 - V)^{N_c} \quad (5.3)$$

This can be re-arranged and re-written as follows:

$$p_c = 1 - [(1 - V)^{N_c}] \quad (5.4a)$$

$$p_c = 1 - \left[ 1 - \left( \frac{N_c V_{EX} V}{V_{EX}} \right) \left( \frac{1}{N_c} \right) \right]^{N_c} \quad (5.4b)$$

where  $V_{EX}$  is the excluded volume of one nanotube. In the limit of an infinite system (i.e.  $V \rightarrow 0$  and  $N_c \rightarrow \infty$ ) both the ratio  $\frac{V}{V_{EX}}$  and the total excluded volume  $V_{EXTOT} = N_c V_{EX}$  have been shown to be constants [Balberg<sup>2</sup>, Balberg<sup>3</sup>]. By expanding Eqn (5.4), we get:

$$p_c = 1 - \exp\left(\frac{-N_c V_{EX} V}{V_{EX}}\right) \quad (5.5a)$$

$$p_c = 1 - \exp\left(\frac{-V_{EXTOT} V}{V_{EX}}\right) \quad (5.5b)$$

$$p_c = 1 - \exp(-N_c V) \quad (5.5c)$$

This provides an analytic expression predicting the percolation threshold,  $p_c$ , as a function of the nanotube volume and the critical number present. The critical number  $N_c$  is not known however but can be calculated from the ratio of total excluded volume to excluded volume (Eqn (5.5b)). In a system of randomly oriented objects, average excluded volumes must be used.

For a hard, capped cylinders of diameter  $d$  and length  $L$  the volume of the cylinder is:

$$V = \frac{1}{8} \left( \frac{4\pi d^3}{3} + 2\pi d^2 L \right) \quad (5.6)$$

In three dimensions, the excluded volume associated with a capped cylinder oriented at an angle  $\gamma$  relative to another cylinder is given by [Balberg<sup>2</sup>]:

$$\begin{aligned} V_{EX} &= \frac{4\pi d^3}{3} + 2\pi d^2 L + 2dL^2 \sin\gamma \\ &= 8V + 2dL^2 \sin\gamma \end{aligned} \quad (5.7)$$

For a randomly oriented system one must average  $\sin\gamma$  over all possible solid angles of stick  $i$  and  $j$  (where  $\theta_i$  and  $\theta_j$  are confined to an angle of  $2\theta_\mu$  around the  $z$ -axis of the system). This gives the *average* excluded volume of a capped cylinder:

$$\begin{aligned} \langle V_{EX} \rangle &= \frac{4\pi d^3}{3} + 2\pi d^2 L + 2dL^2 \langle \sin\gamma \rangle_\mu \\ &= 8V + 2dL^2 \langle \sin\gamma \rangle_\mu \end{aligned} \quad (5.8)$$

One can easily see that in general the average excluded volume of a cylinder is not the same shape as the geometric volume of a cylinder except for the special case of parallel cylinders whereby  $\theta_\mu = 0$  and then  $\langle \sin\gamma \rangle_\mu = 0$ . Then the average excluded volume of a cylinder is simply another cylinder of volume 8 times that of the cylinder itself. The

isotropic case (randomly distributed cylinders) corresponds to  $\theta_\mu = \pi/2$  and then  $\langle \sin \gamma \rangle_\mu = \pi/4$  [Balberg<sup>2</sup>]. In this case:

$$\begin{aligned} \langle V_{EX} \rangle &= \frac{4\pi d^3}{3} + 2\pi d^2 L + \frac{\pi d L^2}{2} \\ &= 8V + \frac{\pi d L^2}{2} \end{aligned} \quad (5.9)$$

The total average excluded volume for a system of randomly oriented capped cylinders has been calculated to be a constant  $\langle V_{EXTOT} \rangle = 1.4$  [Balberg<sup>3</sup>] and hence by combining Eqns (5.5b), (5.6) and (5.9), the percolation threshold for an isotropic system of randomly oriented cylinders can be written as:

$$p_c = 1 - \exp \left( \frac{-1.4 \left( \frac{\pi d^3}{6} + \frac{\pi d^2 L}{4} \right)}{\left( \frac{4\pi d^3}{3} + 2\pi d^2 L + \frac{\pi d L^2}{2} \right)} \right) \quad (5.10)$$

In the limit of a high aspect-ratio cylinder ( $L/d \gg 1$ ), this reduces to the much simpler form of:

$$p_c = 1 - \exp \left( -0.7 \frac{d}{L} \right) \quad (5.11)$$

which in turn can be approximated by:

$$p_c \approx 0.7 \frac{d}{L} \quad (5.12)$$

It can be seen therefore that for a system of randomly dispersed, high aspect-ratio cylinders, the percolation threshold is approximated by the inverse of the aspect-ratio. This derivation assumes that all cylinders are of the same size. Balberg showed that for a system with a distribution of lengths with a mean length  $\langle L \rangle$  [Balberg<sup>3</sup>], the constant

total excluded volume must be replaced by  $\langle V_{EXTOT} \rangle = 1.4 \frac{\langle L \rangle^3}{\langle L^3 \rangle}$  and this leads to a new

expression for the percolation threshold:



$$p_c = 0.7 \frac{\langle L \rangle^3}{\langle L^3 \rangle} \frac{d}{L} \quad (5.13)$$

It should be pointed out that this derivation assumes *geometric* percolation whereby intimate physical contact exists between the filler particles. In reality, in a polymer-nanotube composite system, a polymer coating surrounds each nanotube acting as a barrier between adjacent nanotubes. This coating has been observed by TEM for MWNT composites fabricated with the conjugated polymer PmPV [McCarthy] and also for the insulating polymer polyvinyl alcohol (PVA) [Cadek] (as shown in Figures 2.10 and 2.11 respectively). These physical barriers prevent a geometric network consisting purely of connected nanotubes but the model still holds if the filler particles are considered simply as nanotubes plus an associated polymer coating as illustrated in Figure 5.2. This lack of physical connectivity between the nanotubes requires a charge transport process such as quantum tunnelling or hopping in order for macroscopic conductivity to occur. A non-zero conductivity can also be measured below the percolation threshold. The percolation threshold can then be considered as the volume fraction at which long-range connectivity firstly occurs between polymer-coated nanotubes.

### ***Percolation Exponent***

In an electrical percolation study of various carbon-black/polymer composites [Balberg<sup>4</sup>], three different percolation exponents  $t = 4.0, 2.8$  and  $2.0$  were measured for three different carbon-blacks. The structures of the particles were different ranging from “low-structure” spheres to “high-structure” chain-like aggregates of carbon-black with an aspect-ratio greater than unity. As the structure or aspect-ratio increased, the exponent  $t$  decreased.

Foygel and co-workers [Foygel] expanded the excluded volume model of Balberg to describe this variation of  $t$  with filler aspect-ratio. A computational model studied the variance of percolation threshold,  $p_c$  with decreasing nanotube length and diameter while keeping aspect-ratio constant. This relationship can be described by a power law with

exponent  $\nu$ . The percolation exponent  $t$  scales with this exponent and in  $d$ -dimensions can be written as [Shklovskii]:

$$t = (d - 1)\nu \tag{5.14}$$

The calculated values for a 3-dimensional system consisting of identical randomly distributed and randomly oriented spherocylinders was plotted as a function of aspect-ratio  $a = L/d$ , and this is shown in Figure 5.3.

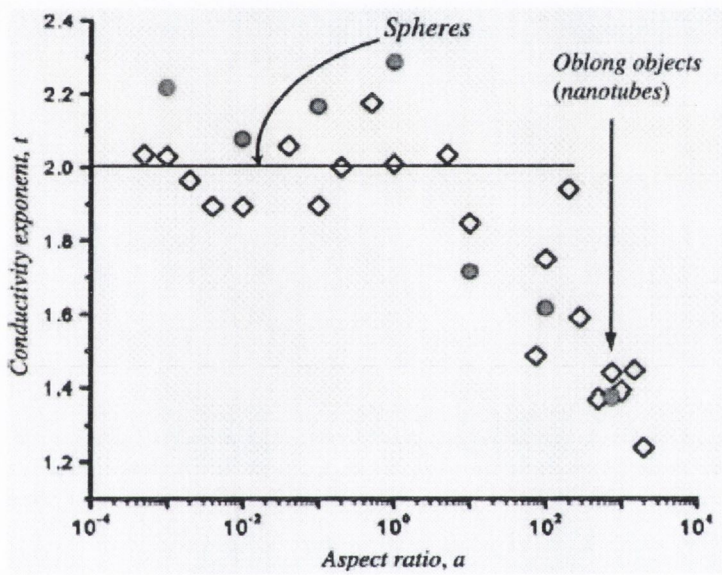


Figure 5.3: Critical exponent  $t$  for 3-dimensional systems of nanotubes as a function of aspect-ratio ( $a = L/d$ ) calculated by Monte Carlo simulation by Foygel et al (from Ref Foygel).

The “universal” value of  $t = 2.0$  does apply to systems with  $a \leq 1$  but clearly  $t$  decreases as aspect-ratio increases (as is the case for nanotubes). Combining this information with Eqn (5.12), the aspect-ratio controls both  $p_c$  and  $t$ . Both are expected to decrease as the aspect-ratio is increased.

### 5.3 Percolation in Carbon Nanotube Systems

The previous section discussed the non-universality of the percolation threshold  $p_c$  and the critical exponent  $t$  for percolating systems that obey the empirical law stated as Eqn

(5.1) and that are composed of large-aspect fillers. Numerous studies on percolation in nanotube-polymer composites appear to verify this non-universality because a wide range of values for  $p_c$  and  $t$  are reported. A summary of various experimental results are summarised in Table 5.1 along with the nanotube type and the matrix. Not every group reports a conductivity prefactor  $\sigma_0$  and therefore the range of measured conductivities is also included.

| Matrix        | Filler                     | Percolation<br>Threshold<br>$p_c$ | Percolation<br>Exponent<br>$t$ | Conductivity<br>Range<br>$\sigma$ (S/m) | Group / Reference |
|---------------|----------------------------|-----------------------------------|--------------------------------|-----------------------------------------|-------------------|
| PmPV and PVA  | Arc-D MWNT                 | $2.9 \times 10^{-4}$              | 1.36                           | $10^{-13} - 10^{-5}$                    | [Kilbride]        |
| PMMA          | Arc-D SWNT                 | $3.3 \times 10^{-3}$              | 2.1                            | $10^{-3} - 10^3$                        | [Benoit]          |
| Epoxy         | CVD MWNT                   | $2.5 \times 10^{-5}$              | 1.2                            | $10^{-9} - 10^0$                        | [Sandler]         |
| Polystyrene   | Functionalised HiPco SWNTs | $4.5 \times 10^{-4}$              | 1.54                           | $10^{-14} - 10^1$                       | [Ramasubramaniam] |
| Polycarbonate | Functionalised HiPco SWNTs | $1.1 \times 10^{-3}$              | 2.79                           | $10^{-13} - 10^2$                       | [Ramasubramaniam] |
| Polystyrene   | Functionalised HiPco SWNTs | $2.5 \times 10^{-3}$              | 2.32                           | $10^{-8} - 10^2$                        | [Blanchet]        |
| Polycarbonate | CVD MWNT                   | $1.4 \times 10^{-2}$              | 2.1                            | $10^{-16} - 10^{-2}$                    | [Potschke]        |
| Polyimide     | Laser Ablation SWNTs       | $5 \times 10^{-4}$                | 1.5                            | $10^{-16} - 10^{-4}$                    | [Ounaies]         |

Table 5.1: Summary of percolation results for polymer-nanotube composites from the Literature. These include the percolation threshold  $p_c$  and critical exponent  $t$ . ‘Arc-D’ stands for ‘Arc-Discharge’ and ‘HiPco’ stands for ‘High Pressure carbon monoxide-CVD’.



The lowest percolation threshold measured to date was  $p_c = 2.5 \times 10^{-5}$  for an epoxy-nanotube composite produced using mechanical shear mixing [Sandler]. This provided a very homogeneous dispersion of nanotubes. A scanning electron micrograph showed that these nanotubes were very long with  $L > 10\mu\text{m}$  ensuring a large aspect-ratio. An interesting note is that this lowest value for  $p_c$  (suggesting largest aspect-ratio) was indeed measured along with the lowest value for  $t$ .

The values for  $p_c$  vary by almost 3 orders of magnitude and exponents were measured in the large non-universal range of  $t = 1.2 - 2.79$ . By transforming the values for  $p_c$  to aspect-ratio  $a = L/d$  using Eqn (5.12), a graph of  $t$  versus aspect-ratio can be plotted similar to Foygel’s graph presented in the last section (Figure 5.3). These transformed data are displayed in Figure 5.4. The experimental data do follow the general trend of that calculated by Foygel demonstrating the usefulness of Figure 5.3.

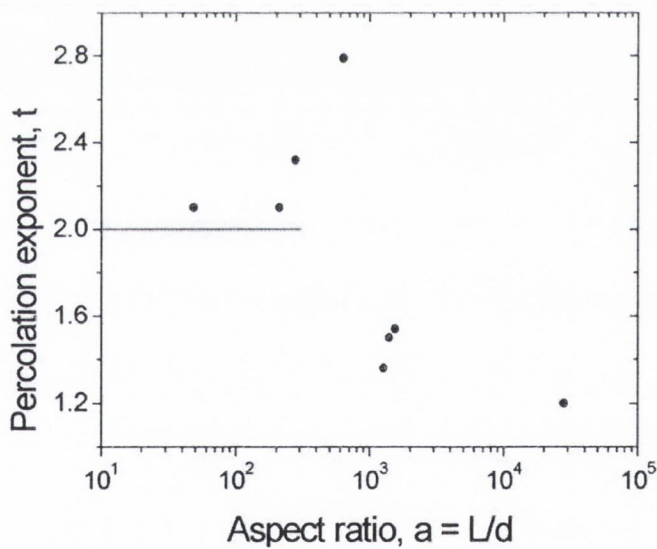


Figure 5.4: Critical exponent  $t$  for 3-dimensional systems of nanotubes as a function of aspect-ratio ( $a = L/d$ ) compiled from the data in Table 5.1.

5.4 Electrical Dependence on Nanotube Volume Fraction

Nanotube Breakdown

The electrical devices studied in this chapter were produced as described in section 3.5. The average composite sample thickness was  $1.5\mu\text{m}$  (see Table 3.3) and the active area was  $6\text{mm}^2$  in each case (see Figure 3.6). At the beginning of testing each sample, a one-off voltage scan extending up to a maximum of 7V was performed. In all samples, this first curve was ohmic up to approximately 4V at which point a large drop in current was observed. Figure 5.5 displays the initial I-V curve for two composite samples (volume fractions  $p \sim 1.3\%$  and  $p \sim 2.6\%$ ) with a characteristic “shark fin” shape. The solid curve was scaled according to nanotube volume fraction relative to the dashed curve and the reason for this is explained later.

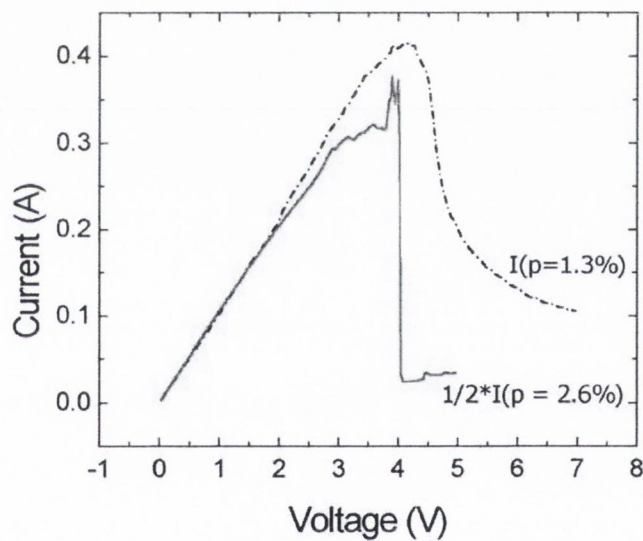


Figure 5.5: Initial scaled I-V curves displaying current carried by “bridging-nanotubes”.

These characteristics are attributed to long nanotubes that extend completely through each sample from one electrode to the other. We expect the nanotubes to be dispersed randomly throughout the matrix with a slight bias favouring those oriented parallel to the electrodes due to spin-coating. This orientational preference should be small however because of the high polymer concentration. Therefore a small fraction of nanotubes are expected to bridge the electrodes directly because the average sample thickness is  $1.5\mu\text{m}$

which is similar to MWNT lengths. Those “bridging-nanotubes” in parallel provide the paths of least resistance and will carry the majority of the current. The nanotubes are metallic and initially the I-V is ohmic. However, at a certain voltage  $V_{br}$ , electrical breakdown of these nanotubes occurs causing a rapid reduction in current. Deliberate electrical breakdown of individual MWNTs has been previously reported [Collins].

Assuming that the number of bridging-nanotubes scales linearly with volume fraction  $p$ , then the current that can be carried should also scale linearly with  $p$  because the nanotubes are in parallel. This is the case for the two composites represented in Figure 5.5 because the scaled I-V curves are identical for small voltages ( $V < 2V$ ). However, because the bridging-nanotubes act in parallel, they each individually feel the same electric field and therefore the breakdown voltage should not vary with MWNT volume fraction. Figure 5.5 shows that this is also the case and  $V_{br} \sim 4V$  is the same for both samples. The actual detail of the breakdown is slightly different for the two samples but this is probably due to the difference in number density of bridging-nanotubes.

After this initial scan, the I-V characteristics remained stable and reproducible over multiple measurements in the voltage range tested. An upper limit of 2.5V was chosen to ensure device stability because multiple measurements were performed at multiple temperatures.

### ***DC Current-Voltage Characteristics***

For all composites, the current-voltage characteristics (I-V curves) were symmetric about  $V = 0$  as expected since the electrodes were both made from gold. All curves displayed ohmic behaviour initially but proceeded to become non-linear somewhere above  $V = 0.5V$ . Two typical room temperature composite I-V curves are shown in Figure 5.6. The general shape of the curves is the same with the difference occurring in the magnitude of the current.



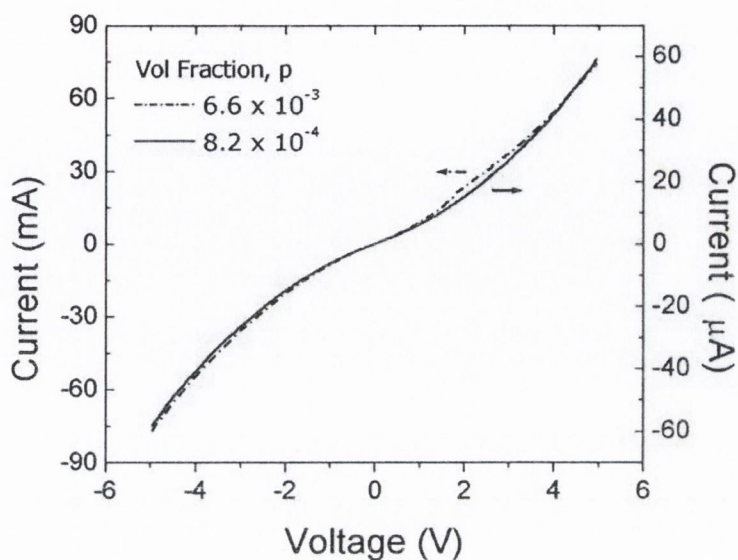


Figure 5.6: Current-voltage characteristics for two composites with MWNT volume fractions  $p = 6.6 \times 10^{-3}$  and  $p = 8.2 \times 10^{-4}$  respectively.

By plotting a log-log graph it was seen that the non-linearity was not due to an abrupt power law changeover (such as ohmic to space charge limited conduction (SCLC)) but was continuously changing). The zero-field, ohmic conductance was calculated for each sample as the slope of the I-V curve around  $V = 0V$ . By scaling for thickness and active area, the DC conductivity  $\sigma_{DC}$  of each sample was calculated and these values are given in Table 5.2.

| MWNT Volume Fraction,<br>$p$ | DC Conductivity<br>$\sigma_{DC}$ (S/m) | DC Conductivity<br>$\sigma_{AC} (\omega \rightarrow 0)$ (S/m) |
|------------------------------|----------------------------------------|---------------------------------------------------------------|
| $6.6 \times 10^{-3}$         | $1.87 \times 10^{-3}$                  | $1.79 \times 10^{-3}$                                         |
| $4.9 \times 10^{-3}$         | $1.95 \times 10^{-3}$                  | --                                                            |
| $1.7 \times 10^{-3}$         | $8.68 \times 10^{-5}$                  | $5.19 \times 10^{-5}$                                         |
| $8.2 \times 10^{-4}$         | $1.25 \times 10^{-6}$                  | $1.24 \times 10^{-6}$                                         |
| $2.1 \times 10^{-4}$         | $4.67 \times 10^{-9}$                  | $1.10 \times 10^{-8}$                                         |
| 0                            | $1.12 \times 10^{-9}$                  | $1.06 \times 10^{-9}$                                         |

Table 5.2: Summary of the conductivity values measured for various PVP-MWNT composites. Column 1 displays the volume fraction  $p$ , columns 2 and 3 display the zero-field DC conductivity ( $\sigma_{DC}$ ) and the zero-frequency limit of electric modulus ( $\sigma_{AC} (\omega \rightarrow 0)$ ).

The impedance of each sample as a function of frequency was measured and this was transformed into the electric modulus  $|\sigma^*|$  for each sample. These curves are displayed in Figure 5.7 for various MWNT volume fractions. The electric modulus for a MWNT-PVP composite can be described by an equivalent circuit consisting of a resistance  $R$  and a capacitance  $C$  acting in parallel as given by Eqn (3.12).

The polymer-only sample can be considered as a pure dielectric (i.e. no resistive element,  $R \sim 0$ ) and in this case Eqn (3.12) reduces such that the electric modulus is simply proportional to frequency. This is observed for the PVP sample, which is frequency dependent over the complete frequency range studied, and has a slope of unity on a log-log scale. In contrast, for the sample with a relatively high MWNT volume fraction of  $p = 6.6 \times 10^{-3}$ , the composite behaves effectively as a pure conductor (i.e. no capacitive element,  $C = 0$ ). In this case, Eqn (3.12) reduces such that the electric modulus is a constant value independent of frequency. In reality, a small yet finite capacitance is present but its contribution to electric modulus only becomes non-negligible at a high frequency (such that  $\omega \sim 1/RC$ ) which explains the slight upturn at  $\omega > 10^6$  rad/s.

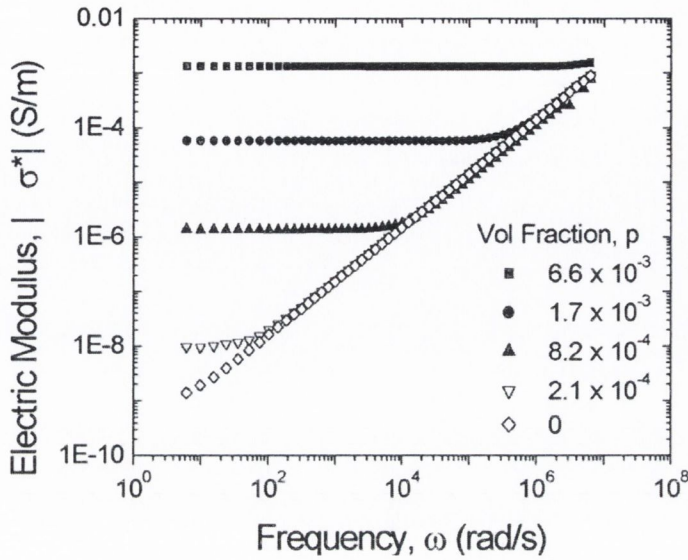


Figure 5.7: Frequency dependence of the electric modulus of composites with various MWNT volume fractions.

For composites in between these two nanotube volume fraction limits, the dielectric (C) and conductive elements (R) are both significant with the former dominating at high frequency and the latter at low frequency. As more nanotubes are added to the polymer, the total resistance of the sample reduces resulting in an up-shift in crossover frequency from a constant electric modulus to a frequency dependent value. This crossover frequency is given by  $\omega \sim 1/RC$ .

The DC conductivity has also been obtained from the zero frequency limit of the AC curves and these values (which are labelled  $\sigma_{AC} (\omega \rightarrow 0)$ ) are given in Table 5.2. It is clear that for  $\omega = 0$ , Eqn (3.12) reduces to Eqn (3.1). The conductivity values from Table 5.2 are plotted on the same graph as a function of nanotube volume fraction (Figure 5.8). A sharp increase in the conductivity, by 6 orders of magnitude from the polymer itself, is observed over a very low volume fraction range. The maximum conductivity measured was  $\sigma \sim 2 \times 10^{-3}$  S/m at a low volume fraction of  $p = 6.6 \times 10^{-3}$ . The conductivity required for electrostatic dissipation is  $\sigma > 1 \times 10^{-4}$  [Miller] and this is actually met for a volume



fraction of  $p < 5 \times 10^{-3}$ . The sharp transition suggests the formation of a percolating network and a possible fit to Eqn (5.1).

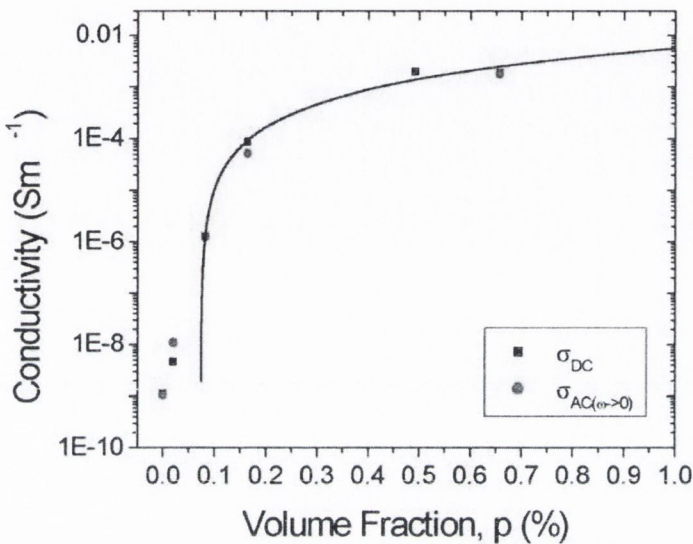


Figure 5.8: Log of conductivity of composites studied in this work as a function of nanotube volume fraction. The solid line is a fit using Eqn (5.1).

Figure 5.7 shows that above a nanotube volume fraction of  $p = 2.1 \times 10^{-4}$ , the behaviour of the electric modulus can no longer be considered purely capacitive (i.e. linearly proportional to frequency over the entire frequency range). The response becomes frequency independent for low frequencies ( $\omega < 10^4$  rad/s) indicating an appreciable conductive element. The percolation threshold was therefore assumed to occur above a nanotube volume fraction of  $p = 2.1 \times 10^{-4}$ . It was found by incrementally adjusting  $p_c$  and applying a linear fit to Eqn (5.1) (on a log-log scale) that a value of  $p_c = 7.4 \times 10^{-4}$  provided the best fit using least squares regression and this is shown in Figure 5.9. This low percolation threshold compares favourably with those reported values in Table 5.1 for other composite systems. A value of  $t = 1.76$  for the percolation exponent and  $\sigma_0 = 21$  S/m were also obtained from the fit.

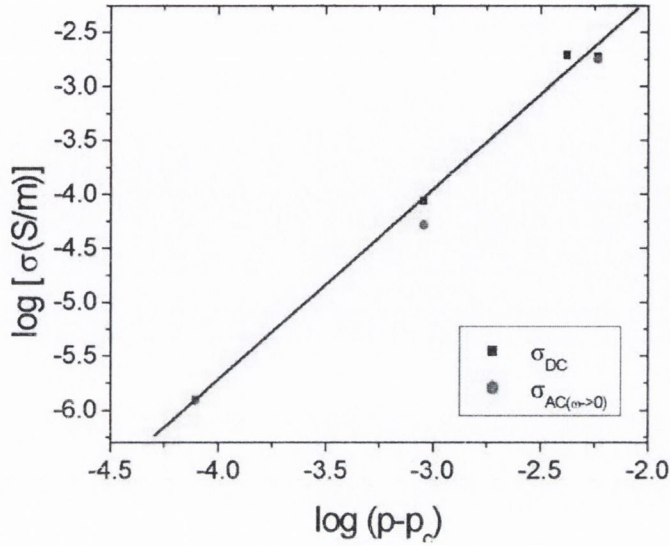


Figure 5.9: Log of conductivity of composites with volume fraction  $p$  above the percolation threshold  $p_c$ , plotted as a function of  $\log(p-p_c)$ , along with the percolation scaling law (Eqn (5.1)).

The MWNTs used in this study have an average diameter and length of 17nm and 2 $\mu$ m respectively as measured from TEM images. Using these values, an estimate for the expected MWNT percolation threshold of  $p_c = 5.95 \times 10^{-3}$  can be calculated using Eqn (5.12). This value overestimates the measured value by a multiple of eight. One explanation for this discrepancy is that a distribution of nanotube lengths occurs in the sample. According to Eqn (5.13), this calculated value for  $p_c$  should then be multiplied by a distribution factor of  $\langle L \rangle^3 / \langle L^3 \rangle \sim 0.12$  suggesting that an appreciable tail towards large lengths occurs. While no actual distribution of lengths has been measured, nanotubes with lengths of up to double the average have been observed by TEM. Physically, it makes sense that the longer-than-average nanotubes contribute significantly to the percolating system, especially when  $\langle L \rangle$  is of the order of the sample thickness. This explanation is supported by the results of Kilbride et al [Kilbride]. Using MWNTs produced in the same generator, the authors measured a value of  $p_c = 2.9 \times 10^{-4}$  for other MWNT-polymer composite systems. This value is of the same order as the value measured here and is even lower than the predicted  $p_c = 5.95 \times 10^{-3}$  for constant lengths.

The percolation exponent was calculated to be  $t = 1.76$ . From the graph of Foygel (shown in Figure 5.3), this corresponds to a nanotube aspect-ratio in the range  $a = 20 - 200$ . Using the average values quoted in the previous paragraph for average diameter and length, this gives a value of 117. These results clearly agree although there is slightly too much scatter in Figure 5.3 to use this graph to estimate the aspect-ratio from  $t$  alone.

The conductivity prefactor was calculated to be  $\sigma_0 = 21 \text{ S/m}$ . As previously mentioned, this value does not represent the intrinsic conductivity of filler particles since Eqn (5.1) only holds for  $(|p-p_c| \ll 1)$ . This number is actually an upper limit for the filler particle conductivity since Eqn (5.1) actually overestimates the real behaviour for large volume fractions. Conductivity experiments performed on individual MWNTs at 300K have measured values in the range  $\sigma = 10^5 - 10^7 \text{ S/m}$  [Dai, Ebbesen]. It is expected therefore that the measured value of  $\sigma_0 = 21 \text{ S/m}$  cannot represent an upper limit for the conductivity of MWNTs themselves. This lends further weight to the idea that the filler particles in our percolation model are polymer-coated MWNTs and the low value for  $\sigma_0$  represents an upper limit for the conductivity of this *composite* filler particle. This value is 4-6 orders lower than expected due to conduction limited by the polymer barrier. Possible conduction mechanisms include quantum mechanical tunnelling or hopping between MWNTs through the polymer. Using MWNTs produced in the same generator, Kilbride [Kilbride] measured a value of  $\sigma_0 \sim 1 \times 10^{-3} \text{ S/m}$  for other MWNT-polymer composites using the semi-crystalline polymers PVA and PmPV. This is 4 orders lower than the measured value above for PVP and can also be explained by polymer coating. Since PVP is 100% amorphous, the nanotubes cannot seed any crystallinity. They will be separated by PVP but this distance should be less than for crystalline coatings of PVA or PmPV (see Figures 2.10 and 2.11). A tunnelling mechanism would be highly sensitive to the inter-nanotube separation and this lack of crystallinity can therefore explain the 4 orders of magnitude difference in these results using effectively identical MWNTs.

It can be shown that inter-nanotube tunnelling is a possible candidate to describe the composite conduction by transforming the conductivity data as a function of MWNT



volume fraction,  $p$  (Table 5.2). Since the MWNTs were uniformly dispersed throughout the polymer by sonication, then the composite conductivity at room temperature can be described by the behaviour of a single tunnel junction [Boettger] given by Eqn (2.11). By geometric considerations the tunnel width  $w$  is dependent on MWNT volume fraction  $p$  as given by Eqn (2.29). Combining these two equations produces the following relationship between conductivity and volume fraction:

$$\sigma = \sigma_0' \exp\left(-p^{1/3}\right) \tag{5.15}$$

where  $\sigma_0'$  is a constant. A graph of  $\ln(\sigma)$  versus  $-p^{1/3}$  is plotted in Figure 5.10 and this displays the expected straight-line relationship indicative of a possible tunnelling mechanism.

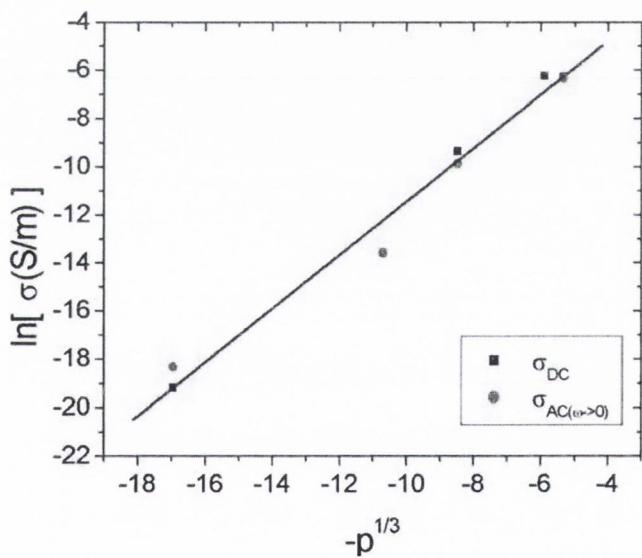


Figure 5.10: Natural log of conductivity versus  $p^{1/3}$ . The solid line is a fit to Eqn (5.15).

In order to investigate the underlying conduction mechanism further, temperature and electric field dependent data for the conductivity are required. These results are presented in the following two sections.

5.5 Electrical Dependence on Temperature

The temperature dependence of the zero-field DC electrical conductivity is plotted in Figure 5.11 for PVP composites at three characteristic MWNT volume fractions: (i) greater than the percolation threshold,  $p_1 > p_c$ , (ii) very close to the percolation threshold,  $p_2 \sim p_c$  and (iii) below the percolation threshold,  $p_3 < p_c$ . The actual volume fractions are given in the Figure caption. In order to directly compare the composites, the conductivities are scaled according to the conductivity measured at  $T = 20\text{K}$ .

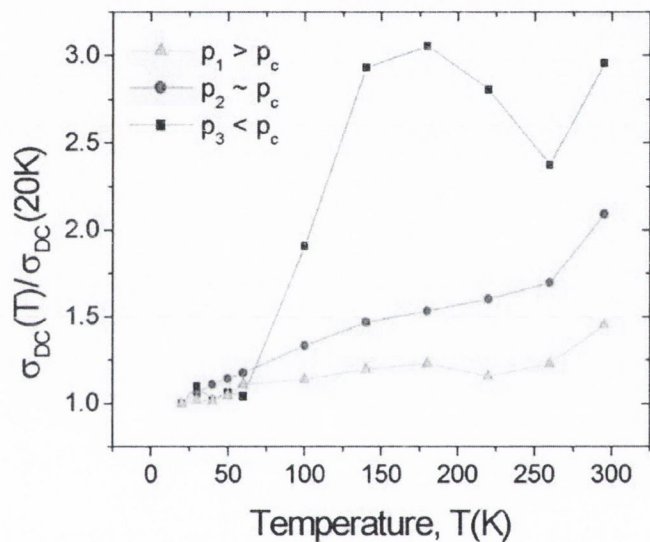


Figure 5.11: Temperature dependence of the conductivity of three composites (scaled relative to their respective conductivity at 20K). The MWNT volume fractions are  $p_1 = 6.6 \times 10^{-3}$ ,  $p_2 = 8.2 \times 10^{-4}$  and  $p_3 = 2.1 \times 10^{-4}$ .

First, as the nanotube volume fraction increases the conductivity is less sensitive to temperature variation. This is expected because with the addition of more nanotubes, the overall composite should become more conductive (or metallic-like). This behaviour has also been reported for high loadings of carbon-black in polyvinyl chloride (PVC) [Sichel] and polyethylene (PE) [Reidy].

The second point to note is the relative insensitivity to temperature of the conductivity for all volume fractions. Even for the most sensitive composite ( $p_3 < p_c$ ) the conductivity

only increases by approximately a factor of 3 over two orders of magnitude of temperature variation. This would appear to rule out a conduction mechanism that is phonon-assisted such as Arrhenius-type direct thermal activation (described by a Boltzmann distribution and written in Eqn (2.13)). This can be ruled out completely by the lack of a straight-line fit of  $\ln(\sigma)$  versus  $1/T$  for any of the composites. A naïve attempt to fit a straight-line to various segments of this plot in order to estimate an activation energy from the slopes gave values for  $\Delta E$  that were actually smaller than the thermal energy! Other conduction mechanisms with this characteristic temperature dependence such as nearest-neighbour hopping or ionic conduction can also be discounted on this basis.

While much care was taken to choose a maximum voltage to ensure device stability, DC measurements at a range of temperatures lead to some scatter in the conductivity data. This is most evident in the sample with  $p < p_c$  in Figure 5.11 as might be expected since this sample was most sensitive to the creation or destruction of even one pathway with an applied bias. Due to this scatter, a simple determination of whether or not the conductivity could be attributed to variable range hopping (VRH) was not so simple as for Arrhenius-type behaviour.

Because of the more slowly varying nature of VRH conductivity with temperature as described by Eqn (2.21), this form of conduction cannot be ruled out immediately. In this case, by plotting  $\ln(\sigma)$  versus  $1/T^x$  for both  $x = 1/2$  and  $x = 1/4$ , it was not clear if a straight line could fit the data. The sample with  $p \sim p_c$  was chosen to further test for VRH because of the apparent lack of scatter in conductivity.

Graphs of  $1/T^x$  versus  $\ln(\sigma)$  were plotted for both  $x = 1/2$  and  $x = 1/4$ . This format was chosen in order to easily display both sets of data on one graph as shown in Figure 5.12. It can be seen that there appear to be two distinct regions for both exponents and these correspond to temperatures of  $T \leq 60\text{K}$  and  $T \geq 100\text{K}$ .



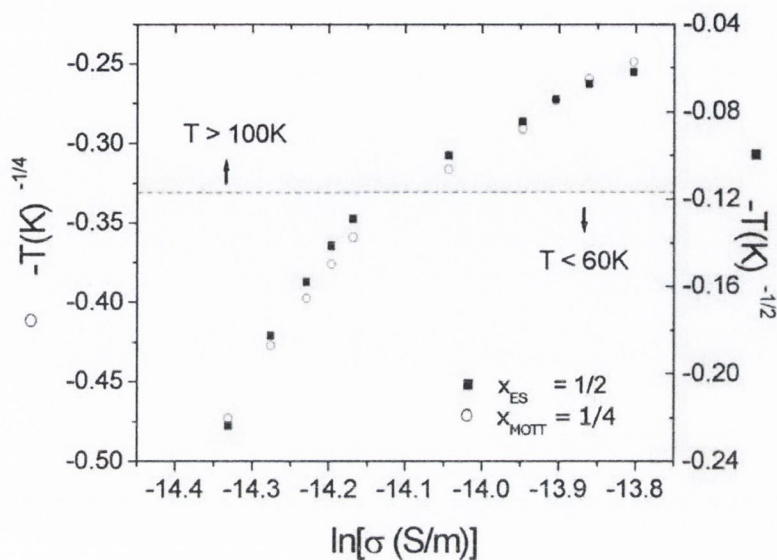


Figure 5.12: Graph of  $-1/T^*$  versus natural log of conductivity for  $x = 1/4$  (Mott) and  $x = 1/2$  (ES) to investigate possible variable range hopping (composite with MWNT volume fraction  $p = 8.2 \times 10^{-4}$ ).

Straight lines were fit to the data for both exponents in both temperature ranges and  $T_x$  (defined in section 2.5) in each case was calculated from the slope (see Table 5.3). There is a large variation in the  $T_x$  values ranging from 3K – 135K. Although straight-line fits are possible, none of the calculated values meet the criteria for variable range hopping (of either type) explained as follows.

|                                        | $T_{1/4}$ (K) | $T_{1/2}$ (K) |
|----------------------------------------|---------------|---------------|
| Temperature range $T \geq 100\text{K}$ | $135 \pm 34$  | $36 \pm 5$    |
| Temperature range $T \leq 60\text{K}$  | $4.2 \pm 0.6$ | $2.9 \pm 0.4$ |

Table 5.3: Variable range hopping temperatures  $T_x$  calculated from the slopes of straight line fits to Figure 5.12.

Adkins [Adkins] showed that a requirement for variable range hopping is that  $T_x$  exceeds  $T$  over the entire temperature range studied. Immediately, this rules out VRH in all cases except possibly Mott VRH for  $T \geq 100\text{K}$ .

Mott's analysis described in section 2.5 requires that  $\alpha R_{ij} \leq 1$  where  $R_{ij}$  is the average nearest-neighbour distance and  $\alpha$  is the inverse localisation length. However, a further requirement for VRH to make physical sense is that  $\alpha R_{opt} > 1$  where  $R_{opt}$  is the optimum hopping distance. If this inequality is not satisfied, then two hopping sites cannot be regarded as separate because the wavefunctions will hybridise. Dawson and Adkins [Dawson] extended Mott's optimisation derivation for VRH to include the general form for the density of states:

$$N(E) = N_v (E - E_F)^v \quad (5.16)$$

introduced in section 2.5. This more general analysis produced the following expression for  $\alpha R_{opt}$  in all dimensions:

$$\alpha R_{opt} = \frac{1}{4} \left( \frac{T_x}{T} \right)^{1/2} \quad (5.17)$$

By requiring  $\alpha R_{opt} > 1$ , this leads to the more stringent criterion for VRH that  $T_x > 16T$  over the temperature range studied. Applying this requirement clearly rules out all values for  $T_x$  calculated in Table 5.3 and variable range hopping can be discounted.

Based on the temperature dependence of the zero-field conductivity alone, fluctuation induced tunnelling provides a possible candidate. Figure (5.13) shows a least-squares fit of Eqn (2.25) to the data for the sample with  $p \sim p_c$ . The fitting parameters are  $T_0 = (135 \pm 21) \text{ K}$ ,  $T_1 = (134 \pm 24) \text{ K}$  and  $\sigma_0 = (1.41 \pm 0.07) \times 10^{-6} \text{ S/m}$ .

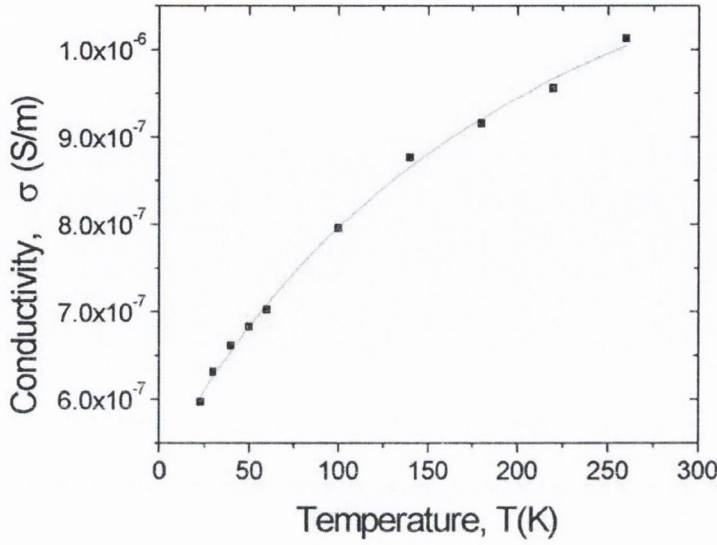


Figure 5.13: Conductivity as a function of temperature for the composite with MWNT volume fraction  $p = 8.2 \times 10^{-4}$ . The solid line is a fit to the fluctuation induced tunnelling model described by Eqn (2.25).

These parameters give a ratio  $T_1/T_0 \sim 1$  and this provides information about the strength of tunnelling since by definition:

$$\frac{T_1}{T_0} = \frac{\pi \chi w}{2} \quad (5.18)$$

where  $\chi$  is the tunnelling constant and  $w$  is the tunnel width. In an analysis of carbon-black/polycarbonate composites, Dawson claims that this ratio must be much greater than 1 as required for a tunnelling mechanism [Dawson]. This is not the case however because in order for a finite tunnelling probability to exist, the width of the barrier must be sufficiently small so that overlap of decaying wavefunctions can occur within the barrier i.e.  $w \sim 1/\chi$ .

The ratio  $T_1/T_0$  makes physical sense for tunnelling to occur but the value of  $T_0$  should reflect the temperature at which the fluctuation effect becomes significant. For  $T \ll T_0$ , a temperature independent conductivity is expected but this is not observed within the lower range of temperatures probed. Equally, at temperatures above  $T \gg T_0$ , Arrhenius



type behaviour is expected but again, the temperature range probed does not reflect this. Connor et al [Connor] observed fluctuation induced tunnelling in carbon-black/poly(ethyleneterephthalate) (PET) composites and similar values for  $T_0$  and  $T_1$  were reported. For a composite with  $p = 0.015$ ,  $T_0 = 132\text{K}$  and  $T_1 = 135\text{K}$  were measured in the temperature range  $T = 25\text{-}300\text{K}$ . It is precisely the high values for  $T_0$  (compared to the Dawson values of  $T_0 \sim 15\text{K}$ ) that reflect the lower temperature sensitivity of conductivity. The merits of this model will be considered further in the next section.

A final note on the temperature dependence of the conductivity of these composites is the consideration of thermal expansion. The thermal expansion coefficient of nanotubes is similar to the in-plane value for graphite of  $\alpha_{ab} = 1 \times 10^{-6} \text{ K}^{-1}$  [Ruoff]. The coefficients of expansion of vinyl polymers are over 2 orders of magnitude larger [Bueche] and therefore any influence on conductivity due to expansion would be dominated by changes in the polymer. Increasing temperature would actually increase the inter-nanotube separation and a decreasing conductivity would be expected ( $d\sigma/dT < 0$ ). Sichel [Sichel] suggested that this effect can act in competition to increasing conductivity due to thermal fluctuations ( $d\sigma/dT > 0$ ) and at some temperature a crossover occurs. This could account for the peak in conductivity in Figure 5.11 at  $T = 180\text{K}$  for the sample with  $p < p_c$ . This sample would be most sensitive to expansion of the inter-nanotube polymer layers but whether this peak is genuine or due to scatter in the data as discussed previously cannot be discerned.

## 5.6 Electrical Dependence on Electric Field

While the temperature dependent results did not conclusively pinpoint which conduction mechanism is involved in these composites, it did rule out a number of candidates such as hopping mechanisms. This section concerns the DC electric field dependence on conductivity. A number of common conduction mechanisms in thin insulating films can be discounted due to the I-V characteristics and these are presented as follows.

The current-voltage characteristics of the sample with  $p \sim p_c$  were transformed into conductivities and these were scaled relative to the zero-field conductivity at  $T = 20\text{K}$ .

Figure 5.14 displays these scaled conductivities as a function of applied DC bias. As mentioned previously, ohmic behaviour is observed for small voltages and then a non-linear dependence occurs.

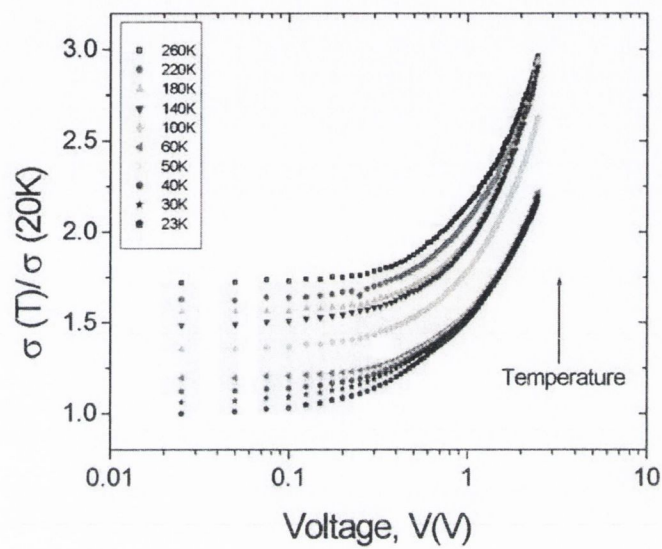


Figure 5.14: Voltage dependence of the conductivity at various temperatures (scaled relative to the zero-field value at  $T = 20\text{K}$ ) for the composite with MWNT volume fraction  $p = 8.2 \times 10^{-4}$ .

To investigate the nature of this non-linear conduction, the I-V data can be plotted as a log-log graph. There is no simple power law that describes the behaviour above the ohmic data (region with slope 1) and in fact a continuously varying slope is observed. This rules out space-charge limited conduction (of any type) which predicts an abrupt changeover from linear to quadratic dependence in current as a function of voltage (slope 2 on a log-log curve). This continuously varying slope suggests that an exponential power law of the type described by Eqn (2.23) could be dominant:

$$I = A \exp(cV^x) \tag{5.19}$$

where A, c and x are constants. A plot of  $V \frac{d(\ln I)}{dV}$  versus  $\ln(I)$  should produce a straight-line graph with a slope equal to the exponent x but this is not the case. Both Schottky emission and the Poole-Frenkel effect can be ruled out on this basis because an

exponent of  $x = \frac{1}{2}$  is expected. Both of these mechanisms equally could have been discounted due to their temperature dependence.

The limiting barrier to conduction in these composites is the inter-nanotube polymer layer. Lamb [Lamb] proposes a number of possible separate conduction mechanisms through thin insulating amorphous films and these include ionic conduction, space-charge limited conduction (SCLC), Schottky emission and the Poole-Frenkel effect and tunnelling. Therefore the only mechanism that can possibly describe the data is some form of tunnelling and due to the temperature dependence of the zero-field conductivity, we return to fluctuation induced tunnelling.

### ***Fluctuation Induced Tunnelling***

This model has been considered due to the temperature dependence of the zero-field conductivity but the theory also predicts a field dependence of tunnelling current. The electric field across each insulating gap consists of two components: the applied field  $E_A$  and a randomly varying field due to thermal fluctuations,  $E_T$ . At sufficiently high applied field such that  $E_T$  can be ignored, the tunnelling current can be described by Eqn (2.30). The value of  $E_T$  is dependent on the capacitance of the barrier which in turn depends on the barrier width,  $w$  and area,  $A$ . It is not easy to estimate values for these parameters because the exact shape of the insulating gaps in our composites is not known. Even though crystalline coating thicknesses around individual nanotubes have been measured for PVA and PmPV from TEM images of  $w \sim 5\text{nm}$ , these may not be directly transferable to nanotubes within the bulk of an amorphous polymer such as PVP. Also, the exact effective area of the junction could vary from anywhere between the cross-sectional area of a MWNT ( $\sim 400\text{nm}^2$ ) to a much smaller area consisting of a small number of atoms because of the curvature of the tip ( $\sim 1\text{nm}^2$ ). Another difficulty is knowing the true value of the local field across the gap itself. Assuming that a conducting pathway consists of nanotubes separated by thin insulating gaps in series, then the total voltage only drops across these gaps and  $E_A$  would be larger than the applied macroscopic field. Setting these difficulties aside, when  $E_A \gg E_T$  then reverse current



due to thermal fluctuations can be ignored and the total tunnelling current is predicted to have the form:

$$I \approx I_0 \exp \left[ -a(T) \left( \frac{V}{V_0} - 1 \right)^2 \right] \text{ where } a(T) = \left( \frac{T_1}{T + T_0} \right) \quad (5.20)$$

for  $V < V_0$  which is related to the potential of the barriers.

A reasonable estimate for  $E_T$  cannot therefore be easily determined but a first guess would be to set  $E_T$  equal to the field value at which deviation from ohmic behaviour has occurred. From Figure 5.14, it can be easily seen that this has definitely occurred by a voltage of  $V_T = 1\text{V}$  for all temperatures and therefore a fit of Eqn (5.20) was attempted to the data above this voltage.

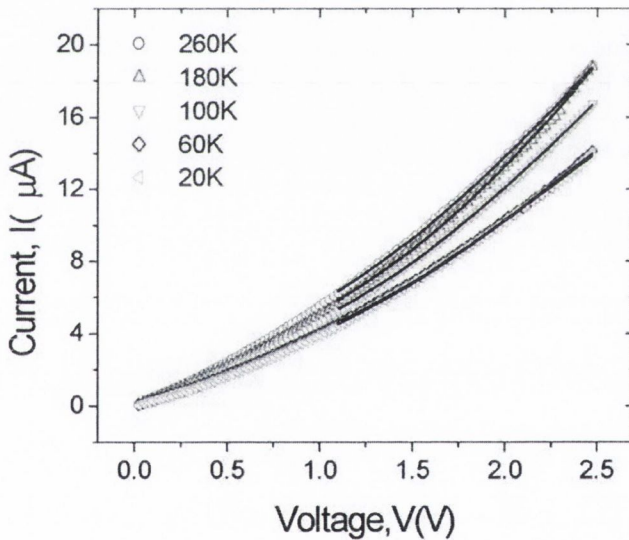


Figure 5.15:  $I$ - $V$  curves at various temperatures for the sample with  $p \sim p_c$ . The solid lines are fits to the data using the fluctuation induced tunnelling Eqn (5.20).

By setting  $I_0$ ,  $a$  and  $V_0$  as free parameters, fits were obtained for each temperature and these would appear to describe the data well as shown in Figure 5.15. The fit parameters are given in Table 5.4.

| Temperature (K) | $I_0$ ( $\mu\text{A}$ ) | $a(T)$ | $V_0$ (V) |
|-----------------|-------------------------|--------|-----------|
| 260             | 31.4                    | 2.90   | 4.28      |
| 220             | 34.1                    | 3.01   | 4.49      |
| 180             | 40.9                    | 3.25   | 4.86      |
| 140             | 30.5                    | 3.10   | 4.16      |
| 100             | 28.5                    | 3.05   | 4.26      |
| 60              | 22.4                    | 2.94   | 4.13      |
| 50              | 20.9                    | 2.88   | 4.01      |
| 40              | 20.3                    | 2.89   | 3.93      |
| 30              | 21.0                    | 2.92   | 4.00      |
| 20              | 20.4                    | 2.94   | 3.88      |

Table 5.4: Fluctuation induced tunnelling fit parameters obtained using Eqn (5.20).

The main problem with these fits however is the set of values obtained for  $a(T)$ . This function should be equal to  $T_1/(T+T_0)$ . Using the values obtained in the previous section of  $T_1 = 134\text{K}$  and  $T_0 = 135$ ,  $a(T)$  should range from 0.34 to 0.87 for the temperature range studied. Clearly there is a discrepancy between these values and it could be due to the choice of start voltage above which the fitting is performed. The voltage of  $V_T = 1\text{V}$  was chosen because non-linear behaviour occurs here. An attempt to fit Eqn (5.20) to the whole dataset (from  $V_T = 0\text{V}$  upwards) at various temperatures resulted in an overestimate in  $a(T)$  of approximately 0.2 in each case. This suggests that a further decrease in  $a(T)$  could occur if  $V_T$  is increased above  $V_T = 1\text{V}$ . It seems unlikely however that this could cause a sufficient change in  $a(T)$  to agree with the values obtained using  $T_1$  and  $T_0$ . This is a major weakness in the applicability of this model to the data and in order to fully resolve it, currents at higher fields need to be measured.

One final point to note is that the conductivities displayed in Figure 5.14 do appear to be converging to some common value at an undetermined voltage  $V > 2.5\text{V}$ . This behaviour is expected as the voltage approaches  $V_0$ . Eqn (5.20) also predicts that the convergence

should occur more quickly at lower temperatures and this can also be seen to happen in Figure 5.14.

### ***Other Tunnelling Mechanisms***

There are a number of reports on non-linear conduction in polymer/carbon-black [Song, Tang] and polymer/graphitic-flake [Chen, Celzard] composites whereby the authors empirically describe the currents as a linear combination of a linear and quadratic voltage. In one instance [Song], this form of current is attributed to a combination of two different tunnelling mechanisms in parallel: Simmon's tunnelling [Simmons] and Fowler-Nordheim field emission [Streetman]. This is highly unlikely however because the electric fields required for both mechanisms are quite different and it is not expected that both should act in parallel. Furthermore, Simmon's tunnelling is used to describe the linear dependence but this type of tunnelling should also introduce an extra non-linear dependence at high fields when field emission is expected. Therefore a combination of linear and quadratic terms would not be expected even if these two processes could occur in parallel.

Celzard et al [Celzard] proposed a combined tunnelling and ionic mechanism in polymer graphitic-flake composites. The current could be written as a product of a power of voltage and an exponential of voltage. The authors could not verify this model due to lack of temperature-dependent data and it is highly unlikely that any ionic conduction takes place in the PVP-MWNT composites.

None of these combined tunnelling processes can describe the field or temperature dependence of the data and are therefore neglected.

## **5.7 Conclusions**

In summary, electrical conductivities were measured for a series of PVP-MWNT composites. These were observed to follow a percolation power law with percolation threshold  $p_c = 7.4 \times 10^{-4}$ , critical exponent  $t = 1.76$  and conductivity prefactor of  $\sigma_0 = 21$  S/m. A percolation model based upon the concept of *excluded volume* can relate  $p_c$  and  $t$



to the MWNT aspect-ratio. The measured value for  $p_c$  suggests that a distribution of MWNT aspect-ratios exists and that the longest nanotubes dominate the overall electrical connectivity. The measured critical exponent  $t$  agrees with the predicted value using the average MWNT aspect-ratio of a  $\sim 117$ . Finally, the measured  $\sigma_0$  can be attributed to a thin coating of amorphous polymer surrounding each MWNT.

Temperature dependence of the conductivity data rules out any thermally activated conduction mechanism such as variable range hopping, suggesting a tunnelling mechanism. Fluctuation induced tunnelling as a possible conduction mechanism cannot be ruled out through temperature dependence results but appears to break down when electric field dependence is analysed. The exact nature of the tunnelling cannot be fully described using the available data. Higher electric field dependent data is needed and therefore thicker composites are required to survive these fields.

## References

- Adkins, C. J. *Journal de Physique*, **1**, 1253, (1989)
- Balberg<sup>1</sup>, I. and Binenbaum, N. *Physical Review B*, **35**, 8749-8752, (1987)
- Balberg<sup>2</sup>, I., Anderson, C. H., Alexander, S., *et al.* *Physical Review B*, **30**, 3933-3943, (1984)
- Balberg<sup>3</sup>, I. *Physical Review B*, **31**, 4053-4055, (1985)
- Balberg<sup>4</sup>, I. *Physical Review Letters*, **59**, 1305-1308, (1987)
- Benoit, J. M., Corraze, B. and Chauvet, O. *Physical Review B*, **65**, 241405, (2002)
- Blanchet, G. B., Subramoney, S., Bailey, R. K., *et al.* *Applied Physics Letters*, **85**, 828-830, (2004)
- Boettger, H. and Bryskin, U. V., *Hopping Conduction in Solids*, (Berlin Verlag Akademie, Berlin, 1986)
- Bueche, F., *Physical Properties of Polymers*, (Wiley Interscience, New York, 1962)
- Cadek, M., Coleman, J. N., Barron, V., *et al.* *Applied Physics Letters*, **81**, 5123-5125, (2002)
- Celzard, A., McRae, E., Furdin, G., *et al.* *Journal of Physics-Condensed Matter*, **9**, 2225-2237, (1997)

- Chen, G. H., Weng, W. G., Wu, D. J., *et al. Journal of Polymer Science Part B-Polymer Physics*, **42**, 155-167, (2004)
- Collins, P. C., Arnold, M. S. and Avouris, P. *Science*, **292**, 706-709, (2001)
- Connor, M. T., Roy, S., Ezquerra, T. A., *et al. Physical Review B*, **57**, 2286-2294, (1998)
- Dai, H. J., Wong, E. W. and Lieber, C. M. *Science*, **272**, 523-526, (1996)
- Dawson, J. C. and Adkins, C. J. *Journal of Physics-Condensed Matter*, **7**, 6297-6315, (1995)
- Ebbesen, T. W., Lezec, H. J., Hiura, H., *et al. Nature*, **382**, 54-56, (1996)
- Foygel, M., Morris, R. D., Anez, D., *et al. Physical Review B*, **71**, 104201, (2005)
- Kilbride, B. E., Coleman, J. N., Fraysse, J., *et al. Journal of Applied Physics*, **92**, 4024-4030, (2002)
- Lamb D. R., *Electrical Conduction Mechanisms in Thin Insulating Films*, (Methuen, London, 1967)
- McCarthy, B., Coleman, J. N., Czerw, R., *et al. Journal of Physical Chemistry B*, **106**, 2210-2216, (2002)
- Miller, B. *Plastics World*, **54**, 73, (1996)
- Onsager, L. *Annals of the New York Academy of Sciences*, **51**, 627, (1949)
- Ounaies, Z., Park, C., Wise, K. E., *et al. Composites Science and Technology*, **63**, 1637-1646, (2003)
- Potschke, P., Dudkin, S. M. and Alig, I. *Polymer*, **44**, 5023-5030, (2003)
- Ramasubramaniam, R., Chen, J. and Liu, H. Y. *Applied Physics Letters*, **83**, 2928-2930, (2003)
- Reidy, R. F. and Simkovich, G. *Journal of Materials Science*, **28**, 799-804, (1993)
- Robertson, J. *Materials Today*, **7**, 46, (2004)
- Ruoff, R. S. and Lorents, D. C. *Carbon*, **33**, 925-930, (1995)
- Sahimi, M., *Applications of Percolation Theory* (Taylor and Francis, London, 1994)
- Sandler, J. K. W., Kirk, J. E., Kinloch, I. A., *et al. Polymer*, **44**, 5893-5899, (2003)
- Scher, H. and Zallen, R. *Journal of Chemical Physics*, **53**, 3759-&, (1970)
- Shklovskii, B. I. and Efros A. L., *Electronic Properties of Doped Semiconductors*, (Springer, Berlin, 1984)
- Sichel, E. K., Gittleman, J. I. and Sheng, P. *Physical Review B*, **18**, 5712-5716, (1978)

- Simmons, J. G. *Journal of Applied Physics*, **34**, 1793-1803, (1963)
- Song, Y. H., Zheng, Q. and Yi, X. S. *Journal of Polymer Science Part B-Polymer Physics*, **42**, 1212-1217, (2004)
- Streetman, B. G. and Banerjee, S., *Solid State Electronic Devices*, (5<sup>th</sup> Ed., Prentice-Hall, London, 2000)
- Stauffer, D. and Aharony, A., *Introduction to Percolation Theory*, (2<sup>nd</sup> Ed, Taylor and Francis, London, 1992)
- Tang, H., Chen, X. F., Tang, A. Q., *et al.* *Journal of Applied Polymer Science*, **59**, 383-387, (1996)
- Zallen, R., *The Physics of Amorphous Solids* (Wiley, New York, 1983)



## Chapter 6

### 6.1 Introduction

Inorganic nanowires based upon a metal-chalcogen-halogen system are a very new and exciting branch of nanomaterial. Unlike carbon nanotubes which have been extensively studied since their own discovery in 1991, relatively little research has been focused on these novel nanomaterials. Whereas carbon nanotubes (especially SWNTs) are generally produced in both metallic and semiconducting forms, these inorganic nanowires are predicted to be completely metallic and highly conducting. This uniformity of electronic type has obvious advantages for applications such as conductive nanowire-polymer composites.

A range of composites has been produced and the room temperature electrical conductivities were measured. These data follow a percolation power law as a function of nanowire volume fraction. The results are discussed after a brief introduction to the particular branch of nanowires studied here.

### 6.2 Nanowire Overview

In an application such as electrostatic shielding that requires metallic-only nanotubes, then two-thirds of all as-produced SWNT material becomes redundant. Alternatively, in order to utilise the rectifying behaviour of semiconducting carbon nanotubes, the metallic nanotubes present in a sample must first be removed. Separation of nanotube types has been achieved both chemically [Chattopadhyay] and physically [Collins] but both these methods have limitations, introduce extra processing steps and realistically only demonstrate “proof-of-principle” separation of small quantities.

It has also been demonstrated that these nanowires can be highly dispersed in a variety of organic solvents through the use of high-power (120W) ultrasonication [Nicolosi<sup>1</sup>, Nicolosi<sup>2</sup>]. It is therefore expected that a nanowire-polymer composite with desirable electrical properties could be achieved. This is due to the ease of dispersal of the filler nanowires and their large intrinsic conductivity.

The as-produced material was obtained from the group of Dragan Mihailovic at the Jozef Stefan Institute in Ljubljana, Slovenia. Molybdenum sulphur iodide ( $\text{Mo}_6\text{S}_{9-x}\text{I}_x$ ) (or MoSI) nanowires were synthesised stoichiometrically using a single-step reaction directly from the elements in a sealed vessel [Vrbanic, Mo6 Inc. Patent]. Scanning electron microscopy (SEM) showed that the material consists of wire-wool-like bundles ranging from 50 to 300nm in diameter and up to 5mm in length. The individual nanowires each have a diameter of 0.94nm. Elemental analysis and thermogravimetric analysis confirmed the composition as  $\text{Mo}_6\text{S}_3\text{I}_6$  and  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  [Vrbanic]. Trace quantities of impurities are present however and these typically consist of  $\text{Mo}_6\text{S}_6\text{I}_2$ ,  $\text{Mo}_2\text{S}_3$  and  $\text{MoS}_2$ . X-ray diffraction analysis (XRD) determined the average structure of the bundles while extended X-ray absorption fine structure measurements (EXAFS) determined the local structure [Meden]. Together, these techniques revealed that the  $\text{Mo}_6\text{S}_{9-x}\text{I}_x$  bundles have an identical skeletal structure independent of  $x$ , and are composed of identical nanowires very weakly bound by van der Waals forces. The latter result means that the bundles can easily be dispersed in a liquid medium, such as an organic solvent or a polymer solution, by ultrasonic agitation. The degree of dispersion depends on the duration of the sonication and the nanowire dilution [Vrbanic]. Density functional theory was used to determine the electronic band structure of  $\text{Mo}_6\text{S}_3\text{I}_6$  nanowires [Meden]. It was determined that the electronic orbital overlap normal to the nanowire axis is very small, reflecting very weak interaction between nanowires. In contrast, the orbital overlap along the nanowire axis was significant and this results in the nanowires displaying semi-metallic behaviour. Preliminary experiments performed on bundles of  $\text{Mo}_6\text{S}_{9-x}\text{I}_x$  nanowires show linear current-voltage characteristics with conductivity values of the order 100 S/m [Nicolosi<sup>2</sup>].

### 6.3 MoSI Nanowire - Polymer Composite Preparation

Similar to carbon nanotubes, the as-produced nanowire material contains unwanted impurities in the form of  $\text{Mo}_6\text{S}_6\text{I}_2$ ,  $\text{Mo}_2\text{S}_3$  and  $\text{MoS}_2$ . Nicolosi et al [Nicolosi<sup>1</sup>] determined that the raw material can be purified through dispersion in a variety of solvents. The best solvents for these nanowires were dimethyl-formamide (DMF), isopropanol, and chloroform while dimethylsulfoxide, water, acetone and ethanol were observed to be

relatively poor. Three phases were identified in the material, two of which were insoluble and one which forms a stable solution. Transmission electron microscopy showed that the stable solution phase consists mainly of bundles of nanowires and this equates to 12% of the raw material. It was also discovered that the diameter of these bundles was dependent on the concentration of nanowires in solution. The average bundle diameter decreased with decreasing concentration due to debundling. A dramatic reduction in average bundle diameter occurred at a concentration of  $C_{NW} = 1 \times 10^{-2}$  mg/mL and very small bundles of two to three nanowires were observed below  $C_{NW} = 3 \times 10^{-3}$  mg/mL. The average bundle length was not observed to vary.

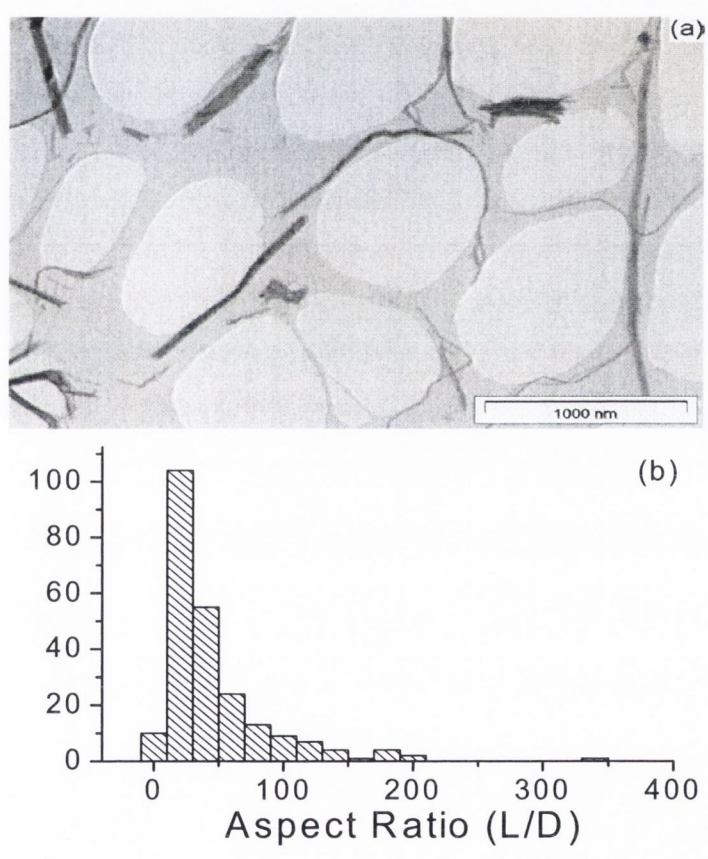


Figure 6.1: (a) TEM image of  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  nanowire bundles dispersed in DMF at high concentration (1 mg/mL) and (b) histogram of the aspect-ratio distribution of these bundles.



The as-produced nanowires were purified by Valeria Nicolosi using a settling time of 96 hours. This powder was then dispersed in DMF with a concentration of  $C_{NW} = 1\text{mg/mL}$  using a high-power (120W) sonic tip for 5 mins. Microscopy studies have shown that this sonication time does not damage the nanowires. TEM was performed on this initial solution as shown in Figure 6.1(a). The nanowires exist in bundles, and lengths and diameters were measured for over 300 separate bundles. The distribution of aspect-ratio is shown in Figure 6.1(b) with a most probable value of approximately 40. The length and diameter distributions (not shown) peaked at values of 1200nm and 40nm respectively. In addition, both displayed a long tail to higher values.

Unlike carbon nanotubes, the purified nanowires remained stably dispersed in a solvent with DMF proving the best. It was therefore logical to consider a polymer matrix that is also soluble in DMF as a medium for the nanowires. This would ensure good coupling of the polymer and the filler nanowires and eliminates any adverse solvent effects. Also, like polyvinylpyrrolidone, by choosing an amorphous polymer it was expected that the lack of crystalline coatings should be advantageous in producing good nanowire networks. For these reasons, the common polymer poly (methyl methacrylate) (PMMA) was chosen.

Composites were prepared in a similar manner to the PVP-MWNT samples in the previous chapter. Various volume fractions from  $p = 2.5 \times 10^{-6}$  to 0.027 were prepared by blending the initial nanowire dispersion ( $C_{NW} = 1\text{mg/mL}$ ) with polymer solutions. Due to the limited quantity of nanowire material available, the polymer stock solution had a relatively low concentration of 2.25mg/mL. For this reason, drop-casting was preferred to spin-coating to ensure film thicknesses of greater than 1 $\mu\text{m}$ . For each volume fraction, the composite dispersion was drop-cast onto an 80nm pre-deposited gold electrode, on a glass substrate, forming a uniform film. These were then dried at 60°C to remove any residual solvent and top gold contacts of thickness 80nm were evaporated onto each film. Film thicknesses were in the range of 3-4 $\mu\text{m}$  as determined by Dektak surface profilometry.

### 6.4 Electrical Results and Discussion

Electrical testing was performed using the same set-up as for the carbon nanotube composites (described in section 3.6). Measurements were performed at room temperature only. AC and DC measurements were performed using a Zahner IM6e impedance analyser over a frequency range 1Hz-1MHz and a Keithley Model 2400 sourcemeter respectively.

From the impedance spectroscopy measurements, the complex impedance ( $Z^*$ ) was obtained as a function of frequency for each sample. This allows the calculation of the electric modulus as a function of frequency,  $|\sigma^*(\omega)|$ , as defined by Eqn (3.7). Figure 6.2 shows the electric modulus versus frequency for a range of different nanowire loadings.

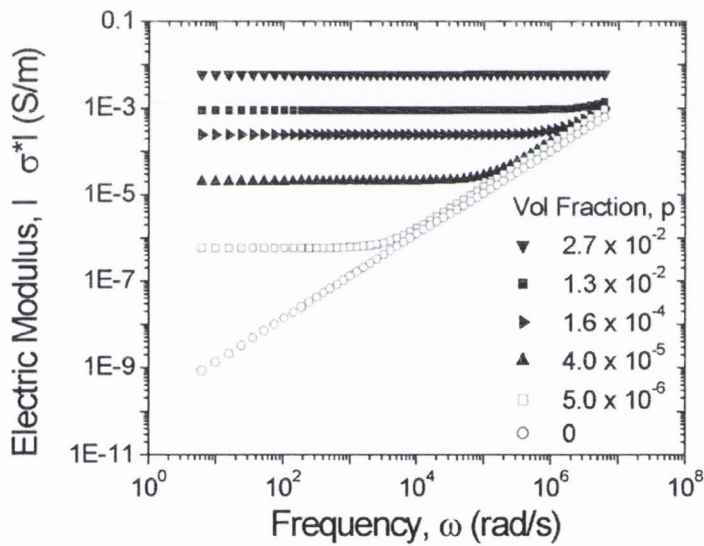


Figure 6.2: Frequency dependence of the electric modulus of composites with various nanowire volume fractions.

The electric modulus for the PMMA sample is frequency dependent over the complete frequency range studied and has a slope of unity on a log-log scale, as expected for a pure dielectric. For the sample with highest nanowire volume fraction, the composite behaves as a pure conductor with no frequency dependence in electric modulus whatsoever. In between these extremes, the composites display both dielectric and conductive behaviour

with the latter dominating at low frequency. The DC conductivity was obtained from the zero frequency limit of these AC curves and these values are labelled  $\sigma_{AC (\omega \rightarrow 0)}$ . The DC conductivity,  $\sigma_{DC}$ , was also calculated from the slope of the current-voltage characteristics, which were ohmic at all voltages. These conductivity values are presented together in Table 6.1.

| MWNT Volume Fraction,<br>p | DC Conductivity<br>$\sigma_{DC}$ (S/m) | DC Conductivity<br>$\sigma_{AC (\omega \rightarrow 0)}$ (S/m) |
|----------------------------|----------------------------------------|---------------------------------------------------------------|
| 0.027                      | 0.0022                                 | 0.0059                                                        |
| 0.021                      | 0.0042                                 | 0.0042                                                        |
| 0.013                      | 0.0024                                 | --                                                            |
| 0.0013                     | 0.0028                                 | $8.8 \times 10^{-4}$                                          |
| $6.4 \times 10^{-4}$       | 0.0022                                 | 0.0022                                                        |
| $3.2 \times 10^{-4}$       | $1.0 \times 10^{-3}$                   | $8.1 \times 10^{-4}$                                          |
| $1.6 \times 10^{-4}$       | $6.7 \times 10^{-4}$                   | $2.5 \times 10^{-4}$                                          |
| $7.9 \times 10^{-5}$       | $5.7 \times 10^{-5}$                   | $5.4 \times 10^{-5}$                                          |
| $4.0 \times 10^{-5}$       | $3.4 \times 10^{-5}$                   | $2.0 \times 10^{-5}$                                          |
| $9.9 \times 10^{-6}$       | $1.8 \times 10^{-5}$                   | $1.9 \times 10^{-5}$                                          |
| $5.0 \times 10^{-6}$       | $6.1 \times 10^{-7}$                   | $5.8 \times 10^{-7}$                                          |
| $2.5 \times 10^{-6}$       | $5.7 \times 10^{-8}$                   | --                                                            |
| 0                          | --                                     | $1.1 \times 10^{-11}$                                         |

Table 6.1: Summary of the conductivity values measured for various PMMA-MoSi nanowire composites. Column 1 displays the volume fraction  $p$ , columns 2 and 3 display the zero-field DC conductivity ( $\sigma_{DC}$ ) and the zero-frequency limit of electric modulus ( $\sigma_{AC(\omega \rightarrow 0)}$ ).

The conductivities of the composites are shown together in Figure 6.3(a) as a function of nanowire volume fraction ( $p$ ) and these values are in good agreement for each sample. A sharp increase in the conductivity, by over 8 orders of magnitude from the polymer itself, is observed over a very low volume fraction range. The maximum conductivity observed



was  $4 \times 10^{-3}$  S/m at  $p = 0.027$ . This sharp increase in conductivity indicates the onset of percolation and can be described by the percolation power law (Eqn (5.1)).

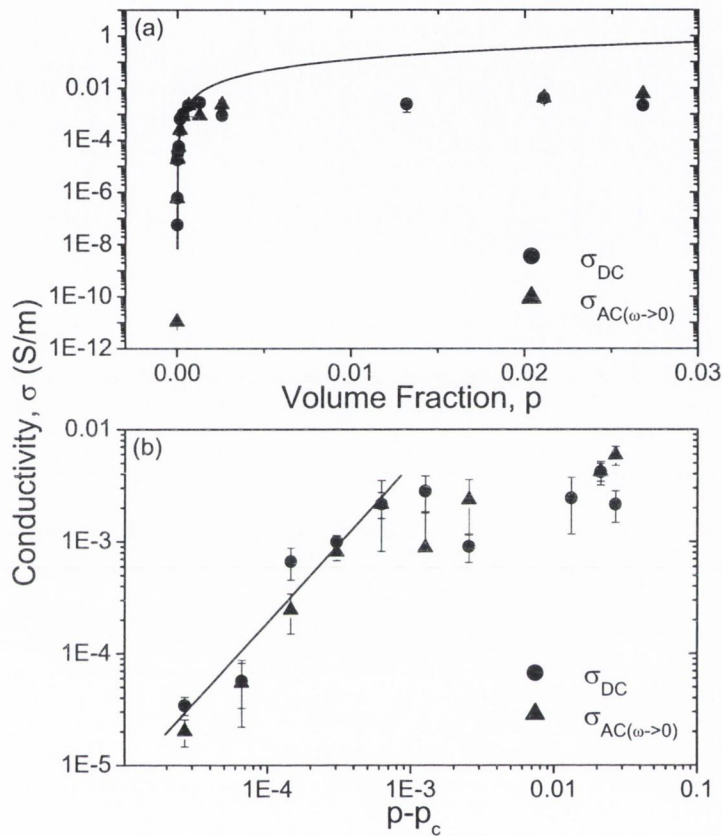


Figure 6.3: Log of conductivity of (a) all composites studied in this work as a function of nanowire volume fraction. The solid line is a fit using Eqn (5.1); (b) those samples with volume fraction  $p$  above the percolation threshold  $p_c$ , plotted as a function of  $\log(p-p_c)$ , along with the percolation scaling law (Eqn (5.1)) for  $p < 1 \times 10^{-3}$ .

Figure 6.2 displays that the electric modulus appears to diverge from purely dielectric behavior by  $p = 5 \times 10^{-6}$  so an initial estimate for the percolation threshold was assumed to occur below this volume fraction. However, it was found by incrementally adjusting  $p_c$  and applying a linear fit to Eqn (5.1) (on a log-log scale) that a slightly higher value of  $p_c = 1.3 \times 10^{-5}$  provided the best fit using least squares regression as shown in Figure 6.3(b).

This is an extremely low percolation threshold and is over 50 times smaller than that observed for MWNTs in PVP. This value compares favourably with the lowest threshold observed previously [Sandler] of  $p_c = 2.5 \times 10^{-5}$  for a carbon nanotube doped system. This value is the lowest measured percolation threshold for any 1-d conductor-insulator composite system to date. A value of  $t = 1.41 \pm 0.08$  was obtained for the conductivity exponent which is in the range previously quoted for similar systems (see Table 5.1 in the previous chapter). From the fit,  $\sigma_0 = (81 \pm 58) \text{ S/m}$  was obtained. It should be pointed out that a good fit is only obtained for  $p \leq 1 \times 10^{-3}$ . Above this value the experimental data deviates sharply from the fit.

These results raise questions about the nature of this low percolation threshold and the sharp divergence of the experimental data from the theoretical curve. As demonstrated in section 5.2, for rod-like fillers, the percolation threshold can be approximated by the inverse aspect-ratio of the filler particles (Eqn (5.12)). Applying this to the measured dimensions of the nanowire bundles used to prepare these samples shown in Figure 6.1, a value of  $p_c \sim 2.5 \times 10^{-2}$  would be expected. Clearly this conflicts with the measured value of  $p_c = 1.3 \times 10^{-5}$ . However as previously mentioned, it has previously been observed [Nicolosi<sup>1</sup>] that dramatic debundling occurs when  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  nanowires are dispersed at concentrations below  $C_{\text{NW}} = 1 \times 10^{-2} \text{ mg/mL}$ . This concentration corresponds to a volume fraction of  $p \sim 1 \times 10^{-3}$  in this study (solution preparation phase). Thus below  $p \sim 1 \times 10^{-3}$  debundling becomes important, resulting in a dispersion of individual nanowires of diameter 0.94nm and lengths ranging up to many microns at lower concentrations. Hence, this leads to a significant increase in aspect-ratio at lower concentrations which implies a much smaller  $p_c$  than predicted for large diameter bundles such as those found at higher concentrations.

Furthermore, according to Balberg's analysis the presence of a distribution of lengths of rod-like fillers can reduce the percolation threshold compared to the case of identical filler particles. In this case Eqn (5.13) should be employed. For isolated nanowires, the diameter  $d = 0.94\text{nm}$  and we can conservatively estimate  $\langle L \rangle \sim 1\mu\text{m}$  giving an aspect-ratio of approximately 1000. This means that Eqn (5.12) provides an upper bound for the

percolation threshold of  $p_c < 6.6 \times 10^{-4}$ . However, for Eqn (5.13) to explain the measured value of  $p_c$  would require  $\langle L \rangle^3 / \langle L^3 \rangle = 0.02$ . This would require the length distribution of the nanowires to be dominated by a very long tail. While this is not impossible, wires of this length would be expected to short out our thin film (3-4  $\mu\text{m}$ ). This would result in a percolation exponent of  $t \sim 1$  which is not what is observed here. It is probable that the low percolation threshold can more properly be explained by weak attractive interactions between nanowires. Interactions of this type can modify the random spatial distribution of nanowires in solution [Vigolo], in this case during the film-drying phase. This could result in the formation of conductive paths at concentrations lower than those expected from purely geometric arguments.

That the average nanowire aspect ratio is approximately 1000 is supported by the computational study of Foygel [Foygel] described in section 5.2. This work showed that for rod-like filler particles, the critical exponent  $t$  falls from its 3-d value of 2.0 as the aspect-ratio is increased. We have measured a value of 1.41 which Foygel's study associates with an aspect-ratio in the range 500-2000 confirming our nanowire length estimate of 1000nm.

The presence of bundles only at higher concentrations also explains the breakdown in the percolation fit in Figure 6.3(b) for  $p > 1 \times 10^{-3}$ . Above this loading level the percolation network consists of nanowire bundles rather than individual nanowires. Such a network will be a less efficient conductor as it will contain fewer conductive paths for a given volume fraction, resulting in conductivities lower than those predicted by the extrapolated percolation fit.

One should also notice that the conductivities of the samples with  $p$  close to  $p_c$  are quite substantial. This could be due to possible doping of the polymer by iodine that has remained intercalated on the nanowires from production. Oxidative doping can occur whereby iodine can extract electrons from the polymer resulting in semi-mobile holes [Roth]. This additional contribution to overall conductivity also explains why the AC



data for the  $p = 5 \times 10^{-6}$  sample deviates from dielectric behaviour even though it is still below the percolation threshold.

While the conductivities displayed by these composites, even at high volume fractions, are modest, conductivities of  $10^{-4}$  S/m are sufficient for electrostatic dissipation applications [Miller]. In this work we observe conductivities of  $10^{-4}$  S/m at volume fractions as low as  $1 \times 10^{-4}$ . This means that extremely low quantities of filler are required resulting in the minimum perturbation of other properties of the host matrix.

## 6.5 Conclusions

In summary, we have shown that  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  nanowires are highly conducting and form a percolation network with very low threshold of  $p_c = 1.3 \times 10^{-5}$ . This appears to be the lowest threshold measured to date for any 1-d conductor/insulator composite system. This result can be explained by the debundling of the nanowires during sample fabrication at low nanowire concentrations. In addition the data shows the importance of the longer nanowires in the sample. The highest measured conductivity was  $4 \times 10^{-3}$  S/m which is large enough for anti-static applications.

## References

- Chattopadhyay, D., Galeska, L. and Papadimitrakopoulos, F. *Journal of the American Chemical Society*, **125**, 3370-3375, (2003)
- Collins, P. C., Arnold, M. S. and Avouris, P. *Science*, **292**, 706-709, (2001)
- Foygel, M., Morris, R. D., Anez, D., *et al.* *Physical Review B*, **71**, 104201, (2005)
- Meden, A., Kodre, A., Gomilsek, J. P., *et al.* *Nanotechnology*, **16**, 1578-1583, (2005)
- Miller, B. *Plastics World*, **54**, 73, (1996)
- Mo6 Inc. Patent - *Quasi-one-dimensional polymers based upon the metal-chalcogen-halogen system*, European Patent Specification PCT/EP04/001870
- Nicolosi<sup>1</sup>, V., Vrbancic, D., Mrzel, A., *et al.* *Journal of Physical Chemistry B*, **109**, 7124-7133, (2005)
- Nicolosi<sup>2</sup>, V., Vrbancic, D., Mrzel, A., *et al.* *Chemical Physics Letters*, **401**, 13-18, (2005)

Roth, S. and Carroll, D. *One-Dimensional Metals*, (2<sup>nd</sup> ed., Wiley-VCH, Weinheim, 2004)

Sandler, J. K. W., Kirk, J. E., Kinloch, I. A., *et al. Polymer*, **44**, 5893-5899, (2003)

Vigolo, B., Coulon, C., Maugey, M., *et al. Science*, **309**, 920-923, (2005)

Vrbanic, D., Remskar, M., Jesih, A., *et al. Nanotechnology*, **15**, 635-638, (2004)

## Chapter 7

### 7.1 Conclusions

In summary, the yield and purity of multi-walled carbon nanotube-containing soot can be maximised by careful control of production parameters. Both yields and relative purities increased with increasing current density and pressure. The optimal production parameters were found to be  $J = 190 \text{ A/cm}^2$  and  $P = 500 \text{ Torr}$ . A yield of up to  $24 \text{ mg/min}$  has been achieved with an approximate MWNT purity of 55% as measured by electron spin resonance. Refinement of this value by including Thermogravimetric (TGA) data reduces this figure to an actual purity of 48%. This is still the highest known figure for any as-produced arc-discharge MWNT soot to date.

We have shown that multi-walled carbon nanotube soot can be effectively purified using a conjugated organic polymer (PmPV) to selectively suspend MWNTs relative to graphitic impurities (GP). The fraction of available MWNTs (or GP) suspended can be measured using ESR. This rises with increasing polymer mass before saturating at approximately 50% by mass with only trace amounts of GP remaining in solution. The actual mass of MWNTs and GP in solution can be measured using TGA. In conjunction with ESR this allows the total mass of MWNTs and GP in the original soot to be calculated giving its purity. Furthermore we can use this data to define and determine proportionality constants relating species mass (MWNT or GP) to ESR signal intensities, eliminating the destructive element (TGA) from the characterisation process. Finally the polymer was removed from the purified composite solutions by Buchner filtration, resulting in a 91% pure nanotube product. Optimisation of this technique could ultimately lead to a yield of up to 40 mg of pristine MWNTs from every 100 mg of soot.

We have also demonstrated that a second conjugated polymer, PFO, can suspend MWNTs effectively with an optimum settling time of 96 hrs. However, PFO also suspends graphitic nanoparticles with a maximum diameter of approximately 100 nm. This can be attributed to the structure of the polymer itself. This polymer is therefore not suitable for efficient purification of MWNTs. Composites produced using MWNTs with



both PmPV and PFO can act as efficient optical limiters and the magnitude of the light pulse dissipation is comparable with the most efficient phthalocyanine compounds.

A series of composite materials were produced using the insulating polymer PVP and MWNTs. Electrical conductivities were measured at a range of temperatures and electric-field values. At room temperature, these were observed to follow a percolation power law with percolation threshold  $p_c = 7.4 \times 10^{-4}$ , critical exponent  $t = 1.76$  and conductivity prefactor of  $\sigma_0 = 21$  S/m. A percolation model based upon the concept of *excluded volume* can relate  $p_c$  and  $t$  to the MWNT aspect-ratio. The measured value for  $p_c$  suggests that a distribution of MWNT aspect-ratios exists and that the longest nanotubes dominate the overall electrical connectivity. The measured critical exponent  $t$  agrees with the predicted value using the average MWNT aspect-ratio of a  $\sim 117$ . Finally, the measured  $\sigma_0$  can be attributed to a thin coating of amorphous polymer surrounding each MWNT.

Temperature dependence of the conductivity data rules out any thermally activated conduction mechanism (such as variable range hopping), suggesting instead a tunnelling mechanism. Fluctuation induced tunnelling as a possible conduction mechanism cannot be ruled out through temperature dependence results but appears to break down when electric field dependence is analysed. The exact nature of the tunnelling cannot be fully described using the available data.

A series of composite materials were produced using the insulating polymer PMMA and novel inorganic nanowires. We have shown that  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  nanowires are highly conducting and form a percolation network with very low threshold of  $p_c = 1.3 \times 10^{-5}$ . This appears to be the lowest threshold measured to date for any 1-d conductor/insulator composite system. This result can be explained by the debundling of the nanowires during sample fabrication at low nanowire concentrations. In addition the data shows the importance of the longer nanowires in the sample. The highest measured conductivity was  $4 \times 10^{-3}$  S/m which is large enough for anti-static applications.

## 7.2 Further Challenges

This body of work has demonstrated many of the advantages gained by incorporating carbon nanotubes (and inorganic nanowires) into a polymeric host. The purification method presented in Chapter 4 is completely non-destructive and could feasibly be scaled-up. There are still a number of challenges in order to fully exploit this scheme. The MWNT soot yield and purity was optimised for the current arc-discharge setup. However, approximately 50% of the original product still consists of impurities. This value could possibly be increased by varying other parameters such as chamber gas, chamber design and by introducing an automated system to control the gap spacing. After this has been maximised, the next question regards polymer choice. The polymer PmPV could only hold up to 50% of the available MWNTs. Other polymers could increase this value further but this requires a detailed knowledge of the interactions between the nanotubes and the polymer. Many research groups are currently studying this problem.

Regarding the electrical characterisation, a number of outstanding issues remain. The model used to predict the percolation threshold relies on the distribution of nanotube lengths and the factor  $\langle L \rangle^3 / \langle L^3 \rangle$ . An intimate knowledge of the distribution is not known however. TEM studies of MWNTs dispersed in organic solvents can provide average values. These would not however describe the distribution of MWNTs that remain preferentially suspended in the polymer. TEM of the composite material is not possible except when diluted to very low concentration which then alters the system being studied. A microscopy technique is required that can probe the nanotube network as it exists embedded in the polymer. Scanning electron microscopy using various accelerating voltages could explore the interior of the material but this introduces its own set of problems such as the issue of charging due to the insulating polymer.

Networks of polymer-coated MWNTs were formed within a polymer matrix. The macroscopic electrical conductivity obeyed a percolation power law as a function of nanotube volume fraction. The exact nature of the underlying conduction mechanism is not fully understood. Thermally activated or assisted conduction mechanisms can be discounted. The dependence of conductivity on nanotube volume fraction and

temperature both point to a form of tunnelling. The precise nature of the tunnelling has not been clarified. Conductivities measured at higher electric fields would be required to fully discount fluctuation induced tunnelling (or verify some other type). For the samples produced in this study, electrical breakdown would occur before these high field values and therefore thicker samples are required. This leads to a final point about the polymer itself. PVP is completely amorphous and does not have good film-forming capability. The samples in this work were produced by spin-coating and were relatively thin ( $\sim 1\mu\text{m}$ ). In order to produce the aforementioned thicker films, this polymer would not be suitable due to its amorphous nature. This property appears to be crucial in allowing large macroscopic conductivities to be observed (due to the absence of crystalline barriers). Therefore a conflict clearly exists between highly conductive nanotube-polymer composites and the robustness of the films. This would have to overcome for any practical application and a solution may lie in the use of diblock co-polymers. One of the polymers could serve as an amorphous coating around the nanotubes (and therefore prevent crystalline growth). The other polymer could then provide the structural integrity and support without jeopardising the conductive nature of the composite. These are exciting challenges and pose many interesting questions about our continuous understanding of carbon nanotubes. Many of the same questions exist for composite materials formed using inorganic nanowires. By increasing our knowledge base of both of these complementary composite systems, solutions to some of the mentioned challenges are possible. These answers can ultimately lead to practical materials which exploit the unique properties of these fascinating nano-materials.



## Appendix A - Publication List

*“Percolation and Charge Transport in carbon nanotube-polymer composites”*

**R. Murphy**, J. N. Coleman and W. J. Blau  
*In Preparation*

*“Observation of Extremely Low Percolation Threshold in  $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$  nanowire/polymer composites”*

**R. Murphy**, V. Nicolosi, Y. Hernandez, D. McCarthy, D. Rickard, D. Vrbancic, A. Mrzel, D. Mihailovic, W. J. Blau and J. N. Coleman  
*Scripta Materialia*, 54, 417-420 (2006)

*“Charge transport effects in field emission from carbon nanotube-polymer composites”*

R. C. Smith, J. D. Carey, **R. Murphy**, W. J. Blau, J. N. Coleman and S. R. P. Silva  
*Applied Physics Letters*, 87, 263105 (2005)

*“Biomolecules as Selective Dispersants for Carbon Nanotubes”*

S. E. Moulton, A. I. Minett, **R. Murphy**, K. P. Ryan, D. McCarthy, J. N. Coleman, W. J. Blau and G. G. Wallace  
*Carbon*, 43, 1879-1884 (2005)

*“Polymer and Carbon Nanostructure Dispersions for Optical Limiting”*

S. M. O’ Flaherty, **R. Murphy**, S. V. Hold, A. Drury, M. Cadek, J. N. Coleman and W. J. Blau  
Kirchberg/Tirol, Austria, AIP Conference Proceedings, New York, 685, 481-485, (2003)

*“Optical limiting properties of carbon nanostructure and polymer dispersions”*

S. M. O’ Flaherty, **R. Murphy**, S. V. Hold, M. Cadek, A. Drury, J. N. Coleman and W. J. Blau  
Proceedings of SPIE Vol. 4991, 194-203 (2003)

*“Material investigation and optical limiting properties of carbon nanotube and nanoparticle dispersions”*

S. M. O’ Flaherty, **R. Murphy**, S. V. Hold, M. Cadek, J. N. Coleman and W. J. Blau  
*Journal of Physical Chemistry B*, 107, 958-964, (2003)

*“Comparative study of two polymer carbon nanotube composites using electron paramagnetic resonance and transmission electron microscopy”*

**R. Murphy**, J. N. Coleman, S. M. O’ Flaherty, M. Cadek, B. McCarthy, A. Drury, R. C. Barklie and W. J. Blau  
Proceedings of SPIE Vol. 4876, 659-667 (2002)

*“Characterisation of nanotube based artificial muscle materials”*

G. Kiernan, V. Barron, D. Blond, A. Drury, J. N. Coleman, **R. Murphy**, M. Cadek and W. J. Blau

Proceedings of SPIE Vol. 4876, 775-782 (2002)

*“High yield, non-destructive purification and quantification method for carbon nanotubes”*

**R. Murphy**, J. N. Coleman, M. Cadek, B. McCarthy, M. Bent, A. Drury, R. C. Barklie and W. J. Blau

*Journal of Physical Chemistry B*, 106, 3087-3091, (2002)

*“Optimisation of the Arc-Discharge Production of Multi Walled Carbon Nanotubes”*

M. Cadek, **R. Murphy**, B. Mc Carthy, A. Drury, B. Lahr, M. in het Panhuis, J. N. Coleman, R. C. Barklie and W. J. Blau

*Carbon*, 40, 923-928, (2002)

*“Purification and processing of carbon nanotubes using self-assembly and selective interaction with a semiconjugated polymer”*

P. Fournet, B. McCarthy, A. B. Dalton, J. N. Coleman, **R. Murphy**, C. Stephan, S. Lefrant, P. Bernier, H. J. Byrne and W. J. Blau

Proceedings of SPIE Vol. 4468, 112-123 (2001)

*“Optimisation of Carbon Nanotube Production by Arc-Discharge”*

M. Cadek, **R. Murphy**, B. McCarthy, B. Lahr, M. in het Panhuis, J. N. Coleman, R. C. Barklie and W. J. Blau

Kirchberg/Tirol, Austria, AIP Conference Proceedings, New York, 591, 179-182, (2001)