



Terms and Conditions of Use of Digitised Theses from Trinity College Library Dublin

Copyright statement

All material supplied by Trinity College Library is protected by copyright (under the Copyright and Related Rights Act, 2000 as amended) and other relevant Intellectual Property Rights. By accessing and using a Digitised Thesis from Trinity College Library you acknowledge that all Intellectual Property Rights in any Works supplied are the sole and exclusive property of the copyright and/or other IPR holder. Specific copyright holders may not be explicitly identified. Use of materials from other sources within a thesis should not be construed as a claim over them.

A non-exclusive, non-transferable licence is hereby granted to those using or reproducing, in whole or in part, the material for valid purposes, providing the copyright owners are acknowledged using the normal conventions. Where specific permission to use material is required, this is identified and such permission must be sought from the copyright holder or agency cited.

Liability statement

By using a Digitised Thesis, I accept that Trinity College Dublin bears no legal responsibility for the accuracy, legality or comprehensiveness of materials contained within the thesis, and that Trinity College Dublin accepts no liability for indirect, consequential, or incidental, damages or losses arising from use of the thesis for whatever reason. Information located in a thesis may be subject to specific use constraints, details of which may not be explicitly described. It is the responsibility of potential and actual users to be aware of such constraints and to abide by them. By making use of material from a digitised thesis, you accept these copyright and disclaimer provisions. Where it is brought to the attention of Trinity College Library that there may be a breach of copyright or other restraint, it is the policy to withdraw or take down access to a thesis while the issue is being resolved.

Access Agreement

By using a Digitised Thesis from Trinity College Library you are bound by the following Terms & Conditions. Please read them carefully.

I have read and I understand the following statement: All material supplied via a Digitised Thesis from Trinity College Library is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of a thesis is not permitted, except that material may be duplicated by you for your research use or for educational purposes in electronic or print form providing the copyright owners are acknowledged using the normal conventions. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone. This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.



Electrical Characterization of Polymer Nanocarbon
Composites and High Yield Exfoliation of
Graphene

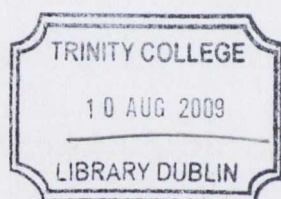
Yenny R. Hernández P.¹

Thesis submitted for the degree of Doctor in Philosophy

School of Physics
Trinity College Dublin

April 21, 2009

¹hernandy@tcd.ie



THO815
8846

Declaration

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 collaborative work mentioned in the list of publications.

I agree that Trinity College Library may lend or copy this thesis on request.



A mis padres, hermanos y abuelos

Amor

The course of true love never did run smooth

A midsummer night dream, act 1, scene 1

William Shakespeare

Abstract

The high aspect ratio, outstanding mechanical properties and high conductivity of carbon nanotubes makes them ideal candidates for polymer reinforced conducting composites. Solution processed composites, based on polyvinylalcohol and multiwalled-nanotubes, have been fabricated for a range of volume-fractions using three solvents; water, 1-methyl-2-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO). Electrical tests were carried out on each composite, demonstrating that the electrical properties depend strongly on the solvent used. The addition of nanotubes resulted in conductivity scaling with volume fraction according to $\sigma = \sigma_0(p - p_c)^t$. A low percolation-threshold of 0.001 was observed for the DMSO and NMP-based composites while a maximum conductivity of $\sim 1\text{S/m}$ was attained for the NMP and water-based composites. A higher percolation-threshold, 0.0042, was observed for the water-based systems. These effects are attributed to the formation of solvent dependent polymer coatings around the nanotubes, which act as tunnelling-barriers thus limiting the conductivity.

Composites based on polyvinylalcohol were also prepared from solution with either carbon nanotubes or carbon nanodisks as fillers. The nanotube based composites displayed percolation thresholds of 0.0042 compared to 0.021 for the nanodisks, which is higher than expected due to disk alignment. The maximum conductivities observed were $\sim 1\text{ Sm}^{-1}$ for both composite types. Values for σ_0 of 20 and 40 S m^{-1} were calculated for nanotubes and nanodisks, respectively.

In order to fully exploit the remarkable properties of graphene a method for its mass production is required. Two main routes are possible: large-scale growth or large-scale exfoliation. In this work, graphene dispersions with concentrations up to $\sim 0.01\text{ mg ml}^{-1}$, produced by dispersion and exfoliation of graphite in or-

ganic solvents such as NMP are presented. This is possible due to the fact that the energy required to exfoliate graphene is balanced by the solvent-graphene interaction for solvents whose surface energies match that of graphene. The presence of individual graphene sheets is confirmed by Raman spectroscopy, transmission electron microscopy and electron diffraction. The dispersion method developed here results in a monolayer yield of ~ 1 wt%, which could potentially be improved to 7-12 wt% with further processing. The absence of defects or oxides is confirmed by X-ray photoelectron, infrared and raman spectroscopies. Semi-transparent conducting films and conducting composites were also produced from graphene dispersions. Solution processing of graphene opens up a range of potential large-area applications, from device and sensor fabrication to liquid-phase chemistry. An alternative method to disperse and exfoliate graphite in order to give graphene suspended in water-surfactant solutions is also presented. The optical characterisation of these suspensions allowed the partial optimisation of the dispersion process. Transmission electron microscopy showed the dispersed phase to consist of small graphitic flakes. More than 40% of these flakes had < 5 layers with $\sim 3\%$ of flakes consisting of monolayers.

Acknowledgements

Doing a PhD is quite an adventure. I have learnt in this past four years that no matter how great you think your ideas are, it takes lots of hard work and perseverance to get them working. This, of course, cannot be done alone. I could not have done it without the support of my supervisor Professor Jonathan Coleman. He supported my ideas when I decided to go to a completely unexplored area and guided me till the very end to what I consider a beautiful and comprehensive study of the dispersion of graphene. I would like to acknowledge Professor Yurii Gun'ko and Professor Werner Blau who provided me with financial and scientific support during my studies. I would also like to acknowledge Dr. Kevin Ryan and Dr. Rob Murphy for the initial training in the composite's preparation and characterisation. I would like to express my gratitude to Alex Gryson for his hard work and enthusiasm during his fourth year project.

I would like to specially thank Dr. Valeria Nicolosi for all of her hard work, enthusiasm and support during the first part of the graphene project. We could not have done it without the rest of the team that believed in us: Fiona, Mustafa, Zhenyu, Sukanta and Michelle. Special thanks also to Professor Iggy McGovern, Brendan Holland, Professor John Boland, Peter Niraj, Dr. Georg Duesberg, Dr. Robbie Goodhue and Dr. Andrea Ferrari for their scientific contribution that made this first big step towards the production of graphene so comprehensive.

I would also like to mention the School of Physics and their technical staff that were always there to answer my questions. John Kelly, Jemmer, Mick, safety Joe, Ken, Rebecca, Una, Pat, Marie, Robbie and Jeanette many thanks to all of you.

I would like to thank the people that help me in the lab and that were also there to provide entertainment and support: Anna, Adam, Denis, Grace, Rob, Sandy, Valeria, David, Estelle, Marjo, Helen, Emer, Rory, Martin, Ronan, Ian, Michele,

Richard, Umar, Chris, Trevor, Eddie, Darren, Niall, Paula, Denise, Evelyn, Phil, Karen, Marguerite and Mustafa. Being a composite group I most probably forget some of the past members of group BU and group CoCo, but to all of them also a big thanks.

Fiona, and Shane, I could not have done it without you. I now consider you guys as my family. A family that resides in Ireland, my second home. I also have friends outside the group: John, Niall and Sean were also there to listen to me and also to provide some entertainment.

My Colombian friends in Ireland have also been a great support throughout these four years: Jose, Patricia, Juan Pablo, Mauricio y Luisa. *Muchas gracias por su consejo y apoyo muchachos.*

Moving to a new country is quite a difficult task and I couldn't have done it without knowing there was people back home cheering up for me. To my friends and family in Colombia a big thanks. *Deywis, gracias por estar siempre a mi lado. No puedo esperar a que nuestros ciclos de vida coincidan de nuevo*

And last but not least, to all the proofreaders of this thesis... thank you and sorry for taking so much of your time.

Contents

1	Introduction	1
1.1	Background and motivation	1
1.2	Thesis outline	3
	References	5
2	Carbon nanotubes and graphene literature review	7
2.1	Physical Properties of Carbon Nanotubes	9
2.2	Polymers	12
2.2.1	Polymer - Carbon Nanotube Composites	14
2.3	Graphene	15
	References	24
3	Materials and methods	25
3.1	Materials	25
3.2	Sample preparation	26
3.3	Methods of Analysis	28
3.3.1	Absorption Spectroscopy	28
3.3.2	Sedimentation	29
3.3.3	Two probe electrical measurements	30
3.3.4	Atomic Force Microscopy - AFM	33
3.3.5	Scanning Electron Microscopy - SEM	34
3.3.6	Transmission Electron Microscopy - TEM	36
3.3.7	Raman Spectroscopy	36
3.3.8	Thermogravimetric analysis - TGA	38
	References	40

4	The effect of solvent choice on the electrical percolation of polymer-nanotube composites	41
4.1	Introduction	41
4.2	Percolation Theory	42
4.2.1	Excluded Volume Theory	43
4.3	Experimental Procedure	47
4.4	Results and Discussion	48
4.5	Conclusions	54
	References	58
5	Comparison of carbon nanotubes and nanodisks as percolative fillers in electrically conducting composites	59
5.1	Introduction	59
5.2	Experimental Procedure	60
5.3	Results and Discussion	62
5.4	Conclusions	70
	References	73
6	High yield exfoliation of graphene in organic solvents	75
6.1	Introduction	75
6.2	Experimental procedure	76
6.3	Results and discussion	78
6.3.1	Dispersion of Graphite	80
6.3.2	Electron diffraction	88
6.3.3	Atomic force microscopy	93
6.3.4	Raman Spectroscopy	94
6.3.5	Film formation and structure	97
6.3.6	X-ray photoelectron spectroscopy	99
6.3.7	Attenuated total reflectance-Fourier transform infrared spectroscopy	102
6.3.8	Presence of residual NMP	103
6.3.9	Thin Film conductivity	105
6.3.10	Composites	106

6.4	Conclusions	106
	References	113
7	Production of graphene by exfoliation of graphite in surfactant – water	115
7.1	Experimental procedure	116
7.2	Results and discussion	116
7.2.1	Extinction Coefficient Determination	116
7.2.2	Concentration Study	118
7.2.3	TEM	120
7.3	Conclusions	123
	References	126
8	Conclusions and future work	127
A	Calculation of the enthalpy of mixing	131
A	Published papers	135

Chapter 1

Introduction

The study and development of materials has influenced civilization in ways we sometimes take for granted. It has marked eras of the human history and it has improved our quality of life immensely. From fabrics that keep us warm, to computers and wires that keep us connected in this new information world, there is always a team of scientists behind tailoring new materials for our use and commodity.

In the 1960's the idea of microtechnology was coming to fruition, however, one scientist envisaged much more for the world of materials science proposing that the limit of miniaturization as deep down at the nanoscale. Feynman's lecture "*there's plenty of room at the bottom*" laid the foundations for what we now call *nanotechnology*. The development of characterization techniques such as Atomic Force Microscopy (AFM) [1] and electron microscopy allowed scientists to engineer new materials from the bottom up permitting more control over their physical properties.

1.1 Background and motivation

In the early 1980's Harold Kroto and David Walton were studying the formation of long carbon chains in atmospheres similar to those found in giant red stars, however, the high temperatures required for this were experimentally challenging. After convincing Richard Smalley, of Rice University (Texas), they started using his laser ablation system which was composed of a high power laser, a graphite target and an inert atmosphere. The soot obtained in this process was analysed using a

mass spectrometer in search of the elusive long carbon chains. To their surprise they found a new family of cage like molecules which were later called fullerenes [2] in honor of the famous architect Richard Buckminster Fuller who designed domes with structures similar to that of C_{60} (figure 1.1)

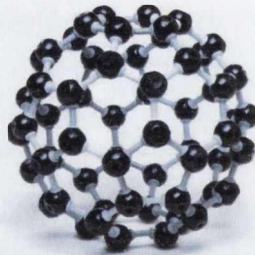


Figure 1.1: Molecular model of a C_{60} molecule

The discovery of fullerenes created hype not seen in materials research in many years. C_{60} was named the molecule of the year by the journal Science in 1991 [3] and the scientists involved in its discovery were awarded the Nobel prize in chemistry in 1996.

In 1991 Sumio Iijima was working in the production of fullerenes and by analyzing the material deposited in his arc discharge system he discovered carbon nanotubes [4]. These are an elongated form of fullerenes with outstanding physical properties (to be discussed in chapter 2). These promising properties came at a price. Nanotubes stick together in bundles that are hard to separate and they are also present as a mixture of metallic and semiconducting tubes, which is not desirable for certain applications. Scientists have slowly managed to solve these problems and applications seem closer to reality than ever before [5].

Carbon nanotube - polymer composites were first prepared and tested in 1994 [6]. Since then, the reported physical properties of these composites have improved immensely thanks to the use of better nanotube dispersions. The mechanical reinforcement of several polymers has been used in applications where carbon fibers were previously predominant (i.e. sport goods) [7]. Due to the high aspect ratio of carbon nanotubes, low loading levels are necessary to increase the conductivity of nanotube-composite materials by several orders of magnitude. This is useful for

applications where transparent contacts and coatings are required.

In 2004 A. Geim and coworkers discovered that it was possible to isolate one monolayer of carbon from graphite [8]. They did it by sticking tape to graphite and repeatedly peeling off layers. For many years isolated graphene was thought not to exist and it was used by theoretical physicists as an "academic material". After Geim's discovery, properties like quantum hall effect and ambipolar field effect were predicted and confirmed experimentally [9]. However, high yield production of graphene still represents a challenge. Chemical functionalisation of graphite to produce functionalised graphene has proven successful [10]. However, the samples produced by this method do not have the properties predicted for pristine graphene even after reduction [11]. In chapter 6 and 7 we introduce two new methods to produce virtually defect free graphene in solution. This opens a new range of possibilities for applications involving graphene.

1.2 Thesis outline

This thesis consists of 7 chapters:

- Chapter 2: An introduction to carbon nanotubes and graphene is presented. Growing techniques, physical properties and possible applications of these materials are discussed. A section on polymer and on polymer composites is also presented
- Chapter 3: A review of the experimental techniques for the sample preparation and characterization is presented. The composites sample preparation protocol was mostly followed from previous experimental work in the group.
- Chapter 4: In this chapter a comparison of the electrical properties of polyvinyl-alcohol - nanotube composites using different solvents is presented. A short literature review of percolation parameters reported by other authors is discussed. The electrical percolation parameters obtained for thick films are analysed using excluded volume theories.
- Chapter 5: Here the influence of the filler geometry on the electrical properties and percolation parameters of polymer nanotube composites is presented.

These sets of data were analysed using excluded volume theories and compared to theoretical predictions on the behavior of this type of system made by other authors.

- Chapter 6: In this chapter a novel method for the dispersion of graphite in organic solvents to give graphene at a high yield is introduced. The successful exfoliation of SWNTs in organic solvents was extended for use in graphite. The exfoliation occurs by matching the surface tension of graphene with the surface tension of the used solvents. Transmission electron microscopy analysis (TEM), electron diffraction and raman spectroscopy confirmed the presence of graphene in solution at a high yield ($\sim 1\text{wt}\%$). Other spectroscopic techniques were also used to check the quality (i.e. defects) of the produced graphene.
- Chapter 7: In this chapter a first step towards the dispersion of graphite in surfactants is presented. Initial TEM analysis confirmed the presence of graphene and few layers graphene in solution
- Conclusions and future work: the experimental results presented in chapters 4 to 7 are summarised together with a discussion of future work that could be undertaken in these areas of research.
- Appendix A: The calculation of the enthalpy of mixing used to explain the exfoliation of graphite to produce graphene in chapter 6 is presented
- Appendix B: A list of the papers published during the course of this work is presented.

References

- [1] D. P. E. Smith, G. Binnig, and C. F. Quate. *Applied Physics Letters*, 49(18):1166, 1986.
- [2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley. *Nature*, 318:162, 1985.
- [3] Koshland Daniel E. *Science*, 254:1705, 1991.
- [4] Sumio Iijima. *Nature*, 354:56, 1991.
- [5] M. Terrones. *International Materials Reviews*, 49(6):325, 2004.
- [6] P. M. Ajayan, O. Stephan, C. Colliex, and D. Trauth. *Science*, 265:1212, 1994.
- [7] J. N. Coleman, U. Khan, and Y. K. Gun'ko. *Advanced Materials*, 18(6):689, 2006.
- [8] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. *Science*, 306:666, 2004.
- [9] A. K. Geim and K. S. Novoselov. *Nature Materials*, 6(3):183, 2007.
- [10] Sasha Stankovich, A. Dikin Dmitriy, H. B. Dommett Geoffrey, M. Kohlhaas Kevin, J. Zimney Eric, A. Stach Eric, D. Piner Richard, T. Nguyen SonBinh, and S. Ruoff Rodney. *Nature*, 442:282, 2006.
- [11] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff. *Carbon*, 45(7):1558, 2007.

Chapter 2

Carbon nanotubes and graphene literature review

For many years carbon was thought to exist in only two crystalline allotropic forms: graphite and diamond (figure 2.1). Diamond is the hardest known natural mineral, which makes it an excellent abrasive when used in a powder form. Each carbon atom in diamond is covalently bonded to four other carbons in a tetrahedron. These tetrahedrons together form a 3-dimensional network of puckered six-membered rings of atoms. The movement of electrons is therefore restricted making diamond electrically insulating. The term graphite comes from the Greek *graphein* which means "to draw/write". Unlike diamond, graphite is able to conduct electricity due to delocalization of the π bond electrons above and below the planes of the carbon atoms. These electrons are free to move and therefore are able to conduct electricity along the plane of the layers. In graphite, each carbon atom uses only 3 of its 4 outer energy level electrons in covalently bonding to three other carbon atoms in a plane. Each carbon atom contributes one electron to a delocalized system of electrons that is also a part of the chemical bonding.

In the 1970s and 1980s carbon fibres were grown by hydrocarbon decomposition at high temperatures in the presence of small diameter transition metal catalyst particles leading to the formation of *straight and parallel carbon layers rolled cylindrically* [1]. Unfortunately, these were not recognized at the time as carbon nanotubes and it was not until the discovery of fullerenes in 1985 [2] that the existence of a new "cage like" family of carbon molecules was considered possible.

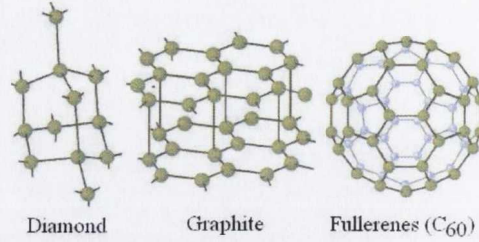


Figure 2.1: Allotropic forms of Carbon

In 1991 Sumio Iijima¹ analyzed “needle like” structures deposited in the anode of an arc discharge system used to produce fullerenes using High Resolution Transmission Electronic Microscopy (HRTEM)[3]. The study revealed that each needle consisted of coaxial tubes of graphene sheets (figure 2.2).

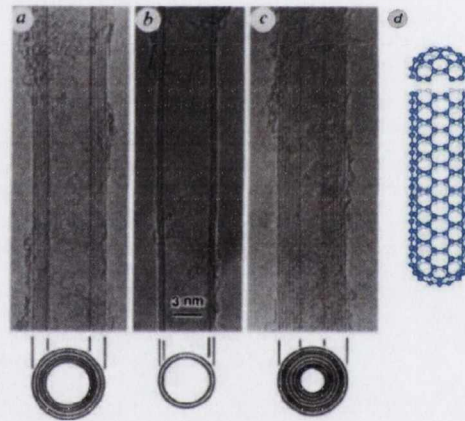


Figure 2.2: MWNTs reported by Iijima in 1991. MWNT diameters interior and exterior d_i and d_0 , N number of walls (a) $N = 5$, $d_0 = 6.7\text{nm}$, (b) $N = 2$, $d_0 = 5.5\text{ nm}$, (c) $N = 7$, $d_i = 2.3\text{ nm}$, $d_0 = 6.5\text{ nm}$ (d) Structural representation of a SWNT

Carbon Nanotube (CNT) diameters are in the range of less than 1nm up to a few tens of nanometers. Their length is in the range of a few hundreds of nanometers up to a few centimeters [4], depending on the growth conditions. They are divided in 2 main classes.

- SWNT (Single Wall Nanotubes) which can be seen as a graphene sheet rolled into a tubular shape.

¹NEC Corp. Tsukuba , Japan

- MWNT (Multi Wall Nanotubes) which can be seen as concentric graphene sheets, similar to a coaxial cable.

In 1993 Iijima (NEC) [5] and Bethune (IBM) [6] reported separately, the observation of SWNTs in samples produced in the presence of catalyst particles.

2.1 Physical Properties of Carbon Nanotubes

The electronic density of SWNTs is a function of their diameter and chirality [7]. This allow us to classify them into three groups: semiconductors of small and wide band gap and metallic nanotubes.

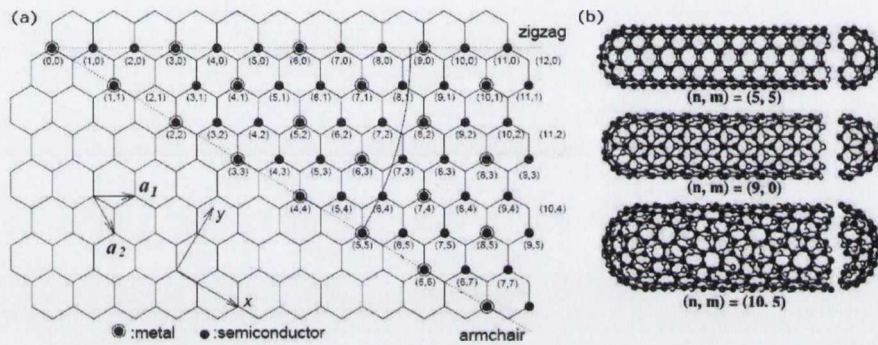


Figure 2.3: (a) Possible vectors specified by the pairs of integers (n, m) for general carbon nanotubes, including zigzag, armchair, and chiral nanotubes. The encircled dots denote metallic nanotubes while the small dots are for semiconducting nanotubes (b) from top to bottom nanotubes armchair, zigzag and chiral

The circumference of a carbon nanotube is expressed in terms of the chiral vector C_h which connects two crystallographically equivalent sites on a 2D graphene sheet (figure 2.3) [8]. The construction depends uniquely on the pair of integers (n, m) which specifies the chiral vector (equation 2.1). Figure 2.3(a) shows the chiral angle θ between the chiral vector C_h and the zigzag direction ($\theta = 0^\circ$) and shows the unit vectors a_1 and a_2 of the hexagonal honeycomb lattice of the graphene sheet. Three distinct types of nanotube structures can be generated by rolling up the graphene sheet into a cylinder (figure 2.3). Zigzag and armchair nanotubes correspond to

chiral angles of $\theta = 0^\circ$ and 30° respectively, and chiral nanotubes correspond to $0^\circ < \theta < 30^\circ$. (figure 2.3(b))

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (2.1)$$

The nanotube diameter d_t is given by:

$$d_t = \sqrt{3}a_{C-C}(m^2 + mn + n^2)^{1/2}/\pi = C_h/\pi \quad (2.2)$$

where C_h is the length of $\mathbf{C}_h$, a_{C-C} is the C-C bond length (0.14 nm), and the chiral angle θ is given by:

$$\theta = \tan^{-1}[\sqrt{3}n/(2m + n)] \quad (2.3)$$

Theoretical calculations indicate that all armchair nanotubes are metallic, as well as zigzag cylinders exhibiting values of $2m + n$ multiple of three [9]. Thus, the metallic conductivity condition for these tubular structures can be written

$$\frac{(2m + n)}{3} = \text{integer} \quad (2.4)$$

Carbon nanotubes (CNTs) have attracted a great deal of attention because their electrical [10], mechanical [11, 12], and thermal [13] properties make them ideal for nanotechnology applications (See table 2.1). Individual SWNT conductivity measurements have confirmed that each SWNT exhibits unique electronic transport [14], which can lead both to metallic and semiconducting behaviour (conductivities at 300 K, of about 8.3×10^5 to 1.9×10^7 S/m, activation energies < 0.3 eV for semiconducting tubes). These results were the first to confirm that geometric differences (i.e. chirality, diameter, etc.) and degree of crystallinity of the tubular structures play a key role in the electronic response. Bundles of SWNTs have been shown to behave as conductors with conductivities of 3×10^6 S/m [14, 15]. Dekker and co-workers carried out the first transport measurements on individual SWNTs, and demonstrated that they behave as quantum wires, in which electrical conduction occurs via well separated, discrete electronic states that are quantum mechanically coherent over long distances [16].

The most common production techniques for carbon nanotubes are: Arc discharge [6, 14, 17, 18], Laser ablation [19] and Chemical Vapor Deposition (CVD) [20–23]. Each of them give a different level of graphitization, impurities, lengths and diameters. Generally purification techniques such as: oxidation [24], acid treatment [25, 26] and annealing are implemented in order to remove the catalyst particles, defects and amorphous carbon present in the raw powder.

Property	SWNT	By comparison
Size	0.6 - 1.8 nm in diameter	Electron beam lithography can create lines 40nm wide, a few nanometers thick
Density	1.33 - 1.40 g/cm^3	Aluminium has a density of 2.7 g/cm^3 .
Tensile Strength	45 to 100 GPa	High-strength steel alloys break at 2 GPa
Resilience	Can be bent at large angles and restraightened without damage	Metals and Carbon fibres fracture at grain boundaries
Current carrying capacity	$10^9 A/cm^2$	Copper wires burn out at $10^6 A/cm^2$
Field emission	Can activate phosphors at $3V/\mu m$	Molybdenum tips require fields of 50 to 100 $V/\mu m$ and have very limited lifetimes
Heat transmission	Predicted to be 6000 $\frac{W}{m \cdot K}$ at room temperature	Nearly pure diamond transmits 3320 $\frac{W}{m \cdot K}$
Temperature Stability	Stable up to 2800°C in vacuum, 750°C in air	Metal wires in microchips melt at 600°C – 1000°C

Table 2.1: Physical properties of Carbon Nanotubes [27]

2.2 Polymers

Organic polymers are long, one dimensional macromolecules, made up of repeating identical building blocks that consist mainly of carbon, oxygen, hydrogen and nitrogen atoms joined to form a chain-like structure [28]. They exist in natural and synthetic forms. The most common natural polymers are: wood, rubber, cotton, wool, leather and silk. Man-made polymers have been studied since the beginning of the 20th century. They are generally divided into two categories:

- Thermoplastics
 - This type of polymers soften when heated and hardens when cooled in a reversible manner.
 - They usually have linear or branched structures.
- Thermosets
 - This type of polymer becomes permanently hard when heat is applied and do not soften upon subsequent heating.
 - They usually have covalently crosslinked structures.

Polymers have a range of applications that far exceeds that of any other class of material available to man. Current applications extend from adhesives, coatings, foams, and packaging materials to textile and industrial fibers, composites, electronic devices, biomedical devices and optical devices. Traditional polymers are electrically insulating. Their valence electrons are used up in covalent bonds and therefore are localised and unable to conduct electricity. In some polymers, however, this is not the case. In π -conjugated polymers, like polyacetylene, alternate single and double bonds are present along the polymer backbone. These electrons become delocalised and therefore are able to move and conduct electricity. Conducting polymers play a key role in organic light emitting diodes (OLEDs) and solar cells [29].

Polyvinyl Alcohol

Polyvinyl Alcohol (PVA or PVOH) is an electrically insulating semi-crystalline polymer. It is soluble in water, dimethyl sulfoxide (DMSO) and N-methylpyrrolidone

(NMP) to name but a few. Its melting point is 230 °C and its density is ~1300 kg/m³ [30]. It has high tensile strength and flexibility. However these properties are dependent on humidity. Absorbed water reduces its tensile strength increasing its elongation and tear strength properties at the same time.

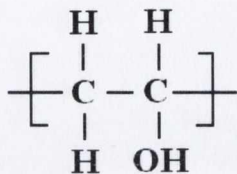


Figure 2.4: Polyvinyl Alcohol monomer

PVA is generally used for coatings, glues and adhesives. Chapter 4 and 5 will discuss the electrical properties of PVA composites using different solvents and different filler particles.

Polystyrene

Polystyrene (PS) is an electrically insulating amorphous polymer soluble in organic solvents like acetone and N-methylpyrrolidone (NMP). Its density is ~1050 Kg/m³ [30]. It is one of the most widely used kinds of plastic. Solid polystyrene is used in disposable cutlery, plastic models and CD and DVD cases. Products made from foamed polystyrene are nearly ubiquitous, for example, packing materials, insulation, and foam beverage cups.

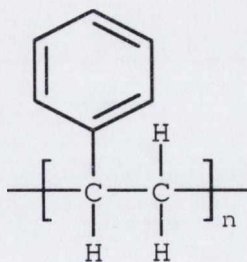


Figure 2.5: Polystyrene monomer

Chapter 6 will discuss the electrical properties of polystyrene-graphene composites.

2.2.1 Polymer - Carbon Nanotube Composites

In the case of carbon nanotubes, the combination of extremely high longitudinal elastic moduli, high thermal and electrical conductivities along the axial direction and low density make them perfect candidates as fillers in polymer composites[31]. Mechanical reinforcement [32], actuators [33], lithium batteries [34], field emission displays [35], antistatic coatings and electromagnetic shielding [36] are the most common applications in which nanotubes are expected to play an important role, therefore extensive research has been conducted in these areas.

In recent years, blends of conducting materials in an insulating host have been extensively studied because of their importance in both basic and applied science [37–39]. Some of this work has focused on polymer hosts such as poly(methylmethacrylate) (PMMA)[40], polyvinylalcohol (PVA) [41] or poly-9-vinyl carbazole (PVK) filled with materials such as carbon black, carbon fibers, and conductive polymers such as polyaniline. In these systems electronic conductivity can be increased by up to 10 orders of magnitude with relatively low filler concentrations [42]. This is significant as it allows the retention of the intrinsic matrix properties such as flexibility.

One of the key problems in composites is dispersion. Carbon nanotubes aggregate in bundles damaging the homogeneity of the composites. These problems have usually been solved by using bulk polymerization, in-situ polymerization [43] and ultra-sonication during the CNT dispersion process [44]. When a conducting polymer is used as a matrix, the addition of nanotubes as a filler drastically increases the electrical transport at relatively low concentrations [45]. Safadi et. al. found that polystyrene/MWNT composite films doubled the tensile modulus, and transform the electrical behaviour from insulating to conductive [46]. Polycarbonate/MWNT composites can also be made electrically conducting when loads of between 1 and 2 wt% MWNTs are embedded in the matrix [47]. In chapter 4 (Table 4.1) some of the reported percolation parameters that characterise the electrical conductivity of polymer-nanotube composites are presented.

2.3 Graphene

Graphene is the name given to each of the hexagonal carbon planes composing graphite (figure 2.6). The chemical intercalation of graphite has been studied for over fifty years [48]. However, such methods [49] give thin graphite sheets or graphene fragments [50] rather than large scale graphene monolayers. The standard response to this problem has been the compromise of complete exfoliation of chemically modified forms of graphene such as graphene oxide or functionalised graphene [51–53].

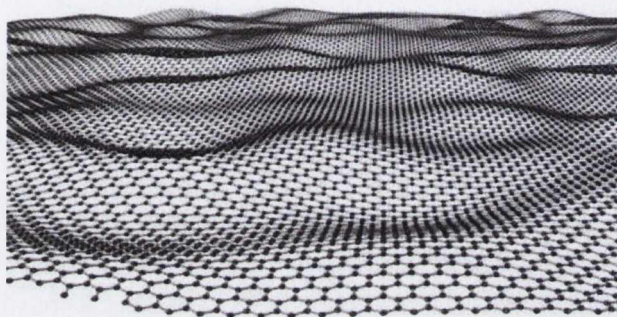


Figure 2.6: Structural model of a graphene membrane. Ripples spontaneously appear due to thermal fluctuations as has been seen experimentally in suspended graphene [54]

The graphene planes in graphite are held together by weak, attractive intermolecular forces called van der Waals forces [55]. The nature of this force is what enables graphite to be broken so easily into thin flakes that make up the mark left on the paper when writing with a pencil. In 2004 Geim and co-workers in Manchester University managed to produce single crystals of graphene by mechanical exfoliation [56]. This result surprised the scientific community because the produced samples were stable at room temperature and of high crystallinity. Their experimental set up consisted of a piece of sticky tape and a piece of graphite. The tape was stuck on the graphite and peeled off repeatedly. Subsequent optical analysis proved the existence of graphene. This process is called *micromechanical cleavage* and it has also been used to produce two dimensional crystals of other materials [57]

Graphene is thin and it is also extremely strong and stiff [58]. In its pure form, graphene, could have a mobility of $\sim 100,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature

which is higher than the values reported for other semiconductors [59, 60]. Although applications that use graphene could still be a few years ahead, fundamental physics, like relativistic quantum mechanics, is being studied at the moment. For example, electrons in graphene, apart from traveling great distances ballistically [56], also do it as if its mass was less than when traveling through conventional metals. This is caused by the interaction with the hexagonal lattice. These new type of *electric charge carriers* are called *Dirac massless fermions* and obey the rules set by Dirac's equation in quantum mechanics [61]:

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \boldsymbol{\sigma} \cdot \mathbf{k} \quad (2.5)$$

where $\mathbf{k}$ is the quasiparticle momentum, $\boldsymbol{\sigma}$ the 2D Pauli matrix and v_F is the Fermi velocity. The speed at which these massless Dirac fermions move is relativistic (around 300 times less than the speed of light), therefore Quantum Electrodynamics (QED) effects could be studied at room temperature on a bench-top experiment. This type of physics was previously studied only by cosmologists and high energy physicists.

One of the interesting effects predicted by QED is called the Klein paradox which describes circumstances in which a relativistic object can pass through any potential energy barrier no matter how high or high wide it is [62]. Heisenberg's uncertainty principle states that certain physical quantities, like position and momentum, cannot both have precise values at the same time. The narrower the probability distribution for one, the wider it is for the other. One of the consequences of this principle is that even though a low-energy particle might seem trapped by a high barrier, there is some probability that the particle will later be found outside that barrier. This is called *quantum tunneling* and the probability of it happening shrinks as the barrier gets higher and thicker. The Klein paradox states that relativistic particles should tunnel through barrier regions of high energy and broad expanse with a 100% probability. One of the consequences of the Dirac equation is the existence of antiparticles. When a relativistic particle pairs up with its antiparticle it doesn't see the barrier and therefore can travel through it. This particle will then unpair from its antiparticle and appear at the other side of the barrier [63]. In Graphene

the Klein paradox becomes a routine effect with readily observable consequences.

Klaus von Klitzing discovered in 1980 that in a 2D electron gas at a temperature close to absolute zero the Hall resistivity becomes quantized taking discrete values of h/ne^2 (where h is the Planck's constant, n is a positive integer and e is the electric charge) [64]. The quantization is so precise that this *Quantum Hall Effect* (QHE) is used as a standard for measuring resistivity. Geim and co-workers measured the QHE of graphene at room temperature [61]. This was a surprise because the QHE had only been measured in metals at very low temperatures. This occurs because the magnetic energy of the electrons (cyclotron energy) in graphene is 1000 times greater than in other materials [65, 66].

Schedin *et.al.* showed that chemical sensors made from graphene are capable of detecting individual events when a gas molecule attaches or detaches on its surface. The adsorbed molecules change the local carrier concentration in graphene by one electron, which leads to step-like changes in resistance. In conventional sensors such resolution has been out of reach of any detection technique, due to fluctuations caused by thermal motion of charges and defects. The intrinsic noise caused by such fluctuations is very low in the graphene case [67]. Other authors have also reported the introduction of graphene in composites [52, 68] to give conducting materials. Recently, functionalized graphene has also been tested for applications in solar cells [69, 70]

Micromechanical cleavage produces graphene at a very low yield. Other production methods like epitaxial growth [71] and graphene functionalization have been developed [51]. However, the electronic properties of graphene are seriously compromised by these production methods. In chapters 6 and 7, two different methods for the production of graphene in solution will be introduced. The first one is the exfoliation of graphite in organic solvents to produce graphene with a high yield. The second one is a first step towards the dispersion of graphite in surfactant systems to produce graphene. It is important to note that this two new methods do not compromise the crystallinity of graphene or its electronic properties which makes them advantageous over other methods to produce graphene in solution.

References

- [1] A. Oberlin, M. Endo, and T. Koyama. *Journal of Crystal Growth*, 32(3):335, 1976.
- [2] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley. *Nature*, 318:162, 1985.
- [3] Sumio Iijima. *Nature*, 354:56, 1991.
- [4] L. X. Zheng, M. J. O'Connell, S. K. Doorn, X. Z. Liao, Y. H. Zhao, E. A. Akhadow, M. A. Hoffbauer, B. J. Roop, Q. X. Jia, R. C. Dye, D. E. Peterson, S. M. Huang, J. Liu, and Y. T. Zhu. *Nature Materials*, 3(10):673, 2004.
- [5] Sumio Iijima and Toshinari Ichihashi. *Nature*, 363:603, 1993.
- [6] D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers. *Nature*, 363:605, 1993.
- [7] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus. *Applied Physics Letters*, 60(18):2204, 1992.
- [8] M. S. Dresselhaus, G. Dresselhaus, Ph Avouris, and Editors. *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*. [In: *Top. Appl. Phys.*, 2001; 80]. 2001.
- [9] Riichiro Saito, Mitsutaka Fujita, G. Dresselhaus, and M. S. Dresselhaus. *Physical Review B: Condensed Matter and Materials Physics*, 46(3):1804, 1992.
- [10] Fangming Du, Robert C. Scogna, Wei Zhou, Stijn Brand, John E. Fischer, and Karen I. Winey. *Macromolecules*, 37(24):9048, 2004.

- [11] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko. *Carbon*, 44(9):1624, 2006.
- [12] J. N. Coleman, U. Khan, and Y. K. Gun'ko. *Advanced Materials*, 18(6):689, 2006.
- [13] S. Berber, Y. Kwon, and D. Tomnek. *Physical Review Letters*, 84(20):4613, 2000.
- [14] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio. *Nature*, 382:54, 1996.
- [15] H. Dai and et al. *Science (Washington, D. C.)*, 272(5263):797, 1996.
- [16] Sander J. Tans, Michel H. Devoret, Hongjie Dai, Andreas Thess, Richard E. Smalley, L. J. Geerligs, and Cees Dekker. *Nature*, 386:474, 1997.
- [17] Ching-Hwa Kiang, III Goddard, William A., Robert Beyers, and Donald S. Bethune. *Carbon*, 33(7):903, 1995.
- [18] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapells, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer. *Nature*, 388:756, 1997.
- [19] Andreas Thess, Roland Lee, Pavel Nikolaev, Hongjie Dai, Pierre Petit, Jerome Robert, Chunhui Xu, Young Hee Lee, Seong Gon Kim, and et al. *Science (Washington, D. C.)*, 273:483, 1996.
- [20] Jing Kong, Hyongsok T. Soh, Alan M. Cassell, Calvin F. Quate, and Hongjie Dai. *Nature*, 395:878, 1998.
- [21] Guangli Che, Brinda B. Lakshmi, Ellen R. Fisher, and Charles R. Martin. *Nature*, 393:346, 1998.
- [22] Hyongsok T. Soh, Calvin F. Quate, Alberto F. Morpurgo, Charles M. Marcus, Jing Kong, and Hongjie Dai. *Applied Physics Letters*, 75(5):627, 1999.
- [23] Cheol Jin Lee, Dae Woon Kim, Tae Jae Lee, Young Chul Choi, Young Soo Park, Won Seok Kim, Young Hee Lee, Won Bong Choi, Nae Sung Lee, Jong Min Kim, Yong Gak Choi, and Soo Chang Yu. *Applied Physics Letters*, 75(12):1721, 1999.

- [24] T. W. Ebbesen, P. Ajayan, H. Hiura, and Tanigaki K. *Nature*, 367:519, 1994.
- [25] Jeong-Mi Moon, Kay Hyeok An, Young Hee Lee, Young Soo Park, Dong Jae Bae, and Gyeong-Su Park. *Journal of Physical Chemistry B*, 105(24):5677, 2001.
- [26] Tak Jeong, Wan-Young Kim, and Yoon-Bong Hahn. *Chemical Physics Letters*, 344(1,2):18, 2001.
- [27] Philip G. Collins and Phaedon Avouris. *Scientific American*, 283(6):62, 2000.
- [28] William D Callister. *Fundamentals of materials Science and Engineering*. Wiley, New York.
- [29] Karsten Fehse, Karsten Walzer, Karl Leo, Wilfried Loevenich, and Andreas Elschner. *Advanced Materials (Weinheim, Germany)*, 19(3):441, 2007.
- [30] Brandrup J. and Immergut E. H. *Polymer Handbook*. Wiley Interscience, New York.
- [31] M. Terrones. *International Materials Reviews*, 49(6):325, 2004.
- [32] P. M. Ajayan, O. Stephan, C. Colliex, and D. Trauth. *Science*, 265:1212, 1994.
- [33] H. Baughman Ray, A. Zakhidov Anvar, and A. de Heer Walt. *Science*, 297:787, 2002.
- [34] Elzbieta Frackowiak and Francois Beguin. *Carbon*, 40(10):1775, 2002.
- [35] Jean-Marc Bonard, Jean-Paul Salvetat, Thomas Stockli, Walt A. de Heer, Laszlo Forro, and Andre Chatelain. *Applied Physics Letters*, 73(7):918, 1998.
- [36] R. Ramasubramaniam, J. Chen, and H. Y. Liu. *Applied Physics Letters*, 83(14):2928, 2003.
- [37] D. S. McLachlan and Michael B. Heaney. *Physical Review B: Condensed Matter and Materials Physics*, 60(18):12746, 1999.
- [38] Umar Khan, Kevin Ryan, Werner J. Blau, and Jonathan N. Coleman. *Composites Science and Technology*, 67(15-16):3158, 2007.

- [39] Milo S. P. Shaffer and Alan H. Windle. *Advanced Materials (Weinheim, Germany)*, 11(11):937, 1999.
- [40] Christophe Stephan, Thien Phap Nguyen, Bernd Lahr, Werner Blau, Serge Lefrant, and Olivier Chauvet. *Journal of Materials Research*, 17(2):396–400, 2002.
- [41] M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolosi, G. Bister, A. Fonseca, J. B. Nagy, K. Szostak, F. Beguin, and W. J. Blau. *Nano Letters*, 4(2):353, 2004.
- [42] I. Musa, M. Baxendale, G. A. J. Amaratunga, and W. Eccleston. *Synthetic Metals*, 102(1-3):1250, 1999.
- [43] Murielle Cochet, Wolfgang K. Maser, Ana M. Benito, M. Alicia Callejas, M. Teresa Martinez, Jean-Michel Benoit, Joachim Schreiber, and Olivier Chauvet. *Chemical Communications*, (16):1450, 2001.
- [44] S. Giordani, S. D. Bergin, V. Nicolosi, S. Lebedkin, M. M. Kappes, W. J. Blau, and J. N. Coleman. *J. Phys. Chem. B*, 110(32):15708, 2006.
- [45] J. N. Coleman, S. Curran, A. B. Dalton, A. P. Davey, B. Mc Carthy, W. Blau, and R. C. Barklie. *Synthetic Metals*, 102(1-3):1174, 1999.
- [46] B. Safadi, R. Andrews, and E. A. Grulke. *Journal of Applied Polymer Science*, 84(14):2660, 2002.
- [47] Petra Potschke, T. D. Fornes, and D. R. Paul. *Polymer*, 43(11):3247, 2002.
- [48] M. S. Dresselhaus and G. Dresselhaus. *Advances in Physics*, 30(2):139, 1981.
- [49] L. M. Viculis, J. J. Mack, and R. B. Kaner. *Science*, 299:1361, 2003.
- [50] X. L. Li, X. R. Wang, L. Zhang, S. W. Lee, and H. J. Dai. *Science*, 319:1229, 2008.
- [51] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff. *Carbon*, 45(7):1558, 2007.
- [52] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff. *Nature*, 442:282, 2006.

- [53] S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, and R. C. Haddon. *Journal of the American Chemical Society*, 128(24):7720, 2006.
- [54] A. Fasolino, J. H. Los, and M. I. Katsnelson. *Nature Materials*, 6(11):858, 2007.
- [55] J. C. Charlier, X. Gonze, and J. P. Michenaud. *Europhysics Letters*, 28(6):403–8, 1994.
- [56] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. *Science*, 306:666, 2004.
- [57] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. *Proceedings of the National Academy of Sciences of the United States of America*, 102(30):10451, 2005.
- [58] Changgu Lee, Xiaoding Wei, Jeffrey W. Kysar, and James Hone. *Science (Washington, DC, United States)*, 321(5887):385, 2008.
- [59] Yijian Ouyang, Paul Campbell, and Jing Guo. *Applied Physics Letters*, 92(6):063120/1, 2008.
- [60] Koichi Saito, Jun Nakamura, and Akiko Natori. *Physical Review B: Condensed Matter and Materials Physics*, 76(11):115409/1, 2007.
- [61] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov. *Nature*, 438:197, 2005.
- [62] Mikhail I. Katsnelson. *Materials Today (Oxford, United Kingdom)*, 10(1-2):20, 2007.
- [63] Andre K. Geim and Philip Kim. *Scientific American*, 298(4):90, 2008.
- [64] K. Von Klitzing, G. Dorda, and M. Pepper. *Physical Review Letters*, 45(6):494, 1980.
- [65] Y. B. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim. *Nature*, 438:201, 2005.
- [66] Antonio Castro Neto, Francisco Guinea, and Nuno Miguel Peres. *Physics World*, 19(11):33, 2006.

- [67] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov. *Nature Materials*, 6(9):652, 2007.
- [68] Yenny Hernandez, Valeria Nicolosi, Mustafa Lotya, Fiona M. Blighe, Zhenyu Sun, Sukanta De, I. T. McGovern, Brendan Holland, Michele Byrne, Yurii K. Gun'Ko, John J. Boland, Peter Niraj, Georg Duesberg, Satheesh Krishnamurthy, Robbie Goodhue, John Hutchison, Vittorio Scardaci, Andrea C. Ferrari, and Jonathan N. Coleman. *Nature Nanotechnology*, 3(9):563, 2008.
- [69] Xuan Wang, Linjie Zhi, and Klaus Muellen. *Nano Letters*, 8(1):323, 2008.
- [70] Junbo Wu, Hector A. Becerril, Zhenan Bao, Zunfeng Liu, Yongsheng Chen, and Peter Peumans. *Applied Physics Letters*, 92(26):263302/1, 2008.
- [71] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. deHeer. *J. Phys. Chem. B*, 108(52):19912, 2004.

Chapter 3

Materials and methods

3.1 Materials

Carbon Nanotubes are mainly produced by electric arc discharge under inert atmospheres [1–3], laser ablation of graphite under inert atmospheres [4, 5] and chemical vapour deposition (CVD)[6]. These techniques produce CNTs at different yields and levels of graphitisation [7]. Catalytic carbon vapor deposition (CCVD) is the growth technique that gives higher yields of SWNT and MWNT [8, 9]. The CNTs used in this work were obtained from Nanocyl¹ where they were produced by CCVD. This technique consists of the decomposition of hydrocarbons in an inert atmosphere at high temperatures (500°C). The decomposed carbon molecules subsequently diffuse into catalyst particles on patterned substrates. Upon saturation, carbon is precipitated in the form of nanotubes. Figure 3.1 shows a schematic of a typical CVD system used for nanotube growth.

Carbon Nanodisks (CNDs) are graphitic microstructures (see Figure 3.2) prepared by pyrolysis of hydrocarbons in a carbon arc [10] (purchased from n-Tec²). This process consists of an industrial scale carbon-arc plasma generator under a continuous flow of hydrocarbon (i.e. heavy oil) at a typical feed rate of 50 - 150 kg h⁻¹ and a reactor pressure of 2-3 bar.

¹www.nanocyl.be, Product code 3100

²www.n-tec.no

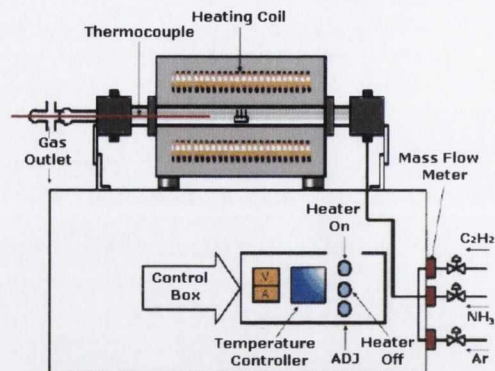


Figure 3.1: Typical setup used in CVD

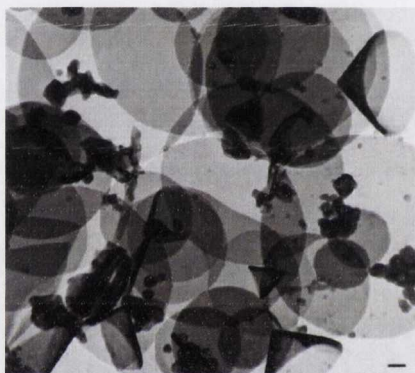


Figure 3.2: TEM image of the microstructures present in the CNDs powder. Scale bar 200nm

The graphite powder used in the majority of experiments was purchased from Sigma-Aldrich (Product Number 332461) and sieved through a 0.5 mm mesh sieve to remove the larger particles.

3.2 Sample preparation

The experiments presented in this thesis are divided into 2 parts: polymer-nanotube composite electrical characterisation and graphene dispersion in organic solvents and surfactant systems.

- Polymer-MWNT and Polymer CND composites: Polymer solutions were prepared by dissolving polyvinylalcohol (PVA), in the relevant solvent at a con-

centration of 30 mg/ml. Composite solutions were prepared by adding a mass of MWNT/CND to each polymer solution. These were then sonicated using a sonic tip for 10 minutes, a sonic bath for 2 hours and then again with a sonic tip for 10 minutes. The dispersions were left for 24 hours to allow any unstable nanotube aggregates to sediment out. These were then removed by decantation. The nanotube mass fraction after sedimentation was measured by comparison with the optical absorbance before and after sedimentation. The solutions were blended down with PVA solutions in the appropriate solvent to give a range of mass fractions. Free-standing films were drop-cast in standard weighting boats. The solvents were removed by evaporation under vacuum at a temperature of 60°C. The films were peeled from the substrates and cut for electrical characterization (Figure 3.3).

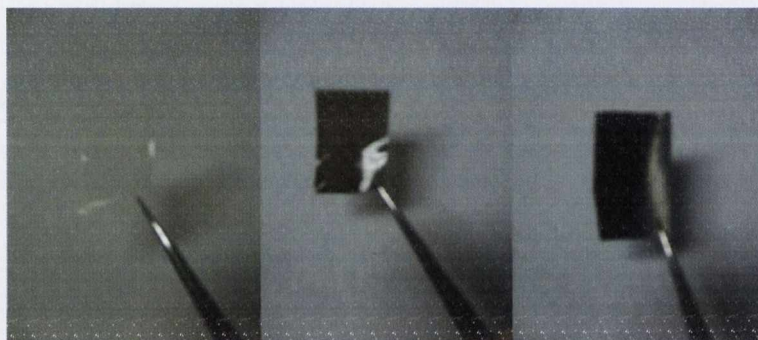


Figure 3.3: PVA-MWNT composite films of 3 different mass fractions 0%, 1% and 2% respectively

- Graphene dispersion in surfactants and organic solvents: Graphite Flakes from Sigma Aldrich were sieved through a 0.5 mm mesh to remove large particles. The sieved flakes were then added to the relevant liquid system at a typical concentration of 0.1 mg/ml. The samples were sonicated in the sonic bath for 30 minutes. The resultant dispersion was then centrifuged for 90 minutes at 500 rpm. The samples were decanted by pouring. The stability of the solutions was subsequently studied using a home-built sedimentation machine. The solutions can then be characterized using electron microscopy and spectroscopic techniques. Furthermore, graphene thin films can be produced by vacuum filtration as described in chapter 6.

3.3 Methods of Analysis

In this section the techniques used in the sample preparation and sample characterisation are reviewed:

In the composite work, the concentration after sedimentation was calculated by the differences in absorbance. Electrical contacts were evaporated on the drop casted composite films for DC and AC characterisation. In order to compare the percolation parameters obtained from the electrical data, the aspect ratio of the nanotubes used was determined via Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Powder conductivities of the starting filler materials were measured using a home-made apparatus (see figure 3.7)

In the dispersion work, absorption spectroscopy was used extensively to quantify the fraction of graphene remaining after centrifugation. The successful exfoliation of graphene from graphite was confirmed by transmission electron microscopy (TEM) and Raman spectroscopy. Thick films of graphene and polystyrene-graphene composites were characterised by SEM and Raman spectroscopy. Electrical characterisation was also carried out on these samples.

3.3.1 Absorption Spectroscopy

In absorption spectroscopy, the absorption of nearly monochromatic incident radiation is monitored as the radiation is scanned over a range of frequencies. The ratio of the transmitted intensity, I , to the incident intensity I_0 , at a given frequency is called the transmittance, T , of the sample at that frequency:

$$T = \frac{I}{I_0}$$

It is found empirically that the transmitted intensity varies with the length, l , of the sample and concentration, C , of the absorbing species according to the **Beer - Lambert law**:

$$I = I_0 10^{-\epsilon Cl} \quad (3.1)$$

The quantity ε is called the **extinction coefficient** [11] which depends on the frequency of the incident radiation and is greatest where the absorption is most intense. The form of equation 3.1 suggests that it is sensible to introduce the **absorbance**, A of a sample at a given wavenumber as

$$A = \log \frac{I_0}{I} = -\log T$$

Then the Beer - Lambert law becomes

$$A = \varepsilon Cl \quad (3.2)$$

A Cary 6000i UV-Vis spectrometer was used to quantify the concentration remaining in the composites/graphene samples after decantation, through the application of equation 3.2.

3.3.2 Sedimentation

The stability of graphene dispersions after centrifugation were measured with the aid of a home-built sedimentation machine (figure 3.4). This apparatus consists of four lasers stacked vertically across from four detectors, with the cuvette placed between them. The transmission of the lasers ($\lambda = 650 \text{ nm}$, pulse duration = 10 ms) through the cuvette could then be measured as a function of time. The transmission of the four lasers through the cuvette was averaged and this was then converted to absorbance using the Beer-Lambert law discussed previously.

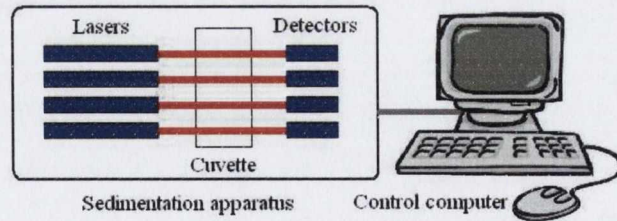


Figure 3.4: Sedimentation apparatus diagram. The cuvette contains the dispersion to be monitored

3.3.3 Two probe electrical measurements

The electrical characterization in this work was mainly done in a two probe configuration. Gold and silver were used as contacts, due to their non-reactive characteristics (the formation of oxides on the contact surface increases the contact resistance of the measurements taken). Contacts were typically 50 nm thick.

The drop cast composite films were peeled off the substrates, cut into 12mm $\times$ 12mm squares and then gold contacts were evaporated on them yielding six sandwich-structure devices with an active area of 6mm² (figure 3.5). Current-Voltage (IV) measurements were performed using a Keithley Model 2400 sourceme-
ter.

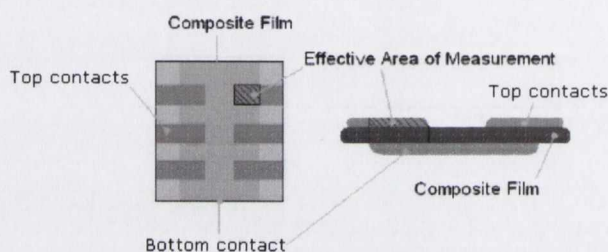


Figure 3.5: Electrical contacts deposited on composite films

Impedance spectroscopy is an established non-destructive tool for analysing electrical properties of insulator/conductor composite materials [12] where the dynamics of bound or mobile charge in the bulk or interfacial regions of a material can be investigated. Impedance vs frequency measurements were performed using a Zahner IM6e impedance spectrometer over a frequency range of 1Hz-1MHz with an applied alternating voltage of 20mV. All AC and DC measurements were made on five devices³ on each sample and subsequently averaged.

Vacuum evaporation

Resistive thermal evaporation is one of the most commonly used metal deposition techniques. It consists of vaporising a solid material by heating it to sufficiently high temperatures and recondensing it onto a cooler substrate to form a thin film.

³In general not all 6 evaporated contacts worked

As the name implies, the heating is carried out by passing a large current through a filament container (usually in the shape of a basket, boat or crucible) which has a finite electrical resistance. The choice of this filament material is dictated by the evaporation temperature and its inertness to alloying/chemical reaction with the evaporant.

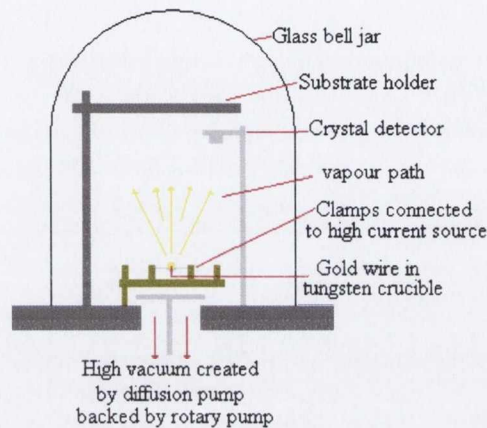


Figure 3.6: Schematic diagram of a evaporation system

Once the metal is evaporated, its vapour undergoes collisions with the surrounding gas molecules inside the evaporation chamber. As a result, a fraction of the vapour is scattered within a given distance during its transfer through the ambient gas. The mean free path for air at 25°C is approximately 45 and 4500 cm at pressures of 1×10^{-4} and 1×10^{-6} mbar respectively [13]. Therefore pressures lower than 1×10^{-5} mbar are necessary to ensure a straight line path for most of the evaporated species and for a substrate-to-source distance of approximately 10 to 50 cm in a vacuum chamber. A good vacuum is also a prerequisite for producing contamination free deposits.

The Edwards 306 thin film coating system was used for the deposition of the contacts referred to in this work; a schematic diagram of such a system is shown in figure 3.6. The system is fitted with an acoustic crystal monitor which is linked to an Edwards film thickness monitor for controlling the amount of metal deposited. The quartz crystal oscillates at a resonance frequency that is linearly dependant on the thickness and mass of the film deposited onto it [14]. To measure the deposition

thickness precisely, the crystal monitor must be provided with information about the material being evaporated, specifically its density and Z-ratio. The Z-ratio is the parameter that corrects the frequency change to a thickness transfer function for the effects of acoustic impedance mismatch between the crystal and the coated material. Gold was the preferred metal to evaporate and tungsten crucibles were used. The chamber pressure before evaporation was $\sim 2 \times 10^{-6}$ mbar. The current used was $\sim 2A$ and the average evaporation time was ~ 25 minutes for a 50nm thick contact. Faster evaporations would require higher currents that could break the crucible.

Powder conductivity measurements

Powder conductivity measurements were taken for carbon disks and MWNTs powders. The setup used is shown in figure 3.7. The powders were deposited in the drilled cavity, E, which is 5mm in diameter. A copper base plate forms the bottom electrode (C). An aluminium rod, of diameter equal to that of the drilled hole, is located on top of the powder as the top contact (D). The resistance across the contacts is measured. A traveling microscope measures the difference in height of the metal rod which is used to determine the powder density.

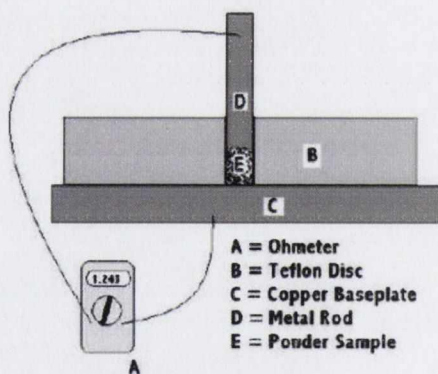


Figure 3.7: Powder conductivity measurement apparatus

Different compressing weights are applied on top of the metal rod and resistance measurements are taken again. Mamunya *et.al.* reported an increase in the conductivity with the applied pressure and the particle size (in the case of metallic

particles)[15].

3.3.4 Atomic Force Microscopy - AFM

The atomic force microscope (AFM) is a very high-resolution scanning probe microscope, with resolutions of up to fractions of a nanometer. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s [16]. Smith *et.al.* designed and built the first AFM in 1986 [17]. The AFM is one of the foremost tools for imaging, measuring and manipulating at the atomic scale. Accurate scanning is enabled by piezoelectric elements that facilitate tiny but accurate and precise movements on electronic command.

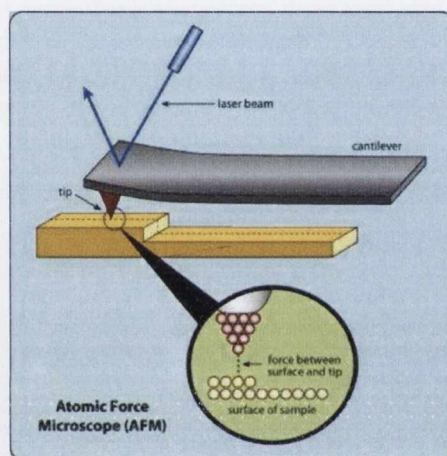


Figure 3.8: Schematic diagram of the AFM

The AFM consists of a microscale cantilever with a sharp tip at its end that is used to scan the sample surface (See figure 3.8). The cantilever is typically silicon or silicon nitride with a tip radius of curvature of 10nm [18]. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the sample, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces and magnetic forces. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge.

If the tip was scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction in order to maintain a constant force, and the x and y directions for scanning the sample. The resulting map of the area represents the topography of the sample.

The primary modes of operation are static (contact) mode and dynamic (tapping) mode. In static mode operation, the static tip deflection is used as a feedback signal. In the dynamic mode, the cantilever is externally oscillated at or close to its fundamental resonance frequency. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. In dynamic contact mode, the cantilever is oscillated such that the separation distance between the cantilever tip and the sample surface is modulated.

The AFM used in this study was a Digital Instruments Multimode SPM with Nanoscope 3A controller. All the images were taken in dynamic (tapping) mode. The substrates on which the samples were deposited and the AFM tips were both made of silicon.

3.3.5 Scanning Electron Microscopy - SEM

In a typical SEM[19], a high voltage is applied to a tungsten filament causing electrons to be emitted. The electron beam is focused by one or two condenser lenses onto a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface (See figure 3.9). The way in which the electrons are thermally emitted and scanned through an area resembles the now old cathode ray televisions.

When an electron beam hits matter, it begins to broaden because of strong elastic scattering effects. Simultaneously, inelastic interactions cause an energy loss of the

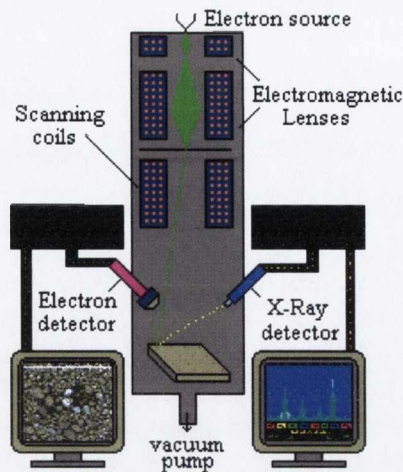


Figure 3.9: Schematic diagram of the SEM

electrons. If the sample is very thick, the energy will be completely transferred to the sample. The overall result is a pear-shaped interaction volume (figure 3.10). The angle and energy at which the electrons are scattered (by elastic and inelastic collisions) in the SEM allows them to be classified as backscattered, auger and secondary electrons. Each of these signals is registered in a different type of detector.

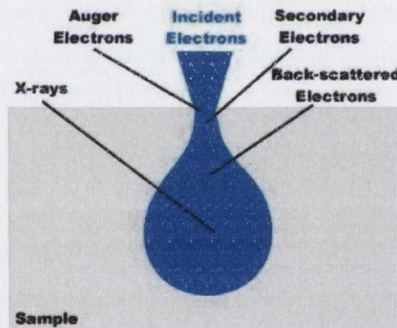


Figure 3.10: Inelastic interactions cause an electron energy loss. For a thick sample, the energy will be completely transferred throughout the volume resulting in a pear-shaped interaction volume

The energy dispersive X-ray (EDX) detector is used to quantify the chemical composition of the sample. The backscattered electrons give information about the mean atomic number of the scanned area in the sample. Usually, brighter areas mean that heavier elements are present compared to other areas. The secondary

electrons give information about the surface topography of the sample [19].

The samples for the SEM need to be both conducting and heat resistant. Although most of the time this is not the case, there are ways to get around the problem. For example, an easy way to characterize a non-conducting sample is to stick it onto a conductive adhesive (made out of copper or carbon). Gold coating the sample is another option if the conductive tape is not enough for successful imaging. Gold is inert and very conducting, two of the main requirements for coating SEM samples. Gold-Palladium⁴ and carbon can also be used as conducting coatings. Biological samples generally require freezing and other preparation techniques for SEM imaging. Even though metal coating generally works for low melting point samples it might be necessary to vary the imaging conditions (i.e. spot size and accelerating voltage) or to use a cooled sample holder (cryo-SEM).

The system used in the work presented in this thesis was the Hitachi S-4300 Field Emission Scanning Electron Microscope equipped with a secondary electrons detector and an EDX detector. The accelerating voltage typically used was 5kV.

3.3.6 Transmission Electron Microscopy - TEM

In TEM the electrons are transmitted through the sample and create an image on a fluorescent screen (see figure 3.11). The transmission process requires more energetic electrons than the SEM, as well as thinner samples. Working voltages in TEM range between 80kV and 300kV. Such high accelerating voltages require an ultrahigh vacuum in order to reduce the scattering of electrons within the column. The samples need to be thinner than 500nm.

Two systems were used in this study: the Hitachi H-7000 and the Jeol 2100. The samples were prepared by dropping a few milliliters of the relevant solution on copper grids (mesh size 400) with a holey carbon coating.

3.3.7 Raman Spectroscopy

The inelastic scattering of photons by molecules is known as the Raman effect. This effect allows the study of the vibrational energy levels of a system. Typically, the ex-

⁴This alloy is preferred over gold due to its smaller cluster size

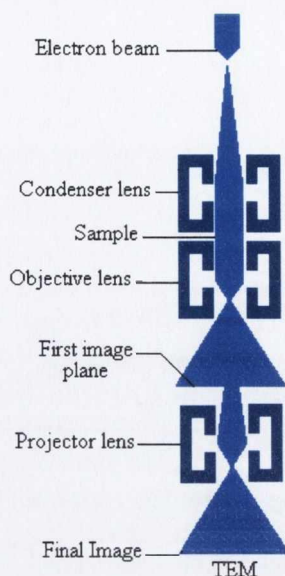


Figure 3.11: Schematic diagram of the TEM

periment consists of a monochromatic beam being reflected off (or passed through) a sample and the radiation that is scattered perpendicular to the beam being monitored. These scattered photons are accounted for by the lower-frequency Stokes radiation from the sample. Other photons may collect energy from the molecules and emerge as higher-frequency anti-Stokes radiation. The component of radiation scattered in the forward direction is known as Rayleigh radiation (Figure 3.12).

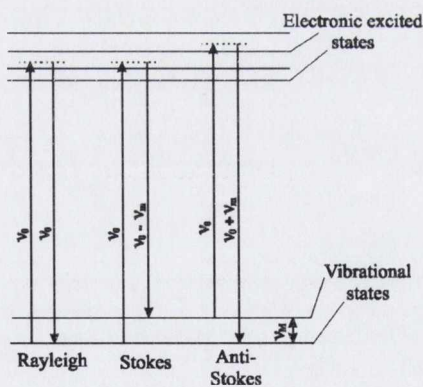


Figure 3.12: Energy levels in Raman spectroscopy.

As the shifts in frequency of the scattered radiation are so small, it is very important that the incident light be monochromatic in order for the shifts to be

observed. The energy shift yields information on the phonon modes in the system. For a vibration mode to be Raman active, the polarisability of the molecule must change with the vibrational direction. Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules. It can act as a fingerprint for the identification of molecules or specific components of larger systems [20].

The Raman Spectroscopy measurements shown in this thesis were taken with the Jobin Yvon Raman System fitted with a Argon laser ($\lambda = 532\text{nm}$)

3.3.8 Thermogravimetric analysis - TGA

Thermogravimetric analysis (TGA) measures physical changes in materials. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation. In chapter 6 the preparation of high volume fraction graphene/polystyrene (PS) composites will be discussed⁵. To prepare this set of composites PS should be used in excess [21] therefore TGA is needed to quantify the amount of PS remaining after filtration. The system used was the Perkin Elmer Pyris 1 TGA. The temperature ranges from 30°C to 900 °C with the typical temperature rate at 10 °C /minute in an oxygen atmosphere.

⁵This set of experiments was conducted by Dr. Fiona Blighe

References

- [1] D. S. Bethune, C. H. Klang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers. *Nature*, 363(6430):605–607, 1993.
- [2] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio. *Nature*, 382(6586):54–56, 1996.
- [3] Ching-Hwa Kiang, William A. Goddard, Robert Beyers, and Donald S. Bethune. *Carbon*, 33(7):903–914, 1995.
- [4] C. Kramberger, M. Loeffler, M. Ruemmeli, A. Grueneis, R. Schoenfelder, O. Jost, T. Gemming, T. Pichler, and B. Buechner. *Physica Status Solidi B: Basic Solid State Physics*, 243(13):3050, 2006.
- [5] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer. *Nature*, 388(6644):756–758, 1997.
- [6] Alan M. Cassell, Jeffrey A. Raymakers, Jing Kong, and Hongjie Dai. *Journal of Physical Chemistry B*, 103(31):6484, 1999.
- [7] M. Terrones. *International Materials Reviews*, 49(6):325, 2004.
- [8] Pavel Nikolaev, Michael J. Bronikowski, R. Kelley Bradley, Frank Rohmund, Daniel T. Colbert, K. A. Smith, and Richard E. Smalley. *Chemical Physics Letters*, 313(1,2):91, 1999.
- [9] Jing Kong, Hyongsok T. Soh, Alan M. Cassell, Calvin F. Quate, and Hongjie Dai. *Nature (London)*, 395(6705):878, 1998.
- [10] A. Krishnan, E. Dujardin, M. M. J. Treacy, J. Hugdahl, S. Lynum, and T. W. Ebbesen. *Nature*, 388(6641):451, 1997.

- [11] P. Atkins & J. de Paula. *Physical Chemistry*. Oxford University Press, 2002.
- [12] J. R. Macdonald. *Impedance Spectroscopy: emphasizing solid materials and systems*. Wiley, 1987.
- [13] R. V. Stuart. *Vacuum Technology, Thin Films and Sputtering*. Academic Press, 1983.
- [14] Daniel James, David V. Thiel, Gillian R. Bushell, W. Ken Busfield, and Alan Mackay-Sim. *Analyst (Cambridge, United Kingdom)*, 119(9):2005, 1994.
- [15] Ye P. Mamunya, H. Zois, L. Apekis, and E. V. Lebedev. *Powder Technology*, 140(1-2):49, 2004.
- [16] Gerd Binnig and Heinrich Rohrer. Scanning apparatus for surface investigation using vacuum-tunnel effect at cryogenic temperatures, 1981.
- [17] D. P. E. Smith, G. Binnig, and C. F. Quate. *Applied Physics Letters*, 49(18):1166, 1986.
- [18] R. Bennewitz E. Meyer, H. J. Hug. *Scanning Probe Microscopy*. Springer-Verlag, 2004.
- [19] Graham Lawes. *Scanning Electron Microscopy and X-Ray Microanalysis*. John Wiley & Sons, 1987.
- [20] M. J. Pelletier. *Analytical Applications of Raman Spectroscopy*. 1999.
- [21] F. M. Blighe, Y. Hernandez, W. J. Blau, and J. N. Coleman. *Advanced Materials*, 19:4443, 2007.

Chapter 4

The effect of solvent choice on the electrical percolation of polymer-nanotube composites

4.1 Introduction

In the area of nanotube based composites, reinforcement [1, 2] and percolation [3] have been demonstrated at extremely low loading levels. This is of huge interest to the aviation and automotive industries for applications such as electromagnetic interference shielding (EMI), electrostatic dissipation and electrostatic painting [4].

Many studies have been carried out in the area of conductive composites formed from nanotubes or nanowires embedded in polymer matrices [3, 5–11]. Most of these studies have been aimed at reducing the percolation threshold; a goal to which nanotubes are perfectly suited due to their large aspect ratio. A more important goal is perhaps to maximize the composite conductivity. With a few exceptions [4, 12, 13] the vast majority of studies appear to reach a maximum conductivity below 1 S/m [3, 6, 10, 11, 14–17]. In general this is due to the conductivity bottleneck caused by the presence of polymer tunneling barriers [6]. It would be extremely useful to understand the factors controlling the formation of the polymer coatings on nanotubes that lead to these tunneling barriers.

One parameter within our control that should strongly affect the properties of the polymer coatings is the solvent choice. This has previously been shown to

have significant effects on the mechanical properties of polymer-nanotube composites [18]. This chapter will investigate the electrical conductivities of polyvinylalcohol (PVA) - MWNT composites using dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and deionized water as solvents. The choice of solvent has also a significant effect on both the percolation threshold and the maximum conductivity. Changes in these properties are attributed to the effect of the solvent on the polymer coatings that form around the nanotubes in the solution phase.

4.2 Percolation Theory

In percolation theory a large change in the physical properties of a composite material occurs when the filler concentration reaches the point at which a connecting cluster throughout the entire volume is formed [19]. This usually occurs over a small concentration range. The volume fraction at which this occurs is called the *percolation threshold*, p_c . p_c depends on many factors including the connectivity of the phases and the size and shape of each phase.

For a set of regular lattice points there are two types of percolation: *site percolation* which considers the lattice vertices as the relevant entities and *bond percolation* which considers the lattice edges as the relevant entities. Site percolation is described by the following scaling law for 2D and 3D systems:

$$\sigma = \sigma_0(p - p_c)^t \quad (4.1)$$

where σ is the conductivity, p_c is the percolation threshold and t is a constant. Equation 4.1 is valid when $p > p_c$ and $(p - p_c)$ is small. As the mass fraction increases beyond the percolation threshold the conductivity increases sharply as conductive paths begin to form. The exponent t was once thought to be universal and to be only dependent on sample dimensionality with calculated values of $t = 1.33$ and $t = 2.0$ for 2D and 3D systems respectively. However, in recent theoretical studies t has been shown to be dependent on the aspect ratio and the size distribution of the filler particles [20].

In the case of polymer-nanotube composites the formation of conductive paths through the insulating matrix (Figure 4.1) leads to a change in conductivity val-

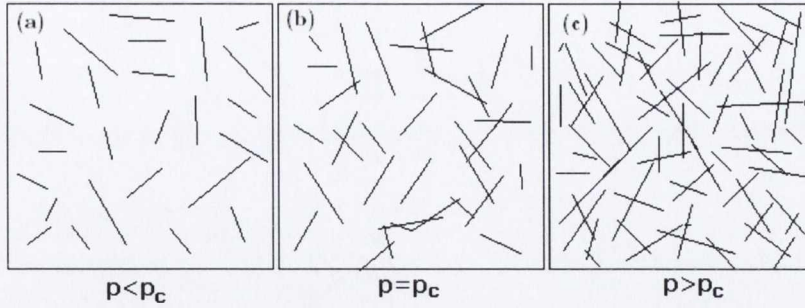


Figure 4.1: Increasing filler concentrations in an insulating volume in the case of "stick like" fillers

ues from 8 to 10 orders of magnitude. The lowest filler concentration needed for a macroscopic conductivity increase (i.e. the formation of an electrical pathway through the sample) has been observed to be as low as 0.005% by volume for some polymer blends [12, 21].

4.2.1 Excluded Volume Theory

In order to predict the percolation threshold of composite systems several theories have been developed. The first and more general one is the *Mean Field Theory* which consists of calculating the average effects of the random resistor network representing the binary mixture of an insulator and a conductor by a homogeneous effective medium. A conductivity equation applicable over a full range of compositions can be determined [22]. *Excluded volume* theories are less general but give similar results when the geometry of the filler particles is known.

The excluded volume can be seen as the volume around an object in which the center of another similarly shaped object is not allowed to penetrate. The excluded volume of a sphere of radius R can be easily shown to be 8 times its volume (assuming they are of the same radii) (figure 4.2(A)). The excluded volume for a capped cylinder, as calculated by Balberg *et.al.* [23] is not as straightforward to calculate as it depends on the orientation of the *stick-like* particles. The excluded area for widthless sticks of the same length (Figure 4.2(B)) is:

$$A_{exc} = (2l)^2 \sin \gamma = 4l^2 \sin \gamma \quad (4.2)$$

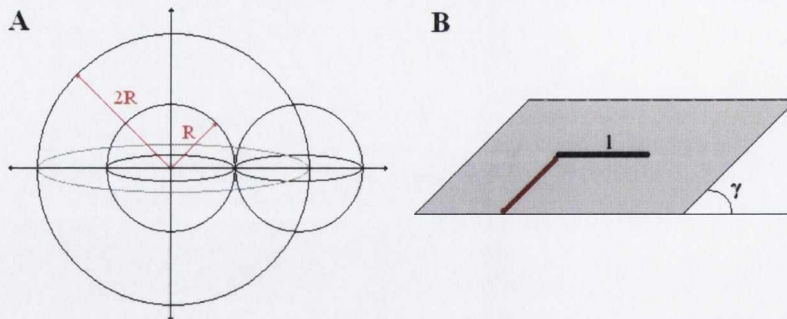


Figure 4.2: (A) Excluded volume for spheres of the same radii (B) Excluded area of widthless sticks

where l is the length of the stick and γ is the angle at which the sticks are oriented relative to one another. Furthermore, assuming random anisotropic orientations the excluded volume of finite width capped cylinders can be written as:

$$V_{ex} = 2d \left(\frac{2\pi}{3} d^2 + \pi dl + l^2 \frac{\pi}{4} \right) \quad (4.3)$$

where d is the diameter of the cylinder and l is its length. The first term of equation 4.3 is the contribution of the caps. The second term is the contribution of the cylinder and the last term comes from the parallelepiped drawn by a cylinder swept around another one averaged over random orientations [23]. Foygel *et.al.* [20] took Balberg's work one step further by calculating, using Monte Carlo simulations, the influence of making the cylinders interpenetrating to the excluded volume. This was found to be almost negligible. In the limit of high aspect ratio cylinders, p_c can be approximated to:

$$p_c = \frac{0.6}{a} = 0.6 \frac{d}{l} \quad (4.4)$$

The ratio between the diameter and the length of the filler particles is known as the aspect ratio (a in equation 4.4). The correlation between the aspect ratio and the percolation threshold has also been reported by several authors [24, 25].

Table 4.1 presents the difference in the percolation parameters reported by different authors. It has been arranged from earlier papers to more recent ones to show how improvements in the dispersion of CNTs has affected the percolation thresholds. It should be noted that a significant percentage of the reported values of t are

CNT	Polymer	Solvent	σ_0 (S/m)	p_c wt%	t	Reference
MWNT	PVA	Water		5%		[26]
SWNT	PMMA			3%		[27]
MWNT	PVA	Water	2×10^{-5}	0.030%	1.36	[6]
SWNT	polyimide	DMF	1.02×10^{-6}	0.050%	1.48	[28]
SWNT	PS	ChCl		0.11% – 0.045%	2.79 – 1.54	[4]
SWNT	Polyimide	DMF	1×10^{-6}	0.05% 1.5		[29]
SWNT	PANI	Xylene	1×10^{-2}	0.3%	2.13 – 2.06	[30]
MWNT	PMMA	Toluene		0.300%	2.4 – 2.15	[31]
SWNT	PVAc	Water	33.4	0.04%	1.9	[14]
MWNT	Epoxy			0.0039% – 0.0021%	1.78 – 1.74	[24]
SWNT	PBT	1,4-butanediol		0.2%		[32]
SWNT	PMMA	DMF		0.39%	2.3	[8]
SWNT	PMMA	Toluene	83	0.330%	2.1	[5]
MWNT	Epoxy			0.50%		[33]
SWNT	PMMA	ChCl		0.17%	2.2 – 1.3	[13]
SWNT	Polyimide	DMA	89.12	0.050%	2.77	[10]
MWNT	PU	THF	6.3×10^5	0.005%	3.1	[12]
MWNT – SWNT	Epoxy			0.005% – 0.050%		[21]
SWNT	PAA	Water		0.046%		[34]
MWNT	PVA	DMSO-Water		<1%		[35]

Table 4.1: Percolation parameters reported by different authors

greater than 2, confirming its non-universal nature.

Electrical Measurements

Assuming that the composites follow Ohm’s law, the direct current (DC) conductivity is written as:

$$\sigma = \frac{I}{V} \frac{l}{A} \quad (4.5)$$

where σ is the conductivity, I the current, V the voltage, A the effective area of measurement, and l is the thickness of the sample.

Applying an alternating voltage, to the sample, of the form:

$$V = V_0 e^{-i\omega t}$$

the current will flow at the same frequency ω , but out-of-phase by an angle δ ,

$$I = I_0 e^{-i(\omega t + \delta)}$$

the impedance is defined by:

$$Z = \frac{V_0 e^{-i\omega t}}{I_0 e^{-i(\omega t + \delta)}} = \frac{V_0}{I_0} e^{i\delta}$$

Hence we can conclude that Z is a complex number

$$Z = |Z| e^{i\delta}$$

$$Z = Z' - iZ'' \quad (4.6)$$

where Z' and Z'' are the real and imaginary part of the impedance, respectively.

The electrical modulus is given by:

$$|\sigma^*| = \frac{1}{|Z|} \frac{l}{A}$$

$$|\sigma^*| = \frac{1}{\sqrt{(Z')^2 + (Z'')^2}} \frac{l}{A} \quad (4.7)$$

The equivalent electrical circuit for composite materials can be expressed as a set of resistors and capacitors connected in parallel (figure 4.3(a)). Part (b) of the same figure shows the ideal behavior of the electrical modulus with frequency.

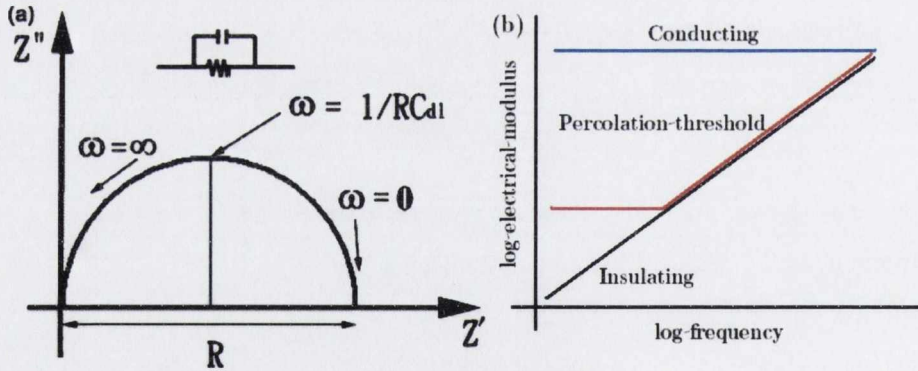


Figure 4.3: (a) A typical complex impedance diagram for a RC circuit in parallel connection (b) Schematic of the electrical modulus behavior of composite samples

The total impedance of the film can be written as

$$Z(\omega) = \frac{R}{1 + R^2 C^2 \omega^2} - i \frac{R^2 C \omega}{1 + R^2 C^2 \omega^2} \quad (4.8)$$

where the first and second terms represent the real and imaginary impedance respectively. The complex plane impedance diagram of a parallel RC circuit has a semi-circle structure (Figure 4.3(a)). The angular frequency (ω) is represented by the semicircle and the maximum value for Z' is the distance from the origin to the point intercepted by the circle at the Z' axis, which is also equal to the resistance R . The maximum value for Z'' arises when the angular frequency $\omega = 1/RC_{dl}$ (where C_{dl} is the double layer capacitance at the electrodes). Hsu *et.al.* have shown recently that these type of graphs are useful for monitoring the nanotube dispersion in composites [36].

In the present study DC (direct current) and AC (alternating current) conductivities were measured. For the DC conductivities I-V (current-voltage) graphs were taken. Given that each nanotube is probably coated with polymer, which acts as a potential barrier to internanotube hopping, it is likely that electrical conductivity in this system is limited by tunneling between conductive regions. This behavior is described by the fluctuation induced tunneling model [37] which takes into account tunneling through potential barriers of varying height due to local temperature fluctuations. In the present case, temperature dependent conductivity was not studied.

4.3 Experimental Procedure

Polymer solutions were prepared by dissolving polyvinylalcohol (PVA), (average molecular weight 30000-70000g/mol) in water, NMP and DMSO at a concentration of 30 mg/ml. Composite solutions were prepared by adding a mass of nanotubes to each of the three polymer solutions such that the partial MWNT concentration was 7.5 mg/ml. These were then sonicated using a sonic tip for 10 minutes, a sonic bath for 2 hours and then again with a sonic tip for 10 minutes. The dispersions were left for 24 hours to allow any unstable nanotube aggregates to sediment out. These were then removed by decantation. This procedure was repeated three times to ensure the complete removal of all aggregates. The nanotube mass fraction after sedimentation was measured by comparison with the optical absorbance before and after sedimentation. The new concentrations were found to be 16%, 10% and 15% for the water, NMP and DMSO based dispersions respectively.

The solutions were blended down with PVA solutions in the appropriate solvent to give a range of mass fractions. Free-standing films were drop-cast in standard weighting boats ($3\text{cm} \times 3\text{cm} \times 1\text{cm}$, polystyrene) for both PVA-Water and PVA-DMSO composites, while teflon boats ($4\text{cm} \times 4\text{cm} \times 1\text{cm}$) were used for the NMP based composites. The solvents were removed by evaporation under vacuum at a temperature of 60°C . The film thicknesses were $\sim 64\mu\text{m}$ and $\sim 38\mu\text{m}$ for the films cast in weighting boats and teflon boats respectively. The films were peeled from the substrates, cut into $12\text{mm} \times 12\text{mm}$ squares and contacted as described in chapter 3. The nanotube volume fractions [1], p , were calculated from the mass fractions by taking the nanotube density [26] to be $1800\text{kg}/\text{m}^3$.

4.4 Results and Discussion

The conductivity increases with the mass fraction and is ohmic in the voltage range studied in all cases and scales with the volume fraction (figure 4.4).

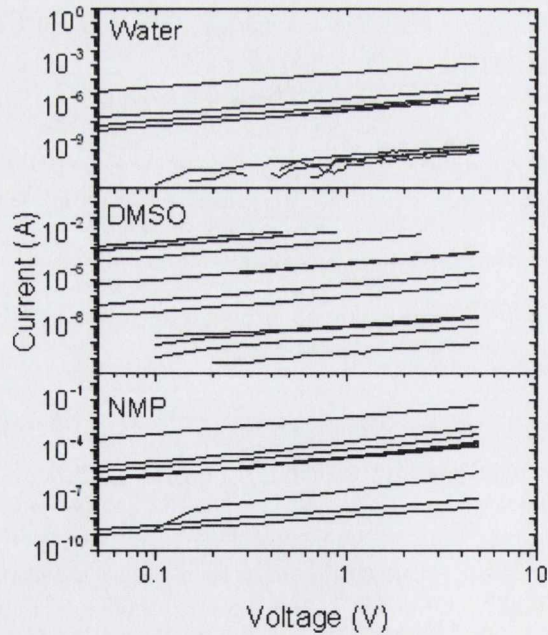


Figure 4.4: Current - Voltage characteristics for the different solvents composites. Each line corresponds to a particular volume fraction starting from 0 in all cases and ending in 0.13, 0.08 and 0.12 for Water, NMP and DMSO respectively

The electrical modulus versus frequency plots show a change from frequency dependent to frequency independent behavior as the nanotube volume fraction increases. This occurs after the first percolation path has been formed, i.e. around the percolation threshold. High volume fraction samples show completely frequency independent behavior (figure 4.5).

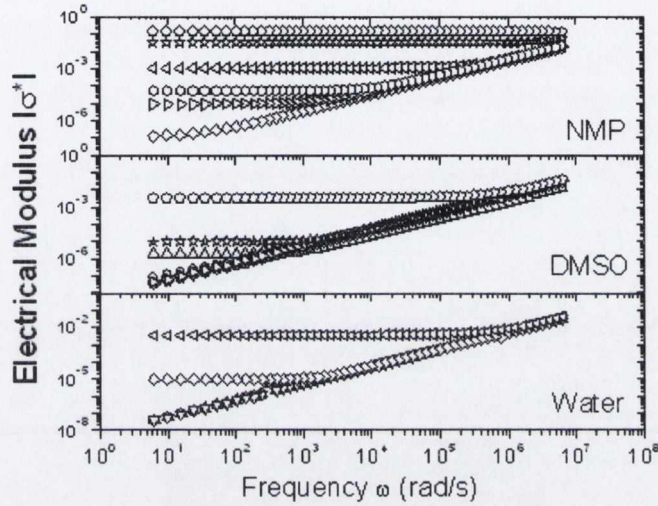


Figure 4.5: Frequency dependent behavior of the electrical modulus for PVA-MWNT composites prepared with 3 different solvents. Each set of data points represents a particular volume fraction starting from 0 in all cases and ending in 0.13, 0.08 and 0.12 for Water, NMP and DMSO respectively

Cole-Cole plots of the imaginary versus real components of impedance show only one semicircle, indicating good film homogeneity [36] (figure 4.4).

This was confirmed by taking SEM images of the crosssectional fracture area for composites prepared with 3 different solvents (figure 4.7)

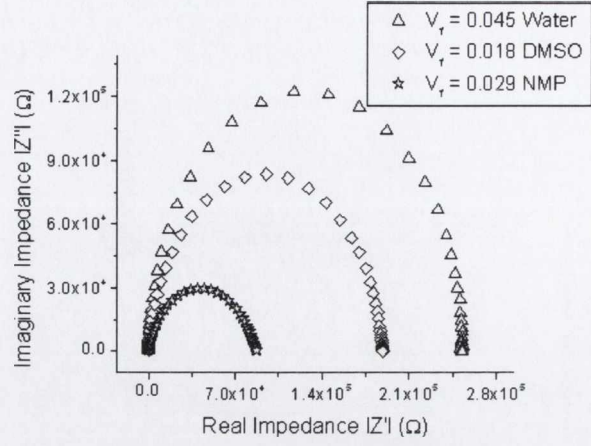


Figure 4.6: Representative Cole-Cole plot for each of the different solvent composites

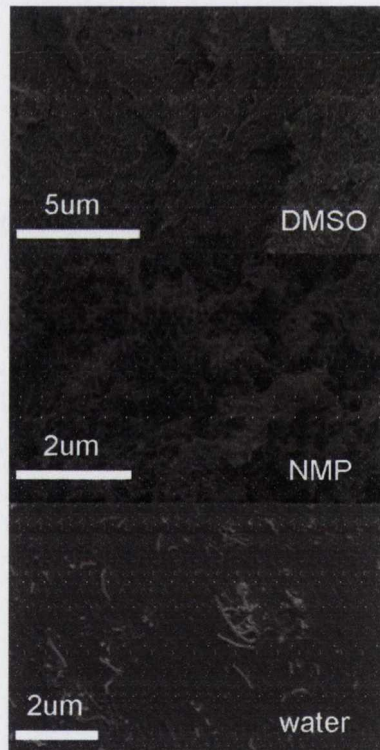


Figure 4.7: SEM images of the crosssectional fracture area for composites using DMSO, NMP and water as solvents. The mass fractions of these composites are 15%, 10% and 5% respectively.

Film conductivities, as derived from the current voltage curves, are presented in figure 4.8 as a function of the nanotube volume fraction for all three composite types. In each case, a sharp increase in conductivity occurs at low volume fractions indicating the formation of a percolation path. However, the conductivity-volume fraction curves vary significantly for the three composite types. In the case of water-based composites, the maximum conductivity achieved is two orders of magnitude lower than that for the NMP or DMSO composites. Equation 4.1 has been fitted to the data as shown in figure 4.9. In all cases, a good fit ($R^2 \sim 1$) was obtained.

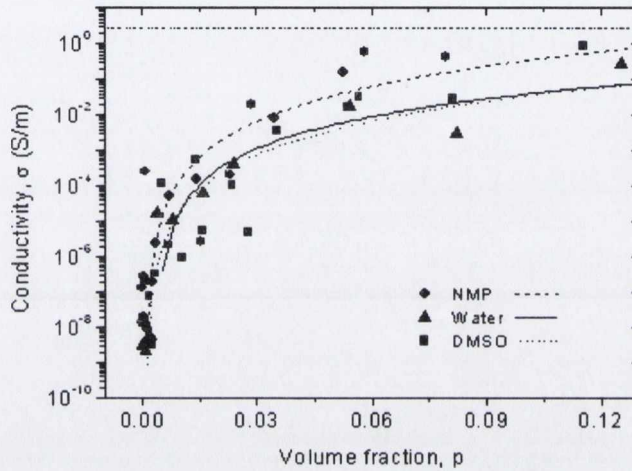


Figure 4.8: DC conductivity versus volume fraction for different solvents. The lines are fits to equation 4.1. The horizontal line is the conductivity of the MWNT powder: $\sigma_{Pow} = 2.7 \text{ S/m}$.

Values of p_c , σ_0 and t were obtained from the fits and are presented in table 4.2. All three parameters vary significantly with solvent choice underlining the role of the solvent in determining the morphology of the polymer and possibly the nanotube network.

The percolation thresholds were found to vary from 1×10^{-3} for the DMSO and NMP based composites to 4×10^{-3} for the water based composites. These values compare favorably with values of 2.5×10^{-5} reported by Sandler et al [3]. These values could be explained by statistical percolation theories based on excluded volume approaches [38]. Such theories generally predict that the percolation threshold

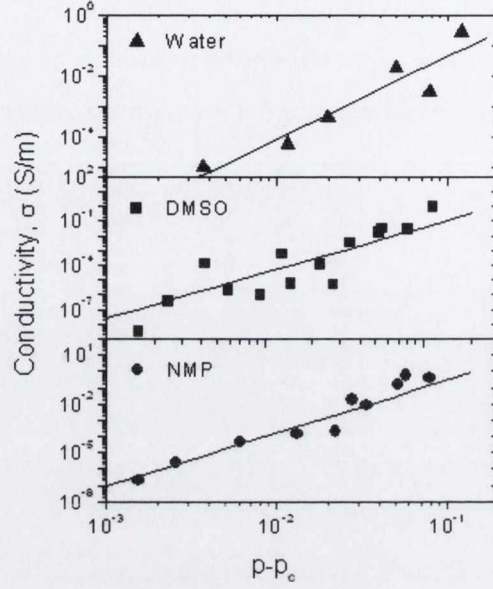


Figure 4.9: Logarithmic plot of the DC conductivity versus $(p-p_c)$.

Solvent	$\log \sigma_0$	$p_c(10^{-3})$	t	R^2
NMP	2.7 ± 0.8	1.0 ± 0.1	3.2 ± 0.8	0.98
DMSO	1.7 ± 0.8	1.0 ± 0.1	3.1 ± 0.4	0.89
Water	1.3 ± 0.8	4.2 ± 0.2	2.7 ± 0.5	0.99

Table 4.2: Percolation parameters obtained in this study

scales inversely with particle aspect ratio (see equation 4.4).

The average length and diameter of the MWNT used in this study were measured by SEM and AFM to be $1.1 \pm 0.4 \mu\text{m}$ and $14 \pm 6 \text{ nm}$ respectively. This gives a lower limit of 0.08 for the percolation threshold. However, it is known that the percolation threshold can be reduced below that expected for a random isotropic network due to modifications to the network topology induced by weak inter-nanotube interactions [39]. In addition, it is known that thick polymer coatings can form around nanotubes in PVA/water solutions [15]. These would reduce the effective aspect ratio resulting in a larger percolation threshold for the water-based composites.

Significant variations in σ_0 are also observed, with values for $\log(\sigma_0/\text{Sm}^{-1})$ of

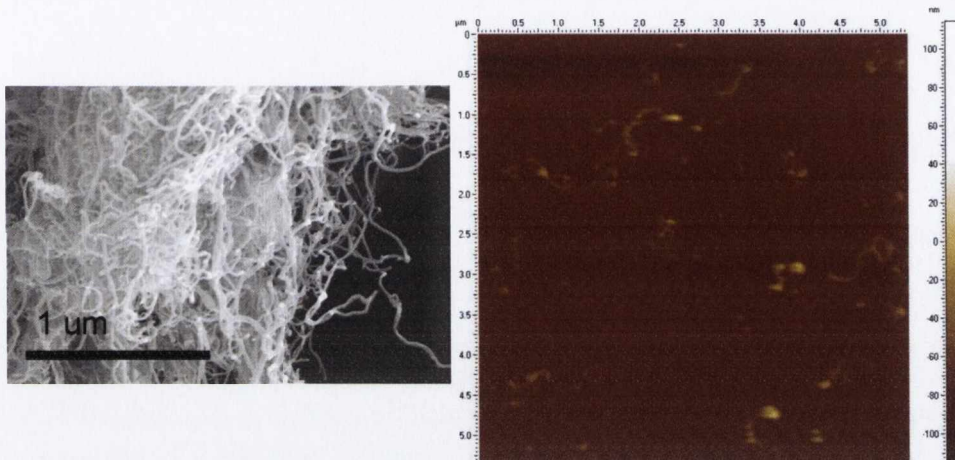


Figure 4.10: SEM and AFM images of the MWNT used in this work

1.3 ± 0.7 , 1.6 ± 0.8 and 2.7 ± 0.8 measured for the water, DMSO and NMP based composites respectively. In solution based composites, a polymer layer always forms around the nanotubes in the solution phase [6]. This means that carriers must tunnel from nanotube to nanotube, significantly reducing carrier mobility. According to Foygel *et.al.*, σ_0 is a measure of the conductivity of the links of the network [20]. In reality, each link can be thought of as a nanotube in series with a tunneling barrier. As the nanotubes are very conductive, σ_0 is controlled by the effective conductance, and hence the thickness of the tunneling barrier. This suggests that, in all cases, the nanotubes are coated with a polymer layer in solution but the layer thickness is very solvent dependent. Typical coating thicknesses then scale with solvent in the order: water > DMSO > NMP. The fact that very thick coatings form in water agrees with previous observations [15, 18, 40]. In addition, this analysis suggests the presence of very thin polymer coatings for the NMP based systems. This is consistent with the fact that the maximum conductivity observed in these systems is very close to the MWNT powder conductivity. This suggests that when using NMP as a solvent, the composite conductivity is limited by the nanotube conductivity more than the presence of tunneling barriers. To corroborate this, a thick free-standing film of MWNTs was prepared by vacuum filtration of an NMP-MWNT dispersion. This type of sample preparation reduces the film porosity and increases the internanotube contacts. The conductivity of this sample was ~ 500 S/m which compares well

with the σ_0 calculated for the PVA-NMP-MWNT composite system (~ 630 S/m). However this comparison does not hold for other solvents as nanotubes are insoluble in most organic solvents.

Values of the exponent, t , of 2.7, 3.0, and 3.2 were observed for the water, DMSO and NMP based systems respectively. In three dimensional systems, the universal value of the exponent is $t = 2.0$ [19]. However, larger values have been reported by many authors (See table 4.1). Balberg [41] predicted that t can be as large as 6 for systems limited by tunneling through high resistance connections between filler particles. In addition, t increases as the distribution of tunneling barrier thicknesses increases. Thus, the combination of relatively low t and σ_0 for the water based samples suggests the presence of thick polymer coatings with reasonably uniform thickness. Recent measurements on similar systems have yielded values of coating thicknesses of 25 ± 10 nm [40]. It should be noted that this error is dominated by measurement error rather than spread in coating thickness. Conversely, for the NMP based systems, the combination of high t and σ_0 suggests a wide range of coating thicknesses, with conduction through the thinner ones dominating. Khan *et.al.* have studied the mechanical reinforcement on similar composites to the ones discussed in this chapter. Differential scanning calorimetry (DSC) measurements confirmed the presence of crystalline coatings on the PVA-Water based composites [18].

4.5 Conclusions

In conclusion, the choice of solvent used during composite preparation is of importance for the final electrical conductivity in composite systems. The presence of polymer coatings around the nanotubes affects all percolation parameters. The fitted value for σ_0 in NMP based composites was over two orders of magnitude larger compared with the water based composites, although the error was very large. For DMSO and NMP based composites a percolation threshold of 1×10^{-3} was observed compared to 4×10^{-3} for the water based system. This shows that careful solvent choice is crucial for the optimisation of the electrical properties of polymer-nanotube composites.

References

- [1] David Blond, Valerie Barron, Manuel Ruether, Kevin P. Ryan, Valeria Nicolosi, Werner J. Blau, and Jonathan N. Coleman. *Advanced Functional Materials*, 16(12):1608, 2006.
- [2] P. M. Ajayan, O. Stephan, C. Colliex, and D. Trauth. *Science*, 265:1212, 1994.
- [3] J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer, and A. H. Windle. *Polymer*, 44(19):5893, 2003.
- [4] R. Ramasubramaniam, J. Chen, and H. Y. Liu. *Applied Physics Letters*, 83(14):2928, 2003.
- [5] O. Chauvet, J. M. Benoit, and B. Corraze. *Carbon*, 42(5-6):949, 2004.
- [6] B. E. Kilbride, J. N. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth, and W. J. Blau. *Journal of Applied Physics*, 92(7):4024, 2002.
- [7] F. Gubbels, S. Blacher, E. Vanlathem, R. Jerome, R. Deltour, F. Brouers, and Ph Teyssie. *Macromolecules*, 28(5):1559, 1995.
- [8] Fangming Du, Robert C. Scogna, Wei Zhou, Stijn Brand, John E. Fischer, and Karen I. Winey. *Macromolecules*, 37(24):9048, 2004.
- [9] H. M. Kim, K. Kim, C. Y. Lee, J. Joo, S. J. Cho, H. S. Yoon, D. A. Pejakovic, J. W. Yoo, and A. J. Epstein. *Applied Physics Letters*, 84(4):589, 2004.
- [10] David S. McLachlan, Cosmas Chiteme, Cheol Park, Kristopher E. Wise, Sharon E. Lowther, Peter T. Lillehei, Emilie J. Siochi, and Joycelyn S. Harrison. *Journal of Polymer Science, Part B: Polymer Physics*, 43(22):3273, 2005.

- [11] 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(3):417, 2006.
- [12] H. Koerner, W. D. Liu, M. Alexander, P. Mirau, H. Dowty, and R. A. Vaia. *Polymer*, 46(12):4405, 2005.
- [13] V. Skakalova, U. Dettlaff-Weglikowska, and S. Roth. *Synthetic Metals*, 152(1-3):349, 2005.
- [14] J. C. Grunlan, A. R. Mehrabi, M. V. Bannon, and J. L. Bahr. *Advanced Materials*, 16(2):150, 2004.
- [15] Jonathan N. Coleman, Martin Cadek, Rowan Blake, Valeria Nicolosi, Kevin P. Ryan, Colin Belton, Antonio Fonseca, Janos B. Nagy, Yurii K. Gun'ko, and Werner J. Blau. *Advanced Functional Materials*, 14(8):791, 2004.
- [16] X. W. Jiang, Y. Z. Bin, and M. Matsuo. *Polymer*, 46(18):7418, 2005.
- [17] D. A. Makeiff and T. Huber. *Synthetic Metals*, 156(7-8):497, 2006.
- [18] Umar Khan, Kevin Ryan, Werner J. Blau, and Jonathan N. Coleman. *Composites Science and Technology*, 67(15-16):3158, 2007.
- [19] Aharony A. Stauffer D. *Introduction to Percolation Theory*. Tailor & Francis, 1992.
- [20] M. Foygel, R. D. Morris, D. Anez, S. French, and V. L. Sobolev. *Physical Review B: Condensed Matter and Materials Physics*, 71(10):104201/1, 2005.
- [21] A. Moisala, Q. Li, I. A. Kinloch, and A. H. Windle. *Composites Science and Technology*, 66(10):1285, 2006.
- [22] D. S. McLachlan and Michael B. Heaney. *Physical Review B: Condensed Matter and Materials Physics*, 60(18):12746, 1999.
- [23] I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner. *Phys. Rev. B*, 30(7):3933, 1984.

- [24] C. A. Martin, J. K. W. Sandler, M. S. P. Shaffer, M. K. Schwarz, W. Bauhofer, K. Schulte, and A. H. Windle. *Composites Science and Technology*, 64(15):2309, 2004.
- [25] Stuart H. Munson-McGee. *Physical Review B*, 43(4):3331, 1991.
- [26] Milo S. P. Shaffer and Alan H. Windle. *Advanced Materials (Weinheim, Germany)*, 11(11):937–941, 1999.
- [27] C. A. Grimes, C. Mungle, D. Kouzoudis, S. Fang, and P. C. Eklund. *Chemical Physics Letters*, 319(5-6):460, 2000.
- [28] Cheol Park, Zoubeida Ounaies, Kent A. Watson, Roy E. Crooks, Joseph Smith, Sharon E. Lowther, John W. Connell, Emilie J. Siochi, Joycelyn S. Harrison, and Terry L. St Clair. *Chemical Physics Letters*, 364(3-4):303, 2002.
- [29] Z. Ounaies, C. Park, K. E. Wise, E. J. Siochi, and J. S. Harrison. *Composites Science and Technology*, 63(11):1637, 2003.
- [30] Graciela B. Blanchet, C. R. Fincher, and F. Gao. *Applied Physics Letters*, 82(8):1290–1292, 2003.
- [31] H. M. Kim, K. Kim, S. J. Lee, J. Joo, H. S. Yoon, S. J. Cho, S. C. Lyu, and C. J. Lee. *Current Applied Physics*, 4(6):577, 2004.
- [32] A. Nogales, G. Broza, Z. Roslaniec, K. Schulte, I. Sics, B. S. Hsiao, A. Sanz, M. C. Garcia-Gutierrez, D. R. Rueda, C. Domingo, and T. A. Ezquerro. *Macromolecules*, 37(20):7669, 2004.
- [33] Young Seok Song and Jae Ryoun Youn. *Carbon*, 43(7):1378, 2005.
- [34] J. C. Grunlan, L. Liu, and Y. S. Kim. *Nano Lett.*, 6(5):911, 2006.
- [35] Yuezhen Bin, Mariko Mine, Ai Koganemaru, Xiaowen Jiang, and Masaru Matsuo. *Polymer*, 47(4):1308, 2006.
- [36] W. K. Hsu, V. Kotzeva, P. C. P. Watts, and G. Z. Chen. *Carbon*, 42(8-9):1707, 2004.

- [37] Ping Sheng, E. K. Sichel, and J. I. Gittleman. *Physical Review Letters*, 40(18):1197, 1978.
- [38] A. Celzard, E. McRae, C. Deleuze, M. Dufort, G. Furdin, and J. F. Mareche. *Physical Review B: Condensed Matter*, 53(10):6209, 1996.
- [39] B. Vigolo, C. Coulon, M. Maugey, C. Zakri, and P. Poulin. *Science*, 309:920, 2005.
- [40] M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolosi, G. Bister, A. Fonseca, J. B. Nagy, K. Szostak, F. Beguin, and W. J. Blau. *Nano Letters*, 4(2):353, 2004.
- [41] I. Balberg. *Physical Review B: Condensed Matter and Materials Physics*, 57(21):13351, 1998.

Chapter 5

Comparison of carbon nanotubes and nanodisks as percolative fillers in electrically conducting composites

5.1 Introduction

For over 30 years composites fabricated from polymers filled with carbon have been used and developed for use in the sports, aviation and automotive industries producing plastics that are both strong and conductive. While carbon black (CB) [1–4] and carbon fibres [5] are routinely used in huge volumes, carbon nanotubes [6–9] and graphene [10, 11] have attracted considerable attention recently due to their unique physical properties properties.

One fundamental difference between carbon black, graphene and carbon nanotubes is geometry. In general, the physical properties of most composites depend to some degree on the shape of the filler [12, 13]. Garboczi et. al. numerically computed the percolation threshold for overlapping ellipsoids[14] to be:

$$p_{c,CNT} = 0.6 \frac{d}{l} \quad p_{c,CND} = 1.27 \frac{l}{d} \quad (5.1)$$

where d and l are the length and diameter of the ellipsoids. The cases studied are

quite useful for the analysis of the data to be discussed in this chapter. As discussed in chapter 4, the excluded volume theory is quite effective for the prediction of percolation thresholds for composite materials. Celzard et. al predicted the excluded volume for randomly oriented disk-shaped fillers as:

$$p_c = 1 - \exp\left(-\frac{\langle V_{ex} \rangle l}{\pi r}\right) \quad (5.2)$$

From equation 5.1 we can see that in the case of nano-disks, the cylinder length might more appropriately be called the disk thickness; however, we refer to it as l in the interests of consistency. r in equation 5.2 is the radius of the disks. $\langle V_{ex} \rangle$ is known in the extreme cases of infinitely thin disks (1.8) and of spheres (2.8) so p_c for disks of finite thickness follows the inequality [15]:

$$1 - \exp\left(-\frac{1.8l}{\pi r}\right) \leq p_c \leq 1 - \exp\left(-\frac{2.8l}{\pi r}\right) \quad (5.3)$$

The strong dependance of the percolation threshold on the aspect ratio [16] is a key factor when choosing a composite filler. Both carbon nanotubes and graphene sheets have large aspect ratios, resulting in composites with very low percolation thresholds [9, 10].

Several groups have studied the electrical properties of composites made from various types of polymer [7, 9, 17–20] and nanotubes [9]. However, no direct comparison has yet been made on the difference between planar and rod-like fillers in the same polymer-solvent system. Chapter 4 showed the influence of the solvent on all the percolation parameters. In this chapter, the electrical conductivities of PVA-based composites using rod-like (multiwalled carbon nanotubes (MWNTs)) and planar (carbon nanodisks [21] (CNDs)) carbon nanomaterials as fillers will be compared.

5.2 Experimental Procedure

CNDs were prepared by pyrolysis of hydrocarbons in a carbon arc [21], while MWNTs were prepared by chemical vapour deposition (CVD). To characterize the geometry of the filler materials Scanning electron microscopy (SEM) and Atomic

Force Microscopy (AFM) images were taken. The raw powder was deposited on conducting carbon tape and a thin gold layer was sputtered onto it for SEM characterization. For the AFM imaging, the samples were dispersed in NMP and drop casted on silicon substrates. Due to the high boiling point of NMP, the samples were dried in a vacuum oven at 70 °C for 3 hours.

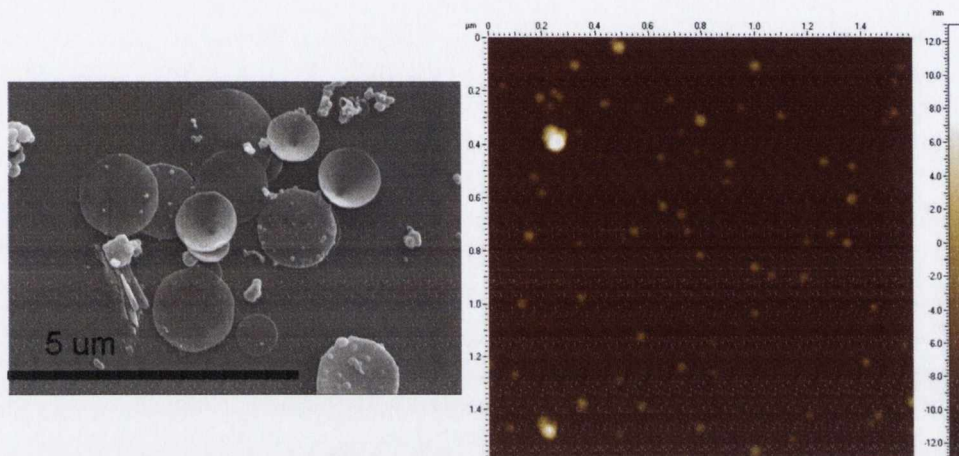


Figure 5.1: SEM and AFM images of the CND raw powder used in this study. Note that a small population of nanocones exist in addition to the disks

The CNDs (figure 5.1) are well graphitized microstructures that appear to be, with a well-defined disk shape. Note also the presence of small quantities of nanocones. This is expected from the sample preparation as reported by Krishnan et.al. ???. The MWNTs are typical of CVD-grown nanotubes in that they are relatively long and contain significant quantities of defects (figure 4.10).

Stock solutions of PVA ($M_w = 30000 - 70000$ kg/mol) in water were prepared at a concentration of 30 mg/ml. The solutions were sonicated for 10 min using an ultrasonic tip¹, followed by 2 h in a low-power sonic bath (70 W) and a further 10 min with the sonic tip. Composite dispersions were prepared by adding MWNTs and CNDs to separate PVA-water solutions with partial concentrations, of 7.5 mg/ml and 10.5 mg/ml, respectively (due to their more compact geometry it was possible to disperse higher levels of disks compared to nanotubes). These were then sonicated using the same regime as before. The solutions were left to sediment for 72 h

¹GEX600, 60 kHz, 120 W

and then decanted. The mass fractions, after decantation, were found by comparing the optical absorbance, A , before and after settling. Assuming the absorption coefficients of the dispersed and sedimenting nanotubes are the same the LambertBeer law can be applied, to write: $A_b/C_b = A_a/C_a$, where the subscripts b and a represent before and after sedimentation, respectively. Calculation of the new concentrations after sedimentation, C_a , then allows the calculation of the new mass fractions to be $\sim 16\%$ and $\sim 20\%$ for the MWNT and CND samples, respectively. These two stock dispersions were then used to prepare a range of composite dispersions with different filler contents.

The stock dispersions were diluted by adding polymer solution to provide a range of dispersions with different nanodisk/nanotube mass fractions. Free-standing films were drop-cast in standard weighing boats ($3\text{ cm} \times 3\text{ cm} \times 1\text{ cm}$, polystyrene) and the water was evaporated in an oven at a temperature of 60°C . The film thicknesses were $\sim 65\mu\text{m}$ on average as measured using a digital micrometer. This relatively high thickness is in order to ensure a minimum sample dimension, significantly greater than 10 times the longest filler dimension as specified by Foygel et al. [13]. The films were peeled off the substrates, cut into $12\text{ mm} \times 12\text{ mm}$ squares and then gold contacts were evaporated onto either side, as described in chapter 2. In this geometry we measure the bulk conductivity perpendicular to the film. The volume fractions, p , were calculated from the mass fractions [22] taking the densities to be 1300 , 1800 and 2000 kg m^{-3} for the polymer, nanotubes and nanodisks, respectively. DC and AC and powder conductivity measurements were taken using the same protocol described in chapter 4. Thin films were prepared by vacuum filtration of dispersions of the nanotubes/ nanodisks in NMP onto Teflon filter papers. Conductivity measurements were made by measuring the film resistance as a function of film length.

5.3 Results and Discussion

DC conductivities were calculated from the slopes of the current-voltage curves (ohmic in the voltage range studied) (figure 5.3). For both fillers, the conductivity increases rapidly as the volume fraction is increased. However, the onset of the

conductivity occurs at higher volume fraction for the disks compared to the MWNT samples. Furthermore, the disks reach slightly higher conductivities than MWNTs. In systems such as these, the onset of conductivity occurs at the percolation threshold, p_c .

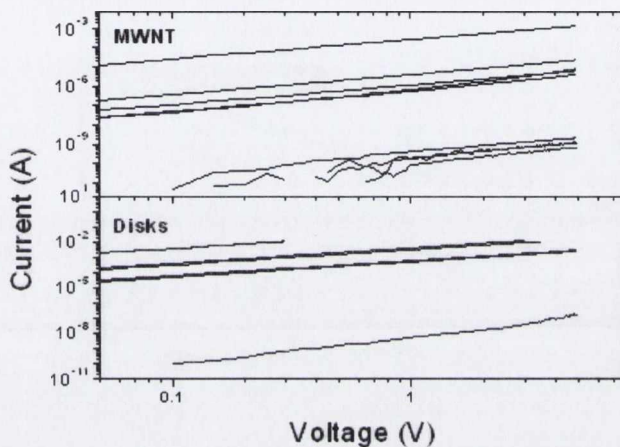


Figure 5.2: IV graphs for both fillers in PVA based composites for volume fractions ranging from 0 in both cases up to 0.12 and 0.15 for MWNT and CND respectively. The slope of each of these graphs is the resistance from which the conductivity can be calculated.

The frequency dependence of the electrical modulus is shown in figure 5.3. At low volume fraction, the conductivity scales linearly with volume as is appropriate for a dielectric. At higher volume fractions the conductivity becomes frequency independent at low frequency, indicating conducting behavior. The transition between these regimes gives the range in which the percolation threshold is located. In addition, Cole-Cole plots display one semicircle for all mass fractions, in both sets of samples, indicating film homogeneity [23] (figure 5.4).

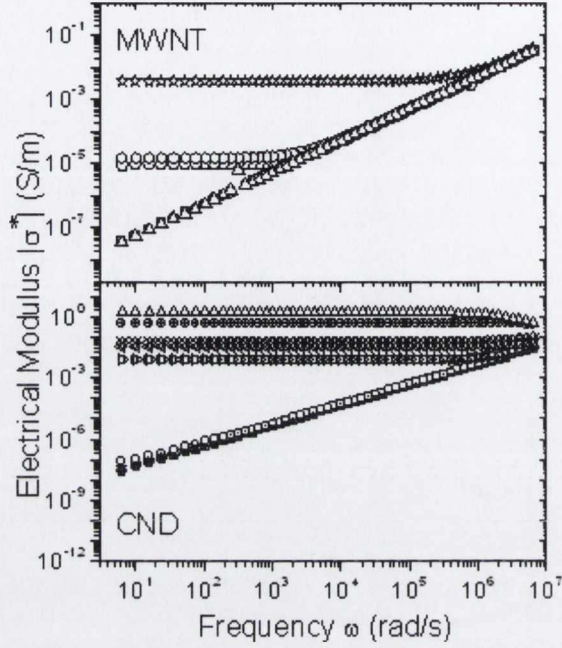


Figure 5.3: Frequency dependent behavior of the electrical modulus for PVA-MWNT and PVA-CND composites for volume fractions ranging from 0 in both cases up to 0.12 and 0.15 for MWNT and CND respectively

The type of non-linear behavior displayed in figure 5.5 can be modeled using the percolation scaling law discussed in chapter 4 [24]. The conductivity data for both tubes and disks was fitted to equation 4.1 in figure 5.3. In both cases a good fit was obtained. The fit parameters obtained are presented in Table 5.1 where they can be compared with typical results from the literature for polymers filled with carbon black [3, 4, 25] (spheres), graphene [10] (sheets) and carbon fibres [26].

The percolation thresholds for disks and tubes were found to be 2.1 ± 0.2 and 0.4 ± 0.02 vol.%, respectively. The latter value is typical for composites filled with nanotubes [27]. There is very little literature, however, on composites based on disk-like fillers. Polymers have been filled with exfoliated graphite to give composites with percolation thresholds as low as 0.1 vol.% [10] and 0.3 vol.% [11].

The length and diameter of the MWNTs and CNDs were estimated by SEM and AFM to be: $d_{CND} = 1.7 \pm 0.6 \mu\text{m}$, $l_{CND} = 7 \pm 3 \text{nm}$, $d_{MWNT} = 14 \pm 6 \text{nm}$ and $l_{MWNT} = 1.1 \pm 0.4 \mu\text{m}$ (Figure 5.7). Using these values, we can calculate the

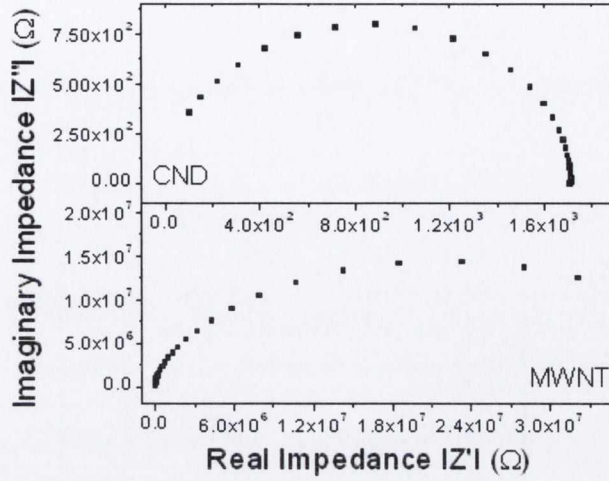


Figure 5.4: Cole-Cole plot for CND and MWNT composites in PVA. $V_{f,CND} = 1.9 \times 10^{-2}$, $\sigma_{DC,CND} = 8.91 \times 10^{-3}\text{S/m}$, $V_{f,MWNT} = 7.7 \times 10^{-2}$, $\sigma_{DC,MWNT} = 8.76 \times 10^{-6}\text{S/m}$

average aspect ratios, which are defined to be the long dimension divided by the short dimension (d/l for disks, l/d for rods), to be ~ 250 and ~ 80 for disks and nanotubes respectively. While the nanodisks have a significantly larger average aspect ratio, equation 5.1 tells us that disk-like objects are less efficient at forming percolation paths than rods. The calculated percolation thresholds are 0.5 ± 0.4 vol% for disks and 0.8 ± 0.6 vol% for the nanotubes. This theoretical result for the nanotubes agrees reasonable well with the experimental result. However, for the disks the experimental value is significantly higher than the theoretical one. It is likely that the disks tend to preferentially orient in the plane of the film during film drying as can occur for nanotubes [28]. This deviation from random orientation would lead to a larger percolation threshold than predicted by equation 4.1.

To test whether the disks were oriented in the film we broke both the nanotube and nanodisk composites films (0.3 vol.%) by tensile extension to reveal fracture surfaces. SEM measurements were made on these (gold-coated) fracture surfaces (Fig. 5.8). In all cases these images are for samples that are below the percolation threshold. For the nanotube-based composites (Fig. 5.8(A)) we can clearly see a number of well dispersed nanotubes protruding from the surface. The nanodisk-

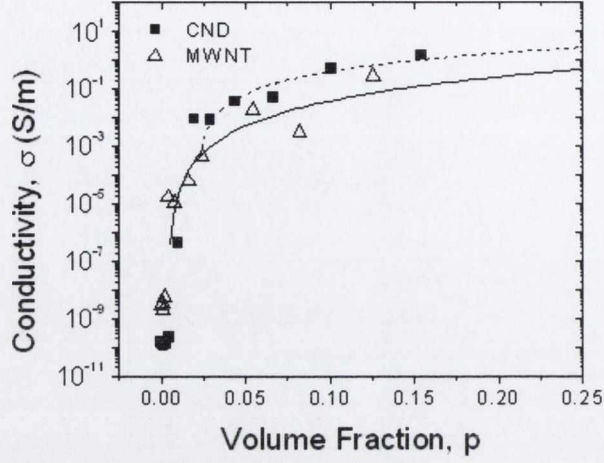


Figure 5.5: DC conductivity versus volume fraction for both MWNT and carbon disks as fillers in PVA based composites.

based composites (Fig. 5.8(B and C)) are more instructive. In these images we can clearly see both disks and the holes they leave on pull-out. It is clear from these images that the disks are extremely well dispersed. In addition, the disks are predominately oriented in the plane of the film. This shows clearly that the high percolation threshold observed in the nanodisk sample is a drying effect as suggested above.

For both nanotube and nanodisk based samples the maximum conductivities measured were similar: 0.27 S/m and 1.5 S/m respectively, achieved at volume

Filler	$p_c(\text{vol}\%)$	$\log(\sigma_0/\text{Sm}^{-1})$	t	Geometry	Reference
Carbon Black	1.1	–	2.17	Spherical	[25]
Carbon Black	17	–	2.9 ± 0.1	Spherical	[4]
Carbon Black	$2.74 - 0.516$	$6.7 - 2.3$	$3.4 - 1.7$	Spherical	[3]
Carbon Nanodisks	2.1 ± 0.2	1.6 ± 0.4	1.8 ± 0.3	Cylindrical – planar	This study
Graphene sheets	0.1	4.9 ± 0.5	2.7 ± 0.2	Planar sheets	[10]
Carbon Fibers	1.1	1.9	2.7	Rod Like	[26]
MWNT	0.4 ± 0.02	1.3 ± 0.8	2.7 ± 0.5	Rod like (high aspect ratio)	This study

Table 5.1: Percolation parameters obtained from fitting the experimental data to equation 4.1

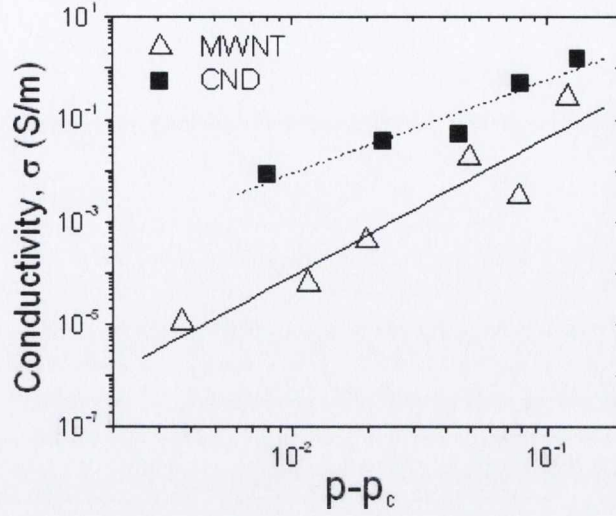


Figure 5.6: Logarithmic plot of the DC conductivity versus $(p - p_c)$. The lines are fits to equation 4.1

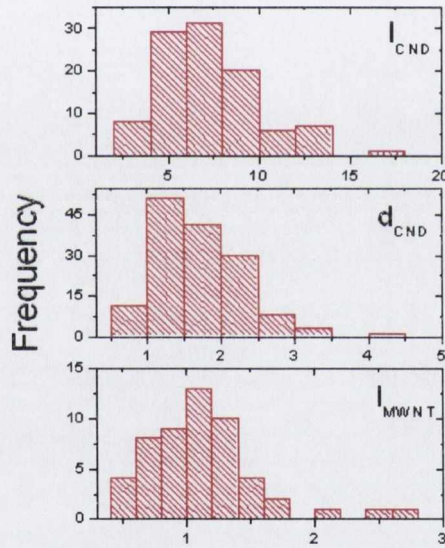


Figure 5.7: Length and diameter of the CNDs and MWNTs used in this study determined from SEM and AFM images. The x axis of each histogram are in nm, μm and μm for l_{CND} , d_{CND} and l_{MWNT} respectively.

fractions of around 15%. By fitting the whole set of DC conductivities as a function of volume fraction to equation 4.1, we can extract values of σ_0 . This parameter gives

an approximate measure of the conductivity of the percolative network. However, it should not be confused with the conductivity of the individual conductive filler particles. This is because, in many polymer based composite systems, the filler particles get coated with a thin layer of polymer in the solution phase, as discussed on chapter 4. This coating may be retained on film drying, resulting in the presence of very resistive inter-filler-particle barriers. The presence of these barriers can result in values of σ_0 that are significantly lower than the conductivity of the individual fillers [13]. In fact, values of σ_0 derived from fitting equation 4.1 to the data in figure 5.3 were $10^{1.60 \pm 0.44} \text{ S/m}$ ($\sim 40 \text{ S/m}$) and $10^{1.33 \pm 0.77} \text{ S/m}$ ($\sim 20 \text{ S/m}$) for disks and tubes respectively. These values are much lower than the expected conductivities of graphitic disks or disordered nanotubes such as those used here, indicating the presence of resistive polymer coatings around both filler types, as it will be discussed later.

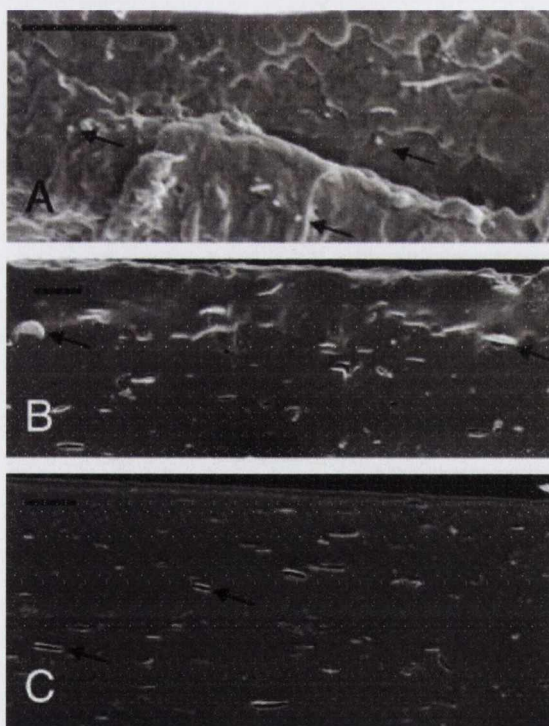


Figure 5.8: SEM images of fracture surfaces of (A) a PVAMWNT composite (~ 0.2 vol.%). The arrows indicate some of the protruding nanotubes. (B) and (C) PVACND composite (~ 0.2 vol.%). The arrows in (B) indicate some of the protruding nanodisks and in (C) some of the holes left by the pullout of the nanodisks.

To put these results in context, conductivity measurements were made, for both disks and tubes, on both the raw powders and on films. The films were made by vacuum filtration of nanodisks/nanotubes dispersed in NMP onto Teflon filter papers. It should be emphasized that both powder and film measurements give a value for the conductivity of a network of either nanodisks or nanotubes in the absence of any polymer. However, it would be expected that the powders and films may display different conductivities due to their different morphologies. The powder conductivities were measured to be ~ 2 S/m for both rods and disks as described in Chapter 3. This low value reflects the granular nature of the powders, suggesting poor electrical connections between grains. The films fabricated from the disks were very brittle, resembling a film of fine powder. Like the powder, they demonstrated low conductivities of 2–9 S/m, again suggesting a granular structure.

In contrast, the nanotube films had much higher conductivities of ~ 500 S/m illustrating their more homogenous nature. Such films, when fabricated from single walled nanotubes, tend to be porous [29] but display high conductivity indicating good electrical contact between nanotubes [30]. Thus, these nanotube films can be thought of as a high volume fraction percolative network where the polymer matrix has been replaced by air. This means that no resistive barriers are present and good electrical connection is expected at nanotube junctions. This is confirmed by the high film conductivity. That the measured σ_0 value for the nanotube composites is significantly smaller than the conductivity of this nanotube film confirms that the composite conductivity is limited by inter-nanotube polymer coatings[31], as suggested above and as observed previously[8].

In contrast, the conductivity of the pure disk film was lower than the value of σ_0 observed for the disk filled composite samples. This can only occur if the disks are themselves conductive but the morphology of the film is such that the overall conductivity is low. However, the fact that σ_0 is low compared to the conductivity expected for such well graphitized materials[21] suggests that either the inter-disk conductivity is limited by the presence of polymer tunneling barriers or that due to the CNDs morphology the probability of inter-disk contact is lower limiting the overall conductivity. Further experiments would be necessary to corroborate these assumptions.

Finally, for the disk based composites, a percolation exponent of 1.8 ± 0.3 was observed, very close to the universal value of 2.0. However, for the nanotube-based composites, a higher value of $t = 2.7 \pm 0.5$ was observed. Balberg has shown that t can be greater than 2.0 in situations where conducting fillers are separated by resistive connections with a distribution of resistivities[32]. This suggests that the polymer coatings surrounding the nanotube tend to have a wide range of thicknesses. That t is so close to 2.0 for the disk based samples suggests that the distribution of polymer coating thicknesses is much narrower for the disk based composites.

5.4 Conclusions

In this chapter it was shown that the percolation threshold depends of the geometry on the filler particles as has been predicted by several authors. While disk-like fillers result in low percolation thresholds, this critical loading level can be reduced even further by using rod-like fillers. For the disk based composites, the percolation threshold deviated significantly from the theoretical value due to film drying effects. In addition, similar conductivities were observed for composites filled with carbon disks compared to carbon nanotubes.

References

- [1] Qian Chen, Piyi Du, Lu Jin, Wenjian Weng, and Gaorong Han. *Applied Physics Letters*, 91(2):022912/1, 2007.
- [2] Hai-Ping Xu and Zhi-Min Dang. *Chemical Physics Letters*, 438(4-6):196, 2007.
- [3] Jiugao Yu, Ning Wang, and Xiaofei Ma. *Biomacromolecules*, 9(3):1050, 2008.
- [4] D. S. McLachlan and Michael B. Heaney. *Physical Review B: Condensed Matter and Materials Physics*, 60(18):12746, 1999.
- [5] Zdenka Rimska, Vojtech Kresalek, and Josef Spacek. *Polymer Composites*, 23(1):95, 2002.
- [6] Valeria Nicolosi, Damjan Vengust, Dragan Mihailovic, Werner J. Blau, and Jonathan N. Coleman. *Chemical Physics Letters*, 425(1-3):89, 2006.
- [7] O. Chauvet, J. M. Benoit, and B. Corraze. *Carbon*, 42(5-6):949, 2004.
- [8] B. E. Kilbride, J. N. Coleman, J. Fraysse, P. Fournet, M. Cadek, A. Drury, S. Hutzler, S. Roth, and W. J. Blau. *Journal of Applied Physics*, 92(7):4024, 2002.
- [9] J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer, and A. H. Windle. *Polymer*, 44(19):5893, 2003.
- [10] Sasha Stankovich, A. Dikin Dmitriy, H. B. Dommett Geoffrey, M. Kohlhaas Kevin, J. Zimney Eric, A. Stach Eric, D. Piner Richard, T. Nguyen SonBin, and S. Ruoff Rodney. *Nature*, 442:282, 2006.
- [11] Guohua Chen, Wengui Weng, Dajun Wu, and Cuiling Wu. *European Polymer Journal*, 39(12):2329, 2003.

- [12] C. A. Martin, J. K. W. Sandler, M. S. P. Shaffer, M. K. Schwarz, W. Bauhofer, K. Schulte, and A. H. Windle. *Composites Science and Technology*, 64(15):2309, 2004.
- [13] M. Foygel, R. D. Morris, D. Anez, S. French, and V. L. Sobolev. *Physical Review B: Condensed Matter and Materials Physics*, 71(10):104201/1, 2005.
- [14] E. J. Garboczi, K. A. Snyder, J. F. Douglas, and M. F. Thorpe. *Physical Review E: Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics*, 52(1-B):819, 1995.
- [15] A. Celzard, E. McRae, C. Deleuze, M. Dufort, G. Furdin, and J. F. Mareche. *Physical Review B: Condensed Matter*, 53(10):6209, 1996.
- [16] I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner. *Physical Review B*, 30(7):3933, 1984.
- [17] F. Gubbels, S. Blacher, E. Vanlathem, R. Jerome, R. Deltour, F. Brouers, and Ph Teyssie. *Macromolecules*, 28(5):1559, 1995.
- [18] Fangming Du, Robert C. Scogna, Wei Zhou, Stijn Brand, John E. Fischer, and Karen I. Winey. *Macromolecules*, 37(24):9048, 2004.
- [19] H. M. Kim, K. Kim, C. Y. Lee, J. Joo, S. J. Cho, H. S. Yoon, D. A. Pejakovic, J. W. Yoo, and A. J. Epstein. *Applied Physics Letters*, 84(4):589, 2004.
- [20] David S. McLachlan, Cosmas Chiteme, Cheol Park, Kristopher E. Wise, Sharon E. Lowther, Peter T. Lillehei, Emilie J. Siochi, and Joycelyn S. Harrison. *Journal of Polymer Science, Part B: Polymer Physics*, 43(22):3273, 2005.
- [21] A. Krishnan, E. Dujardin, M. M. J. Treacy, J. Hugdahl, S. Lynum, and T. W. Ebbesen. *Nature*, 388(6641):451, 1997.
- [22] David Blond, Valerie Barron, Manuel Ruether, Kevin P. Ryan, Valeria Nicolosi, Werner J. Blau, and Jonathan N. Coleman. *Advanced Functional Materials*, 16(12):1608, 2006.
- [23] W. K. Hsu, V. Kotzeva, P. C. P. Watts, and G. Z. Chen. *Carbon*, 42(8-9):1707, 2004.

- [24] Aharony A. Stauffer D. *Introduction to Percolation Theory*. Tailor & Francis, 1992.
- [25] Marco T. Connor, Saibal Roy, Tiberio A. Ezquerria, and Francisco J. Balta Calleja. *Physical Review B: Condensed Matter and Materials Physics*, 57(4):2286, 1998.
- [26] Jun Xu, John P. Donohoe, and Jr. Pittman, Charles U. *Composites, Part A: Applied Science and Manufacturing*, 35A(6):693, 2004.
- [27] Jaime C. Grunlan, Ali R. Mehrabi, Michael V. Bannon, and Jeffrey L. Bahr. *Advanced Materials (Weinheim, Germany)*, 16(2):150, 2004.
- [28] Milo S. P. Shaffer and Alan H. Windle. *Advanced Materials (Weinheim, Germany)*, 11(11):937, 1999.
- [29] C. J. Frizzell, M. in het Panhuis, D. H. Coutinho, Jr. Balkus, K. J., A. I. Minett, W. J. Blau, and J. N. Coleman. *Physical Review B: Condensed Matter and Materials Physics*, 72(24):245420/1, 2005.
- [30] Zhuangchun Wu, Zhihong Chen, Xu Du, Jonathan M. Logan, Jennifer Sippel, Maria Nikolou, Katalin Kamaras, John R. Reynolds, David B. Tanner, Arthur F. Hebard, and Andrew G. Rinzler. *Science*, 305(5688):1273, 2004.
- [31] Jonathan N. Coleman, Martin Cadek, Rowan Blake, Valeria Nicolosi, Kevin P. Ryan, Colin Belton, Antonio Fonseca, Janos B. Nagy, Yurii K. Gun'ko, and Werner J. Blau. *Advanced Functional Materials*, 14(8):791, 2004.
- [32] I. Balberg. *Physical Review B: Condensed Matter and Materials Physics*, 57(21):13351, 1998.

1. The first part of the paper is devoted to a general discussion of the problem.

2. In the second part, we consider the case of a single particle.

3. The third part is devoted to the case of a system of particles.

4. In the fourth part, we consider the case of a continuous medium.

5. The fifth part is devoted to the case of a system of continuous media.

6. In the sixth part, we consider the case of a system of particles and continuous media.

7. The seventh part is devoted to the case of a system of particles and continuous media.

8. In the eighth part, we consider the case of a system of particles and continuous media.

9. The ninth part is devoted to the case of a system of particles and continuous media.

10. In the tenth part, we consider the case of a system of particles and continuous media.

11. The eleventh part is devoted to the case of a system of particles and continuous media.

12. In the twelfth part, we consider the case of a system of particles and continuous media.

Chapter 6

High yield exfoliation of graphene in organic solvents

6.1 Introduction

Graphene is one of the most exciting nano-materials [1] due to the unique physical properties that have recently been demonstrated. For example, due to the details of its electronic structure, charge carriers in graphene behave as massless Dirac fermions [2] which means that it is possible to test quantum electrodynamics effects on a bench top experiment, as discussed on chapter 2. Furthermore, effects such as an ambipolar field effect [3], room temperature quantum Hall effect [4, 5] and breakdown of the Born-Oppenheimer approximation [6] are observed. However, as was the case in the early days of nanotube research, graphene still suffers from a problem that is critical for its mass-scale exploitation: it cannot yet be made with high yield.

The standard procedure used to make graphene is micromechanical cleavage [7]. This yields the best samples to date, with mobilities up to $200,000 \text{ cm}^2/\text{Vs}$ [8, 9]. However, single layers are a negligible fraction amongst large quantities of thin graphite flakes. Alternatively, growth of graphene is also achieved by annealing *SiC* substrates, to produce samples that are in fact composed of a multitude of domains, most of them sub-micrometer, and not spatially uniform in number, or in size over larger length scales [10–12]. A number of works have also reported graphene growth on metal substrates [13–16], but this would require the sample transfer to insulating

substrates in order to make useful devices, either via mechanical transfer or, via solution processing.

Recently, a large number of papers have described the dispersion and exfoliation of graphene oxide (GO) [17–20]. This material consists of graphene-like sheets, chemically functionalised with compounds such as hydroxyls and epoxides, which stabilise the sheets in water [21]. However, this functionalisation results in considerable disruption of the electronic structure of the graphene. In fact GO is an insulator [22] rather than a semi-metal and is conceptually different from graphene. While the functionalities can be removed by reduction, large defect populations, which continue to disrupt the electronic properties remain [17, 21]. Thus, a non-covalent, solution-phase method to produce significant quantities of defect free, un-oxidised graphene is required.

In this chapter a novel *solution based* method for the successful exfoliation of graphene at high yield is presented. This work builds upon over fifty years of study into chemical exfoliation of graphite [23] (and references within). Previously, intercalated graphite could be partially exfoliated by reactions involving the intercalant [24, 25], through thermal shock [26] or by acid treatment of expandable graphite [27]. However, such methods give thin graphite sheets or graphene fragments [27] rather than large scale graphene mono-layers. The standard response to this problem has been the compromise of complete exfoliation of chemically modified forms of graphene such as graphene oxide or functionalised graphene [19, 21, 28]. However such materials are not graphene as they are insulators containing numerous structural defects [21, 28], which cannot, so far, be fully removed by chemical treatment [21]. This work is an extrapolation from the successful exfoliation of SWNTs from bundles by matching the surface tension of them with the surface tension of organic solvents [29–31]. Many variables are yet to be optimised and studied but this is a first big step towards the high yield production of graphene in solution for applications.

6.2 Experimental procedure

Recently, carbon nanotubes have been successfully exfoliated in a small number of solvents such N-methylpyrrolidone (NMP) [32, 33]. Such exfoliation occurs because

the strong interaction between solvent and nanotube sidewall means that the energetic penalty for exfoliation and subsequent solvation becomes small [29, 30, 34]. The dispersion of graphite in organic solvents to produce graphene is a completely new area of research therefore several parameters had to be tuned¹:

- Type of starting graphite powder: There are several types of graphite powders and flakes in the market but in order to assure the high quality of the starting material Raman spectra and scanning electron microscopy (SEM) imaging was taken. Graphite has a distinctive Raman Spectra and, in particular, Ferrari *et.al.* [35] recently showed that the graphene spectra evolves with the number of layers allowing an unambiguous identification of it.

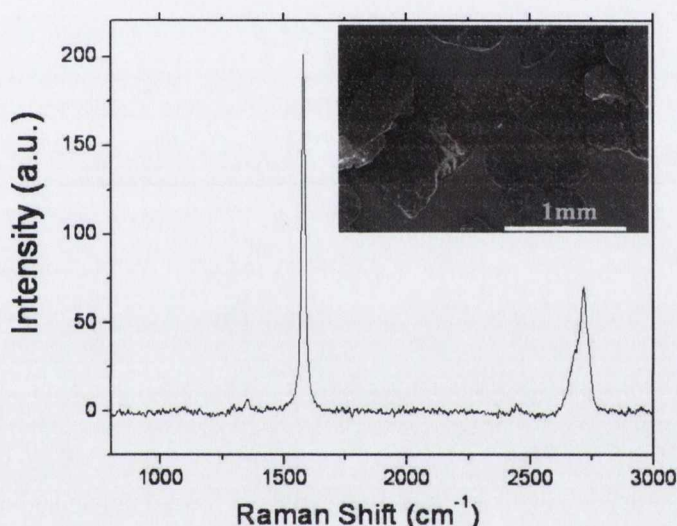


Figure 6.1: Raman Spectra of the starting material. SEM image of sieved graphite (inset)

The best starting material available to us for solution processing of graphite was supplied by Sigma Aldrich (product number 332461, batch number 06106DE)(See figure 6.1(inset)). The size distribution of these flakes is quite broad therefore they were sieved through a 0.5 mm mesh to remove the larger particles.

- Type of sonication: TEM analysis showed that the sonication in the sonic

¹The initial study was done using NMP and the tuned parameters were subsequently extrapolated to other organic solvents

bath (Model Ney Ultrasonic) was more efficient for graphene exfoliation than sonication with the sonic tip. This type of sonication has been successful for the dispersion of CNTs but it compromises the quality of the flakes in the graphene case.

- Sonication time: ~ 30 minutes is the ideal sonication time for graphene dispersion in organic solvents. Longer sonication times compromise the quality of the flakes. The dispersion of graphene is generally independent of the bottle size. Sonication in round bottom flasks should be avoided as the graphene flakes cannot withstand the energy of the standing wave created on its surface.
- Centrifugation time: The resultant dispersion was then centrifuged using a Hettich Mikro 22R centrifuge for 90 minutes at 500 rpm. The samples were decanted by pouring. The sediment can subsequently be used to prepare new dispersions where further exfoliation occurs. While moderate levels of sedimentation and aggregation occur within three weeks of centrifugation, the dispersions remain of high quality at least five months after preparation.
- Initial concentration: A starting graphite concentration of 0.1 mg/ml gave the highest percentage of graphite/graphene remaining after centrifugation. Transmission electron microscopy (TEM) analysis also showed a higher yield of exfoliated graphene flakes at this concentration in comparison to higher starting concentrations.

6.3 Results and discussion

After tuning the initial concentration (0.1 mg/ml), four solvents that had previously shown to disperse CNTs were selected for the dispersion of graphite. These were: 1-Methyl-2-pyrrolidinone (NMP), γ -Butyrolactone (GBL), N,N-Dimethylacetamide (DMA) and 1,3-Dimethyl-2-Imidazolidinone (DMEU). The samples were sonicated and centrifuged as described in the previous section. The decanted dispersions were characterised by UV-vis-IR absorption spectroscopy with the absorption coefficient, α , plotted versus wavelength in figure 6.3. The spectra are featureless in the visible-IR region as is expected from theory [36].

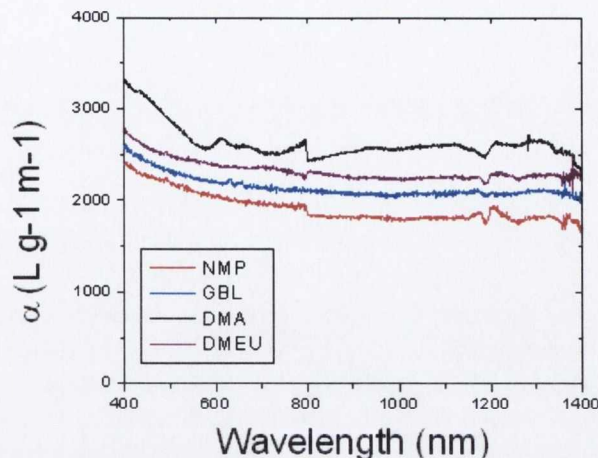


Figure 6.2: Absorption spectra for graphene dispersed in NMP, GBL, DMA and DMEU at concentrations from 3 to 9 $\mu\text{g/ml}$

To calculate the concentration of material remaining after centrifugation, the extinction coefficient of graphene dispersed in solution was calculated. To do this, relatively large volumes ($\sim 500\text{ml}$) of the graphite dispersion were filtered through polyvinylidene fluoride (PVDF) membranes (pore size: 100 nm). Careful measurements of the filtered mass, accounting for residual solvent, gave the concentration of dispersed phase after centrifugation. This procedure was repeated for three other solvents known to successfully disperse nanotubes[31]: N,N-Dimethylacetamide (DMA), γ -Butyrolactone (GBL) and 1,3-Dimethyl-2-Imidazolidinone (DMEU). Each of these four dispersions was diluted a number of times and the absorption spectra recorded. The absorbance (660 nm) of the dispersed phase divided by the cell length is plotted versus concentration in figure 6.3, showing Beer-Lambert behavior for all solvents; $\langle \alpha_{660} \rangle = 2460 \text{ L g}^{-1}\text{m}^{-1}$.

Shown in figure 6.4 is a sedimentation curve measured on a sample of graphite dispersed in NMP that had previously been centrifuged and had the sediment removed by decantation. The concentration of the dispersed phase in NMP falls over time. This shows that the centrifugation step does not remove all unstable material from the dispersion. Approximately 28 wt% of the dispersed phase sediments out over a period of 1 to 3 weeks. This data can be analysed using sedimentation theory

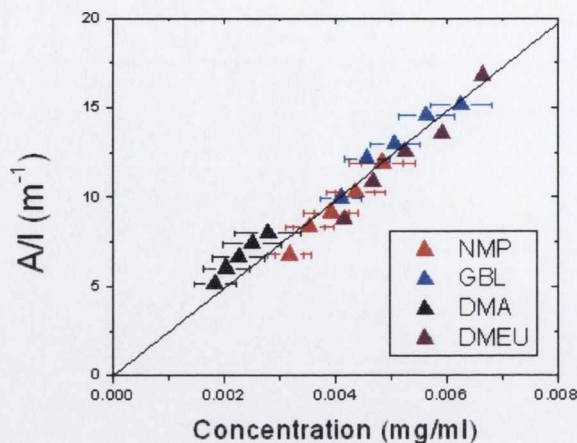


Figure 6.3: Optical absorbance ($\lambda = 660$) divided by cell length (A/l) as a function of concentration.

(see fit in figure 6.4) by fitting with a bi-exponential, suggesting the presence of two sedimentation phases and one stable phase [37]. Two time constants are identified: a short time-constant ($\tau_1 = 1.4$ hrs) component, represents sedimentation of a very small population of large graphitic flakes which were not removed when separating the supernatant after centrifugation. (Decantation by pouring is relatively inefficient. Subsequent decantations were made by taking the top 50% of the centrifuged dispersion). This represents only 4.3wt% of the total mass of graphite/graphene in the sample. The second sedimenting phase represents 22.4wt% of the sample mass and has a much longer time constant ($\tau_2 = 152$ hrs) indicating much smaller sedimentating objects which we believe to be large flakes of multilayer graphene. Note that there is also a non-sedimenting phase, which consists of the bulk of the sample (71.6wt%). This phase is associated with small graphene monolayers and multilayers.

6.3.1 Dispersion of Graphite

It is clear that graphite can be dispersed in some solvents. The exfoliation of graphite gives multilayer structures with <5 layers in NMP, GBL and DMEU if not other solvents. In addition, significant quantities of individual monolayers are present.

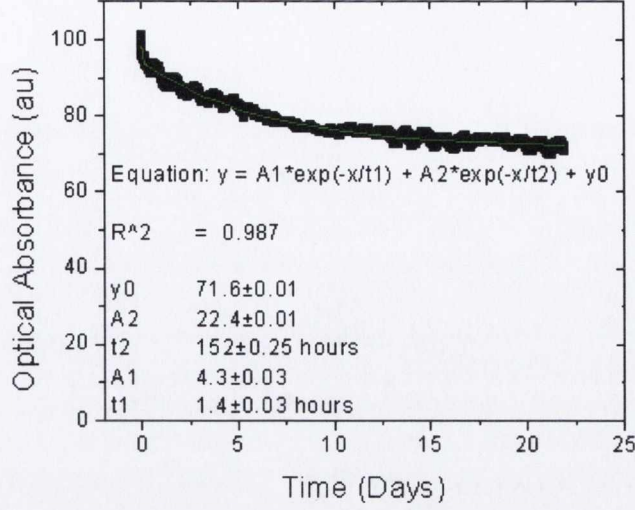


Figure 6.4: Sedimentation curve for graphene dispersed in NMP measured after centrifugation in a home built apparatus[37].

Such exfoliation can only occur if the net energetic cost is very small. This energy balance is expressed as the enthalpy of mixing (per unit volume) which we can approximately calculate in this case to be (See Appendix 1):

$$\frac{\Delta H_{Mix}}{V_{Mix}} \approx \frac{2}{T_{flake}} (\delta_G - \delta_{Sol})^2 \phi \quad (6.1)$$

where $\delta_i = \sqrt{E_{Sur}^i}$ is the square root of the component surface energy, T_{flake} , is the thickness of a graphene flake and ϕ is the graphene volume fraction. Reminiscent of the Hildebrand-Scratchard equation[38], this shows the enthalpy of mixing is dependent on the balance of graphene and solvent surface energies. For graphite the surface energy is defined as the energy per unit area required to overcome the van der Waals forces when peeling two sheets apart.

From equation 6.1, a minimal energy cost of exfoliation is expected for solvents whose surface energy matches that of graphene. To test this we dispersed graphite in a wide range of solvents. By measuring the optical absorbance (660nm) after centrifugation and using the average absorption coefficient ($\alpha_{660} = 2460 Lg^{-1}m^{-1}$) to transform absorbance into concentration we can quantify the amount of graphite / graphene dispersed as a function of solvent surface energy (calculated from surface tension [39, 40]) as shown in figure 6.5.

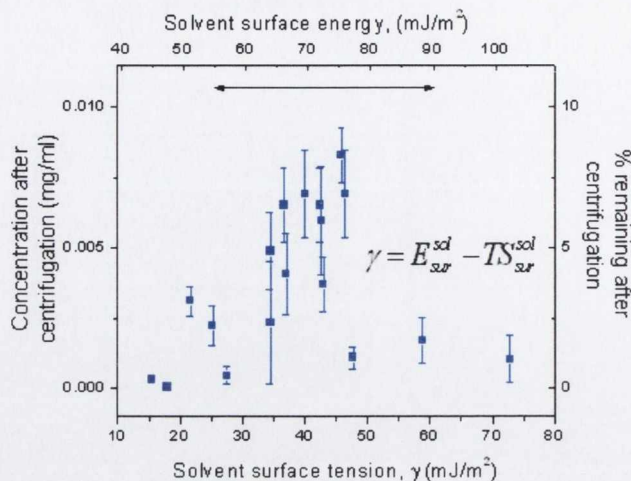


Figure 6.5: Graphene concentration measured after centrifugation for a range of solvents plotted versus solvent surface tension. This data was converted from absorbance using $A_{660}/l = \langle \alpha_{660} \rangle C$ with $\langle \alpha_{660} \rangle = 2460 \text{ Lg}^{-1}\text{m}^{-1}$. The original concentration, before centrifugation, was 0.1 mg/ml. Shown on the right axis is the percentage of material remaining after centrifugation. On the top axis, the surface tension has been transformed into surface energy using a universal value for surface entropy of $\sim 0.1 \text{ mJ/m}^2\text{K}$. The horizontal arrow shows the approximate range of the reported literature values for the surface energy of graphite [41–44]

As predicted, the dispersed concentration shows a strong peak for solvents with a surface energy very close to literature values of nanotube/graphite surface energy [41–44], that is $\sim 70 - 80 \text{ mJ/m}^2$. Coupled with Equation 6.1, this strongly suggests that not only is the enthalpy of mixing for graphene dispersed in good solvents very close to zero, but the solvent-graphene interaction is van der Waals rather than covalent. In addition, it predicts that good solvents are characterised by surface tensions in the region of $40\text{--}50 \text{ mJ/m}^2$. Also, we can tell from these data that for the best solvent (Benzyl Benzoate), 9.1% by mass of the original material remained after centrifugation.

The twelve best solvents as characterised by the fraction of graphite/graphene remaining after centrifugation are listed on table 6.1.

It is crucial to ascertain the exfoliation state of the material that remains dis-

Solvent	Surface Tension (mJ/m^2)	% Remaining after centrifugation	error
Benzyl Benzoate	45.95	9.1	1.1
NMP (1-Methyl-2-pyrrolidinone)	40.1	7.6	1.7
GBL (γ -Butyrolactone)	46.5	7.6	1.7
DMA (N,N-Dimethylacetamide)	36.7	7.2	1.4
DMEU (1,3-Dimethyl-2-Imidazolidinone)	42.5	7.2	1.4
NVP (1-Vinyl-2-pyrrolidone)	42.7	6.6	2.1
N12P (1-Dodecyl-2-pyrrolidone)	34.5	5.4	1.5
DMF (N,N-Dimethylformamide)	37.1	4.5	1.6
DMSO (Dimethylsulfoxide)	42.98	4.1	1.0
IPA (Isopropanol)	21.66	3.4	0.6
N8P (1-Octyl-2-pyrrolidone)	34.5	2.6	2.4
Acetone	25.2	2.5	0.8

Table 6.1: Best solvents by fraction of graphene/graphite remaining after centrifugation

persed after centrifugation. First, the state of the initial graphite powder was examined. SEM studies (figure 6.1(inset)) show the starting powder to consist of flakes of lateral size $< 500\mu m$ and thickness $< 100\mu m$. In comparison, the sediment separated after centrifugation contains flakes, which are much smaller, with lateral size measured in tens of microns with thicknesses of a few microns (figure 6.6(A)). We note that, as the crystallite size in the starting powder was $> 150\mu m$, the preparation procedure must result in tearing of the crystallites. This process may be similar to sonication induced fragmentation of carbon nanotubes[45].

It is possible to investigate the state of the material remaining dispersed using TEM simply by dropping a small quantity of each dispersion onto holey carbon grids². Crucially, this technique is much simpler than that previously used to prepare graphene for TEM [46], which involved under-etching of graphene placed on

²holey carbon is the name used in electron microscopy to describe an amorphous thin layer of carbon that is evaporated on TEM grids to give additional support to the samples.

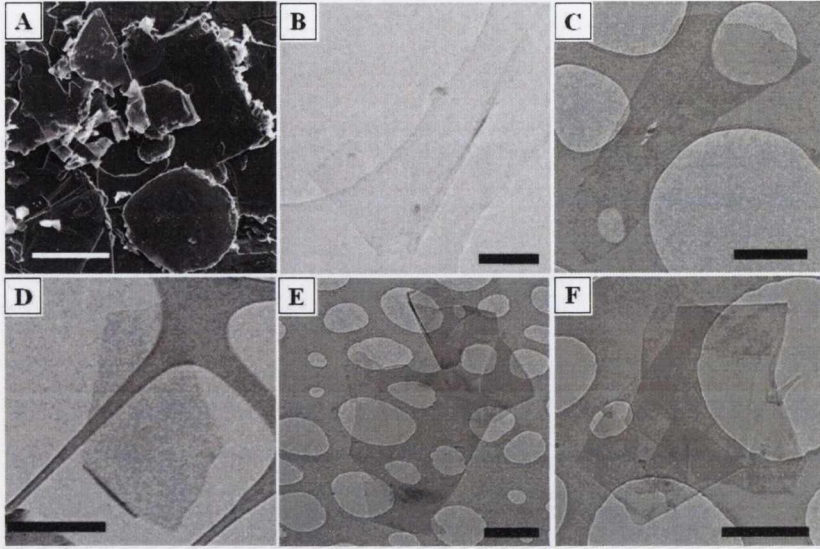


Figure 6.6: A) SEM image of sediment after centrifugation (scale: 25 μm). B), C) and D) Bright field TEM images of single layer graphene flakes deposited from GBL, DMEU and NMP respectively (scale: 500nm). E) A folded graphene sheet (bright field, deposited from NMP). F) Multi-layer graphene (bright field, deposited from NMP) (scale: 500nm).

a silicon substrate, and immediately shows one advantage of having graphene solutions. Shown in figure 6.6(B-F) are bright field TEM images of objects typically observed. Generally three classes of objects were found. The first, as shown in figure 6.6(B-D), are graphene monolayers. Secondly, in a number of cases a single folded graphene layer is observed (figure 6.6(E)). Thirdly, bi-layer and multi-layer graphenes are also observed (figure 6.6(F)). In all cases, these objects have lateral sizes of typically a few microns. In some cases the sheet edges tend to scroll and fold slightly. However, large objects with thickness of more than a few layers were not seen. Thus it is believed that, in these samples, graphite has been almost completely exfoliated to give monolayer and few-layer graphene. By analysing a large number of TEM images (figure 6.8), paying close attention to the uniformity of the flake edges, flake thickness statistics can be generated (figure 6.7).

The mass fraction of graphene, (mass of monolayer graphene/mass of all flakes, M_{Ind}/M_T) can be calculated as:

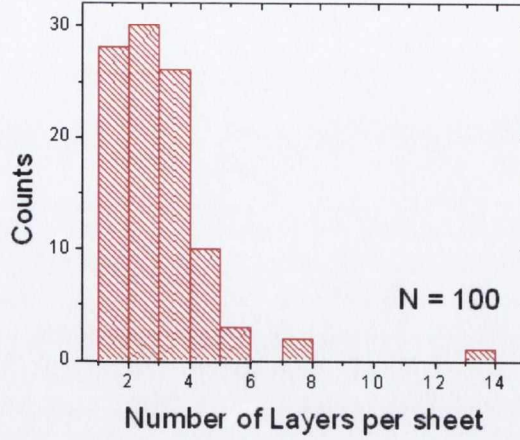


Figure 6.7: Histogram of the number of visual observations of flakes as a function of the number of monolayers per flake for NMP dispersions

$$\frac{M_{Ind}}{M_T} = \frac{\sum_{Individuals} A_{monolayer}}{\sum_{All\,flakes} N_{monolayer} A_{monolayer}} \quad (6.2)$$

where $A_{monolayer}$ is the area of a monolayer and $N_{monolayer}$ represents the number of monolayers in a given flake. The mass fraction was calculated to be 11.8% for the aforementioned NMP based sample. By combining this with the fraction of material remaining after centrifugation, χ we can estimate the total yield of graphene, Y . Y is defined as the mass of graphene produced divided by the starting mass of graphite: $Y = M_{Ind}/M_T \times \chi$. This gives $Y = 0.83\%$ for the NMP based sample.

Overall, the number fraction of monolayer graphene in NMP dispersions can be estimated as 27% with a solution-phase monolayer mass fraction of $\sim 12\%$, leading to an overall yield (mass of monolayers / starting graphite mass) of $\sim 1\%$ (see tables 6.2 and 6.3 for statistics). In fact, the sediment can also be recycled to produce dispersions with number and mass fractions of monolayer graphene of $\sim 18\%$ and 7% respectively. This suggests the possibility of full sediment recycling and the eventual increase of the yield towards 7-12wt% (relative to the starting graphite mass). We also carried out TEM studies on dispersions prepared from DMEU and GBL immediately after centrifugation. In both cases mono-layers were found. The mono-layer number densities and mass fractions were calculated as 6% and 2.1% respectively for DMEU and 4% and 1.5% for GBL (Table 6.3).

Solvent	N_{flakes}	$N_{monolayers}$	$N_{multilayers}$	Monolayer number fraction
NMP, $t = 0$	100	27	73	27%
NMP, $t = 4$ weeks	106	7	99	4.3%
NMP, $t = 5$ months	94	4	90	6.6%
NMP, $t =$ recycled sediment	100	18	82	18%
DMEU, $t = 0$	49	3	46	6%
GBL, $t = 0$	47	2	45	4%

Table 6.2: Statistics associated with analysis of the TEM images for samples deposited from NMP based dispersions immediately after centrifugation, four weeks after centrifugation and 5 months after centrifugation. Also included in this table are the statistics calculated for a dispersion prepared by re-dispersing a portion of the sediment from the original NMP based dispersion in fresh NMP. Finally we present statistics relating to the TEM analysis of dispersions based on DMEU and GBL. The last column on the right shows the number fraction of monolayers for each case under study

Solvent	$\frac{M_{Ind}}{M_T}$	χ	$Y = \frac{M_{Ind}}{M_T} \times \chi$
NMP, $t = 0$	11.8 %	7%	0.83%
NMP, $t = 4$ weeks	1.8%	7%	0.13%
NMP, $t = 5$ months	1.1%	7%	0.08%
NMP, $t =$ recycled sediment	6.7%	7%	0.47%
DMEU, $t = 0$	2.1%	6.5%	0.14%
GBL, $t = 0$	1.5%	6.9%	0.10%

Table 6.3: In this table the mass fraction of graphene (number of monolayers / total number of flakes), the fraction of material remaining after centrifugation (χ) and the overall yield of graphene are presented

Recycling of the sediment

We attempted to recycle the sediment separated from the original graphene/NMP sample by centrifugation. To do this the sediment was dried and used it to prepare a new dispersion in fresh NMP, in exactly the same way as the original dispersion was made. After centrifugation, this dispersion was analysed using TEM. A significant

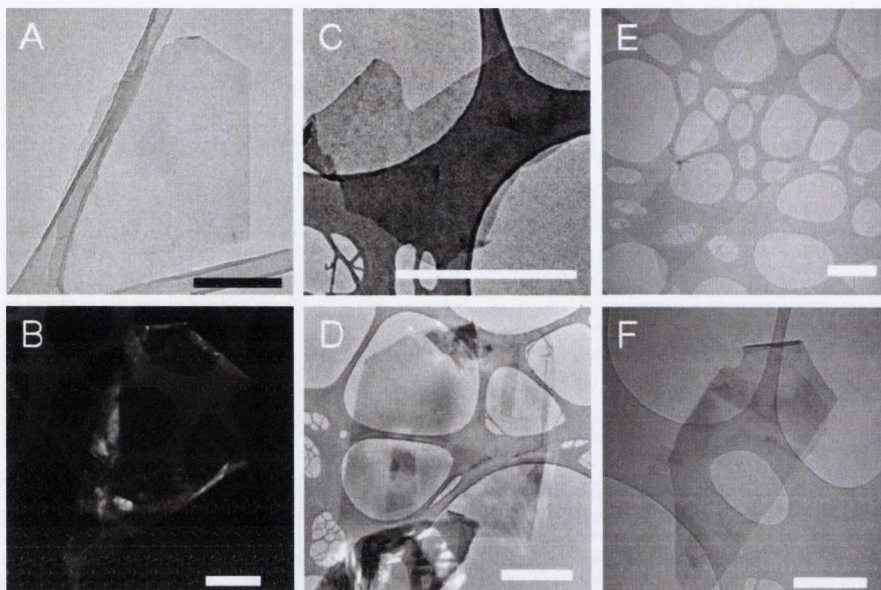


Figure 6.8: Representative TEM images of monolayer graphene flakes in NMP based samples A) immediately after centrifugation, B) immediately after centrifugation showing scrolling (dark field image), C) four weeks after centrifugation, D) five months after centrifugation, E) and F) prepared by recycling the sediment left over while producing the sample shown in A) and B). E) monolayer F) bilayer. In all cases the scale bar is 500 nm.

number of graphene monolayers were observed in addition to large quantities of multi-layers. An example of an image of such a monolayer is shown in figure 6.8(E) with a bilayer shown in figure 6.8(F). A histogram of the number of monolayers per multilayer is shown in figure 6.9. Analysis of the data presented in the histogram allows the calculation of the number density of monolayers and the mass fraction of monolayer graphene to be 18% and 6.7% respectively. These values are similar to those obtained from the original dispersions. This is an important point as it means that the sediment can be effectively recycled. Thus, the real yield of monolayer graphene is not given by $Y = M_{Ind}/M_T \times \chi$, as described above (0.83%) but is actually much larger with a maximum value given by $Y_{max} = M_{Ind}/M_T$. This allows us to estimate the maximum yield as between the values of M_{Ind}/M_T calculated for the recycled sample and the $t=0$ sample; i.e. between 6.7% and 11.8%.

Stability against re-aggregation

Minimal re-aggregation occurs in the dispersion phase over short time frames. The vast majority of the flakes observed in the $t = 0$ sample have Bernal stacking³. However, two multilayers which showed diffraction patterns with a number of six-fold patterns rotated slightly from each other, indicative of random stacking were also found [47]. We suggest that we observe Bernal stacking for multilayers which were never exfoliated and random restacking for flakes that did exfoliate but have subsequently re-aggregated in the dispersion phase.

We studied re-aggregation over longer timescales by carrying out TEM analysis on dispersions allowed to stand undisturbed for timescales of both 4 weeks and 5 months. Sample images are in figure 6.8(C and D). Shown in figure 6.9 are histograms of the number of graphene layers per flake for these samples, in comparison to the $t = 0$ sample. For both the 4 weeks and 5 months old samples, we see small but significant amounts of aggregation compared to $t = 0$. This aggregation can be quantified by a decrease in monolayer number fraction and mass fraction for the aged samples relative to the $t = 0$ sample (tables 6.2 and 6.3). However, both the aged samples contained individual monolayers, demonstrating a reasonable degree of stability. It should be noted that the ensuing aggregation can be reversed at any time by mild sonication. It should be pointed out that it is not clear what happens to the adsorbed NMP after aggregation. However, as aggregation is reversible, NMP could get trapped between the aggregated sheets.

6.3.2 Identification of monolayer graphene by electron diffraction

A more definitive identification of graphene can be made by analysis of electron diffraction patterns [48]⁴. As an example of this, in figure 6.10 (A and B) what appear to be a graphene monolayer and a graphene bi-layer respectively are shown. Figure 6.10(B) is particularly interesting as the right side of the flake consists of at least two layers while on the left side, a single mono-layer protrudes. Shown in figure ??(C) is the normal incidence electron diffraction pattern of the flake in (A). This

³Images and analysed taken by Dr. Valeria Nicolosi

⁴Electron diffraction patterns taken by Dr. Valeria Nicolosi

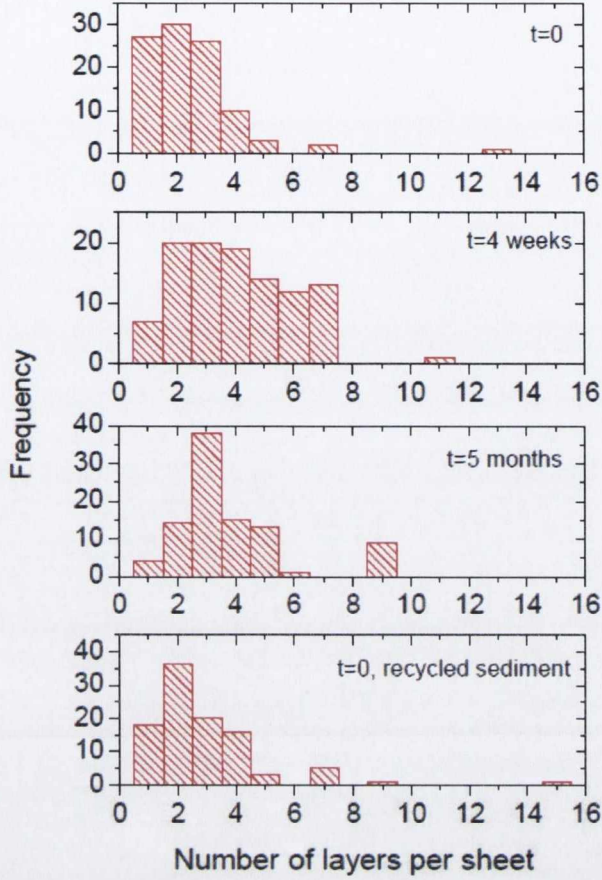


Figure 6.9: Histograms of the number of graphene layers per flake from samples prepared from NMP based dispersions, immediately after centrifugation and both 4 weeks and 5 months after centrifugation. Statistics are also presented for a sample prepared from re-suspended sediment collected from the original graphene/NMP sample and re-suspended in pure NMP.

pattern shows the typical six-fold symmetry expected for graphite/graphene [46, 48] allowing us to label the peaks with the Miller-Bravais (hkl) indices. Shown in figure ??(D and E) are normal incidence selected-area diffraction patterns for the flake in (B), taken with beam positions close to the black and white dots respectively. This means we expect one pattern (D) to reflect monolayer graphene while the other (E) will reflect multi-layer graphene. In both cases we see a hexagonal pattern similar to that in (C). The main difference between (D) and (E) is that for the multi-layer

(E), the 2110 spots appear to be more intense relative to the 1100 spots. This is an important observation, as for graphene multi-layers with Bernal (ABA) stacking, computational studies have shown that the intensity ratio, $I\{1100\}/I\{2110\} < 1$, while for mono-layers $I\{1100\}/I\{2110\} > 1$ [49]. Virtually all the objects identified in all the images as multi-layers displayed $I\{1100\}/I\{2110\} < 1$, demonstrating that Bernal stacking rather than AA stacking is predominant in these samples [49].

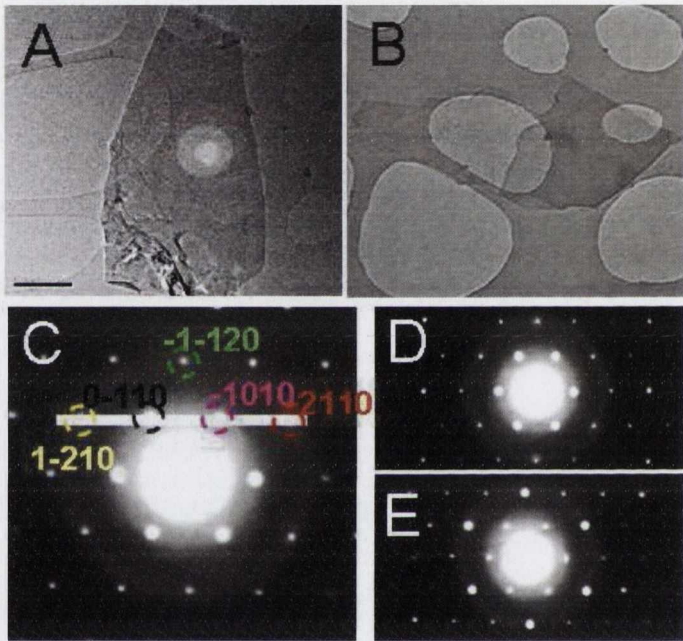


Figure 6.10: A) and B) HRTEM images of solution cast monolayer and bi-layer graphene respectively. C) Electron diffraction pattern of the sheet in A). The peaks are labelled using Miller-Bravais indices. The same labels also apply to the patterns in D) and E). D) and E) Electron diffraction patterns of the sheet shown in B). The pattern in D) was taken from the position marked with the black spot where the sheet is one layer thick. The pattern in E) was taken from the position marked with the white spot where the sheet is clearly two layers thick.

This identification of Bernal stacking in these thin multi-layers allows us to definitively differentiate mono-layer graphene from multi-layer graphene by inspection of the intensity ratio; $I\{1100\}/I\{2110\}$. To do this, we plot a line section through the (1-210)-(0-110)-(-1010)-(-2110) axis for the patterns in C, D and E in figures 6.10 are shown in figure 6.11 F, G and H. In F and G we can clearly see that the

inner peaks, (0-110) and (-1010), are more intense than the outer ones, (1-210) and (-2110), confirming that both the flake in A, and the region marked by the black dot in B, are monolayer graphene. Conversely, H clearly shows inner peaks that are less intense than the outer ones confirming that the area around the white dot in B consists of more than one layer. Further confirmation of the presence of monolayer graphene can be found by measuring the diffraction peak intensity as a function of tilt angle.

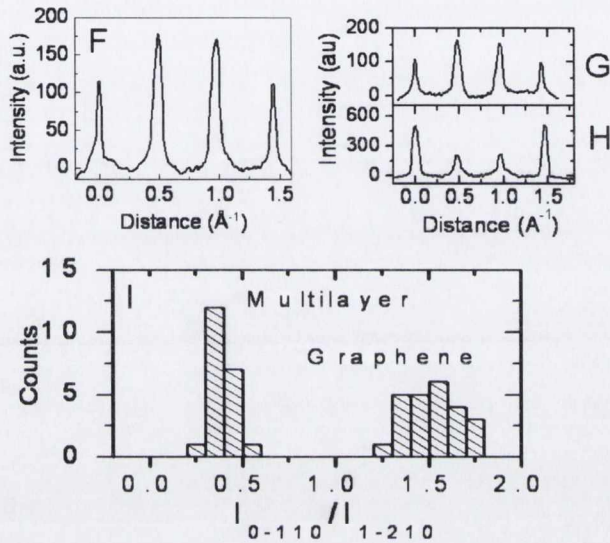


Figure 6.11: F), G) and H) Diffracted intensity taken along the 1-210 to -2110 axis for the patterns shown in C), D) and E) (fig 6.10) respectively. I) Histogram of the ratios of the intensity of the 1100 and 2110 diffraction peaks for all the diffraction patterns collected. A ratio greater than 1 is a signature of graphene.

The diffraction pattern of 45 flakes was taken before measuring the intensity ratio; $I_{\{1100\}}/I_{\{2110\}}$. These ratios are plotted as a histogram in figure 6.11(I). We clearly see a bimodal distribution with peaks centred at $I_{\{1100\}}/I_{\{2110\}} = 0.35$ and $I_{\{1100\}}/I_{\{2110\}} = 1.5$ representing multilayer and monolayer graphene respectively. These results agree well with reported experimental intensity ratios of $I_{\{1100\}}/I_{\{2110\}} \sim 0.4$ for a bilayer and $I_{\{1100\}}/I_{\{2110\}} \sim 1.4$ for monolayer graphene[48]. Though this data suggests a yield of 51% monolayer graphene, this is certainly an over estimate as selected area electron diffraction can give mono-layer

like patterns for multi-layers such as that in figure 6.10(B), when the beam is incident on a protruding monolayer. Better statistics can be found by counting the number of monolayers per flake as shown in figure 6.7. However, electron diffraction can be used to check the accuracy of the image analysis showing that it can reproducibly be used to identify monolayer graphene, thus confirming the results presented in figure 6.7.

Evidence of exfoliation from angle dependent electron diffraction

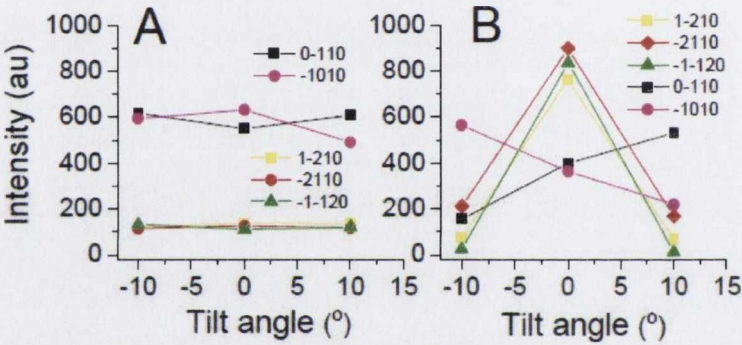


Figure 6.12: Diffracted intensity for a range of spots as a function of tilt angle for a monolayer (A) and a bilayer (B).

Further confirmation of the presence of monolayer graphene can be found by measuring the electron diffraction peak intensity as a function of tilt angle. For monolayer graphene, the peak intensity is insensitive to angle while for multi-layer graphene, the intensity can change dramatically with tilt angle [46, 48]. Shown in figures 6.12(A and B) are diffraction intensity versus tilt angle data for two flakes identified both visually and from electron diffraction intensity ratios as monolayer and bilayer respectively. As expected the monolayer flake shows angle invariant diffraction intensities while the multilayer shows a collapse of diffracted intensity for the {2110} peaks as the sample holder is tilted to $\pm 10^\circ$. This is further confirmation of the presence of graphene and of our ability to identify it visually.

6.3.3 Atomic force microscopy

The graphene/graphite dispersions were deposited onto various substrates by spraying with an airbrush⁵. The advantage of this technique is that it allows deposition onto any surface. In principle, any film thickness can be made, from sub-monolayer to many nanometres thick, by controlling the volume of liquid deposited. The sub-monolayer films of graphene were prepared by spraying 1ml at a nitrogen pressure of 2 bar from a distance of 4–5cm away from the sample⁶. This procedure is generally repeated a second time after drying in an oven at 100°C for 15 minutes to increase the number of deposited flakes. Residual solvent was removed by annealing under forming gas⁷ at 400°C for 4 hours prior to AFM measurements.

The amount of deposited material was generally low enough that we observed isolated sheets. However, when spraying from a high concentration aggregated sheets were also seen (figure 6.13(A and B)). While the majority of sheets were relatively thick: 2–5 nm (figure 6.13(A)), we also saw significant numbers of thinner objects, which we identify as monolayers. Such objects are typically 1–2 nm in height (figure 6.13(A, B and C)) rather than 0.3 nm, in line with the observations of others [17, 19]. However, sometimes we measure objects that have very well defined edges but have larger than expected thickness, even up to 2.6 nm (figure 6.13(D)). Well defined edges were a distinctive signature of monolayers in TEM taken in this study. In fact, by checking the electron diffraction pattern for monolayers identified by their edges shows that edge-identification of monolayers is accurate. Thus, we suggest that the object in figure 6.13(D) is a monolayer. That the thickness is much larger than expected is probably due to a combination of chemical contrast issues and the presence of a residual NMP between the monolayer and the Si wafer substrate. Note the similarity between the shape and size of the graphene sheet in figure 6.13(C) and that imaged by TEM in figure 6.8(C) (or those in figure 6.6). This ability to deposit individual sheets is important because it opens up the possibility of preparing samples for electronic applications.

⁵www.graphics.co.uk

⁶Samples sprayed and imaged by Peter Niraj

⁷a mixture of up to 10% hydrogen in nitrogen

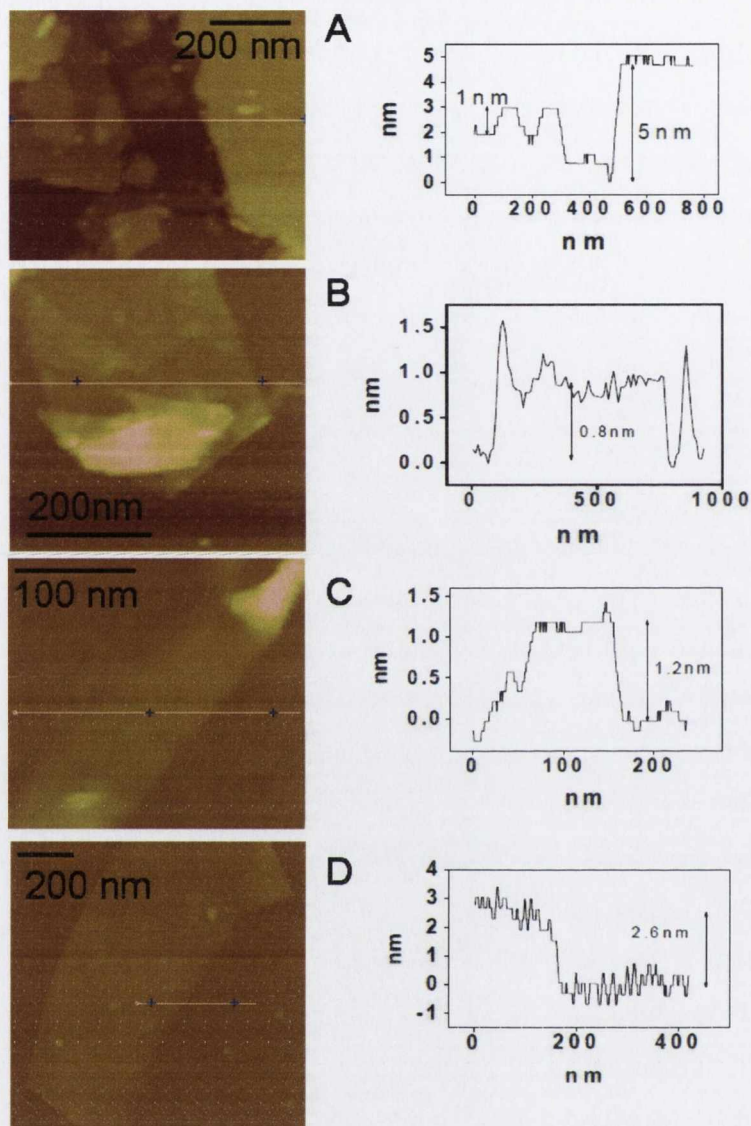


Figure 6.13: AFM images of a number of flakes observed in this study. The flakes in C) and D) are believed to be monolayers.

6.3.4 Raman Spectroscopy

Graphene can be identified in terms of number and orientation of the layers by means of elastic and inelastic light scattering, such as Raman [35] and Rayleigh spectroscopies [6, 50]. Raman spectroscopy also allows monitoring of doping and defects [6, 51, 52]. Raman spectroscopy is a fast and non-destructive method for the characterization of carbons [53]. Their spectra show common features in the

800-2000 cm^{-1} region: the G and D peaks, which lie at around 1560 and 1360 cm^{-1} respectively (see figure 6.15(D)). The G peak corresponds to the E_{2g} phonon at the Brillouin zone centre. The D peak intensity is not related to the number of graphene layers, but only to the amount of disorder [54, 55]. Indeed, when moving from graphite to nanocrystalline graphite, the ratio between the intensity of D and G peak, $I(D)/I(G)$, varies inversely with the size of the crystalline grain [54–56]. The 2D peak is the second order of the D peak. This is a single peak in monolayer graphene, whereas it splits in four bands in bi-layer graphene, reflecting the evolution of the band structure [35].

Evidence of exfoliation from Raman spectroscopy

Figure 6.14 plots the Raman spectra for individual flakes deposited from solution onto a marked holey carbon TEM grid (400 mesh). The use of grids as substrates allows the confirmation of the nature of the flakes observed in the TEM, and it helps to later find the same flake with the Raman spectrometer. These spectra have small or non-existent D bands, indicating an absence of defects. It is possible to identify the number of layers from the shape of the 2D peak [35]. The top spectrum displays a very sharp 2D peak, identifying it as a monolayer. The graphene monolayer studied here is the same one shown in figure 6.6(D) and had dimensions of $\sim 1\mu\text{m}$. This small size makes these monolayers difficult to find, even on a marked TEM grid. The second spectrum has a 2D band shape typical of graphene bilayers. The third can be identified from the 2D band as a graphene multilayer with less than 5 layers. A spectrum for bulk graphite is shown for comparison. The fact that monolayers, bilayers and multi-layers (<5 layers) can be detected, confirms again that the method presented here can successfully exfoliate bulk graphite.

The value of this work is that it demonstrates a method to produce graphene with high yield in the liquid phase. It is important to note that the liquid phase production of graphene oxide (GO) is already well established [17–19, 21, 57]. However, while reduction of GO can remove some of the oxygen, Raman spectroscopy shows that a large amount of structural defects remain [17, 21]. The presence of these defects alters the electronic properties relative to pristine graphene, strongly suppressing the π electrons delocalisation, and massively decreasing the mobility [17].

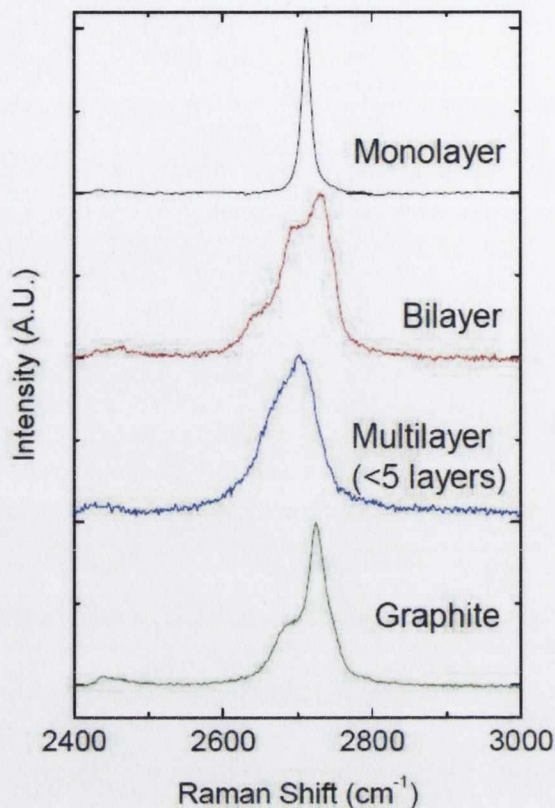


Figure 6.14: 2D Raman spectra for individual flakes deposited from dispersion on a marked holey carbon TEM grid (400 mesh). The shape of the 2D peak allows identification of the number of layers per sheet. The top spectrum is for a graphene monolayer while the second represents a graphene bilayer. The third can be identified as a graphene multilayer (<5 layers). A spectrum for bulk graphite is shown for comparison. The graphene monolayer studied here is the same one shown in figure 2E.

It is then critical to further validate that we are not producing graphene oxide or a related version of derivatised graphene. This was done by a combination of X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). In addition we must demonstrate that we are not generating structural defects during the graphene preparation process.

6.3.5 Film formation and structure

We can briefly illustrate the potential of this method of graphene production by using it to make thin graphene films⁸. Thin films were prepared by vacuum filtration of the relevant dispersions onto either polyvinylidene fluoride (PVDF) membranes (pore size: 100 nm) or porous alumina membranes (pore size: 20 nm). A relatively large volume, 400 mL, of dispersion was filtered to give films weighing 2-4 mg, depending on the dispersion concentration. Such films are typically 5 microns thick. Initial sample drying was carried out in a vacuum oven at room temperature at a pressure of $\sim 10^{-3}$ mbar. Subsequently, in some cases, annealing was carried out to remove residual solvent using a vacuum tube furnace from GERO Hochtemperaturfen GmbH. The samples were heated to 400°C for 4 hours in either vacuum or forming gas. These films could then be used for further analysis, notably optical and electron microscopy and Raman spectroscopy. Note that the position and width of the Raman 2D line shown in figure 6.15 indicates the presence of graphite rather than graphene [35]. This could be caused by re-aggregation of graphene or by a prevalence of multilayer flakes.

Both optical and SEM images indicate that the films consist of random arrays of multilayer flakes. Optical imaging (figure 6.15(A)) shows the films to consist of a uniform background embedded with objects of $\sim 1-10\mu\text{m}$ in size. SEM imaging (figure 6.15(B)) coupled with Raman spectroscopy (figure 6.15(D)) point to these large objects being flakes of graphite (i.e. have more than ~ 5 layers). Zooming in on the background region (figure 6.15(C)) indicates that the bulk of the material consists of small thin flakes with sizes of $\sim 0.5-2\mu\text{m}$. These are very similar to the flakes observed by TEM (see figure 6.6 and figure 6.9). Raman spectroscopy shows these flakes to be <5 layers thick (figure 6.15(D)). In addition, it should be noted that these films are not totally uniform. It is clear that the mean thickness is significantly larger than the nominal value of 30nm, indicating significant free volume. In addition thickness variations are evident with the membrane occasionally visible.

⁸films prepared by Mustafa Lotya

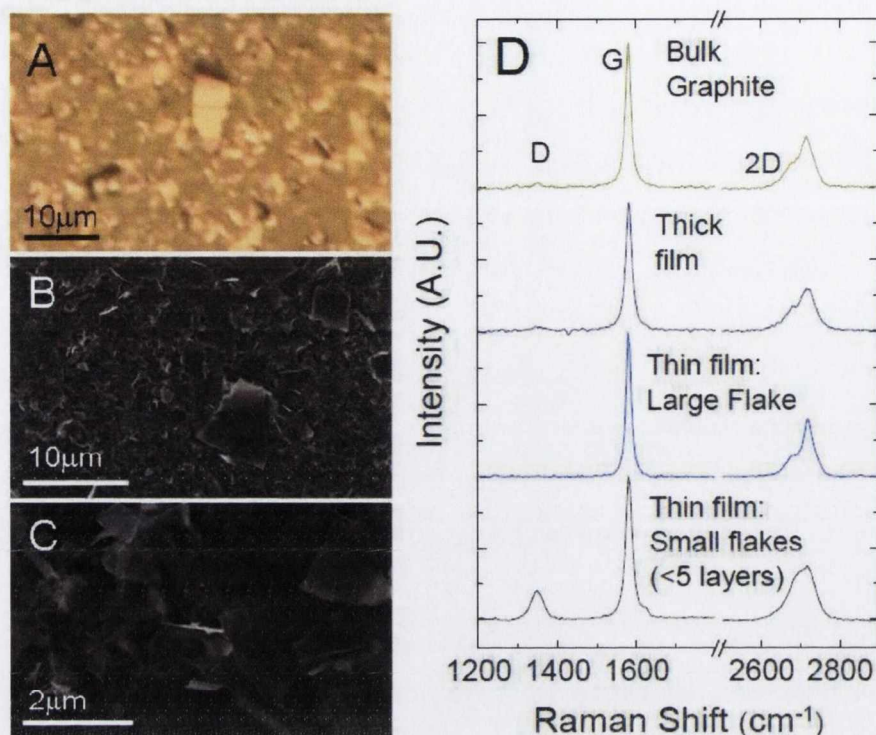


Figure 6.15: Analysis of the surface of a thin graphene film with a nominal thickness of 30 nm. A) Optical image. B) and C) SEM images. D) Raman spectra for a thick film and a thin film taken by focusing the beam on both large and small flakes. For comparison, spectra taken from bulk graphite and from a vacuum deposited thick film are also shown.

Raman of films

While figure 6.5 suggests a van der Waals type solvent-graphene interaction, it is crucial to rule out any inadvertent basal-plane functionalisation, which could alter the electronic structure. Figure 6.16 are Raman spectra of thin films of graphite/graphene prepared by vacuum filtration onto alumina filters. The G line ($\sim 1580 \text{ cm}^{-1}$) and 2D line ($\sim 2700 \text{ cm}^{-1}$) are visible in all cases while the D peak ($\sim 1350 \text{ cm}^{-1}$) is very weak or absent, except for the spectra of small flakes ($\sim 0.5\text{--}2 \text{ }\mu\text{m}$) which show edge effects[35]. This indicates that the solution based exfoliation process does not introduce significant structural defects, such as epoxides covalently bonded to the basal plane [21]. In addition Raman spectra were recorded for individual flakes deposited on marked TEM grids allowing us to identify monolayers,

bilayers and multilayers from the shape of the 2D band, emphasising the quality of our exfoliation (figure 6.14). The lack of pronounced D bands in these individual flakes demonstrates the lack of defects. Furthermore, we have used X-ray photoelectron spectroscopy and infra red spectroscopy to show the absence of oxidation typically associated with GO [17, 18]. These experiments show that high-quality, un-oxidised graphene in solution can be produced at a high yield.

The Raman spectrum of the region of the thin films characterised by small flakes was also noted (figure 6.15D). The shape of the 2D band is indicative of thin multilayers (<5 layers). This is an important observation as it indicates that very little aggregation occurs in the film formation stage. Eda *et.al.* observed monolayers in their graphene oxide films [17]. However, their films were very thin (<2nm) resulting in less opportunity for aggregation in the film formation phase. In addition, their flakes were effectively charged [18] which would minimise aggregation. The films prepared for this work were from dispersions of monolayer and multilayer graphene not graphene oxide. These flakes are therefore uncharged and the lack of large scale aggregation is surprising. However this lack of aggregation is balanced by the presence of residual NMP adsorbed to the flakes.

It is important to note that, as shown in figure 6.15(D), a small D band is always present in the spectra of films of small flakes. However, this is not surprising. The small flakes are 0.5-2 μm in diameter. As the laser spot size is 1-2 μm , there will always be a large quantity of edges seen by the beam. These act as defects and are expected to give a D band of similar width to that observed here. The lack of broadening of the G peak also confirms that the D peak comes from edges and not from diffuse structural disorder in the samples. Taken together with the data for films, this is very strong evidence that the dispersion process does not introduce defects to the basal plane of the graphene.

6.3.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was carried out on thin (~ 30 nm) vacuum filtered films that had been vacuum dried (10^{-3} mbar) at room temperature⁹. Measurements were done on both the as prepared films (to be referred to as un-

⁹Experiments conducted by Professor Ignatious T. McGovern and Brendan Holland

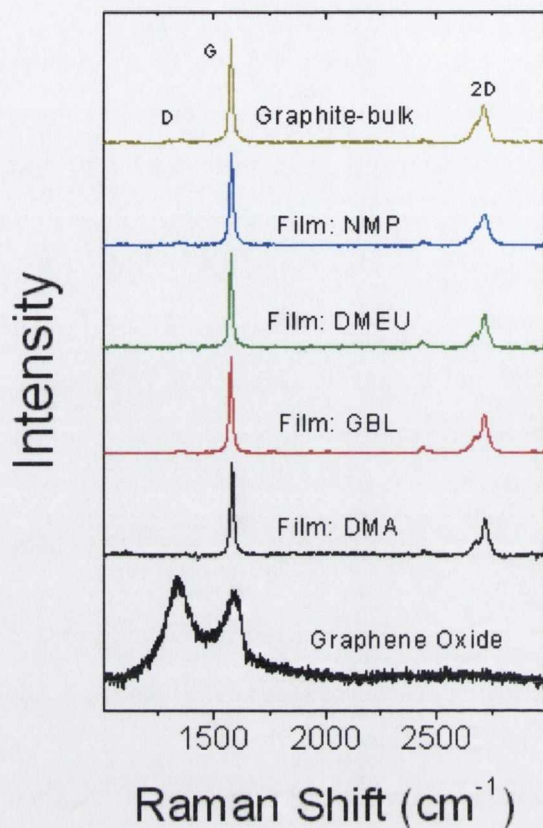


Figure 6.16: Raman spectra taken for graphite/graphene films. The top is untreated graphite powder. The next four spectra are for thick of graphene/graphite flakes deposited from NMP, DMEU, GBL and DMA by vacuum filtration onto PVDF filter papers. Furthermore, for comparison purposes, an spectrum of a thin film of graphene oxide is shown.

annealed) and on a film that was subsequently heated in a tube furnace in vacuum (10^{-3} mbar) to 400°C for four hours, to try and remove residual NMP (to be referred to as annealed). Spectra were recorded at 10 eV pass energy and 2 mm slits, with a resolution of 0.85 eV.

XPS spectra were recorded for the un-annealed sample before and after *in vacuo* heating at 600°C to remove atmospheric adsorbates such as CO_2 , CO , O_2 and N_2 . Employing reasonable cross-section and escape depth approximations, nitrogen *1s* core level intensities imply nitrogen concentrations of 1.9 atom% and 1.5 atom% before and after *in vacuo* heating. Such a small change implies that *in vacuo* heat-

ing removed adsorbates such as N_2 but leaves the majority of the NMP trapped in the film. We can use the latter value to estimate a residual NMP content of $\sim 11\text{wt}\%$. Similar nitrogen contents were observed for the annealed sample suggesting that heat treatment is inefficient at removing NMP from the interior of these graphene/graphite films.

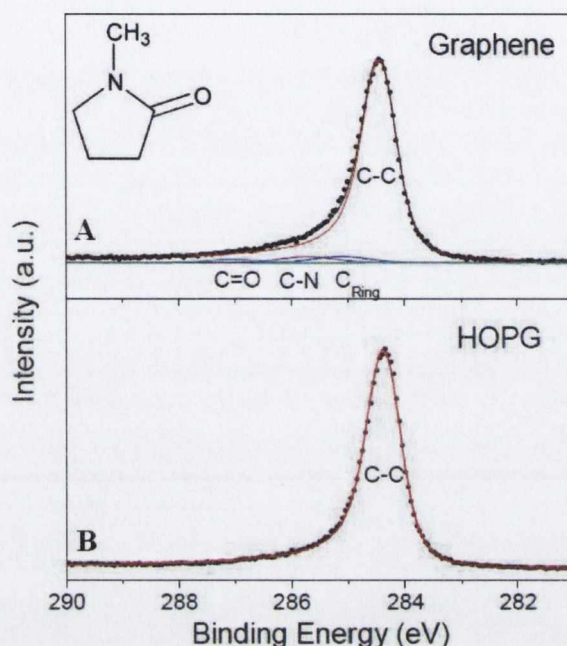


Figure 6.17: A) XPS spectra for thin (~ 30 nm) film produced by vacuum filtration of an NMP based dispersion and dried in a vacuum oven at room temperature. Inset: structure of the NMP molecule B) XPS spectrum of HOPG. In both cases the Shirley background has been removed. Fit lines are labelled as: C–C, graphitic carbon; C_{Ring}, Carbon in the NMP ring bonded to two hydrogen atoms; C–N, carbon in the NMP molecule bonded to a N atom; C=O, Carbon in the NMP ring double bonded to an oxygen atom.

Carbon $1s$ core level spectra are shown in figure 6.17. Spectrum A is from an un-annealed graphene sample which was subjected to *in vacuo* heating at 600°C while spectrum B is from a clean highly oriented pyrolytic graphite sample (HOPG). Spectrum A has been fitted to the following features: principally, a HOPG spectrum including a Shirley background and three small Voigt features at 0.7, 1.6 and 2.6 eV higher binding energy than the graphite peak. These features are representative

of the two carbon atoms in the NMP ring that are not bonded to N or O, the two carbon atoms that are bonded to N and the carbonyl carbon, respectively. These features have been fitted to the spectrum in the intensity ratio 2:2:1, respectively, as would be expected for NMP. For visual clarity the Shirley background has been removed from both spectra. As can be seen, a very good fit is obtained considering only the graphite-like carbon and the NMP carbon (and the Shirley background).

As described above, nitrogen *1s* core level intensity implies an estimated 1.5 atom% N in the in vacuo heat treated samples. As each NMP nitrogen atom is associated with 5 NMP carbon atoms we can estimate that ~8% of the carbon *1s* peak is due to NMP carbons. This compares well with the combined intensity of the remnant (non-graphite-like) features of 7% of the total carbon *1s* signal. Thus, this level of solvent residue in graphene provides a reasonable explanation of spectrum A. Both estimates of percentage, however, are individually subject to potential error. A much firmer conclusion is that there is no discernible trace of graphene oxide in this sample. Similar general conclusions can be drawn for the annealed graphene film. Graphene oxide is generally manifested in XPS by a large C–O peak at 286.2 eV [17, 21, 58]. Even after reduction and annealing at up to 1100°C, traces of C–O are still observable by XPS [58]. Here no C–O peak is clearly observable. In addition the remnant features around 286 eV can be attributable to residual solvent. Thus, the XPS data strongly suggests that solvent processing does not result in any observable oxidation of the resultant graphene/graphite. This allows us to confirm that the structures observed by TEM are graphene rather than graphene oxide.

6.3.7 Attenuated total reflectance-Fourier transform infrared spectroscopy

Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR - FTIR) spectra were measured for thin films, similar to those shown in figure 6.15, deposited from NMP dispersions onto alumina membranes by vacuum filtration¹⁰. The films were dried under vacuum (10^{-3} mbar) at room temperature. One film was subsequently annealed at 400°C for 4 hours in an Ar/H₂ purged atmosphere to remove NMP. The FTIR spectra for both vacuum dried and annealed samples are shown in

¹⁰Measurements conducted by Mustafa Lotya and Michele Byrne

figure 6.18 and are virtually featureless. This is in sharp contrast to the spectra for graphene oxide published by Li *et.al.* [18], which contain intense spectral features around 1700 cm^{-1} attributable to carboxyl groups. Again this is further evidence that we produce graphene rather than some form of derivatised graphene.

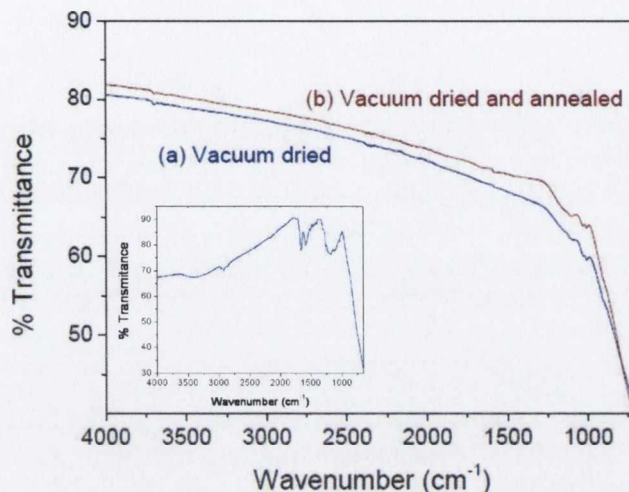


Figure 6.18: ATR-FTIR spectra for vacuum dried and annealed graphene films. These spectra show no evidence of carboxyl groups which generate features around 1700 cm^{-1} . Inset: Graphene oxide spectrum.

6.3.8 Presence of residual NMP

NMP is a high boiling solvent which, coupled with the fact that it is also thought to bind well to graphitic surfaces [30], means that it may be difficult to completely remove NMP from the sample. We have characterised the presence of NMP both for as-prepared samples which have been dried at room temperature under vacuum (10^{-3} mbar)(to be referred to as un-annealed) and on films that were subsequently heated in a tube furnace in vacuum (10^{-3} mbar) to 400°C for four hours in an attempt to remove residual NMP (to be referred to as annealed). We have used three techniques to characterise the presence of NMP; XPS, combustion analysis and AFM.

Combustion analysis was carried out on powder recovered from NMP based dispersions using a Thermo Deltaplus Continuous Flow Isotope Ratio Mass Spectrome-

ter (CF-IRMS) with a CE Instruments 1112 Flash elemental analyser interfaced via a Conflo III¹¹. Nitrogen was detected at a level of ~ 1.5 atom% in the un-annealed sample but was not observed in the annealed sample. Taking into account the resolution of the instrument, this means a nitrogen content of <0.9 atom% in the annealed sample. These values correspond to NMP contents by weight of $\sim 11\%$ and $<7\%$ respectively. XPS was carried out on thin filtered films giving nitrogen contents of ~ 1.5 atom% before and after annealing corresponding to contents of NMP by weight of $\sim 11\%$. These results are reasonably close given the different sample types used.

Technique	N content, unannealed (atom%)	N content, annealed (atom%)	NMP content, unannealed (wt%)	NMP content, annealed (wt%)
XPS	~ 1.5	~ 1.5	~ 11	~ 11
Combustion Analysis	~ 1.3	<0.9	~ 10	<7
AFM	—	—	Large amounts visible	None visible

A third, non-quantitative method was also used; AFM. It was found that NMP tends to coalesce into nano-scale puddles on SiO₂. These puddles can be observed by AFM. In the un-annealed sample large quantities of puddles are observed. After annealing all puddles are removed. Thus we believe that NMP is almost totally removed from monolayer films by annealing at 400°C for 4 hours. We note however, that the presence of NMP between flakes and substrate (as suggested by AFM) cannot be ruled out. Taken together, these results suggest that NMP cannot be fully removed from thin films or powdered samples, with a residual 10% content. This translates to approximately one NMP molecule per 75 graphene carbons. These molecules are most likely trapped on the internal surface of the powder/film. However, monolayer films have no internal surface, allowing almost complete solvent removal.

¹¹Measurements carried out by Dr. Robbie Goodhue

6.3.9 Thin Film conductivity

Thin graphene films were made by vacuum filtration as described above¹². It proved virtually impossible to remove these films from the alumina membrane so all measurements were made on films on the membranes. All films were approximately 30 nm thick. The sheet resistance of thin films of multilayer graphene were measured by the four-point probe technique¹³. The transparency was measured by comparing the transmitted intensity of a HeNe laser (632nm) through the graphene film on alumina to the transmitted intensity through the alumina alone. Three sample types were prepared. In the first case, after vacuum filtration, the film was dried in a vacuum oven (10^{-3} mbar) at room temperature overnight. This sample had a transmittance of 61% and a sheet resistance of $R_s = 7.2 M\Omega/\square$. The conductivity of this film was relatively low: ~ 5 S/m. These results are comparable to that obtained by Eda *et.al.* for GO films reduced and annealed ($R_s \sim 1 M\Omega/\square$)[17].

Such vacuum dried films were then treated in two ways to improve the conductivity. The first involved heating to 300°C in an oven in ambient conditions for 2 hours¹⁴. This resulted in a slight decrease in transmittance to 42%. However the sheet resistance decreased dramatically to $R_s = 7.1 k\Omega/\square$. For a thickness of 30 nm this implies a conductivity of 5000 S/m. The second treatment involved annealing in Ar/H₂ (nominally 90%/10%) at 250°C for 2 hours. Again the transmittance decreased to 42%. However the sheet resistance dropped dramatically to $R_s = 5.1 k\Omega/\square$, equivalent to a conductivity of 6500 S/m. This latter value is very close to that observed for films prepared from reduced GO by Li *et.al.* (7000 S/m) [18]. It should be noted that these conductivities can almost certainly be improved upon. As shown in figure 6.15, these films are much thicker than the nominal 30nm. This thickness is that expected if the sheets were close packed. The fact that there is so much free volume means that the number of inter-sheet junctions is much lower than that expected for a dense film. Thus we expect that densification and alignment would result in a significant increase in conductivity as is the case for carbon nanotube films.

¹²Samples prepared by Mustafa Lotya

¹³Measurements conducted by Dr. Sukanta De

¹⁴Samples annealed by Dr. Georg Duesberg and Dr. Satheesh Krishnamurthy

6.3.10 Composites

Composite dispersions were prepared by adding 3-7g polystyrene to a graphite dispersion in NMP (concentration ~ 0.01 mg/ml, volume ~ 400 ml). This was then sonicated for 15 mins in a sonic bath. Composite films were prepared by the film formation method described above. It should be noted that most of the polymer was lost through the filter paper. The graphene/graphite mass fraction was measured by TGA¹⁵ to be in the range 60-85%. At these high volume fractions, the films are very non-uniform as shown in the SEM image in figure 6.19.



Figure 6.19: SEM image of the cross section of a polymer-composite film deposited on a PVDF membrane.

Electrical measurements were made by measuring the film resistance as a function of film length. The electrical conductivity of the resultant composite films are shown in figure 6.20 and range from ~ 50 S/m for the lowest mass fraction composite to ~ 700 S/m for the graphene/graphite only film. It is not clear why the conductivity of the graphene/graphite only film deviates from that measured for the thin films. However it is likely to be due to thickness dependent changes in the film morphology.

6.4 Conclusions

In conclusion, we have demonstrated a scalable, high yield method to produce high-quality, un-oxidised graphene from powdered graphite. By using certain solvents, graphene can be dispersed at concentrations of up to 0.01 mg/ml. Raman and SEM analyses show that these films consist predominately of thin graphene multilayers with less than 5 layers. X-ray photoelectron spectroscopy measurements show that these films have $\sim 11\text{wt}\%$ residual NMP after drying at room temperature at $\sim 10^{-3}$

¹⁵measurements taken by Dr. Fiona Blighe

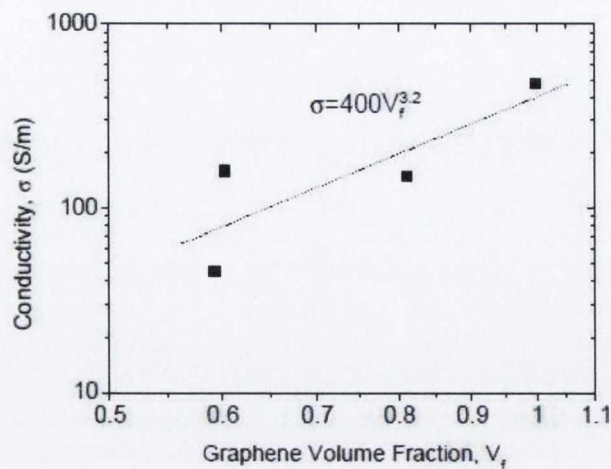


Figure 6.20: Conductivity of polystyrene composite films prepared by vacuum filtration. The dotted line is a percolation fit with an exponent of 3.2.

mbar. This value remained unchanged after a subsequent vacuum anneal at 400°C. Combustion analysis gives an NMP content of ~10wt% after room temperature drying ($\sim 10^{-3}$ mbar) which can be reduced to <7wt% after annealing. These films have conductivities of ~6500 S/m, similar to reduced graphene oxide films [18] and optical transparencies of ~42%. We also demonstrate polystyrene-graphene composites in NMP at high volume fraction. We measured the conductivity of such composites as a function of graphene volume (figure 6.8) to scale from 50 S/m for a 70 vol% film to 700 S/m for a film of graphene/graphite. These values are comparable to the most conductive polymer-nanotube composites [59] and significantly higher than those quoted for graphene-oxide based composites [19]. Finally, we have deposited graphene monolayers on SiO₂ surfaces via spray coating, demonstrating that this processing method can potentially be used to prepare samples for microelectronic applications.

References

- [1] A. K. Geim and K. S. Novoselov. *Nature Materials*, 6(3):183, 2007.
- [2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov. *Nature*, 438:197, 2005.
- [3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. *Science*, 306:666, 2004.
- [4] Y. B. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim. *Nature*, 438:201, 2005.
- [5] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, and A. K. Geim. *Science*, 315(5817):1379, 2007.
- [6] S. Pisana, M. Lazzeri, C. Casiraghi, K. S. Novoselov, A. K. Geim, A. C. Ferrari, and F. Mauri. *Nature Materials*, 6(3):198, 2007.
- [7] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. *Proceedings of the National Academy of Sciences of the United States of America*, 102(30):10451, 2005.
- [8] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer. *Solid State Communications*, 146(9-10):351, 2008.
- [9] Xu Du, Ivan Skachko, Anthony Barker, and Eva Y. Andrei. *Nature Nanotechnology*, 3(8):491, 2008.
- [10] C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, D. Mayo, T. B. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer. *Science*, 312:1191, 2006.

- [11] Taisuke Ohta, Farid El Gabaly, Aaron Bostwick, Jessica L. McChesney, Konstantin V. Emtsev, Andreas K. Schmid, Thomas Seyller, Karsten Horn, and Eli Rotenberg. *New Journal of Physics*, 10(Feb.), 2008.
- [12] S. Y. Zhou, D. A. Siegel, A. V. Fedorov, F. El Gabaly, A. K. Schmid, A. H. C. Neto, D. H. Lee, and A. Lanzara. *Nature Materials*, 7(4):259, 2008.
- [13] S. Marchini, S. Gunther, and J. Wintterlin. *Physical Review B*, 76(7), 2007.
- [14] A. L. V. de Parga, F. Calleja, B. Borca, M. C. G. Passeggi, J. J. Hinarejos, F. Guinea, and R. Miranda. *Physical Review Letters*, 1(5), 2008.
- [15] Peter W. Sutter, Jan-Ingo Flege, and Eli A. Sutter. *Nat Mater*, 7(5):406, 2008.
- [16] Y. Pan, N. Jiang, J.T. Sun, D.X. Shi, S.X. Du, F. Liu, and H.-J. Gao. *ArXiv:0709.2858*, 2008.
- [17] Goki Eda, Giovanni Fanchini, and Manish Chhowalla. *Nature Nanotechnology*, 3(5):270, 2008.
- [18] D. Li, M. B. Muller, S. Gilje, R. B. Kaner, and G. G. Wallace. *Nature Nanotechnology*, 3(2):101, 2008.
- [19] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff. *Nature*, 442(7100):282, 2006.
- [20] X. Wang, L. J. Zhi, and K. Mullen. *Nano Letters*, 8(1):323, 2008.
- [21] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff. *Carbon*, 45(7):1558, 2007.
- [22] I. Jung, M. Pelton, R. Piner, D. A. Dikin, S. Stankovich, S. Watcharotone, M. Hausner, and R. S. Ruoff. *Nano Letters*, 7(12):3569, 2007.
- [23] M. S. Dresselhaus and G. Dresselhaus. *Advances in Physics*, 30(2):139–326, 1981.
- [24] L. M. Viculis, J. J. Mack, and R. B. Kaner. *Science*, 299:1361, 2003.

- [25] Cristina Valles, Carlos Drummond, Hassan Saadaoui, Clascidia A. Furtado, Maoshuai He, Olivier Roubeau, Luca Ortolani, Marc Monthieux, and Alain Penicaud. *Journal of the American Chemical Society*, 130(47):15802–15804, 2008.
- [26] G. H. Chen, W. G. Weng, D. J. Wu, C. L. Wu, J. R. Lu, P. P. Wang, and X. F. Chen. *Carbon*, 42(4):753–759, 2004.
- [27] X. L. Li, X. R. Wang, L. Zhang, S. W. Lee, and H. J. Dai. *Science*, 319(5867):1229, 2008.
- [28] S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, and R. C. Haddon. *Journal of the American Chemical Society*, 128(24):7720, 2006.
- [29] S. Giordani, S. D. Bergin, V. Nicolosi, S. Lebedkin, M. M. Kappes, W. J. Blau, and J. N. Coleman. *Journal of Physical Chemistry B*, 110(32):15708, 2006.
- [30] S.D. Bergin, V. Nicolosi, S. Giordani, A. de Gromard, L. Carpenter, W.J. Blau, and J.N. Coleman. *Nanotechnology*, 18(45):455705, 2007.
- [31] S.D. Bergin, V. Nicolosi, P.V. Streich, S. Giordani, Z. Sun, A.H. Windle, P. Ryan, N.P.P. Niraj, Z.T. Wang, L. Carpenter, W.J. Blau, J.J. Boland, J.P. Hamilton, and J.N. Coleman. *Advanced Materials*, 20(10):1876, 2008.
- [32] C. A. Furtado, U. J. Kim, H. R. Gutierrez, L. Pan, E. C. Dickey, and P. C. Eklund. *Journal of the American Chemical Society*, 126(19):6095–6105, 2004.
- [33] T. Hasan, V. Scardaci, P. H. Tan, A. G. Rozhin, W. I. Milne, and A. C. Ferrari. *Journal of Physical Chemistry C*, 111(34):12594, 2007.
- [34] B. J. Landi, H. J. Ruf, J. J. Worman, and R. P. Raffaele. *Journal of Physical Chemistry B*, 108(44):17089, 2004.
- [35] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim. *Physical Review Letters*, 97(18), 2006.
- [36] D. S. L. Abergel and V. I. Fal’ko. *Physical Review B*, 75(15), 2007.

- [37] V. Nicolosi, D. Vrbancic, A. Mrzel, J. McCauley, S. O'Flaherty, C. McGuinness, G. Compagnini, D. Mihailovic, W. J. Blau, and J. N. Coleman. *Journal of Physical Chemistry B*, 109(15):7124–7133, 2005.
- [38] J.H Hildebrand, J.M. Prausnitz, and R.L. Scott. *Regular and related solutions*. Van Nostrand Reinhold Company, New York, first edition, 1970.
- [39] J. Lyklema. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 156(1-3):413, 1999.
- [40] N. G. Tsierkezos and A. C. Filippou. *Journal of Chemical Thermodynamics*, 38(8):952, 2006.
- [41] L. X. Benedict, N. G. Chopra, M. L. Cohen, A. Zettl, S. G. Louie, and V. H. Crespi. *Chemical Physics Letters*, 286(5-6):490, 1998.
- [42] L. A. Girifalco and R. J. Good. *Journal of Physical Chemistry*, 61(7):904, 1957.
- [43] M. Hodak and L. A. Girifalco. *Chemical Physics Letters*, 350(5-6):405, 2001.
- [44] R. Zacharia, H. Ulbricht, and T. Hertel. *Physical Review B*, 69(15), 2004.
- [45] S. H. Jeong, O. J. Lee, K. H. Lee, S. H. Oh, and C. G. Park. *Chemistry of Materials*, 14(4):1859, 2002.
- [46] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth. *Nature*, 446(7131):60, 2007.
- [47] Shigeo Horiuchi, Takuya Gotou, Masahiro Fujiwara, Toru Asaka, Tadahiro Yokosawa, and Yoshio Matsui. *Applied Physics Letters*, 84(13):2403, 2004.
- [48] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, D. Obergfell, S. Roth, C. Girit, and A. Zettl. *Solid State Communications*, 143(1-2):101, 2007.
- [49] S. Horiuchi, T. Gotou, M. Fujiwara, R. Sotoaka, M. Hirata, K. Kimoto, T. Asaka, T. Yokosawa, Y. Matsui, K. Watanabe, and M. Sekita. *Japanese Journal of Applied Physics Part 2-Letters*, 42(9AB):L1073, 2003.

- [50] P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim. *Applied Physics Letters*, 91(6):063124/1, 2007.
- [51] C. Casiraghi, S. Pisana, K. S. Novoselov, A. K. Geim, and A. C. Ferrari. *Applied Physics Letters*, 91(23):233108/1–233108/3, 2007.
- [52] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari, and A. K. Sood. *Nature Nanotechnology*, 3(4):210–215, 2008.
- [53] Carlo Ferrari Andrea and John Robertson. *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences*, 362(1824):2477, 2004.
- [54] A. C. Ferrari and J. Robertson. *Physical Review B: Condensed Matter and Materials Physics*, 61(20):14095, 2000.
- [55] F. Tuinstra and Jack L. Koenig. *Journal of Chemical Physics*, 53(3):1126, 1970.
- [56] Diane S. Knight and William B. White. *Journal of Materials Research*, 4(2):385, 1989.
- [57] Dmitriy A. Dikin, Sasha Stankovich, Eric J. Zimney, Richard D. Piner, Geoffrey H. B. Dommett, Guennadi Evmenenko, SonBinh T. Nguyen, and Rodney S. Ruoff. *Nature (London, United Kingdom)*, 448(7152):457–460, 2007.
- [58] Hector A. Becerril, Jie Mao, Zunfeng Liu, Randall M. Stoltenberg, Zhenan Bao, and Yongsheng Chen. *ACS Nano*, 2(3):463, 2008.
- [59] F. M. Blighe, Y. Hernandez, W. J. Blau, and J. N. Coleman. *Advanced Materials*, 19:4443, 2007.

Appendix A

Calculation of the enthalpy of mixing

Professor Jonathan Coleman (TCD) extrapolated the theory he developed for the exfoliation of Carbon nanotubes by matching their surface tension with the surface tension of organic solvents. The calculation goes as follows:

Consider an isolated volume of solvent, V_{sol} , and an isolated mass of graphite, M_G . The graphite can be considered as arranged in flakes of thickness T_1 and area, A_1 . The number of such flakes is $N_1 = M_G / \rho_G T_1 A_1$, where ρ_G is the graphite density.

The enthalpy of mixing of solvent and graphite can be found by calculating the energy required to separate all molecules (solvent/graphene sheet) to infinity minus the energy to bring them back together in the form of a solvent-graphite dispersion, but with flakes of different thickness. This can be divided into five energetic components.

1. The energy required to separate all graphene sheets to infinity is given by the energy required to create the surfaces associated with the individual graphene sheets and so is related to the effective graphite surface energy, E_{sur}^G , which can be thought of as the inter-sheet binding energy per unit area of surface.

$$E_1^G = N_1 \left[\left(\frac{T_1 A_1}{t A} \right) 2A - 2A_1 \right] E_{sur}^G \quad (\text{A.1})$$

where the term in the round brackets represents the number of graphene sheets

per flake and the second term in the square brackets represents a correction for the outer surface of the flake. Here, t and A are the thickness and area of individual graphene sheets.

2. The energy required to remove all the solvent molecules to infinity is given by

$$E_1^{Sol} = V_{Sol} E_{Coh}^{Sol} - A_1^{Sol} E_{sur}^{Sol} \quad (A.2)$$

where E_{Coh}^{Sol} is the solvent cohesive energy, E_{sur}^{Sol} is the solvent surface energy and A_1^{Sol} is the external surface area of the solvent.

3. The energy retrieved by bringing the graphene sheets back from infinity to form N_2 flakes of thickness, T_2 , and length, L_2 , is similar to E_1^G and is given by

$$E_2^G = N_2 \left[\left(\frac{T_2 A_2}{t A} \right) 2A - 2A_2 \right] E_{sur}^G \quad (A.3)$$

Where $N_2 = M_G / \rho_G T_2 A_2$

4. We can also calculate the energy released by bringing the solvent molecules back from infinity to form a liquid but leaving voids to accommodate the reconstituted flakes:

$$E_2^{Sol} = V_{Sol} E_{Coh}^{Sol} - A_2^{Sol} E_{sur}^{Sol} - A_{Inter}^{G-Sol} E_{sur}^{Sol} \quad (A.4)$$

Here A_2^{Sol} is the new solvent (outer) surface area, while A_{Inter}^{G-Sol} is the surface area of the voids, which will accommodate the flakes.

5. Finally we must calculate the interfacial energy associated with placing the flakes in the voids:

$$E_2^{G-Sol} = 2A_{Inter}^{G-Sol} E_{Inter}^{G-Sol} = 2N_2 2A_2 E_{Inter}^{G-Sol} \quad (A.5)$$

where E_{Inter}^{G-Sol} is the solvent-graphite binding energy per unit area. The factor of two comes from the fact that we are passivating two surfaces, that of the graphene and that of the solvent. The enthalpy of mixing is given by:

$$\Delta H_{Mix} = E_1^G + E_1^{Sol} - (E_2^G + E_2^{Sol} + E_2^{G-Sol}) \quad (A.6)$$

This can be calculated using the expressions outlined above. A number of approximations can be made. One is that the solvent external surface area is the same before and after mixing with the graphite $A_2^{Sol} \approx A_1^{Sol}$, a reasonable approximation at low graphite content. In addition, we assume that the flakes that exist in the graphite powder are much larger than those in the dispersion ($T_1 \gg T_2$). Including these approximations, this works out to be

$$\Delta H_{Mix} \approx 2 \frac{M_G}{T_2 \rho_G} [E_{Sur}^G + E_{Sur}^{Sol} - 2E_{Inter}^{G-Sol}] \quad (A.7)$$

Finally, we note that the volume fraction of graphite, ϕ , is given by $\phi = M_G / \rho_g V_{Mix}$, where V_{Mix} is the volume of the mixture. Then:

$$\frac{\Delta H_{Mix}}{V_{Mix}} \approx 2 \frac{\phi}{T_2} [E_{Sur}^G + E_{Sur}^{Sol} - 2E_{Inter}^{G-Sol}] \quad (A.8)$$

In general, for materials that interact predominately by dispersive interactions we can estimate G_{Inter}^{G-Sol} from the geometric mean approximation¹:

$$E_{Inter}^{G-Sol} \approx [E_{Sur}^G E_{Sur}^{Sol}]^{1/2} \quad (A.9)$$

Substituting this in above we get

$$\frac{\Delta H_{Mix}}{V_{Mix}} \approx \frac{2}{T_{flake}} (\delta_G - \delta_{Sol})^2 \phi \quad (A.10)$$

where $\delta_i = \sqrt{E_{Sur}^i}$ and where we write T_2 as T_{flake} for clarity.

The solvent surface energy, E_{Sur}^{Sol} , is related to the surface tension, γ^i , by²:

$$\gamma = E_{Sur}^{Sol} - T S_{Sur}^{Sol} \quad (A.11)$$

¹Hildebrand J. H. *et.al.* Regular and related solutions: the solubility of gases, liquids and solids, Van Nostrand Reinhold Company (New York) 1970. Girifalco, L. A. and Good, R. J. Journal of Physical Chemistry, 61, 904 (1957)

²Lyklema, J. Colloids and Surfaces, A: Physicochemical and Engineering Aspects. 156(1-3), 413 (1999)

where S_{Sur}^{Sol} is the solvent surface entropy. The surface entropy is a generic liquid property that tends to have values in the range 0.07-0.14 mJ/m²K. Liquids of a given class tend to have very similar values of S_{Sur}^{Sol} , with DMF and toluene for example shown to have values close to $S_{Sur}^{Sol} = 0.11 \text{ mJ/m}^2 \text{ K}$ ³. Thus, we take the universal value to be $\sim 0.1 \text{ mJ/m}^2 \text{ K}$ and use this to transform between γ and S_{Sur}^{Sol} in figure (surface energy).

³Tsierkezos, Nikos G. and Filippou, Alexander C., Journal of Chemical Thermodynamics, 38(8), 952 (2006)

Appendix A

Published papers

- **Broadband Nonlinear Optical Response of Graphene Dispersions.** Jun Wang, Yenny Hernandez, Mustafa Lotya, Jonathan N. Coleman, Werner J. Blau. *Advanced Materials* 2009, 21, 1–6.
- **Carbon Nanotube - Polymer Nanocomposites for Field Emission Cathodes.** Thomas Connolly, Richard C. Smith, Yenny Hernandez, Yurii Gun'ko, Jonathan N. Coleman and J. David Carey. *Small* 2009, 5(7), 826–831.
- **Preparation of buckypaper-copper composites and investigation of their conductivity and mechanical properties.** Michele T. Byrne, Yenny R Hernandez, Tom Connaty, Jonathan N. Coleman, Yurii Gun'ko. *Chem Phys Chem* 2009, 10(5), 774–777.
- **Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions.** Mustafa Lotya, Yenny Hernandez, Paul J King, Ronan J Smith, Valeria Nicolosi, Lisa S Karlsson, Fiona M Blighe, Sukanta De, Zhiming Wang, IT McGovern, Georg S Duesberg and Jonathan N Coleman. *JACS* 2009, 131(10), 3611–3620.
- **High-yield production of graphene by liquid-phase exfoliation of graphite.** Hernandez, Yenny; Nicolosi, Valeria; Lotya, Mustafa; Blighe, Fiona M.; Sun, Zhenyu; De, Sukanta; McGovern, I. T.; Holland, Brendan; Byrne, Michele; Gun'Ko, Yurii K.; Boland, John J.; Niraj, Peter; Duesberg, Georg;

- Krishnamurthy, Satheesh; Goodhue, Robbie; Hutchison, John; Scardaci, Vittorio; Ferrari, Andrea C.; Coleman, Jonathan N. *Nature Nanotechnology* 2008, 3(9), 563-568.
- **Observation of percolation-like scaling - far from the percolation threshold - in high volume fraction, high conductivity polymer-nanotube composite films.** Blighe, Fiona M.; Hernandez, Yenny R.; Blau, Werner J.; Coleman, Jonathan N. *Advanced Materials* 2007, 19(24), 4443-4447.
 - **Comparison of carbon nanotubes and nanodisks as percolative fillers in electrically conductive composites.** Hernandez, Yenny R.; Gryson, Alex; Blighe, Fiona M.; Cadek, Martin; Nicolosi, Valeria; Blau, Werner J.; Gun'ko, Yurii K.; Coleman, Jonathan N. *Scripta Materialia*, 2008, 58(1), 69-72.
 - **Observation of extremely low percolation threshold in $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ nanowire/polymer composites.** Murphy, Robert; Nicolosi, Valeria; Hernandez, Yenny; McCarthy, Denis; Rickard, David; Vrbancic, Daniel; Mrzel, Ales; Mihailovic, Dragan; Blau, Werner J.; Coleman, Jonathan N. *Scripta Materialia* 2006, 54(3), 417-420.