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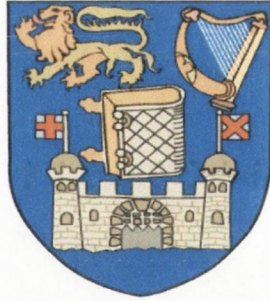
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Mechanical Reinforcement Effects of Carbon Nanotube Polymer Composites

By

Martin Cadek

A thesis submitted for the degree of

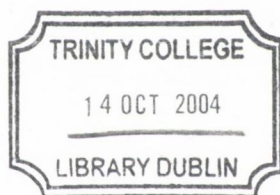
Doctor of Philosophy

at the

University of Dublin



Department of Physics
Trinity College Dublin
December 2003



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This work is dedicated to my grandmother

Martha Cadek, Geb. Ohnesorge

(^{}1st July 1913 – [†]17th December 1995)*

*If I saw farther than others, than only because
I stood on the shoulder of giants
(Sir Isaac Newton)*

*Das schönste Glück des denkenden Menschen ist, das Erforschliche erforscht zu haben
und das Unerforschliche zu verehren
(Johann Wolfgang von Goethe)*

*Naděje není přesvědčení o něčem s dobrým výsledkem,
ale jistota o významu, lhostejná na výsledku.
(Václav Havel)*

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Abstract

The effect of varying current density and pressure during arc-generation on the yield and purity of multi walled carbon nanotube containing carbon soot has been studied in this work. Various soots were produced and characterised qualitatively using transmission electron microscopy and quantitatively using electron paramagnetic resonance and thermal gravimetric analysis. It was found that both yield and purity increase as current density and pressure are increased.

Multi walled carbon nanotubes were investigated as potential mechanical reinforcement agents in two hosts, polyvinyl alcohol (PVA) and poly(9-vinyl carbazole) (PVK). It was found that, by adding various concentrations of nanotubes, both Young's modulus and hardness increased by factors of 1.8 and 1.6 at 1 wt% in PVA and 2.8 and 2.0 at 8 wt% in PVK, in reasonable agreement with the Halpin–Tsai theory. Mechanical investigations here were performed by nano-indentation. In addition, the presence of the nanotubes was found to nucleate crystallisation of the PVA. This crystal growth is thought to enhance matrix-nanotube stress transfer. Moreover, microscopy studies suggest extremely strong interfacial bonding in the PVA-based composite. This is manifested by the fracture of the polymer rather than the polymer-nanotube interface.

As a next step tensile tests were carried out on free-standing composite films of polyvinyl alcohol and six different types of carbon nanotubes. Significant increases in Young's modulus by up to a factor of two were observed in all cases. However, theories such as Krenchel's rule-of-mixtures or the Halpin-Tsai-theory could not

explain the relative differences between composites made from different tube types. However, it is possible to show that the reinforcement scales linearly with the total nanotube surface area in the films. In addition, in all cases crystalline coatings around the nanotubes were detected by calorimetry suggesting similar polymer-nanotube interfaces. This supports the fact that the reinforcement is critically dependent on the polymer-nanotube interfacial interaction. Theoretical models to calculate the ultimate tensile strength and the crystalline polymer coating thickness around carbon nanotubes have been developed.

In order to show the possibility of industrial applications for carbon nanotube reinforced engineering polymer composites a range of multi walled carbon nanotubes and carbon nanofibres were mixed with a polyamide 12 matrix using a twin-screw micro-extruder. The resulting blends were spun to produce a series of reinforced polymer fibres. Dispersion, mechanical and thermal properties were studied using electron microscopy, tensile testing and differential scanning calorimetry.

Chapter 1

Introduction

1.1 Historical Background on Advanced Composites

Compared to the historical development over the last couple of hundred years, the past century witnessed a dramatic development in material science, addressing mainly the strength to weight ratio of materials. Over the past five decades the improvement of polymeric composite materials has become more and more important. Due to the progress in technology the need for lighter and stronger materials is more and more crucial. This is due to the high requirements of industry regarding quality, safety and weight in order to cut down production costs and energy consumption of automobiles and aeroplanes etc.

In the mid 1950's the U.S. Air Force identified the promise for early applications of a new class of materials – advanced composites – and established its feasibility by the fabrication of raw fibres with exceptional high strength and modulus to weight ratios. The practical fabrication of graphite fibres was essential for the development of advanced composite materials. The National Aeronautics and Space Administration (NASA) and the U.S. Air Force supported many research and technology programs, which led to the first composite applications for aircraft and space vehicles in the early 1970's. Thus it took only 2 decades from the laboratory research to an application. This can be compared to the first introduction of aluminium into aircraft which took over 30 years and this is still in development¹.

However, the largest market for the use of advanced composite materials is believed to be the automotive industry in order to create lighter weight automobiles to reduce fuel consumption. In the case of aeronautic and space applications a compromise in combining aluminium and advanced composite materials was pressed forward.

1.2 Discovery of Carbon Nanotubes

Research on novel reinforcement agents has been performed since the early 1970's – 1980's when for the first time tubular fibrils with dimensions in the nanometer range were reported by Obermerlin and Endo *et al.*²⁻⁵. They were found as a by-product in the synthesis of vapour grown carbon fibres. These were produced by the decomposition of hydrocarbons at high temperatures in the presence of transition metal catalyst particles of <10nm diameter. However, they were not fully understood and no detailed systematic study was reported in these early years of nanotube research⁶.

Another pioneering breakthrough leading to the systematic study of carbon filaments of very small diameters was the discovery of a third allotrope of carbon – the C₆₀ molecule or Buckminster Fullerene - by Kroto, Curl and Smalley⁷. Before 1985 carbon was thought to exist only in 2 forms: the 3-dimensional ordered crystalline graphite (diamond, sp³ hybridised form of carbon) and the 2-dimensional ordered graphite (sp² hybridised form of carbon). Fullerenes (C₆₀) were the first member of a new family of carbon structures, in the form of a spherical cage. C₆₀ consists mainly of hexagons with the incorporation of twelve pentagons giving sufficient positive curvature for it to close into a sphere.

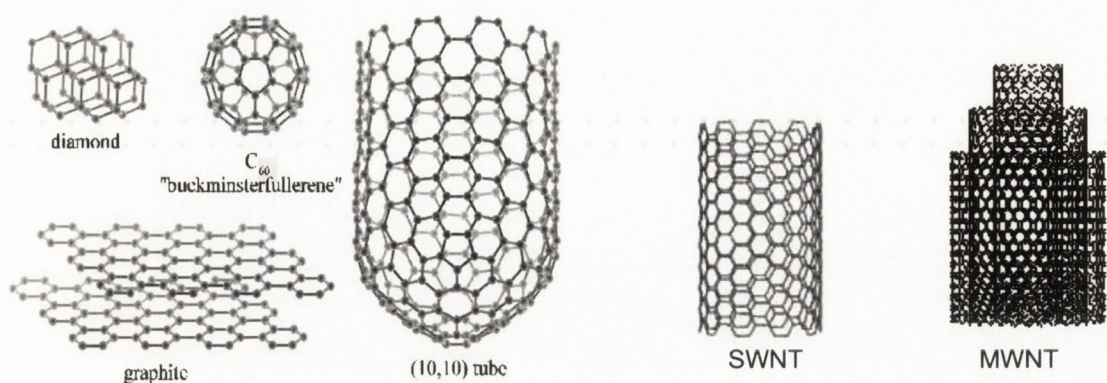


Figure 1-1: Allotropes of carbon; diamond, graphite, fullerene, and nanotubes (single and multi walled)

The discovery of C₆₀ had an impact which extended far beyond the confines of academic chemical physics and marked the beginning of a new era in carbon science^{8,9}. Kroto, Curl and Smalley were awarded with the Nobel Prize in Chemistry in 1996 for the discovery of the Fullerene molecule. Fullerenes are also known as 'Buckminster Fullerenes' or just 'Buckyballs'. The name was given to the new molecules in honour of the famous architect R. Buckminster Fuller who designed and built geodesic domes. This architectural style is very similar to the structure of these molecules and is based of the regular truncated icosahedron which was already known to Leonardo da Vinci in about the year 1500¹⁰.

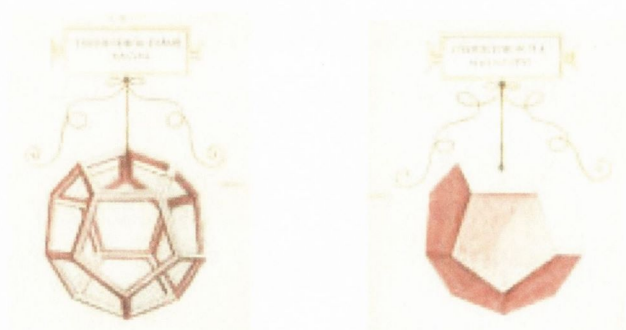


Figure 1-2: A regular truncated icosahedron from an Italian translation of the "Libellus" published in 1509 by the mathematician Luca Pacioli in his book "De Divina Proportione." The design is thought to be by Leonardo da Vinci¹⁰.

Krättschmer and Huffman¹¹ then tried to improve the production method of the newly discovered Fullerenes in order to upscale the yields. They found a novel method to produce these molecules by a simple arc method where graphite is vaporized in an atmosphere of helium, and the collected soot on the vessel walls contains C₆₀ and C₇₀ (an additional member of the Fullerene family, consisting of 70 carbon atoms) in macroscopic amounts. This method was published in 1990 in *Nature* and showed that this simple way of producing bulk amounts of Fullerenes was accessible to any laboratory.

Therefore, it stimulated a deluge of research which led to the intensive investigation of the chamber wall soot by Iijima (NEC Laboratory in Tsukuba, Japan) and finally to the cylindrical hard deposit which is formed on the graphite cathode after arc-evaporation and previously discarded as disposable material. The deposit consists of a hard shell and soft soot with a whole range of novel graphitic structures and mostly striking of all the long tubules with a perfect linear structure. This discovery of multi-walled carbon nanotubes (MWNT) was in 1991. In 1993 Iijima also discovered that carbon nanotubes can consist of only one shell¹² – single-walled carbon nanotubes (SWNT) followed by Bethune *et al.*¹³ (IBM Almaden Laboratory, U.S.A.).

Since these discoveries carbon nanotubes (CNT) are seen as the future material for advanced composite materials. Many other applications have been predicted such as super strong fibres¹⁴, biomedical devices, light emitting diodes with low energy consumption^{15,16}, actuators for artificial muscles¹⁷, extremely small transistors¹⁸, flat field emission displays¹⁹, superconductors²⁰ and super capacitors¹⁴, just to mention a few. This is due to their extraordinary mechanical, electrical and thermal properties²¹. In the field of polymer composite reinforcement it is believed that they will replace

materials such as steel or aluminium because of their extraordinary high modulus and strength. They are known to have a density normalised modulus which is 19 times that of steel and a density normalised strength a factor of 56 times higher²²⁻²⁴. The thermal conductivity²⁵ is known to be twice as high as that of the best known thermal conductor – diamond^{21,22,25}. CNT behave at low temperature ($\sim 0.55\text{K}$) as superconductors^{20,22} and have been found to act as super capacitors¹⁴.

Unfortunately, there were many problems to be solved during the past decade in order to transfer the outstanding possibilities of CNT into applications. The quantity of CNT which could be produced had to be up scaled. Nowadays it is possible to produce kilograms of CNT but for commercial applications there is a need to produce then in the tonnes range with constant quality of the product. Furthermore, there was a purity problem of the as produced CNT soot. Purification methods had to be found^{26,27} which do not destroy the structure of nanotubes and therefore their favourable properties. Another extremely important issue for the mechanical reinforcement and enhanced conductivity of polymer composites was the dispersion of CNT in a polymer matrix. CNT tend to form agglomerates due to their size. The reasons CNT tend to entangle are because of their lengths of several microns and due to their small diameters and hence low high flexibility.

The most important issue to be solved for mechanical applications was the interfacial bonding between a CNT and a polymer matrix in order to ensure that an applied load is transferred to the strong CNT rather to the relative weak polymer. This can only be ensured if the wetting behaviour between the polymer matrix and the CNT is sufficient and if a strong interaction takes place such as van de Waals bonding or covalent bonding between the carbon nanotube surface and the polymer matrix. Due to the perfectly graphitic structure of some CNT, and therefore their complete inertness, it is relatively complicated to achieve covalent bonding.

In this work the aforementioned problems will be addressed. The motivation of this work was to find solutions to increase the quantity of CNT and their purity as well as their dispersion and interaction in a polymer matrix in order to create a strong polymer composite as a step towards applications with outstanding mechanical, electrical and thermal properties. Furthermore, the reinforcement mechanism has to be understood and explained.

1.3 Thesis Outline

The major materials studied in this thesis are a range of polymers, such as thermoplast and thermoset materials and all of the available different types of carbon nanotubes in terms of production methods. In Chapter 2 the properties of all of the materials used will be reviewed. This includes their mechanical and electrical properties.

Chapter 3 will explain several preparation method for the materials used in this study. This will be divided into several parts such as the production of CNT and several production methods for the preparation of different forms of polymer composites these include thin polymer films, free standing polymer films, melt spun polymer fibres and bulk polymer material all reinforced by CNT. Furthermore, the non-destructive carbon nanotube purification method used in this study will be explained.

Shown in Chapter 4 is the optimisation process for the arc discharge production method of CNT. Quantity and quality of carbon nanotube yield will be investigated

using electron paramagnetic resonance, thermal gravimetric analysis and transmission electron microscopy.

In Chapter 5 the mechanical and thermal properties as well as the morphology of CNT thin film polymer composites will be discussed. Two different polymer hosts were used and placed on glass substrates. Nano-indentation was performed to investigate the mechanical properties and differential scanning calorimetry measurements were performed in order to investigate the thermal properties and the morphology of the materials. Transmission electron microscopy micrographs are shown to understand the bonding behaviour between polymer and CNT.

Further work in the second section of this Chapter will show composite solutions placed on polished Teflon dishes instead of glass substrates in order to obtain free standing composite films. Mechanical properties were measured by tensile testing and nano-indentation. Furthermore, dynamic mechanical testing was performed as well as differential scanning calorimetry to investigate thermal properties and morphology.

The third section of this Chapter describes a way of improving the interfacial bonding of CNT and several polymer matrices, covalent functionalisation of CNT with polymer chains has been performed. Mechanical measurements were performed by tensile testing.

In Chapter 6 a production method of CNT composite fibres is shown using double screw extrusion. A range of different CNT and carbon nanofibres were dispersed in different thermoplastic materials followed by fibre drawing. Nano-indentation, tensile testing, differential scanning calorimetry and x-ray diffraction measurements were

performed. Scanning electron microscopy micrographs are shown to investigate the dispersion and the orientation of CNT in the composite fibres.

Finally, Chapter 7 concludes all of the work completed in this thesis by reviewing all of the results achieved and presented here. Furthermore, it will describe the implications of this research and the areas of future work are considered.

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Chapter 2

Materials & Backgrounds

2.1 Introduction

This chapter will give an overview of the production methods of various carbon nanotubes and their physical properties. A non-destructive purification method is explained which was applied for all nanotube samples. Moreover, a description of all polymer matrices used in this work in addition to the used nanotube material will be given. Furthermore, there will be a detailed explanation about the material properties in this work as well as the known theoretical predictions and rules to reinforce polymer composites with carbon fibres.

2.2 Experimental Background

Carbon Nanotubes (CNT) can be synthesised in a range of different ways. In this section the three most common production processes are introduced. Arc-discharge and laser ablation methods involve the condensation of carbon atoms generated from the evaporation of highly pure solid graphite sources. The temperatures involved in these methods are close to the melting temperature of graphite, approximately 3000-4000°C. When the evaporated carbon atoms condense, carbon nanotubes are formed under certain circumstances such as in a helium atmosphere at constant pressure. Processing temperatures for the third method - chemical

vapour decomposition (CVD) of carbon containing gases - are much lower at around 550-750°C. In addition it will be shown how properties such as length, structure and diameters for the different production methods change as well as the advantages and disadvantages regarding composite reinforcement. Moreover, a non-destructive purification method will be introduced as previously reported CNT purification methods such as heat or acid treatments¹⁻⁴ are common to use but they are destructive and therefore they harm the intrinsic mechanical and electrical properties of CNT. Other non-destructive purification methods such as chromatography⁵ and microfiltration⁶ show scale up problems.

2.2.1 Nanotube Growth Methods

Arc-Discharge

The first known method for the production of both multi walled carbon nanotubes (MWNT) and single walled carbon nanotubes (SWNT) was developed by Krätschmer and Huffman⁷ in 1990 and was formerly used for the production of Fullerenes. This method was subsequently optimised by Ebbesen and Ajayan⁸ for the production of nanotubes. More refined optimisation in 2001 is explained in Chapter 4 of this work and elsewhere⁹⁻¹¹. The Krätschmer generator (shown in Figure 2-1) usually consists of a cylindrical steel chamber where two opposing graphite rods are ignited in a helium atmosphere by currents passing through the carbon anode and cathode.

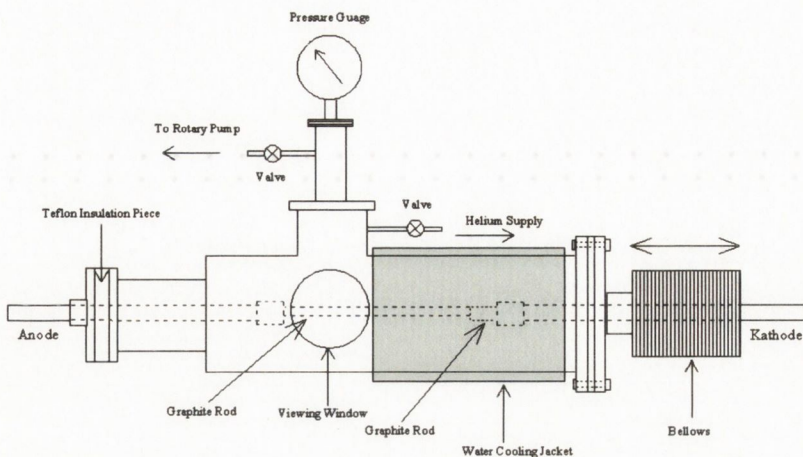


Figure 2-1: Schematic of the arc-discharge generator

Arc- discharge has been found to be an excellent method for producing both high quality MWNT and SWNT. Iijima *et al.*¹² and Bethune *et al.*¹³ reported in 1993 that this method using a cathode containing metal catalysts (such as cobalt, iron or nickel) mixed with graphite powder results in chamber wall soot containing SWNT.

MWNT can be produced using this method by controlling the helium pressure and the arcing current. Sublimed graphite from the anode condenses onto the cathode in the form of a deposit with hard outer shells and a soft core containing MWNT. Arc-discharge MNWT consist of straight graphitic walls running parallel to the tube axis indicating an excellent crystallinity with only a few defects. They have lengths in the order of tens of microns and diameters ranging from 5-50 nm. The by products of the arc-discharge process are multi-layered graphitic particles polyhedral in shape, turbo stratic graphite and carbon onions.

Laser ablation

Another method to grow high quality SWNT is the laser ablation method. It was first demonstrated in 1996 by Smalley's group¹⁴ and has prompted a lot of interest due to the scale-up possibilities of this discontinuous process. Thess *et al.*¹⁴ showed that the synthesis could be carried out in a horizontal flow tube under a flow of inert gas at a controlled pressure. In this set-up the flow tube is heated to $\sim 1200^{\circ}\text{C}$ by a furnace. Laser pulses enter the tube and strike a target consisting of a mixture of graphite and 0.5 atomic percent of a metal catalyst such as Co or Ni. SWNT condense from the laser vaporisation and are deposited on a collector outside the furnace zone. During laser ablation, a flow of inert gas is passed through the growth chamber to carry the grown nanotubes downstream to be collected.

Chemical Vapour Decomposition (CVD)

An alternative to arc discharge and laser ablation is the catalytic growth of nanotubes. This method is based on the decomposition of a hydrocarbon gas over a transition metal to grow nanotubes in a chemical vapour deposition (CVD) reactor such as the one shown in Figure 2-2.

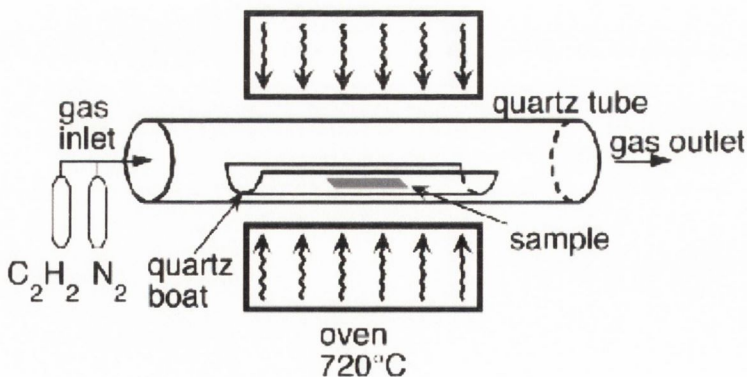


Figure 2-2: Schematic diagram of a CVD deposition oven

Carbon filaments and fibres have been produced by thermal decomposition of hydrocarbons since the 1960's¹⁵⁻¹⁸. Usually, a catalyst is necessary to promote the growth. A similar approach was used for the first time in 1993 by Yacaman *et al.* to grow MWNT from the decomposition of acetylene over iron particles.

For the production of MWNT acetylene is usually used as the source of carbon atoms at temperatures typically between 600 – 800°C. To grow SWNT the temperature has to be significantly higher (900 – 1200°C) due to the fact that SWNT have a higher energy of formation. In this case carbon monoxide or methane must be used because of their increased stability at higher temperatures as compared to acetylene.

2.3 Non-Destructive Purification Method of MWNT

While previous researchers have carried out systematic studies on the effect of production conditions on nanotube yield and purity, quantitative characterisation tools have not been available¹⁹⁻²². Until recently only the qualitative techniques of transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Raman spectroscopy have been used to study nanotube production. However, Coleman *et al.*²³ have shown that electron paramagnetic resonance (EPR) can be used to measure nanotube content in non-magnetic systems, such as arc discharge produced multi-walled nanotube containing soot.

The purity of arc discharge nanotube containing soot was measured using the method discussed in reference²⁴. Multi walled nanotube containing soot was added to a solution of poly(*m*-phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene)

(PmPV)²⁵ (Figure 2-3) in toluene and sonicated for several hours. PmPV was synthesised in our laboratories using a Horner polycondensation reaction²⁶. Shown in Figure 2-4 a) is a schematic of this purification process. Figure 2-4 b) shows the simulation of a van der Waals interaction between a single walled carbon nanotube and a single PmPV molecule^{27,28}. Due to the long side-chains of PmPV the polymer/nanotube formation stays suspended in solution with toluene. This solution is allowed to settle for 48 hours to let the graphitic impurities form a sediment on the bottom of the sample bottle. This sediment is separated from the nanotube containing solution by careful decantation giving a purified nanotube solution. Both the sediment and the solute are then dried and weighed for analysis. Nanotube content in both fractions and hence purity can then be measured by electron paramagnetic resonance (EPR) and thermal gravimetric analysis (TGA).

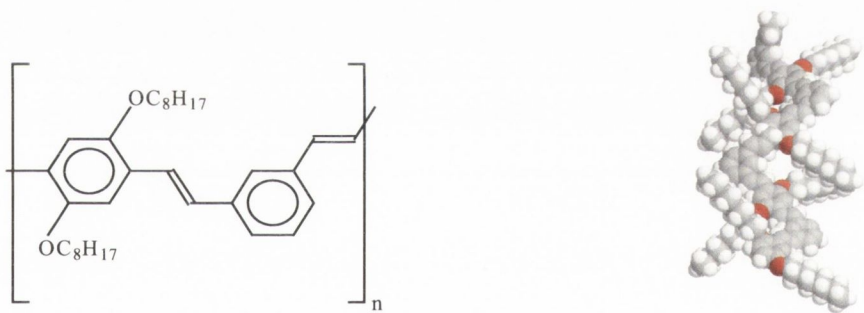


Figure 2-3: a) Molecular structure of poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV) b) Geometry optimised structure of PmPV²⁸.

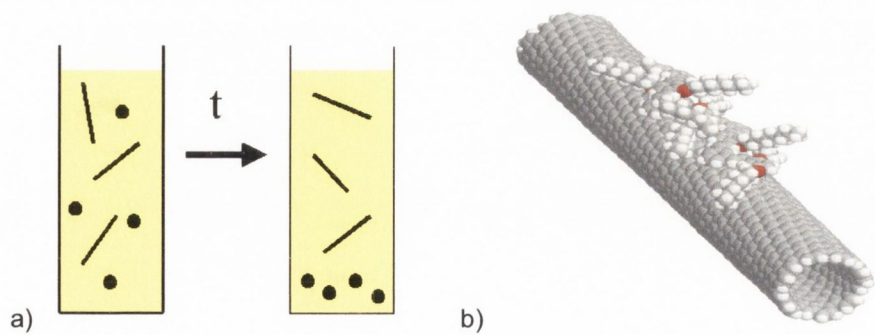


Figure 2-4: a) Schematic of purification process b) Simulation of interaction between poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)(PmPV) and a carbon nanotube²⁸.

Other materials such as polyvinyl alcohol (PVA) and poly(9-vinyl carbazole) (PVK) can be used for this purification method as well. Unfortunately, not with the same success as PmPV, since these materials do not hold as many CNT in solution. The mentioned materials will be described in the next section in more detail.

2.4 Physical Structure of Carbon Nanotubes

A geometrically perfect CNT can be considered as a 2 dimensional hexagonal lattice of carbon scrolled up to form a concentric cylinder with two caps (hemispheres of fullerenes) on each end of the cylinder. They can consist of only one shell (single walled carbon nanotubes - SWNT) or multiple shells (multi walled carbon nanotubes – MWNT). The separation spacing of the walls in MWNT is constantly 0.34 nm, which is very close to the basal plane spacing in graphite (0.335 nm)¹². MWNT usually have diameters between 5-50 nm and lengths of 1-50 μm depending on the synthesis method. SWNT have diameters of around 1nm and lengths in the same range as MWNT. The smallest diameter for a SWNT is known to be 0.4 nm.

The two-dimensional hexagonal lattices of carbon can be rolled up in several different ways which effects the electrical properties of a CNT. If the graphite sheet is rolled up around its x-axis (shown in Figure 2-5) the CNT becomes a so called “zig-zag” tube. If it is scrolled around its y-axis it is called an “arm-chair” CNT. Every other CNT in between these extremes is known as a chiral CNT.

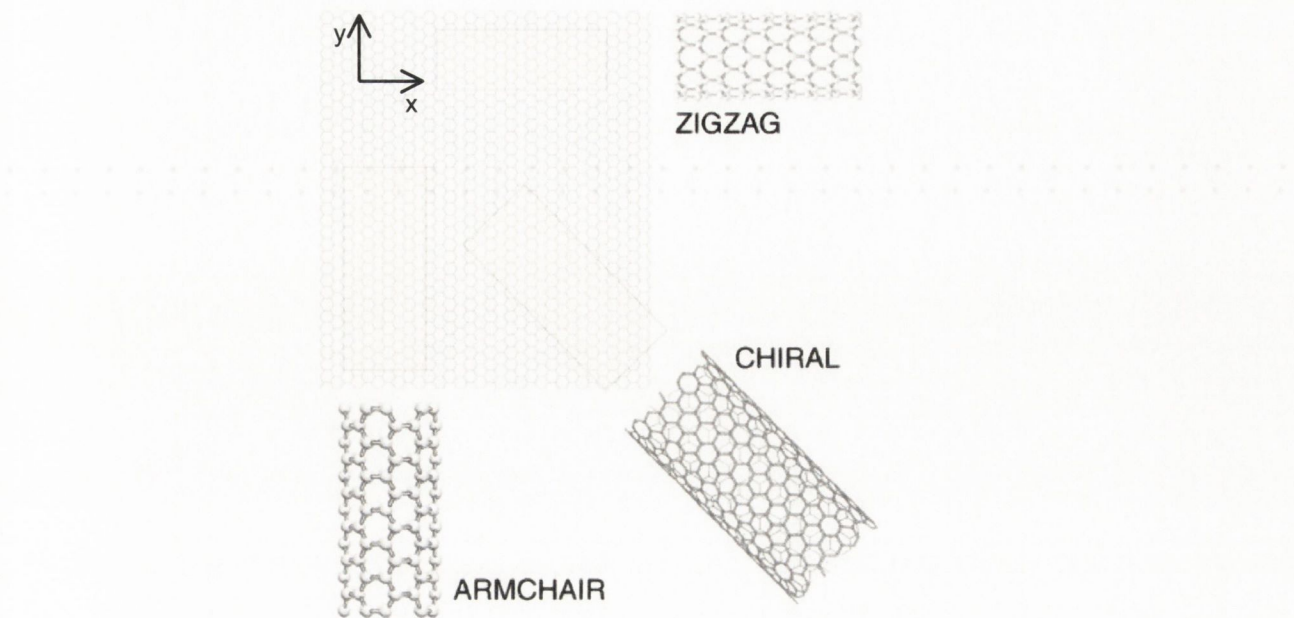


Figure 2-5: Different possibilities of scrolling a 2 dimensional hexagonal lattice of carbon into a carbon nanotube

Shown in Figure 2-6a and b are the two most symmetric possible structures for nanotubes. Figure 2-6a represents an ‘armchair’ and Figure 2-6b a ‘zig-zag’ CNT. In practice it is believed that most CNT do not have these highly symmetric forms but have structures in between in which the hexagons are arranged helically around the tube axis, as shown in Figure 2-6c.

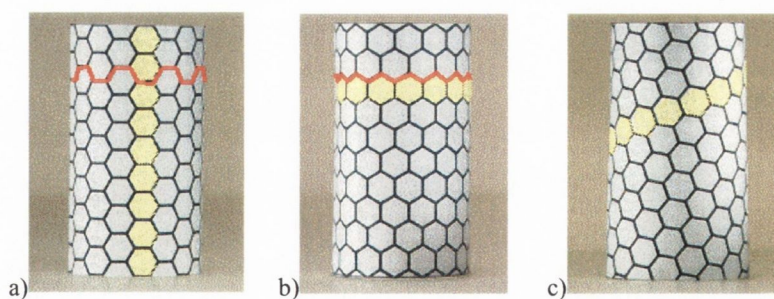


Figure 2-6: Model of an a) ‘armchair’ b) ‘zig-zag’ and c) chiral carbon nanotube

These structures are in general known as chiral and can be formed with a screw axis along the long axis of the tubule. These general CNT can be described mathematically of either 2 integers **n** and **m** or in terms of the diameter of the tube **d**

and the chiral angle θ between 0° - 30° which are shown in Figure 2-7 where the chiral vector is $\mathbf{c}$

$$\mathbf{c} = n \mathbf{a}_1 + m \mathbf{a}_2$$

Equation 2-1

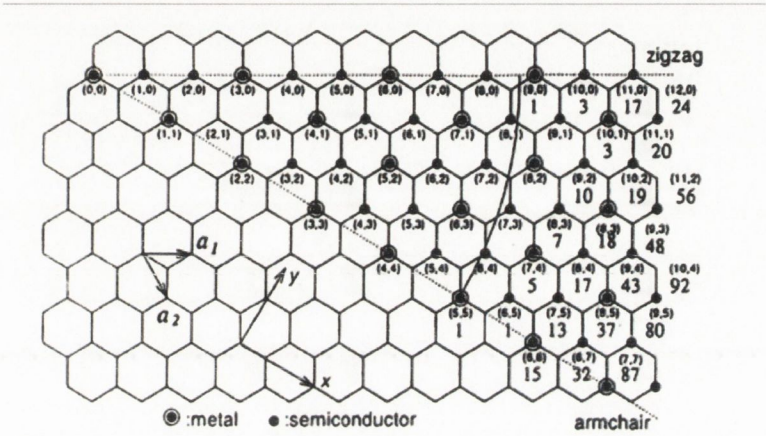


Figure 2-7 Possible vectors specified by the pairs of integers (n, m) for general carbon nanotubes, including armchair, zig-zag and chiral nanotubes.

The electronic properties of a CNT are known to differ depending on their chirality vector. It can be seen in Figure 2-8 that an ‘armchair’ CNT shows metallic behaviour and is therefore electrically conductive whereas ‘zig-zag’ and chiral CNT show semi-metallic behaviour where the bandgap varies inversely with diameter. Ropes of single walled nanotubes have been measured having a resistivity of $10^{-4} \, \Omega \cdot \text{cm}$ at $300 \, \text{K}$ ¹⁴, making them the fibres with the highest known conductivity. Individual tubes have been observed to conduct electrons ballistically, without scattering, with coherence lengths of several microns²⁹.

In addition, they can carry a current density of $>10^9 \, \text{A/cm}^2$ which is known to be the highest in any known material³⁰.

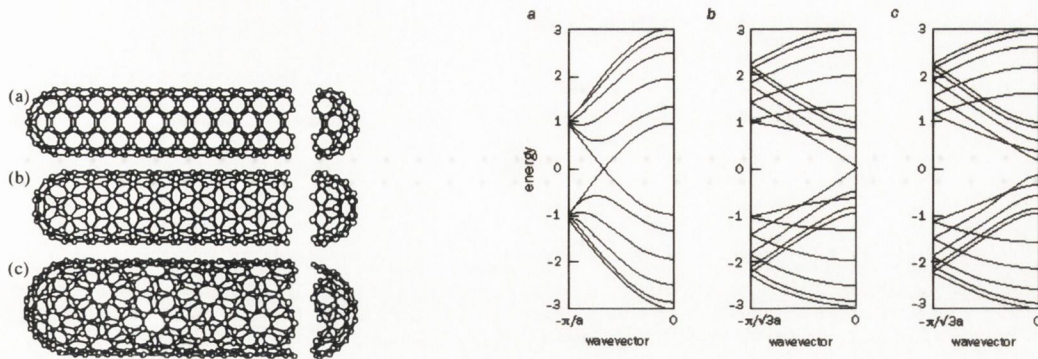


Figure 2-8: Band structure calculations for single walled carbon nanotubes; a) shows a metallic nanotube with a finite density of states at the Fermi energy b) shows a semi conducting nanotube with zero bandgap whereas c) shows semi-conducting behaviour with non-zero bandgap

In conventional materials the Young's modulus varies from a few GPa to up to 600 GPa for the hardest materials, such as diamond and SiC. Since nanotubes were discovered by Iijima³¹ it was speculated that they could have values of Young's modulus far over 600 GPa, given that the in-plane C-C bond in graphite is one of the strongest chemical bonds known in nature (the C_{11} elastic constant in graphite is 1.060 TPa³²). The first realistic evidence in this respect was provided by Treacy *et al.*³³. By monitoring the amplitude of the thermal oscillations of the free tips of anchored MWNT at a range of temperatures, it was possible to obtain an estimation of the Young's modulus of MWNT. The mean value of the Young's modulus obtained was 1.8 TPa. At this point it has to be mentioned that the statistical errors of their measurements were large where the data for individual nanotubes ranged from values of 0.4 TPa to up to 4.15 TPa.

Although this value reported by Treacy *et al.*³³ is now generally accepted to be slightly too large, it is nevertheless indicative of the extraordinary mechanical properties of carbon nanotubes. Other methods were reported by Salvatet and Forró *et al.*³⁴⁻³⁶ where Atomic Force Microscopy (AFM) was used in order to bend different types of carbon nanotubes with the AFM tip on small diameter membranes. Values in

the range from 0.1 TPa for catalytical grown MWNT and 1TPa for arc-discharge grown MWNT were determined. Several simulation studies confirmed further values for carbon nanotubes in the TPa region.

2.4.1 Arc-Discharge Grown Multi and Single Walled Carbon Nanotubes

Arc-Discharge grown multi and single walled carbon nanotubes (AMWNT) are known to be the nanotubes with the best graphitic structure. They are straight and stiff (due to no defects in the graphite structure). Diameters for AMWNT are typically $24\text{ nm} \pm 10\text{ nm}$. Length distribution for arc-discharge carbon nanotubes is $1\text{ }\mu\text{m} \pm 0.5\text{ }\mu\text{m}$. This method involves the production of impurities such as turbo stratic graphite, amorphous carbon and carbon onions. Purity (amount of AMWNT) of the as produced soot varies between 10-50%. Optimised yields for the production of arc-discharge produced nanotube material is several grammes per day with a purity of approximately 50% after the optimisation of this process^{9,11}. Further details regarding purity and quality of this product are shown in Chapter 4 of this work.

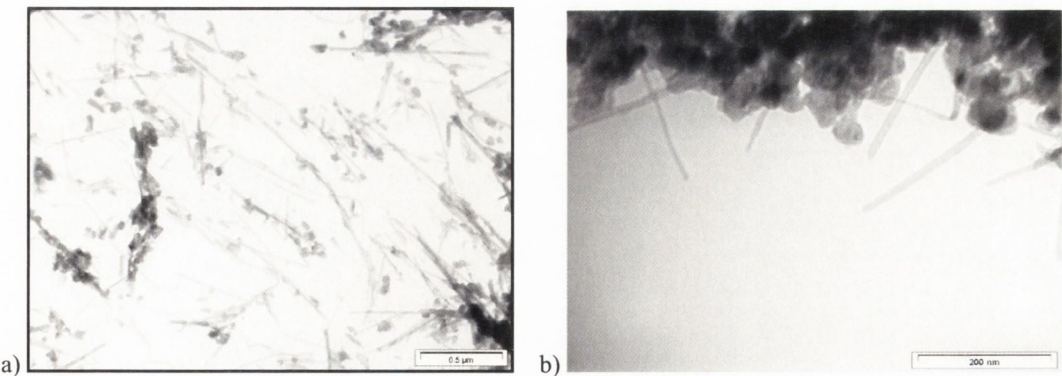


Figure 2-9: Transmission electron microscopy micrographs of a) arc-discharge produced multi walled carbon nanotubes and b) arc-discharge produced single walled carbon nanotubes

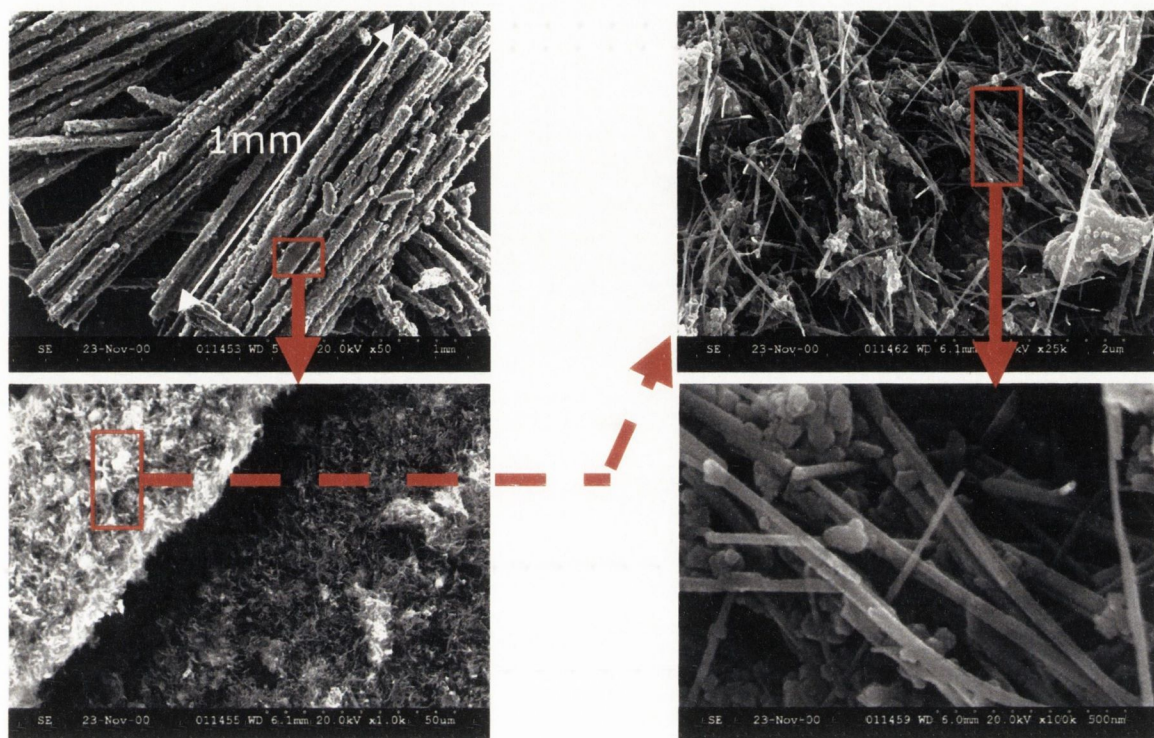


Figure 2-10: Scanning electron microscopy micrograph of multi walled carbon nanotubes produced by the arc-discharge method. A zoom series from macroscopic resolution to the nano scale is shown containing as-produced soot, fibrous material of soot, nanotubes and their impurities.

In the case of arc grown single walled carbon nanotubes (ASWNT), catalytical particles are included in the soot. In addition to the other difference that ASWNT are found on the chamber walls rather than in the catalytic deposit. The soot is non fibrous but very volumetric with an extremely low weight per volume and therefore is hard to process.

2.4.2 Catalytic Vapour Decomposition Grown Multi and Double Walled Nanotubes

Additionally used carbon nanotubes in this work were produced by catalytic vapour decomposition of acetylene or ethylene. MWNT used in this study were synthesised by decomposition of ethylene at 700°C on cobalt/aluminium oxide $\text{Co/Al}_2\text{O}_3$ and purified by refluxing in 40% sodium hydroxide (NaOH) for 24 h. Afterwards they were placed in concentrated Hydrochloric acid (HCl) for 15 hours followed by annealing under vacuum at 500°C for 5 hours. This method is highly destructive and therefore defects are present.

These produced nanotubes exist with different shapes and diameters. The following used MWNT were produced by the University of Namur/Belgium and are named in this work from now on NMWNT. They are also commercially available at Nanocyl S.A./Belgium. Shown in Figure 2-11a are classical catalytic grown MWNT with lengths of up to 50 μm and diameters in the range $15 \pm 5 \text{ nm}$. The nanotubes shown were purified by a destructive oxidation method described elsewhere^{2,37} and were found to contain more than 95% of NMWNT after the purification process. They are highly entangled and therefore very hard to disperse in polymer composites. Their curvature indicates high amounts of structural defects such as dangling bonds as well a pentagons and heptagons along with the main hexagonal structure.

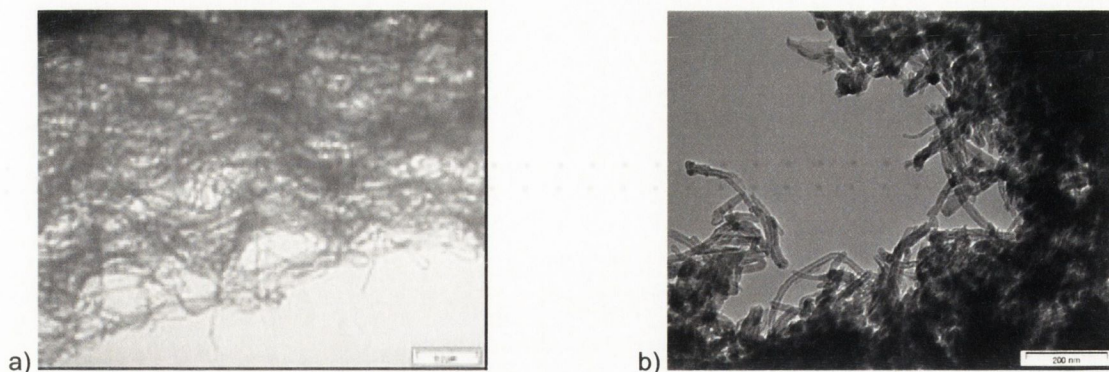


Figure 2-11: a) Highly entangled and purified catalytic grown multi walled carbon nanotubes b) hydroxy-functionalised catalytic grown multi walled carbon nanotubes using ball milling under hydrogen atmosphere.

Figure 2-11b shows NMWNT produced by ball milling of the as produced and purified product shown in Figure 2-11a. Ball milling under hydrogen results in much shorter NMWNT with functional hydroxyl groups (OHMWNT) at the defects which are usually at the breaking surface induced by ball milling³⁷.

In addition “thin MWNT” produced in a similar way to the double walled nanotubes (DWNT) were used in this study. Diameter sizes can be varied by changing the catalyst particle size and the production conditions such as temperature and pressure. Furthermore, diameters of nanotubes can be changed by the use of different catalysts. Thin-MWNT and DWNT were purchased from Nanocyl S.A, Namur/Belgium and are shown in Figure 2-12.

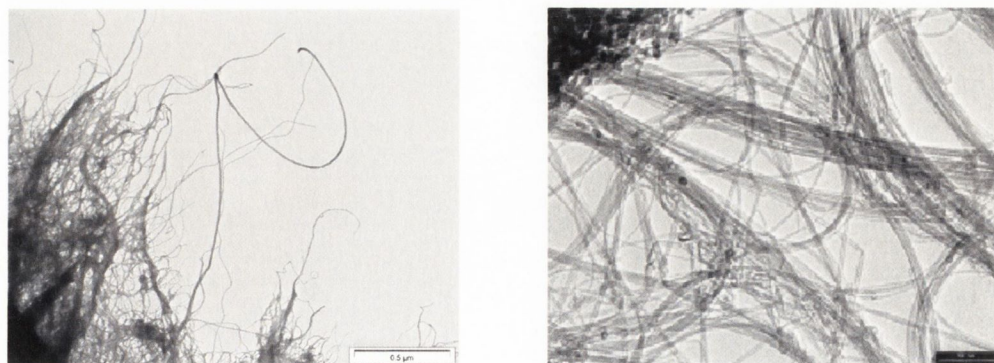


Figure 2-12: Transmission electron microscopy micrographs of a) “thin” multi walled carbon nanotubes and b) double walled carbon nanotubes

DWNT consist of only 2 graphite cylinders and therefore only have a diameter of 2.3-3.3 nm. The purity of the as delivered product is >95%. Thin-MWNT have the same purity but show a larger diameter. The average diameter was found to be 12 ± 10 nm and their lengths are known to be as long as 50 μm . However, measurements of (100) thin-MWNT (dispersed in chloroform) showed an average length of 1.8 ± 0.08 μm . This can be observed in the length distribution diagram of Figure 2-13a where data were determined by a Lorentzian fit. Lengths of thin-MWNT were measured using several TEM micrographs such as shown in Figure 2-13b.

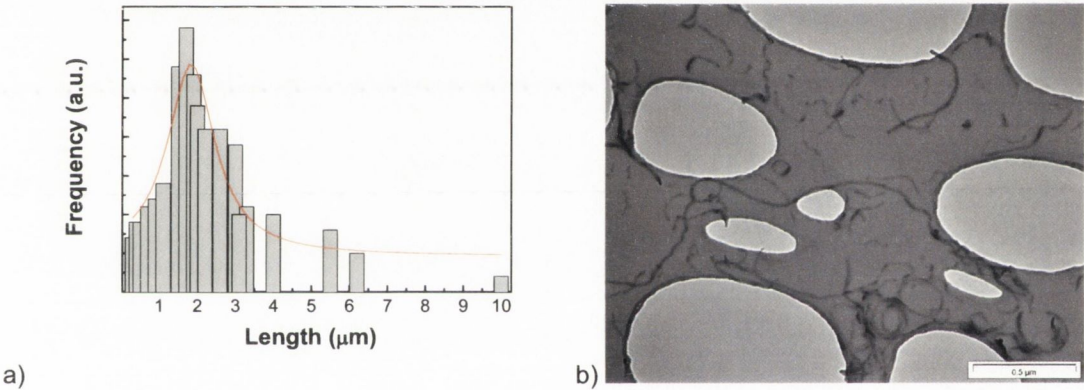


Figure 2-13: a) Length distribution diagram for thin multi walled carbon nanotubes measured from b) transmission electron microscopy micrograph of thin multi walled carbon nanotubes dispersed in chloroform

Thin-MWNT used in Chapter 8 were furthermore functionalised with hydroxyl and amine groups^{38,39} by ball-milling to improve their dispersion properties.

An additional sample from the University of Orléans (OMWNT)⁴⁰, similar to the catalytic MWNT produced in Namur was obtained. An equivalent production method was used but with cobalt/magnesium oxide (Co/MgO) as the catalyst. Moreover, the purification method differs from the former sample. Here, purification⁴¹ by hydrochloric acid was used resulting in a 98% pure sample shown in Figure 2-14. As

this purification method is destructive structural defect are present⁴². Average diameters of these nanotubes are 16 ± 5 nm with lengths of up to 50 μm .

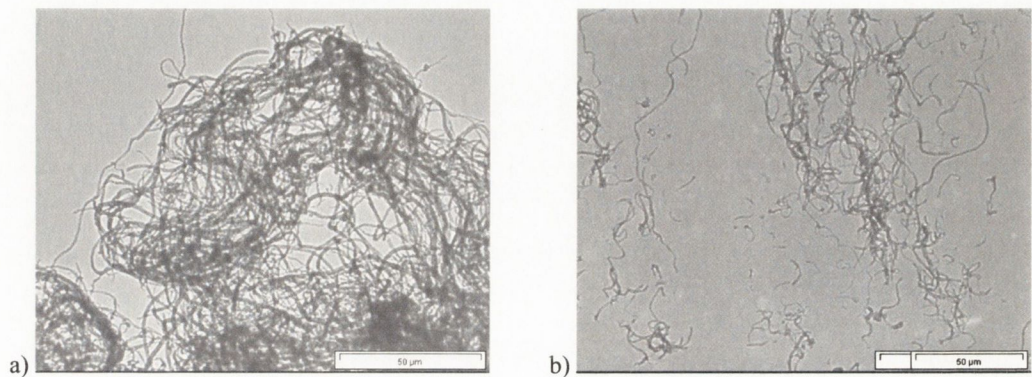


Figure 2-14: Purified catalytic grown multi walled carbon nanotubes using cobalt/magnesium oxide as catalyst⁴⁰.

For further work shown in Chapter 9, commercially available carbon nano fibres (CNF) (Pyrograf III[®], PR-19) were purchased from Applied Science Inc., U.S.A. and used (Figure 2-15a) in addition to aligned catalytic grown multi walled nanotubes (aMWNT) produced at the University of Cambridge, UK⁴³ as shown in Figure 2-15b.

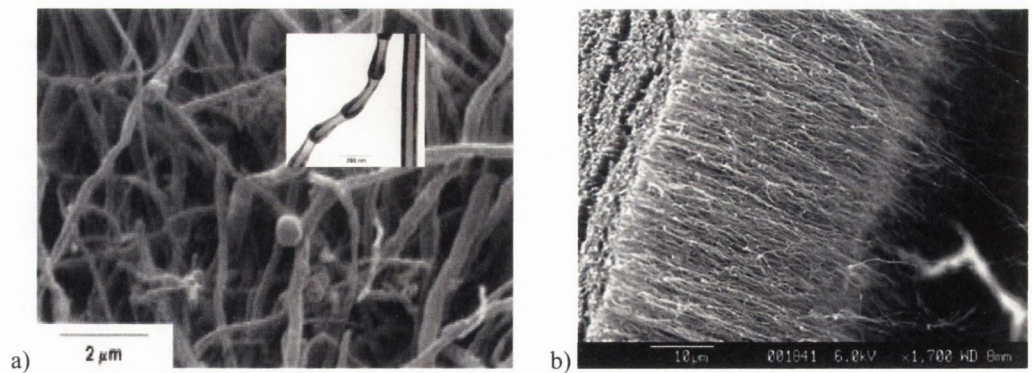


Figure 2-15: Scanning microscopy micrographs of a) carbon nano fibres and their bamboo-like structure and b) aligned multi walled carbon nanotubes

CNF are produced by a similar method as catalytic grown CNT but have larger diameters and contain more defects and are therefore not as strong and stiff as CNT.

Shown in Figure 2-15a (top corner) is a typical bamboo like structure of CNF. Their length distribution varies from 30-100 μm and diameters are in the range of 100-200 nm. Production costs are much lower than for CNT and production yields are in the kilogram range. However, CNT are still only produced on the gram scale. Aligned catalytic grown MWNT diameters range between 40-50 nm and have lengths of 50 μm ⁴³. These highly aligned MWNT are produced on substrates under a mixed helium argon atmosphere (1:3) at 760°C.

2.4.3 High Pressure Decomposition of Carbon Monoxide (HipCO) Grown Single Walled Carbon Nanotubes

High pressure decomposition of carbon monoxide produced single walled carbon nanotubes (HipCO-SWNT) do consist of only one graphite shell and their ends consist of hemispheres of Fullerenes. Their diameters are as small as 0.7-1.4 nm and lengths range between 100-1000 nm.

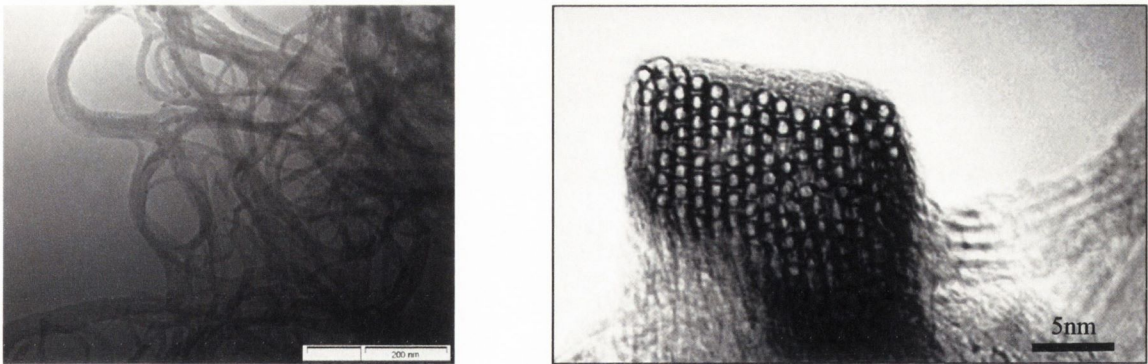


Figure 2-16: High pressure decomposition of carbon monoxide produced single walled carbon nanotubes a) transmission electron microscopy micrograph of single walled carbon nanotube ropes and b) scanning electron microscopy micrograph of a single nanotube rope by Thess et al.¹⁴

An important structural aspect of these single walled nanotubes differs from other nanotubes. All SWNT have the ability of self-organisation into "ropes" which consist

of many tubes running together along their length in contact with each other. These ropes are much longer than any individual tube in them. Whereas single tubes are usually about 1 micron in length, these ropes are essentially endless, branching off from each other and joining others again. Shown in Figure 2-16 diameters of HipCO-SWNT-ropes are typically 5-10 nm. This results in a significant problem regarding reinforcement of polymer composites as the nanotubes can not be dispersed reasonably which is essential for the reinforcement mechanism. The interfacial bonding between single nanotubes in ropes held together by van der Waals forces is comparable to the bonding between the interface of nanotube and polymer matrix. The main difficulty is the dispersion of HipCO-SWNT-ropes in polymer matrices and this will be further discussed in Chapter 5.

2.4.4 Polymer functionalised multi walled carbon nanotubes

In order to avoid the problem mentioned in previous section regarding bundle formation and interfacial bonding between nanotube and polymer matrix, carbon nanotubes were chemically prepared. The smallest diameter multi walled carbon nanotubes were covalently attached to the polymer chains of the reinforcing matrix to ensure a uniform dispersion of nanotubes in the polymer matrix and a strong interfacial interaction.

It has been reported earlier that Fullerenes such as C_{60} are able to react with lithium alkyl and Grignard reagents giving alkylated metal fullerides e.g. $RC_{60}-Li^{+44-46}$. However, while much research on organometallic chemistry of fullerenes has been performed, not much of the corresponding nanotube research has been done. It is well known that nanotubes contain several different structures apart from the main

hexagonal shape such as pentagon and heptagon rings. These sites are potentially reactive and can be attacked by nucleophiles such as lithium alkyls.

Purified “thin”-MWNT were reacted with n-BuLi in tetra hydro furan (THF) under argon at ambient temperature resulting in a green solution. After this treatment the dispersability of the nanotubes in THF increases significantly. The process results in formation of air and moisture sensitive lithium functionalised nanotube products which are extremely reactive. This hybrid can react with any halogen containing species with an elimination of the lithium halide. For example, reaction with SnBr_2 resulted in the formation of Sn-C bonds on the nanotube surface. Reactions with alkyl halides gave correspondent alkyl adducts with a very high solubility in organic solvents. More importantly, lithiated MWNT have also been functionalised by reaction with chlorinated polypropylene (cPP) to produce nanotubes covalently bonded to polypropylene (cPP-MWNT). These materials are expected to interact strongly with a polypropylene matrix in composite systems and will be further discussed in Chapter 6.

2.5 Advanced Polymer Composites

A composite material consists of two or more phases and is artificially created, as opposed to a material that occurs or forms naturally. In addition, the constituent phases are chemically dissimilar and separated by a distinct interface. Polymer matrix composites consist of a polymeric phase, either resin or thermoplastic material, with e.g. glass, carbon or aramid fibres (Kevlar[®]) as reinforcing media. They are used in many applications of daily life such as automotive parts, aircraft parts,

plastic pipes, storage containers, sports equipment, and pressure vessels or even for bullet-proof vests (Kevlar[®]).

Glass fibre reinforced composites those are produced in the largest quantities. This is due to the low costs of the glass fibre production. Furthermore, they are relatively easy to produce. Glass fibres are relatively strong and when embedded in a polymeric matrix they produce a composite having a very high specific strength. When coupled with various plastics they possess a chemical inertness that renders the composite useful in a variety of corrosive environments. There are several limitations to this group however. Even though they possess high strength they are not very stiff and do not show much rigidity which is necessary for certain applications. Most fibreglass composites are limited to an application temperature of below 200°C depending on the quality of fibres and the polymer matrix.

Carbon is a high-performance fibre material which is the most often used reinforcement agent in advanced polymer matrix composites. This is because carbon fibres have the highest specific modulus and strength⁴⁷ of all reinforcing fibre materials even at elevated temperatures. At room temperature, carbon fibres are not affected by moisture or a wide variety of solvents, acids or bases. The fibre production process has become less expensive over time due to the large scale production of fibres in industry. Moreover, the composite formation is relatively inexpensive and therefore cost effective. Carbon fibres are not completely crystalline but consist of both graphitic and non-crystalline regions. These non-crystalline areas are devoid of the 3-dimensional ordered arrangements of hexagonal carbon networks that are characteristic of graphite. Diameters usually range between 4-10 µm and lengths can be discontinuous or chopped. Polymer composites reinforced with carbon fibres are extensively used in extreme sports equipment as well as in automotive and aircraft parts and space applications.

Aramid fibres were only introduced in the early 1970's. They have high modulus and strength comparable to graphite fibres. Kevlar[®] fibres are especially desirable due to their exceptional high strength to weight ratio, which is superior to metals. The tensile moduli are higher than all other known polymeric fibres but they are relatively weak in compression. The material is known for its toughness, impact resistance, and resistance to creep and fatigue failure. The suitable temperature range for Kevlar fibres varies between -200°C and 200°C. Aramid fibres are known to be chemically resistant to most solvents and chemicals. As reinforcement agents, Kevlar[®] fibres are mostly used in epoxies or polyester materials. Since the fibres are relatively flexible and somewhat ductile they can be used for most common textile operations. Typical and most commonly known applications for Kevlar[®] fibre reinforced polymer composites are bullet-proof vests, sporting equipment, tyres, and ropes.

Other known fibre reinforcement materials are boron, silicon carbide, and aluminium oxide. These materials are used to a much lower degree. Most commonly used polymer matrix materials for glass fibre reinforced polymer composites are polyesters, vinyl esters and epoxies. There exists a large spectrum of different resin formulations which provide a wide range of material properties. For high temperature applications the more expensive polyimide resins are used. Specific types of polyimide resins are polyetheretherketone (PEEK), polyphenylene sulphide (PPS), and polyetherimide (PEI). These materials are known to have a thermal stability of up to 330°C and are mainly used for space applications⁴⁸.

A new generation of reinforcement agents are expected to be carbon nanotubes (CNT) which were firstly introduced scientifically in the early 1990's by the electron microscopist Sumio Iijima^{12,31} (NEC Laboratories, Japan). Since this pioneering work

of Iijima the study of carbon nanotube reinforcement of polymer composites has progressed rapidly^{18,49-73} regarding purity of CNT soot, dispersion of CNT in polymer matrices and investigations on the interaction between matrix and CNT.

2.5.1 Poly(vinyl alcohol) in H₂O-solution

It has been 80 years since poly(vinyl alcohol) (PVA) was first obtained and 50 years since it was commercialised (by Dupont), and is still used in many industrial fields. PVA is a synthetic semi-crystalline polymer with excellent film-forming and emulsifying capabilities. This versatile polymer offers high tensile strength, high modulus, flexibility, acid and alkali resistance, abrasion resistance, UV resistance and a high oxygen and aroma resistivity⁷⁴. It is also characterised by its water solubility, which makes this material environmentally friendly. PVA has low electrical and thermal conductivity. With these excellent properties, it has a wide range of applications in industry such as fabrics, building reinforcing materials, package materials, ropes and meshes. Due to the afore mentioned oxygen and aroma barrier, PVA is often used as a barrier material e.g. in fuel tanks or multi layer films.

PVA is called as such because of its analogy to other related vinyl polymers which are as well polymerised of vinyl monomers. As vinyl alcohol it can not be isolated as a monomer therefore it has to be prepared from other vinyl polymers that can undergo suitable chemical transformations. The source for large productions of PVA is poly(vinyl acetate). The molecular weight distribution can be controlled either by the preparation method or by fractionation and selection. The tacticity has become under reasonable control through reliable measurements and novel preparative methods⁷⁵.

A major polymerisation problem is the degree of deacylation or deetherification of the primary polymer. Shown in Figure 2-17 are the two common reaction possibilities for the production of PVA⁷⁵.

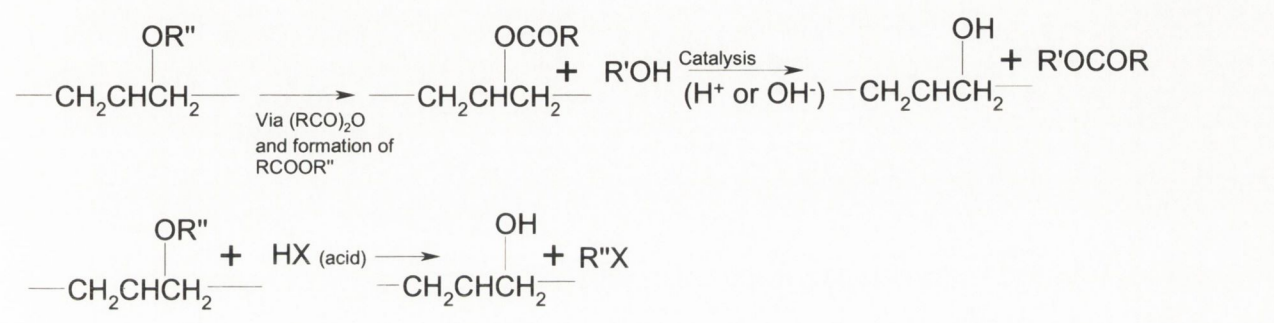


Figure 2-17: General polymerisation steps for poly(vinyl alcohol)

PVA is a light, white solid powder when pure and can be obtained in a range of molecular weights from a few thousand to about a million. As mentioned before the common solvent for PVA is water but other solvents can be used as well. However, they are rare and it is difficult to process solutions made using them⁷⁵.

PVA used in this work (Figure 2-18) contains an average molecular weight ranging between 30,000 to 70,000 g/mol and a density of 1.26 g/cm³. It is available in solid state as white powder and was used for composite production as delivered.

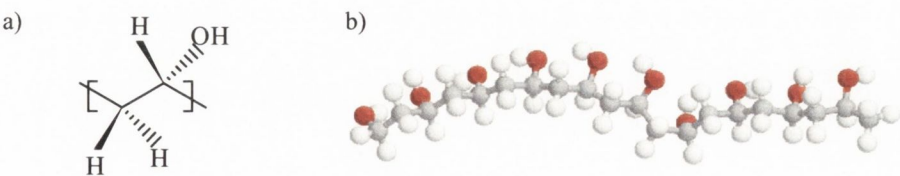


Figure 2-18: a) Chemical structure of poly(vinyl alcohol). b) Optimised structure of poly(vinyl alcohol)⁷⁶

2.5.2 Poly(9-vinyl carbazole) in Dichloromethane

Poly(9-vinyl carbazole) (PVK) (Figure 2-19 and Figure 2-20) is a typical photo conducting conjugated amorphous polymer and is mainly used for hole transport layer applications such as in light emitting diodes^{77,78}. Due to its large band gap PVK is transparent to visible light and has an excellent hole mobility. Composites with C₆₀ were recently investigated by Wang *et al.*⁷⁹ in order to examine the photovoltaic response. He found that the transient photo voltage of a two layer PVK/C₆₀ film revealed that the photo induced electron transfer between PVK and C₆₀ molecules results in a very fast mechanism of charge separation.

PVK used for this work is in crystal form when in solid state. It has an average molecular weight of 1,100,000 g/mol and a density of 1.2 g/cm³. The solvent for PVK is dichloromethane (DCM) with a purity of 99.6%, density of 1.325 g/cm³ and a boiling point of 38-39°C.

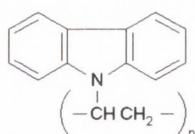


Figure 2-19: Chemical structure of poly(9-vinyl-carbazole)

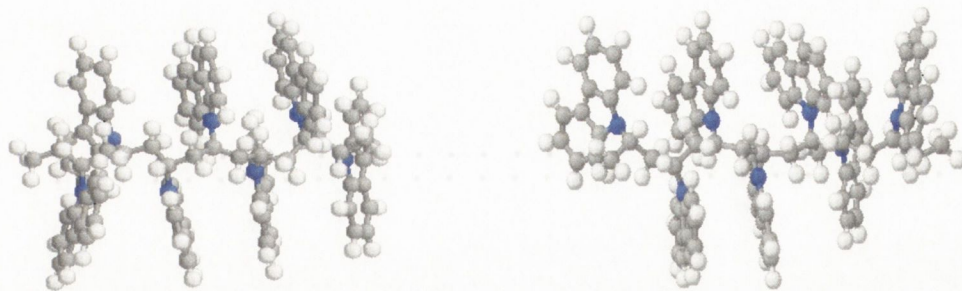


Figure 2-20: Optimised structure of poly(9-vinyl-carbazole)⁸⁰

2.5.3 Polyamide 12

Nylon[®] was discovered in 1938 by Du Pont and was the first known thermoplast material. Most commonly used types of Nylon[®] are Nylon[®]-6 and Nylon[®]-6.6 and are used in commercial production as fibres for textile and engineering applications. Its technical name is polyamide. Another important Nylon[®] is polyamide 12 (PA12). It represents only a small fraction of the fibre market but is known for its excellent strength to toughness ratio. The PA12 used in this work was produced and delivered by Degussa AG/Germany (VESTAMID L1700).

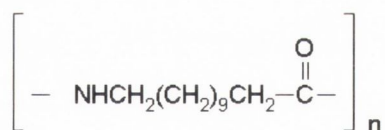


Figure 2-21: Chemical structure of polyamide 12

PA12 is a linear aliphatic, semi-crystalline thermoplast with a density of 1.02 g/cm³ and is used for applications such as precision engineering components which are materials with exceptional mechanical and thermal properties such as high stiffness and toughness, low creep and excellent thermal resistance. This makes them valuable in the manufacturing of structural products such as gears, bearings, electronic devices and automotive parts.

PA12 is known to be hygroscopic but compared to other polyamide materials it saturates at <1.6 wt% of water uptake while maintaining excellent dimensional mechanical stability and electrical properties. Its melting temperature is between 190-230°C.

2.6 Theoretical Background & Characterisation methods

Fibre reinforcement of polymer composites has been performed since the early 1950's and several theoretical models have been developed to date. Reinforcement parameters of the resulting composite, such as elasticity modulus or strength, are not only dependent on the matrix and fibre elastic modulus and length and diameter distribution of the fibres but also on other extremely important parameters such as distribution and orientation of the reinforcing agent and the interaction between filler and polymer matrix. This has to be taken into consideration when developing a theoretical model. The most commonly used models for fibre reinforced polymer composite are the aggregate model^{81,82}, Cox-shear-lag Theory^{83,84} and the rule of mixture⁸⁵. The aggregate model was found to be very precise only for nearly unidirectional orientation of the fibres⁸⁶ therefore other parameters must be taken into consideration.

2.6.1 Mechanical Properties of Polymer Composites

Young's modulus, Y is in general is the ratio of stress to strain when deformation is totally elastic and is a measure of material stiffness. It quantifies the resistance that a material presents against deformation in a particular direction.

Y is therefore usually defined by the following expression:

$$Y_m = \frac{F}{A_0 \cdot \varepsilon} \left[\frac{N}{m^2} = Pa \right] (a)$$

Equation 2-2

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l - l_0}{l_0} (b)$$

Where **F** stands for the applied force, **ε** for the strain, **l₀** is the initial length and **Δl** the length when the force is applied to the specimen. **A₀** describes the initial sample cross section or the cross section of the indent in case of nano-indentation.

Hardness, **H** is the resistance of materials to plastic deformation, usually measured by indentation. However, the term may also refer to resistance to scratching, abrasion, or cutting. It is the property of a material which gives it the ability to resist being permanently deformed (bent, broken, or have its shape changed) if a load is applied.

$$H = \frac{F}{A} \left[\frac{N}{m^2} = Pa \right]$$

Equation 2-3

Here **H** stands for hardness, **F** for the applied force and **A** for the area of the indent. The Nano Hardness Tester (NHT) seen in Figure 2-22a, better known as nanoindenter or ‘Berkovich’ indenter, is a high precision instrument for the determination of the nano mechanical properties of thin polymer films, coatings and substrates. The Young's modulus and hardness, of soft, hard, brittle or ductile materials can be determined⁸⁷ using the NHT. The NHT operates as follows: A diamond pyramid shape indenter tip (Figure 2-23a) normal to the sample surface, with a known geometry, is driven into the sample by applying an increasing load up to some preset value (Figure 2-22b). As seen in Figure 2-22c) the load is gradually

decreased until partial or complete relaxation of the sample has occurred. Load and displacement are recorded continuously throughout this process to produce a load displacement curve from which the nano-mechanical properties such as Young's modulus, hardness, stress-strain studies, time dependant creep measurement, fracture toughness, plastic and elastic energy of the sample material can be calculated.

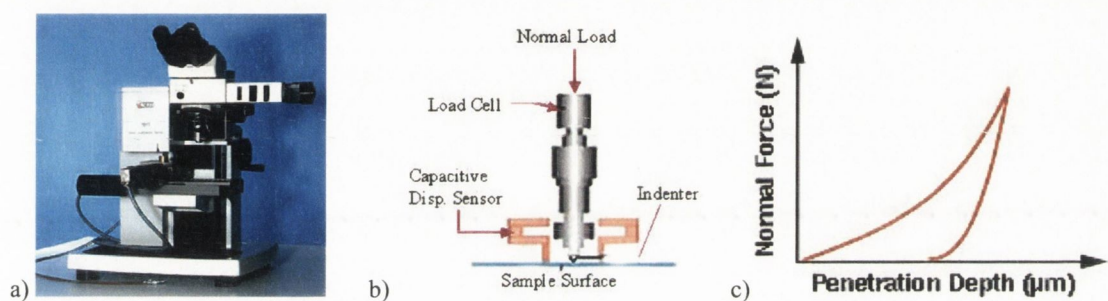


Figure 2-22: a) Nanoindenter device b) schematic diagram of nanoindenter and c) classical load-displacement curve of nano-indentation

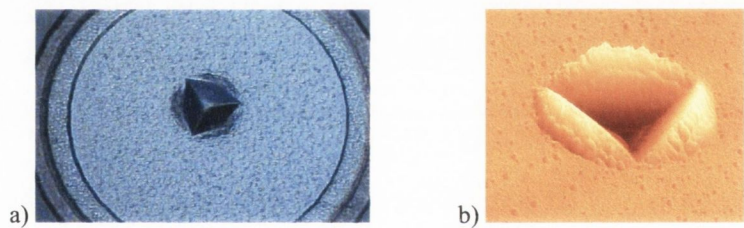


Figure 2-23: a) Pyramidal shape of a nano hardness tester tip. b) AFM micrograph of imprint on the material surface of a nano hardness tester tip.

The nano-indentation procedure has to be repeated for certain times at different sample positions to achieve average values of mechanical properties. This is to avoid measurements of hard particles such as dust or other impurities by the indenter tip.

Nano-indentation tests measure hardness by indenting a testing specimen, i.e. thin polymeric film, using very small, on the order of a couple of μ -Newton indentation forces, and measuring the depth of the indentation. Young's modulus can be

determined by calculations of the slope in the linear elastic deformation region. These tests are based on a technology that allows precise measurement and control of the indenting forces and precise measurement of the indentation depths. By measuring the depth of the indentation, progressive levels of applied force are measurable on the same piece. This allows the tester to determine the maximum indentation load that is possible before the hardness is compromised and the film is no longer within the testing range. This also allows a check to be completed to determine if the hardness remains constant even after an indentation has been made.

One of the most common mechanical stress-strain tests is performed in tension using a tensile testing device (Figure 2-25a). To perform tensile testing a number of specimens are deformed with a gradually increasing tensile load that is applied uniaxially along the long axis of the specimen, usually until the fracture of the sample occurs. Specimens are mounted at its ends into holding grips of the testing apparatus. The tensile testing device is designed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous load and the resulting elongation. The output of the test is recorded and usually plotted as stress (σ) versus strain (ϵ) shown in Figure 2-24a and Figure 2-24b.

Several mechanical properties that are important in designing a material can be obtained from the stress-strain curve⁸⁸. The most relevant are tensile modulus (Y), which can be obtained as the slope in the elastic (linear) region. Furthermore, yielding point (P_Y) and yielding strength (S_Y), which is the point or the stress respectively, at the end of the elastic regime where plastic deformation begin, as shown in Figure 2-24a. Ultimate tensile strength (S) and the elongation at break (ϵ_b) are the maximum of the stress-strain curve where fracture occurs. The energy needed to break the specimen, also called toughness (T), can be calculated from the

integral under the stress-strain curve. These single property points can be found in Figure 2-24a.

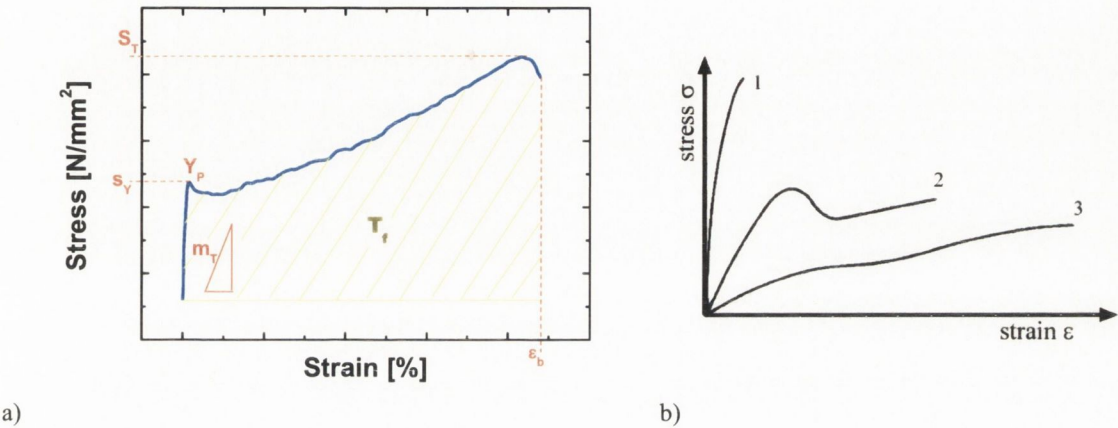


Figure 2-24: Classical stress strain curves for a) thermoplast material with single property positions and b) material properties of different polymer material groups⁸⁹.

If the tested material consists of a brittle structure, such as a typical thermoset material (epoxy based systems), fracture will occur directly at the end of the linear-elastic regime. No yielding occurs when tensile testing these materials. The elongation at break for epoxy thermoset materials is usually in the range of 3-4%. This behaviour can be explained by the usually high curing density of thermoset materials and therefore the small mash-width between the single curing points. The brittle behaviour in a stress-strain curve corresponds to graph 1 in Figure 2-24b⁸⁹. The tensile modulus is calculated of the slope of the linear-elastic stress-strain curve. Graph 2 represents the classical behaviour of a thermoplast material such as polypropylene. Tensile modulus and ultimate tensile strength are usually lower than thermoset materials, but the fracture strain is considerably higher as can be observed in Figure 2-24b. Elongations at break for a polypropylene can be up to 800%. For a classical thermoplast material the deformation occurs as follows: As a first step the stress increases proportional to the strain when a force is applied to the specimen. In

this linear region the tensile modulus can be determined by calculating the slope of the linear region. At the end of the linear-elastic region the polymer chains in the amorphous sections of the polymer start to align from their entanglements with the effect that the material is creeping. This point is called the yielding point. Furthermore, possibly available fillers (fibres) start to orient at this point parallel to the polymer chains and therefore towards the applied force due to the flowing of the polymer matrix. A stress drop usually occurs while the yielding process. Once the polymer chains are fully aligned the stress increases non-proportional to the elongation until the ultimate tensile strength is reached. Here the stress usually drops back to zero once the specimen breaks abrupt.

The third graph in Figure 2-24b shows a typical behaviour of an elastomeric material such as rubber. These materials can reach fracture strains of several hundreds of percents. This is due to the larger mesh-width compared to the thermoset material. The yielding point is not as distinctive as for a thermoplast material. Usually the material does not deform plastically.

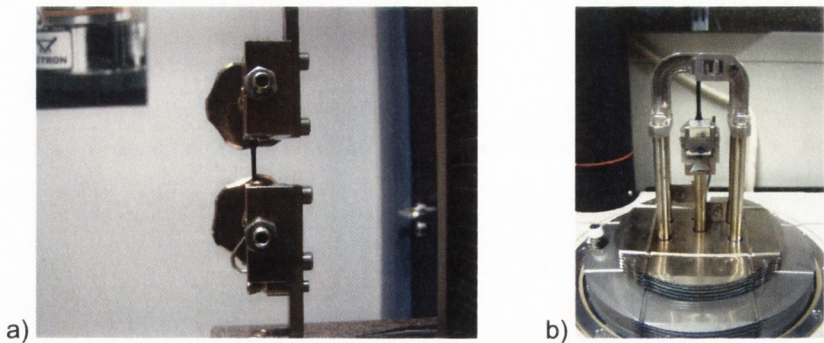


Figure 2-25: a) Tensile testing equipment and b) dynamic mechanical thermal analyser, both set up for tensile testing of thin polymer films and standardised thin polymer tensile bars analysis.

$$\sigma = \frac{F}{A_0} \left[\frac{N}{m^2} = Pa \right] \quad \text{Equation 2-4}$$

$$\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} \cdot 100 [\%] \quad \text{Equation 2-5}$$

$$Y = \frac{\sigma}{\varepsilon_l} \left[\frac{N}{m^2} = Pa \right] \quad \text{Equation 2-6}$$

Here σ stands for the applied stress, A_0 is the origin cross sectional area before the measurement was performed, ε_l is the elongation of the sample in the linear-elastic region, L describes the length of the sample after testing and L_0 is the origin length. Tensile modulus is described as Y .

2.6.2 Thermal Properties of Polymer Composites

The transition from the energy-elastic stage of a polymer (glassy condition - solid) to the entropy-elastic stage (rubbery condition - viscous) is called the glass transition. Here the mobility of polymer chains is reactivated by passing the glass transition temperature range (T_g) while heating up a polymer sample. When cooling down the sample polymer chains freeze when passing T_g . In the T_g range where amorphous polymer (or the amorphous regions in a semi-crystalline polymer) changes from a hard and relatively brittle condition to a viscous or rubbery condition. In this temperature region, many physical properties such as hardness, brittleness, thermal expansion, and specific heat undergo rapid changes. Therefore, when heated through T_g the coefficient of thermal expansion and the specific heat capacity (C_p) of

a polymer increases while the modulus decreases. In case of PVA C_p shows a proportional relationship to the temperature $[T^{\circ}C]^{75}$.

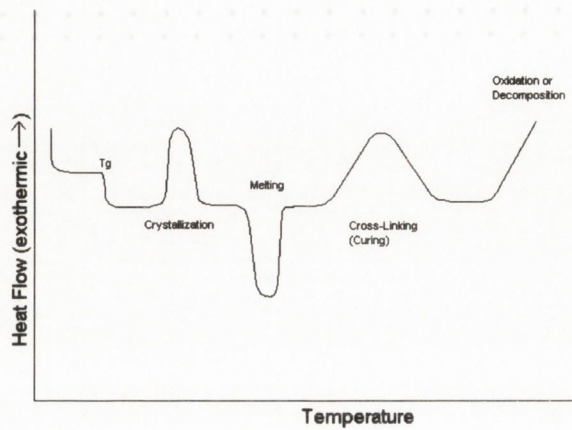


Figure 2-26: Typical differential scanning calorimetry graph for polymeric materials

Amorphous polymers show a steeper transition step at the glass transition temperature as no crystalline regions are available. Therefore, all polymer chains begin to reorient in the same temperature region. Whereas, in the case of semi-crystalline polymers the glass transition region is broader. Melting can only occur in semi-crystalline polymers. Therefore, the melting temperature, T_m defines the temperature region where all crystal regions of a semi-crystalline polymer change from the solid crystalline state to the amorphous liquid state. Here, no weight loss or chemical changes occur. The energy needed for the melting process of the crystals is described by the endothermic enthalpy change (ΔH_m) and can be calculated as the area under the melting peak shown in Figure 2-26. The broadness of the melting peak is dependent on the crystal size distribution of the polymer structure. When cooling the melt energy is dissipated to build up the new crystalline structure. Both T_g and T_m are strongly depending on the thermal history of the polymer sample as well as on the heating speed. Lower heating rates promote post crystallisation or crystal size changes.

Differential scanning calorimetry (DSC) is used to precisely determine the **T_g** and **T_m** of a material. Here two identical aluminium pans are heated according to a preset temperature program under an inert atmosphere, usually Helium, in order to avoid reactions such as oxidation of the investigated material, by oxygen from the atmosphere. The difference in energy needed to heat the sample pan relative to the reference pan is measured, and the change in enthalpy can then be calculated. Exothermic and endothermic reactions can be observed directly from a DSC curve as shown in Figure 2-26, indicating melting or a change in material conditions.

Using the measured enthalpy of melting (**ΔH_m**), determined from the area under the melt peak, the crystallinity of a semi-crystalline polymer composite can be calculated. This is achieved by dividing **ΔH_m** by the theoretically calculated enthalpy for a 100% crystalline polymer, **H_c**, and multiplying by 100% in order to achieve the percentage value for polymer crystallinity (Shown in Equation 2-7). It has to be pointed out at this stage that **H_c** does not exist in reality as polymers do never show 100% crystallinity.

$$C = \frac{\Delta H_m}{H_c} \cdot 100\%$$

Equation 2-7: Calculation for crystallinity of semi-crystalline polymers

Where **C** stands for the crystallinity, **ΔH_m** is the enthalpy needed to melt all crystals involved in the polymer matrix resulting from the calculated integral of the melting peak, and **H_c** stands for the theoretical enthalpy value of a 100% crystalline polymer.

Curing of thermoset polymer composites is an exothermal irreversible reaction in a certain temperature range where one component of a thermoset, i.e. the resin, interacts chemically with its hardener resulting in a covalently bonded network (mesh). If temperature decreases further it is followed by the destructive decomposition of the composite. Decomposition of a polymer composites can be more precisely investigated using thermal gravimetric analysis (TGA) where the different weight losses of a material can be investigated while increasing the decomposition temperature.

2.6.3 Electron Microscopy

Transmission electron microscopy (TEM) is here used to characterise the structure of the CNT produced and the interaction between polymer and the nanotube surface. A TEM consists of an electron source (heated tungsten filament), a condenser system (electromagnet), a sample stage, an objective lens and a projection system. A mono-energetic beam passes the condenser system through which it is guided by an applied magnetic field. The condenser lens widens the beam and projects it over the whole sample. After transmission through the sample film it passes the projection system (lens) which forms an image and projects it on the phosphor screen. To record images it is possible either to replace the screen with a photographic film or a CCD system⁹⁰. The sample has to be assembled on special copper grid (4mm in diameter) which is covered with a support film of formvar. The electron beam has to penetrate the sample film fully which limits the thickness and nature of the sample film to be tested.

High resolution TEM (HRTEM) can resolve structures down to the atomic scale and is capable of resolving individual shells of multi walled nanotubes. It images the structure by transmitting an electron beam (high energy electrons) through a sample. At this high energy the electrons have a shorter wavelength than light which results in the high resolution.

Scanning electron microscopy (SEM) here is used to characterise carbon nanotube purities and the interaction between polymers and carbon nanotubes. The SEM electron gun generates an electron beam from a tungsten filament. This filament is a loop of tungsten which acts as the cathode. When a voltage is applied to the tungsten loop, heating occurs and electrons are emitted. The anode, which is positive with respect to the filament, forms a powerful attractive force for the electrons accelerating them towards the anode. This beam is condensed by a condenser lens, and focused to a sharp point on the sample by the objective lens. The scan coils are energised, therefore creating a magnetic field which deflects the beam back and forth in a controlled pattern. The pattern of deflection of the electron beam is reproduced as an identical pattern of deflection in a cathode ray tube, allowing an image to be observed.

The electron beam hits the sample where secondary electrons are produced from the target. These are collected by an additional detector and are converted to a voltage which is amplified. This amplified voltage is then applied to the grid of the cathode-ray-tube and causes the intensity of the spot of light to change. Thousands of these spots do exist on the image with variations in their intensity that corresponds to the topography of the sample. SEM samples can only be investigated under high vacuum in order to ensure stability of the electron beam i.e. the reaction of other molecules

with the electron source or electrons in the beam could result in ionisation. Furthermore, the transmission of the electron beam through the optic column would be hindered by other molecules.

2.6.4 Quantification technique for carbon nanotubes

The electron paramagnetic resonance (EPR) technique involves the resonant absorption of microwaves by electrons with unpaired spins in the presence of a magnetic field⁹¹. It has been previously shown that this technique can be used to measure nanotube content^{92,93} in non-magnetic systems. EPR signals for nanotube soot consist of a superposition of two Lorentzian curves, representing nanotubes and graphitic impurities²⁴, respectively. The ratio of the area under the deconvoluted nanotube curve to the total area gives a relative measure of the nanotube content in the soot. However, this value is only an approximation of the absolute purity of MWNT soot. Using the purification method described in the previous section by Coleman *et al.*⁹² and by employing thermal gravimetric analysis (TGA) it is possible to calculate the absolute value of purity.

2.6.5 Rule of Mixture

The Rule-of-Mixture describes a simple theoretical model which was often used in the past to calculate Young's moduli of carbon fibre reinforced polymer composites. Other methods have been based on various forms of the Rule-of-Mixture such as:

$$E_{\parallel} = v_f E_f + v_m E_m [Pa] (a)$$

$$E_{\perp} = \frac{E_f E_m}{E_m v_f + E_f v_m} [Pa] (b)$$

Equation 2-8: Rule-of-Mixture a) parallel and b) perpendicular to the principal fibre orientation

Where $E_{\parallel}$ and $E_{\perp}$ are determined moduli parallel and perpendicular to the principal fibre orientation direction in a continuous unidirectional fibre system

The rule of mixture was further modified by Halpin and Tsai⁸³ and was already earlier reported to describe the reinforcement of carbon nanotube composites^{54,62,94}.

2.6.6 Halpin-Tsai Theory

The Halpin-Tsai equation is a simple approximate form of the generalised self consistent micromechanics solution developed by Hill^{95,96}. The modulus values based on this equation agrees reasonable well with the experimental values for a variety of reinforcement geometries⁹⁶. For randomly oriented nanotubes the Halpin-Tsai equation is expressed as

$$E_{random} = \frac{3}{8} E_{11} + \frac{5}{8} E_{22} [Pa]$$

$$E_{11} = \frac{1 + 2 \left(\frac{l_f}{d_f} \right) \eta_L V_F}{1 - \eta_L V_f} E_m [Pa]$$

$$E_{22} = \frac{1 + 2 \eta_T v_f}{1 - \eta_T v_f} E_m [Pa]$$

Equation 2-9: Halpin-Tsai Equation for randomly oriented fillers⁹⁶

where E_{11} and E_{22} are longitudinal and transversal components of composite properties such as modulus. The aspect ratio (l/D) is the length over diameter ratio for the nanotubes and V_f is the volume fraction of nanotubes dispersed in the polymer matrix. The η parameters are given by

$$\eta_L = \frac{\left(\frac{E_{NT}}{E_M}\right) - 1}{\left(\frac{E_{NT}}{E_M}\right) + 2\left(\frac{l_{NT}}{d_{NT}}\right)}$$

$$\eta_T = \frac{\left(\frac{E_{NT}}{E_M}\right) - 1}{\left(\frac{E_{NT}}{E_M}\right) + 2}$$

$$E_C = \left[\frac{3}{8} \frac{1 + 2\left(\frac{l_{NT}}{d_{NT}}\right)\eta_L V_{NT}}{1 - \eta_L V_{NT}} + \frac{5}{8} \frac{1 + 2\eta_T V_{NT}}{1 - \eta_T V_{NT}} \right] E_M [Pa]$$

Equation 2-10: Halpin-Tsai Equation applied on carbon nanotube composites^{54,62,94,96}

Indices used for different modulus are as follows; composite (**C**), matrix (**M**) and nanotubes (**NT**).

2.6.7 Cox-shear-lag Theory

Further modifications on the Rule-of-Mixture were performed by Cox *et al.*⁸⁴ to derive his shear lag analysis:

$$E_c = E_m (1 - v_f) + E_f v_f \left(1 - \frac{\tanh\left(\frac{\beta \cdot l}{2}\right)}{\left(\frac{\beta \cdot l}{2}\right)} \right) [Pa]$$

Equation 2-11: Cox-shear-lag Theory^{84,86}

Where the last terms in brackets is explained as the fibre length correlation factor, with l as the fibre length and β stands for the stress built up at the fibre ends and is calculated by:

$$\beta = \frac{1}{r} \left[\frac{E_m}{E_f (1 + \nu) \ln \left(\frac{r}{l} \right)} \right]^{1/2}$$

Equation 2-12: Fibre length correlation factor for Cox-shear-lag Theory^{84,86}

Here E_m stands for the matrix modulus, ν for the Poisson's ratio, v_f is the volume fraction, r the fibre radius.

Several assumptions had to be made such as: The fibre and matrix remained elastic in their mechanical response, the interface between the fibre and the matrix has to be perfect and there is no axial force transmitted through the fibre ends.

Hence, the rule of mixture for randomly oriented fibres can be written as:

$$E_c = E_m (1 - v_f) + \eta_l \eta_0 E_f v_f [Pa]$$

Equation 2-13: Krenchel's expression for short carbon fibre composite derived from the rule of mixture for randomly oriented fibres, modified by Cox⁸⁴

where η_l is the fibre-length correction factor and η_0 stands for the so called Krenchel orientation efficiency factor^{84,86}.

Perfect alignment, for long carbon fibres, can be assumed if the Krenchel and the fibre-length correction factor equal one. This modified rule of mixture is called the Krenchel's expression for short carbon fibre composites and was applied for several

studies of carbon nanotube reinforcement of polymer fibres and composites by Sandler *et al.*^{63,97,98}.



2.6.8 Krenchel’s Orientation Efficiency Factor

The Krenchel orientation efficiency factor is explained as follows:

$$\eta_0 = \sum_n a_{fn} \cos^4 \alpha_n / \sum_n a_{fn}, \text{ where } \sum_n a_{fn} = 1$$

Equation 2-14: The Krenchel orientation efficiency factor

where a_{fn} is the ratio between the cross sectional area presented by a group of fibres oriented at an angle α_n to the applied load direction and the total area of all the fibres at a given cross-section of the composite. The number of groups is designated by $n = 1, 2, 3, \dots, n$ ⁸⁶.

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Chapter 3

Sample Preparation & Characterisation

methods

3.1 Introduction

A common technique to produce one of the employed types of carbon nanotubes will be described in this Chapter. Furthermore, all investigated polymer matrices will be introduced. It will be shown how the composites were prepared in order to manufacture thin or free standing polymer films, highly oriented thin polymer fibres and macroscopic specimens. In the second part of this Chapter it will be shown how these composites were characterised using common methods such as, electron microscopy, spectroscopy and thermal analysis.

3.2 Polymer Composite and Nanotube Sample Preparation

3.2.1 Production of Arc-Discharge MWNT

The multi walled carbon nanotubes used for this work were produced using a 'Krätschmer generator' (see Chapter 2) in laboratories of Trinity College^{1,2} and of the Technical University of Hamburg-Harburg (shown in Figure 3-27). The generator used at Trinity College consists of a cylindrical steel chamber with dimensions of approximately 350 mm in length and 100 mm in diameter.

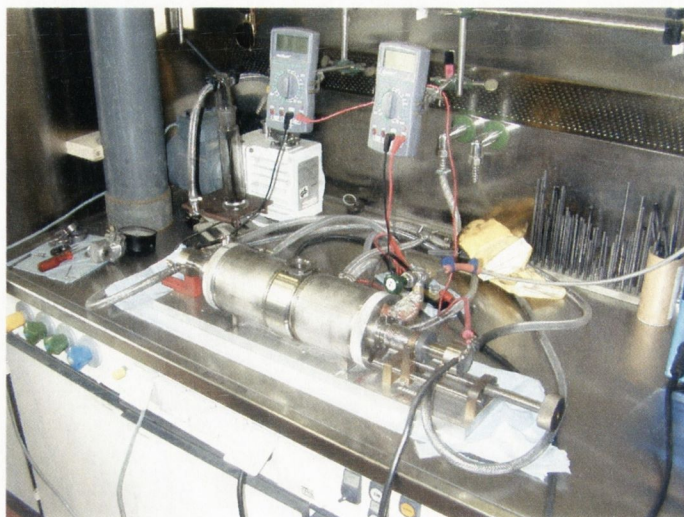


Figure 3-27: Krätzschmer generator for the production of arc-discharge grown multi and single walled carbon nanotubes at the University of Hamburg-Harburg.

Enclosed in the chamber are two graphite electrodes, a stationary cathode (diameter 6.15 mm) made of 99.5% pure graphite and a 99.998% pure, moveable anode (diameter 4.2 mm). In case of the generator used in Hamburg the stationary and the moveable electrodes have the same diameters of 6.15mm and purities of 99.998%.

Electrodes for the anode were cut into a length of 270 mm and the tips were polished parallel to each other with fine sand paper. The cathode electrode was also polished.

Water cooling was switched on after placing the electrodes in the chamber of the generator. Parallelism of the long axis of both electrodes had to be ensured before a vacuum of 10 Torr was applied. Electrode holders were then mechanically fixed.

Afterwards the chamber was “flushed” with Helium gas and repeated three times to ensure that all particles and gases were evacuated from the chamber. The vacuum was stabilised after the third flushing at a constant Helium atmosphere of 500 Torr. A

constant current was generated by a DC generator and driven between the electrodes, which were in contact, before slowly separating them until a voltage drop of 23 V (27 V for generator in Hamburg) was established. The anode position was continuously adjusted to keep voltage drop between the electrodes as close to 23 V

as possible. During this process the anode sublimes and the nanotubes are found condensed as a deposit on the anode. During production the gas pressure was constantly adjusted to minimise pressure fluctuations. The production process had to be interrupted when the anodic graphite rod was consumed and production parameters become unstable. Therefore the DC supply was switched to zero and the chamber was flushed with Helium in order to evacuate all produced gases and nano particle from the generator. After cooling down the generator was opened and the cathodic deposit, which consists of a hard shell and a soft fibrous shell containing carbon nanotubes, was manually separated from each other. This CNT containing soot can be further investigated regarding purity or can be used as reinforcement and conducting agents for polymer composites.

3.2.2 Production of Polymer Solutions

Two different concentrations (polymer to solvent) were used to produce polymer films. 10 g/L solution was used to produce thin polymer films which were placed on glass substrates and 30 g/L solution produced for macroscopic polymer films which were drop cast on polished Teflon discs. Hence, for the thin polymer films, 30 mg of polyvinyl alcohol (PVA) powder was placed in a glass sample bottle and dissolved in 3 ml deionised water by mixing with a sonic tip for 1 minute using an amplitude of 20%. This was followed by a mild sonication using an ultra sonic bath for 20 minutes. In case of the macroscopic polymer films, 300 mg of PVA was dissolved in 10 ml of deionised water using the same sonication procedure described above with an additional sonication time to dissolve the higher mass of PVA. For this concentration samples had to be placed in the ultra sonic bath for two additional hours. After sonication, 25 wt% of arc-discharge produced MWNT containing soot was added into the polymer solutions and mixed for one more minute with the sonic tip. The sample

bottle was subsequently placed in an ultrasonic bath for 2 hours to ensure a homogenous dispersion.

The same procedure was performed for poly(9-vinyl carbazole) (PVK). An additional mild ultra sonication of 20 minutes was implemented here to dissolve PVK completely in dichloromethane (DCM) before the arc-discharge MWNT containing soot was added.

A different mixing procedure and concentration of only 1 wt.% (CNT/PVA solution) had to be used for CNT other than the arc-discharge produced MWNT. Here, after CNT nanotubes were added to the solution, a 5 min sonication procedure was performed using the ultra high power sonic tip at an amplitude of 20%. Afterwards samples were placed for gentle sonication in a low power sonic bath for 2 hours followed by an additional 5 min sonication step using the high power sonic tip. This procedure had to be performed with the intention of breaking up the entanglements of the longer CNT.

After sonication the sample bottles of all polymer solutions were allowed to settle for 24 hours forming a sediment on the bottom of the sample bottle. The sediment and solute were separated after careful decantation.



Figure 3-28: Sample bottles of blended range of polyvinyl alcohol/ carbon nanotube solutions (Foam appears after sonification. Solution is for a long term stable)

For thin polymer film samples 1 ml of the resulting composite solution was taken from the sample bottle by an automatic dropper and placed into a new sample bottle. This amount of polymer composite solution was blended with 1 ml of same concentrated pure polymer solution and mixed with the sonic tip for 1 further minute. This procedure was repeated 4 times in order to get a CNT containing soot mass fraction range of 25 wt% / 12 wt% / 6.25 wt% and 3.125 wt%. In the case of the polymer solutions for the free standing polymer films 4ml of polymer solution were taken from the high mass fraction sample and blended in the same way resulting in the desired concentrations. Later TGA investigations showed that real mass fractions for these concentrations were 2 wt% / 1 wt% / 0.5 wt% and 0.25 wt%.

In all other cases concentrations were found to be <1 wt% / <0.5 wt% / <0.25 wt% and <0.125 wt%. This will be explained in detail in the thermal gravimetric analysis section of this Chapter.

Following equation was applied to transform mass fractions of CNT into volume fraction values:

$$V_f = \frac{1}{1 + \left(\frac{\rho_{NT}}{\rho_{Pol}} \right) \left(\left(\frac{1}{m_f} \right) - 1 \right)}$$

Equation 3-15

Where V_f stands for the volume fraction and m_f for mass fraction of CNT added to the polymer, ρ_{NT} and ρ_{Pol} for the densities of CNT and polymer matrix respectively. Nanotube densities were assumed and compared from earlier work of D. Qian *et al.*³ Mass fractions have to be inserted as absolute values.

3.2.3 Preparation of Glass Substrate Polymer Films

To produce thin films on a glass substrate for the nano-indentation procedure two common film preparation methods were applied: drop casting and spin coating.

For both methods 1cm² glass substrates were cleaned using a 1/10 Decon/water solution. The substrates were placed into the solution and sonicated in a low power ultra sonic bath for 20 minutes. Afterwards the Decon/water solution was washed off with deionised water. The substrates were placed into a beaker with acetone and sonicated in the ultra sonic bath for another 20 minutes. Following this, the glass substrates were placed into a beaker with 2-propanediol and boiled on a hot plate to evaporate the solvent. The dried substrates were stored in Petri dishes.

Afterwards, the cleaned glass substrates were pre heated to 60°C and as much as possible of the PVA solute was dropped onto the glass substrates using a pipette. The substrate was allowed to dry for 1 hour in a 60°C pre-heated oven. This method results in a randomly oriented MWNT / PVA composite film as will be shown in electron microscopy micrographs in following Chapter.

The same glass substrates as used for the drop casting method were placed onto a spinning dish. Spinning speed was adjusted to 1500 rpm. Five layers of PVK solute was dropped onto the spinning substrate and dried while spinning for 1 minute for each layer. In between every layer the sample was placed into an 80°C pre-heated

oven for 30 minutes to achieve a good layer binding due to the polymer chain reorientation.

The film thickness was measured using a nano scratch tester from SCEM Instruments S.A. and found to be $>1\text{ }\mu\text{m}$ on average.

3.2.4 Manufacturing of Free Standing Polymer Films

An additional method similar to the drop casting method described above was used to produce polymer films. Here, free standing polymer films were produced by casting of 1 ml of PVA nanotube solution on macroscopic blank polished Teflon dishes (30 mm in diameter). Polymer solutions were sonicated for 1 minute before dropping the polymer solutions on the Teflon discs using the ultra high power sonic tip with an amplitude of 20%.

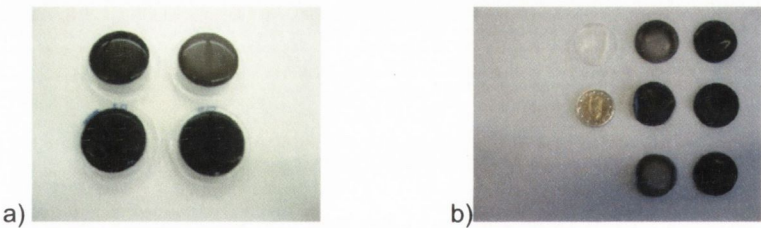


Figure 3-29: a) polyvinyl alcohol/nanotube solutions on Teflon substrate and b) dried free standing polyvinyl alcohol/ carbon nanotube films

Afterwards the sample should be allowed to rest for several minutes to eradicate air bubbles caused from the sonication procedure. This additional sonication step was only performed if the sample was stored for several days before the film production. Otherwise bubble formation will occur during film formation. It has to be ensured that no bubbles are formed on the surface of the polymer solution after dropping the solutions with the automatic pipette. If bubbles do exist, they have to be manually removed using an ordinary glass pipette. The dishes containing the polymer

nanotube solution were then placed into a 60°C preheated oven to allow the solvent to evaporate and form a composite film. This procedure was repeated 4 times resulting in a ~0.5 mm thick free standing polymer film after taking it off the non adhering Teflon substrates. PVA/CNT films were then cut into of 10x4 mm strips using a razor blade in order to perform microscopy and mechanical and thermal testing. Films were dried for an additional hour at 60°C immediately before testing procedures.

3.2.5 Polymer Functionalised Carbon Nanotube Polymer Composites

Production of chlorinated polypropylene (cPP) free standing polymer films, reinforced with carbon nanotubes functionalised with chlorinated polypropylene (cPP-MWNT), is similar to the earlier described method in previous section. 150 mg cPP was dissolved as a 30 g/L solution with 5 ml tetrahydrofurane (THF) using an high power ultra sonic tip for 1 minute with an amplitude of 20%. Afterwards, the sample bottle was placed for mild sonication in an ultra sonic bath for 2 hours. 1.5 mg of cPP-MWNT were added to the polymer solution followed by a 5 minute sonication procedure using the high power sonic tip at 20% amplitude and an additional 2 hours of mild sonication in the ultra sonic bath. This was followed by an additional sonication process using the high power sonic tip for 5 additional minutes at 20% amplitude. The solution was allowed to settle for 24 hours in order for undissolved particles to sediment from solution. Decantation was then used to separate the polymer solution, rich in cPP-MWNT, from the unwanted sediment material.

2ml of the resulting solution was blended into 4 different mass fractions in the same way as described in the previous section resulting in nanotube concentrations of: <1 wt% / <0.5 wt% <0.25 wt% and <0.125 wt%.

1ml of each solution was dropped using an automatic pipette onto a polished Teflon disc and placed into a 50°C preheated oven in order to allow THF to evaporate. This was repeated twice resulting in approximately 300 µm thick free standing polymer film which could be easily peeled from the Teflon substrate. These films were cut into 4x10 mm strips in order to perform further investigations.

3.2.6 Sample Preparation of Polymer Fibres

Polyamide 12 (PA12) was delivered as polymer pellets and dried overnight at 80°C^{4,5}. All multi walled carbon nanotubes were used as produced and as described in Chapter 2 previously. Here, arc grown multi walled carbon nanotubes (AMWNT)², entangled catalytic grown multi walled carbon nanotubes from Namur (NMWNT)⁶ and aligned catalytic grown multi walled carbon nanotubes (aMWNT)⁷ were used in addition to commercial carbon nanofibres grade PR-19-PS (CNF) purchased from Applied Sciences Inc., U.S.A. .

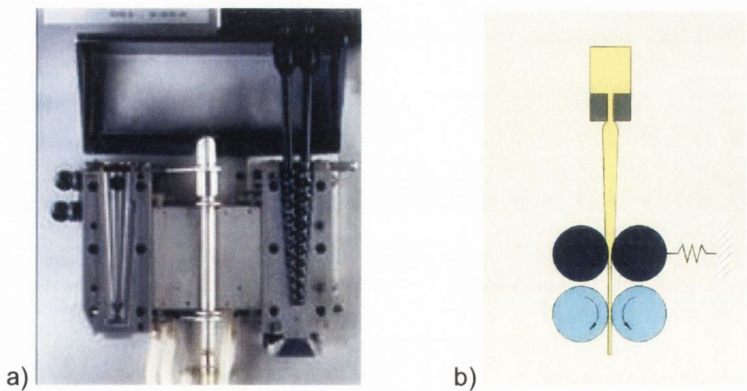


Figure 3-30: Polymer fibre production tools: a) Twin-screw microextruder with melt stream returning system b) scetch of MFI and wind up unit for fibre spinning.

PA12 and MWNT were blended in a twin-screw micro-extruder^{4,5,8,9} (produced by DSM Geleen/The Netherlands), at a temperature of 220°C with 80 rpm. The melt was mixed for 5 minutes using a melt stream return system. Afterwards, the extrudate

was chopped into moderate pieces and re-melted in a melt-indexer at 220°C. A single strand was then spun from a 1mm die, and wound up at 0.5 m/s resulting in a fibre of 125µm in diameter. The filler rates for the produced nano-composites fibres were realised for AMNT and aMWNT: 1.25 wt%, 2.5 wt%, 5 wt%. CNF: 5 wt%, 10 wt% and 15 wt%. NMWNT: 1.25 wt%, 2.5 wt%, 5 wt% and 10 wt%. This was dependent on the availability of the nanofillers and the melt viscosity after the addition of nano-fillers to the composite.

All produced Nylon[®]-fibres were subsequently cut into short segments and embedded in a cold mounting polymer matrix, usually used for microscopic analysis, manufactured by MetPrep Ltd. Two parts of Quick-set[®] powder was mixed with one part Quick-set[®] liquid and pored into cylindrical moulds. Fibres were embedded in the matrix allow curing for several minutes. The surface of the cylindrical fibre embedment was then ground and polished in order to perform nano-indentation measurements.

3.3 Characterisation of Carbon Nanotubes and their Composites

In this section details about sample preparation for the methods used to analyse their composites will be explained. These techniques include transmission and scanning electron microscopy along with spectroscopic analysis such as electron paramagnetic resonance. Furthermore, preparation techniques for thermal gravimetric analysis and differential scanning calorimetry will be described.

3.3.1 Transmission Electron Microscopy

All nanotube soot and polymer nanotube solutions were characterised by transmission electron microscopy (TEM) carried out using a Hitachi H7000 electron

microscope, capable of a magnification of 600k. The accelerating voltage used was 100 keV.

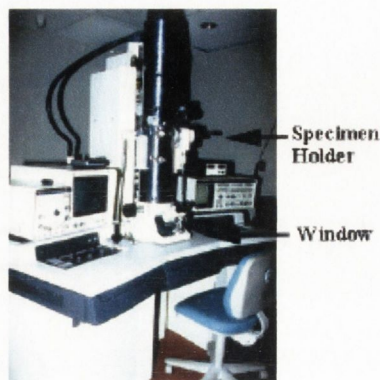


Figure 3-31: Hitachi H7000 Transission Electron Microscope¹⁰.

All TEM investigations were carried out on formvar coated copper grids. To prepare nanotube samples, 10 mg of carbon nanotube soot was dispersed in 1ml ethanol by sonication using a high power sonic tip with an amplitude of 20% for 2-3 minutes. For polymer/nanotube solution samples no additional preparation was necessary. After sonication TEM grids were either dipped into the solutions or solution was dropped onto the grids using a pipette. Grids were allowed to dry while free standing in the air using special tweezers.

3.3.2 Scanning Electron Microscopy

All scanning electron microscopy investigations were carried out using a Hitachi S-4300 Field Emission Scanning Electron Microscope. Acceleration voltages ranged between 10 keV and 30 keV depending on the stability of the sample and the resolution required. Resolution of the Hitachi S-4300 is 1.5 nm at 15 keV. Nanotube/polymer pull-out length measurements were carried out using a 45° sample holder.



Figure 3-32: Hitachi S-4300 Field Emission Scanning Electron Microscope.

For SEM investigations, all samples were shock cooled in liquid nitrogen and broken using pliers or tweezers depending on the thickness of the material. Resulting fractures surfaces using this sample preparation were very plain and brittle, no yielding of the polymer matrices could occur due to the very low temperature. In order to obtain a conducting surface on the polymer specimens gold sputtering of the samples was performed. Thicknesses of the gold layer are estimated to be 15-20 nm. Investigation of the raw nanotube material was carried out by placing double sided adhesive tape on SEM holders and dropping nanotube power on the tape. Gold sputtering was performed afterwards.

3.3.3 Electron paramagnetic resonance

Electron paramagnetic resonance measurements were made at room temperature using a 100 kHz field modulation and a microwave frequency of approximately 9.7 GHz. Samples for electron paramagnetic resonance (EPR) analysis were prepared as follows. For powder samples (soot or sediment) approximately 5 mg of powder was placed in a spin free quartz tube for analysis. In the case of the solutions, approximately 0.3 ml containing around 7 mg of material was placed on spin free

quartz plate and dried in a vacuum oven. These samples were then analysed using EPR^{1,2,11,12}. EPR investigations were performed by Robert Murphy.

3.3.4 Thermal gravimetric analyses

Thermal gravimetric analysis (TGA) was performed using a Mettler TG50 thermal analysis unit and a Perkin Elmer TGA Diamond power compensation instrument. A sample of approximately 10mg of either CNT or polymer films containing CNT is placed into an aluminium oxide crucible and positioned inside a temperature programmable furnace. This is heated through a predetermined temperature profile and continuously purged to remove volatile products. Its weight is continuously monitored and plotted as a function of temperature or time.

3.3.5 Differential Scanning Calorimetry

Thermal properties such as glass transition temperature (T_g) and melting temperature range (T_m) of semi-crystalline polymer were examined using differential scanning calorimetry (DSC) with 2 different devices: Perkin Elmer Diamond DSC power compensation instrument and TA Instruments DSC 2920. Approximately 10mg of polymer material was placed for both DSC devices into standard aluminium pans with caps for DSC experiments and positioned inside a temperature programmable furnace. The furnace is heated through a predetermined temperature profile and continuously purged to remove volatilised products. Its energy consumption is compared to a reference sample and continuously monitored and plotted as a function of temperature or time.

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Chapter 4

Experimental Optimisation of

Arc Discharge Carbon Nanotube Production

4.1 Introduction

In this Chapter a method to improve the arc-discharge production process of multi walled carbon nanotubes is described. Therefore, the production yields and lengths of arc-discharge grown multi walled carbon nanotube have been improved. Optimisation of the 'Krätschmer' generated nanotube production process was performed by variation of production parameters and evaluated by transmission electron microscopy, thermal gravimetric analysis and electron paramagnetic resonance. Production yields and purity could be improved dramatically. Lengths of the resulting nanotubes could be increased shown on transmission electron microscopy micrographs. Furthermore, production time could be minimised drastically.

4.2 Arc-discharge production process

The arc discharge process, developed by Krätschmer and Huffman^{11,114} in the early 1990's and subsequently improved by Ebbesen and Ajayan², was optimised by varying the current densities in 5 A/cm² steps. The current density band was varied

from 165 A/cm² to 195 A/cm². In addition to the current, variations of the Helium pressure in the Krätschmer generator has been increased from 300 Torr to 500 Torr in steps of 100 Torr. In order to study the effects on the ambient production parameters, investigations using transmission electron microscopy micrographs were made in order to quantify the results. The resulting qualitative yield values were subsequently established using electron paramagnetic resonance and thermal gravimetric analysis to maintain quantitative results of the yields.

4.3 Production yields of cathode deposit soot investigated by gravimetric analysis

Various nanotube containing soot samples were produced by arc discharge at a variety of pressures and current densities, as described in the previous section. During the production process the anodic graphite sublimed before forming a deposit on the cathode of the 'Krätschmer generator'. This deposit clearly shows two distinct microstructures; a hard outer shell consisting of an inseparable pyrolytic graphite mass and an inner core region, which consists of loosely packed columns aligned in the axial direction of the deposit. These columns are made up of straight, rigid, multi-walled nanotubes, closed carbon nano-particles and turbostratic graphite. This nanotube containing core region was manually separated from the shell and weighed by a highly sensitive electronic balance. Yields of carbon nanotube containing soot are plotted in Figure 4-1 for each parameter variation step. Yield is defined as the mass of carbon nanotube soot, separated from the shell material, divided by the production time displayed in minutes. It can clearly be seen from this graph that the yield increases as the current density and pressure increase. For current densities of 165 A/cm² and pressures of 300 Torr low yields are observed in the region of 2.6

mg/min, whereas for the sample with increased Helium pressure shows slightly higher production yields in the region of 3.0 mg/min. Whereas, when the current densities and pressures are increased to 180-185 A/cm² and 400 Torr respectively, the yield plateaus at regions of between 6-12 mg/min. Increasing, for instance, the current density to 180 A/cm² while leaving the Helium pressure at 400 Torr results in almost a 3-fold increase of production yield of 8.7 mg/min compared to the low current density samples. When increasing the current density to 190 A/cm² but leaving the Helium pressure low at 300 Torr the increase of yields are increased almost by a factor of 4. This indicates that current density is the more important parameter on the production yields. However, more successful was the combination of high pressure of Helium and high current density, which resulted in an 8-fold increase in yield. Here the production parameters resulted in increasing the yields sharply to 22 mg/min for the 195 A/cm² and 500 Torr Helium pressure and to 24 mg/min yield for 190 A/cm² current density and 500 Torr Helium pressure.

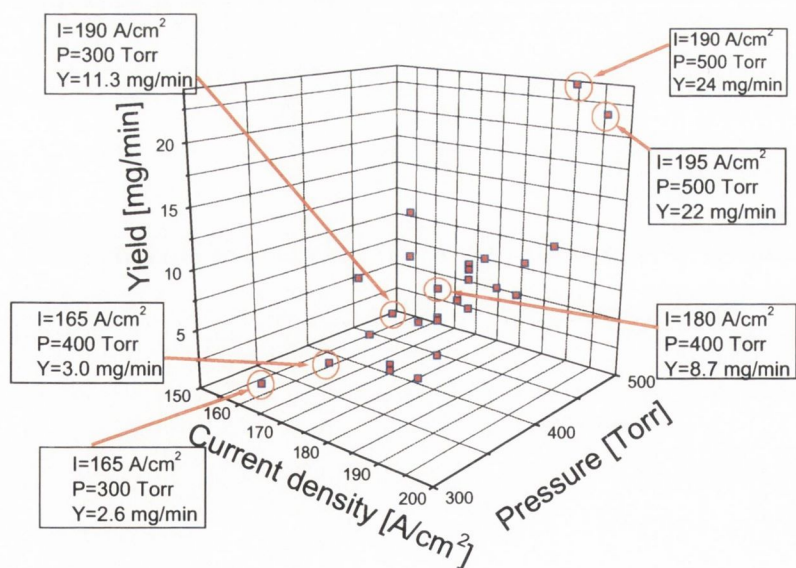


Figure 4-1: Yield of nanotubes, in mg/min, as a function of production parameters, current density and pressure.

These results are limited due to the small diameter of the graphite rods used in these experiments. Repeating these results on a newly developed Krätschmer generator, which allowed the use of larger diameter graphite rods (6.15 mm² diameter rods compared with 4.2mm²), production parameters such as voltage were increased from 23 V to 27 V. During the production process the voltage was subsequently further increased of up to 31 V in order to avoid the resulting current density drop due to increasing resistance while deposit length growth. Using the previous determined optimum process parameters (current density 190 A/cm² /Helium pressure 500 Torr) resulted in production yields of 23.3 mg/min. However, due to the larger diameter rod a higher mass of 700 mg per production run (30 minutes) could be achieved, whereas only 260 mg per run (12 minutes) could be produced with the smaller diameter graphite rods. Therefore setting up time is reduced. Furthermore, due to subsequent increases in voltage during the production process no amorphous core could be found while separating the soft core from the hard shells. This occurs only after a third of the production time, due to an increase in the electrical resistance as a result of increasing cathode deposit length. This could be minimised with voltage increase during the production process.

4.4 Production yields of deposit soot investigated by transmission electron microscopy

In order to study the effect of the described variation of production parameters on the soot microstructure, TEM images were compared for nanotube content, for a range of samples, The lowest yield sample produced with a current density of 165 A/cm² and Helium pressure of 300 Torr, a mid yield sample produced at a high current density of 190 A/cm² and a low Helium pressure of 300 Torr, and two highest yield samples

produced at Helium pressure of 500 Torr and current densities of 190 A/cm² and 195 A/cm², were compared using this technique.

The results can be seen in Figure 4-2a, b, c and d respectively. It can be clearly seen from these micrographs that there are relatively more nanotubes in the high yield samples, compared with the low and mid yield samples. Furthermore, it can certainly be seen that the carbon nanotubes in the high yield samples are much longer than the low and mid yield samples. No curvature or bending of the nanotubes can be observed in these micrographs suggesting that these carbon nanotubes are completely graphitised. This further shows that the purity is substantially increased with increasing current densities and Helium pressures. It should be noted at this point, that these micrographs are representative of a large number of TEM images analysed for each sample.

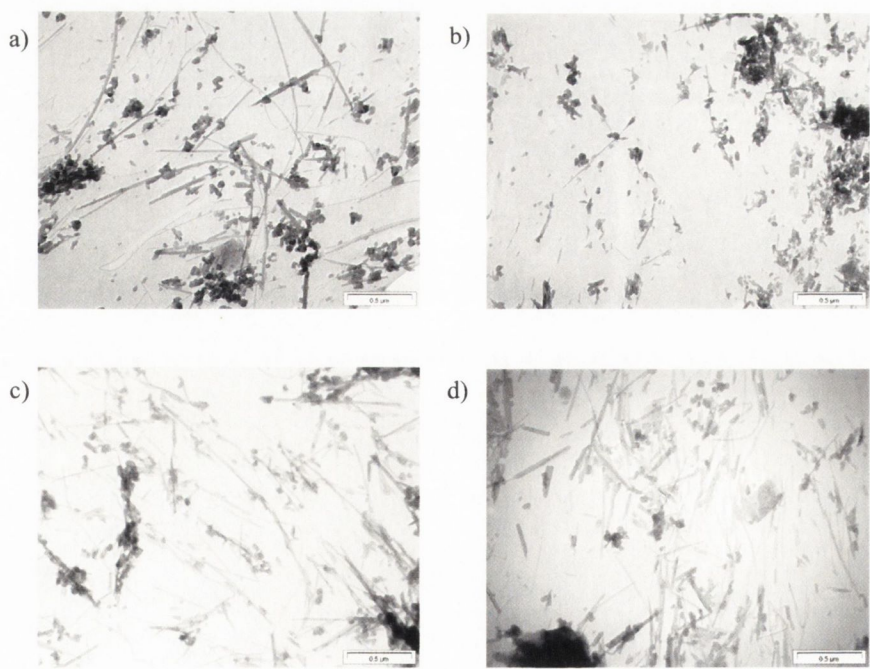


Figure 4-2: Transmission electron microscopy micrographs of MWNT containing soot generated using different production parameters a) low yield (2.6 mg/min) produced with low pressure (300 Torr) and low current density (165 A/cm²), b) mid yield (11.3 mg/min) produced with low pressure (300 Torr) and high current density (190A/cm²), c) high yield (22 mg/min) produced with high pressure (500 Torr) and high current density (195 A/cm²) and d) high yield (24 mg/min) produced with high

pressure (500 Torr) and high current density (190 A/cm²). Figures b) and c) represent samples B) and C) described in Figure 4-3 (scale bar is 0.5 micron).

4.5 Quantitative determination of production yield

In order to quantify the observed increase in purity, electron paramagnetic resonance measurements (EPR) were carried out by Robert Murphy. These were performed at room temperature using 100 kHz field modulation and a microwave frequency of approximately 9.7 GHz. Samples for electron paramagnetic resonance (EPR) analysis were prepared as follows. For powder samples (soot or sediment) approximately 5 mg of powder was placed in a spin free quartz tube for analysis. In the case of the solutions, approximately 0.3 ml containing around 7 mg of material was placed on spin free quartz plate and dried in a vacuum oven at 60°C. These samples were then analysed using EPR^{27,35,37,113}.

Complex spectra as shown in Figure 4-3 can be fitted to individual Lorentzian lines representing individual species (in this case multi walled carbon nanotubes and impurities) with the area under the absorption curve proportional to that mass of the species present. EPR spectra were measured for this specific low yield sample (**A**) with current densities of 180 A/cm², Helium pressure of 400 Torr (8.7 mg/min). Furthermore, a mid yield sample (**B**) produced with 190 A/cm² current density and Helium pressure of 300 Torr with a production yield of 11.3 mg/min and a high yield sample (**C**), 195 A/cm² current density, 500 Torr Helium pressure and a production yield of 22 mg/min. In this graph, spectrum **B** corresponds to sample **b** in Figure 4-2 while spectrum **C** corresponds to sample **c**. The EPR spectra are shown in Figure 4-3. The shoulder (marked with arrow) at high field has been shown^{46,47,106} to represent the nanotube component of the sample. The ratio of the nanotube curve area to the total signal area, (I_{EPR}) is a relative measure of the purity of each sample.

At this point it is important to note that this ratio is representative of, but not equal to the sample purity as the magnetic spin susceptibility for MWNT is not equal to that for graphitic impurities. These ratios were calculated by fitting Lorentzian's to the EPR absorption curve and were 35%, 41% and 55% respectively for the three samples discussed above (Figure 4-3). This result clearly shows that the purity increases as the current density and pressure are increased.

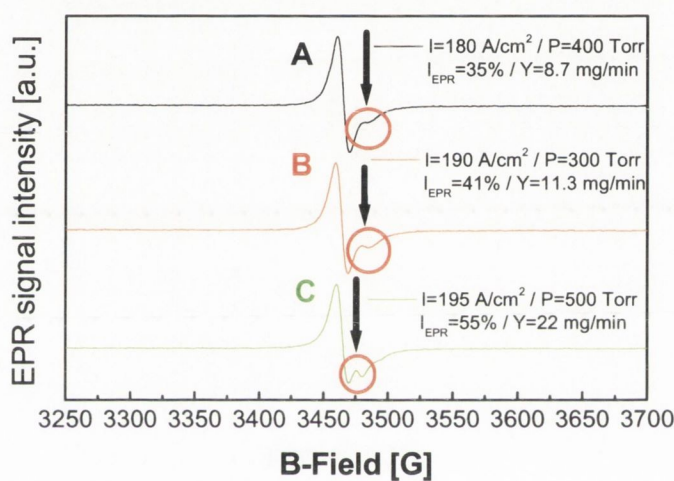


Figure 4-3: Electron paramagnetic resonance (EPR) spectra with an increase in purity.

In order to calculate the absolute purity of sample **C** the method described in Chapter 2 and elsewhere^{18,19} was used. This involved purification of the soot using a conjugated polymer solution which suspends some of the nanotubes while the rest of the nanotubes and all of the impurities sediment out of solution (shown in Chapter 2.1.3). Both nanotube and impurity content in sediment and solution can then be measured using EPR and TGA.

EPR spectra for soot, sediment and solution are shown in Figure 4-4. Each curve consists of low and high field absorption lines representing impurities and nanotubes

respectively. Both soot and sediment spectra display significant impurity components while the nanotube component in the sediment is reduced relative to the soot line. This clearly shows that after decantation most impurities are in the sediment. However, in the solute graph it is seen that the high field peak predominates. This shows that this solution is rich in nanotubes with only trace amounts of graphitic impurities.

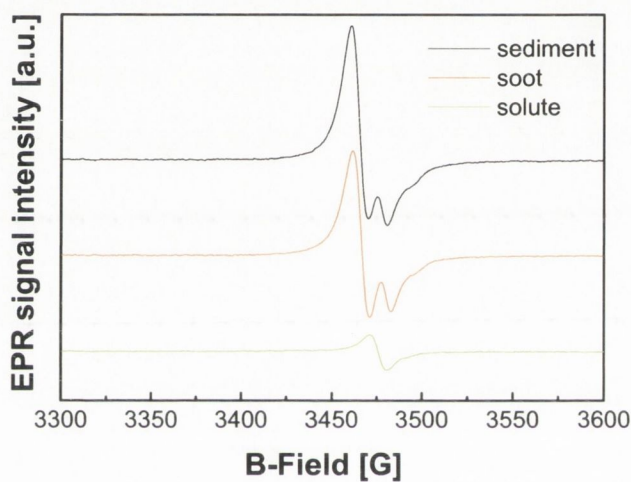


Figure 4-4: Electron paramagnetic resonance spectra for the purest sample [sample C, 190 A/cm², 500 Torr, yield 24 mg/min, absolute purity 48%).

Each of the spectra described above were integrated and fitted to 2 Lorentzian's, representing nanotubes and impurities. The areas under each curve were calculated to represent the entire mass of each species (nanotube or impurity) in each phase (sediment or solution)¹¹⁵. Then, by comparing the intensity of the nanotube component of the solute with the total nanotube component (solute and sediment) it was possible to calculate the fraction, by mass, of nanotubes remaining in solution¹¹⁵. In this case 21% by mass of the nanotubes added to the polymer remained in solution, no impurities could be observed.

4.6 Thermal gravimetric analysis for nanotube soot quantification

Thermal gravimetric analysis (TGA) results for the PmPV composite sample described above with sample **C**, current density 195 A/cm² and Helium pressure of 500 Torr are shown in Figure 4-5. The middle curve represents the TGA trace for a free standing film made from the purified polymer-nanotube solution. In comparison, the TGA traces for a pure PmPV film and the untreated soot are also shown. It is clear from this graph that the PmPV alone has been almost completely oxidised by approximately 700°C. In the higher temperature region of 750-850°C degradation of the nanotubes can be observed. Between 700°C and 750°C virtually no oxidation occurs, corresponding to a plateau in the TGA curve representing the nanotube component. Correcting for the residual mass of polymer remaining, this composite curve indicates that the fraction of the composite due to nanotubes is 5% by mass. Knowing the total solute mass, (64.6 mg) allows the calculation of the mass of nanotubes held in solution as 2.0 mg. Given the EPR result showed that 21% of all nanotubes were held in solution, the total initial mass of nanotubes can be calculated (in the raw soot of 20.1 mg) as 9.52 mg. This gives an absolute nanotube purity of the raw soot of 48%.

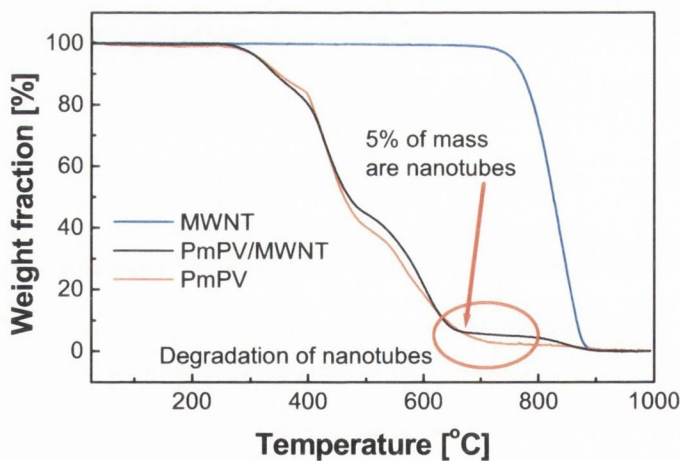


Figure 4-5: TGA curves for polymer (PmPV), composite (PmPV/MWNT) and the multi-walled carbon nanotube sample with the highest purity.

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Chapter 5

Experimental Polymer Composite Films

5.1 Introduction

This Chapter will describe a series of reinforced polymer matrices produced by different polymer film forming methods. The first section of this Chapter describes two film forming methods where two different polymer matrices, poly(vinyl alcohol) and poly(9-vinyl carbazole), reinforced by arc grown multi walled carbon nanotubes (AMWNT) are compared in terms of mechanical and thermal properties. These film production methods were drop-casting, where the polymer/nanotube solution was dropped on a glass substrate and the solvent evaporates in an oven, and spin-coating, where the solvent of the polymer/nanotube solution was evaporated by spinning the samples. The advantage of these film forming methods are that only a minute amount of polymer/nanotube solutions are necessary to create polymer film samples. The disadvantage is that at both film production methods the polymer composite films are placed on glass substrates. As the mechanical measurements on the thin polymer films placed on glass substrates were in this section performed by nano-indentation a certain film thickness (~1 micron) had to be achieved to avoid glass effects. As the glass substrate is much harder the values for mechanical properties would be negatively affected on the real value. Nano-indentation is performed by a pyramid shaped diamond indenter who measures the elastic deformation of the material. Young's modulus and hardness of the polymer

composites can be calculated with this method. This was performed in a depth region of only a few tenths of a micrometer of the surface layer to avoid the earlier mentioned influences on the measurements. In order to compare this novel determination method for the Young's modulus and hardness of extremely thin polymer composite films, further investigations of the mechanical results using a different production method was performed. Therefore, free standing polymer composite films and a traditional measurement technique -tensile testing- was performed and compared with the nano-indentation results.

Instead of placing polymer films on glass substrates, polymer solutions were dropped onto non-adhering Teflon discs. After evaporation of the solvents the composite material could easily be removed resulting in free standing films. This could only be performed with one of the formerly used polymer matrices, poly(vinyl alcohol), as film forming difficulties occurred for poly(9-vinyl carbazole). Mechanical properties of free standing polymer composite films could be measured using a standard analysis method - tensile testing. Here the polymer films were stretched until they break. Elastic and plastic deformations and the necessary energy to break the polymer composite films supplied important information on the mechanical properties of these novel materials. Furthermore, results for both film forming methods using differential scanning calorimetric analysis showed that including CNT to the semi-crystalline poly(vinyl alcohol), the crystallinity of the matrix increases dramatically with increasing mass fractions of carbon nanotubes. This was found to be an important effect as crystallinity occurs on the nanotube surface. It is therefore believed that the total surface area of the involved nanotube must play a significant role on the reinforcement effect. Thus, a range of differently produced CNT with varying diameters was used to reinforce this standard polymer matrix. It was found that the highest surface area of CNT relative to the volume of polymer film showed the

highest reinforcing effects. Therefore, CNT with the smallest diameter showed the highest increase of mechanical properties. Further evidence on the diameter effect will be shown in an additional section where small diameter nanotubes were used for investigations on the mechanical properties.

The interfacial shear strength between nanotube and polymer chain is limited by the relatively weak van der Waals forces. Thus, functionalisation of thin MWNT was performed by covalently bonding polymer chains directly onto the nanotubes followed by dispersion of the functionalised CNT in the same polymer matrix. This method can be further improved but has already shown significant reinforcing effects for only very small volumetric amount of reinforcing agents.

Here, the mechanical and thermal properties of CNT composites will be presented for differently produced polymer samples and matrices. These are compared with each other using different measurement methods and different types of CNT. Furthermore, morphology of the polymer composite will be investigated in order to explain the interaction between nanofillers and polymer matrix. In addition a range of transmission electron microscopy micrographs will be shown to visualise these interactions.

5.2 Thin polymer composite films on glass substrates

5.2.1 Mechanical nano-indentation test

Values for Young's modulus and hardness for thin and free standing poly(vinyl alcohol) films were obtained by nano-indentation¹⁻³ using a SCEM Instruments Nano-hardness tester. Nine indentation points were measured for all samples using a 3x3 matrix with a distance of 50 μm between each indent. The maximum indentation

force for both thin and free standing polymer composite films was 0.5 mN with a loading/unloading rate of 1 mN/min.

The measured values were averaged and errors were shown by the standard deviation. These data were plotted versus the volume fraction of the introduced arc grown MWNT.

In order to plot the data versus the volume fraction and fit theoretical curves shown later in Figure 5-3 the involved mass fractions of AMWNT were transferred into volume fraction values by assuming a density for perfectly graphitised MWNT of 2.16 g/cm^3 ⁴ and a polymer density of 1.3 g/cm^3 for both polymers. In addition Young's modulus for MWNT was taken to be 1 TPa in agreement with recent research studies of Lourie and Wagner⁵ where Raman spectroscopy was performed in order to measure the compressive deformation of nanotubes embedded in a polymer matrix. Young's moduli for pure polymer matrices were needed for the transformation and were determined in the compression mode by nano-indentation. They were found to be 6.9 GPa and 2.1 GPa for PVA and PVK respectively. As these values seem to be very high it is possible that a glass effect took place in this experiment. Therefore, the values were normalised, for comparison reason as shown in Figure 5-3, by dividing the results with the reference modulus value of PVA.

Significant increases in Young's modulus and hardness were observed for both AMWNT reinforced polymer matrices. In the case of the PVA based composite an increase from 6.9 GPa to 12.5 GPa and 291 MPa to 474 MPa was recorded for Young's modulus and hardness values respectively up to an approximate nanotube loading level of 0.5 vol.%. This corresponds to an increase of 182% in the case of Young's modulus and 163% in hardness which is shown in Figure 5-1.

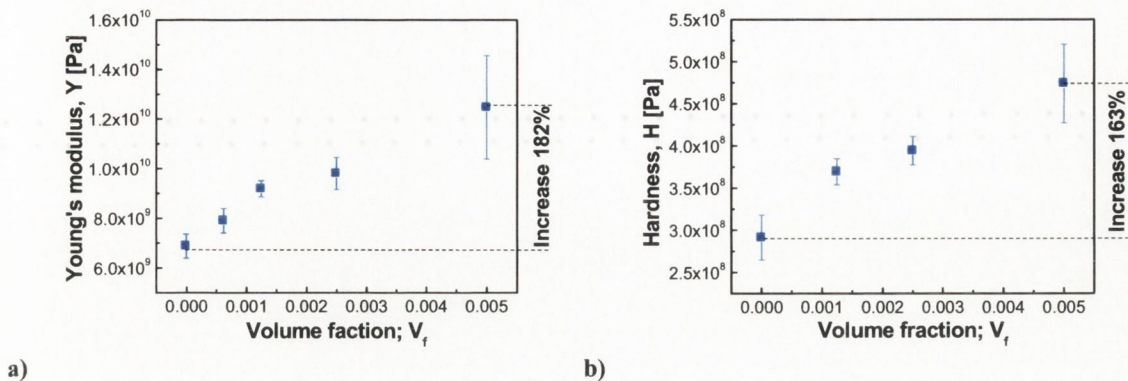


Figure 5-1: Increase of mechanical properties such as a) Young's modulus increase of 182% while adding 0.5 Vol.% of multi walled carbon nanotubes and b) hardness, 163% for polyvinyl alcohol by adding only 0.5 Vol.% of multi walled carbon nanotubes

Similar results were observed for PVK based composites as shown in Figure 5-2. Young's modulus increased from 2.1 GPa for pure PVK to 5.7 GPa for the 5 vol.% sample. Likewise, hardness values increased linearly from 310 MPa for pure PVK to 614 MPa for the 5 vol.% sample before levelling off. This corresponds to increases of 273% and 198%, respectively.

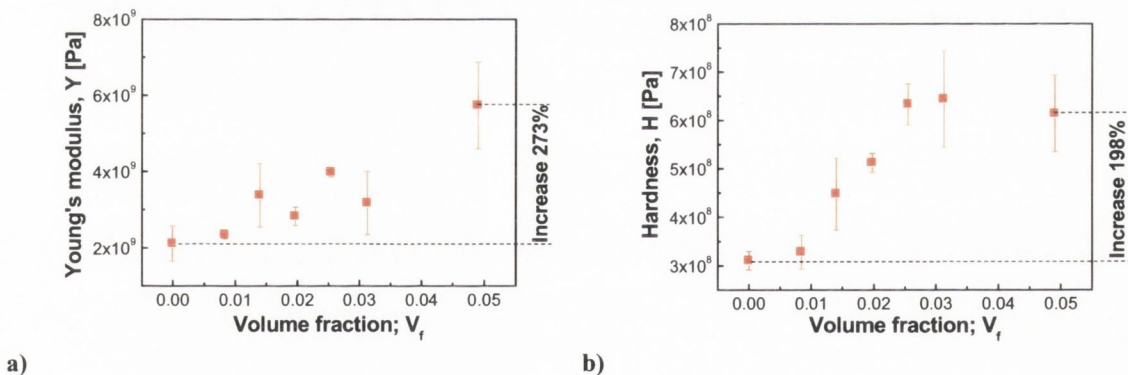


Figure 5-2: a) Young's modulus increase of 273% for poly(9-vinyl carbazole) by adding 5 volumetric percent of multi walled carbon nanotubes b) Hardness increase of 198% for poly(9-vinyl carbazole) by adding 5 volumetric percent of multi walled carbon nanotubes.

Qian and co-workers⁴ have shown in previous work that Young's modulus for nanotube reinforced polymer composites can be modelled using the Halpin-Tsai

theory. The modulus values based on this equation agree reasonably well with the experimental values for a variety of reinforcement geometries⁶.

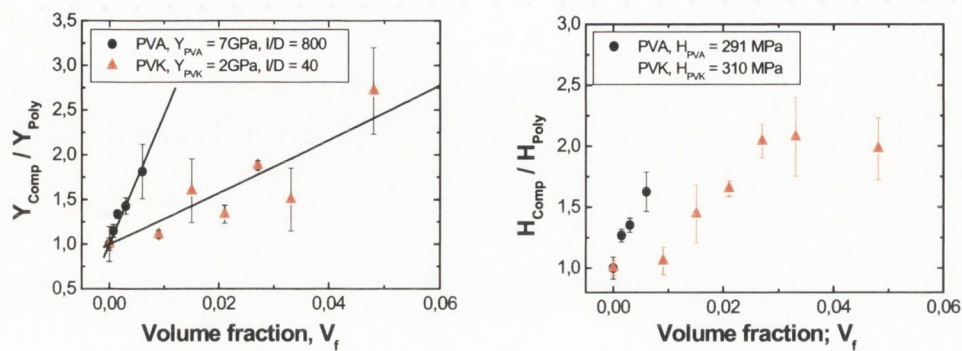


Figure 5-3: Increases for both polyvinyl alcohol and poly(9-vinyl carbazole) in a) normalised Young's modulus versus volume fraction of multi wall carbon nanotubes fitted with theoretical predictions of Halpin and Tsai and b) normalised hardness versus volume fraction of multi wall carbon nanotubes

Shown in Figure 5-3a are normalised Young's moduli values for both PVA and PVK plotted versus volume fraction of AMWNT in addition to a fit to the Halpin-Tsai equation. It can clearly be seen that the values measured with the nano-indenter do indeed fit in reasonable agreement with the theoretically calculated Young's moduli for PVA and PVK respectively.

As Y was assumed to be 1 TPa, the aspect ratio is a free parameter and can be obtained from a fit to the Halpin-Tsai equation. The aspect ration (l/D) values obtained were 800 and 40 for the PVA and PVK composites respectively. This result is unexpected though as the same batch of AMWNT was used to produce each composite and the true aspect ratio, as measured by TEM is close to 100. However, as the Halpin-Tsai equation is derived assuming perfect stress transfer it is likely that the difference in predicted aspect ratios is a measure of the stress transfer for both matrices. This result shows that the interfacial bonding is far superior for the PVA matrix. In order to understand the differences in interfacial bonding for the two host polymers DSC measurements were carried out in the following section.

The relatively large increase of mechanical properties of these polymers by the introduction of CNT suggests a relative homogeneous dispersion of CNT in the polymer matrices and a strong interfacial bonding between polymer chains and nanotubes. Homogeneous dispersion and strong bonding between filler and matrix is essential for the reinforcing of polymers with CNT. In case of eventual bundle formation the reinforcement is expected to be lower as the total surface area of the fillers is decreased. In addition, to this the interfacial bonding between single nanotubes in bundles is weak as only van der Waals forces interact. These issues will be further investigated by TEM and is shown in a subsequent section.

5.2.2 Thermal Analysis

Thermal properties such as decomposition temperature of the used polymer were examined by thermal gravimetric analysis (TGA) using a Mettler TA 4000 DSC analyser. Furthermore, glass transition and melting temperatures were determined by differential scanning calorimetry (DSC) (TA Instruments DSC-2920). Approximately 10 mg of free standing polymer films were used in both methods for all polymer composites. Aluminium oxide crucibles were used to perform TGA experiments under a constant air flow of 10 L/min. The temperature ranges for TGA were between 25-1000°C. Standard aluminium pans and caps were used in the case of the DSC experiments. Heating and cooling rates were 10°C/min for both polymer samples. In order to measure all results under the same circumstances the analysis of the data was performed on the second heating run in each case. Liquid nitrogen was used as a coolant in the DSC apparatus and Helium as a purge gas. In DSC experiments the temperature was increased from 0°-220°C for PVA and 0°-300°C in the case of PVK. True nanotube mass fractions were measured by thermo gravimetric analysis (TGA) and found to range between 0.1-1 wt.% for PVA shown in Figure 5-4a, whereas in

case of PVK the true mass fraction was found to vary between 1.5-8 wt.% shown in Figure 5-4b.

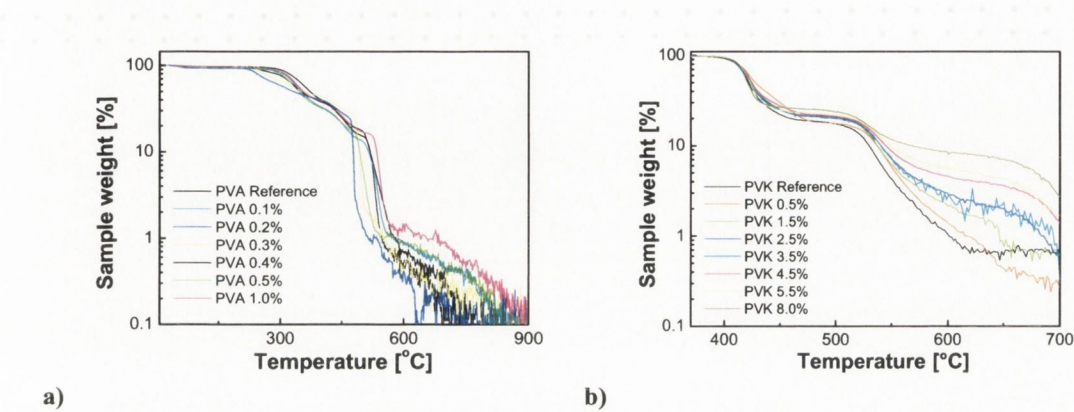


Figure 5-4: Thermal gravimetric analysis graph for the determination of the true weight fraction of carbon nanotubes involved in a) polyvinyl alcohol and b) poly(9-vinyl carbazole)

As shown in Figure 5-5a it is very obvious that AMWNT have a strong influence on the thermal properties of polymers. Pure PVK samples show typical thermal behaviour for an amorphous polymer. Only one glass transition point (T_{g2}) can be observed with no melting peak. However, it can be observed that by introducing AMWNT to the polymer matrix a second glass transition point appears, named T_{g1} . This phenomenon can be observed for all nanotube reinforced PVK composites and may be explained by the formation of a second polymer phase due to the interaction of the AMWNT with the polymer matrix⁷.

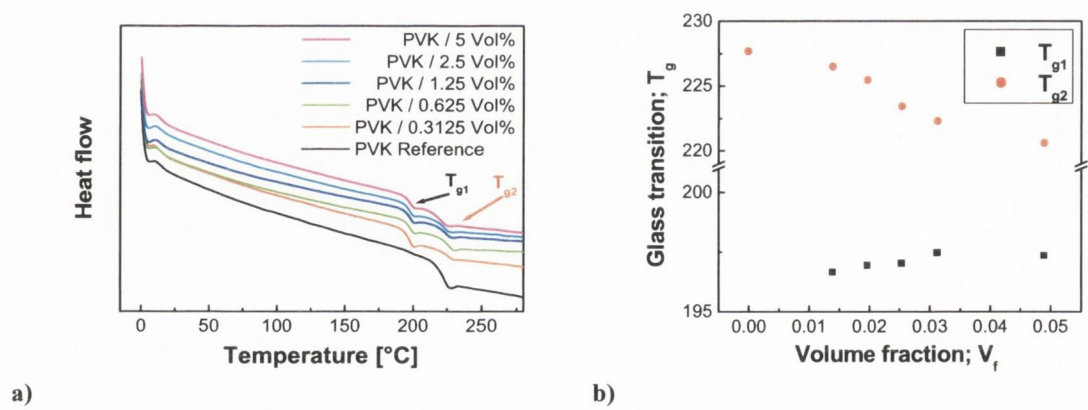


Figure 5-5: a) Differential scanning calorimetry graph of poly(9-vinyl carbazole) b) Glass transition temperatures of poly(9-vinyl carbazole) reinforced with multi walled carbon nanotubes.

In addition a shift in T_{g2} can be observed. Thermal conductivities of AMWNT are known to be $>6000 \text{ W/K}\cdot\text{m}^8$. Thus, in the local region around the nanotubes, polymer chain reorientation can occur earlier as the temperature in the local nanotube region is higher than the average temperature of the polymer. Therefore, T_{g2} decreases from 228°C to 220°C (Figure 5-5b).

A different effect can be observed in the case of polyvinyl alcohol (PVA). Here is shown in Figure 5-6a that PVA demonstrates typical semi-crystalline behaviour. A melting peak can clearly be observed in the high temperature region.

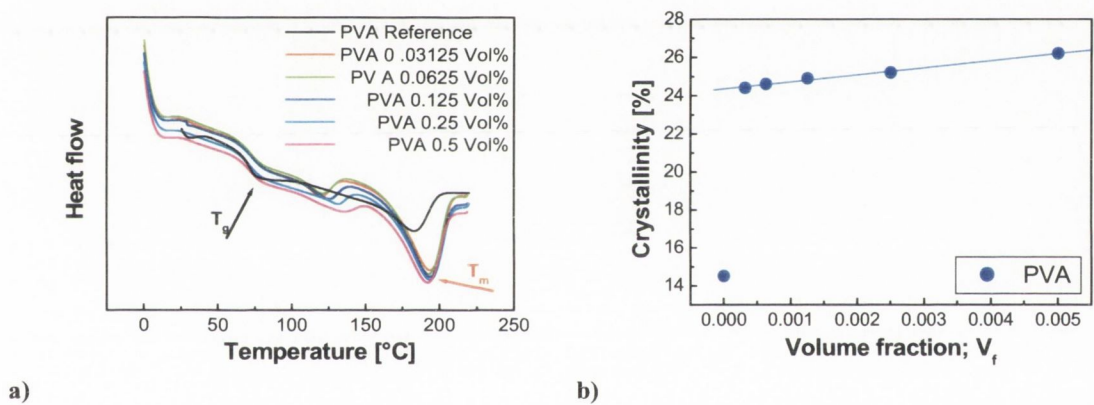


Figure 5-6: a) Differential scanning calorimetric graph for polyvinyl alcohol and arc grown multi walled carbon nanotubes and b) Graph on the amount of crystallinity plotted versus the mass fraction of multi walled carbon nanotubes

The melting peak temperature (T_m) for pure PVA was found to be 180°C and increased up to almost 200°C by adding only 0.5 vol% of AMWNT to the PVA matrix. Also it can be observed that in case of the composite samples melting and re-crystallisation of smaller crystals occur shortly before the main melting peak. This is a known phenomenon for a large crystal size distribution⁹⁻¹¹. Furthermore, a significant increase of the area under the melting peak, which is proportional to the crystallinity of the polymer matrix, was observed. Crystallinity for pure PVA was found to be only

14%, whereas this value increased rapidly by adding only 0.0625 vol.% of AMWNT to 24% with further linear increase of up to 27% for 0.5 vol.% of AMWNT added to the PVA matrix material (shown in Figure 5-6b). The slope of the linear fit in Figure 5-6b was found to be 3.7. It was determined in order to calculate the crystalline coating of polymer chains around the CNT using Equation 5-2 in following microscopy section. In general, the presence of modifier particles, such as CNT, even at low loading fractions, influences the crystallinity behaviour of semi-crystalline polymer matrices. The development of polymorphism, for example, is a common effect in other semi-crystalline polymer matrices reinforced with layered silicate particles^{10,12,13} as well as for other PVA nano-composites¹⁴. This relates very well to the high increase in mechanical properties recorded since the interfacial bonding between polymer and nanotube surface is much higher when the amount of crystallinity in a polymer matrix is increased.

Crystalline polymer matrices show much higher mechanical properties due to the higher interaction interface in an oriented system rather than point interactions in an amorphous non-oriented system as shown in sketch below.

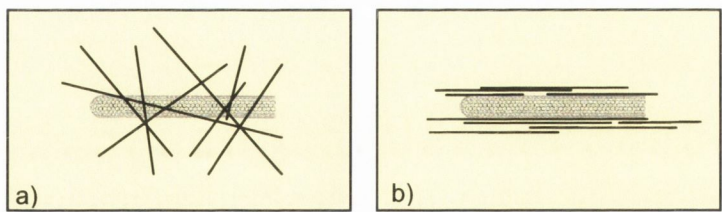


Figure 5-7: Sketch of a) amorphous polymer chain point interactions and b) oriented area interactions of crystalline polymer chains

The glass transition temperature, T_g for PVA dropped from 75°C to 50°C for all samples reinforced with AMWNT. As an explanation for this behaviour the same effect can be explained as for the PVK earlier in this section. Since, thermal conductivity should increase dramatically due to the addition of superb thermal conductors, polymer chains can reorient locally earlier hence T_g drops significantly.

The non-isothermal differential scanning calorimetry diagrams in this section have shown a hetero-nucleation effect associated with the introduced carbon nanotubes into poly(9-vinyl carbazole) and polyvinyl alcohol. Similar effects have been reported for silicate nano-particles dispersed in PVA and a range of different semi-crystalline thermoplastic polymer materials^{7,10,11,14-16}. It was shown in these studies that the nucleation effect were the most prominent in small loading fractions, in agreement with the observed results in Figure 5-5a and b and Figure 5-6a and b. Furthermore, these nucleation effects give evidence that the degree of crystallinity follows the trend of increasing surface area of carbon nanotubes. This will be further investigated and discussed in Chapter 5-3.

5.2.3 Transmission Electron Microscopy

To characterise the dispersion of CNT in the polymer matrices and the interaction between the AMWNT surface and the polymer chains, transmission electron microscopy (TEM) investigations were carried out using a Hitachi H7000 electron microscope. The operating accelerating voltage was typically 100 keV. All TEM investigations were carried out on formvar coated copper grids.

Shown in Figure 5-8a is a TEM micrograph focused on one point in a PVA film which had torn after exposure to a concentrated electron beam in the electron microscope. By magnifying the right hand part in Figure 5-8a a nanotube can be observed protruding from the polymer fracture zone. It is likely that local heating of the film by the beam caused contraction resulting in the nanotube being pulled from the polymer film. However, a higher magnification image, shown in Figure 5-8c clearly shows this nanotube coated with a thin layer of polymer. From the DSC measurements it can be said that these layers of polymer must be of crystalline nature.

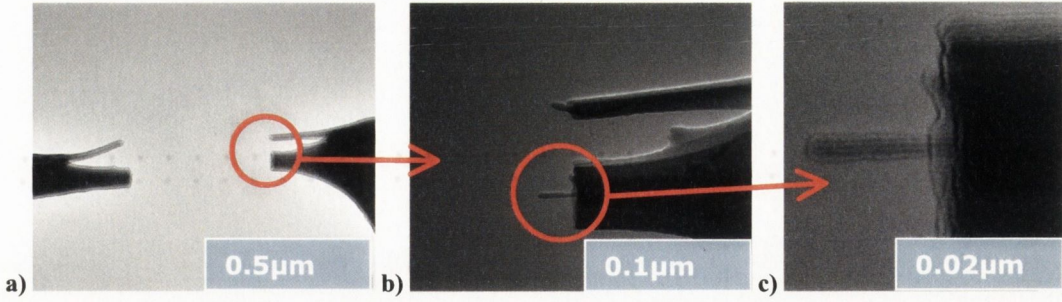


Figure 5-8: Transmission electron microscope micrograph for polyvinyl alcohol with an arc grown multi walled carbon nanotube sticking out showing a strong interaction between nanotube and polymer matrix

This is a very important and remarkable result as it shows that the polymer film did not break at the polymer-nanotube interface but in the polymer matrix. This suggests that the interfacial stress (τ) between AMWNT and the PVA matrix is stronger than the shear stress of the polymer ($\sigma_{\text{SHEAR}}=41$ MPa). Furthermore, detailed calculations can be made using Equation 5-1.

$$F_p < F_{\text{INTERFACE}}$$

$$F_p = \sigma_{\text{SHEAR}} \cdot A_p$$

$$F_{\text{INTERFACE}} = \tau \cdot A_{\text{INTERFACE}}$$

$$\sigma_{\text{SHEAR}} \cdot A_p < \tau \cdot A_{\text{INTERFACE}}$$

$$\sigma_{\text{SHEAR}} \cdot l \cdot 2\pi(R + b) < \tau \cdot l \cdot 2\pi R$$

$$\sigma_{\text{SHEAR}}(R + b) < \tau R$$

$$\Rightarrow \tau > \sigma_{\text{SHEAR}} \cdot \frac{(R + b)}{R} \quad \text{Equation 5-1}$$

Here, F_p is the shear force needed to break the polymer; $F_{\text{INTERFACE}}$ stands for the shear force needed to break the interface between the polymer coating and the nanotube. Furthermore, A stands for the surface area of the interface ($A_{\text{INTERFACE}}$) and the polymer coating (A_p) around the nanotube. R is the radius of the carbon

nanotube (12 nm), l stands for the pull-out length (200 nm) in Figure 5-8c and b describes the crystal coating thickness which can be calculated from equation 5-4. This equation was easily derived by relating the thickness of the crystalline coating to the volume fraction of nanotubes by considering the crystallinity as two components. One that linked with the bulk polymer and the second component associated with the CNT. Assuming a cylindrical geometry for the CNT nucleated coating, an equation for the composite crystallinity C , as a function of the number of CNT in the polymer film, N , can be written. In this equation the first term relates to the bulk polymer crystallinity, whereas the second part is related to the CNT induced crystallinity.

$$C = \frac{V_0 + N \left[\pi(R+b)^2 l_{NT} - \pi R^2 l_{NT} \right]}{V} \quad \text{Equation 5-2}$$

where V_0 is the volume of crystallinity regions not associated with CNT, R is the average CNT radius, b is the average thickness of the crystalline coating, l_{NT} is the CNT length and V is the film volume. In addition the CNT volume fraction, V_f is defined as follows:

$$V_f = \frac{N \pi R^2 l_{NT}}{V} \quad \text{Equation 5-3}$$

Combining these two equations gives the expression for the crystallinity as a function of volume fraction shown in equation 5-4¹⁷.

The slope of the linear fit of crystallinity values versus volume fraction of CNT determined in Figure 5-6b was found to be 3.7. Therefore, the crystalline PVA coating thickness around AMWNT could be calculated using Equation 5-4 and was found to be 14 nm.

$$a) C = V_f \left[\frac{b^2}{R^2} + \frac{b}{R} \right] + \frac{V_0}{V}$$

Equation 5-4

b)

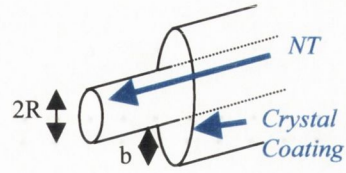


Figure 5-9: a) Model to calculate the thickness of crystalline coating of polymer on carbon nanotubes and b) Schematic of crystalline coating of a carbon nanotube

Further calculations using Equation 5-1 show that, the interfacial stress (τ) between PVA and the AMWNT must be therefore > 88.8 MPa. From earlier reported theoretical calculations for amorphous polymers of Wagner *et al.*¹⁸ and further experimental work of Wagner and Barber *et al.*^{18,19} it was found that covalently bonded polymers show a interfacial strength of <50 MPa whereas, van der Waals interacting polymer chains show only 10 MPa of interfacial strength. Crystalline interaction between polymer chains and fillers are well known to be larger than amorphous ordered polymer chains, therefore the calculated value of $\tau > 88$ MPa is in reasonable agreement with the predictions of Barber and Wagner *et al.*^{18,19}.

5.3 Free standing PVA/CNT films

In order to further investigate the results shown in the previous section of this Chapter, free standing macroscopic polyvinyl alcohol (PVA) films were produced and analysed. Similar mechanical results for these free standing films were obtained as for the substrate films. Then the effect of the reinforcing mechanism was investigated with a range of differently produced carbon nanotubes. A theoretical model to explain the reinforcement effects has been developed and is presented in this section.

Furthermore, direct comparison between nano-indentation results and tensile tested results are shown.

5.3.1 Mechanical tensile testing

Tensile testing is a standard mechanical test and was carried out in this part of the study using a Zwick Z100 tensile tester. To plot the applied force versus the deformation strain of the sample, a 100N load cell was used. A position controlled cross head speed of 0.5 mm/min was applied to obtain mechanical properties such as tensile modulus, E , yielding point, P_Y and stress, S_Y , ultimate tensile strength, S and the energy needed to break the polymer sample known as toughness, T . Furthermore, the elongation at break, ϵ_B , was determined using this method.

Shown in Figure 5-10 are the normalised tensile moduli for composite films containing 6 different nanotube types plotted versus the volume fraction of CNT. Double walled carbon nanotubes (DWNT), catalytic multi walled CNT from Namur (NMWNT), catalytic multi walled CNT from Orléans (OMWNT), hydroxyl functionalised multi walled CNT (OHMWNT), arc grown multi walled CNT (AMWNT) and HipCO grown single walled CNT (HipCO). An increase in tensile modulus of up to a factor of 2 was observed at very low loading levels. In most cases straight lines can be fit. In the case of the DWNT the linear curve fits only at low volume fractions. This is probably due to bundle formation for higher volume fractions.

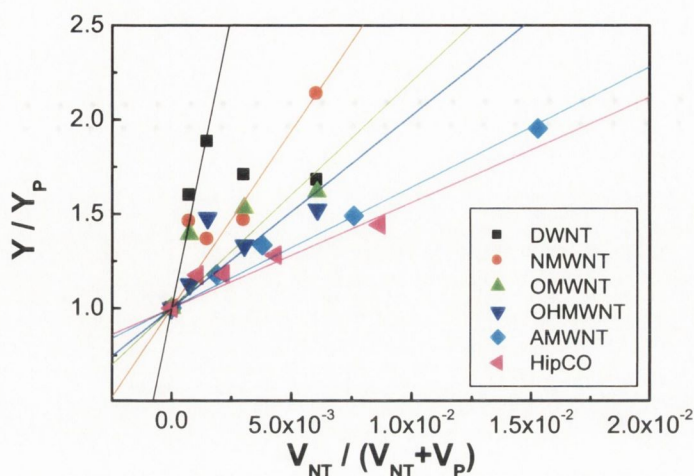


Figure 5-10: Normalised tensile modulus plot versus volume fraction of nanotubes per volume of polymer film

Two of the most common theories for classical polymer reinforcement used to analyse these types of curves are the modified Krenchel's rule-of-mixtures²⁰ and the Halpin-Tsai-theory²¹. Analysis using the modified Krenchel's rule-of-mixtures gives the nanotube tensile modulus while if the NT modulus and diameter are known, analysis using Halpin-Tsai-theory gives the NT length. These parameters have been calculated in all cases and are presented in Table 5-1 along with the expected values and the slopes of the fit curves shown in Figure 5-10. With the exception of the nanotube length for the AMWNT none of these calculated values match well to the expected values. This suggests that neither of these theories apply well to these samples.

Tubes	Diameter, d	Slope, m	Coating, b	Rule of mixtures		Halpin-Tsai	
				Y_c (calculated)	Y_c (predicted)	Length (calculated)	Length (predicted)
DWNT	2.8 nm	622	12 nm	5.1 TPa	~1 TPa	200 μ m	2 μ m
NMWNT	14 nm	188	16 nm	1.4 TPa	<0.1 TPa	500 μ m	<50 μ m
OMWNT	16 nm	120	12 nm	0.9 TPa	<0.1 TPa	500 μ m	<50 μ m
OHMWNT	15 nm	102	35 nm	0.8 TPa	<0.1 TPa	500 μ m	<50 μ m
AMWNT	24 nm	64	10 nm	0.5 TPa	~1 TPa	3 μ m	1-2 μ m
SWNT	9nm(bundles)	56	-	0.4 TPa	-	-	-

Table 5-1: Shown in columns 2-4 are the measured NT diameters, slopes of the normalised modulus versus volume fraction curves and crystalline coating thickness. Presented in columns 5-8 are the calculated and predicted Young's moduli and lengths of carbon nanotubes using the rule of mixtures and the Halpin-Tsai theories. Modulus for PVA is 1.9 GPa. The measured values for diameter (column 2) and the predicted values for NT modulus (column 6) were used to calculate the NT length from Halpin Tsai theory.

Empirically, it can be seen from Table 5-1 that the slopes, m do not scale with the expected modulus or length. However, as the NT diameter increases the slope tends to decrease. To study this observation in more detail the slope of the reinforcement is plotted versus the NT diameter on a log-log scale in Figure 5-11.

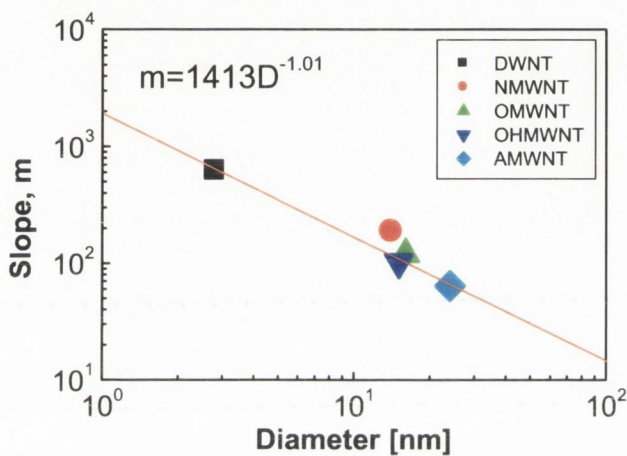


Figure 5-11: Reinforcement decrease (slope, m) versus increase of nanotube diameter on a log-log scale

A straight line of slope close to -1 could be fitted to this data. This is clearly indicating that the reinforcement is inversely proportional to the nanotube diameter. It can be shown that this suggests that the increase in normalised modulus is proportional to the total nanotube surface area, **SA**, per unit volume of polymer film. To test this hypothesis the x-axis of Figure 5-10 can be transformed to represent the total **SA** per volume. This is shown in Figure 5-12.

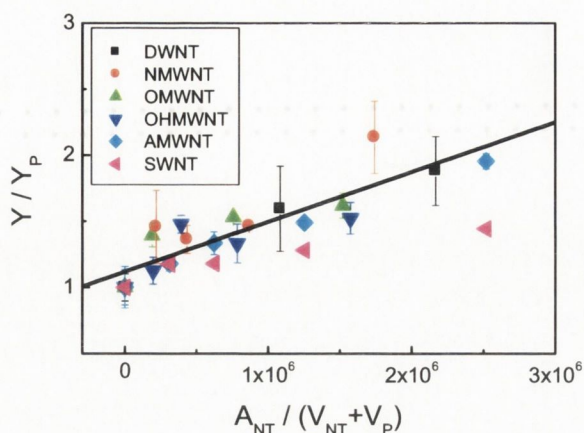


Figure 5-12: Normalised tensile modulus for all polymer/nanotube samples plotted versus the total surface area per volume of all composite films. Linear dependency of total surface area is shown for all samples apart from HipCo-SWNT due to bundle formation. Volume fractions for nanotubes were calculated from the added mass fractions using equation 3-15 shown in Chapter 3.

It can be observed that all data points apart from the HipCO-SWNT fall on the same universal curve. This clearly shows a dependency of the reinforcement of polymer composites using CNT on the total nanotube **SA**. In case of HipCO-SWNT, reinforcement is lower than predicted by this model. This can be explained by the fact that bundle formation is known to occur for these materials. This results in a lower level of reinforcement in these materials due to SWNT slippage in the bundles^{22,23} as interfacial interaction between single nanotubes is lower than interfacial interaction between CNT and polymer chains.

5.3.2 Thermal analysis – DSC/TGA

Thermal properties of free standing PVA films such as the T_g and T_m of this semi-crystalline polymer were examined using a Perkin Elmer Diamond DSC power compensation instrument. A sample of approximately 10 mg of free standing PVA film was placed into a standard aluminium pan with cap for DSC experiments.

Heating rates were 40°C/min for a temperature range of 0°-220°C . Helium was used as purge gas and liquid nitrogen as a coolant for the DSC apparatus. In order to study the crystallisation behaviour of PVA/CNT composites a cooling rate of 40°C/min was chosen.

As the surface area appears to play a fundamental role in the reinforcement mechanism it is important to understand the nature of the interface for each composite type. To do this, DSC measurements were carried out on all films. Shown in Figure 5-13a are the melting peaks of the nanotube filled high volume fraction PVA films. In all cases a large melt peak was observed at approximately 170°-210°C indicating a degree of polymer crystallinity in all composites.

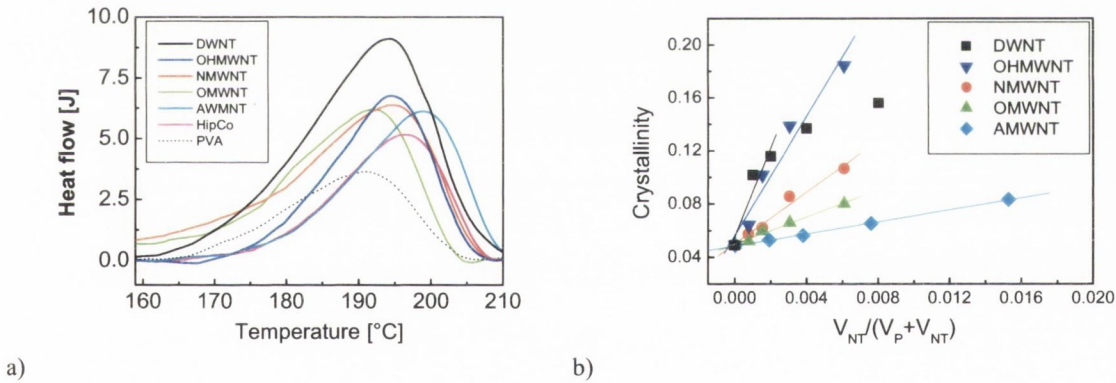


Figure 5-13: a) Crystallisation peaks of all high volume fraction carbon nanotubes samples added to free standing polyvinyl alcohol polymer composite films. b) Linear crystallinity increase for all composites versus volume fraction of carbon nanotubes per volume of composite film

This crystallinity was observed to increase with nanotube content. Shown in Figure 5-13b is the linear increase of crystallinity for all PVA/CNT samples plotted versus the volume fraction of CNT present. The linear increase in crystallinity suggests that each CNT has a crystal coating with a thickness that is constant for each nanotube type.

This shows that all samples used in this study had a similar (crystalline) polymer nanotube interface.

As shown in previous section it is possible to calculate the thickness of this coating from the slope of the crystallinity versus volume fraction graph using Equation 5-2. This model gives crystal coating thickness ranging from 10 nm for AMWNT to 35 nm for OHMWNT. The calculated values are given in Table 5-1. This result is interesting as it shows that PVA can crystallise on the surface of both well graphitised nanotubes such as AMWNT and poorly graphitised nanotubes such as those that are catalytically grown. This suggests that the crystallinity is not templated by the hexagonal lattice of the nanotube but can occur on any cylindrical NT surface. This is in good agreement with predictions by Coleman and Ferreira²⁴.

Thermal gravimetric analysis (TGA) on free standing PVA films was performed using a Perkin Elmer Diamond TGA power compensation instrument. Samples of approximately 10mg of either CNT or polymer films containing CNT were placed into an aluminium oxide crucible and positioned inside a temperature programmable furnace. TGA was performed under a constant air flow of 20 L/min using a heating rate of 10°C/min from 25°-1000°C.

It was found that a maximum of 1.8 wt% of AMWNT could be dispersed in PVA/H₂O solution. In all other cases, analysis of the real mass fractions was extremely difficult as they were <1 wt%. As not all CNT could be dispersed due to their entanglement it can only be estimated for the other samples that <1 wt% of CNT were dispersed. TEM micrographs showed that only short catalytic grown CNT disperse in the polymer solutions. Longer tubes were not able to disperse due to their entanglement, thereby forming a sediment in the sample bottle. Sediment and solution were separated by decantation of PVA solutions.

5.3.3 Electron microscopy – TEM/SEM

In order to characterise the dispersion of arc and catalytic grown MWNT and HipCO grown SWNT in polyvinyl alcohol transmission and scanning electron microscopy was carried out. TEM investigations were performed using a Hitachi H7000 electron microscope. The operating accelerating voltage was typically 100 kV. All TEM investigations were carried out on formvar coated copper grids. SEM micrographs were prepared using a Hitachi S-4300 field emission scanning electron microscope performed with an electron acceleration voltage range of 10-30 kV.

Shown in Figure 5-14a and b are TEM micrographs of several arc grown multi walled carbon nanotubes dispersed in PVA. Focusing on a single AMWNT shown in Figure 5-14b clearly visualise the PVA coating around the tubule.

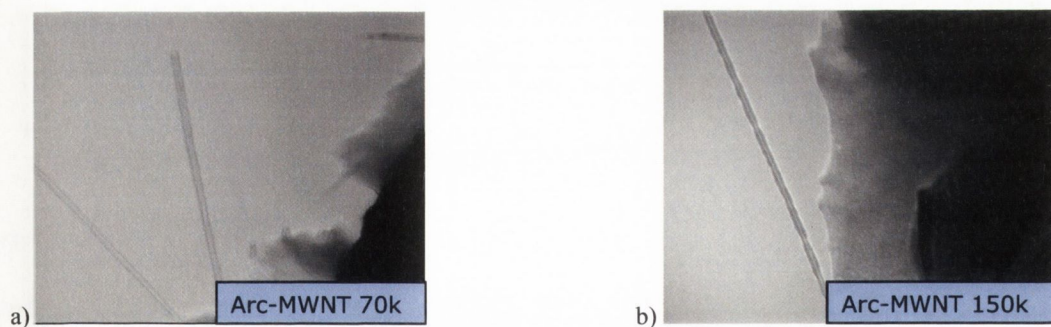


Figure 5-14: Transmission electron microscopy micrographs of arc grown multi walled carbon nanotubes dispersed in polyvinyl alcohol

Randomly oriented catalytic grown multi walled carbon nanotubes can be observed in both micrographs shown in Figure 5-15a and b. Figure 5-15a shows NMWNT dispersed in polyvinyl alcohol, whereas Figure 5-15b shows OMWNT in the same matrix. Both samples are showing relative homogenous dispersion and only small amounts of agglomerates or impurities such as catalytic particles.

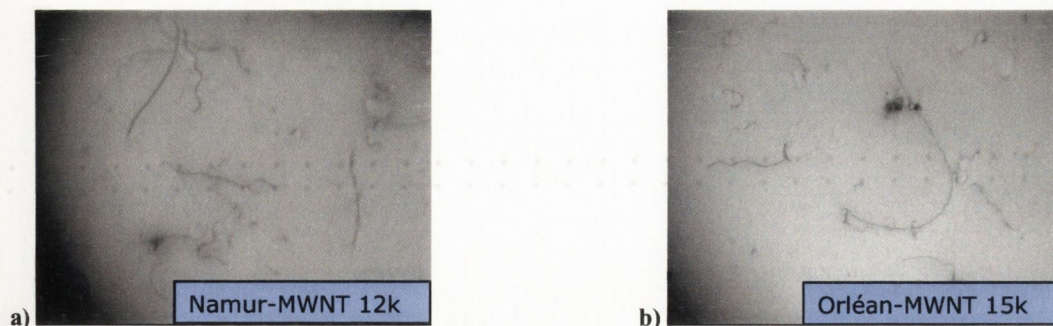


Figure 5-15: Transmission electron microscopy micrographs of a) catalytic grown multi walled carbon nanotubes from Namur and b) catalytic grown multi walled carbon nanotube from Orléans. Both samples are dispersed in polyvinyl alcohol

Figure 5-16a and b shows SEM micrographs from the identical composites as shown in Figure 5-15a and b.

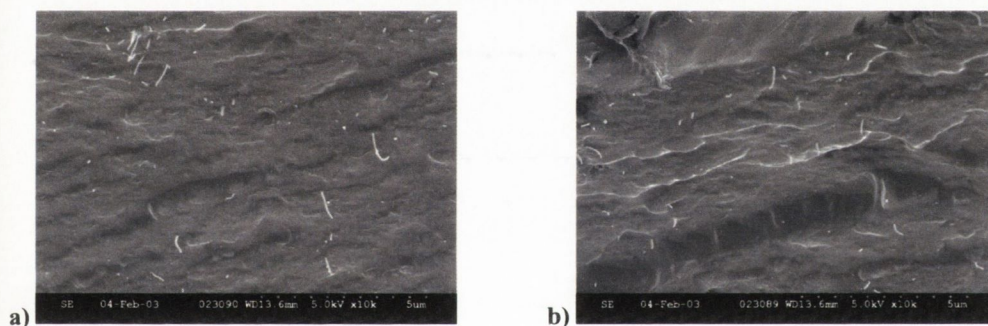


Figure 5-16: Scanning electron microscopy micrograph of the dispersion of catalytic grown multi walled carbon nanotubes in polyvinyl alcohol. a) Shows multi walled carbon nanotubes from Namur and b) from Orléans

Here the cross sectional areas (also seen in Figure 5-17a and b) are shown from free standing PVA films after performing mechanical tensile testing. Determined pull-out lengths from the SEM micrographs were found to be the same for both samples ranging between 0.5-2 μm .

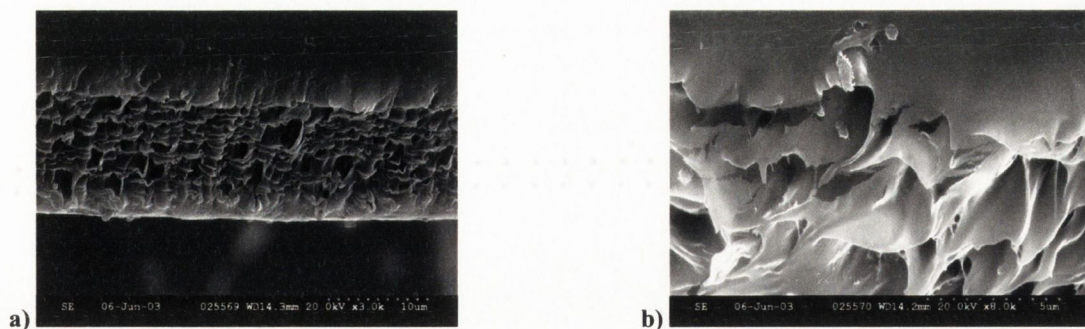


Figure 5-17: Scanning electron microscopy micrograph of cross sectional area of free standing polyvinyl alcohol films reinforced by catalytic grown carbon nanotubes

In case of HipCo-SWNT included in PVA local homogenous dispersion could be observed (Figure 5-18a) as well as agglomerates and bundle formation of PVA coated SWNT shown in Figure 5-18b.

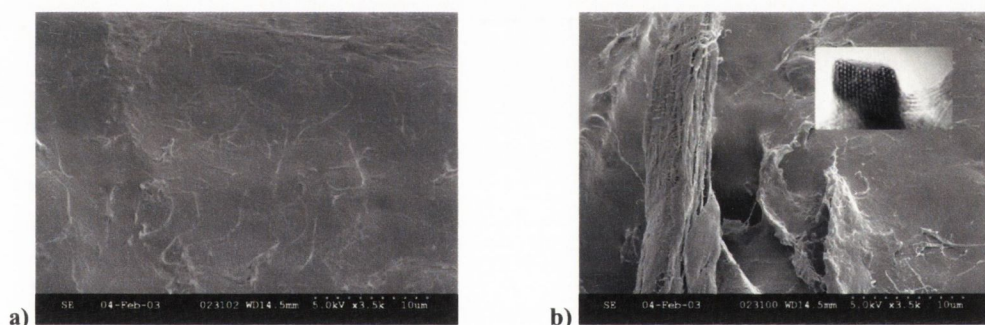


Figure 5-18: Scanning electron microscopy micrographs of the a) dispersion of HipCO single walled carbon nanotubes in polyvinyl alcohol and b) local bundle formation of HipCO single walled carbon nanotubes in polyvinyl alcohol. Additional micrograph in b) shows cross sectional area of a bundle of intrinsic HipCO-single walled carbon nanotubes²⁵ without polymer coating.

The bundle formation of SWNT shown in Figure 5-18b corresponds to the observations in former results section where HipCO-SWNT could not achieve as high reinforcement values as MWNT and low volume fraction samples of DWNT in PVA.

5.3.4 Comparison between nano-indentation and tensile results

In order to show that both nano-indentation and tensile testing can be performed to investigate mechanical properties of nanocomposites the results are directly compared with each other. Shown in Figure 5-19 are normalised Young's moduli for PVA free standing films and PVA thin glass substrate films plotted versus the volume fraction of AMWNT added to the polymer matrices.

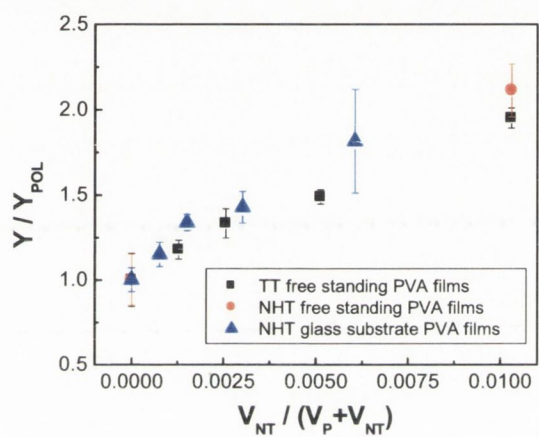


Figure 5-19: Comparison of nano-indentated and tensile tested Young's moduli on glass substrate and free standing polyvinyl alcohol polymer composite reinforced with arc grown multi walled carbon nanotubes

Nano-indentation was performed on a glass substrate PVA film as well as for a free standing PVA film with the same volume fraction of AMWNT. This was compared to a third set of results for a tensile tested free standing PVA film. It can be clearly observed that all tested samples fall onto the same line and are therefore comparable. This is an important result as many doubts existed on the validity of mechanical results on nanocomposites measured by nano-indentation.

5.4 Thin-MWNT/PVA free standing composite film

From the study in the former section of this Chapter it was found that ‘small’ diameter carbon nanotubes showed the highest increases in mechanical properties for polyvinyl alcohol. Therefore, in order to maximise mechanical properties of PVA/CNT composites ‘small’ diameter MWNT (thin-MWNT) were used in this section. As these CNT are multi shell CNT they do not tend to form bundles such as single walled CNT and have much larger surface areas and therefore higher reinforcement potential.

5.4.1 Electron Microscopy – SEM/TEM

To characterise the dispersion and interaction of CNT and the polymer matrix transmission electron microscopy (TEM) investigations were carried out using a Hitachi H7000 electron microscope. The typically used accelerating voltage was 100 keV. All TEM investigations were carried out on formvar coated copper grids.

Due to the relatively small diameters of thin-MWNT of only 12-14 nm they consist of relatively large surface areas (**SA**). Lengths of the thin-MWNT were found to range between 1 and 10 micron as shown in Figure 5-20 and b. The average length was determined to be 1.8 microns.

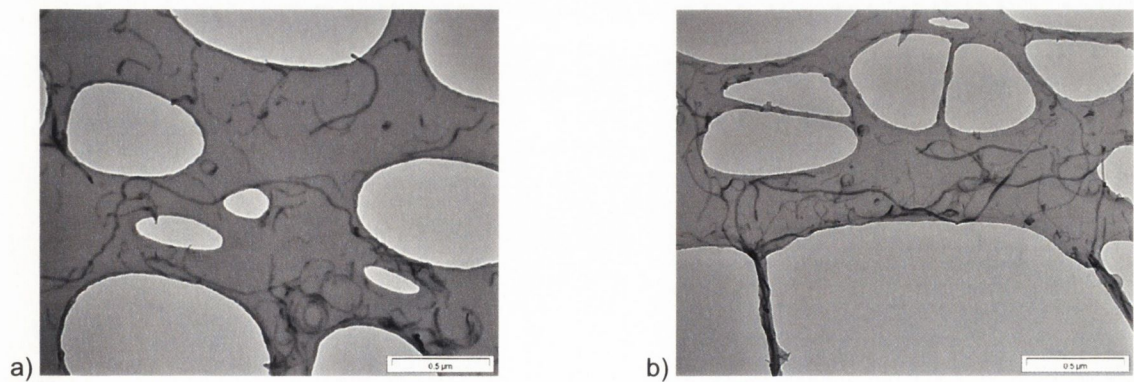


Figure 5-20: a) Transmission electron microscopy micrograph on thin multi walled carbon nanotubes and b) length distribution diagram for thin multi walled carbon nanotubes. Both dispersed in chloroform

Shown in Figure 5-21 is the fracture surface of PVA polymer composite strips after the tensile test was performed. These micrographs were taken using a Hitachi S-4300 field emission scanning electron microscope with an acceleration voltage of 30 KV and under ultra high vacuum. Pull-out lengths of thin-MWNT were measured and found to be on average 0.53 μm . This is in reasonable agreement with the measured length of approximately 2 μm , taken from the TEM micrograph in Figure 5-20a and b, as the total length of a nanotube can be assumed to be 4 times its pull-out length. This results from the fact that if fracture occurs, a nanotube is pulled out of the side of the break where the embedment length is shorter. This means that the pull-out length can vary from zero to maximum the half of the nanotube length. Therefore, the average length can be assumed to be a $\frac{1}{4}$ of the total nanotube length. A newly developed theoretical model in a later section will show an even closer agreement of the length of thin-MWNT dispersed in a PVA composite.

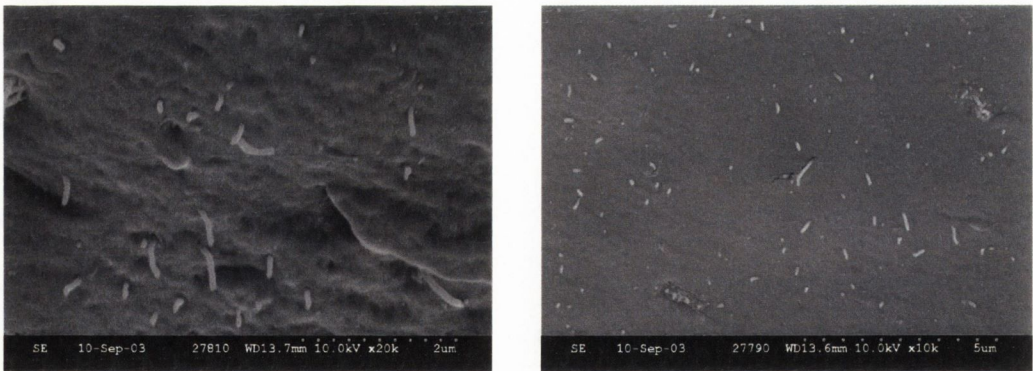


Figure 5-21: Scanning electron microscopy micrographs for small diameter multi walled carbon nanotubes in polyvinyl alcohol. Micrographs show the cross sectional area of tensiled polymer composite strips. Nanotubes here are pulled-out $\frac{1}{4}$ of their whole length

5.4.2 Mechanical tensile testing

Tensile testing was carried out using a Zwick Z100 tensile tester. A 100 N load cell was used to measure the applied force and deformation strain of the samples. A position controlled cross head speed of 0.5 mm/min was applied. Polyvinyl alcohol (PVA)/thin-MWNT composite solutions were produced in the exact same way as described for all former samples in this Chapter. Also the free standing films were prepared equally for tensile testing measurements and thermal analysis to determine crystallinity.

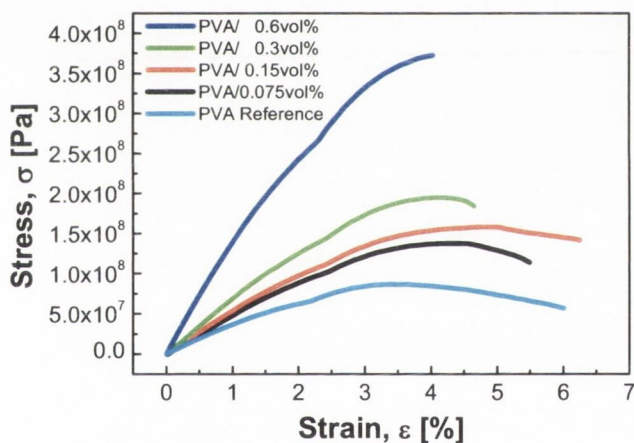


Figure 5-22: Representing stress-strain curves for polyvinyl alcohol composite reinforced with thin multi walled carbon nanotubes.

Figure 5-22 shows representing stress-strain curves for PVA composite reinforced with a range of different volume fractions of thin-MWNT. It can be observed that the stress to break the sample is increasing significantly while the strain is decreasing with increasing volume fraction of thin-MWNT. Furthermore, the slope of the increasing stress, and therefore the tensile modulus, increases dramatically while adding only 0.6 vol% of thin-MWNT to the PVA matrix.

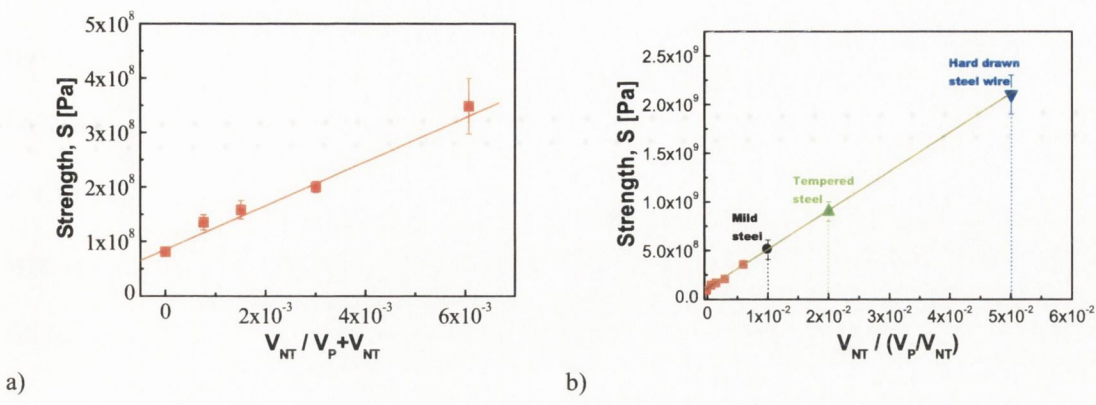


Figure 5-23: a) Increase of tensile strength versus volume fraction of polyvinyl alcohol/thin multi walled carbon nanotube composites. b) Scale up to potential reinforcement for polyvinyl alcohol thin multi walled carbon nanotube composites.

Shown in Figure 5-23a is a plot of the increase in tensile strength of PVA versus volume fraction of thin-MWNT. It can clearly be seen that the strength increases by 300% from 100 MPa for pure PVA to 400 MPa for the composite reinforced by only 0.6 vol% of thin-MWNT. It can be further seen in Figure 5-23b that the value of 400 MPa is relatively close to the tensile strength of mild steel. By fitting a straight line to the obtained results from Figure 5-23a it can be seen in Figure 5-23b that only 1 vol.% of thin-MWNT could increase the tensile strength of the PVA to the same value as for mild steel and in the case of 2 vol.% filler content of thin-MWNT, tensile strength could be increased to a value of 1 GPa which corresponds to the value of tempered steel. If it would be possible to disperse 5 vol.% of thin-MWNT in the PVA matrix a strength value of a hard drawn steel wire (2 GPa) could be achieved.

In the case of tensile modulus an increase of a factor of 4 could also be achieved. Shown in Figure 5-24a is the linear increase of tensile modulus versus volume fraction of thin-MWNT. Tensile modulus could be raised from 1.8 GPa to 7 GPa. In Figure 5-24b it can be observed that the energy needed to break the PVA films reinforced with thin-MWNT increases as well. The increase is not completely linear

as the uncertainty in the obtained values was relatively large. This can be explained by the sensitivity of the polymer films to damage such as cracks or air inclusions etc. Nevertheless, a raised average value for toughness can be observed. For the pure PVA film the energy to break the polymer film was averaged around $5 \times 10^6 \text{ J/m}^3$ whereas for the samples containing 0.6 vol.% of thin-MWNT an average value of $9 \times 10^6 \text{ J/m}^3$ was observed.

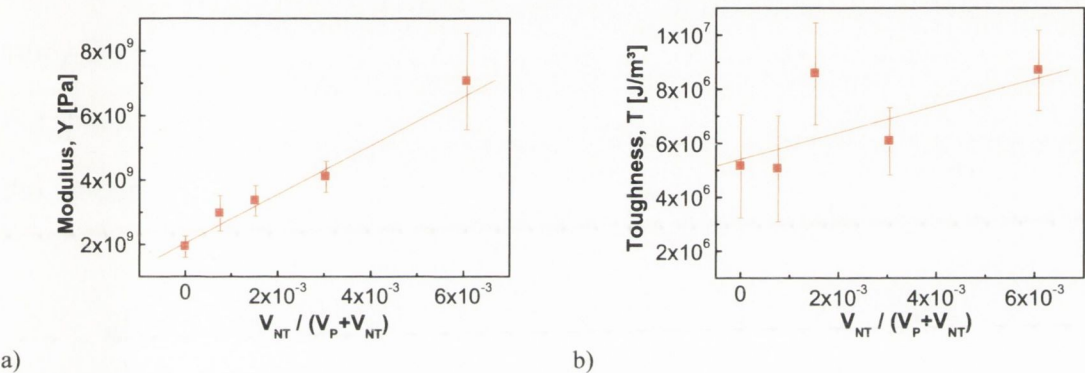


Figure 5-24: Plot for polyvinyl alcohol reinforced with thin multi walled carbon nanotubes. a) Increase in tensile modulus from 1.8 GPa to 7 GPa and b) toughness values increase from $5 \times 10^6 \text{ J/m}^3$ to $9 \times 10^6 \text{ J/m}^3$

When fitting Krenchel's Rule-of-Mixture²⁶ to the determined dataset of tensile modulus, shown in Figure 5-1a using 1.92 GPa for the pure polymer modulus and 7.54×10^{11} as the slope of the increase, the Young's modulus of thin-MWNT was calculated to be 752 GPa. This value for thin-MWNT is unrealistically high as Forró *et al.* predict a Young's modulus for catalytical grown multi walled carbon nanotubes of only 10-100 GPa²⁷. Krenchel assumed iso-strain behaviour in the composite system which is in this case not realistic due to the curvature of the thin-MWNT. This result predicts that Krenchel's Rule-of-Mixture is not applicable for calculations on the Young's modulus of carbon nanotubes reinforced polymer matrices.

5.4.3 Morphological measurements - DSC

Thermal properties of free standing PVA films reinforced with thin-MWNT were examined by a Perkin Elmer Diamond DSC power compensation instrument. Approximately 10 mg of a free standing polymer film was placed to a standard aluminium pan and covered with a cap to perform the DSC experiment. Heating rates here were 40°C/min for a temperature range of 0°C-220°C. Helium was used as purge gas and liquid nitrogen as a coolant for the DSC apparatus. Cooling rates to study the crystallisation behaviour were also 40°C/min.

For thin-MWNT/PVA composites the crystallinity increased dramatically while raising the amount of filler content. This can be observed in Figure 5-25a and b.

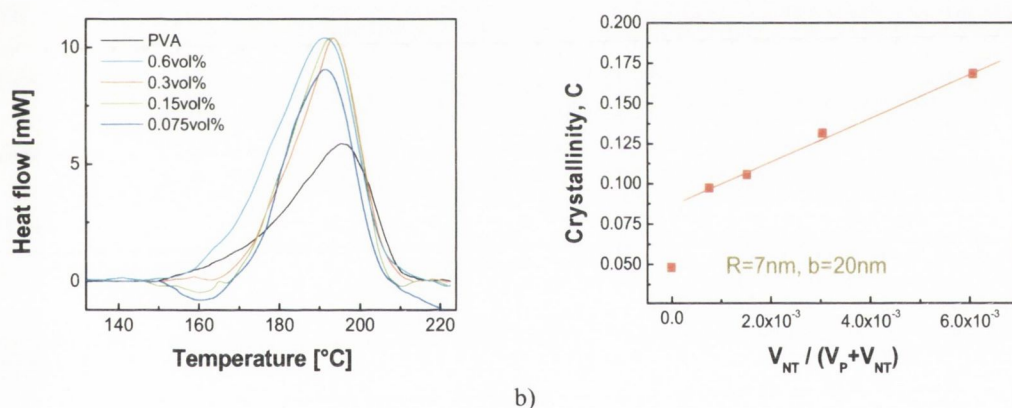


Figure 5-25: Graph of a) melting peak of polyvinyl alcohol reference and composite samples with thin multi walled carbon nanotubes and b) crystallinity plot of polyvinyl alcohol versus volume fraction of thin multi walled carbon nanotubes

A broad melting peak can be observed between 160°C and 210°C with increasing area of the melting peaks. This shows an increase in the amount of crystals in the PVA matrix and is plotted in Figure 5-25b versus the volume fraction of thin-MWNT added to the PVA matrix. When adding only 0.075 vol% of thin-MWNT to the PVA matrix the crystallinity increased sharply from 5% to 10% followed by a smooth linear increase from 10% to 17.5% while adding 0.6 vol% of thin-MWNT to the PVA matrix.

The crystalline coating thickness was calculated on Equation 5-2 in previous section and found to be 20 nm. This confirms earlier statement that when the crystalline coating is increased, by decreasing the diameter of MWNT, the mechanical properties can be improved dramatically.

5.5 Theoretical model for tensile strength calculations

In order to understand and calculate the breaking mechanism for a polymer reinforced with CNT a model was developed and is shown in Figure 5-26. Perfect nanotube alignment is assumed in the model. Nanotubes are symbolised by the bold black line whereas the dotted line next to the CNT symbolises the crystalline polymer layer interacting with the CNT. Two breaking mechanisms have to be taken into consideration. Firstly, the crystalline polymer matrix around the nanotubes has to be broken apart and secondly the pure polymer has to break up in tension to destroy the composite sample. This has been taken into consideration in Equation 5-5.

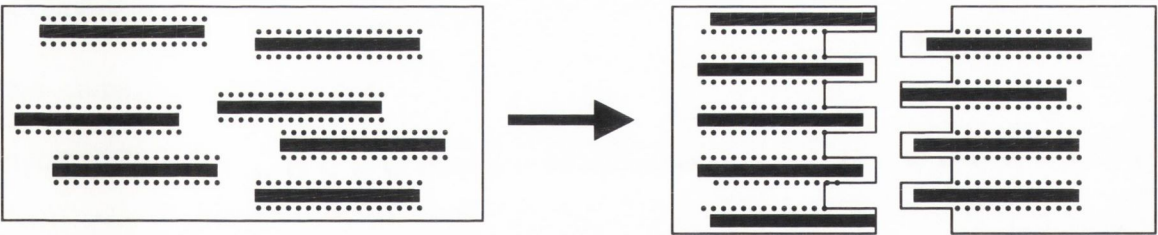


Figure 5-26: Breaking mechanism for carbon nanotube reinforced polymer composites

The theoretical model to calculate the ultimate tensile strength for nanotube reinforced polymers shown in Equation 5-5 has been developed by Coleman and Cadek *et al.* and is derived elsewhere¹⁷.

$$S = \left[\frac{R+b}{R} \right] \left[f(\theta) \frac{l}{2R} S_{p'} - \left(\frac{R+b}{R} \right) S_p \right] V_F + S_p [Pa]$$

Equation 5-5: Theoretical model for the calculation of the ultimate tensile strength for polymers reinforced with carbon nanotubes

Where **S** stands for the ultimate tensile strength of the composite, **S_{p'}** for the shear strength of the polymer, **S_p** is the tensile strength of the matrix, **R** stands for the radius of the CNT, **b** for the crystal coating thickness calculated from Equation 5-1. In a previous section of this Chapter, **V_f** stands for the volume fraction of CNT added to the polymer matrix, **f(θ)** is a orientation constant for the CNT in the polymer matrix and is equal to 1 when perfect alignment of CNT can be considered. Using this model it was possible to calculate the length, **l**, of thin-MWNT which were used as the reinforcing agent in the PVA. The parameter **R** was measured using TEM and found to be 7 nm, **b** was calculated using Equation 5-2 from previous section in this Chapter and found to be 20 nm. The value **S_{p'}** for PVA is known to be 41 MPa^{17,28}. The values **S_p** were used from the determined results of Section 5.3.2. The length of thin-MWNT was calculated to be 3.7 μm which stands in reasonable agreement with the previously reported value which was determined by transmission electron microscopy micrographs.

5.6 Free standing cPP/cPP-MWNT film

Multi walled carbon nanotubes (MWNT) with smaller diameters (thin-MWNT) were functionalised with chlorinated polypropylene polymer chains in order to achieve covalent bonding and therefore stronger interfacial interaction between CNT and polymer chains. These functionalised CNT were added to a chlorinated polypropylene polymer matrix and analysed optically by transmission and scanning

electron microscopy, mechanically by tensile testing, and thermally using differential scanning calorimetry.

5.6.1 Electron microscopy - SEM/TEM

Transmission electron microscopy (TEM) investigations were carried using a Hitachi H7000 electron microscope. The typically used accelerating voltage was 100 keV. All TEM investigations were carried out on formvar coated copper grids.

Shown in transmission electron microscopy micrographs in Figure 5-27 are the thin-MWNT functionalised with chlorinated polypropylene and dispersed in a chlorinated polypropylene matrix.



Figure 5-27: Transmission electron microscopy images of thin multi walled carbon nanotubes covered with chemically bonded chlorinated polypropylene

It can clearly be seen that cPP not only interacts with the CNT but also a thick layer of polymer wraps around the cPP-MWNT indicating a strong chemical interaction between polymer and CNT.

Scanning electron microscopy micrographs were taken using a Hitachi S-4300 field emission scanning electron microscope performed with an electron acceleration voltage of 30 KV. In the scanning electron microscopy micrographs of Figure 5-28

pull-out studies of cPP-MWNT in chlorinated polypropylene are shown. The cross sectional areas after the tensile test experiment are shown.

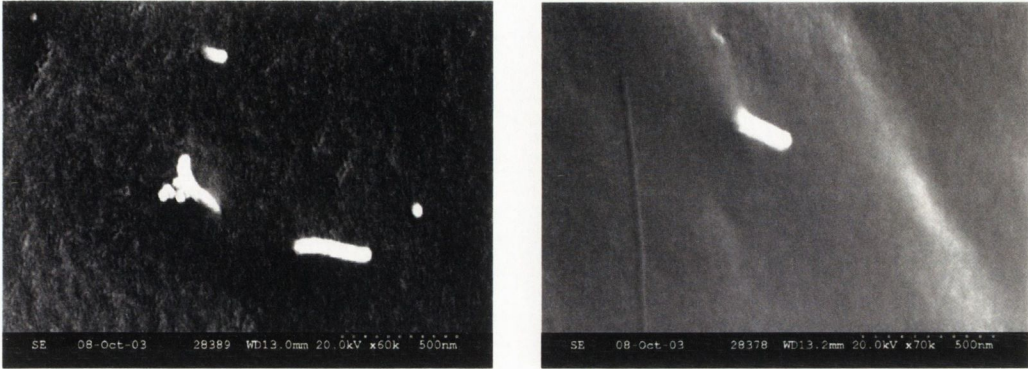


Figure 5-28: Scanning electron microscopic pull-out studies of thin multi walled carbon nanotubes functionalised with chlorinated polypropylene and dispersed in a polypropylene matrix

It can be observed in Figure 5-28 that cPP-MWNT are oriented due to the shearing of the polymer while being pulled apart with elongations of up to 800%. Pull-out lengths were found to be 500 nm which is in quite reasonable agreement to the measured length of thin-MWNT (2 μm) taken from previous TEM images (Figure 5-20).

5.6.2 Mechanical tensile testing

To perform tensile testing a Zwick Z100 tensile tester was used with a 100 N load cell in order to obtain the applied force and deformation strain of the samples. A position controlled cross head speed of 0.5 mm/min was applied for all samples tested. Free standing polypropylene samples reinforced with cPP-functionalised thin-MWNT were prepared in the exact same way as the PVA free standing films in order to perform tensile testing measurements and thermal analysis to determine crystallinity. Tensile testing was carried out with representative stress strain curves as shown in Figure 5-29a. Substantial increases in mechanical properties are observed as the

nanotube concentration is increased. On average, as the content of thin-MWNT is increased to 0.6 vol%, Young's modulus increases by a factor of 3 from 1.7 GPa for pure cPP to over 5.2 GPa as shown in Figure 5-29b. For all volume fraction samples, 6-10 films were measured. Determined values were averaged and the standard deviation was calculated.

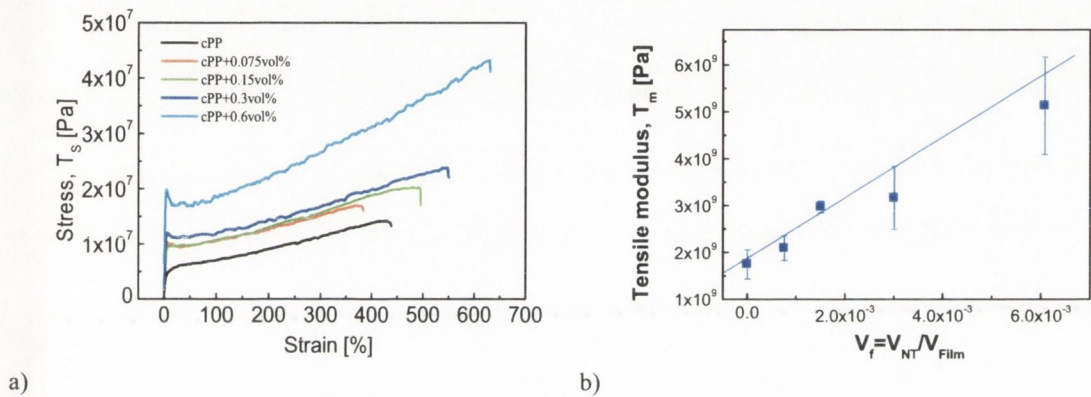


Figure 5-29: a) Stress-strain curves for thin multi walled carbon nanotubes functionalised with chlorinated polypropylene dispersed in a polypropylene matrix. b) Tensile modulus increase by a factor of 3 while increasing volume fraction of thin multi walled carbon nanotubes to 0.6%

Moreover, both the tensile strength and the energy to break, shown in Figure 5-30a and b), are increase dramatically by a factor of 2.5 for ultimate tensile strength, from 12 MPa to 30 MPa, and a factor of 4 in the case of toughness from 3.8×10^7 J/m³ to 1.4×10^8 J/m³. Extrapolating these values to 10 vol% of cPP-MWNT is resulting in a yielding strength of 140 MPa which is comparable to brass.

When calculating the Young's modulus for thin-MWNT using these data points in combination with Krenchel's Rule-of-Mixture with the determined slope from Figure 5-29b of 6.48×10^{11} and a Young's modulus of 1.74×10^9 GPa for the pure polymer matrix results in a nanotube modulus of 646.3 GPa. This value is unrealistically high compared to Youn'g modulus values for catalytic grown MWNT calculated from Forró *et al.*²⁷ and is therefore not reliable.

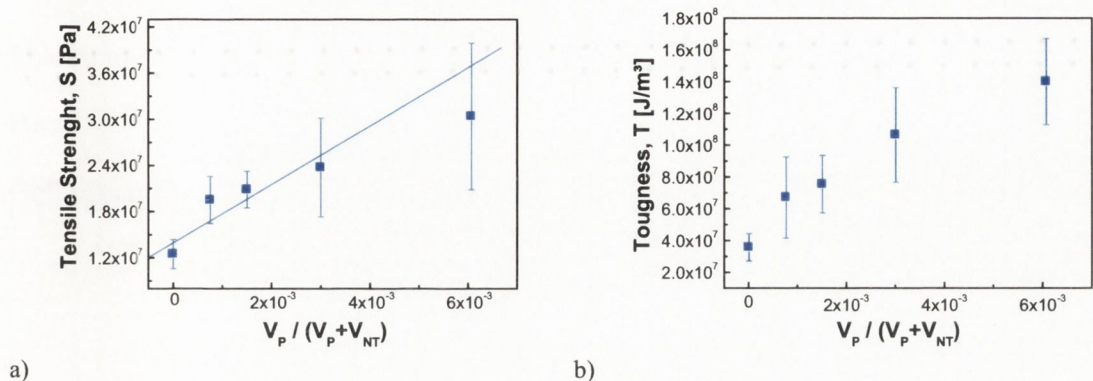


Figure 5-30: Increase of mechanical properties such as a) tensile strength plotted versus volume fraction of chlorinated polypropylene functionalised thin multi walled carbon nanotubes and b) Toughness increase versus volumetric nanotube filler content.

The graph in Figure 5-31a shows the increase of yielding strength plotted versus the amount of CNT added to the matrix. These values were raised from 6 MPa to 17 MPa. In the case of the strain at break (ϵ_B), values could be increased from 380% to 540% when adding 0.6 vol% of cPP functionalised thin-MWNT to the polymer matrix.

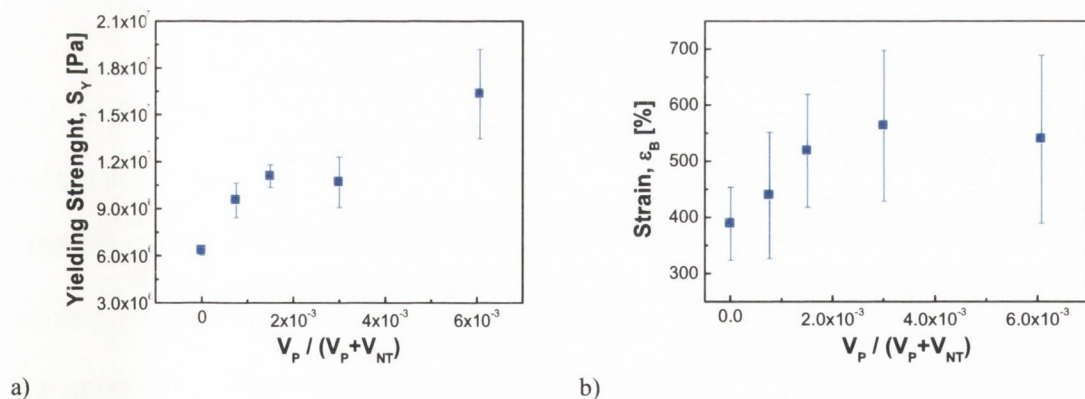


Figure 5-31: Increase of a) yielding strength plotted versus volume fraction of chlorinated polypropylene functionalised thin multi walled carbon nanotubes and b) Strain values where polymer collapses versus volumetric nanotube filler content.

5.6.3 Thermal analysis - DSC

Thermal properties of free standing cPP-films reinforced with chlorinated polypropylene functionalised thin-MWNT were examined using a Perkin Elmer

Diamond DSC power compensation instrument. For each volume fraction a sample of approximately 10mg of the free standing cPP film was placed into a standard aluminium pan closed with an aluminium cap in order to perform DSC experiments. Heating and cooling rates were 20°C/min for a temperature range of 0°C-210°. Helium was used as purge gas and liquid nitrogen as a coolant for the DSC analyser.

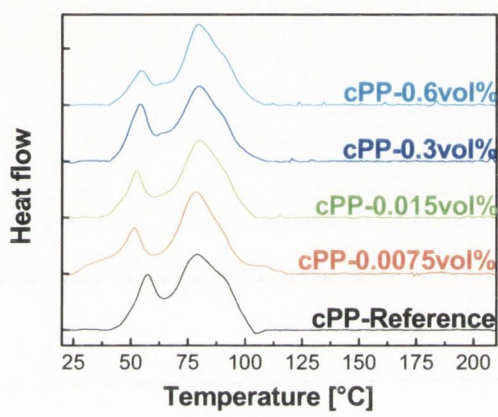


Figure 5-32: First thermal heating graph of differential scanning calorimetry. Shown are two melting peaks for chlorinated polypropylene reinforced with thin multi walled carbon nanotubes functionalised with chlorinated polypropylene polymer chains.

Due to the chosen temperature range the glass transition temperature could not be determined. Literature confirms a glass transmission temperature of polypropylene of -18°C²⁹. During the first thermal heating of the cPP/cPP-MWNT composites two melting peaks were found. The first peak occurred in the region of 50°-60°C whereas the second peak appeared from 60°-100°C. It can be observed in Figure 5-32a that the first melting peak decreases in size with increasing volume fraction of cPP/MWNT. The second melting peak shows a constant size. Nevertheless, calculations of crystallinity resulted in ~5% and did not rise significantly when adding cPP-MWNT to the chlorinated polypropylene. This value is reasonable agreement with the relative low melting temperature for cPP as for highly crystalline iso-tactic

polypropylene with a crystallinity of up to 70-80% melting occurs at 175°C²⁹. Due to the larger amorphous phase of chlorinated polypropylene compared to an iso-tactic polypropylene the drop in T_m seems to be realistic. The second melt peak and its behaviour when adding cPP-MWNT can not be explained by the literature. Different crystal sizes could be an explanation.

When cooling from 200°C-0°C with a cooling rate of 20°C/min no recrystallisation occurs. Surprisingly, a melting peak, but only one, could be observed in the second thermal heating run shown in Figure 5-33.

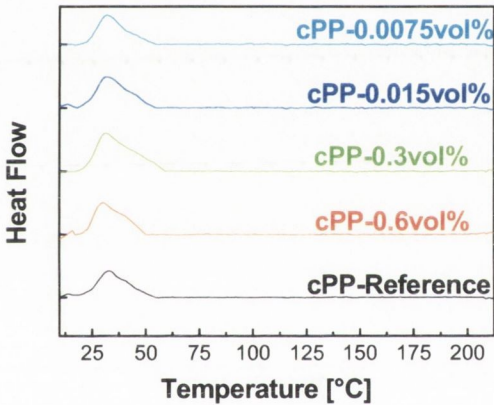


Figure 5-33: Second thermal heating graph of differential scanning calorimetry for chlorinated polypropylene reinforced with thin multi walled carbon nanotubes functionalised with chlorinated polypropylene. The second melting peak could not be observed in the second run.

The melting peak of the second run of cPP is reduced to the range of 25°-50°C for pure cPP and slightly less for the cPP/cPP-MWNT composites. The down shift phenomenon of T_m can be explained by the absence of the large size crystals observed in the first heating and the increased heat dispersion due to the introduction of a thermal conductor. Therefore, locally melting can occur as the thermal insulation properties of the polymer is nearby a nanotube decreased. The absence of the crystallisation peaks when cooling was unexpected due to the small melting peaks at

the second heating. Probably the cooling rate was chosen to high, hence the relative small amount of crystallisation was not registered by the DSC apparatus.

5.6.4 Model of CNT functionalisation with polymer chains

The mechanical increase of cPP-functionalised thin-MWNT in chlorinated polypropylene described in the previous section is relatively high but expectations were much higher due to the covalent bonding of the polymer chains to the CNT. As shown in the previous section there was no crystallinity increase for cPP while adding cPP-MWNT. This suggests that the local break occurs between the bonded polymer of the cPP-MWNT and the matrix. Shown in Figure 5-34a is the schematic of the functionalisation effect of the polymer and the thin-MWNT, where the polymer chains are parallel bonded at several points to the nanotube length axis. This is not wanted as the area where the polymer chains can entangle with the polymer matrix is not maximised. Due to this effect the increases in mechanical properties were not as high as expected.

Hence, shown in Figure 5-34b, is the desired situation where polymer chains are only bonded at the ends of the polymer chains to the nanotube. The resulting perpendicular functionalisation guarantees a maximal area of polymer chains which are covalently bonded to a nanotube corresponding to the polymer chain length. This means that the polymer chains occupy significant volume in the vicinity of the nanotube surface. In this case it is unlikely that fracture will occur at the polymer-nanotube interface as this would require the breaking of a large number of covalent bonds. Instead it is likely that the fracture surface will be displaced from the polymer-nanotube surface by a distance **b**.

Fracture surface

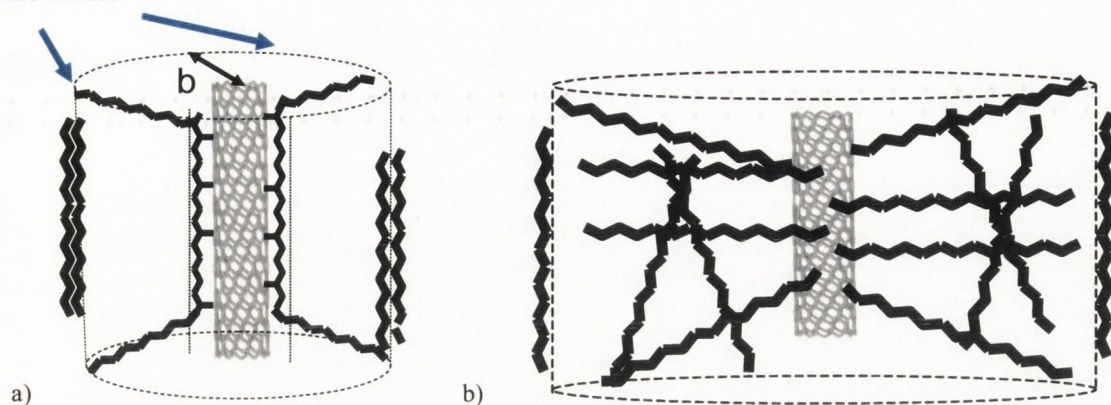


Figure 5-34: Schematic of the functionalisation effects: a) actual situation with multiple bonding points and b) desired situation with only one coupling point and perpendicular position of the polymer chains to the nanotube.

In this case only the relatively weak inter-polymer van der Waals bonds have to be broken. Assuming that the polymer shear strength is approximately equal to the tensile strength we can apply Equation 5-4 to the determined cPP data shown in Figure 5-30a. Analysis gives a value of $b=52$ nm. This is reasonable as it would be expected that the relatively long, covalently attached polymer strands are occupying a significant volume around the nanotube.

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Chapter 6

Experimental Polymer Fibres

6.1 Introduction

This Chapter describes the mechanical, thermal and microscopic analysis of melt blended polyamide 12 (Nylon[®]) fibres reinforced with a range of differently produced multi walled carbon nanotubes (MWNT) and carbon nano fibres (CNF). A twin-screw micro extruder was used to disperse the nano-fillers and the resulting blends were spun in order to produce thin Nylon[®]-composite fibres using a melt flow index analyser in combination with a wind-off unit. Two different standard mechanical testing techniques, nano-indenter and dynamic mechanical thermal analyser, were used to evaluate the mechanical properties such as Young's modulus, hardness, tensile strength and yielding strength of the polymer composite fibres. In addition to this, classical morphology determination and decomposition behaviour of the polymer composite fibres was performed using differential scanning calorimetry and thermal gravimetric analysis. In order to investigate the dispersion and the wetting behaviour of the nano-fillers in the polymer composite, scanning electron microscopy was performed. Moreover, for identification of the different nano-fillers, Raman spectroscopy was performed^{1,2} and in order to describe the alignment of the dispersed carbon nanotubes X-ray diffraction measurements were performed on the different Nylon[®]-composite fibre samples and are shown elsewhere^{1,2}. This work was accomplished in cooperation with three university partners and two industrial partners

in the framework of the European network project, CNT-Net: Trinity College Dublin, the University of Cambridge/U.K., the Technical University of Hamburg-Harburg/Germany, Degussa AG Mahl/Germany, DSM Research Geleen/The Netherlands^{1,2}. The university partners Dublin, Cambridge and Hamburg produced the polymer composite fibres and the university partners Dublin and Cambridge prepared, performed and analysed the above mentioned investigations. The industrial partners provided polymeric material and processing equipment in order to manufacture the samples.

6.2 Mechanical Analysis

6.2.1 Nano-indentation

In order to perform nano-indentation³⁻⁵ on Nylon[®]12-composite fibres they had to be embedded into a polymeric cold mounting embedding material as described in detail in Chapter 2.3.3. Values for Young's modulus and hardness for all PA12 fibre samples were obtained using a SCEM Nano-hardness-tester. Eight indentation points were measured for all samples using a 2x4 matrix with distances of 30 µm in between each indent. Exact indentation positions were determined using an optical microscope to ensure that all indents are carried out on the actual fibres. Fibre thickness was found to be 125 µm measured by an optical microscope. All measured values were averaged and the standard deviation calculated. The maximum indentation force for PA12 fibre samples was 100 mN with loading/unloading rates of 200 mN/min.

Shown in Figure 6-1a are averaged values of Young's modulus as measured by nano-indentation and plotted versus the volume fraction of aligned catalytic grown multi walled carbon nanotubes (aMWNT). For a volume fraction of 1.7 vol% of

aMWNT the modulus increased by a factor of 1.5 compared to the 0.4 vol% sample from 1.1 GPa to 1.7 GPa. It has to be pointed out that measurements of the reference sample could not be performed on the nano-indenter due to technical reasons but compared to the PA12 reference sample obtained by tensile testing, the Young's modulus value of 0.8 GPa, fits reasonably. Compared to the reference value the mechanical increase was of a factor of 2 while adding 1.7 vol% aMWNT.

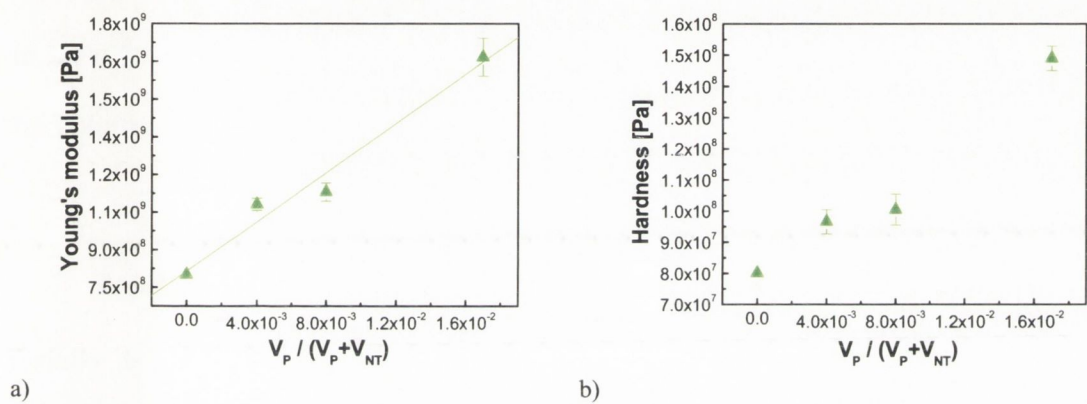


Figure 6-1: Nano-indentation results on polyamide12 fibres reinforced with aligned catalytic grown multi walled carbon nanotubes. a) Young's modulus plotted versus volume fraction of carbon nanotubes and b) hardness plotted versus volume fraction of carbon nanotubes

When fitting a line to these data points a slope of 4.9×10^{10} was calculated. Using this value in Krenchel's Rule-of-Mixture results a Young's modulus for aMWNT of 49.8 GPa. This value is in reasonable agreement from earlier calculations by Forró *et al.*⁶ where values for catalytical grown MWNT are predicted to be in the range of 10-100 GPa. Obviously Krenchel's Rule-of-Mixture does apply here. The difference to former results could be explained as crystalline coating can not be observed around the nano-fillers. For all earlier reported results in this thesis a crystalline coating around the nano-fillers could be observed. This could be explained in the different structure of the polymer matrix. The polymer back bone of Nylon[®]12 obviously does not tend to wrap around a CNT in such a way as i.e. poly(vinyl alcohol) does. Further investigations have to be performed in order to explain this phenomenon.

In case of the hardness measurements determined by nano-indentation it can also be observed that the hardness increases linearly with increasing nanotube content as shown in Figure 6-1b. Here the value at a volume fraction of 1.7 vol % of aMWNT increased from 95 MPa for the 0.4 vol % sample to 150 MPa. This is corresponding to 158%. It has to point out that the value for the pure PA12 was taken from the literature and was measured by Rockwell hardness test. Nevertheless, the value of 80 MPa for pure PA12 fits reasonable to the linear increase of PA12 when increasing the volume fraction of aMWNT.

6.2.2 Dynamic Mechanical Thermal Analyser

Tensile testing of individual PA12 fibre segments was performed using a TA Instruments 2980 Dynamic Mechanical Thermal Analyser (DMTA). A special fibre clamping device was mounted and measurements were performed using a constant force ramp of 0.1 N/min. Measurements were carried out at 25°C with a gauge length of 5.5 mm. At least 3 fibres were tested for each mass fraction of nano-filler and filler type. The maximum elongation of the Nylon[®]-samples was limited to approximately 400% due to the design of the clamping device. Therefore, a conclusive analysis of ultimate tensile strength and toughness could not be evaluated as some of the tested samples did break at an elongation >400%.

As shown in the stress-strain curves in Figure 6-2a the elongation to break the Nylon[®]-fibres reinforced with aligned catalytic grown MWNT (aMWNT) is approximately 400%. As further can be observed there is a two-stage yielding behaviour between 3 and 30% strain. This is followed by a stress plateau up to the region of 190% strain. As the experimental set-up was force controlled no yielding drop occurred. The stress plateau appeared due to strain induced crystallisation

effects after initial fibre necking. Initial yielding points were increased from 20 MPa for neat PA12 to 30 MPa for the 1.7 vol.% filled aMWNT PA12 fibre sample. Secondary yielding points were raised from 30 MPa for the neat PA12 to 40 MPa for the 1.7 vol.% aMWNT PA12 fibre sample. In the case of the PA12 sample reinforced with entangled catalytic grown MWNT from Namur (NMWNT), shown in Figure 6-2b, the same two-stage yielding behaviour followed by a stress plateau could be observed. Initial yielding points were raised from 20 MPa for the pure PA12 sample to 50 MPa for the 3.6 vol.% NMWNT filled PA12 fibre sample. As can be seen in Figure 6-2b the high mass fraction sample does not show neither the two-stage yielding behaviour nor the stress plateau. Furthermore, a decrease of elongation to break can be observed. The neat PA12 sample shows an elongation to break >400% whereas with increasing weight% of NMWNT the elongation to break decreases approximately to 150-200% for the high mass fraction sample. The ultimate tensile strength in this case is roughly constant for all mass fractions but decreased slightly compared to the neat PA12 sample. Stress plateaus can be observed in Figure 6-2b in the same region of up to 190% apart from the high mass fraction sample.

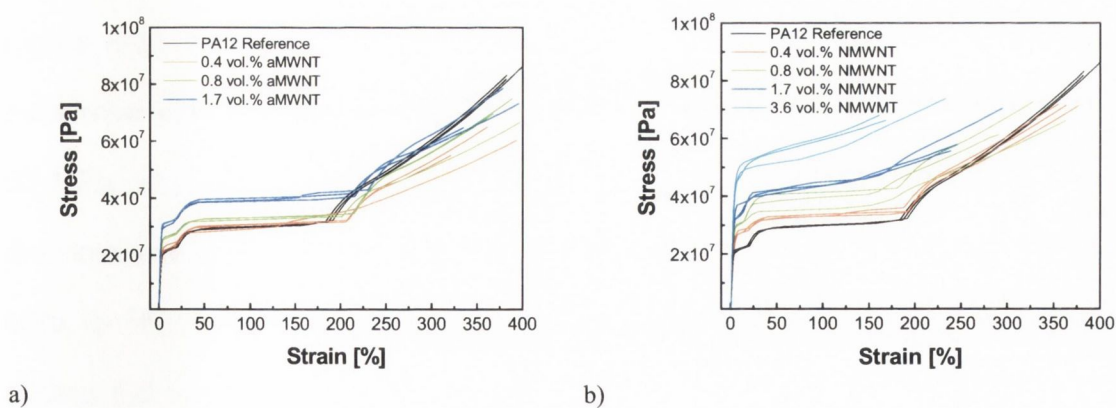


Figure 6-2: Stress-strain curves for polyamide 12 catalytic grown multi walled carbon nanotubes a) aligned catalytic multi walled carbon nanotubes and b) entangled catalytic multi walled carbon nanotubes

All produced samples showed necking behaviour between the grips which subsequently propagated toward the clamps. The observed occurrence of the characteristic two-stage yielding point could be observed for all other produced PA12 fibre samples up to a volume percent of nano-fillers of 1.7 vol.% for carbon nanotubes (CNT) and 3.6 vol.% for carbon nanofibres (CNF). At higher loading fractions the effect changed to single yielding behaviour followed by a steady stress increase.

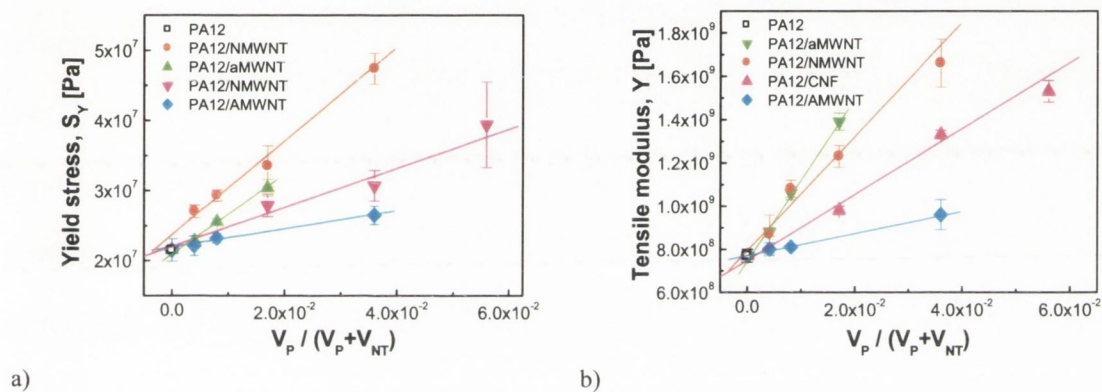


Figure 6-3: Increase of a) yielding stress plotted versus the volume fraction of nano-fillers and b) Tensile modulus plotted versus the volume fraction of nano-filler content

As already mentioned previously and seen in Figure 6-2a and b it can be observed in Figure 6-3a that the yielding stresses were raised linearly for all Nylon®-samples reinforced with nano-fillers. The highest increase in yielding stress, from 20 MPa to 50 MPa, was observed for NMWNT at a volume fraction of 3.6%. When observing the slopes of the linear fits it is followed by aMWNT where the yielding stress was 30 MPa for the 1.7 vol.% CNT sample. CNF were doubling the yielding stress while adding 5.6 vol.% to the PA12 matrix whereas AMWNT-soot did not increase this value significantly.

Figure 6-3b shows a comparative plot of the Nylon®-fibre tensile modulus as a function of filler volume fraction. It can be clearly observed that stiffness of the nano-

composites increases linearly with the volume fraction increase of the nano-fillers. It can further be observed that aMWNT shows the steepest increase followed by NMWNT. The highest modulus could be observed for the 3.6 vol.% sample of NMWNT where a factor of 2.25 could be observed for the increase of stiffness from 0.8 GPa for the neat PA12 to 1.7 GPa for the 3.6 vol.% sample. CNF were increasing the sample stiffness of PA12 by a factor of 2 while adding 5.6 vol.% to the PA12 matrix. As already observed in Figure 6-3a and b AMWNT did not increase significantly the mechanical properties of melt blended PA12 due to agglomeration effects of the graphitic impurities contained in the sample as shown in later section of this Chapter (Figure 6-6d). Shown in Table 6-1 are the slopes of the linear fits of Figure 6-3b and the calculated Young's modulus values using Krenchel's Rule-of-Mixture. These calculations resulted in nanotube moduli which are in reasonable agreement with Young's moduli values of catalytic grown MWNT determined of Forró *et al.*⁶. In case of the AMWNT the value does not agree with the theory as they are known to have a Young's modulus of 1 TPa^{7,8}.

Nano-filler	Slope, m	Young's modulus, Y
aMWNT	3.75×10^{10}	36.7 GPa
NMWNT	2.64×10^{10}	25.6 GPa
CNF	1.52×10^{10}	14.4 GPa
AMWNT	5.09×10^9	4.3 GPa

Table 6-1: Calculated values for Young's moduli using Krenchel's Rule-of-Mixture on used nano-fillers.

As reported already in previous section Krenchel's Rule-of-Mixture does apply using this production method of nano-composites. The difference to former results reported in this thesis is the crystalline coating around the nano-fillers which can be neither confirmed by electron microscopy nor by the differential scanning calorimetry

analysis. For all earlier reported results in this thesis a crystalline coating around the nano-fillers could be observed.

6.3 Thermal Analysis

In order to investigate the thermal properties, such as decomposition behaviour, glass transition and melting temperatures, of the produced PA12 nano-composites thermal gravimetric analysis and differential scanning calorimetry were performed. All produced nano-particle filled Nylon[®]-fibres were cut into small pieces, tested and analysed.

6.3.1 Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was carried out using a Mettler TG50 thermal analysis unit. 10 mg of the PA12 nano-composite fibre or plain nano-filler were placed into an aluminium oxide crucible and heated up in air using a heating rate of 10°C/min from 25-1000°C. This was performed under a constant air flow of 20 L/min. All PA12 samples were held initially at 100°C for 1 hour in order to remove any water present.

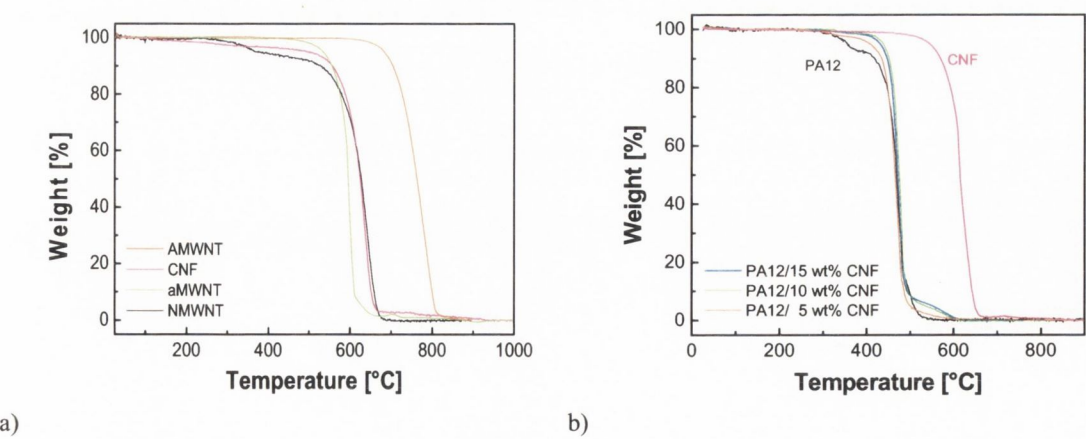


Figure 6-4: a) Comparative weight loss plot of all used nano-fillers versus the temperature increase and b) weight loss of polyamide 12 reinforced with nano-fillers plotted versus temperature increase

Figure 6-4a shows the decomposition behaviour of all nano-fillers used in this Chapter. It can be clearly observed that AMWNT illustrate the best decomposition behaviour as they begin decomposition only at 700°C. However, CNF already show slight decomposition at 200°C levelling off until 600°C followed by a sharp weight loss. Similar results can be observed for NMWNT where 10 weight% of the material decomposes as low as 300°C. The remainder of the material decomposes at only 600°C. In case of aMWNT the material decomposes at 500°C with no earlier effects. This is an indicator for the well graphitised aMWNT and the perfect structure of AMWNT. In case of NMWNT and CNF the initial weight loss suggests the presence of small amounts of amorphous carbon.

Representative for the thermal stabilisation effect of nano-fillers it can be observed in Figure 6-4b that CNF are increasing the thermal stability in polymer composites. It can be seen that the pure PA12 matrix decomposes in a two step process. A weight loss of about 10% occurs at 350°C followed by a second weight loss at 450°C. All nano-fillers stabilise this weight loss effect for the PA12 matrix. This effect can be observed in Figure 6-4b in case of the PA12 sample reinforced with CNF. Similar effects could be observed earlier on other polymers and are thought to relate to radical capture by the nanotube surface^{1,2,9,10}

All other produced nano-composite samples in this Chapter did confirm these observations. The weights remaining after complete decomposition of the polymer matrix are qualitatively consistent with the weight fracture of nanotubes added to the Nylon[®] matrix. However, quantitatively the obtained masses are slightly lower than

the nano-fillers added, presumably because of the inevitability of lost material during the production of the nano-composite.

6.3.2 Melting and Crystallisation behaviour – DSC

Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer series 7 machine operating at 10°C/min shown in Figure 6-5a. Heating ramps from 0°C to 210°C were used. Before cooling back to 0°C, samples were held isothermal at 210°C for 5 minutes in order to remove the thermal history of the polymer composite fibres.

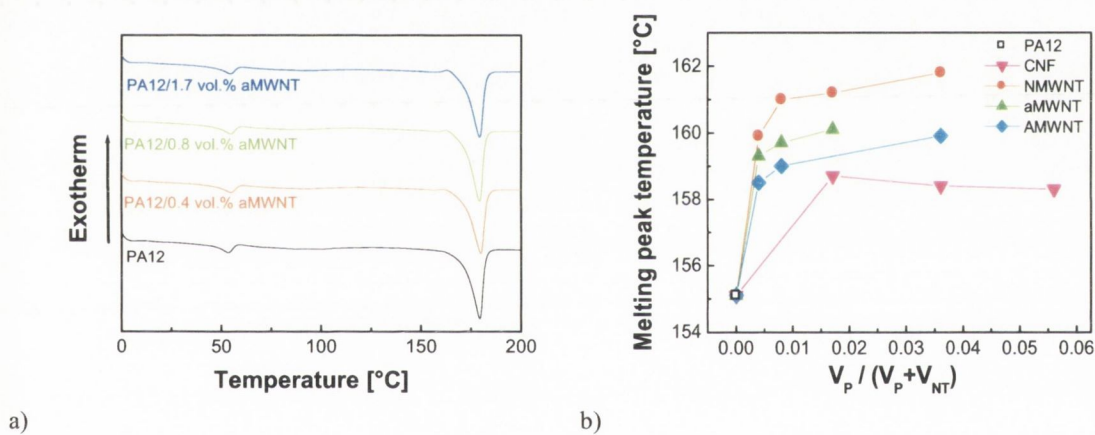


Figure 6-5: a) First heating of differential scanning calorimetry data obtained for aligned catalytic grown multi walled carbon nanotubes in polyamide12 nano-composite fibres, with increasing filler loading fraction, at 10°C/min heating rate b) Non-isothermal crystallisation study of all polyamide 12 nano-composite samples.

In Figure 6-5a the non-isothermal DSC thermographs from as-spun PA12 composite fibre reinforced with aMWNT can be observed. Three different filler contents of aMWNT are shown in addition to the pure Nylon[®]-sample as a comparison sample. All observed curves show similar shapes. As can be observed the glass transition occurs at around 50°C for all samples and is therefore not influenced by the nano-fillers. In addition all curves show an endothermic melting peak above 170°C which is associated with melting of the crystallites. Neither the melting peak temperature nor

the shape of the melting peak show significant changes in shape or size compared to the pure PA12 composite fibre sample. In order to establish a comparative degree of crystallinity for all nano-composite samples the melting peak area was evaluated and normalised to the fraction of polymer present. This approach led to a roughly constant degree of crystallinity ranging between 23% and 27%. This calculation was based on a melting enthalpy for a 100% crystalline PA12 sample of $209.34 \text{ J/g}^{1,2,10}$. Shown in Figure 6-5b is a comparative plot of a non-isothermal crystallisation study for all nano-composites produced in this Chapter where the melting peak temperature is plotted versus the volume fraction of nano-fillers. Samples were heated to 210°C and held for 5 minutes isothermal prior to cooling at 10°C/min . In case of the pure PA12 sample a single narrow crystallisation peak at around 155°C could be observed. In all other cases the nano-composites revealed an increase in crystallisation temperatures. This was depending on the filler-type and content. In the case of NMWNT the crystallisation temperature was increased to 162°C for the 3.6 vol.% composite sample. Figure 6-5b further shows that all nano-fillers used in this Chapter are acting in PA12 as nucleation agents as with increasing nanotube volume fraction an increase of the nucleation temperature can be observed. This effect seems to be most prominent for low filler loading fractions below 1.7 vol.% and can be explained by the enhancement of thermal conductivity when introducing thermal conductors such as carbon nanotubes. Here the heat can be faster deducted out of the composite sample and local crystallisation can occur in the area of the nano-fillers. Similar effects were observed in Chapter 5.2.2 in the case of poly(9-vinyl carbazole) and poly(vinyl alcohol).

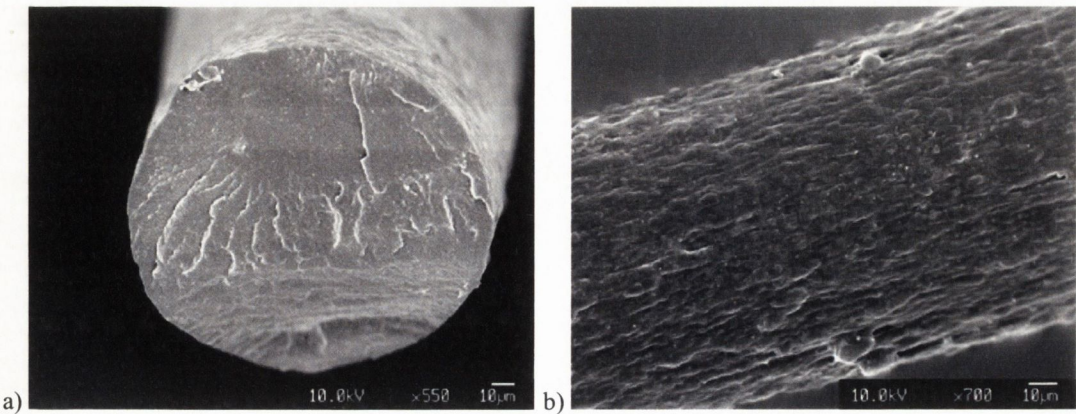
6.4 Electron Microscopy

In order to obtain and compare the dispersion and wetting behaviour of the nano-fillers in the composite, scanning electron microscopy (SEM) was performed. Composite samples were fractured under liquid nitrogen and mounted for observation in a JEOL 6430F FEG SEM, operating at 10kV acceleration voltage after sputtering with chromium.

Macroscopically all of the as-spun Nylon[®]12 nano-composite fibres appeared to be of good quality regarding surface finish and uniformity of diameter apart from the PA12 sample filled with AMWNT. All nano-composite fibre samples, regardless of the filler content, were coloured uniformly, non-transparently, black.

6.4.1 Dispersion and Wetting of Nano-fillers in PA12 fibres- SEM

Typical SEM micrographs of the nano-composite fibres can be seen in Figure 6-6 and Figure 6-7 which indicates the high level of dispersion for all catalytic grown nano-fillers, although occasional small agglomerates can be observed in the NMWNT as well. This can be explained by the higher degree of entanglement of the NMWNT material and is shown in Figure 6-6b and Figure 6-7b.



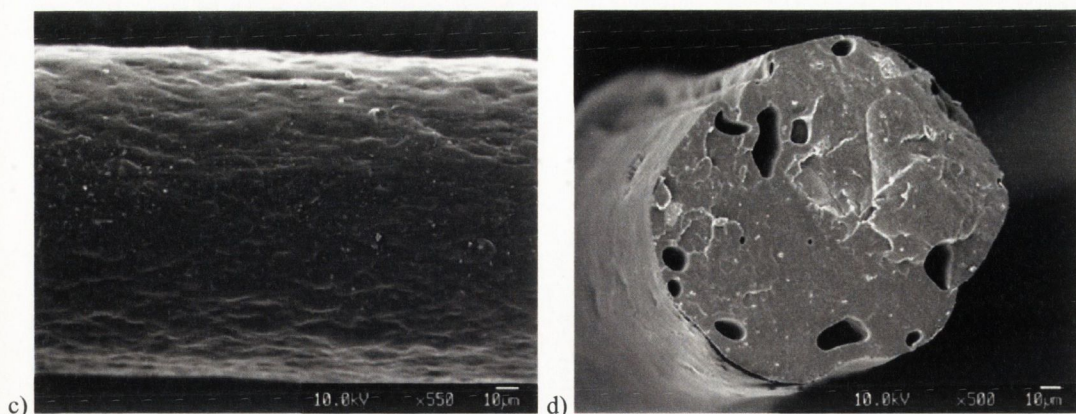
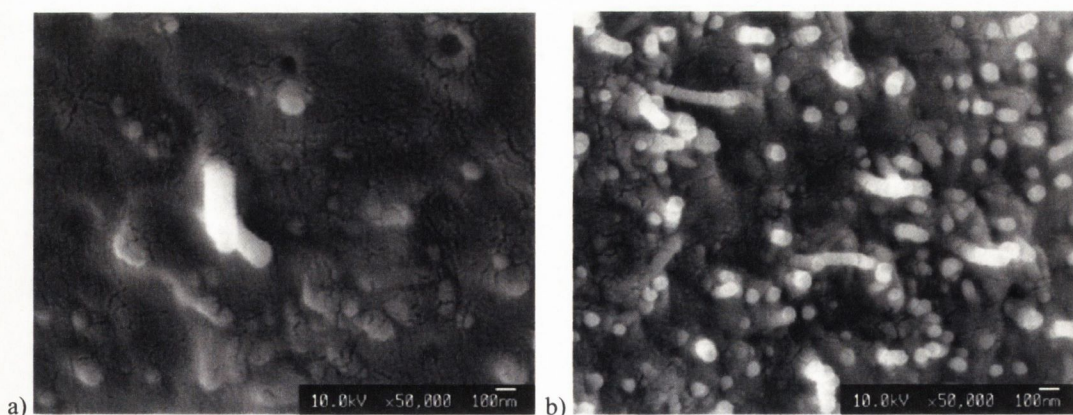


Figure 6-6: Scanning electron microscopy micrographs of polyamide 12 nano-composite fibres, containing a) 3.6 volume % carbon nano fibres, b) 3.6 volume % entangled catalytic grown multi walled carbon nanotubes, c) 1.7 volume % aligned catalytic grown multi walled carbon nanotubes and d) 1.7 volume % of arc grown multi walled carbon nanotubes

In the case of the AMWNT, dispersion was on a poorer level with aggregate formation leading to voids within the fibre which is clearly shown in Figure 6-6d and Figure 6-7d. This can be explained by the impurities involved in the as produced AMWNT material. These are fused together by the contaminating graphite. Highest dispersion level is shown in the more straight aMWNT and CNF which can be observed in Figure 6-6a and c and Figure 6-7a and c. Agglomerates can not be observed and the polymer seems to interact well with aMWNT and CNF.



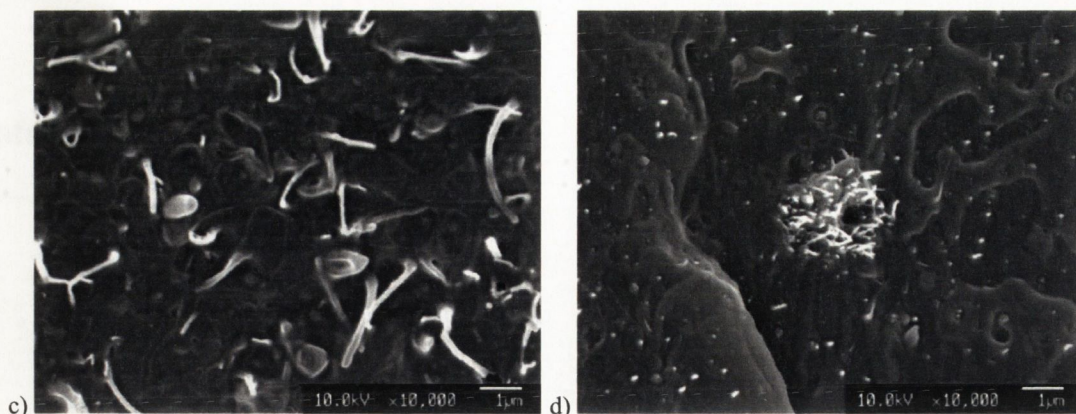


Figure 6-7: Higher resolution Scanning electron microscopy micrographs of polyamide 12 nano-composite fibres, containing a) 3.6 volume % carbon nano fibres, b) 3.6 volume % entangled catalytic grown multi walled carbon nanotubes, c) 1.7 volume weight% aligned catalytic grown multi walled carbon nanotubes and d) 1.7 volume % of arc grown multi walled carbon nanotubes

Maximum pull-out length were measured using SEM and found to range between ~300-500 nm for CNF, ~1 micron for NMWNT, ~0.5 μm for AMWNT and reach ~3-4 micron in case of the aMWNT/PA12 nano-composite sample. AMWNT were found to have lengths of 1-2 micron. Therefore, the measured pull-out length is reasonable as the pull-out average length is $\frac{1}{4}$ of the total length which results from the fact that if breakage in a CNT reinforced composite sample occurs a nanotube is pulled out from that side where the embedment length is shorter. This means that the pull-out length must vary between zero and the half of the nanotube length. However, aWMT and CNF are known to be significantly longer than 4 times their measured pull-out length in Figure 6-7a and c. This indicated that breakage of the CNF and aMWNT must have occurred when breaking these composite samples.

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Chapter 7

Conclusions & Future work

7.1 Conclusions

7.1.1 Optimisation of the arc-discharge production process

In a first step of this work it was shown that both the yield and purity of multi-walled carbon nanotube containing soot produced by the arc-discharge method can be maximised by careful control of production parameters such as current density and pressure. Both yields and relative purities increased with increasing current density and pressure with yields of up to 24 mg/min achieved for high current densities (190 A/cm²) and high pressures (500 Torr). This trend was supported using transmission electron microscopy. From electron paramagnetic resonance and thermo gravimetric measurements nanotube purity was measured quantitatively. This purity was shown to increase to 48% in the highest yield case. This extremely high purity value, for arc discharge produced carbon nanotube, shows that careful choice of current and pressure are critical to the optimisation of nanotube production. Furthermore the yield of nanotube containing soot per run could be dramatically increased by increasing the electrode size from 4.2 mm to 6.15 mm. Compared to the small diameter graphite rods the yield of production soot could be more than doubled from 260 mg to 700 mg per run. Furthermore, due to the optimised parameters the graphitic core part which hindered the manual separation process significantly could be avoided, therefore the separation process was dramatically simplified.

Thus, the arc-discharge method possesses much unrealised potential for the production of large quantities of high quality and high purity carbon nanotubes.

7.1.2 Polyvinyl alcohol thin film composites on glass substrates

The mechanical and thermal properties of amorphous and semi-crystalline multi walled carbon nanotube reinforced polymer films, drop cast on glass substrates, have been studied by nano-indentation and differential scanning calorimetry. In both cases significant increases in Young's modulus and hardness were observed. For polyvinyl alcohol increases in Young's modulus and hardness were observed of a factor of 1.8 and 1.6 respectively. These increases could be achieved while adding only 0.5 volume percent of arc grown multi walled carbon nanotubes. In the case of poly(9-vinyl carbazole) based composites the Young's modulus and hardness was increased by a factor of 2.7 and 2 respectively on addition of 5 volume percent of arc grown multi walled carbon nanotubes to the polymer matrix. In terms of thermal properties it was shown that the multi walled carbon nanotubes have a strong influence on glass transition and melting temperatures for the semi-crystalline polyvinyl alcohol. The crystallinity increased significantly while adding only 0.5 volume percent of arc grown multi walled carbon nanotubes to the matrix while poly(9-vinyl carbazole) does not show crystallization effects. The crystallinity increase of polyvinyl alcohol results in an extremely strong interfacial interaction between nanotube and polymer and is the major reason for the reinforcement of polyvinyl alcohol. In the case of the amorphous poly(9-vinyl carbazole) a second phase appeared when multi walled carbon nanotubes were added to the polymer. Furthermore, transmission electron microscopy micrographs clearly show that when under stress, the polyvinyl alcohol polymer matrix failed rather than the polymer

nanotube interface. This indicated an excellent interfacial interaction, suggesting that nanotubes are exceptional candidates for the reinforcement of polyvinyl alcohol.

7.1.3 Polyvinyl alcohol free standing films and diameter variation of carbon nanotubes

In order to perform macroscopic mechanical testing and compare these to previous nano-indentation results free-standing poly(vinyl alcohol) composite films were produced. Furthermore, to study the mechanical reinforcing effect of carbon nanotubes a range of different diameters was incorporated into poly(vinyl alcohol) free standing polymer films. A general increase of mechanical properties such as Young's modulus by a factor of up to 2 could be observed while adding only 0.6 vol% of CNT to polyvinyl alcohol. It was further observed that with the increasing diameter of the carbon nanotubes, the mechanical properties of the polymer composites, such as tensile modulus and tensile strength, decreased linearly on a double logarithmic plot. Therefore, the Young's modulus of the carbon nanotubes did not play the major role in this study as there were major differences of an order of magnitude in the nanotube moduli used in this study. Hence, it can be said that the reinforcing effect of carbon nanotubes is strongly dependant on the total surface area of carbon nanotubes per volume of polymer film. In order to establish this observed result an additional batch of small diameter carbon nanotubes were introduced in the same polymer matrix and found to increase the tensile modulus and strength by a factor of 4. Ultimate tensile strength for poly(vinyl alcohol) could be increased from 100 MPa to 400 MPa and tensile modulus from 1.8 GPa to 7 GPa while adding only 0.6 vol% of carbon nanotubes. This is an extraordinarily high value for a polymer composite and ranges in the region of mild steel. The major result is that if higher volume

fractions can be achieved to disperse in the poly(vinyl alcohol), a reinforcement in the region of tempered steel can be achieved when adding only 2 vol.% of carbon nanotubes and in case of 5 vol% of carbon nanotube a strength value of hard drawn steel wire would be achieved. This is a remarkable step forward to an industrial application.

This work was important to show that even poorly graphitised and hence low modulus nanotubes can be effective as reinforcement agents. This is probably due to the fact that for most polymers the polymer-nanotube interfacial stress transfer is low with values typically less than 50MPa. This means that the full potential of the nanotubes can never be addressed. This results in virtually no difference between nanotubes with $Y=1$ TPa and $Y=0.1$ TPa in terms of polymer reinforcement. As the interface of the carbon nanotubes appears to be the same in all cases it seems clear that the level of reinforcement is determined by the PVA-nanotube interfacial stress transfer. This demonstrates the critical importance of the interfacial stress transfer.

7.1.4 Polypropylene reinforced with polymer functionalised carbon nanotubes

In order to increase the interfacial stress transfer, free standing polymer films were produced reinforced with low diameter multi walled carbon nanotubes. These nanotubes were modified by functionalisation. The difference in this modification process is that not only functional groups were bound to the nanotube but whole polymer chains were covalently bond to the carbon nanotubes. This leads to a reinforcing effect of a factor of 4 and in the case of the fracture toughness an increase from 3.8×10^7 J/m³ to 1.4×10^8 J/m³. Furthermore, tensile modulus could be

increased by a factor of 4 from 1.7 GPa to 5.2 GPa and ultimate tensile strength was increased by a factor of 2.5 from 12 MPa to 30 MPa. Also the yielding strength (6 MPa – 17 MPa) and the elongation at break (380% - 540%) could be dramatically increased by only adding an amount of 0.6 vol.% of polymer chain functionalised small diameter multi walled carbon nanotubes. This result is remarkable but not as high as expected. It will be further improved by modifying the bonding of polymer chains to the carbon nanotubes. This is another approach to an industrial application of carbon nanotube reinforced polymer composites.

7.1.5 Extrusion of polyamide 12 fibres reinforced with carbon nanotubes

Investigations were carried out using a mass production method for polymer processing. A micro twin screw extruder was used in order to investigate the dispersion behaviour and the reinforcing effect of carbon nanotubes in a fibre spun engineering polymer. As polymer matrix polyamide 12 was chosen and reinforced with a range of different carbon nanotubes. Reinforcing effects determined by nano-indentation were obtained. Here the Young's modulus of the polyamide 12 could be increased by a factor of 1.5 from 1.1 GPa to 1.7 GPa while adding 5 weight % of aligned catalytic grown multi walled carbon nanotubes. In case of tensile testing the tensile modulus could be increased from 0.8 GPa for pure polyamide to 1.7 GPa for a filler fraction of 10 weight% of entangled catalytic grown multi walled carbon nanotubes. Here the aligned carbon nanotubes could increase the tensile modulus from 0.8 GPa to only 1.4 at a filler content of 5 weight %. This is in reasonable agreement to the nano-indentation results. Carbon nanofibres did raise the tensile modulus to 1.5 GPa when 15 weight% were added to the polyamide 12 matrix. Yielding points could be increased from 20 MPa for pure polyamide 12 to 50 MPa for

all nanotube reinforced polymer fibre composites. The thermal stability could be increased for all samples dramatically. Where for the neat polymer sample first decomposition effects could be observed already at 280°C the decomposition temperature for the composite was stable until 380°C in case of the 15 weight % filled carbon nano-fibre sample and was also observed for all other polyamide composite fibres. In the case of crystallinity all carbon nanotubes introduced to the polyamide acted as a nucleation agent when cooling from 210°C to room temperature. Crystallisation temperature was increased by 5°C when adding 10 weight% of carbon nanotubes. Observations from the electron micrographs confirm that melt blending leads to homogenous dispersions of purified carbon nanotubes and carbon nano fibres in polyamide 12 polymer composites which is essential for a strong reinforcement effect.

7.2 Future work

In order to further investigate the mechanical reinforcement effects of carbon nanotubes in polymer composite systems the work, reported in this thesis, will be followed by further investigations regarding the variation in the carbon nanotube diameters. The gap between the bundle forming single and double walled carbon nanotubes and small diameter multi walled carbon nanotubes will be minimised. Furthermore, there will done investigations on large diameter multi walled carbon nanotubes in order to see “the other extreme”.

In addition, several crystallinity and molecular weights of polyvinyl alcohol will be investigated to be able to learn more regarding the crystallisation behaviour when

adding carbon nanotubes to a polymer matrix. The iso-tacticity will be an additional issue of ongoing research on polyvinyl alcohol and carbon nanotubes.

Moreover, thermal processes to maximise the crystallinity in a polymer matrix will be performed in addition to alignment of the introduced carbon nanotubes in the polymer matrix in order to achieve iso-strain behaviour in the polymer composite systems.

Regarding functionalisation of carbon nanotubes, new work is ongoing where not only chlorinated polypropylene but a range of different polymer chains are covalently attached to the carbon nanotubes. Here the importance will be concentrated on the more prominent perpendicular functionalisation by only attaching the ends of the polymer chains to the carbon nanotube. This will increase the area around the nanotube in order to interact to as many polymer chains as possible and therefore increase the bonding area around the nanotube to a maximum related to the polymer chain length.

Appendix - Publication list

First author journal paper

1. "Optimisation of the Arc-Discharge Production of Multi-walled Carbon Nanotubes"
M. Cadek, R. Murphy, B. McCarthy, A. Drury, B. Lahr, M. i. h. Panhuis, J. N. Coleman, R. Barklie, and W. J. Blau, *Carbon*, **40**, 923-928 (2002)
2. "Morphological and Mechanical Properties of Carbon Nanotube Reinforced Semi-crystalline and Amorphous Polymer Composites"
M. Cadek, J. N. Coleman, V. Barron, K. Hedicke and W. J. Blau, *Applied Physics Letters*, **81**, 5123-5125 (2002)
3. "Reinforcement of polymers with carbon nanotubes: the role of nanotube surface area"
M. Cadek, J. N. Coleman, K. P. Ryan, V. Nicolosi, G. Bister, A. Fonseca, J. B. Nagy, K. Szostak, F. Béguin and W. J. Blau, *Nano Letters*, **4**, 353 (2004)
4. "High performance nanotube reinforced plastics: The mechanism of strength increase"
J. N. Coleman, **M. Cadek**, V. Nicolosi, K. Ryan, R. Blake, F. Liégeois, A. Fonseca, J. B. Nagy, Y. Gounko, and W. J. Blau, *Advanced Functional Materials*, **in press** (2004)

Co-author journal paper

5. "High yield, non-destructive purification and quantification method for carbon nanotubes"
R. Murphy, J. N. Coleman, **M. Cadek**, B. McCarthy, M. Bent, A. Drury, R. C. Barklie and W. J. Blau, *Journal of Physical Chemistry B*, **106**, 3087 (2001)
6. "Experimental Observation of Scaling Laws for AC and DC Conductivity in Polymer-Carbon Nanotube Composite Thin Films"
B. E. Kilbride, J. N. Coleman, P. Fournet, **M. Cadek**, A. Drury and W. J. Blau, *Journal of Applied Physics*, **92**, 4024-4030 (2001)
7. "Nonlinear optical response of Multi Walled Carbon Nanotube dispersions"
S. M. O'Flaherty, S. V. Hold, **M. Cadek**, A. Drury, J. N. Coleman and W. J. Blau, *Journal of the Optical Society of America B*, **20**, 49-58 (2002)
8. "Material investigation and optical limiting properties of carbon nanotube and nanoparticle dispersions",
S. M. O'Flaherty, R. Murphy, S. V. Hold, **M. Cadek**, and W. J. Blau, *Journal of Physical Chemistry B*, **107**, 958-964 (2002)
9. "Experimental Observation of Scaling Laws for AC and DC Conductivity in Polymer-Carbon Nanotube Composite Thin Films"
B. E. Kilbride, J. N. Coleman, P. Fournet, **M. Cadek**, A. Drury and W. J. Blau, *Virtual Journal of Nanoscale Science & Technology*, **6**, (14) (2002)

10. "Nonlinear optical response of Multi Walled Carbon Nanotube dispersions"
S. M. O'Flaherty, S. V. Hold, **M. Cadek**, A. Drury, J. N. Coleman and W. J. Blau, *Virtual Journal of Ultrafast Science – Condensed Matter Physics*, **2**, (1) (2003)
11. "Nonlinear optical response of Multi Walled Carbon Nanotube dispersions"
S. M. O'Flaherty, S. V. Hold, **M. Cadek**, A. Drury, J. N. Coleman and W. J. Blau, *Virtual Journal of Nanoscale Science & Technology - Carbon Nanotubes, C60, and Related Studies*, **7**, (4) (2003)
12. "A comparative study of melt spun polyamide-12 fibres reinforced with carbon nanotubes and nanofibres"
J. K. W. Sandler, S. Pegel, **M. Cadek**, F. Gojny, M. v. Es, J. Lohmar, W. J. Blau, K. Schulte, A. H. Windle, and M. S. P. Shaffer, *Polymer*, **45** (6) 2001-2015 (2003)
13. "Carbon Nanotube nucleated crystallinity in a conjugated polymer composite"
K. P. Ryan, S. M. Lipson, A. Drury, **M. Cadek**, M. Ruether, S. M. O. Flaherty, V. Barron, B. McCarthy, H. J. Byrne, W. J. Blau, and J. N. Coleman, *Journal of Physical Chemistry B*, **submitted** (2003)
14. "Spectroscopic Ellipsometry of a Polymer Nanotube Composite"
C. R. Belton, E. Tousaerre, G. Kranzelbinder, **M. Cadek**, A. Drury, J. N. Coleman, J. Zyss and W. J. Blau, *Advanced Functional Materials*, **submitted** (2003)

First author conference proceeding

15. Optimisation of Carbon Nanotube Production by Arc-Discharge"
M. Cadek, R. Murphy, B. McCarthy, B. Lahr, M. in het Panhuis, J. N. Coleman, R. C. Barklie and W. J. Blau, *AIP Conference Proceeding*, **591**, 179-182 (2001)
16. "Mechanical and Thermal Properties of CNT and CNF Reinforced Polymer Composites"
M. Cadek, B. Le Foulgoc, J. N. Coleman, V. Barron, J. Sandler, M. S. P. Shaffer, A. Fonseca, M. V. Es, K. Schulte, and W. J. Blau, *AIP Conference Proceeding*, **633**, 562-565, (2002)
17. "Mechanical and Thermal Properties of Multiwalled Carbon Nanotube Reinforced Polymer Composites"
M. Cadek, B. Le Foulgoc, J. N. Coleman, V. Barron, and W. J. Blau, *ICCE/9, San Diego, CA*, **9**, 85 (2002)
18. "Mechanical and Thermal Properties of Carbon Nanotube Reinforced Polymer Composite"
M. Cadek, J. N. Coleman, V. Barron, K. Hedicke and W. J. Blau, *Journal Proceedings SPIE*, **4876**, 676-685 (2002)
19. "Effect of Nanotube Type on the Enhancement of Mechanical Properties of Free-Standing Polymer/Nanotube Composite Films"
M. Cadek, J. N. Coleman, D. Blond, A. Fonseca, J. B. Nagy, K. Szostak, F. Béguin and W. J. Blau, *AIP Conference Proceeding*, **685**, 269-277 (2003)

Co-author conference proceeding

20. "Effect of Nanotube Inclusions on Polymer Morphology in Composite Systems"
J. N. Coleman, K. P. Ryan, M. S. Lipson, A. Drury, **M. Cadek**, M. in het Panhuis, R. P. Wool, and W. J. Blau, *AIP Conference Proceeding*, **633**, 557-561 (2002)
21. "Nanosecond nonlinear optical extinction in dispersed multi walled carbon nanotubes excited at 532 nm"
S. M. O'Flaherty, S. V. Hold, **M. Cadek**, A. Drury, J. N. Coleman and W. J. Blau, *Journal Proceedings SPIE*, **4876**, 750-758 (2002)
22. "Photoluminescence quenching and degradation studies to determine the effect of Nanotube Inclusions on Polymer Morphology in conjugated polymer-carbon nanotube composites"
K. P. Ryan, S. M. Lipson, S. M. O'Flaherty, V. Barron, **M. Cadek**, A. Drury, H. J. Byrne, R. P. Wool, W. J. Blau, J. N. Coleman, *Journal Proceedings SPIE*, **4876**, 361-369 (2002)
23. "Characterisation of Nanotube Based Artificial Muscle Material"
G. Kiernan, V. Barron, D. Blond, A. Drury, J. N. Coleman, R. Murphy, **M. Cadek**, and W. J. Blau, *Journal Proceedings SPIE*, **4876**, 775-783 (2002)
24. "Spectroscopic analysis of the intermolecular interactions of gamma cyclodextrin and carbon nanotubes"
G. Chambers, C. Carroll, G. F. Farrell, A. B. Dalton, **M. Cadek**, M. McNamara, E. Cummins, M. i. h. Panhuis, and H. J. Byrne, *Journal Proceedings SPIE*, **4876**, 667-675 (2002)
25. "Comparative study of two polymer carbon nanotube composites using electron paramagnetic resonance and transmission electron microscopy"
R. Murphy, J. N. Coleman, S. M. O'Flaherty, **M. Cadek**, B. McCarthy, A. Drury, R. C. Barklie, and W. J. Blau, *Journal Proceedings SPIE*, **4876**, 569-667 (2002)
26. "Polymer and Carbon Nanostructure Dispersions for Optical Limiting"
S. O'Flaherty, R. Murphy, S. Hold, A. Drury, **M. Cadek**, J. N. Coleman and W. J. Blau, *AIP Conference Proceeding*, **685**, 481-484 (2003)
27. "Mechanical Properties of Hybrid Polymer Nanotube Systems"
J. N. Coleman, **M. Cadek**, A. B. Dalton, E. Munoz, J. Razal, R. H. Baughman and W. J. Blau, *Journal Proceedings SPIE*, **in press**, (2003)
28. "Nanotube- and Nanofibre-reinforced Polyamide-12 Fibres"
M. S. P. Shaffer, J. K. W. Sandler, S. Pegel, A. H. Windle, F. Gojny, K. Schulte, M. Cadek, W. J. Blau, J. Lohmar, and M. v. Es, *MRS Conference Proceeding*, **in press**, (2003)

Patents

29. "Invention Related onto a Nanotube Composite Material"
M. Cadek, J. N. Coleman and W. J. Blau, *E.U & U.S. Patent*, **submitted, (2003)**

Thesis

30. "Investigations on Toughening of Novel Epoxy Resins"
M. Cadek, Diploma Thesis, University of Applied Science Darmstadt, **(2000)**