Chemically Modified Carbon Nanotube and Polymer Composites for Improved Mechanical and Acoustic Performance

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Abstract

This study has been undertaken in order to develop a new nanocomposite acoustic material via incorporation of multi-walled carbon nanotubes (MWCNTs) into the conventional damping material–polyvinyl acetate (PVAc). Usually MWCNTs are added into polymers to strengthen its stiffness only. Here, properties of stiffness and damping are both required for the cone/diaphragm to improve sound features of the speakers. The work provides perspectives on MWCNT covalent modification and the effect of MWCNT surface chemistry on the acoustic performance of the nanotube composites.

To achieve this goal, a detailed examination of the chemical modification of MWCNTs was carried out and a series of matrix-compatible MWCNTs were produced. The oxidation and amidation of the MWCNTs provide fundamental insight to the formation of oxidative fragments and the covalent reactivity of the MWCNTs, which has largely been ignored previously.

In the MWCNT carboxylation step, the oxidation debris generated from the etching of the nanotube lattice remains immobilised on the MWCNT surface. Their structure and solubility are similar with soil fulvic acids (FAs). The number of surface groups (e.g. phenol, lactone and carboxylic) after the removal of oxidative debris was determined by acid-base titrations, providing clear understanding of the amount of the covalently attached acidic groups on oxidised MWCNTs. Removal of FAs is of great importance as it can eliminate the unfavourable physical adsorption of polymer chains and improve the efficiency of MWCNT covalent modification.

A comprehensive set of experiments has been conducted to characterise the chemical reactivity of covalently attached carboxylic groups on MWCNT surface. It was realised that although the total number of oxygen-containing groups increased with prolonged oxidation time, the actual chemical reactivity of the carboxylic groups decreased. This is an important finding particularly in the understanding of chemistry of surface functionalities on MWCNTs and optimisation of the acid-oxidation conditions. PVAc chains were covalently linked to the MWCNT surface via free radical polymerisation; results revealed that the vinyl sites pre-anchored on MWCNTs lead to better grafting efficiency and thermal resistance of the grafted polymer. These data were confirmed by the transmission electron microscopy (TEM), differential scanning calorimetry and thermogravimetric analysis results.

Hot pressing of the casted films was adopted to fabricate MWCNT/PVAc composites with controlled dimensions free from air bubbles, where the pressing temperature is increased with pressure and time. The use of polymer grafted MWCNTs results in good distribution and interfacial adhesion as confirmed by TEM analysis. The stiffness is increased by 45% ± 10% when incorporated with 1wt% polymer coated MWCNTs, whereas damping is dropped by 17%. By contrast, the pristine MWCNTs induced limited improvement over the stiffness of up to 26% ± 10% and a good preservation of damping ability. The governing factors for stiffness and damping performance of the nanocomposites are discussed in terms of filler fraction percentage and MWCNT modification.
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Author Declaration

I declare that the research contained in this thesis, unless otherwise formally indicated within the text, is the original work of the author. The thesis has not been previously submitted to this or any other university for a degree, and does not incorporate any material already submitted for a degree.

Signed

Dated
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<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
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<tr>
<td>AIBN</td>
<td>Azobisisobutyronitrile</td>
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<tr>
<td>ASTM</td>
<td>American society for testing of materials</td>
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<td>CNTs</td>
<td>Carbon nanotubes</td>
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<td>CVD</td>
<td>Chemical vapour decomposition</td>
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<td>DMA</td>
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<td>DMF</td>
<td>Dimethylformamide</td>
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<td>DSC</td>
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<td>DWCNTs</td>
<td>Double-walled carbon nanotubes</td>
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<tr>
<td>EDAC</td>
<td>1-ethyl-3-(3-dimethylaminopropyl) carbodiimide</td>
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<td>FA</td>
<td>Fulvic acid</td>
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<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
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<td>IR</td>
<td>Infrared</td>
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<td>MWCNTs</td>
<td>Multi-walled carbon nanotubes</td>
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<td>NHS</td>
<td>N-hydroxysuccinimide</td>
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<td>PAH</td>
<td>Polycyclic aromatic hydrocarbons</td>
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<td>PBI</td>
<td>Polybenzimidazole</td>
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<td>Polycarbonate</td>
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<td>Polyimide</td>
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<td>Polymethylmethacrylate</td>
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<td>PS</td>
<td>Polystyrene</td>
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<td>Abbreviation</td>
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<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
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<td>PVAc</td>
<td>Polyvinyl acetate</td>
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<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SWCNTs</td>
<td>Single-walled carbon nanotubes</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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Chapter one:

Introduction
1.1. Mechanical damping of loudspeakers

Loudspeaker is an electroacoustic transducer where the electrical signal can be converted into an acoustic wave most often through vibrating a cone/diaphragm. The input electrical signal in the voice coil generates a mechanical force via electromagnetic coupling. The cone/diaphragm moves accordingly and a suspension system helps it return to neutral position after excitation, therefore a sound is produced (figure 1.1). The motion of the cone must respond simultaneously with the electrical signal without any additional vibrations so as to reproduce sound in its true form. Cones/diaphragms made from light weight and highly stiff materials such as diamond and carbon fibres are the key factors in the successful design of tweeter and mid-range drivers. However, stiff materials exhibit poor mechanical damping. The damping capacity of the cone materials is of crucial importance in reducing resonant vibration from the cone itself (Eargle 2003). Significant efforts have been spent on promoting vibration control via the use of new cone materials with polymer coating which has high stiffness associated with good damping property.
Given the better ratio of stiffness to weight compared with other polymer fibres, woven Kevlar fibres derived from polyamide have been utilised in cone/diaphragm since the 1980s. PVAc, a rubbery synthetic polymer used to seal the fabric cones, also improves damping. Figure 1.2 shows the simulation results of cone displacement as a sinusoidal force (6000 Hz) is applied to the bottom of the cone. It is can be seen that the mechanical waves propagate along the cone radius. In the case of cone with PVAc coating (figure 1.2 (B)), the mechanical wave is significantly damped by the time it reaches the surround on the edges compared with that of cone without PVAc. So far, the combination of Kevlar cone and PVAc is considered as one of the best composite in loudspeaker production (figure 1.3), exhibiting high elastic property and damping at the same time. However the performance of Kevlar cones can be further improved in time of response if it is possible to raise the Young’s modulus of PVAc without sacrificing its damping. Therefore, in this project, we are trying to improve Young’s modulus and damping properties of PVAc by incorporation of MWCNTs.
Figure 1.2 Simulation of a drive unit (A) with and (B) without PVAc coating (Copyright© Bowers&Wilkins)
1.2. CNT/polymer composites for improving stiffness and damping

1.2.1. Mechanical properties of CNTs

It is difficult to directly measure the mechanical performance of individual CNTs due to their nanoscale size and in-situ generated impurities. Therefore the initial understanding of the CNT mechanical behaviour was largely based on theoretical calculations. It has been estimated that CNTs consisting of single or multi-layers of graphene sheets are high stiffness materials and have Young’s modulus analogous to the in-plane Young’s modulus of graphite, which is around 1060 GPa (Ruoff et al. 1995). In numerical results of the SWCNTs, the obtained Young’s moduli are very scattered due to the uncertainty of exact value of CNT wall thickness. Some of the reported results can be as high as 6 TPa and it has been judged as less accurate in which wall thickness is considered as equivalent to the ratio of the bending to
tension rigidity. Actually it has been proved that this ratio is not a constant and it depends on the type of loading (Huang et al. 2006). Comparison between numerical and experimental results, Young’s modulus of about 1.0-1.3 TPa should be reliable and reasonable results of the SWCNT (Krishnan et al. 1998. Salvetat et al. 1999).

Furthermore, it has been proved by both experiment and theory calculations that Young’s modulus of nanotubes is affected by their structures defects, number of wall layers etc (Salvetat et al. 1999, Tu et al. 2002). The SWCNTs with less degree of disorder present higher Young’s modulus which is the best choice for mechanical applications in the research studies. However MWCNTs are relatively low cost offering advantage in large-scale industrial development.

1.2.2. Young’s modulus of CNT/polymer composites

Young’s modulus, which reflects the stiffness of a polymer composite, is defined as the ratio of stress to strain in the linear elastic region, which can be derived from the tensile tests under static forces. In addition, Young’s modulus measured under vibration condition is commonly used in characterising viscoelastic materials because of their frequency dependent property. The following mathematical model has been established for estimating Young’s modulus of CNT/polymer composites (Soboyejo et al. 2003).

\[ E_c = K_1 V_{CNT} E_{CNT} + (1-V_{CNT})E_m \]

In this model, \( E_c \), \( E_{CNT} \) and \( E_m \) are elastic moduli of the final composite, CNTs and polymer matrix, respectively. \( V_{CNT} \) is the volume fraction of CNTs. \( K_1 \) is the CNT reinforcing
efficiency parameter which is limited by CNT alignment, length and stress transfer etc. (Soboyejo et al. 2003).

Selections of polymers have been utilised as matrix materials in CNT composites for stiffness improvement, such as epoxy (Schadler et al. 1998), PS (Qian et al. 2000), PMMA (Hwang et al. 2004), PVA (Shaffer et al. 1999, Cadek et al. 2004), etc. Table 1.1 summarises some examples of Young’s modulus of matrix materials and their random distributed CNT composites. Results indicated that the CNT composites had a very limited increase in the mechanical performance, which could be due to weak interface interactions and CNT orientation state (Haggenmueller et al. 2000, Coleman et al. 2006).

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>Matrix</th>
<th>(E_{\text{polymer}}) (GPa)</th>
<th>(E_{\text{composite}}) (GPa)</th>
<th>CNT content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD-MWCNTs</td>
<td>PVOH</td>
<td>~ 6.3</td>
<td>~ 12.6</td>
<td>60 wt%</td>
</tr>
<tr>
<td>CVD-MWCNTs</td>
<td>PS</td>
<td>1.2</td>
<td>1.69</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Arc-MWCNTs</td>
<td>PVA</td>
<td>7</td>
<td>12.6</td>
<td>0.6 vol%</td>
</tr>
<tr>
<td>CVD-MWCNTs</td>
<td>PS</td>
<td>1.53</td>
<td>3.4</td>
<td>2.5 vol%</td>
</tr>
<tr>
<td>CVD-MWCNTs</td>
<td>High density PE</td>
<td>0.98</td>
<td>1.35</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Arc-MWCNTs</td>
<td>PMMA</td>
<td>0.71</td>
<td>2.34</td>
<td>1 wt%</td>
</tr>
<tr>
<td>DWCNTs</td>
<td>PVA</td>
<td>2</td>
<td>3.6</td>
<td>0.2 vol%</td>
</tr>
<tr>
<td>CVD-MWCNTs</td>
<td>PVA</td>
<td>2</td>
<td>4.2</td>
<td>0.6 vol%</td>
</tr>
<tr>
<td>CVD-MWCNTs</td>
<td>PVA</td>
<td>1.9</td>
<td>7.04</td>
<td>0.6 vol%</td>
</tr>
</tbody>
</table>

Table 1.1 Modulus of polymer blank and CNT/polymer composites (Taken from Coleman et al. 2006).

Therefore the major concern regarding nanocomposites is how to effectively transfer loading from polymer matrix to CNTs, thus obtaining individual performance of CNTs on the
nanoscale. Poor load transfer mainly arises from the insufficient CNT distribution and weak interfacial adhesion between the filler and polymer matrix (Salvetat et al. 1999, Ajayan et al. 2000). Moreover, the obtained mechanical performance of nanocomposites varied depending on the weight/volume fraction, purity, production procedure and configurations of the CNTs.

Chemical functionalisation of CNTs is accepted as an important approach to disentangle CNT bundles and improve interfacial integrity between CNTs and polymer matrix (Gojny et al. 2003). It is usually shown that functionalised CNT/polymer composites yield considerable improvement in mechanical properties compared with composites containing raw CNTs. Mechanical performance of 2.5 wt% SWCNT/PVA reported by Paiva et al. was shown to have only a moderate increase of 35% compared with the blank, and 55% increase in the case of same quantity of functionalised MWCNTs (Paiva et al. 2004).

1.2.3. Damping performance of CNT/polymer composites

Proper damping materials include rubbery polymers, void containing and amorphous materials as they can absorb more energy than stiff materials. The capacity of the damping is expressed by the loss modulus (E’’) which can be obtained by multiplying loss factor (η) or damping ratio (ζ) with Young’s modulus (E’). The loss factor can be evaluated by DMA or free vibration tests. In addition to achieve high Young’s modulus, increasing damping is another goal for CNT/polymer composites for certain applications i.e. acoustic, aerospace and civil systems (Deng et al. 2007). Both theoretical and experimental work showed that CNTs support matrix materials against deformation when the applied force (σ1 or σ2) is lower than the critical interfacial stress (τcr), however they can debond from the matrix once the applied
forces ($\sigma_3$) is higher than the critical stress, leading to interfacial slippage and energy absorption, which forms the mechanism of damping enhancement (figure 1.4) (Hölscher et al. 1998, Falvo et al. 1999, Rajoria et al. 2005). Thus CNT composites with lower interfacial stress criteria have higher damping capacity. It is recognised that damping can be further strengthened by increasing the amount of CNTs and using CNTs of small diameters which potentially increase the interfacial contact areas (Zhou et al. 2004). Figure 1.5 (A) reveals CNTs pulled out from a polymer matrix after three-point bending tests (Lau et al. 2002). The ‘pull out’ effect indicates good damping as CNTs slip out of the surrounding matrix (Ajayan et al. 2006), but this is not expected to occur for the case of stiffness reinforcement as the CNTs cannot take maximum loading and break together with matrix (figure 1.5 (B)).

Figure 1.4 Mechanism of damping performance of CNT composites (taken from Rajoria et al. 2005).

High Young’s modulus and high damping ratio are incompatible requirements as standard damping materials are usually soft but stiff materials such as metals are not good at damping (Kireitseu et al. 2008). However a number of engineering and acoustic applications require
Young’s modulus and damping at the same time in order to reduce vibration levels (Rivin 1999). By adding CNTs into polymers, it is possible to simultaneously improve Young’s modulus and loss factor. It is believed that the strong interface interactions are able to offer effective stress transfer to reinforcing fillers, resulting in high Young’s modulus. In the meanwhile, the interfacial sliding between CNTs and matrix materials can absorb energy, resulting in good damping property. Thus the interface between CNTs and the parent material plays a crucial role in damping and stiffness. It was found that high interfacial strength can increase Young’s modulus but not damping. However, good CNT distribution may solve this problem which can enlarge the ‘contact’ area between CNTs and surrounding polymers and in turn increase the chance of interfacial sliding.

Here are some research studies on stiffness and damping properties of CNT/polymer composites. Jin et al. have measured the DMA behaviour of melt-processed CNT/PMMA composites and results showed that Young’s modulus increased up to 27-fold with addition of 26% of MWCNTs and the loss factor remained (Jin et al. 2000). Suhr et al. reported that sandwich structured MWCNT/epoxy composite exhibited viscoelastic properties, its loss factor increased by 1400% however the Young’s modulus was the same as epoxy blank (Suhr et al. 2005). Rajoria et al. reported that there is a 700% increase in loss factor for CNT/epoxy composites, but no obvious change in stiffness, with the addition of 5 wt% of pristine MWCNTs (Rojoria et al. 2005). So far, it is still lack of study on how to engineer interface of CNT/polymer composites to increase both damping and stiffness.
Figure 1.5 SEM images of (A) CNTs pulled out from polymer matrix after three-point bending tests; (B) CNTs break in the PP (Taken from Lau et al. 2002, Funck et al. 2007)
1.3. Processing methods for CNT/polymer composites

1.3.1. Solution mixing

The basic method for producing CNT/polymer composites is mixing CNTs with a polymer solution, which is suitable for processing both thermoplastic and thermosetting polymers. This method is considered the most successful approach to synthesis of CNT/polymer composites as numerous studies have demonstrated that surface modification can effectively change the dispersibility of CNTs. In addition, the cost of solution mixing is usually lower than other polymer processing methods. In this approach, CNTs functionalised by multi-step chemical or physical treatment are firstly dispersed in a polymer solution in water or an organic solvent. In the case of thermoplastic polymers, solvents are evaporated in a controlled way to allow the polymer to re-solidify (Tang et al. 2003). For thermosetting polymers, an additional hardening and curing procedure is required (Gojny et al. 2003). Up to now, CNTs have been mixed with a wide range of polymer matrices using this method, such as PS (Fragneaud et al. 2008), PMMA (Kshiwagi et al. 2007), PVA (Cadek et al. 2002), PC (Ramasubramaniam et al. 2003), PBI (Okamoto et al. 2008), PI (Bellayer et al. 2008) and epoxy resin (Sandler et al. 2003), to produce advanced nanocomposites for mechanical, electrical and thermal applications. The major concern in using the solution mixing method is that any residual solvent can impose negative influence on the properties of nanocomposites, therefore may hinder large scale industrial applications (Esawi et al. 2009).
1.3.2. Melt blending

The melt blending process involves dispersing CNTs into polymer melt by mechanical shear forces using extrusion, injection or compression moulding. This method has advantages of making nanocomposites for large scale production and the final material shape is well controlled through moulding; however it suffers from poor CNT dispersion as mechanical forces are usually applied for only a few minutes and are not enough to disaggregate CNT bundles in polymer melt of high viscosity. Currently a microcompounder is frequently used in preparing nanocomposites in the experimental stage through controlling the mixing time and screw speed; meanwhile it can also provide rheological characterisation of materials (Pötschke et al. 2004).

1.3.3. In-situ polymerisation

Instead of mixing CNTs with pre-synthesised polymers, an alternative way for producing nanocomposites is to add CNTs into the polymerising solution. In an early example of this method used by Cochet et al, CNTs were dispersed in polyaniline (Cochet et al. 2001). The main shortcoming of this method is the control of polymer molecular weight because CNTs could interrupt the chain progression by attaching with polymer radicals (Jia et al. 1999).
1.4. CNT structures

A SWCNT can be regarded as a graphene sheet rolled into a cylinder of around 2 nm in diameter and up to few µm in length (Tans et al. 1997, Saito et al. 1998). Depending on the rolling vector \( C_h = na_1 + ma_2 \), it has two highly symmetrical structures: armchair \((n = m)\) and zigzag (either \( n = 0 \) or \( m = 0 \)) (figure 1.6). The other known structures are known as chiral CNTs (Dai et al. 2001, Balasubramanian et al. 2005). By repetitive insertion of rolled graphene sheets into a concentric formation, a structure representative of MWCNTs is produced, presenting a diameter of 5-40 nm, several µm length and a layer spacing of 0.3–0.4 nm (Shang et al. 2005).

![Figure 1.6 The chiral vector \((n, m)\) determines how the graphene sheets roll up into a CNT tube (Taken from Dai et al. 2001).](image)

The TEM technique provides morphological details of CNTs. The first TEM images of MWCNTs were obtained by Radushkevich et al. in 1952, however the (002) lattice could not be resolved due to the limitation of the microscope (figure 1.7 A) (Radushkevich et al. 1952, Monthioux et al. 2006). In 1991, MWCNTs were synthesised by arc discharge method in an
attempt to produce fullerenes. This time, the MWCNT layer stacking arrangement was clearly showed in TEM images (figure 1.7 B) (Iijima 1991). Since then, CNTs have attracted enormous attention and various tubular configurations have been observed. For instance, it was found that in some cases a different number of layers are formed on the two sides of the central core and the interlayer spaces are not evenly distributed (Harris 1999) (figure 1.7 C). Branched CNTs showing ‘elbow connection’ may have positive impact on their electronic property. (Wang et al. 2006, Kiang et al. 1996) (figure 1.7 D). It has been suggested that coiled CNTs with regular spiral structures could enhance the interfacial bonding between CNTs and the polymer matrix, therefore they are considered as a promising filler of structural nanocomposites (figure 1.7 E) (Wen et al. 2001, Lau et al. 2006). Bamboo-like CNTs having separated inner cavity have shown excellent electrochemical behaviour (Heng et al. 2005) and lithium storage capacity (Wang et al. 2003). (Lin et al. 2005) (figure 1.7 F).
Figure 1.7 A. The first TEM picture of MWCNTs (Radushkevich et al. 1952); B. High resolution TEM image of MWCNTs (Iijima 1991); C. MWCNTs with different number of layers on two sidewalls (Harris 1999); D. Bent MWCNTs (Kiang et al. 1996); E. Coiled MWCNTs (Wen et al. 2001); F. Bamboo-like MWCNTs (Lin et al. 2005) (Taken from

In reality, CNTs tend to form macroscopic aggregates of a few micrometers which are driven by the strong van der Waals interactions of 0.5 eV per nanometer (Dyke et al. 2004). The CNT clumps decreases the reinforcing aspect ratio. A major direction of CNT research has been focused on disaggregating CNTs, forming solutions of individual CNTs in water or common organic solvents through physical and chemical surface treatment.
1.5. CNT synthesis methods

1.5.1. Arc discharge evaporation method

The arc discharge technique played an important role in the development of CNTs as MWCNTs were first synthesised without the presence of any catalysts (Iijima 1991). The process is very similar to C60 production except that there is a short distance between two electrodes. In the process of direct current (DC) arc discharge through two high purity graphite electrodes (shown in figure 1.8) under He atmosphere and low pressure, carbon on the cathode is continuously vaporised and subsequently condensed on the surface of the anode. The product is also called ‘soot’ which inner core contains CNTs. In 1993, Iijima et al. were able to produce SWCNTs by using a catalyst (Fe) containing graphite electrode and arcing in methane-argon atmosphere (Iijima et al. 1993, Bethune et al. 1993). Later, SWCNTs were successfully produced by Qin et al with the diameter of only 0.4 nm, which are the smallest CNTs that can exist stably (Qin et al. 2000).

With this method, the main concerns are yield and cost. Until now yield has been around 40% using Rh-Pt/Y-Ni mixtures as catalysts (Saito et al. 1998, Shi et al. 1999); cost remains a problem due to the demand of high purity graphite electrodes, catalysts and an inert gas.
1.5.2. CVD method

CVD has been used for over a hundred years to produce carbon filaments (Schultzenberger et al. 1890, US patent 4663230). In 1993 it was successfully applied for the synthesis of CNTs, (Santiesteban 1993). It is now a commonly adopted method for the commercial production of CNTs because of low cost production, high yield and capacity for industrial scale-up. The process (shown in figure 1.9) involves the pyrolysed carbon atoms decomposed on a catalytic substrate. Furthermore, by choosing the right type of hydrocarbon (e.g methane) and catalyst (e.g CoO or Fe$_2$O$_3$), SWCNTs and DWCNTs are obtained (Kong et al. 1998, Peigney et al. 2001). It was observed that CVD-formed-CNTs contained more defects along the sidewalls and tips compared with CNTs produced by the arc-discharge method, which can be attributed to the relatively low temperatures involved in the CVD method (~1000 °C) and different growth mechanisms (Thien et al. 2002).
The CVD method has been optimised in order to achieve large quantity production and novel configuration. The HiPCO process, in which CO is thermally decomposed under high pressure (up to 10 atm) and Fe(CO)$_5$ is used as catalytic precursor, is one of the most productive and effective methods for SWCNT synthesis (Nikolaev et al. 1999). Wang et al synthesised 50 kg d$^{-1}$ of MWCNTs with the fluidised-bed reactor, which is the highest production reported so far (Wang et al. 2002). Enhanced plasma CVD has been demonstrated to be an effective technique to produce vertically-aligned nanotubes (Tanemura et al. 2001). In 2007, researchers at the University of Cincinnati successfully grew 18 mm long aligned MWCNT arrays (Wendy et al. 2007).

### 1.5.3. Laser ablation

Another strategy to grow CNTs is the use of laser ablation, which was first demonstrated in 1996 by Smalley's group (Yakobson et al. 1996). Figure 1.10 is the schematic set up of laser ablation. In this process the flow tube is heated to ~1200°C by a tube furnace. Laser pulses enter the tube and strike a target consisting of a mixture of graphite and a metal catalyst such as Co or Ni. CNTs condense from the laser vaporisation plume and are deposited on a
collector outside the furnace zone. At high temperatures, CNTs with good crystallinity and purity can be obtained (Thess et al. 1996, Guo et al. 1995, Yudasaka et al. 1997). However, a complicated set up and low yield limits its wide applications.

![Laser Ablation](image)

Figure 1.10 Set up for laser ablation in the production of CNTs

### 1.6. CNT purification

The crude CNT samples contain a large number of in-situ generated impurities, such as amorphous carbon, fullerenes, graphitic nanoparticles, and catalyst materials. In some production cases, impurities can account for up to 70% of the final material. Physical techniques (e.g. filtration, centrifugation, chromatography) could not effectively remove large amount of amorphous and spherical carbon particles which are adhered to CNT main structures (Ebbesen et al. 1994, Hou et al. 2008). Oxidation combined with acid washing has been found to be an effective method to overcome this problem, with the idea based on CNT crystalline structures being more thermally and chemically stable than carbonaceous particles and metal catalysts. In 1994, oxidation was initially conducted in air at 700°C for CNTs formed by arc discharge, however less than 1% of the final product was left which was summarised as a small difference in oxidation reactivity between CNTs and impurities (Ebbesen et al. 1994). Then liquid-phase oxidation (e.g HNO₃, H₂SO₄, mixture of HNO₃ and
H₂SO₄) was developed. Results revealed that a high yield of CNTs with smooth surface and high crystalinity was obtained (Hiura et al. 1995). Figure 1.11 shows TEM images of crude SWCNTs ((A) and (B)) and SWCNT after HNO₃ purification ((C) and (D)) (Dujardin et al. 1998). Most of the impurities were effectively removed, leaving ca. 1% of metals which were detected by XPS. In order to fully eliminate nano-sized carbon and catalyst particles, multi-step purification processes combining acid oxidation, air oxidation and annealing have been reported, which produced thick and highly ordered CNT bundles (Martínez et al. 2003). However it is important to understand that oxidation parameters are different and dependent on the configuration of CNTs (e.g MWCNTs, SWCNTs) and production methods (Dillon et al. 1999), and even for different CNT batches or different synthesis apparatuses, purification parameters may vary.
Figure 1.11 TEM images of crude SWCNTs (A) and (B); SWCNTs after purification (C) and (D) (Taken from Dujardin et al. 1998)
1.7. CNT solubility

1.7.1. Solubility of pristine CNTs

Pristine CNTs tend to form large bundles (~10-30 nm in diameter for SWCNTs) and do not disperse well in water or organic solvents due to strong van der Waals interaction between tubes and large specific surface (1500 m² g⁻¹ for SWCNTs) (Wang et al. 2009). Figure 1.12 presents the visual appearance of raw CNT (TMSpetsmash, Ukraine) suspensions in acetone, water, and dichloromethane after sonication for 20 minutes. It is clearly showed that CNTs completely fell out of solvents. A study of solubility of raw SWCNTs (obtained from HiPCO method) identified 1,2-dichlorobenzene as the most suitable solvent (table 1.2) and their solubility varied from 35-95 mg L⁻¹ depending on the solvent polarity (Bahr et al. 2001). Other high polar solvents, such as dimethylformamide, N-methylpyrrolidone, and hexamethylphosphoramide were also considered promising options to solvate pristine CNTs (Ausman et al. 2000). It was also concluded that solubility of pristine CNTs largely depends on their length (Chen et al. 1999), impurity, (Bahr et al. 2001), structural rigidity (Hirsch 2002) and solvent polarity. However, it should be pointed out that by mechanical forces only, i.e. shear forces and micro turbulences, it is difficult to disentangle raw CNTs into individual tubes, and the resulted CNT aggregates will weaken the mechanical, electrical, and thermal conductive properties of final composites.
1 - Introduction

Figure 1.12 Visual appearance of CVD produced MWCNTs in (A) acetone; (B) water and (C) dichloromethane

<table>
<thead>
<tr>
<th>Solvent</th>
<th>mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>95</td>
</tr>
<tr>
<td>Chloroform</td>
<td>31</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>25</td>
</tr>
<tr>
<td>1-Bromo-2-methylnaphthalene</td>
<td>23</td>
</tr>
<tr>
<td>N-Methylpyrrolidinone</td>
<td>10</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>7.2</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>4.9</td>
</tr>
<tr>
<td>1,2-Dimethylbenzene</td>
<td>4.7</td>
</tr>
<tr>
<td>Pyridine</td>
<td>4.3</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>2.6</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>2.3</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
</tr>
<tr>
<td>1,3-Dimethylbenzene</td>
<td></td>
</tr>
<tr>
<td>1,4-Dimethylbenzene</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2 SWCNT (CVD, HiPCO process) solubility in a variety of solvents at room temperature after sonication for 1 hour, (b) indicates that solubility in these solvents is less than 1mg L⁻¹) (Taken from Bahr et al. 2001)

1.7.2. Solubility of modified CNTs

It has been found that surface functional groups and molecules attached to the surface of CNTs, stabilise their dispersions at much higher concentrations compared with raw/unfunctionalised nanotubes (Kharisov et al. 2009). Early examples of improving CNT solubility through chemical functionalisation were provided by the Haddon group. They
reported that shortened SWCNTs (100-300 nm in length) bearing carboxylic groups covalently connected with amines, through reactive alkyl chlorides, had around 85% solubility in dichloromethane and THF. Individual tubes were observed in these suspensions by AFM images (Chen et al. 1998, Hamon et al. 1999). However, short-length CNTs are not desired for certain practical applications, such as material reinforcement, as the composite strength and Young’s modulus increase with respect to aspect ratio (ratio of length to diameter) (Fu et al. 1998, Fu et al. 2009). To overcome this problem, long SWCNTs (~1 µm) soluble in THF (> 0.5 mg mL⁻¹) were prepared by oxidation with dilute nitric acid and subsequent ionic modification with long chain aliphatic amines (Chen et al. 1999). Georgakilas et al. reported an excellent solubility of SWCNTs after 1.3-dipolar cycloaddition reaction, which resulted 50 mg mL⁻¹ stable suspension, this is perhaps the most soluble SWCNTs reported in literature (Georgakilas et al. 2002). Solubility of modified CNTs varied with each other in different studies, however it is extremely difficult to compare which chemical reaction works more efficiently as the results strongly depend on the quality of CNTs, i.e. integrity, defect sites, length, diameter and structural rigidity.

Another approach to improve CNT solubility is to utilise polycyclic aromatic hydrocarbons (e.g. phthalocyanines, polyaryleneethynylene), surfactants (e.g. Triton X-100, SDS) or long chain polymers, which can be physically attached on the CNT surfaces due to π-stacking or polymer wrapping (figure 1.13) (Nakashima et al. 2007). The major advantage of this method is that it does not require aggressive chemical treatments which cause oxidative etching. Liu et al. reported that physical grafting of copolymer polystyrene-g-(glycidyl methacrylate-co-styrene) resulted in a solution with good concentration of 0.55 mg mL⁻¹ of MWCNTs in ethanol in contrast with raw HiPCO MWCNTs showing less than 0.001 mg mL⁻¹ dispersibility in ethanol (Bahr et al. 2001, Liu et al. 2006). Other polystyrene copolymers
were also shown to increase CNT dispersibility up to around 0.066 mg mL\(^{-1}\) in chloroform by sonication of pristine MWCNTs with polystyrene copolymers at 70 °C (Zhao et al. 2008), which is twice the solubility compared to that of raw HiPCO MWCNTs (table 1.2, Bahr et al. 2001).

1.8. Chemical modification of CNTs

A number of covalent reactions on the CNT surface have been reported. The functional groups/molecules are chosen for their solubility in solvents, their particular chemical, thermal and mechanical properties probably as well as the reactivity in subsequent reactions. The combination of the unique properties of CNTs and functional groups increase the possibilities for synthesising polymer composites having high-performance of excellent stiffness, electrical, thermal conductivity. By comparing covalent linkages with physically adsorbed interactions, it is anticipated that covalent bonding would provide a more stable connection between functional molecules and the CNT lattice, which is able to increase the interaction between CNTs and polymer matrix in nanocomposites (Bartholome et al. 2008); however,
covalent modification is limited through the requirement of long reaction periods and complicated experimental procedures.

1.8.1. CNT chemical reactivity

Electrophilic reagents containing a diene such as carbenes and nitrenes are able to react with \( \pi \) electrons of CNTs to form a cyclic group under moderate temperatures and in the presence of a Lewis acid as a catalyst (Gergely et al. 2007). Similarly, reactions between 1,3-dipolar compound such as azomethine and CNTs can produce five-membered ring addition to the CNT sidewalls (Lu et al. 2003). The sidewall addition is mainly determined by the curvature of CNT lattice. Bahr et al reported that one in every twenty carbon atoms in the CNTs were functionalised with aryl diazonium compounds which is found very promising in developing CNT-based molecular electronic devices (Bahr et al. 2001, Bahr et al. 2002).

Instead of utilising \( \pi \) electrons of CNTs, chemical reactions of CNTs can take place on defect sites, which are caused by the curvature of the graphitic lattice, the production process or oxidative treatments. End caps, which are under greater strain compared with the sidewalls, are more susceptible towards chemical reactions (Britz et al. 2006). It has been reported that \(~5\%\) of carbon atoms exist as defect sites in pristine CNTs, which will be further increased by acidification process (Mawhinney et al. 2000).
1.8.2. CNT chemical reactions based on carboxylic groups

Figure 1.14 depicts the typical steps for conducting CNT chemistry on carboxylic groups, which involves amidation through either nucleophilic acyl substitution reaction or carbodiimide assisted amine coupling. In this project, carboxylation and subsequent carbodiimide and NHS activated amidation of CNTs are the points of focus (figure 1.15).

![Figure 1.14 A typical route for CNT chemical reactions based on carboxylic sites](image)

Carboxylic groups can be easily formed on CNT surface along with other oxygen containing groups through solution or gas phase oxidation (figure 1.15) (Ros et al. 2002, Chirila et al. 2005).
Carboxylic groups have been characterised via both qualitative and quantitative methods (Boehm 2002). Compared with the semi-quantitative instrumental techniques, such as XPS and IR, Boehm titration is a more direct and simple technique to quantify the type and number of acidic groups present on oxidised CNTs (Wang et al. 2009). However, recent publications have highlighted that some of the formed carboxylic groups are perhaps not covalently bound to the CNT surface as was first assumed. In 2007 Verdejo et al. (Verdejo et al. 2007) and Salzmann et al. (Salzmann et al. 2007) reported that the majority of the carboxylic groups are attached to the oxidation debris adsorbed on the CNT surfaces. Treatment with NaOH solution is able to remove this debris due to the introduction of negative charge on the protonated CNT fragments.

Generally, there are two approaches in the formation of an amide bond from carboxylated CNTs. One is the reaction with thionyl chloride (SOCl₂), which forms reactive acyl chloride
groups (Bosshard et al. 1959). The main product, MWCNT-acylchloride, reacts with species possessing \(-\text{NH}_2\) groups through a nucleophilic acyl substitution reaction forming amide compounds (figure 1.16). The limitations of this reaction are it has to be performed in dry conditions, as SOCl$_2$ is very sensitive to water and the \textit{in-situ} generated HCl can further neutralise the unreacted amine which reduces the reaction yields (figure 1.17) (Paula, Organic Chemistry 5$^{\text{th}}$ edition). Using this approach, the early work showed that the shortened SWCNTs (100-300 nm in length) reacted with long chain aliphatic amines (Chen et al. 1998) or alkyl aryl amines (Hamon et al. 1999) (shown in figure 1.18) to produce soluble SWCNTs. It is also been reported that allylamine (Yang et al. 2006) was attached to MWCNT-acylchloride, leaving a vinyl group as a new active site, useful in the synthesis of polymer grafted CNTs through free radical polymerisation reaction (shown in figure 1.19).

\[
\text{R-COCl} + \text{NH}_2\text{-R}' \xrightarrow{} \text{R-CONH-R'} + \text{HCl}
\]

Figure 1.16 Amide formation through nucleophilic acyl substitution reaction

\[
\text{HCl} + \text{H}_2\text{N-R}' \xrightarrow{} \text{R'-NH}_3^+\text{Cl}^-
\]

Figure 1.17 Formation of a by-product of an ammonium salt

Figure 1.18 Scheme illustrates the formation of amide bonds with SWCNTs (Taken from Hamon et al. 1999)
Alternatively, coupling of small molecules or biomolecules (e.g. protein) with amine groups to CNTs can be conducted through carbodiimide chemistry (figure 1.14), in which the carbodiimide (e.g. dicyclohexyl carbodiimide, diisopropyl carbodiimide, EDAC) reacts with the carboxylated CNTs to form O-acylisourea intermediate, followed by reaction with the amine to produce an amide derivative and urea as a by-product (figure 1.20 A and B) (Crosslink reagents, Pierce Technical Handbook). This approach is convenient as the reaction is conducted at room temperature without being limited by pH and it is useful for many applications (Saito et al. 2002). One particular example is the coupling of ferritin protein to MWNCTs reported by Jiang et al. (figure 1.21), which can be observed under TEM due to the phase contrast between the CNT and ferritin molecules (figure 1.22) (Jiang et al. 2004). Different ureas are produced in the carbodiimide promoted amidation, but only EDAC was shown to give water soluble by-products that can be easily eliminated by water washing (Montalbetti et al. 2005).
Figure 1.20 Amide bonds can be formed through carbodiimide chemistry (Taken from Cross Link Reagents, Pierce Technical Handbook)

Figure 1.21 MWCNTs covalently modified with ferritin (Taken from Jiang et al. 2004)

Figure 1.22 TEM image of ferritin-MWCNT conjugates (Taken from Jiang et al. 2004)
1.8.3. CNT functionalisation with polymer and biomolecules

Figure 1.23 List of possible approaches in modification of CNTs with polymers (Tsubokawa 2005)

CNTs functionalised by covalent attachment of polymers/biomolecules exhibit a good interaction with matrix materials and promise solubility because the grafted long chain structures are able to overcome the substantial inter-tube attractions more effectively. Figure 1.23 (Tsubokawa 2005) displays possible routes for grafting polymers/biomolecules with CNT surface.

Among them, the ‘grafting from’ method is considered the most common approach in which polymerisation is conducted in the presence of initiators/monomers attached CNTs. Initiators for atom transfer radical polymerisation (Choi et al. 2005), reversible addition fragmentation transfer polymerisation (Cui et al. 2004) and nitroxide mediated radical polymerisation (Fan et al. 2006) have been successful covalently attached to CNT surface and the following
polymerisation successfully produced corresponding polymer grafted CNTs. The ‘grafting from’ method has been reported to generate a good degree of functionalisation and thermal stability due to the pre-attachment of initiators and monomers or reactive molecules. Furthermore the degree of polymerisation can be controlled by varying the ratio of monomer to initiator, which is observed by varied thickness of the grafted polymer coating on CNT surfaces (Kong et al. 2004).

The ‘polymer reaction’ method is accomplished by a reaction between ready-made polymers and reactive groups on CNT surfaces (figure 1.24) (Sham et al. 2006). Large biomolecules such as DNA, enzyme and proteins were also covalently attached to CNT surfaces through the similar mechanism (figure 1.21) (Dwyer et al. 2002, Jiang et al. 2004).

Figure 1.24 An example of ‘Polymer reaction’ method shows reaction between epoxy with amine group on CNT (Taken from Sham et al. 2005).

The ‘grafting onto’ method is easily carried out by trapping of growing/living polymer radicals as CNTs are a strong free radical scavenger (Lee et al. 2006). This method can be associated with ‘graft from’ method where in-situ polymerisation takes place. The main
shortages of this approach are low grafting efficiency (ratio of grafted polymer to MWCNTs) (Tsubokawa 2005) and lower thermal stability of grafted polymers.
Chapter two:

The surface acidity of oxidised MWCNTs and the influence of *in-situ* generated FAs
2.1. Introduction

MWCNTs can be considered as a series of SWCNTs, i.e. grapheme sheets rolled into seamless cylinders, arranged coaxially with regularly increasing diameter (Bhushan et al. 2004). Nitric acid is one of the most frequently used agents in the oxidation of CNTs (Burghard et al. 2005). Initially, oxidation begins at the tube ends, where the distribution of pentagons entails greatest lattice strain (Yao et al. 1998), leading to tip opening CNTs (Tsang et al. 1994, Dujardin et al. 1998, Liu et al. 1998). As high curvature in the nanotubes structure is prevalent, the sidewalls are also under strain and attacked under prolonged oxidation, which leads to a dramatic increase in the amount of carbon possessing phenol, lactone, quinone, carboxyl and ether groups (Esumi et al. 1995, Hiura et al. 1995). Based on these oxygen-containing functions, the subsequent organic or inorganic modification of the CNTs surface has been reported, which demonstrated an improvement in the solubility of CNTs and broadened their applications (Zhao et al. 2004, Lin et al. 2006).

The oxidative treatment of CNTs also leads to erosion of their structure (Tsang et al. 1993, Ajayan et al. 1993, Tran et al. 2007). It was observed that as the shortening and thinning of the CNT layers occurred, carbonaceous debris was produced (Hu et al. 2003). Recently it was found that after the nitric acid oxidation of SWCNTs the carbonaceous fragments remain adsorbed on the CNT surface and act as the major contributor to acidic functionality (Salzmann et al. 2007). This has also been demonstrated with MWCNTs (Verdejo et al. 2007), in which ca. 50% reduction in the number of acidic groups occurred after the oxidised fragments were removed from the surface with sodium hydroxide solution.
In this chapter, the nature of the carbonaceous fragments generated under MWCNT oxidation with concentrated nitric acid and their contribution to surface acidity was studied. These highly polar, yellow colour and water soluble species are proved to be complex PAH structures bonded with oxygen containing functional units, which are apparently similar to the structure of FAs in humic substance. According to this concept, oxidation fragments of MWCNT were termed as FAs in this work. The true number of covalently bound surface acidic functional groups (e.g phenol, lactone and carboxyl) on MWCNTs was determined as a function of oxidation time.

2.2. Fulvic acids, materials, experiments and characterisation methods

2.2.1. Fulvic acids

Fulvic acids (FAs) is an important organic environmental compound formed from the biological transformation of dead cells, which can be found in river water, coal and ocean water (Saparpakorn et al. 2007). It is composed of a mixture of polycyclic aromatic and aliphatic carbons associated with oxygen containing functional groups and soluble in water in all pH regions. Its aqueous solution is light yellow to yellow-brown in colour. FAs collected from different sources have different compositions. The hypothetic model of FAs is shown in figure 2.1 (Buffe et al. 1977).
2.2.2. Materials

MWCNTs (figure 2.2), CVD grown, 99.5% purity, were obtained from TMSpetsmash, Ukraine;

Buffer solutions pH 4 (Phthalate) and pH 7 (Phosphate) were obtained from Fisher Scientific;

50WX2-100 Dowex ion exchange column, DAX-8 resin, ammonium rhodanide (NH$_4$SCN), HNO$_3$ (70%), KBr, NaCO$_3$, NaHCO$_3$, NaOH, NaCl and HCl (37%) were obtained from Sigma-Aldrich Company Limited.
2.2.3. Oxidation of MWCNTs

100 mg of MWCNTs were refluxed in nitric acid (70 %, 30 mL) for 1, 3, 6, 9, 14, 24, and 48 hours separately at 100 °C. After cooling to room temperature, they were vacuum-filtered through a 0.22 μm Millipore polycarbonate membrane and washed with 200 mL of deionised water each time until a neutral pH of the filtrate was reached. The oxidised MWCNTs were dried in a vacuum oven at 105 °C for 24 hours.
2.2.4. Preparation of oxidative fragments extracted MWCNTs

The acid oxidised MWCNTs were refluxed in 1.0M NaOH (100 mL) for 1 hour, washed and filtered until a neutral pH was achieved, and then incubated at room temperature in NaOH 0.5M (100 mL) to fully remove any residual fragments. The obtained MWCNTs were then incubated at room temperature in 0.5M HCl (200 mL) to regenerate the acidic sites.

2.2.5. Isolation and purification of oxidative fragments

To extract oxidative fragments from carbon nanotubes, the oxidised MWCNTs were refluxed with aqueous NaOH (1.0M), as described in 2.2.3, and the filtrate was collected and acidified with HCl. Purification of oxidative fragments was achieved by adapting standard methods for isolation and purification of FAs (Nobili et al. 1990). This solution was passed through a column containing a non-ionic DAX-8 resin to adsorb fulvic substances from solution (Peuravuori et al. 2002). After loading, the column was washed with purified water to remove excess HCl and NaCl. The oxidative fragments were then released by addition of half a column bed of 0.1M NaOH and the coloured fraction was collected. To remove NaOH, the solution was passed through a 50WX2-100 Dowex ion exchange column, until Na\(^+\) was completely removed. The purified oxidative fragments were collected and dried.
2.2.6. Boehm titration

In most cases, surface functionalities (such as carboxyl, lactone or phenol) on MWCNTs can be regarded as oxyacids, which have different proton dissociation ability. In 1964, Boehm (Boehm et al. 1964) proposed a method to determine the distribution of the major surface oxygen-containing functional groups of carbon by reacting with bases of varying strength (table 2.1). Weak base HCO$_3^-$ (pKa = 6.4) is only sufficient to react with moderately strong acids, carboxylic groups; whilst strong base OH$^-$ is able to neutralise all surface oxyacids. CO$_3^{2-}$ with basicity in between HCO$_3^-$ and OH$^-$ (pKa = 10.25) can react additionally with lactones in comparison with HCO$_3^-$.

<table>
<thead>
<tr>
<th>Incubating solution</th>
<th>Surface group neutralised</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO$_3$</td>
<td>Carboxylic (including carboxylic anhydride)</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>Carboxylic and lactone</td>
</tr>
<tr>
<td>NaOH</td>
<td>Carboxylic, lactone, and phenol</td>
</tr>
</tbody>
</table>

Table 2.1 Major surface functional groups with different acidities can react with three base solutions

In a typical Boehm titration process, 20 mL of 0.01M base solution (NaOH, Na$_2$CO$_3$, NaHCO$_3$) in 0.1 M NaCl was pipetted slowly into a vial containing oxidised MWCNTs. NaCl is used as the background to help deprotonation to reach equilibrium. The vial was sealed and placed in a shaking incubator (25 °C) at 150 rpm for 24 hours. Samples were then filtered and 5 mL aliquots were removed and titrated with 0.01M HCl in 0.1M NaCl solution. A blank sample which contained no MWCNTs was also titrated as described. Titrations were performed in triplicate and the pH was monitored using a pH meter (Hanna pH20). Results
were presented as volume of HCl (mL) against pH and their corresponding first order derivative profiles to evaluate the neutralisation points.

The number of surface groups (expressed as milliequivalents of surface groups per grams of MWCNTs, meq g\(^{-1}\)) can be calculated by the following equation:

\[
a = \frac{(C_0 - C_1)V}{m}
\]

Where \(a\) = number of surface groups (meq g\(^{-1}\)), \(C_0\) = concentration of starting base solution (eq L\(^{-1}\)), \(C_1\) = concentration of base filtrate after incubation of MWCNT products, which is calculated by \(C_1V_1 = C_2V_2\) (eq L\(^{-1}\)) (\(C_2\), \(V_2\) stand for HCl concentration and volume at neutralisation point), \(V\) = volume of base solution (mL) and \(m\) = mass of MWCNT products (usually between 0.05 – 0.1g).

2.2.7. XPS spectroscopy

XPS measurements were made using an AXIS ULTRA XPS spectroscope, Mono Al Anode electric current of 10 mA and ultra high vacuum conditions of pressure less than 10\(^{-7}\) Pa (carried out at Northwestern Polytechnical University, China). X-ray energy can excite electrons from their atomic orbits and the level of energy required is measured; thus it is possible to evaluate the elemental composition and electronic state of each element (Yue et al. 1999). A non-linear curve fitting programme provided by Surface Science Instruments XPS system was applied in order to determine the peak width and the binding energy. 90° electron take-off-angle, which probes the sampling depth of around 10 nm, was used to
collect data. For examining oxidised MWCNTs and amine attached MWCNTs, C\text{1s}, O\text{1s} and N\text{1s} peaks were obtained.

2.2.8. Identification of oxidative lattice fragment structures

To determine the oxidative lattice fragment structures, the nitric acid reflux washing and NaOH filtrate obtained from a 6 hour-oxidised MWCNTs were characterised by the following instrumental techniques: UV-Vis spectroscopy, fluorescence spectroscopy and HPLC-mass spectroscopy.

2.2.8.1. UV-Vis spectroscopy

UV-Vis spectroscopy provides evidence for the presence of organic structures with conjugated double/triple bonds and polyaromatic structures as UV and visible light (ranging from 200–800 nm) have the necessary energy to cause π to π* electron transition (Fuentes et al. 2006). Nitric acid reflux washing and a diluted NaOH filtrate of oxidised MWCNTs were placed respectively in 1cm quartz cuvette and the absorption spectra were recorded using a Varian Cary 50 Spectrometer in the wavelength range from 190 to 800 nm.

It has been reported that MWCNTs have near featureless absorption bands (Buffa et al. 2005), while SWCNTs have unique optical properties due to their one-dimensional electronic states (Strano et al. 2003). Thus it is possible to indicate SWCNT modification as a
consequence of disruption of their electronic structures using UV-Vis spectrometer. In the typical SWCNT UV-Vis spectra (figure 2.3), SWCNTs functionalised with polymer chains showed an obvious decrease over absorption intensity, which gives evidence of the interruption of electronic structure after covalent modification (Mountrichas et al. 2008).

Figure 2.3 UV-Vis spectra for pristine SWCNTs and SWCNTs functionalised with PS (Taken from Mountrichas et al. 2008)

2.2.8.2. Fluorescence spectroscopy

Using the same type of electromagnetic radiation, ultraviolet and visible light, fluorescence spectroscopy is a complementary technique for UV-Vis spectroscopy, which records the emitted energy when the excited electrons relax into ground state. Sample preparation was the same as for UV-Vis analysis and the fluorescence spectra were recorded with Varian Eclipse Spectrometer. The contour map generated from a series of excitation wavelengths in the range from 200 to 600 nm, allowed us to evaluate the distribution of aromatic compounds on a single sample of oxidised MWCNT alkaline filtrate.
2.2.8.3. HPLC-mass spectroscopy

HPLC-mass spectroscopy is a technique combining the separation ability of HPLC with the sensitivity of mass evaluation by mass spectrometry. Equipped with a separation column filled with a non-polar chromatographic material of octadecylsilyl silica, each component is recorded in HPLC plots according to its retention time. The separated components are introduced into a mass spectrometer (figure 2.4), in which analytes are vaporised and ionised in the presence of strong electric field and the generated ion beam is directed and focused into the orthogonal acceleration stage of a flight tube. Ions with different masses are accelerated and fly into the reflector which is also called a field-free drift region; ions are then fell back to the detector and separated in terms of their velocities. An equation that describes the motion of charged particles is shown below:

\[(m/Q)a = E + V \times B\]

Here \(m/Q\) stands for the mass to charge ratio, \(a\) is the acceleration, \(E\) is the electrical field, \(V\) is ion velocity and \(B\) is the magnetic field. Precise time for ions to get back to detector is measured for determining the ion velocity; \(m/Q\) therefore can be determined.

In the case of MWCNT oxidative lattice fragments, their composition is very complex and varies as a function of oxidation period. Use of HPLC-mass spectrometer (Bruker Micro Time-of-Flight) with the \(m/z\) analysing range between 20 to 20,000 allowed us to evaluate the molecular mass of each separated component and suggest possible structures.
2.3. Results and discussion

2.3.1. Generation of oxidative fragments and their possible structures

The nitric acid reflux washing was collected and examined with UV-Vis and fluorescence spectroscopy. A broad peak in the UV-Vis spectrum and strong fluorescence emission were detected implying the presence of in-situ generated oxidative fragments leached into the aqueous solution. These fragments may carry fused aromatic rings with double bond substitutes generated in the process of MWCNT oxidation. The remaining oxidised
MWCNTs did not yield any further fluorescence when subsequently refluxed in HCl (1.0 M), implying that aqueous HCl could not dissolve fluorescent species from oxidised MWCNTs.

When incubated in aqueous NaOH the oxidised MWCNTs yielded an orange-brown filtrate (figure 2.5 (a)). A solution of ammonium rhodanide was added in the obtained NaOH filtrate, however no red colour was developed, indicating that iron metal catalysts from the CNT growth process were removed after 1 hour nitric acid treatment and the orange-brown colour of the filtrate was not caused by the dissolution of iron oxide.

UV-Visible spectroscopy of the alkaline filtrate for 6-hour-oxidised MWCNTs exhibited broad absorption peak with a shoulder at \( \lambda = 280 \) nm (figure 2.6 (a) red) which is associated with benzene ring structure and conjugated double/triple bonds. When the filtrate was neutralised with HCl, the UV spectrum (figure 2.6 (a) blue) showed a similar profile with a shoulder at 216 nm. In both cases, the absorption profile has a long tail into the blue region. Fluorescence spectra of the same neutralised alkaline filtrate showed the presence of three emission peaks (figure 2.6 (b) – peaks 1, 2 and 3) at 416, 521 and 615 nm when excited at 300, 450 and 550 nm respectively. The spectra shown in figure 2.6 indicate the presence of a chromophore and fluorophore typical of a mixture of PAHs with conjugated double (or triple) bonds, which supports the notion that oxidative fragments were generated by breaking apart from the graphene lattice during acid oxidation and could only be removed by an alkali solution.

Considering our observations of optical spectra of the alkaline filtrate, the coloured NaOH filtrate of oxidised MWCNTs is believed to contain solubilised PAH species with oxygen contained groups substitutes. Addition of HCl to the filtrate did not lead to any precipitation.
even at pH as low as 1.0. Thus it supports the notion that MWCNT oxidative fragments and FAs have similar structures. (Thurman et al. 1981). Thus the water-soluble species was deemed to be FAs, which appears light yellow in acidic conditions (figure 2.5 (b)). Furthermore the fluorescence distribution profile of the oxidative fragments (figure 2.6 (b)) is found similar to those of other reported FAs (Westerhoff et al. 2001).

Figure 2.5 (a) Water soluble fragments from oxidised MWCNTs in aqueous NaOH has an orange-brown colour, which (b) changes to yellow after acidification with HCl.
The surface acidity of oxidised MWCNTs and the influence of *in-situ* generated FAs

![Figure 2.6](image)

Figure 2.6 (a) UV-Visible spectra of MWCNT-derived oxidative fragments in NaOH solution (red) and neutralised with HCl (blue); (b) fluorescence contour map of oxidative fragments in water at neutral pH

The extracted oxidative fragments or FAs were characterised by HPLC–mass spectroscopy giving the separation profiles (figure 2.7 (a)) and molecular mass distribution of these complex aromatic mixtures (figure 2.7 (b)). The HPLC UV detector observing peaks occurring between 3.0 - 3.4 minutes exhibited the highest intensity and mass spectrometry confirmed the closest molecular formula for the most intensive peak at 391.25 m/z as C₁₆H₉₉O₁₀, taken as the parent ion. It is speculated that the compound consists of two fused benzene rings with extended double (or triple) bonds and oxygen containing functionality which agrees with the optical spectra results. The less intensive peaks around 391.25m/z at 311.21, 355.24, 443.29, 487.32, 531.35 and 575.38 were separated by 44m/z intervals, indicating that FA components may differ from each other by the same fragment, most likely a carboxylic group. The mass spectra of each HPLC peak revealed the presence, in addition to the main peak taken as the parent ion, of low intensity signals at higher masses and therefore indicated that each peak detected within HPLC may comprise more than one FA structure having a similar polarity and therefore similar retention time but different masses.
The surface acidity of oxidised MWCNTs and the influence of in-situ generated FAs

The leaching of FAs from MWCNTs occurred only in alkaline conditions indicating that after their formation during nitric acid oxidation, a significant portion remained immobilised on the carbon surface. Once the acid oxidised MWCNTs were washed free of the nitric acid, the MWCNT – FA systems were stable in acid or neutral solutions. After the removal of FAs, an alkaline filtrate obtained from oxidised MWCNTs appeared colourless and no fluorescence activity was detected, thus indicating that an alkaline reflux and shaking with an addition of alkaline solution at room temperature are sufficient to remove all FAs from the MWCNT surface. This can be explained by the introduction of a negative charge on the protonated FAs, which promotes inter- and intra-molecular repulsion (figure 2.8) (Plaschke et al. 1999). It can be further enhanced by the presence of MWCNTs that have surface acidic groups, which also become negatively charged at higher pHs.
Figure 2.8 Introduction of negative charge on FAs by NaOH solution

Figure 2.9 shows an incomplete fullerene structure that initially was used to represent glassy carbons (Harris 2004). FAs or CNT oxidative fragments generated in-situ by cutting and peeling off CNT lattice chains, are thought of bearing some resemblance with these imperfect sp² carbon networks. FAs also contain a number of sp³ hybridised carbons connected with oxygen-functional groups.

Figure 2.9 Representation of glassy carbon (Taken from Harris 2004)
2.3.2. The effect of oxidative fragments on MWCNT surface acidity

Compared with the semi-quantitative instrumental techniques, such as XPS and IR, Boehm titration is a more direct and simple technique to quantify the acidic groups present on oxidised MWCNTs (Boehm et al. 2002).

Figure 2.10 Acid-base titration profiles and its first-order derivative of MWCNTs oxidised with nitric acid for 3 hours (a) before and (b) after removal of immobilised FAs

When MWCNTs with fulvic acids are used in a titration, a double drop in the pH profile is observed (figure 2.10 (A)). This is clearly present in the derivative profile, revealing two peaks clearly separated. Whereas, when MWCNTs without fulvic acids are titrated, only a
2 – The surface acidity of oxidised MWCNTs and the influence of *in-situ* generated FAs

single drop in the pH profile is present. However, due to the small number of HCl additions around the single equivalence point can lead to minor variations in the rate at which the pH drops on continuous addition of HCl and therefore the derivative of the pH curve appears to contain a double peak. Nonetheless, this is only an artefact of the minor variation in the rate at which the pH changes between a strong acid and a depleted strong base and is not a systemic feature of additional equivalence points.

Figure 2.11 The mean (n=3) total concentration of acidic groups on oxidised MWCNTs before and after FA removal, in which overall acidic groups were neutralised with NaOH (0.01M) solution

Figure 2.11 shows the total number of acidic groups which were detected by NaOH for oxidised MWCNTs before and after FA extraction as a function of oxidation time. The extraction of FAs reduces the number of surface acidic groups and at certain oxidation times can account for up to a 43% loss. This result demonstrates that FAs make a significant contribution to the overall acidity of the oxidised MWCNTs if they are not removed.
2.3.3. Distribution of acidic groups on oxidised MWCNTs after FA removal

Figure 2.12 shows the distribution of different acidic groups (phenol, carboxyl and lactone) on oxidised MWCNTs after extraction of FAs. The removal of FAs is regarded as a necessary step to provide an accurate determination of MWCNT surface acidic group functionality. Titration profiles for sodium carbonate and hydrocarbonate filtrates against HCl are shown in figure 2.13 (A) and (B), where the endpoints occur *ca.* pH 6. By calculation, the amount of phenol and lactone groups on oxidised MWCNTs can be obtained.

![Figure 2.12 Distribution of acidic functional groups on oxidised MWCNTs after FA removal](chart.png)
Figure 2.13 Titration profiles of 9 hour-oxidised MWCNT neutralised with (A) Na₂CO₃ and (B) NaHCO₃ against HCl
The total number of acidic groups increased with oxidation time except for a drop at 24 hours oxidation. The phenol groups were the largest fraction of the acidic groups within the first 6 hours of oxidation, whereas the amount of lactone groups remained almost the same during this period and only slightly increased at longer oxidation times. The number of carboxylic groups gradually increased and became the dominant fraction after 9 hours of acid treatment.

Between 14 and 24 hours of nitric acid oxidation, the number of acidic groups actually decreased, in particular that of lactone and phenol groups. XPS analysis of MWCNTs (figure 2.14) with immobilised FAs revealed peaks at 280.82 eV-287.12 eV and around 550 eV, which indicated the presence of carbon and oxygen in the oxidised carbon nanotubes (Biniak et al. 1997). Peaks for nitrogen were not observed; therefore the loss of acidic groups was not due to possible surface nitration of the MWCNTs in a reaction competing with FA production.

Figure 2.14 High-resolution XPS full scan spectrum of 6 hours oxidised MWCNTs with immobilised FAs

Several factors might account for the drop in the number of acidic groups in this period. It might occur as the result of the MWCNT lattice structure erosion (Tsang et al. 1993).
Additionally, the transformation rate of the existing functional groups into gaseous CO and CO$_2$ (Yue et al. 1999) may be higher than the rate of generating new surface groups and therefore contribute to the decrease in the total number of surface acidic groups between 14 and 24 hours. At 48 hours each type of acidic group (phenol, lactone and carboxyl) and their total number increased again exceeding the 14-hour values. It is likely that the nanotube lattice became severely destroyed at this stage (Tasis et al. 2003), creating new defect sites and facilitating formation of more functional groups. The number of carboxyl groups covalently bound to the MWCNT structure increased from 0.139 to 0.830 meq g$^{-1}$ when the oxidation time extended from 1 to 48 hours.

2.3.4. MWCNTs non-covalent modified with FAs

Figure 2.15 A simplified scheme of the generation of covalently bound surface acidic groups and FAs. The immobilised FAs are deprotonated and leach out in OH$^-$ solution and are re-adsorbed to the MWCNT surface upon protonation with acids.
After the removal of FAs from oxidised MWCNTs, they can be re-adsorbed to the nanotube surface upon mixing an acidified solution of the extracted FAs with oxidised MWCNTs (at a pH ca. 2) and shaking at room temperature for 1 - 2 hours (figure 2.15). The solution separated afterwards, by filtration or centrifugation, is colourless and no longer bears the UV-Vis absorption or fluorescence profiles, as shown in figure 2.6 (a) and (b), confirming that the FAs have transferred from solution onto the MWCNT surfaces. This approach has also been successful in the stabilisation of the aqueous dispersion of unfunctionalised, purified MWCNTs.

It has been reported that aqueous dispersion of CNTs could be stabilised through the addition of naturally occurring humic and fulvic acids (Hyung et al. 2007) acting in a fashion similar to surfactants. Purified MWCNTs were shaken with an excess of MWCNT-derived FAs in HCl solution, followed by centrifugation to remove any large aggregates. The dark grey supernatant (figure 2.16 (A)) is stable for at least two months. On contacting with 1.0 M NaOH solution, precipitation of the MWCNTs occurred (figure 2.16 (B)) due to leaching out of the surface adsorbed FAs.

Figure 2.16 (A) An aqueous dispersion of purified MWCNTs stabilised with adsorbed FAs and (B) the separation of MWCNTs from water after addition of 1.0 M NaOH solution
Boehm titration results for unfunctionalised MWCNTs and FAs physically adsorbed MWCNTs showed an increase in the total number of surface acidic groups from 0.16 ± 0.024 meq g\(^{-1}\) for the starting material to 0.71 ± 0.02 meq g\(^{-1}\) detected by NaOH, which matched the number of acidic groups present on MWCNTs after 6 hours of nitric acid oxidation. The FA adsorption - desorption process has been repeated successfully five times with the oxidised MWCNTs obtained from different manufacturers, including Tsinghua-Nafine (China), Thomas Swan (UK), and commercially available Arry Nano carboxylated MWCNTs (Germany).

### 2.3.5. The role of pH for the FA adsorption and desorption on MWCNT surface

It is thought that several factors contribute to FA physical adsorption to MWCNTs. These include the large surface area and hydrophobicity of CNTs, which makes them energetically favourable to interact with hydrophobic parts of molecules (Britz et al. 2006). At low pH values FAs are protonated, thus becoming more absorbable to the MWCNT surface. It is reasonable to assume that CNT surface is also favourable for non-covalent \(\pi\) - \(\pi\) stacking interaction with the aromatic fragments of FA molecules (Gómez et al. 2003) akin to a strong attraction between other aromatic molecules and the \(\pi\)-bonded network of the graphene surface (Katz et al. 1994). As for the mechanism of FA desorption, as explained in 2.3.1, at high pH FAs and oxidised MWCNT surfaces acquire negative charge which strengthens the inter-molecular repulsion.
2.4. Conclusions

Nitric acid oxidation of MWCNTs generates covalently bound acidic surface groups and strongly adsorbed molecular by-products. Based on the UV-Vis and fluorescence spectra of the alkaline filtrate from oxidised MWCNTs, the molecular products are assumed to be PAH with extensively substituted oxygen-containing functional groups. They remain soluble in water under all pH conditions and are therefore classified as FAs as opposed to humic acids which are insoluble at low pH. Using HPLC - mass spectroscopy analysis it has been found that the NaOH - extracted FAs comprise a mixture of complex aromatic structures. FAs remain immobilised on the MWCNTs surface at acidic and neutral pHs, but can be desorbed into an alkaline solution.

Acid-base titration of oxidised MWCNTs revealed that FAs account for up to 43% of the surface acidity of MWCNTs. After FA removal, surface carboxylic groups became the dominant moieties after 6 hours of oxidation. Oxidation over 24 hours causes destruction of the MWCNT structure. The protonated, solubilised FAs can be readsorbed onto the surface of oxidised or unfunctionalised MWCNTs, which assists the stability of MWCNT suspension in the aqueous phase.
Chapter three

Covalent reactivity of carboxylated MWCNTs
3.1. Introduction

Chemical reactions involving carboxylated CNTs are usually undertaken through covalent bonding with other molecules (e.g. synthetic polymer chains, biomolecules etc.) in order to improve MWCNT stability and selectivity. However, the covalent reactivity of carboxylated CNTs has largely been taken for granted; indirect analytical techniques (such as IR, XPS, Raman etc.) used to monitor their reactions are insufficient to prove the chemical transformations of CNT surface groups (Moreno-Castilla et al. 2000, Yang et al. 2006). The failure to recognise the presence as well as the removal of in-situ generated oxidative lattice fragments has compounded the problem.

In 1998 it was found that acid-oxidised SWCNTs produced graphene fragments and that basic solutions could be used for their removal (Rinzler et al. 1998). Remarkably, a large number of subsequent papers that described the preparation and chemical functionalisation of carboxylated CNTs overlooked the steps required to remove such species. Studies in 2007 indicated that SWCNT surface immobilised carbonaceous fragments, resulting from the acid-oxidation of SWCNTs, may be the sole carrier of the carboxylic groups rather than CNTs themselves (Salzmann et al. 2007). In the case of acid-oxidised MWCNTs undergoing similar base washing, it has been demonstrated that between 57-70% of the total number of surface groups are actually covalently attached to the MWCNT structure depending on the oxidation period, with the remainder connected to surface immobilised oxidised lattice fragments (Wang et al. 2009, Chapter 2 section 2.3.2). The results suggest that previously reported chemical reactions targeting the carboxylic groups on CNTs were likely to have occurred, in part or in full, on the oxidised lattice fragments or FAs, rather than carboxylated MWCNTs as such. In addition, the location and density of the generated carboxylic groups, i.e. –COOH
located within the MWCNT internal layers, could have the negative impact on their accessibility therefore decreasing the grafting efficiency.

Thus we sought to investigate the direct assessment of the covalent reactivity of carboxylated MWCNTs with covalently bound –COOH groups, which was conducted before and after coupling an amine species through a carbodiimide coupling technique. We chose the carbodiimide activated amidation for the reaction assessment because: (1) the reaction is easy to handle and operate at room temperature; (2) compared with amidation via acylchloride-CNTs, amine molecules can be directly coupled to carboxylated-MWCNTs in a one step procedure (Wang et al. 2005); (3) it can be used to functionalise CNTs with other amine species, including long chain amine, amine monomers and initiators (H₂N-R-CH=CH₂, H₂N-R-CH₂Cl, H₂N-R-C(CH₃)₂Br etc.) and biomolecules (DNA, proteins etc); (4) it can be carried out in aqueous media using a water soluble carbodiimide.

3.2. Materials, experiments and characterisation methods

3.2.1. Materials

MWCNTs, CVD grown, 99.5% purity, were obtained from TMSpetsmash, Ukraine;

Acetonitrile (spectroscopy grade, +99%), and buffer solutions pH 4 (phthalate) and pH 7 (phosphate) were obtained from Fisher Scientific;
Water soluble carbodiimide EDAC, NHS, glutamic acid, NaCl, NaHCO₃ and n-butylamine were obtained from Sigma-Aldrich Company Limited. Chemical structures of EDAC and NHS are shown in figure 3.1.

Figure 3.1 Chemical structures of (A) EDAC; (B) NHS

### 3.2.2. Covalent conjugation of n-butylamine to carboxylated MWCNTs

MWCNTs were oxidised and purified according to previously described experimental conditions, with particular emphasis on the extraction of acid-oxidative fragments and the regeneration of surface acidic groups (details outlined in section 2.2.2 and 2.2.3). Typically, MWCNTs oxidised for 6, 24 and 48 hours after removal of all physically adsorbed fragments, were sonicated in acetonitrile to disaggregate the bundles and then stirred with EDAC and NHS (10-fold excess over the number of –COOH groups) at room temperature for 18 hours; a sample was retained for titration analysis. NHS was introduced in order to enhance the coupling yield. A 20-fold excess of n-butylamine to the number of –COOH groups was added and stirred for a further 18 hours. The nanotubes were filtered, washed until neutral pH and then dried in a vacuum oven at 40°C for 48 hours. There is a mixture of amide groups and an ionic salt-like complex formed by electrostatic reaction between -COO⁻ and -NH₃⁺ groups on MWCNT surfaces. To remove the ionic complex, the samples were incubated in HCl (2M) for 4 hours, then washed and dried. The above reaction procedure is highlighted in figure 3.2.
The process was also repeated without the addition of EDAC and NHS in order to solely obtain the ionic complex, and no HCl purification was employed (figure 3.3).

![Figure 3.2](image1.png)

Figure 3.2 Generation of acid-oxidised MWCNTs with covalently bound carboxylic groups and their conversion to the final amide product

![Figure 3.3](image2.png)

Figure 3.3 Direct reaction between n-butylamine with carboxylated MWCNTs for the production of purely ionic complex

**3.2.3. Covalent conjugation of glutamic acid to carboxylated MWCNTs**

Glutamic acid (figure 3.4) was coupled to carboxylated MWCNTs using the same conditions as in n-butylamine coupling to demonstrate that carbodiimide generated O-acylisourea group on the MWCNTs reacts with amine (figure 3.5 (B) shows the chemical structure of O-acylisourea). Electrostatic complexes were washed with HCl solution then deionised water until neutral pH. The sample was dried in vacuum oven for 48 hours at 100 °C. Figure 3.5 presents the reaction sequence.
Figure 3.4 Chemical structure of glutamic acid

Figure 3.5 (A) Acid oxidation of MWCNTs (1) followed by formation of the O-acylisourea intermediate (2) and coupling with glutamic acid to form the final amide MWCNTs (3); (B) Chemical structure of O-acylisourea, MWCNT-COO-NHS.
3.2.4. TEM

A beam of electrons usually formed by thermionic emission from tungsten filaments is applied as ‘light’ source in TEM, enabling resolution at nanometer scale (figure 3.6). Once the accelerated electron beam interacts with a material in vacuum, some electrons are directly transmitted through and parts are diffracted. An objective lens is placed in the back focal plane to select the electron beam. A bright-field image is obtained with only transmitted electrons whilst a dark-field image (also called diffraction image) is achieved by only diffracted electrons. The transmitted and diffracted electrons are magnified by a series of intermediate and projector lenses. The final images are displayed on a fluorescent screen. For TEM imaging of MWCNTs in bright-field mode, when the electron beam is perpendicular to the tube length, the contrast of scattering is relatively weak at the top of a CNT as there is a smaller number of atoms in \((hkl)\) plane (figure 3.7, site H) aligned with electron beam, but the electron scattering would be relatively strong at the both sides as the \((00\ell)\) plane (figure 3.7, site V) contains a large amount of atoms with the same orientation as electron beam (Iijima et al. 1991).
Figure 3.6 TEM operation in (a) bright field and (b) diffraction mode (Copyright ©iNano centre)
The TEM technique allows identification of the concentric structures of MWCNTs after oxidation etching and attached polymer morphology. In this project, a Hitachi 7100 TEM (University of Sussex) and a JEOL JEM2200FS (Toyo University) were employed to image the oxidised MWCNTs (this chapter) and polymer grafted MWCNT products (chapter 4). MWCNT products were first dispersed in THF via sonication for 30 minutes. A drop of suspension was taken and dried on 400-mesh Cu grid supported by a carbon film.

### 3.2.5. Boehm titration

All samples were analysed using Boehm titration via incubating MWCNTs in NaHCO$_3$ (0.01M)/NaCl (0.1M) solution and titrating with HCl (0.01M) for detecting carboxylic groups, as described in section 2.2.5.
3.2.6. Spectroscopic techniques

IR, Raman and XPS spectroscopy are often used in the identification of MWCNT surface functionalities. Electromagnetic radiations employed in IR and Raman are very similar and these two techniques cause molecular vibrations.

3.2.6.1. IR spectroscopy

IR radiation between 800-4000 cm\(^{-1}\) causes stretching and bending vibrations in organic molecules due to the change of dipole moment, which helps to identify the types of functional groups in a compound. The incident beam excites molecules to vibration modes and the absorbed frequencies can reflect the mass of atoms, bonding type of the molecules, etc. A source of IR wavelengths is required and the time of scanning only takes a few seconds, however the results obtained could not differentiate every single frequency in terms of intensity, therefore a mathematic technique known as Fourier transformation which is able to achieve this transforming calculation is built into the computer (figure 3.8).

![In-situ built up Fourier transformation](image-url)

Figure 3.8 The *in-situ* built up Fourier transformation is able to convert raw interferograms into frequency-intensity spectrum (Taken from Introduction to Fourier Transform Infrared Spectrometry, Copyright © Thermo Nicolet Corporation 2001)
In the case of analysing MWCNTs, particularly IR radiation with the wavelength between 4000 to 1500 cm\(^{-1}\) causes vibrations of MWCNT surface functional groups, such as carboxylic, amine, and polymer chains. However one concern about the IR technique is the high IR absorbance feature of MWCNTs (Yang \textit{et al.} 2006). Grinding MWCNTs with KBr and pressing into a pellet effectively increases the light transition; however it is still difficult to gain absorbance signals from a low number of surface groups on MWCNTs.

A single-beam JASCO FT/IR - 4000 spectrometer was used for characterising MWCNTs and their derivatives. The spectra were recorded over 25 scans from 800–4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\), the signal to noise ratio is 22,000:1. In order to eliminate noise coming from MWCNTs high absorbance, the obtained spectra were smoothed with a 25 convolution width.

### 3.2.6.2. Raman spectroscopy

When lights interact with a molecule causing vibration, a very small number of emitted photons would relax back to a vibration state with higher energy instead of ground state, which was referred as Raman scattering or Stokes scattering. The energy difference between incident light and photons experiencing Raman scattering is measured.

Depending on the vibration mode, a Raman spectrum for a MWCNT product generates two characteristic bands: the G mode (occurring around 1500 – 1600 cm\(^{-1}\)), which is related to the vibration of MWCNT main structure; and the D mode (occurring around 1350 cm\(^{-1}\)), which is affected by domains of disordered impurity of MWCNTs. There is an additional D’ band
occurring at ~1615 cm\(^{-1}\) indicating the presence of defect sites and anchored molecules (Osswald et al. 2007). Unlike IR spectroscopy, which offers information on types of functional groups, Raman spectroscopy is mainly used to evaluate the intensity of structure defects (\(I_D/I_G\)) of MWCNTs. It has been shown that D mode was strengthened after covalent modification due to an increase in the number of sp\(^3\) carbon atoms and distortion of \(\pi\) electron networks (Yokoi et al. 2005). Research also showed that the G mode of pristine MCNTs was shifted around 30 cm\(^{-1}\) after a chemical reaction (Titus et al. 2007). Raman spectrum within the range of 200 – 500 cm\(^{-1}\), also known as Radial Breathing Mode (RBM), is sensitive to the nanotube diameter and it is a characteristic band for SWCNTs, as MWCNTs always have much larger concentric structures and RBM are never observed (Dresselhaus et al. 2007).

3.3. Results and discussion

3.3.1. Images of oxidised MWCNTs

![Figure 3.9 TEM image of a 6 hour oxidised MWCNT with a magnified insert (top left) revealing lattice fringes. Second insert (bottom right) reveals MWCNT after 48 hour oxidation](image)

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Figure 3.9 shows a typical TEM image of a MWCNT after 6 hours oxidation in nitric acid. The oxidation causes erosion of the outermost layers comprising the sidewall of the nanotubes (indicated by black arrows). In carbon nanotubes obtained by chemical vapour deposition, the numerous lattice defects account for the initial sites of thermal (Bom et al. 2002) and chemical oxidation (Zhang et al. 2003). Extending the oxidation time can destroy larger areas of the upper layers, invoking peeling and complete de-shelling, and expose subsequent internal layers to the oxidative conditions. The terminated edge of the outer layer (figure 3.6 top-left insert, black arrow) lies on the top of a bifurcation state (white arrow) and possibly further lattice defects in a parallel locale, which may promote further oxidation along these sites towards the centre of the tube. Faint fringes can be observed (to the left of the black arrow in figure 3.9, top-left insert), which may indicate an outer layer peeling after oxidation (Osswald et al. 2007). Further extension of the chemical oxidation time leads to excision of large sections of the sidewall (figure 3.9, lower right insert, white arrow), as well as full opening of the nanotube tip, which can be terminated with oxygen-containing groups.

3.3.2. Properties of O-acylisourea intermediate

Figure 3.10 The changes of carboxylic groups in the process of amidation with glutamic acid
Figure 3.10 shows the reaction sequence along with the changes of carboxylic groups for each MWCNT derivative. The number of carboxylic groups in the starting pristine MWCNTs was 0.005 meq g\(^{-1}\). After refluxing in nitric acid and removing the oxidative fragments, the number of covalently attached carboxylic groups on MWCNTs was determined to be 0.215 meq g\(^{-1}\). In the amidation process, we isolated the intermediate compound formed from the treatment of acid-oxidized MWCNTs with EDAC and NHS, i.e. MWCNT-COO-NHS, which revealed a drop in the number of carboxylic groups detected (0.066 meq g\(^{-1}\)), corresponding to a 70% conversion of the covalently bound carboxylated groups. The stability of the intermediate under acid washing and acid-base titrations raises an important question as to whether the EDAC-NHS activated MWCNTs further converts to the amide or remains in the O-acylisourea form. Therefore the intermediate was reacted with a dicarboxylic aliphatic amine, such as glutamic acid, so that numerous carboxylic groups would be available for detection. Titration results revealed a 5-fold increase of the number of carboxylic groups (0.348 meq g\(^{-1}\)) over the intermediate (0.066 meq g\(^{-1}\)) and 42% increase over the starting acid-oxidised MWCNTs (0.215 meq g\(^{-1}\)), thus demonstrating that the intermediate does undergo further transformation.

### 3.3.3. Covalent reactivity of carboxylated MWCNTs

The progress of the coupling reaction follows a similar profile in each sample where the number of carboxylic groups detected for 6, 24 and 48 hours of MWCNT oxidation decreased once reacted with \(n\)-butylamine, in the presence of EDAC and NHS (figure 3.11, product B). Meanwhile, the formation of an ionic complex was confirmed through the reaction without EDAC and NHS, where the number of carboxylic groups detected decreased.
Covalent reactivity of carboxylated MWCNTs

These two groups of residual carboxylic sites are very close in value, which suggests that both functionalisation strategies are equally efficient and up to 30% of the covalently bound carboxylic groups do not participate in chemical reactions. In order to obtain a pure covalently reacted MWCNT-amide (product C), HCl washing is necessary to remove ionic products. The covalent reactivity of the carboxylic groups undergoing a EDAC-NHS mediated amidation with n-butylamine was determined to be 78, 58 and 65 % for 6, 24 and 48-hour acid-oxidised MWCNTs respectively. Curiously, the number of carboxylic groups covalently reacted for the 6 and 48 hour oxidised MWCNTs was approximately the same (about 0.334 meq g⁻¹) despite an increase in the total number of carboxylic groups of extended oxidation time. An important conclusion is that extending the oxidation time does not necessarily increase the number of reactive carboxylic group sites.
A number of factors could affect the covalent reactivity of the carboxylated MWCNTs. First, in the case of sterically hinderance, the size of the EDAC, NHS and amine molecules may restrict their accessibility to the carboxylic groups; in addition, the generation of sterically hindered carboxylic sites across two adjacent layers at longer oxidation times may occur, where the acid-erosion cuts through two or more walls of the nanotube. Second, with the possible formation of carboxylic anhydride groups, particularly at extended oxidation times (Boehm 2002), only one acyl group is transformed per molecule of anhydride in the reaction with the amine, which results in a lower percentage of carboxylic reactivity. Third, there is also competition between the generation of the covalent amide and the ionic carboxylate.
3.3.4. Characterisation utilising spectroscopic techniques

3.3.4.1. Raman spectroscopy

Raman spectra of acid-oxidised MWCNTs after removal of the oxidative lattice fragments (MWCNT-COOH), MWCNT amide derivative (MWCNT-CONH-butyl) and the ionic MWCNT carboxylate formed without EDAC-NHS (MWCNT-COO⁻⁺NH₃-butyl) were obtained with excitation at 633 nm (figure 3.12). The spectra of MWCNTs oxidised for 48 hours featured a D band peak at 1206 cm⁻¹ and a broad band, which comprises a G band around 1491 cm⁻¹ and D' band around 1523 cm⁻¹. The R value (I_D/I_G) was calculated to be 2.4. The covalently bound amide and ionic carboxylate generated Raman profiles similar to pristine MWCNTs, however the G and the D' bands become separable; both systems gave R values of 2.5. Therefore, despite the addition of n-butylamine, the disordered fraction remains approximately the same compared with oxidised MWCNTs. There is a small shift of G mode for MWCNT-CONH-butyl (1209 cm⁻¹) and MWCNT-COO⁻⁺NH₃-butyl (1207 cm⁻¹) compared with the MWCNT-COOH (1206 cm⁻¹) indicating the amide groups introduce lattice strain, therefore strengthen the C-C vibration.
Figure 3.12 Raman spectra of the 48 hour acid-oxidised MWCNT after removal of oxidative fragments (MWCNT-COOH), purified amide MWCNT derivative (MWCNT-CONH-butyl) and ionic carboxylate MWCNT complex (MWCNT-COO⁻⁺NH₃-butyl)
Table 3.1 Comparison of the parameters in the Raman spectra.

<table>
<thead>
<tr>
<th></th>
<th>D band (cm⁻¹)</th>
<th>G band (cm⁻¹)</th>
<th>D' band (cm⁻¹)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT-COOH</td>
<td>1206</td>
<td>1491</td>
<td>1523</td>
<td>2.4</td>
</tr>
<tr>
<td>MWCNT-CNH-butyl</td>
<td>1209</td>
<td>1494</td>
<td>1523</td>
<td>2.5</td>
</tr>
<tr>
<td>MWCNT-COO⁻·NH₃-buty l</td>
<td>1207</td>
<td>1495</td>
<td>1522</td>
<td>2.5</td>
</tr>
</tbody>
</table>

3.3.4.2. IR Spectroscopy

The high absorbance of the MWCNT structure renders all the spectra to possess nearly featureless profiles: absorbance between 1600 – 1800 cm⁻¹ is ascribed to C=O of carboxylic, lactone, and amide functionalities (Mawhinney et al. 2000), however spectra of oxidised MWCNTs and their derivatives look very similar to each other (figure 3.13 (A)); absorbance within 3400 – 3500 cm⁻¹ is associated with amine group (Ramanathan et al. 2005), again it showed no difference between MWCNT derivatives (figure 3.13 (B)).
3 – Covalent reactivity of carboxylated MWCNTs

(A)

- Ionic \(n\)-butylamine - MWCNTs complex
- Amide MWCNTs
- Amide MWCNTs + ionic complex
- Oxidised MWCNTs
- Pristine MWCNTs
Figure 3.13 IR spectra of the MWCNTs and their amine modified derivatives at (A) wavenumbers between 1800 – 1600 cm\(^{-1}\) and (B) wavenumbers between 3700 – 2800 cm\(^{-1}\)
3.3.4.3. XPS Spectroscopy

In XPS spectra of oxidised MWCNTs without oxidative fragments and amide MWCNTs, deconvolution of C\(_{1s}\) gives four peaks (figure 3.14 (A) and (B)), which can be associated with C-C, C-O, C=O and carbonates. However, with amide MWCNTs (figure 3.14 (B)), the C=O signal and N-C=O signals (~288 eV) (Ramanathan et al. 2005) could not be resolved by the Gaussian sum function within the XPS software, thus rendering it difficult to monitor the changes of –COOH to –CONH. In the case of O\(_{1s}\) spectra (figure 3.14 (C) and (D)), two distinctive peaks were resolved, corresponding to C-O and C=O. An N\(_{1s}\) peak (ca. 399.50 eV) (Gabriel et al. 2006) was resolved in the covalently bound amide compound and no N\(_{1s}\) signals were detected present in the unreacted oxidised sample (figure 3.14 (e) and (f)).

<table>
<thead>
<tr>
<th></th>
<th>Acid-oxidised MWCNTs</th>
<th>Amide MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding energy (eV)</td>
<td>Area%</td>
</tr>
<tr>
<td>C(_{1s})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>283.95</td>
<td>61.8</td>
</tr>
<tr>
<td>C-O</td>
<td>285.25</td>
<td>24.1</td>
</tr>
<tr>
<td>C=O</td>
<td>288.17</td>
<td>6.4</td>
</tr>
<tr>
<td>Carbonate</td>
<td>290.42</td>
<td>7.7</td>
</tr>
<tr>
<td>O(_{1s})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-O</td>
<td>532.82</td>
<td>47.4</td>
</tr>
<tr>
<td>C=O</td>
<td>531.17</td>
<td>52.6</td>
</tr>
<tr>
<td>N(_{1s})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O=C-N</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 3.2 Comparison of parameters of XPS spectra.
3 – Covalent reactivity of carboxylated MWCNTs

(A)

<table>
<thead>
<tr>
<th>Label</th>
<th>BE (eV)</th>
<th>FWHM</th>
<th>Height</th>
<th>Gauss</th>
<th>Asymm</th>
<th>Norm. Area</th>
<th>Rel. Area</th>
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<tr>
<td>A</td>
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<td>10402.7</td>
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<td>0.0%</td>
<td>15349.1</td>
<td>61.8%</td>
</tr>
<tr>
<td>B</td>
<td>265.25</td>
<td>2.58</td>
<td>2184.38</td>
<td>100.0%</td>
<td>0.0%</td>
<td>6001.73</td>
<td>24.1%</td>
</tr>
<tr>
<td>C</td>
<td>268.17</td>
<td>2.45</td>
<td>612433</td>
<td>100.0%</td>
<td>0.0%</td>
<td>1599.69</td>
<td>6.4%</td>
</tr>
<tr>
<td>D</td>
<td>290.42</td>
<td>3.31</td>
<td>540.251</td>
<td>100.0%</td>
<td>0.0%</td>
<td>1503.96</td>
<td>7.7%</td>
</tr>
</tbody>
</table>

Acid-oxidised MWCNTs

Peak Fit Baseline: 293.45 to 281.45 eV
Reduced Chi-Square: 1.709

C-C
C-O
carbonate
C=O
3 - Covalent reactivity of carboxylated MWCNTs

(B)

<table>
<thead>
<tr>
<th>Label</th>
<th>BE (eV)</th>
<th>FWHM</th>
<th>Height</th>
<th>Gauss</th>
<th>Asymm</th>
<th>Norm. Area</th>
<th>Rel. Area</th>
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<td>7287.5</td>
<td>63.5%</td>
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<td>1364.32</td>
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<td>3218.16</td>
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<tr>
<td>C</td>
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<td>318.906</td>
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<td>59.2761</td>
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Peak Fit Baseline: 291.85 to 292.15 eV
Reduced Chi-Square: 1.005

C-C
C-O
carbonate
C=O
Covalent reactivity of carboxylated MWCNTs

<table>
<thead>
<tr>
<th>Label</th>
<th>BE (eV)</th>
<th>FWHM</th>
<th>Height</th>
<th>Gauss</th>
<th>Asym</th>
<th>Norm. Area</th>
<th>Rel. Area</th>
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<tr>
<td>A</td>
<td>532.82</td>
<td>1.96</td>
<td>1907.015</td>
<td>100.0%</td>
<td>0.0%</td>
<td>1850.49</td>
<td>47.4%</td>
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<tr>
<td>B</td>
<td>531.17</td>
<td>2.01</td>
<td>1664.53</td>
<td>100.0%</td>
<td>0.0%</td>
<td>2065.77</td>
<td>52.6%</td>
</tr>
</tbody>
</table>

Acid-oxidised MWCNTs

Peak Fit Baseline: 535.25 to 526.75 eV
Reduced Chi-Square: 1.414

C-O

C=O
Covalent reactivity of carboxylated MWCNTs

![Graph showing binding energy vs. height with peaks labeled C=O and C-O for Amide MWCNTs.]

<table>
<thead>
<tr>
<th>Label</th>
<th>BE (eV)</th>
<th>FWHM</th>
<th>Height</th>
<th>Gauss</th>
<th>Asymm</th>
<th>Norm. Area</th>
<th>Rel. Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>533.17</td>
<td>2.06</td>
<td>646.786</td>
<td>100.0%</td>
<td>0.0%</td>
<td>140.22</td>
<td>45.6%</td>
</tr>
<tr>
<td>B</td>
<td>531.32</td>
<td>2.14</td>
<td>714.461</td>
<td>100.0%</td>
<td>0.0%</td>
<td>162.97</td>
<td>53.4%</td>
</tr>
</tbody>
</table>

Peak Fit Baseline: 538.05 to 528.35 eV
Reduced Chi-Square: 1.525
Covalent reactivity of carboxylated MWCNTs

(E)

Acid–oxidised MWCNTs

Binding Energy, [eV]
Figure 3.14 XPS analysis of acid oxidised MWCNTs C\textsubscript{1s} (A) O\textsubscript{1s} (C) N\textsubscript{1s} (E) and amide MWCNTs C\textsubscript{1s} (B) O\textsubscript{1s} (D) and N\textsubscript{1s} (F).
3.4. Conclusions

In conclusion, the covalent reactivity of the covalently bound carboxylic groups is between 58-78% in the presence of coupling agents such as EDAC and NHS, and extended oxidation time does not increase the number of reactive species. Oxidative fragments and ionic carboxylates can be removed, thus leaving a pure covalent system. Techniques such as Raman, IR and XPS have their limitations in monitoring the reaction progress and giving an accurate description of the reactivity of MWCNT surface groups and their composition. This work bespeaks of the need to re-examine existing functionalised CNT-based composites used for the mechanical reinforcement of bulk polymers to ensure that attachment of polymer molecules occurs on the CNT rather than detachable fragments.
Chapter four

Formation of polymer grafted MWCNTs via free radical polymerisation
4.1. Introduction

To achieve the best dispersibility of MWCNTs, as well as improve the mechanical and damping performances of PVAc bulk polymers, modification of MWCNTs with a layer of PVAc was undertaken via free radical polymerisation with the vinyl units covalently bound MWCNTs.

Figure 4.1 shows the reaction sequence of grafting PVAc from MWCNTs by a three-step procedure: (1) oxidation; (2) amidation and (3) free radical polymerisation. It has been understood that step (1) and (2) could influence the polymer covalent grafting efficiency by the formation of non-covalently attached functional groups (Wang et al. 2009, Wang et al. 2010). For example, in the nitric acid oxidation process of MWCNTs, the in-situ generated oxidative fragments are very likely to lead to undesirable side reactions where coupling of polymer chains onto these carbonaceous fragments occurs (chapter 2, Wang et al. 2009). In the amidation step, compounds containing both the amine and an alkene group such as allylamine (CH$_2$=CH-CH$_2$-NH$_2$) are expected to form amide linkages with carboxylated MWCNTs through carbodiimide promoted amidation, leaving a vinyl unit as the end group. However study of covalent reactivity of carboxylated MWCNTs has shown that up to half of the grafted n-butylamine stayed in the form of carboxylate salts caused by direct acid-base reaction between amine and MWCNT-COOH groups, which competes against the amide conversion (chapter 3, Wang et al. 2010). The oxidation fragments and ionic complexes can be eliminated by washing with NaOH and HCl solutions, respectively.

In step (3) of free radical polymerisation process, co-polymerisation of MWCNT-allylamine complex and vinyl acetate is initiated by benzoyl peroxide at 70 °C to yield the corresponding
PVAc grafted MWCNTs. This reaction scheme has been adopted for synthesising polystyrene grafted MWCNTs (Yang et al. 2006). However, MWCNTs are good electron acceptors of free polymer radicals due to their high electron affinity (ca. 2.65 eV) (Watts et al. 2003, Lee et al. 2006). Therefore, instead of propagation of polymer chains solely from functional groups on MWCNTs, parts of the polymer radicals can be terminated by carbon atoms in the MWCNT lattice (figure 4.2).

Figure 4.1 Production of PVAc grafted MWCNTs via a three-step procedure
Moreover by conducting *in-situ* free radical polymerisation in the presence of pristine MWCNTs without any chemical treatment, various polymer radicals are capable of being directly grafted to MWCNT surfaces (Jia et al. 1999, Park et al. 2002). Without the preoxidation and amidation, this polymer grafting process can be easily conducted within short periods.

This chapter explores the modification of MWCNTs with PVAc by free radical polymerisation of pristine MWCNTs and vinyl-functionalised MWCNTs. The vinyl-terminated MWCNTs are able to bond a wide range of polymers formed from alkene or substituted alkene monomers. It has been reported that a higher grafting efficiency (weight fraction of the grafted polymer) occurs for polymerisation resulting from initiator bonded...
MWCNTs compared with pristine MWCNTs (Kong et al. 2004, Tsubokawa 2005). However, there have been no reports concerning the difference in modification efficiency and thermal stability in the case of utilising pristine MWCNTs and vinyl-MWCNTs in free radical polymerisation. The final products referred as: MWCNT-PVAc and MWCNT-C=C-PVAc, were characterised by TEM, UV-Vis spectroscopy, TGA and DSC.

4.2. Materials, experiments and characterisation methods

4.2.1 Materials

MWCNTs, CVD grown, 99.5% purity, were obtained from TMSpetsmash, Ukraine;

Acetonitrile (spectroscopy grade, +99%), and buffer solutions pH 4 (phthalate) and pH 7 (phosphate) were obtained from Fisher Scientific;

EDAC, NHS, allylamine, PVAc (molecular weight ~100,000) were obtained from Sigma-Aldrich Company Limited.

4.2.2. Vinyl – functionalised MWCNTs

MWCNTs oxidised for 6 hours and free from oxidative lattice fragments (details described in section 2.2.2 and 2.2.3) were sonicated in acetonitrile to disaggregate the MWCNT bundles and then stirred with EDAC and NHS (10-fold excess over the number of –COOH groups, ~5
meq g$^{-1}$) at room temperature for 18 hours; allylamine (20-fold excess over the number of –COOH groups, ~10 meq g$^{-1}$) was added and stirred for a further 18 hours. The nanotubes were filtered then washed with deionised water and methanol until pH neutral; *in-situ* produced carboxylate salts were removed by washing with excess HCl (2M) and deionised water until pH neutral. MWCNTs with covalently attached allylamine, referred to as MWCNT-CH=CH$_2$, were then dried in a vacuum oven at 40$^\circ$C for 48 hours (figure 4.1, reactions (1) and (2)).

**4.2.3. Free radical polymerisation with vinyl – functionalised MWCNTs**

The MWCNT-CH=CH$_2$ complex was mixed with the vinyl acetate monomer in a 1:200 mass ratio. Polymerisation was conducted in the presence of benzooyl peroxide (1:10 of benzooyl peroxide to vinyl acetate) and under N$_2$ at 70 $^\circ$C for 24 hours. The PVAc covalently grafted MWCNTs (MWCNT-C=C-PVAc) were washed with excess toluene and THF, until the filtrate produced no precipitate upon contact with hexane, indicating that no free polymer was present in the sample (figure 4.1. reaction (3)). The final product was dried in a vacuum oven at 40$^\circ$C for 48 hours.

**4.2.4. Free radical polymerisation with pristine MWCNTs**

Pristine MWCNTs were mixed with vinyl acetate monomer in a 1:200 mass ratio. Polymerisation was carried out under the same conditions as grafting PVAc from vinyl-functionalised MWCNTs, in the presence of benzooyl peroxide (1:10 of benzooyl peroxide to
Formation of polymer grafted MWCNTs via free radical polymerisation

vinyl acetate) and N₂ at 70 °C for 24 hours. The final product (MWCNT-PVAc) was washed with an excess of toluene and THF until no precipitation occurred upon contact with hexane. The final product was dried in a vacuum oven at 40°C for 48 hours.

4.2.5. Solubility measurement

100 mg of MWCNT-C=C-PVAc was sonicated in 200 mL of THF for 10 min. The suspension was then centrifuged at 4500 rpm for 20 min to sediment out any large particles. The dark supernatant was decanted and another 200 ml of THF was added to the precipitate, sonicated, and centrifuged again. This was repeated until no dark solution was obtained implying that all soluble MWCNT-C=C-PVAc sample had passed into the supernatant solution. The residual solid was dried under vacuum oven at 40 °C for 48 hours and weighed. The solubility of MWCNT-C=C-PVAc was determined by the ratio of soluble MWCNTs to the volume of THF used. The solubility value was obtained from three measurements to ensure consistency.

4.2.6. Boehm titration

The concentration of surface –COOH groups on oxidised MWCNTs free from oxidative lattice fragments and MWCNT-CH=CH₂ was measured using NaHCO₃ (0.01M)/NaCl solution as described in section 2.2.5.
4.2.7. Thermal gravimetric analysis

TGA can be used to examine thermal stability, oxidation profiles and the composition of MWCNT-polymer hybrids (Jin et al. 2000). It monitors the weight change of a sample upon heating. When materials are heated, weight loss or increase occurs because of physical processes, such as solvent evaporation, and chemical reactions, such as sample decomposition or sample reaction with the gaseous atmosphere provided. For this highly sensitive method, only a few micrograms of a sample are required. The atmosphere is usually air or an inert gas (N₂). In order to determine the relative amount of grafted PVAc on MWCNTs, thermal gravimetric analysis of MWCNT products was conducted using Perkin Elmer 7 analyser under N₂ with a heating rate of 10 °C in the temperature range between 50-600 °C where pristine MWCNTs are still thermally stable but PVAc is not.

4.2.8. Differential scanning calorimetry measurement

The principle of differential scanning calorimetry is based on measuring the difference of the heat flow rate between samples under investigation and a blank reference. The samples and reference are both heated and controlled in an identical temperature environment. Specifically for polymer materials, there is a heat absorption and evolution associated with certain phase transitions (e.g. glass transition, crystallisation, melting or decomposition) (Jin et al. 2007). PVAc is a typical thermoplastic material which undergoes glass transition and thermal decomposition. In the case of PVAc grafted MWCNTs, the polymer is expected to undergo thermal decomposition, which will be presented as a sharp exothermic peak. An equal amount of each sample was measured three times and heated at 10 °C min⁻¹ ramp in order to
reduce the effect of sample mass and heating rate on the shape and position of the decomposition peaks (Ruegg et al. 1977). N\textsubscript{2} was used as purge gas and the samples were sealed in 40 µL aluminium pans.

4.2.9. Optical light microscopy

Optical light microscope allows the observation of objects at relatively small magnifications (15×, 20× and 50×) by visible light. It is unable to resolve individual nanotubes; however it can identify CNT bundles at the micrometer level. The magnification value used here is 20×.

4.3. Results and discussion

4.3.1. Boehm titration

The HCl–NaHCO\textsubscript{3} titration results revealed that 0.31 meq g\textsuperscript{-1} of –COOH for oxidised MWCNTs free from oxidative fragments was reduced to 0.12 meq g\textsuperscript{-1} after amidation with allylamine. Therefore nearly 0.20 meq g\textsuperscript{-1} of acidic groups on MWCNTs were transformed to amide groups, showing 65% of covalent conversion, which agreed with the carboxylic reactivity measured through n-butylamine attachment (chapter 3, figure 3.7).
4.3.2. Solubility of MWCNT-C=C-PVAc

MWCNT-C=C-PVAc shows a better solubility in CHCl₃ compared with MWCNT-PVAc, giving the suspension a visually intensive black colour with over one month stability (figure 4.3). A solution of MWCNT-C=C-PVAc in THF shows no colour intensity difference to their suspension in CHCl₃. Solubility of MWCNT-C=C-PVAc in THF was measured as ~0.0875 mg mL⁻¹, which is 22 times larger than the raw HiPCO MWCNTs reported (Nikolaev et al. 1999, Bahr et al. 2001).

![Figure 4.3 Saturated suspension of (A) MWCNT-PVAc and (B) MWCNT-C=C-PVAc in CHCl₃](image)

4.3.3. Morphology of grafted PVAc on MWCNTs under TEM

TEM images of raw MWCNTs and PVAc grafted MWCNTs are shown in figure 4.4. Some dark cloudy areas can be seen for the pristine MWCNTs, indicated by the arrows, which correspond with bulky amorphous carbon (figure 4.4 (A)). The pristine MWCNTs possess sidewalls with diameters ranging between 15-25 nm (figure 4.4 (A) and (B)).
4 – Formation of polymer grafted MWCNTs via free radical polymerisation

(A)  
(B)  
(C)  
(D)  
(E)  
(F)
TEM images of MWCNT-PVAc (figure 4.4 (C) and (D)) show the diameter along the tube ranging between 15-35 nm. The enlarged diameter of up to 10 nm is the result of PVAc attachment on MWCNT surfaces. However it can be seen that some MWCNTs have not been coated with polymer as the diameter did not change (figure 4.4 (D)). This might be due to the free radical polymerisation proceeding very quickly and there was insufficient time for the polymer radicals to attack every tube. In addition, it is believed that MWCNT clumps could not be fully disaggregated by a magnetic stirrer in a polymerising solution with increasing viscosity.

Images of (E) and (F) for MWCNT-C=C-PVAc samples show discrete clusters reflecting polymer deposition on MWCNT surface, presumably on the grafted vinyl sites. Moreover, fraction of the polymer radicals can be bonded directly with carbon atoms on MWCNTs as the electron transfer from the unpaired electrons of polymer radicals to MWCNTs, giving an apparent increase of wall thickness for samples of MWCNT-PVAc. The observed diameters varied from 15-40 nm (figure 4.4 (G) and (H)), indicating that up to 20 nm polymer coating
on MWCNT surface occurred. With such a wide diameter distribution of polymer covering, it is implied that polymer grafting did not happen uniformly under the conditions used.

4.3.4. UV-Vis spectra

![UV-Vis spectra of PVAc grafted MWCNTs in CHCl₃](image)

Figure 4.5 UV-Vis spectra of PVAc grafted MWCNTs in CHCl₃

The UV-Vis absorption spectra of both MWCNT-PVAc and MWCNT-C=C-PVAc in CHCl₃ are featureless with the absorption intensity gradually decreasing from 250-800 nm (figure 4.5), which is in good agreement with the early reports of suspensions consisting of MWCNTs functionalised with other polymer chains (Baskaran et al. 2004).
4.3.5. TGA characterisation

(A)

(B)

Weight loss (%) vs. Temperature (°C)

- MWCNTs, 2.2%
- MWCNT-C=C, 5%
- MWCNT-PVAc, 15.4%
- MWCNT-C=C-PVAc, 20.3%
Figure 4.6 TGA profiles of (A) commercial PVAc; (B) MWCNTs and their derivatives; TGA and their derivative curves of (C) MWCNT-PVAc and (D) MWCNT-C=C-PVAc. Experiments were performed under N₂ at a heating rate of 10 °C min⁻¹.
TGA of commercial PVAc beads with narrow molecular weight distribution performed under nitrogen, revealed two weight loss steps and the maximum loss for each step occurred at 355 °C and 441 °C (figure 4.6 (A)).

In figure 4.6 (B), pristine MWCNTs have a good thermal stability with 2.2% of total weight loss up to 600 °C. The initial mass loss started from 150 °C, which is attributed to the CVD growth defects and small amount of impurities (around 0.5% in the formation of amorphous carbon and catalyst residues as provided according to the manufacture specification). The vinyl–functionalised MWCNTs (MWCNT-CH=CH₂) have a weight reduction of 5% until 600 °C, which is caused by the surface functional groups. PVAc grafted MWCNTs prepared by two methods, MWCNT-C=C-PVAc and MWCNT-PVAc, showed 20.1% and 15.4% mass decrease at 600 °C, respectively, proving that the vinyl-functionalised MWCNTs have the ability to attach more PVAc than direct polymerisation onto the surface of pristine MWCNTs. However the grafting ratio achieved by these two approaches was not significantly different, possibly due to the steric limitation of the functional groups and grafted polymer on MWCNT surfaces.

TGA and and their derivative profiles of MWCNT-PVAc and MWCNT-C=C-PVAc are shown in figure 4.6 (C) and (D). MWCNT-PVAc exhibits a derivative peak at 301 °C due to the degradation of the covalently grafted polymer. MWCNT-C=C-PVAc, possessing a polymer coating grafted mainly from vinyl groups, shows a highest weight loss at 311 °C. Samples of MWCNT-PVAc showed less thermal stability, which might be explained by the low molecular weight of grafted polymer as the growth of the polymer chains is inhibited by massive π electron clouds and polymer propagating chains are terminated by the MWCNTs in a very random way. Vinyl groups on MWCNTs, on the other hand, are expected to initiate
polymerisation and generate polymers of higher molecular weight. This conclusion is consistent with TEM study in which polymer clusters were clearly observed on the sidewalls of vinyl-MWCNTs. Moreover, the vinyl-modified MWCNTs may display more effective restrictions in contrast with pristine MWCNTs on the chain motions of PVAc upon heating.

4.3.6. DSC characterisation

![DSC curves](image)

Figure 4.7 DSC curves of oxidised MWCNT, MWCNT-CH=CH₂, MWCNT-PVAc and MWCNT-C=C-PVAc in the temperature ranging from 180 to 470 °C
Formation of polymer grafted MWCNTs via free radical polymerisation

<table>
<thead>
<tr>
<th>Samples</th>
<th>Decomposition peak position</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT-PVAc</td>
<td>303 ± 5 °C</td>
</tr>
<tr>
<td>MWCNT-C=C-PVAc</td>
<td>321 ± 7 °C</td>
</tr>
</tbody>
</table>

Table 4.1 Thermal decomposition temperatures of MWCNT-PVAc and MWCNT-C=C-PVAc

In order to confirm that the grafted PVAc molecules are covalently bound rather than physically adsorbed, pristine MWCNTs and MWCNT-CH=CH$_2$ were stirred with PVAc/THF solution (0.05 g mL$^{-1}$) for 24 hours at 70 °C. The samples were separated via filtration and washed with THF until the filtrate did not generate a precipitate in hexane, indicating that the entire free polymer was removed. Both MWCNT products were not soluble in THF and their featureless DSC performance confirmed that PVAc had not adsorbed on the MWCNT surface.

The temperature of maximum weight reduction derived from the TGA profiles may not reflect the real polymer decomposition temperature as MWCNTs with surface functional groups such as lactone, phenol and carbonyl showed continuous weight loss between 150-600 °C, which overlapped with PVAc loss (figure 4.6 (B)). Therefore DSC was conducted for MWCNTs and their derivatives in order to confirm the decomposition peak of grafted PVAc on MWCNTs. Since the position of the characteristic exothermic peak may slightly vary from each measurement, every analysis was repeated in triplicate. The oxidised MWCNTs free from lattice fragments (MWCNT-ox-6hrs) and MWCNTs modified with vinyl groups (MWCNT-CH=CH$_2$) showed near featureless plots within the investigated region indicating that small surface functional groups, such as carboxyl and amide, were not detectable in DSC (figure 4.7). Samples of MWCNT-PVAc and MWCNT-C=C-PVAc show the exothermic peaks, which confirms the covalent attachment of nanotubes by PVAc. Mean
decomposition temperatures are 303 and 321 °C for MWCNT-PVAc and MWCNT-C=C-PVAc, respectively (table 4.1), which supports our TGA results that polymer chains developed from surface functional groups degrade more slowly compared with the polymer grafted onto the pristine MWCNT surface.

4.3.7. Dispersion of polymer covalently grafted MWCNTs in PVAc solution

As MWCNT-C=C-PVAc showed good solubility in THF and thermal stability, their ability to disperse in polymer solution was studied. In preparing PVAc/THF solution, PVAc was dissolved in THF with a concentration of 0.05 g mL⁻¹. MWCNT-C=C-PVAc were sonicated in THF for 10 minutes and then added to PVAc/THF solution. The mixture appears macroscopically homogeneous with an intensive black colour, implying that the grafted PVAc layers can help to disperse MWCNTs in polymer solution effectively. To compare the dispersion ability, the same quantity of pristine MWCNTs were sonicated in THF for 6 hours and subsequently added to PVAc/THF solution. However they failed to form fine dispersion and MWCNT clumps were observed with the naked eye. A drop of both mixtures was taken, dried and analysed under light microscope. MWCNT-C=C-PVAc presents a remarkable improvement of dispersion ability in polymer solution compared with pristine MWCNTs, indicating the polymer coating on the MWCNT surface is very effective in breaking tube-tube interactions (figure 4.8 (B)). Separation of CNTs in polymer solution is of great technical importance as it ensures a high dispersion quality of CNTs in bulk nanocomposites. However some large particles \textit{ca.} ~1\,\mu\text{m} size, still remained particularly under large-scale production of nanotube polymer suspensions implying that it is necessary to prolong the sonication time in accordance with CNT amount. Light and dark grey unfilled circles are
ascribed to the trapped air bubbles generated in the process of pressing cover slip on the microscope slide.

Figure 4.8 Light microscopy of (A) pristine MWCNTs and (B) MWCNT-C=C-PVAc in PVAc/THF solution
4.4. Conclusions

Production of PVAc covalently grafted MWCNTs was achieved by free radical polymerisation in the presence of pristine MWCNTs and vinyl-functionalised MWCNTs. A higher grafting efficiency and thermal stability of PVAc grafted from vinyl-MWCNTs was supported by TGA, DSC and TEM, implying the pre-attached vinyl groups may produce new polymer chains of higher molecular weight and effectively confine the deformation of polymer chains under heating. MWCNT-C=C-PVAc exhibited a considerable increase in their dispersibility in polymer solution, which ensures the production of homogeneous MWCNT composites.
Chapter five:

Stiffness and damping performance of MWCNT/PVAc composites
5 – Stiffness and damping performance of MWCNT/PVAc composites

5.1. Introduction

PVAc is an elastomeric, thermoplastic material which can be produced by free radical polymerisation of vinyl acetate in the presence of an initiator such as AIBN or dibenzoyl peroxide. It is frequently utilised as an adhesive for wood and papers. For loudspeaker production, PVAc is employed as a backing material for Kevlar cone in order to seal the fabric cones and reduce resonant vibrations due to its capacity for energy absorption as a rubbery material.

The most important material properties to maximise cone performance are high stiffness and good damping. The impressive Young’s modulus of MWCNTs (~1 TPa) (Kashyap et al. 2008) and interfacial sliding between fillers and matrix materials (Suhr et al. 2005) suggest that MWCNTs combined with PVAc can yield a new acoustic material with good stiffness and damping characteristics at the same time, therefore improving frequency response. Moreover, introducing MWCNTs into a viscoelastic material such as PVAc should be more effective to increase its stiffness performance than other semi-crystalline matrixes (Jin et al. 2000).

Numerous studies have been conducted on CNT/polymer composites for mechanical reinforcement, however few examples can be found specifically regarding CNT/PVAc materials. Dynamic mechanical analysis of pristine MWCNT/PVAc composite was undertaken by Choi et al. and the results showed that Young’s modulus increased by 10%, but damping has not changed (Choi et al. 2007).
CNTs chemically modified with polymers lead to a better dispersibility and interfacial bonding, particularly when grafting the same polymer being used as the matrix material (Fragneaud et al. 2008, Wang et al. 2008). In general, strong interfacial adhesion encourages the use of CNTs as the reinforcing fillers, which in turn promotes stiffness and strength. On the other hand, good integration reduces frictional energy dissipation, which limits the material’s damping performance (Gorga et al. 2006). Therefore addition of polymer grafted MWCNTs is a promising approach to design stiff materials. But this does not mean that polymer grafted MWCNTs will lead to a weak damping of the polymer composites as good distribution of MWCNTs creates enlarged interfacial contacting areas, which has a potential advantage of high frictional energy. Understanding the effect of polymer coating of MWCNTs on damping behaviour of the composites requires greater attention as the stiffness and damping characteristics are relevant to many commercial applications (e.g. acoustic and mechanical engineering), and it has not been established how to engineer the interface between CNTs and the matrix to enhance the Young’s modulus and preserve damping.

In this chapter, composites of PVAc covalently grafted MWCNTs in bulk PVAc were produced with varied filler fraction amounts of MWCNTs in order to improve stiffness and keep damping character of the matrix material. Optimised vibration-damping tests were carried out and a 3D Finite Element Model was used to evaluate the Young’s modulus of the prepared nanocomposites. To overcome the difficulties in processing PVAc composites arising from air bubbles generating upon heating of its glass transition temperature, hot pressing was applied to the composite films made initially by solution casting. For comparison, pristine MWCNTs and PVAc water-based emulsions were applied as an optional filler and composite matrix, respectively.
5.2. Materials, experiments and characterisation methods

5.2.1 Materials

MWCNTs, CVD grown, 99.5% purity, were obtained from TMSpetsmash, Ukraine;

PVAc beads, molecular weight of ~100,000, were obtained from Sigma-Aldrich Company Limited;

PVAc emulsion, particle size of ~1µm, viscosity of 33 poises under room temperature, was provided by B&W Company.

Triton X-100, non-ionic surfactant, viscous colourless liquid, which is popular in suspending CNTs in aqueous solution.

Figure 5.1 Chemical structure of Triton X-100.

5.2.2. MWCNT treatment

The aggregation size and dispersibility of MWCNTs in PVAc are largely dependent on the modification treatment of MWCNTs. Here, the as-produced MWCNTs were treated in four different ways:
1. Purified MWCNTs: the pristine MWCNTs were air oxidised at 200 °C for 1 hour then refluxed in 2M HCl for 2 hours to remove catalyst particles and amorphous carbon;

2. Oxidised MWCNTs without oxidative fragments: details described in section 2.2.3;

3. Triton X-100 coated MWCNTs: 500 mg of as-prepared MWCNTs were suspended in deionised water through sonication. 4 times mass amount of Triton X-100 was added, sonicated for 10 minutes, the suspension was shaken at room temperature for 24 hours allowing physical adsorption of Triton X-100 onto MWCNT surfaces (Jiang et al. 2003). The product was washed with excessive amount of deionised water through vacuum filtration to remove free surfactant.

4. PVAc covalently grafted MWCNTs (MWCNT-C=C-PVAc): details described in sections 4.2.2 and 4.2.3.

In figure 5.2, oxidised and surfactant-coated MWCNTs showed good solubility in water determined by their visual appearance and their suspension being stable for a few months.

Figure 5.2 Solubility of 1. Pristine MWCNTs; 2. Purified MWCNTs; 3. 6 hours oxidised MWCNTs; 4. Surfactant–coated MWCNTs in water
5.2.3. SEM

SEM is a useful tool for indentifying and characterising the surface morphology of CNT/polymer composites as the electron beam, which has a high energy ranging from a few hundred eV to thousands of eV, is used for scanning of the sample surface. When the incident beam scans the sample, a SEM detector captures secondary electrons or backscattered electrons that are scattered from the sample. Magnification of SEM is able to reach to 500,000 times. Here the SEM images were obtained with Zeiss Supra 55VP, with electron energy of 1.5 kV and 2 kV. Pieces of MWCNT/PVAc composites were fractured after immersion in liquid nitrogen and mounted onto SEM stubs glued with a conductive paste.

5.2.4. Measurement of loss factor and Young’s modulus of MWCNT/PVAc composites

This test refers to a standard method for measuring dynamic mechanical properties of materials (ASTM E756 – 05), which is able to obtain the loss factor through the measured resonance frequencies of the MWCNT/PVAc composites. To eliminate experimental errors, the samples were measured 20 times to obtain the average resonant frequency and its standard deviation.
5 – Stiffness and damping performance of MWCNT/PVAc composites

5.2.4.1. Loss factor

5.2.4.1.1. Sample requirement and experiment setup

For soft, non-self-supported material under vibration analysis, Oberst beam test is often recommended, in which the investigated material is bonded to a supporting platform made from a rigid material such as aluminium. The resonance frequencies are determined by subtracting the influence of the substrate from the response of the mounted sample (figure 5.3).

![Figure 5.3 Oberst beam test](image)

By increasing the sample thickness, a soft material can be transformed into a self-standing beam for vibration tests. This sample formation requires a larger amount of material compared with Oberst beam tests; however it simplifies the sample preparation by eliminating the need of Al substrate (figure 5.4).

In our experiments, self-standing composites beams were applied.

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In the experiment setup (figure 5.5), the composite beams of 5 cm long, 1 cm wide is mounted on a heavy, rigid fixture, excited with a signal containing frequencies of 100 – 5 KHz by means of an electromagnetic transducer. The test assumes that the clamped section is not taken into consideration. The beam displacement is measured by a laser sensor and the response spectrum of excited frequencies versus displacement is recorded.
5.2.4.1.2. Estimation of loss factor from resonant frequency

The peak in the frequency response spectrum defines the beam resonance frequency. Therefore, the loss factor, which is the ratio of the half-power bandwidth to the resonant frequency, can be calculated from equations 5.1. The half-power bandwidth is the frequency difference between the upper 3 dB down point and the lower 3 dB down point (figure 5.6).

\[ \eta = \frac{\Delta f}{f_r} \]  

(eq. 5.1)

Figure 5.6 Illustration of half-power bandwidth

Here, \( \eta \) is loss factor; \( n \) denotes mode shape which defines the relative displacement of each single point on the specimen under excitation. \( f_n \) is the resonant frequency of mode \( n \) and \( \Delta f \) is the half-power bandwidth of the mode (ASTM E756 - 05). The higher resonant frequency, the more complex the vibration mode is (Blevins, 2001) (figure 5.7). Because of the high damping and low stiffness of PVAc, only the first vibration mode can be excited for the uniform PVAc beams (\( n = 1 \)).
Unlike rigid materials, the frequency response spectrum for viscoelastic materials often generates broad, noisy peaks; therefore it is difficult to estimate the resonant frequency visually. Figure 5.8 shows the frequency response spectrum for 0.5 wt% pristine MWCNT/PVAc composites. An advanced formulation, $H(\omega)$ (eq. 5.2), which is a least square criterion, is used to simulate and curve fit the experimental frequency response to help identify resonant frequency (figure 5.9) (Richardson MH et al. 1982).

\[
H(\omega) = \frac{\sum_{k=0}^{m} a_k s^k}{\sum_{k=0}^{n} b_k s^k} \mid s = j(\omega) \quad \text{(eq. 5.2)}
\]
Figure 5.8 Frequency response spectrum for 0.5 wt% pristine MWCNT/PVAc composite. The Y-axis represents sample displacement.
5.2.4.2. Estimation of Young’s modulus

The equation 5.3 is frequently used to estimate the Young’s modulus from the resonant frequency, sample size and density.

\[ E = \frac{12\rho L^4 f_n^2}{a_n^2 t^2} \]  (eq. 5.3)

In eq.5.3, \( E \) is Young’s modulus (Pa), \( \rho \) is the beam density (kg m\(^{-3}\)), \( L \) is the beam length (m), \( n \) denotes mode shape which defines the relative displacement of each single point on
the specimen under excitation. \( f_n \) is the resonant frequency for mode \( n \) (Hz), \( t \) is the beam thickness (m), \( a_n \) is the coefficient for mode \( n \), where \( a_1 = 0.55959 \).

However in equation 5.3, it is assumed the dimensions of the beam cross section to be much smaller than the length of the beam. In order to avoid this approximation a 3D Finite Element (FE) Model (PAFEC software package) is used to estimate the material Young’s modulus (figure 5.10). A forced response linear model with 3D elements is used. The input parameters are sample geometry, density, damping ratio and poisson ratio which is a constant of 0.3 for all PVAc and their MWCNT composites. In the FE analysis, it is assumed that:

- Constraints: the edge of the sample is clamped to an infinitely rigid surface,
- A force is applied at the end of the beam and the resulting displacement is calculated at the same node,
- A viscoelastic material law is applied for the material: it is defined as a complex dynamic Young's modulus.

All the parameters are known apart from the Young’s modulus, which is adjusted until the simulated displacement matches the measured one.
5.3. Results and discussion

5.3.1. MWCNT/PVAc emulsion-based composites

5.3.1.1. Preparation

Purified and modified MWCNTs (oxidised and Triton X-100 physically coated MWCNTs) which have good water solubility were chosen to form an emulsion-based composite. A T18 basic ULTRA-TURRAX (IKA) homogeniser equipped with a S25N–8G dispersing element was applied to disperse MWCNTs into PVAc emulsion. According to the technical data for the dispersing tool, particle size can be cut down to 10 µm.
5.3.1.2. Optical morphology

Figure 5.11 shows the dispersion of purified MWCNT/PVAc emulsion-based composite after homogenisation for 4 minutes, 10 minutes and 20 minutes, for which prolonged treatment shows enhanced homogeneous dispersion and smaller MWCNT particles of around ~10 µm. It should also be noted that efficient dispersion of MWCNTs occurs after 10 minutes.
Surfactant coated and oxidised MWCNTs show increased solubility in water over purified MWCNTs (as shown in figure 5.2). However they did not show any improvement of dispersion in PVAc emulsion compared to pristine MWCNTs, indicating that functional groups on MWCNT surface did not influence their dispersion in solutions of high viscosity (figure 5.12).

Figure 5.11 Optical micrographs for 0.5 wt% purified MWCNT/PVAc nanocomposites prepared by homogenisation of (A) 4 minutes (B) 10 minutes and (C) 20 minutes.
5.3.2. MWCNT/PVAc bead-based composites

Functionalised MWCNTs did not show improved dispersion in PVAc emulsion; therefore PVAc beads soluble in THF were selected to facilitate dispersibility of MWCNTs. Pristine MWCNTs, PVAc covalently grafted MWCNTs (MWCNT-C=C-PVAc) that exhibited strong solubility in THF were introduced as composite fillers.

5.3.2.1. Preparation of MWCNT-PVAc solution mixture

Details of production of MWCNT-PVAc solution mixture using pristine MWCNTs and MWCNT-C=C-PVAc were described in 4.3.6. Here, MWCNT content of 0.1, 0.5 and 1 wt% with respect to the mass of PVAc matrix were incorporated in PVAc matrix.
5.3.2.2. Layer casting

An Al mould (15 × 5 × 0.2 cm) composed of five 1 cm specimens was designed to form Oberst tests and the four surrounding sides are easily separated from the substrate (figure 5.13). Each beam forms the base of MWCNT composites in Oberst test. The prepared MWCNT-PVAc mixture was poured on the mould, layer by layer, until a 2 mm thickness was obtained. We have found that composite beams with 2 mm thickness took few months to prepare due to the slow drying of each individual layer. The problem was compounded by the fact that PVAc has a low glass transition temperature, so the whole mixture can only be dried under ambient conditions to avoid generating bubbles in the composite films when the temperature rises above the glass transition temperature. The composite density was measured as 1.03 g cm\(^{-3}\), which is lower than PVAc matrix of 1.19 g cm\(^{-3}\) and MWCNTs between 1.3–1.4 g cm\(^{-3}\). The voids were clearly visible in the cross-sections of the samples.
Figure 5.13 (A) Pure PVAc and (B) 0.5 wt% pristine MWCNT/PVAc composite on Al mould
5.3.2.3. Film casting and hot pressing

To overcome the problems associated with layer casting method, such as long time of sample preparation and structural defects, film casting and hot pressing were utilised to prepare bulk MWCNT/PVAc composite sheets without Al substrate. Therefore, uniform, non-supported sample with relatively large thickness of 3 mm were manufactured and used instead of Oberst beam in vibration-damping tests.

Composite films were made by drying the MWCNT-PVAc solution mixture on a glass mould (15 cm × 15 cm × 2 mm) for 1 week under room temperature. Films with an average thickness of ~0.2 mm were obtained, which were then hot pressed into composite sheets with a thickness of 3 mm. Approximately 20 composite films were placed into a 15 × 15 cm steel mould. To avoid bubbles being generated in the composite during hot pressing, the pressure load was increased with time under a constant temperature of 50 °C (figure 5.14). In addition, pressure was released at every 20 minutes to avoid air trapping (figure 5.14). Finally temperature was reduced to ambient at a holding pressure of 9 MPa. Figures 5.15 and 5.16 show the prepared 0.5 wt% pristine MWCNT/PVAc composite with 3 mm thickness.
Figure 5.14 Relationship between time and pressure during hot press procedure

Figure 5.15 Composite sheet of 0.5 wt% pristine MWCNT/PVAc of 15 × 15× 0.3 cm
Figure 5.16 Photograph of a composite beam of 5 cm length and 3 mm thickness, which is ready for vibration-damping test
5.3.3. SEM morphology

Figure 5.17 SEM morphology of (A) 0.5 wt% MWCNT/PVAc composite and (B) 0.5 wt% MWCNT-C=C-PVAc/PVAc composite
The imaged nanocomposites contain 0.5 wt% pristine MWCNTs (figure 5.17 (A)) and polymer grafted MWCNTs (figure 5.17 (B)) respectively. The bright dots in the images are regarded as MWCNTs due to their high conductivity (So et al. 2007). MWCNTs were found distributed in PVAc matrix homogeneously in both cases. Clumps of polymer grafted MWCNTs are smaller than pristine MWCNTs, proving that covalently attached polymer layers weaken the inter-tube attractions and promote the MWCNT dispersibility in matrix. It is important to eliminate composite defects formed by large CNT aggregates and achieve effective load transfer (Lee et al. 2007); therefore good dispersion of CNTs is the first essential in production of nanocomposites.
Figure 5.18 High magnification of SEM morphology of (A) 1 wt% pristine MWCNT/PVAc composite and (B) 1 wt% MWCNT-C=C-PVAc/PVAc composite
Interaction between MWCNTs and the matrix material is another important contributor influencing of stiffness and damping. Direct evidence of poor interfacial bonding is MWCNTs pulled out from matrix instead of being broken within matrix (Ajayan et al. 2000). The pulling out of MWCNTs which can be taken as an evidence for crack bridging was proved to effectively enhance damping of a composite (Gojny et al. 2004, Seshadri et al. 2007), hence strengthen the vibration reduction ability of the cones in loudspeaker. In figure 5.18, it is clearly observed that larger amount of pristine MWCNTs are pulled out from the PVAc matrix compared with polymer grafted MWCNTs, indicating that the interfacial adhesion of pristine MWCNTs and matrix is not as good as that of polymer grafted MWCNTs, which is consistent with the published results (Bal et al. 2007). Nevertheless, some clumping of polymer grafted MWCNTs are observed in composites particularly with 1 wt% loading, which creates the local defects under forces and the interfacial spillage is expected to be higher in the region nearby these structural defects.
### 5.3.4. Stiffness and damping performance of the composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resonant frequency (Hz)</th>
<th>Loss factor</th>
<th>Young’s modulus (GPa)</th>
<th>Loss modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVAc</td>
<td>1127 ± 34</td>
<td>0.47 ± 0.015</td>
<td>1.00 ± 0.030</td>
<td>0.47 ± 0.030</td>
</tr>
<tr>
<td>0.1 wt% MWCNT/PVAc</td>
<td>1059 ± 72</td>
<td>0.45 ± 0.015</td>
<td>0.88 ± 0.065</td>
<td>0.40 ± 0.054</td>
</tr>
<tr>
<td>0.1 wt% MWCNT- C=C - PVAc/PVAc</td>
<td>1069 ± 45</td>
<td>0.51 ± 0.025</td>
<td>0.90 ± 0.040</td>
<td>0.46 ± 0.022</td>
</tr>
<tr>
<td>0.5 wt% MWCNT/ PVAc</td>
<td>1285 ± 71</td>
<td>0.40 ± 0.015</td>
<td>1.30 ± 0.075</td>
<td>0.52 ± 0.051</td>
</tr>
<tr>
<td>0.5 wt% MWCNT- C=C - PVAc/PVAc</td>
<td>1151 ± 50</td>
<td>0.42 ± 0.015</td>
<td>1.26 ± 0.055</td>
<td>0.53 ± 0.032</td>
</tr>
<tr>
<td>1 wt% MWCNT/ PVAc</td>
<td>1152 ± 63</td>
<td>0.46 ± 0.025</td>
<td>1.26 ± 0.070</td>
<td>0.58 ± 0.065</td>
</tr>
<tr>
<td>1 wt% MWCNT- C=C - PVAc/PVAc</td>
<td>1355 ± 62</td>
<td>0.39 ± 0.020</td>
<td>1.45 ± 0.065</td>
<td>0.57 ± 0.05</td>
</tr>
</tbody>
</table>

Table 5.1 Loss factor and Young’s modulus results of MWCNT/PVAc nanocomposites, errors bars are derived from the standard deviation
5 – Stiffness and damping performance of MWCNT/PVAc composites

The results of vibration-damping tests on pristine and PVAc grafted MWCNT/PVAc composites are shown in table 5.1. It is noted that the resonant frequency has its largest value for 1 wt% MWCNT-C=C-PVAc/PVAc composite compared to the other composite beams. Therefore, the loss factor which is frequency dependent, is at its lowest for composite with 1 wt% MWCNT-C=C-PVAc as compared to other samples (figure 5.19).
In general, Young’s modulus increases as a function of MWCNT concentration (see trendline, figure 5.19) but there is no difference between composites with pristine MWCNTs and PVAc covalently grafted MWCNTs until mass fraction of MWCNT reaches to 1 wt%. According with the rules of mixtures (chapter 1, section 1.2.2), it is able to estimate that $K_1$ equals to 0.046 for 1 wt% MWCNT-C=C-PVAc/PVAc composites providing Young’s modulus of MWCNTs is 1 TPa. It is also observed that 0.1% weight fraction of MWCNTs is not sufficient to improve the Young’s modulus of the polymer matrix.

![Figure 5.20 Loss modulus of MWCNT/PVAc composites](image)

The average loss modulus of the PVAc composites (figure 5.20), which is determined via multiplying Young’s modulus by loss factor, increases with MWCNT content, displaying a good combination capacity of damping and stiffness. There is no difference in the loss modulus between composites of pristine MWCNTs and PVAc covalently grafted MWCNTs indicating that the MWCNT functionalised with polymer could not facilitate the damping capacity of the nanocomposites. Although at 1 wt% mass fraction, PVAc covalently grafted MWCNTs is more effective in reinforcing Young’s modulus, loss factor is decreased.
Therefore, the loss modulus, which is proportional to the Young’s modulus and loss factor, was not influenced by the MWCNT surface chemistry.

5.3.5. Glass transition temperature of the composites

Glass transition temperature allows to evaluate the molecular mobility of PVAc after addition of MWCNTs and their vibration damping (Sperling et al. 2003). Composites of 1 wt% of nanotube, showing the biggest improvement of loss modulus, were measured with differential scanning calorimetry. It can be seen that MWCNT-C=C-PVAc shows the highest glass transition temperature, then MWCNT-PVAc and pure PVAc, indicating polymer grafted MWCNTs exhibit better effect in retaining motions of polymer chains than that of pristine MWCNTs upon heating, which agrees with the results of loss factors.

Figure 5.21 DSC profiles of PVAc, 1 wt% MWCNT/PVAc and 1 wt% MWCNT-C=C-PVAc/PVAc in the temperature range of -10-120 °C with a heating rate of 20 °C/min.
5.4. Conclusions

We described a route suitable for the large-scale production of MWCNT/PVAc composites that possess controlled dimensions. Two forms of PVAc nanocomposites have been made, emulsion-based and PVAc bead-based. They both present challenges in the dispersion of MWCNTs to form composites of good quality. High viscosity PVAc emulsion prevents modified MWCNTs from being effectively dispersed and the dispersion state became solely dependent on the limitations of the homogeniser. With a PVAc bead-based solution, it is possible to add an excess of solvent in order to reduce the viscosity. Herein, the MWCNTs especially MWCNTs with covalently grafted polymers are much easier to disperse in PVAc solution compared with the PVAc water-based emulsion.

Hot pressing using a stepped pressure increase programme shows a marked improvement in removing air bubbles and generates more homogeneous and condensed MWCNTs composites with controlled dimensions. It is found that at high MWCNT filler fraction levels, polymer composites with covalently modified MWCNTs yield better Young’s modulus compared with that of pristine MWCNTs. Addition of 1 wt% of pristine MWCNTs in PVAc maintained damping, but there was a limiting reinforcement in stiffness. The loss modulus, expressing the combination of damping capacity and stiffness, increased with MWCNT filler fraction levels, but was not influenced by MWCNT surface modification.
Chapter six:

Conclusions
The oxidation of the MWCNTs for different periods of 1, 3, 6, 9, 14, 24 and 48 hours with 70% of nitric acid causes the generation of significant amount of physically adsorbed oxidative fragments. The structures of these fragments correspond to polycyclic aromatic hydrocarbons extensively substituted with oxygen-containing functional groups, as confirmed by HPLC-mass spectroscopy, fluorescence and UV-Vis spectroscopy. The MWCNT-oxidative fragments are soluble in strong acidic environment (pH = 1). They are termed as fulvic acids as their solubility and structures are analogous to fulvic substance extracted from soils or natural river waters. It was found that oxidative fragments can be adsorbed to pristine MWCNT surface at low pH and de-adsorbed in the presence of high pH buffers. Oxidative fragments were removed by NaOH solution and acid-base titration showed that the total number of functional groups decreased by up to 43% after the removal of FAs, effectively eliminating the involvement of non-covalent interaction in the process of covalent modification. The number of carboxyl groups covalently bound to the MWCNT structure increased from 0.139 to 0.830 meq g\(^{-1}\) when the oxidation time extended from 1 to 48 hours.

The conversion percentage of carboxylic groups to amide groups was measured to evaluate the feasibility and reactivity of functional groups on MWCNTs. Notion of long time oxidation would provide more carboxylic groups on MWCNT surface for subsequent reaction is frequently taken for granted. Titration results showed that the number of reactive carboxylic groups did not increase with oxidation time, but remained the same after 6 and 48 hours oxidation. This may be due to the generation of sterically hindered carboxylic sites and carboxylic anhydrides especially at extended oxidation times. It was concluded that up to 42% of carboxylic functional groups do not participate in the covalent transformation due to steric hindrance and ionic reaction. The FTIR spectra of oxidised MWCNTs and their amide derivatives were found featureless as those of the pristine MWCNTs. The intensity ratio of
Conclusions

The disordered-to-graphite band revealed by Raman spectra did not change after amidation reaction. The amide band was resolved in XPS N\textsubscript{1s} signal, however XPS is unable to monitor the transformations of carboxylic groups by C\textsubscript{1s} signal as the peak of carboxylic acids and amide groups could not be distinguished by XPS peak fitting programme.

PVAc was coupled to the MWCNT surface by free radical polymerisation using vinyl functionalised MWCNTs and pristine MWCNTs as the precursor material. Polymer clusters and an increase of the tube diameter of ~20 nm were observed with TEM images, however the non-uniform distribution of tube wall thickness implies that the weak dispersion state of MWCNTs in magnetic stirring assisted polymersing solution. A more successful polymer grafting method is based on utilising vinyl-MWCNTs, where the covalently bound vinyl groups initiate PVAc polymerisation resulting in 20.3% grafting yield and thermal stability of 321 ± 7 °C of attached polymers. On the other hand, polymer coupled to the surface of pristine MWCNTs exhibited lower polymer percentage of 15% and lower thermal stability of 303 ± 5 °C. Due to the covalent linkage of polymer chains, MWCNTs had a good solubility in polymer solution of around 20 times higher than reported in literature, which ensures good dispersion and interfacial compatibility of their polymer composites.

The shear mixing and MWCNT chemical modification did not improve distribution of MWCNTs in PVAc emulsion matrix and the micrographs displayed nanotubes staying in big clumps with the size of ~10 μm, therefore PVAc beads and polymer grafted MWCNTs were selected for composite preparation. MWCNT/PVAc composites with controlled dimensions were produced by layer casting and hot pressing, in which temperature was increased and pressure was released regularly allowing the dissipation of the trapped air. SEM images showed improvement in dispersion and interfacial interaction of composites with polymer.
grafted MWCNTs, which is consistent with previous references. By improving the standard ASTM tests using a frequency response function $H(\omega)$ and a 3D Finite Element Model, Young’s modulus was calculated and it turns out to be improved by 45% with the addition of 1 wt% polymer grafted MWCNTs. Results revealed that high weight fraction and covalent modification treatment of MWCNTs are the dominant factors for the purpose of attaining good stiffness properties of PVAc composites. Additionally, MWCNT surface modification did not improve loss factor of the PVAc composites. The combination stiffness and damping capacity, expressed by the loss modulus, increased with MWCNT filler fraction levels by up to 23%, but was not influenced by MWCNT surface modification.
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