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CHEMISTRY OF SINGLE WALL CARBON NANOTUBE DERIVATIVES

BY

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ABSTRACT

CHEMISTRY OF SINGLE WALL CARBON NANOTUBE DERIVATIVES

By
Haiqing Peng

Single wall carbon nanotubes (SWNTs) are novel materials with unique chemical and physical properties: they are the strongest fiber ever made; they have outstanding thermal conductivity and unique one dimensional electrical conductivity; their weight is light and their individual size is only 0.4 to several nm in diameter.

A wide range of applications of SWNTs were proposed including high performance polymer composites, field emitter for flat panel display, energy storage, molecular electronics and biomedical applications, etc. Functionalization of SWNTs has been an important pathway to utilize SWNTs for many of these applications.

This thesis studies the fluorination of SWNTs, electrochemical properties of fluorinated SWNTs as a cathode material in lithium batteries and oxidative properties and thermal stabilities of fluorinated SWNTs in a binary metal compound matrix.
This thesis also studies functionalization of SWNTs through a free radical addition process, in which radicals were from the thermal decomposition of organic diacyl peroxides including lauryl peroxide, benzoyl peroxide, succinic acid peroxide and glutaric peroxide. Functionalized SWNTs prepared from this method have improved solubility in various common organic solvents. They are characterized with a variety of techniques including Raman, FTIR, TGA/MS, TEM and solid state $^{13}$C NMR. A parallel study on C60 fullerene is also included.

The succinic acid peroxide is of particular interest for functionalization because it can attach ethylenecarboxyl groups (-CH$_2$CH$_2$COOH) to the sidewall of SWNTs. The sidewall acid groups, after reacting with thionyl chloride and diaminines, are converted to terminal amine groups, which can form covalent bonds with epoxy polymers to prepare SWNT reinforced epoxy polymer composites. Mechanical tests show that the tensile strength, elongation and storage modulus of epoxy are greatly improved (25~30%) with 1 weight percent of SWNTs addition.
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Chapter One: Introduction to single wall carbon nanotubes

1.1 Discovery of fullerene and carbon nanotubes

In 1985, to explore the long carbon chain molecules which had previously been detected in the interstellar medium, Harry Kroto, an astrophysical chemistry professor at the University of Sussex, UK, came to Rice University to work with Professors Robert Curl and Richard Smalley who had developed a powerful technique in which a laser was used to vaporize graphite into helium gas. In their collaborative research, they and their students discovered a variety of carbon clusters as expected and they also found under certain conditions, a species containing 60 carbon atoms was dominating. This species was determined to have the form of a common soccer ball or a "truncated icosahedron" in which carbon atoms occupy each vertex because only in this form all the valences were satisfied so it was more stable than other cluster species.¹ This species is fullerene C₆₀ that consists of 60 sp² carbon atoms. Its structure consists of 20 hexagons and 12 pentagons like a soccer ball. It has 90 edges but all are not identical. The edges between the two hexagons are 1.42 Å and edges between a hexagon and a pentagon are 1.44 Å. All the carbons are identical so they have only one NMR signal at 142.7 chemical shifts.
Fullerene C60 was selected "Molecule of the Year" for 1991 by *Science* magazine. The Editors stated that "Fullerene science exhibits the classic profile of a major scientific breakthrough. Buckyballs were found by accident by researchers asking a completely different question. Then they were steadily explored - until they became widely available and the field exploded. Now, buckyball scientists are enjoying the exponential phase, in which almost everything is new and the unexpected is the expected. Eventually, the action will focus on a few promising research veins and the practical applications will bloom". As the editors predicted, researchers all over the world have explored the basic science and applications of fullerenes and the field has spawned an important new area of exploration: carbon nanotubes.

Carbon nanotubes are tube-shape sp2 carbons while C60 fullerene are ball-shape sp2 carbons. In 1991, Electron microscopist Sumio Iijima at the NEC research lab in Japan discovered multi-layer graphite sheet cylinders when he was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. The material he discovered is now called multi wall carbon nanotubes (MWNTs). Another breakthrough came
Figure 1.1: The first observed SWNTs: (a) shows electron diffraction pattern of the first observed SWNTs and (b) shows one individual SWNTs with diameter of 1.37 nm.
in 1993 when Iijima and his coworker added a catalyst such as cobalt to the graphite electrodes of the standard arc-evaporation apparatus. They found extremely fine carbon tubes with single-layer walls which are now called single wall carbon nanotubes (SWNTs).\(^3\) The first SWNT observed by Iijima was shown in Figure 1.1.

In 1995, Smalley and coworkers used their laser-vaporization apparatus similar to that used in making C60, by adding cobalt or nickel catalysts, they produced gram quantity of SWNTs.\(^4\) The SWNTs produced by this method were commercially available from tubes@rice to researchers all over the world before HiPco process was introduced a few years later. Currently, the most efficient way to prepare SWNTs is believed to be the high pressure - high temperature carbon monoxide (HiPCO) disproportionation process with iron pentacarbonyl as the catalyst. This technique requires temperature from 900 to 1100 °C and pressures from 30 to 50 atm. It was reported that by using this method gram quantity of SWNTs could be produced daily\(^5,6\). The smallest SWNTs reported have diameters of about 0.4 nm and the longest SWNTs that were about 20 cm long were produced by a joint team from the U.S. and China\(^7,8\).
Figure 1.2: Basic structures of SWNTs
1.2 Structures and properties of SWNTs

Single wall carbon nanotubes (SWNTs) are considered seamless graphite sheet cylinders with diameters between 0.4 nm to several nm. Graphite sheets consist of hexagonal structures, so there can be various ways to roll up a graphite sheet into a seamless nanotube. Figure 2 shows a graphite sheet where individual carbon atoms are labeled \((m, n)\) for naming the nanotube, which is formed by wrapping up the graphite sheet.\(^9\) As Figure 1.2 shows, if one uses the direction between \((0, 0)\) carbon atom and \((10,10)\) carbon atom as the opening of the nanotube (as Figure 2 (b) shows) to roll up the graphite sheet into a nanotube with an axis perpendicular to the \((0,0)\) to \((10, 10)\) direction, a \((10, 10)\) nanotube is made. By using the same method, a \((19,0)\) nanotube can also be made as shown by Figure 1.2 (b).

Ideally, hemisphere caps close the ends of the nanotubes. Figure 2(b) also shows that the \((10,10)\) nanotube has the “arm-chair” configuration and the \((19,0)\) nanotube has the “zig-zag” configuration at the end opening. Theoretical calculation indicated that a nanotube is considered metallic while the difference of \(n\) and \(m\) is a multiple of 3.\(^{10}\) Thus all arm-chair SWNTs are metallic and one third of zig-zag SWNTs are metallic. Besides “Zig-Zag” and “Arm-Chair”, there can be other \(n\) and \(m\) selections as Figure 2(a) shows, they are called chiral SWNTs.
SWNTs have unique properties: they have unique one-dimensional electrical conductivity; they are the toughest, strongest fiber ever made; they are excellent thermal conductors and they are only nanometers in diameter.\textsuperscript{11, 12, 13}

1.3 Potential applications of SWNTs

Because of their outstanding properties, many applications of SWNTs have been proposed and some of them have been realized in laboratories. Because of the metallic or semi-conductive property and extremely small size, SWNTs are expected to be excellent electron emitters for flat panel displays. The first flat panel display using SWNTs as electron emitters were made in the Samsung Advanced Institute of Technology in 1999.\textsuperscript{14} The low turn-on voltage and high brightness were achieved and it clearly demonstrated the SWNTs potential applications in flat panel display. In the United States, Dupont and Motorola are also trying to develop commercial SWNT flat panel displays.

Researchers from Delft Institute of Technology of the Netherlands reported a study in which an individual SWNT bridged two closely separated platinum electrodes ("source" and "drain" electrodes which was on a silicon surface coated with an insulating silicon oxide layer). Applying an
electric field to the silicon turns on and off the flow of current across the nanotube, by controlling the movement of charge carriers onto the nanotube.\textsuperscript{15} This study described the prototype of a computer transistor whose physical size could be significantly smaller than the current silicon transistor that is typically more than 100 nanometers and made by using HF etching and modern lithographic techniques.

SWNTs are hollow and well-divided materials with large surface areas which can be useful for hydrogen storage for hydrogen fuel cells. Liu and coworkers reported a study in which they found 4.2\% hydrogen (weight percent) could be absorbed to SWNTs at room temperature and under moderately high pressure (10 megapascal). 78.3\% absorbed hydrogen could be released at room temperature and under ambient pressure.\textsuperscript{16} Chen and coworkers found that 20\% and 14\% (weight percent) hydrogen uptake could be achieved by using Li and K doped multiwall carbon nanotubes (MWNTs).\textsuperscript{17}

SWNTs are extremely tough materials and researchers from UTD have developed a procedure for spinning composite carbon nanotube fibers that are tougher than spider silk and any other natural or synthetic organic fiber reported so far. They used SWNTs and lithium dodecyl sulfate in a coagulation-based spinning process that produced nanotube-polyvinyl
alcohol gel fibers and converted them to hundred-meter-long fibers whose diameter was about 50 μm. The prepared fibers exhibited twice the stiffness and strength and 20 times the toughness of steel wire of the same weight.\textsuperscript{18}

Besides the above mentioned applications, SWNTs can also be useful in many other areas such as energy management, high performance composites, catalyst supports and biomedical applications.
Chapter two: Fluorinated single wall carbon nanotubes

2.1 Fluorination of SWNTs

Single wall carbon nanotubes (SWNTs) are novel materials with broad potential applications, but there are many factors that limit their applications. For example, because of their long fiber nature, the as prepared SWNTs form tangled bundles with sizes between 20 to several hundred nanometers when they are produced in mass quantity. The SWNT tangled bundles can not be dissolved in common solvents without help from sonication or surfactants. Furthermore, the SWNTs are considered chemically inert, which imposes additional difficulty in chemical reactions necessary for biomedical, polymer composite and other applications. Sidewall functionalization of SWNTs can help to create repulsive forces between the individual bundled SWNTs, and this will help to disperse SWNTs and create chemical opportunities. So functionalization is an important pathway to make use of SWNTs.

Sidewall functionalization of SWNTs has been an attractive area to researchers and a variety of functionalization techniques have been reported, such as fluorination, phenylation by using aryl diazonium salts, nitrene addition, concentrated HNO$_3$/H$_2$SO$_4$ cutting and following consequent
amine reactions,\textsuperscript{22,23} and alkylation by using fluoronanotubes as precursors to react with organic lithium reagents, Grignard reagents and amines,\textsuperscript{24,25,26} etc.

Among all the above-mentioned functionalization techniques, fluorination by using elemental fluorine is the only solid/gas reaction and the degree of functionalization can be relatively well controlled by controlling the reaction temperature. In addition, fluorination can achieve the highest degree of functionalization: one fluorine atom to every two carbon atoms of SWNTs (C\textsubscript{2}F). Furthermore, fluoronanotubes are not only used as precursors for further functionalizations, but also can be used as intermediates for carbon nanotube cutting. In the cutting process, low F/C ratio fluoronanotubes were pyrolyzed at high temperature (900\degree C) in argon to obtain nanotubes in the range of 20 to 200 nanometers.\textsuperscript{27}

Edward Mickleson and coworkers first performed SWNTs fluorination studies.\textsuperscript{19} In their studies, laser oven produced SWNTs,\textsuperscript{4} with an average diameter 1.3 nm, were reacted with 10\% fluorine at 250, 325 and 400 \degree C for 4 hours. Their study concluded at 250 \degree C the C\textsubscript{2}F stoichiometry was obtained and when the fluorination temperature was higher than 325 \degree C significant destruction happened. In order to maintain tube-like structure of SWNTs, the C\textsubscript{2}F stoichiometry should not be surpassed. The fluoronanotube
could be defluorinated while they were sonicated with hydrazine in tetrahydroforan solution: \( \text{CF}_n + \frac{3}{2}n \text{N}_2 \text{H}_4 \rightarrow \text{C} + n \text{HF} + \frac{3}{2}n \text{N}_2 \).

In this thesis, laser oven produced SWNTs were fluorinated with 10% fluorine gas at 250 °C for 12 hours with HF as a catalyst and high-pressure CO (HiPco) produced SWNTs, whose average diameter is 1 nm, were fluorinated at 150 -160 °C to achieved the C\(_2\)F stoichiometry. Figure 2.1 shows schematic illustration of the fluorination setup and Figure 2.2 shows the real picture of the fluorination setup. At 250 °C, HiPco SWNTs would have been burned away by fluorine gas. The HiPco SWNTs’s lower fluorination temperature for C\(_2\)F stoichiometry reflects their higher reactivity compared with laser oven SWNTs. The higher reactivity originates from their smaller diameter, i.e., the strain energy of smaller diameter nanotubes is higher. This experimental result is supported by theoretical calculation results reported by Bettinger and coworkers. Their calculation results shown that the strain energy of SWNTs is proportional to the reciprocal of the square of the SWNT diameters.\(^{28}\) Similar to fluorinated Laser oven SWNTs, HiPco SWNTs can also be defluorinated by using hydrazine in THF solution. All the SWNTs used in this study were purified by air oxidation (250 °C) and removal of the Fe catalyst residue by HCl sonication method.
Figure 2.1 Schematic illustration of fluorination setup
Figure 2.2: Fluorination setup
developed by Chiang and coworkers. After purification, the iron content is typically less than 1 %( weight).

2.2 Fluoronanotubes as cathodes in a lithium battery

2.2.1 Introduction

The lithium/carbon monofluoride (CFx) battery, a popular commercial product, was first developed by Matsushita in Japan in the 1970s and later made under license by RayOVac. Their open circuit potential is ~3 Volt and the power density is relatively high. Because of their outstanding thermal stability and low self-discharge rates (0.5%/year at 65 °C), they are highly suitable for long term tasks and were particularly chosen for electronic devices in space shuttles. They were also preferred in a computer motherboard for memory backup because a computer gets hot after a long term usage. In the market, the coin size lithium/carbon monofluoride batteries belong to the BR series and lithium/manganese dioxide belong to the CR series, the series types can be easily found on the back of the batteries. A RayOVac coin size lithium/ carbon monofluoride battery can work reliably 7 to 9 years. The carbon monofluoride (CFx) could be manufactured from several kinds of starting materials such as coal, graphite, etc. Their performance characteristics as a cathode material in lithium batteries were fully investigated. After C60 fullerene was discovered in
1985 and produced in mass amount, They were fluorinated and their electrochemical properties as a cathode material in a lithium battery were also studied.\textsuperscript{31} After multi wall carbon nanotubes were discovered, the behavior of fluorinated multi wall carbon nanotubes in an electrochemical cell was also investigated, where the nanotubes were made by decomposition of acetylene over silica-supported cobalt catalysts and fluorinated by F\textsubscript{2}/HF/IF\textsubscript{2} at room temperature or 500 °C.\textsuperscript{32}

2.2.2 Battery design and performance testing

Fluoronanotubes (C\textsubscript{2}F) made from laser oven produced SWNTs and HiPco SWNTs were used as cathode materials and lithium foil (Aldrich) was used as the anode in the batteries. The configuration of the battery is shown in Figure 2.3, the diameter and thickness of the battery were 0.8 and 0.1 inch respectively. Inside the Teflon holder and stainless steel cover, lithium and fluorotubes were separated by a porous polyethylene membrane that was soaked with 1 M LiBF\textsubscript{4} in 1,2-dimethoxyethane and propylene carbonate (1 to 1 ratio in volume). LiBF\textsubscript{4} (Aldrich) was vacuum dried at 100 °C for 24 h; the 1,2-dimethoxyethane and propylene carbonate were distilled to remove water. The cell construction operations were all performed in a drybox filled
Figure 2.3: Schematic illustration of a lithium/fluorotube electrochemical cell. (1) Teflon holder, (2) stainless steel (cathode), (3) stainless steel (anode), (4) lithium foil, (5) porous polyethylene membrane soaked with electrolyte, (6) fluorotubes, (7) Ti current collector, (8) rubber separator.
with argon to prevent any effects from oxygen and moisture and the battery was kept inside the drybox for testing at all times.

The Raman spectra of SWNTs and fluoronanotubes were obtained before the fluoronanotube was fluorinated and assembled into the lithium battery. After the cell was discharged across a resistance load at room temperature, the fluoronanotube cathode material was collected and rinsed with methanol and dried at 70 °C in a vacuum oven for 12 hours before the Raman spectrum was taken. The discharged and rinsed cathode material was heated at 800 °C for 1 h in an argon atmosphere for annealing before the Raman spectrum of the annealed material was taken. All the Raman spectra were obtained with a Renisaw 1000 micro-Raman system with a 780 nm wavelength laser source. The FTIR spectra of the fluorotube cathode material were also collected before and after discharging the cell by using a Thermal Nicolet Nexus 870 FTIR system with an ATR accessory.

The performance of the fluoronanotube cathode was tested by a series of discharging experiments as described by the following. Samples of fluoronanotubes with masses 6 mg, 20 mg, and 40 mg were dispersed in DMF (Aldrich) with the same amount of graphite powder (Aldrich, 1 to 2 µm particle size). The mixture was filtered to obtain fluoronanotube/graphite membranes that were vacuum-oven dried at 70 °C for more than 4 hours
before it was placed in the lithium battery as cathodes. A comparison between the discharge performances of carbon monofluoride (CF$_x$) and fluoronanotube cells was also made. 20 mg fluoronanotubes or 20 mg CF$_x$ (where $x \approx 1$, MARCHEM, Houston) in DMF with 20 mg SWNTs and filtered to obtain membranes that could be placed in cells as cathodes. The use of SWNTs rather than graphite powder facilitated the formation of membranes, with comparable physical properties. The electrochemical cells with fluoronanotubes or CF$_x$ were discharged across a 2 kΩ resistor load; real time voltage across the resistor was monitored and recorded by a Vernier Labpro system. The open circuit voltages of lithium electrochemical cells with CF$_x$, fluorinated laser oven SWNTs and HiPco SWNTs as cathodes were measured at various cathode loads. This was done by replacing the 2 kΩ resistor with a 200 kΩ resistor for a certain period of time after the cell had been discharged at 2 kΩ for a period of time. After recording the voltages across the 200 kΩ resistor, the system was switched back to 2 kΩ to continue the discharge. This measurement and discharge program was repeated until the cell was exhausted. By integration using the discharge curve, the open circuit voltages versus percentage of the cathode utilized were obtained and plotted. Fluorinated HiPco SWNTs were partially discharged, and the Raman spectra were obtained to determine if the
discharge had any size dependence. A sample of 1 mg pure fluorotubes was used as cathode and discharged. The discharged fluorotubes were rinsed with methanol and water to remove the organic solvents and the electrolyte. A SEM image was obtained after drying.

2.2.3 Cathode performance and thermochemistry calculations

Raman spectra have been very important tools in single wall carbon nanotubes (SWNTs) research. The Raman spectra of SWNTs have been studied extensively and a lot of useful information could be obtained from a Raman spectrum. A series of Raman spectra collected from pristine SWNTs, fluororanotubes, fluororanotubes after being discharged in the lithium battery and fluororanotubes after being discharged and annealed are shown in Figure 2.4. As spectrum A in Figure 2.4 shows, the laser oven SWNTs material has a strong tangential mode at 1590 cm\(^{-1}\) that is independent of nanotube diameter and \(A_{1g}\) radial breathing modes (RBM) near 203 cm\(^{-1}\) that are useful in determining the distribution of nanotube diameters. Spectrum B shows the Raman spectrum for fluororanotubes made from laser oven SWNTs. As expected, a strong new peak at 1284 cm\(^{-1}\) appeared which could be assigned to sp3 carbon stretching. The appearance of this peak has become a strong evidence for sidewall
Figure 2.4: Raman spectra of fluoronanotubes (Laser oven SWNTs) before and after discharge. (A) purified SWNTs; (B) fluoronanotubes; (C) after discharge; (D:) after discharge and annealing.
functionalization of SWNTs because pristine SWNTs do not have this peak. Spectrum C shows the Raman spectrum for discharged fluoronanotubes, where both radial breathing and tangential modes are recovered, indicating that during the process of discharging the fluorotubes lose fluorine anions and are reduced to their original state. The following represents the overall reaction.

\[ C_2F(\text{fluoronanotube}) + Li = C_2(\text{SWNTs}) + LiF \]

As spectrum C shows, the sp3 carbon peak (1293 cm\(^{-1}\)) did not completely disappear. This may indicate that a small degree of disorder happened during the fluorination and defluorination (discharge) process. The same phenomenon is also observed while hydrazine is used to reduce the fluorotubes.\(^9\) As was the case for hydrazine reduction, it is seen in spectrum D in Figure 2.4 that the \(~1293\) cm\(^{-1}\) peak is significantly decreased and shifted to 1285 cm\(^{-1}\) by annealing the discharged fluorotubes at 800 °C under an argon atmosphere for 1 hour.

The FTIR spectra of the fluoronanotubes before and after the cell discharge are shown in Figure 2.5 spectra A and B. The peak at \(~1195\) cm\(^{-1}\)
Figure 2.5: FTIR spectra of fluoronanotubes (laser oven SWNTs) before and after discharge. (A) fluoronanotubes; (B) discharged fluoronanotubes
in spectrum A can be assigned to highly polar carbon-fluorine stretching. The FTIR spectrum of the discharged fluorotubes shown in spectrum B confirmed that discharging the cell breaks the carbon-fluorine bonds, as indicated by the disappearance of the carbon fluoride stretch. SEM images of fluorotubes before and after discharge are shown in Figure 2.6. Image A shows the fluoronanotubes and image B shows the fluoronanotubes after being discharged. They show that after fluorine removal, the nanotube ropes appear unchanged.

The fluoronanotube/lithium batteries with 6, 20, or 40 mg fluoronanotubes (produced from laser oven SWNTs) mixed with the same amount of graphite powder as cathode materials were each discharged across a 2 kΩ resistance load. The respective discharging curves are shown in traces a, b, and c in Figure 2.7. Traces b, b', and b'' in Figure 2.7 represent the discharging curves of 20 mg of fluoronanotubes mixed with graphite powders, without mixing with graphite powders, and mixed with 20 mg SWNTs. The similarity between b, b', and b'' indicates that addition of graphite or SWNTs as conductive media was not necessary under our experimental conditions. The discharging curve of the cell with 20 mg CF₆ mixed with the same amount of SWNTs as the cathode is shown by trace d.
Figure 2.6: SEM images of fluoronanotubes before and after discharge. (A) fluoronanotube; (B) discharged fluoronanotube
Figure 2.7: Trace a: discharging curve of 6 mg fluoronanotube cell at 2 kΩ; Trace b: discharging curve of 20 mg fluoronanotube cell at 2 kΩ; Trace b': discharging curve of 20 mg fluoronanotube cell (no graphite) at 2 kΩ; Trace b'' : discharging curve of 20 mg fluoronanotubes cell at 2 kΩ; Trace c: discharging curve of 40 mg fluoronanotube cell at 2 kΩ; Trace d: discharging curve of 20 mg CFₓ cell at 2 kΩ. In traces a, b, and c, fluoronanotubes were mixed with same amount of graphite as cathodes; in trace b', only fluoronanotubes were used; in traces b'' and d, fluoronanotubes and CFₓ were mixed with the same amount of SWNTs.
in Figure 2.7. Comparison of the trace b with d indicates the fluoronanotube cell lasted a shorter time, consistent with the fact that the fluorine content of fluorotubes is lower than that of CF₅, while the higher voltage of the fluoronanotube cell indicates that the carbon-fluorine bonds of fluoronanotubes are weaker than that of the carbon monofluoride (CF₂). The power discharged to reach a voltage of 1.5 V for the 20 and 40 mg fluorotube cells and the 20 mg CF₅ cell are 0.024, 0.063, and 0.047 W·H. This corresponds to 0.0027, 0.0036, 0.0038 W·H per mg fluorine, respectively. The discharge curves for fluoronanotubes show two distinct slopes with the inflection point occurring when ~65-70% of the fluorine has been removed. The last ~35% fluorine appears more strongly bonded to the nanotube. This may suggest that fluoronanotubes(C₂F) are first converted to C₄F while fluorine is removed.

Wood et al. fitted the experimental heats of formation of known CF₅
and obtained \( \Delta H_f^\circ \) (CF₅) = -(44x +3x²), for \( x = 1 \), \( \Delta H_f^\circ = -47 \) kcal/mol, which was in agreement with the experimental result of - 46.7 ± 1 kcal/mol.\(^{36}\) It was also in agreement with Bettinger and coworker's computation result of -46.8 kcal/mol where carbon monofluoride was made by fluorination of a graphite sheet.\(^{28}\) Bettinger and coworkers also investigated the heat of formation of fluoronanotubes. Their calculations showed that for armchair
(10,10) carbon nanotubes, the heat of formation of fluorotubes (C₂F) was -35.6 kcal/mol. The overall cell reactions in a fluoronanotube cell and in a carbon monofluoride cell are shown in the following:

\[ \text{C}_2\text{F} \text{(fluoronanotube)} + \text{Li} = \text{C}_2\text{(SWNTs)} + \text{LiF} \quad \text{(Equation 1)} \]

\[ \text{CF} \text{(carbon monofluoride)} + \text{Li} = \text{C} \text{(graphite)} + \text{LiF} \quad \text{(Equation 2)} \]

Previous studies have shown that SWNTs were slightly more unstable than graphite and the difference was estimated to be 1.0 kcal/mol for (10,10) nanotubes. By using \( \Delta H^\circ \) (fluorotubes) = -35.6 kcal/mol and \( \Delta H^\circ \) (carbon monofluoride) = -46.8 kcal/mol, the heat of reaction (\( \Delta H_r \)) of eq 1 is 9.2 kcal/mol less than that of eq 2. If one assumes that both reactions have approximately the same \( T\Delta S \), then \( \Delta G_{eq1} \) is 9.2 kcal less than \( \Delta G_{eq2} \) where \( \Delta G = \Delta H - T\Delta S \), then using \( E = -\Delta G/nF \), and obtain

\[ E_{eq1} - E_{eq2} = (\Delta G_{eq2} - \Delta G_{eq1})/nF \quad \text{(Equation 3)} \]
This equation suggested that the voltage of the fluorotube cell will be 0.40 V higher than that of a carbon monofluoride \((\text{CF}_x)\) cell. This assumes that the fluorotubes \((\text{C}_2\text{F})\) were produced from \((10,10)\) armchair nanotubes. The diameter of a \((10,10)\) SWNT is 1.3 nm, which is similar to the diameter of laser oven SWNT. In Figure 2.8, traces a, b, and c represent fluorinated laser oven SWNTS, HiPco SWNTs, and carbon monofluoride lithium batteries, respectively. The voltage of battery with the fluorinated laser oven SWNT is ~0.7 V higher than that of carbon monofluoride battery and its discharge curve slope is steeper. The voltages were obtained across 200 k\(\Omega\) resistors while the cells were stepwise discharged at 2 k\(\Omega\). At high resistance like 200 k\(\Omega\), the voltages measured are very close to the open circuit voltages that represent the theoretical cell potential. That the voltage of fluorinated laser oven SWNTs battery was ~0.7 V higher than that of the \(\text{CF}_x\) cell is in reasonable agreement with the theoretical value of 0.40 V. It is also worth noting that the battery of fluorinated laser oven SWNTs has a 0.10 V higher potential than the battery of fluorinated HiPco SWNTs. It is known that HiPco SWNTs have a smaller average diameter 1 nm, similar to that of \((8,8)\) SWNTs. For \((8,8)\) SWNTs, the heat of formation in terms of \(\text{C}_2\text{F}\) is calculated as -37.5 kcal/mol, 1.9 kcal/mol lower than \((10,10)\) tubes.\(^{28}\)
Figure 2.8: Trace a: open circuit voltage of fluorinated laser oven SWNTs vs cathode percentage; Trace b: open circuit voltage of fluorinated H-SWNTs vs cathode percentage; Trace c: open circuit voltage of CF$_x$ vs cathode percentage
This suggested that the battery voltage of fluorinated laser oven SWNTs will be ~0.08 V higher than the battery voltage of fluorinated HiPco SWNTs. This is consistent with the difference between traces a and b in Figure 2.8. It is interesting to note that during discharging the potential of the cell drops more rapidly for the fluoronanotube cell than for the carbon monofluoride cell. At 80% discharge, a change of 0.7 V has occurred for the fluoronanotube battery as compared to 0.2 V for the carbon monofluoride battery. This indicates that the average apparent carbon-fluorine bond energy increases as the system is discharged. A 0.7 V change indicates a bond energy change of 16 kcal/mol. A change in apparent bond energy would occur if the larger diameter fluorotubes are selectively defluorinated before the small diameter tubes. However, based on a calculation of bond energy versus tube diameter, one expects a change of 0.2 V rather than 0.7 V. Thus we suggest that the large change is due to a carbon-fluorine bond energy dependence on the extent of sidewall fluorination. This suggests that carbon-fluorine bonds are the strongest when the nanotube is only slightly fluorinated. To test for the question of diameter-selective defluorination, we partially discharged a fluorinated HiPco SWNT battery. Raman spectra of the partially discharged sample are compared to the initial unfluorinated
Figure 2.9: Raman spectra of (A) HiPco SWNTs. (B) partially discharged fluorinated HiPco SWNTs.
sample in Figure 2.7. The breathing mode region (150-300 cm\(^{-1}\)) includes very similar relative intensities for the various peaks. This indicates that diameter selective defluorination is not occurring and supports the suggestion that carbon fluorine bond energies are dependent on the extent of sidewall fluorination. This is also in agreement with the theoretical calculation result that fluorinated nanotubes have several kinds of isomers with different stabilities.\(^{37}\)

2.2.4 Conclusions

It is worth pointing out that although higher battery potentials from fluoronanotubes battery than from carbon monofluoride battery could be obtained, it did not mean that fluorinated SWNTs are superior to carbon monofluoride as cathodes in lithium electrochemical cells at this point of time. Fluoronanotubes cost more and have lower fluorine content. But it is very interesting to measure the cell potential difference when the fluorinated sheet-like graphite or fluorinated roll-like SWNT cathodes are used. Obviously the difference arises from the shapes of the cathode materials. Furthermore, we have found that the cell potential is diameter dependent when we compare the fluorinated laser oven SWNTs and HiPco SWNTs cathodes, and this result is in agreement with the thermodynamic
calculations. This conventional electrochemical method can offer quantitative comparisons between well-defined nanostructures.

2.3 Oxidative properties and thermal stabilities of fluoronanotubes

2.3.1 Introduction

The novel applications of fluoronanotubes as reinforcing materials in organic/inorganic matrix composites have become an attractive research area and are currently under extensive study. For these novel applications, knowledge of the chemical compatibility of the fluoronanotubes with various inorganic matrix materials is essentially important. However, related information about the chemical stability and reactivity of fluoronanotubes in solid inorganic media has not yet been thoroughly studied. In comparison, the reactivity of fluorinated fullerenes, C_{60} F_{x},^{38,39} toward the inorganic salts (e.g., sodium iodide) was investigated earlier, and the fluorofullerenes were reported to behave as a weak oxidants and fluorinating agents in these systems.^{40} In this thesis, the experimental data obtained in the course of studies of the series of solid compositions of fluoronanotubes with some binary inorganic compounds of group 5, 6, and 7 elements are presented. These data indicate that the fluoronanotubes are not chemically inert in these
systems but exhibit oxidative properties in the redox reactions occurring under various temperatures.

2.3.2 Reactions with binary metal compounds

After the fluoronanotubes were prepared by using the method described in section 2.1 of this thesis, they were mixed in 1:1 weight ratio with powders of commercially available binary inorganic compounds of group 5, 6, and 7 elements and ground thoroughly with a mortar and pestle. This procedure was carried out in a nitrogen filled dry box. The inorganic compounds studied included the halides (KBr, KI, LiI, LiBr, LiCl, NaCl, ZnI₂), oxides (Li₂O, Fe₂O₃, PbO, MnO), sulfides (Li₂S and ZnS), zinc selenide (ZnSe), lithium nitride (Li₃N), and aluminum phosphide (AlP). Some reactions required only activation by mechanical grinding to proceed at room temperature. In the other cases the ground fluoronanotubes/inorganic compound mixtures were heated at elevated temperatures in a flow of argon to observe the effect of temperature on the reactions. The solid reaction products were analyzed by X-ray diffraction on a Siemens powder diffractometer with a Cu source and by Raman and Attenuated Total Reflection-Fourier transformed infrared (ATR-FTIR) spectroscopies, with the use of a Renishaw System 1000 micro-Raman instrument operating with an AlGaAs diode 780.6 nm laser and a Thermonicolet Nexus 670 FTIR
spectrometer. The particular advantage of using Raman analysis here is its sensitivity to SWNTs. The SWNTs show strong characteristic Raman peaks even at very low concentration, due to strong resonance effects.\textsuperscript{41} The gaseous and volatile products formed were identified with the help of the TGA/MS technique, with the use of a TA Q-series 500 instrument coupled to a Pfeiffer ThermoStar quadrupole mass spectrometer. Argon was always used in the TGA/MS runs as a purging gas.

2.3.3 Oxidative properties and thermal stability

Spectrum A and B in Figure 2.10 show the Raman spectra of the purified HiPco SWNT and the fluoronanotubes respectively. In the spectrum A, breathing modes of HiPco SWNTs are observed in the range from 200 to 263 cm\textsuperscript{-1}, and the tangential mode at 1591.0 cm\textsuperscript{-1}. In the spectrum B, both of these modes are weakened and a significant new peak appears at 1288.8 cm\textsuperscript{-1} because of the existence of sp\textsuperscript{3} carbons in the fluoronanotubes, similar to laser oven SWNTs described in last section. The infrared spectrum of a fluoronanotubes, shown in Figure 2.11, exhibits two peaks at 1214.3 and
Figure 2.10. The Raman spectra of cleaned HiPco single-wall carbon nanotubes (A) and of fluoronanotubes (B).
Figure 2.11: The FTIR spectrum of fluoronanotubes made from HiPco SWNTs.
1102.1 cm\(^{-1}\), which belong to the carbon-fluorine bond stretching. The peak at 1539.3 cm\(^{-1}\) most likely originates from the stretching vibration of the conjugated carbon-carbon bonds, which is activated as a result of the addition of fluorine atoms to the SWNT sidewall. The reason for observed splitting of the carbon-fluorine absorption into two significant peaks could be related to the broad range of the diameters in the pristine HiPco SWNTs. Slight heating of the ground mixture of the fluoronanotubes and lithium iodide powder (1:1 ratio), placed in a glass vial, led to evolution of a purple vapor, which quickly condensed on the inside of the vial. When water was added to this mixture, the initially formed purple-colored solution turned blue after the addition of soluble starch, indicating the formation of elemental iodine as the result of oxidative action of the fluoronanotubes on LiI. The Raman spectrum of the ground mixture was shown in Figure 2.12, where a notable recovery of peaks typical for breathing and tangential modes of SWNTs, suggesting that the fluoronanotubes lost a significant amount of fluorine and were reduced by the LiI. It is worth noting that this spectrum resembles the Raman spectrum of the fluoronanotubes, used as the cathode in the fluoronanotubes/lithium batteries after they were partially discharged. The Raman data were confirmed by the observation of a dramatic reduction in peak intensity of the carbon-fluorine stretching in the FTIR spectrum.
Figure 2.12: Raman spectrum of the ground mixture of fluoronanotubes with LiI
and by SEM/EDX elemental analysis.

It is found that fluorine is not completely removed from fluoronanotubes, even with excess potassium iodide added. This result is in agreement with our observation that the stability of the carbon-fluorine bond depends on the extent or type of fluorination in the previous section of this chapter. The X-ray diffraction pattern obtained for the fluoronanotubes showed only a broad hump between $2\theta = 10 - 25^\circ$ and no sharp peaks. In contrast, in the XRD pattern of the fluoronanotube/LiI ground mixture (Figure 2.13), peaks at $2\theta = 38.9, 45.2,$ and $65.4^\circ$, matching the lithium fluoride cubic cell, have been observed. These results strongly suggest that in the system studied the redox reaction between fluoronanotubes and LiI occurred. Mixtures of fluoronanotubes with other iodides, such as KI and ZnI$_2$, were also examined. We found that the grinding and subsequent heating of these mixtures at 100°C for 1 h in a flow of argon causes similar changes in the Raman features and the starch solution color as noted for the LiI matrixes, although at a higher temperature. The other halide/fluoronanotube mixtures, particularly those with LiBr and LiCl, were also studied by the same approach.
Figure 2.13: XRD pattern of fluoronanotubes/LiI ground mixture
The Raman spectra and XRD patterns of products from the fluoronanotubes/LiBr(LiCl) suggested the defluorination of fluoronanotubes and the formation of lithium fluoride through a reaction similar to that observed for fluoronanotube/LiI mixtures. The volatile products of these reactions were studied by the TGA/MS instruments by heating the 1:1 ratio ground mixture in a flow of argon and monitoring the evolving gases with an on-line mass spectrometer. The corresponding temperature-dependent on-line mass spectra, detected for lithium bromide and lithium chloride matrixes, are shown in Figures 2.14 and 2.15, respectively. The strong evolution peaks for bromine and chlorine isotopes observed in these experiments are in agreement with their natural abundance. These TGA/MS data clearly indicate the formation of halogen molecules during the process of stepped heating of these mixtures up to 600 °C, whereas the evolution of Cl₂ has been detected at a higher temperature than that for Br₂ (350 °C vs. 200 °C). It is interesting to note that in comparison with lithium salts, similar heating of potassium bromide or
Figure 2.14: The on-line TGA/MS of bromine evolution in the reaction of fluoronanotubes with lithium bromide.
Figure 2.15: The on-line TGA/MS of chlorine evolution in the reaction of fluoronanotubes with lithium chloride.
potassium chloride with fluoronanotubes in a TGA/MS instrument led to the observation of only negligible evolution of bromine or chlorine.

Mixtures of fluoronanotubes with some metal compounds of group 6 elements in the periodic table were also studied. It was found that lithium sulfide is easily oxidized by fluoronanotubes even at room temperature. This reaction is initiated and completed simply by grinding the mixture. The Raman spectrum of the solid reaction products is shown in Figure 2.16. This spectrum indicates an almost complete recovery of the peaks of breathing and tangential modes of the nanotubes, although the peak of residual sp$^3$ carbon is still noticeable, unlike in the spectrum of purified pristine SWNTs. The corresponding XRD pattern was found to be similar to that shown in Figure 2.11, identifying the lithium fluoride. In a continuation of the analyses, the solid product mixture was placed in the carbon disulfide solvent and mixed thoroughly, the insoluble solids were discarded, and the carbon disulfide decant was transferred to a watch glass. After the carbon disulfide evaporated completely, a hollow yellow bead was formed. Elemental EDAX analysis indicated that this yellow material was sulfur. These results show that fluoronanotube readily oxidize the sulfide anion to elemental sulfur. In their turn they are reduced to the SWNTs after removal
Figure 2.16: The Raman spectrum of the reaction products of fluoronanotubes with lithium sulfide.
of the fluorine, yielding lithium fluoride as a by-product. In opposition to this, a very minor chemical reaction of the fluoronanotubes with an excess of powdered zinc sulfide at room temperature was detected. However, heating this mixture at 100 °C in a flow of argon for 24 h produced dramatic changes, as determined by Raman and XRD measurements. It was found that the breathing and tangential mode peaks had significantly recovered in the Raman spectrum. In the XRD pattern, shown in Figure 2.17, the peaks at $2\theta = 30.0^\circ, 24.2^\circ$, and $36.1^\circ$ match the major fingerprints of the zinc fluoride orthorhombic cell.\textsuperscript{42} The other peaks at $2\theta = 38.3^\circ, 47.3^\circ$, and $56.2^\circ$ coincide with the features of the zinc sulfide cell; however, the origin of the peak at $26.7^\circ$ remains unclear. Zinc selenide matrixes have also been examined. Based on the Raman spectrum changes, it was found that zinc selenide had removed a significant amount of fluorine from the Fluoronanotubes already at room temperature. Additional fluorine was removed from the fluoronanotubes when the mixture was heated at 100 °C in a flow of argon for 24 h. The ground mixture was also treated with carbon disulfide solvent as described in the previous paragraphs. The brown solid left on the watch glass after the evaporation of the solvent was proved by EDX analysis to be elemental selenium.
Figure 2.17: The XRD pattern of the reaction products of fluoronanotubes with zinc sulfide.
Several oxides, including Li2O, Fe2O3, PbO, and MnO, were also studied, and no reaction with the fluoronanotubes was observed at temperatures up to 200 °C.

The reactions fluoronanotubes with several commercially available compounds of group 5 elements, such as aluminum phosphide (AlP) and lithium nitride (Li3N) were studied as well. The Raman spectra of the ground aluminum phosphide powder mixture indicated the ongoing defluorination reaction of fluoronanotubes already at room temperature. The expected formation of elemental phosphorus in this reaction remains unconfirmed. Lithium nitride mixtures were studied similarly, but no chemical reaction was observed at room temperature. Nevertheless, after the ground mixture of the fluoronanotubes and lithium nitride was heated at 200 °C for 1 h under the flow of argon, it was found that in the Raman spectrum, taken there after, the peaks of breathing and tangential modes of the SWNTs had significantly intensified. The XRD pattern indicated the formation of lithium fluoride due to a chemical reaction occurring under elevated temperatures. The TGA/MS studies of this reaction provide evidence for the formation of nitrogen. The on-line MS data (Figure 2.18) show the evolution of Nitrogen (m/z=28) peaking in the temperature range of 220–300 °C.
2.3.4 Conclusions

This study demonstrates that the chemical inertness of fluoronanotubes cannot be simply taken for granted. Fluorinated SWNTs are in general significantly less inert toward the same compounds than fluorographite. Indeed, fluoronanotubes were shown to chemically react as oxidants with several binary metal compounds of group 5, 6, and 7 elements, even at room temperature, to produce the corresponding elements of group 5, 6, and 7 and metal fluorides, and in their turn to be reduced to a SWNT. The overall oxidation properties of fluoronanotubes in these solid matrixes depend on the nature of the inorganic compound and temperature conditions used. The information obtained on chemical stability and oxidation properties of the fluoronanotubes will be useful for their mechanical processing in various inorganic matrixes to be applied for the preparation of SWNT-reinforced nanocomposite materials.
Figure 2.18: The TGA/MS of nitrogen evolution in the reaction of fluoronanotubes with lithium nitride.
Chapter 3: Sidewall functionalization of SWNTs with organic peroxides

3.1 Introduction

The sidewall functionalization of single wall carbon nanotubes (SWNTs) is a promising pathway in improving their solubility for application and processing, e.g., in mechanically reinforced nanocomposites, and also in producing nanotube derivatives with a tailored properties or specific useful properties.\(^4\) However, the examples of the SWNTs sidewall derivatization chemistry are somewhat limited. The radical additions studied involve perfluoroalkyl and aryl radicals, produced photochemically or by electrochemical reduction, in contrast to a larger variety of known radical reactions of fullerenes.\(^4\)

This chapter describes the functionalization of SWNTs by covalent sidewall attachment of free radicals thermally generated from organic diacetyl peroxides, such as lauroyl and benzoyl peroxides, commonly available and used as radical initiators in polymerization reactions.\(^4\) Succinic acid peroxide and gluutaric acid peroxide, which could not be commercially obtained, were also synthesized in our laboratory and used to functionalized SWNTs.
Organic diacyl peroxides, RC(O)OO(O)CR, where R could be aliphatic, aromatic or some other group, readily decompose to release carbon dioxide and form free radicals R upon mild heating as the following shows:

\[ \text{RCOOOCR} \xrightarrow{\text{heat}} 2R^\cdot + 2\text{CO}_2 \]

In this chapter, the radicals used are phenyl, undecyl, 2-carboxyl-ethyl(CH₂CH₂COOH) and 3-carboxyl-propyl radicals(CH₂CH₂CH₂COOH). The latter two are of particular interest because they contain carboxylic acid functional groups. So far, the functionalization study of carbon nanomaterials with the carboxylic acid function-terminated moieties is limited, and the successful case of the fullerene C₆₀ is to utilize a two step process (Bingel 2+1 cycloaddition reaction followed by deesterification) yielding the carboxylated methanofullerene structures.⁴⁶,⁴⁷ A similar process was shown to be much less efficient when applied to pristine SWNTs because of their lower reactivity to carbene addition via Bingel-type reaction.⁴⁸,⁴⁹ In earlier studies of single wall carbon nanotubes, the carboxylic acid functional groups have been created so far only on their
open ends and to some degree on the partially etched ("unzipped") side walls.

3.2 Peroxide functionalization reactions

3.2.1 Materials

Raw SWNTs, used in this study, were produced by the HiPco process in the Professor R. E. Smalley Carbon Nanotechnology Laboratory at Rice University. Such prepared HiPco SWNTs have an average diameter of 1 nm. The iron impurity in the raw HiPco SWNTs was removed by wet air oxidation and a consequent hydrochloric acid rinse as described previously.29 The iron metal content in the HiPco SWNT material is approximately 1%. The last step of purification was done by annealing of the SWNTs at 800 °C in an argon atmosphere for 2 hours. The benzoyl peroxide and lauryl peroxide were purchased from Aldrich. The succinic and glutaric anhydrides, used as precursors for preparation of dicarboxylic acid peroxides, were also purchased from Aldrich. Terminal dimines-ethylene diamine, 4,4'-methylenebis(cyclohexylamine), and diethyltoluenediamine - were purchased from Air Products and Resolution Performance Inc.

3.2.2 Synthesis of succinic acid peroxide and glutaric acid peroxide:
Scheme 3.1

\[
\begin{align*}
\text{HOOC} & \quad + \quad \text{H}_2\text{O}_2 \\
& \quad \rightarrow \\
\text{HOOCCH}_2\text{CH}_2\text{COOCCH}_2\text{CH}_2\text{COH}
\end{align*}
\]

Scheme 3.2

\[
\begin{align*}
\text{HOOC} & \quad + \quad \text{H}_2\text{O}_2 \\
& \quad \rightarrow \\
\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOCCH}_2\text{CH}_2\text{CH}_2\text{COH}
\end{align*}
\]
10 g of succinic or glutaric anhydride fine powder were added to 20 ml of ice cold 8% hydrogen peroxide and stirred for 30 minutes until all powder dissolved and a white gel-like solution was formed, using an ice bath to keep the temperature below 25 °C at all time. The solution was filtered with a 1 μm pore size PTFE membrane (Cole Palmer). The peroxide products were left on the membrane and were washed with small amount of water and air-dried for 10 minutes. The white peroxide products were collected from the membrane into a glass vial and vacuum dried at room temperature for 24 hrs. Approximately 6.5 g of each peroxide, succinic acid peroxide and glutaric acid peroxide, were obtained using this one step procedure reported earlier by Clover et al. The reaction equations are shown in Scheme 3.1 and Scheme 3.2. ATR-FTIR spectra of both peroxides (Figure 3.1 and Figure 3.2) show similar features: a broad band in the 3000-3500 cm⁻¹ region due to the carboxylic O-H stretches, absorbance peaks of the C-H stretchings in the 2850-3000 cm⁻¹ range, absorption peaks near 1700 cm⁻¹ characteristic of the acid carbonyl groups, and a peak at ~1812 cm⁻¹ assigned to the peroxide carbonyls. The solid state ¹³C NMR spectra of succinic acid peroxide show methylene carbon peaks at 28.8, and 24.7 ppm and two carbonyl carbon peaks at 179.7, and 168.7 ppm, of glutaric acid.
Figure 3.1: FTIR spectrum of prepared succinic acid peroxide
Figure 3.2: FTIR spectrum of prepared glutaric acid peroxide
Figure 3.3; $^{13}$C NMR spectrum of prepared succinic acid peroxide
Figure 3.4: Solid state $^{13}$C NMR spectrum of glutaric acid peroxide
peroxide shows three methylene peaks at 33.0, 28.4, and 19.0 ppm and two carbonyl peaks at 182.2 and 170.3 ppm. The $^{13}$C NMR spectra are shown in Figure 3.3 and Figure 3.4.

3.2.3 Functionalization reactions of SWNTs

To Functionalize SWNTs, the following procedure was developed. Purified SWNTs (50 mg) were placed into a 250 ml flask filled with 50 ml dry o-dichlorobenzene and sonicated (17 W/55 kHz Cole Palmer bath) for 30 minutes to obtain the SWNT suspension solution. The latter was heated at 80-90 °C for 10 days while adding each day 0.5 g of peroxides, i.e. benzoyl peroxide, lauroyl peroxide, succinic acid peroxide or glutaric acid peroxide. The functionalization could also be done by adding more peroxide reactants each time to shorten the total reaction time, for example: 2 grams/day. But because every peroxide has its fixed half life time at a certain temperature, adding more peroxide each time may not be the most efficient way for functionalization. After reactions were completed, the products were washed by pouring them into a 500 ml Erlenmeyer flask containing large amount of solvents such as hexane and chloroform, sonicating for 15 to 30 minutes and then filtering using a 0.2 μm pore size
Scheme 3.3

\[ \text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{C}_1\text{H}_2 \xrightarrow{\text{Heat}} \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \xrightarrow{\text{Heat}} \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \]

Scheme 3.4

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \xrightarrow{\text{Heat}} \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \xrightarrow{\text{Heat}} \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \xrightarrow{\text{Heat}} \]

\[ \text{H}_2\text{C}_1\text{H}_2\text{O}_2 \text{O}_2 \text{C}_1\text{H}_2\text{H}_2\text{H}_2 \]
Scheme 3.5

\[
\text{HO-CCH}_2\text{CH}_2\text{COOCCH}_2\text{CH}_2\text{COH} \rightarrow \text{HO-CCH}_2\text{CH}_2\cdot + \text{CO}_2
\]

Scheme 3.6

\[
\text{HO-CCH}_2\text{CH}_2\text{CH}_2\text{COOCCH}_2\text{CH}_2\text{CH}_2\text{COH} \rightarrow \text{HO-CCH}_2\text{CH}_2\text{CH}_2\cdot + \text{CO}_2
\]
PTFE Cole Palmer membrane. Collected the products from the filter paper and repeated this dispersing and sonication procedure one more time. When succinic acid peroxide and glutaric acid peroxide were used for reaction, tetrahydrofuran (THF) and ethanol should be used to wash. Finally, the functionalized SWNTs were collected from the filter paper and vacuum dried at 70 °C over night. The functionalization reactions using the four peroxides are shown in scheme 3.3, 3.4, 3.5 and 3.6. When fluoronanotubes were also used as starting materials to react with peroxides the fluorines were found to be substituted by phenyl, undecyl groups, etc.

3.2.4 Consequent reactions

The decomposition of succinic acid peroxide and glutaric acid peroxide created 2-carboxyl-ethyl and 3-carboxyl-propyl radicals, which could attach to the sidewall of SWNTs to form carboxylic acid containing side-chain groups. The carboxylic acid groups offer chemical opportunities for further reactions. One interesting reaction is the synthesis of amides. The SWNT amide derivative was prepared from 20 mg of acid-functionalized SWNT placed into a dry 100 ml flask, 20 ml of thionyl chloride was added and the mixture stirred for 12 hours. The reaction mixture was vacuum filtered through a 0.2 μm pore size membrane thereafter and the obtained precipitate flushed with a large amount of dry acetone. The solid precipitate
Scheme 3.7

\[
\text{SWNT-CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{SOCl}_2} \text{SWNT-CH}_2\text{CH}_2\text{COCl} \xrightarrow{\text{Ethylene diamine}} \text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{NH}_2
\]

Scheme 3.8

\[
\text{SWNT-CH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{SOCl}_2} \text{SWNT-CH}_2\text{CH}_2\text{CH}_2\text{COCl} \xrightarrow{4,4'-\text{methylenebis (cyclohexylamine)}} \text{CH}_2\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{NH}_2
\]

Scheme 3.9

\[
\text{SWNTs-CH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{SOCl}_2} \text{SWNTs-CH}_2\text{CH}_2\text{CH}_2\text{COCl} \xrightarrow{\text{diethyltoluenediamine}} \xrightarrow{120 \, ^\circ\text{C}} \text{CH}_2\text{CH}_2\text{CH}_2\text{CONH-C}_6\text{H}_4\text{C}_6\text{H}_5
\]
was dried briefly and then placed into a 100 ml flask containing 20 ml ethylenediamine, the mixture stirred at room temperature for 12 hours, then poured into a large amount of ethanol and sonicated for another 10 minutes. The batch was filtered through a 0.2 µm pore size membrane and flushed with a large amount of ethanol. The SWNT-derivative was collected on a membrane and dried overnight in a vacuum oven at 70 °C. A similar procedure was applied for preparation of more amides by using other diamines, for example: 4,4'-methylenebis(cyclohexylamine) and diethyltoluenediamine, unlike ethylenediamine and 4,4'-methylenebis(cyclohexylamine) proceeding at room temperature the reaction with diethyltoluenediamine required heating at 120 °C for 12 hours. 4,4'-methylenebis(cyclohexylamine) and diethyltoluenediamine are both curing agents commonly used in the polymer industry. Scheme 3.7, 3.8 and 3.9 shows the reactions.

3.2.5 Characterization methods

The Raman spectra of purified and functionalized SWNTs were collected with a Renishaw 1000 microraman system with a 780 nm laser source. For the ATR-FTIR spectral measurements a Thermal Nicolet Nexus 870 FTIR system with an ATR accessory was used. The spectra in the UV-Vis-NIR range were taken using a Shimadzu 3101 PC UV/Vis/NIR
spectrometer. The thermal degradation and volatile products evolution analyses were performed with a TGA/MS instrument which includes a Q500 Thermal Gravity Analyzer coupled with a Pfeiffer Thermal Star mass spectrometer.

For the solid state MAS NMR studies, a Bruker (50.3 MHz $^{13}$C, 200.1 MHz $^1$H) NMR spectrometer was used. The spectra were obtained with each sample packed in a 4-mm outer diameter rotor, which was spun at 7.5 kHz for the pristine SWNTs and at 11.0 kHz for the functionalized SWNTs. This results in spinning sidebands to appear well outside the sp$^2$ and sp$^3$ center band regions of interest (149 ppm upfield or downfield from the center band in case of SWNTs and 219 ppm upfield or downfield from a center band for the functionalized SWNTs). Each spectrum was obtained with a 4.5-μs 90° $^{13}$C pulse and a 32.9-ms, proton-decoupled FID, followed by a 180-s relaxation delay for the SWNTs or a 45-s relaxation delay for each of the functionalized SWNTs. In the experiments, a total of 1320 scans (66.0 hr) for the SWNTs, 7152 scans (89.5 hr) for the SWNT-CH$_2$CH$_2$COOH, 4984 scans (62.3 hr) for SWNTs-CH$_2$CH$_2$CH$_2$COOH, and 3560 scans (44.5 hr) for the SWNT amide derivative SWNTs-CH$_2$CH$_2$CONHCH$_2$CH$_2$NH$_2$ were used. Each FID was processed with 50 Hz (1 ppm) of line broadening. The spectra were phase corrected. A fourth-order polynomial was then applied
to the baseline over the region from $\delta$ 315 to $-70$ to create a nearly flat baseline after the polynomial was subtracted from the spectrum. For the functionalized C$_{60}$ sample, C$_{60-}(\text{CH}_2\text{CH}_2\text{COOH})_n$, available,$^{51}$ a 7-mm OD rotor could be used, which was spun at 7.0 kHz. The spectrum was obtained with a 3.8-$\mu$s 90° $^{13}$C pulse and a 32.9-ms, proton-decoupled FID, followed by either a 15-s relaxation delay (10,440 scans, 43.6 hr) or a 45-s relaxation delay (2132 scans, 26.7 hr) to make a rough determination of the relative relaxation rates of the various types of carbons. CPMAS spectra of succinic acid peroxide and glutaric acid peroxide were quickly scanned with 5 kHz MAS, a 1-ms contact time, 32.9-ms FID, and 5-s relaxation delay.

3.2.6 Solubility measurement of Functionalized SWNTs

Several functionalization approaches were reported improving the solubility of SWNTs in a variety of organic solvents including isopropanol, hexane, chloroform etc., but the solubility measurement method was not described,$^{19, 20, 21, 24, 25, 39}$ i.e. there is not a commonly accepted method to obtain and determine a saturated SWNTs solution. It is commonly believed that SWNTs exist in solutions as bundles except in the decant of SWNTs in SDS aqueous solution,$^{52}$ saturated SWNTs solutions prepared from different methods may have different bundle sizes and distributions. Thus solubility results may not be comparable. In this thesis, saturated SWNT solutions
were all prepared in the following method: 25 mg of SWNTs or their derivatives were added to 200 ml of solvents in a 250 ml glass bottle and sonicated for 120 minutes. The SWNTs or their derivatives were dispersed during the sonication. After sonication, the solutions settled for 24 hours. During the settling, it is believed that larger bundle of SWNTs should have precipitated to the lower level of the solution. After the settling, the upper 150 ml of solution were obtained from the glass bottle and filtered through a 0.2 μm Teflon membrane. The SWNTs or their derivatives were left on the membrane and peeled off from the membrane. After being dried in vacuum oven at 70 °C, they were weighed for exact weight for solubility. All solubility measurements were performed as described here to obtain comparable results.

3.3 Characterization results and discussions

3.3.1 Undecylated and phenylated SWNTs

Raman and UV-Vis-NIR spectra showed clear evidences for functionalizations using benzoyl and lauryl peroxide. In the Raman spectra shown in Figure 3.5, the observed decrease of the typical purified HiPco SWNTs breathing and tangential mode peaks at 200–263 and 1591 cm⁻¹, respectively, along with the substantial increase of the sp³ carbon peak at
Figure 3.5: The Raman spectra of A: pristine SWNTs, B: undecylated SWNTs, C: phenylated SWNTs and D: the phenylated SWNTs after heating in Ar to 800 °C.
1291 cm \(^{-1}\) provide a diagnostic indication of disruption of the graphene pi-bonded electronic structure of the side walls, suggesting their covalent functionalization. This is further confirmed by their solution phase UV-Vis-NIR spectra (Figure 3.6) which show typical van Hove singularities of SWNTs disappeared after sidewall functional group attachment because of the disruption of electron energy levels.

The FTIR spectra of the functionalized SWNTs, obtained by using the attenuated total reflectance (ATR) attachment, are shown on Figure 3.7. The weak peaks in the 3060–3020 cm \(^{-1}\) range in the spectra of phenylated SWNTs made from benzoyl peroxide reaction with pristine SWNTs and fluoronanotubes (shown under A and B, respectively) characterize the aromatic carbon-hydrogen stretches of phenyl groups attached to the SWNTs, while the peaks at 2919 and 2850 cm \(^{-1}\), which appear after washing the reaction product with CHCl\(_3\) followed by drying in a vacuum oven, belong to aliphatic carbon-hydrogen stretches. Several stronger absorptions in the 1600-1400 cm \(^{-1}\) can be attributed to phenyl ring skeleton stretches and a broad peak at 1105 cm \(^{-1}\) to the carbon-fluorine stretch. The attachment of long-chain undecyl groups to SWNTs and fluoronanotubes is
Figure 3.6: UV-Vis-NIR spectra of pristine and functionalized SWNTs. (A) purified pristine SWNTs, (B) phenylated SWNTs
Figure 3.7: ATR-FTIR spectra of functionalized SWNTs:
(A) Phenylated SWNTs made from pristine SWNTs
(B) Phenylated SWNTs made from fluoronanotubes1b,
(C) undecylated SWNTs made from pristine SWNTs,
(D) undecylated SWNTs made from fluoronanotubes
indicated in the spectra of C and D, by observation of prominent peaks of the carbon-hydrogen stretches in the 2980-2800 cm\(^{-1}\) range and an absorption of carbon-hydrogen deformation mode at 1465 cm\(^{-1}\). In addition, a mid-intensity band at 1547 cm\(^{-1}\) and a doublet at 1202, 1145 cm\(^{-1}\) due to an activated carbon-carbon and a residual carbon-fluorine stretches, respectively, are present in the spectra D.

Further evidence for covalent functionalization of SWNTs has been provided by thermal degradation analyses (TGA) in the 50–1000 °C range coupled with the on-line monitoring of volatile products either by MS or FTIR techniques. For instance, the TGA/MS data of phenylated SWNTs (Figure 3.8) show the evolution of phenyl groups started at ~250 °C and peaked at 400 °C, indicated by a major peak on the m/z 77 and a smaller peak on the m/z 78 ion current vs. time traces a and b, respectively, and their partial dimerization to biphenyl (m/z 154) volatizing at a higher temperature (trace d). These data confirm that the detected phenyl groups originate from the functionalized SWNTs and not from the reaction by-products, such as biphenyl or benzoic acid ester \(\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5\), indicated by a very small peak on the m/z 105 (trace c), i.e. if biphenyl or benzoic acid ester
Figure 3.8: TGA/MS analysis of evolution products from phenylated SWNTs. Ion current vs. time plots for m/z ions (a) 77, (b) 78, (c) 105, (d) 154.
C₆H₅COOC₆H₅ exist as byproducts, the 154 peak would have come at lower temperature and 105 peak would be dominating. The TGA/FTIR (Figure 3.9) analysis of another sample, undecylated SWNTs, also shows a major derivative peak which corresponds to the loss of undecyl groups. This was concluded by synchronizing this peak with the maximum on the chemigram of the carbon–hydrogen stretch region (2800–2980 cm⁻¹) in FTIR spectra of volatile products (inset on Figure 3.9). Analysis of the same SWNT-derivative, by variable temperature pyrolysis-EIMS confirmed the TGA/FTIR data by indicating the major loss of undecyl radical, C₁₁H₂₃, and their dimer at about 350–400 °C (peaks in EIMS at m/z155 and 310, respectively). The thermal degradation of functionalized SWNTs results in formation of bare wall nanotubes, indicated by restoration of their features in the Raman spectra taken for solid residues after TGA analyses. Functionalized SWNTs by TEM. Indeed, a high resolution TEM image of undecylated SWNTs specimen (Figure 3.10) clearly shows individual nanotubes with long-chain substituents joined to their side-walls. The reactions of benzoyl peroxide with the SWNTs and fluoronanotubes were found to proceed more readily in the solid state, while functionalization using lauroyl peroxide has been efficient only in the solution phase.
Figure 3.9:
(a) Weight loss plot, (b) Derivative plot. Inset shows a synchronized chemigram of volatile products monitored by FTIR spectrum in the 2800–2980 cm\(^{-1}\) region.
Figure 3.10: High resolution TEM image of individual undecyl functionalized SWNTs
The solubility of the pristine SWNTs, prepared phenylated SWNTs and undecylated SWNTs were measured with the method described in the last section of this thesis. It was found that 3.5 mg pristine SWNTs could be dissolved in 150 ml otho-dichlorobenzene (ODCB), while, by comparison, 8.8 mg of phenylated SWNTs and 9.3 mg of undecylated SWNT could be dissolved in 150 ml ODCB. These solubility data clearly show that functionalization improves the SWNT's solubility in organic solvent.

3.3.2 Acid functionalized SWNTs

The SWNT reactions with succinic acid peroxide and glutaric acid peroxide are of particular interest because the reactions attach pendant alkyl carboxyl groups to the SWNT sidewall. The reaction schemes are shown in Scheme 3.5 and 3.6. The alkyl carboxyl groups not only greatly improved the solubility, but also create opportunities for further reactions. This thesis presents a detailed study of these two reactions and characterizations of the products.

Figure 3.11 shows Raman spectra of pristine SWNTs, SWNTs-CH$_2$CH$_2$COOH, SWNTs-CH$_2$CH$_2$CH$_2$COOH and SWNTs-CH$_2$CH$_2$COOH after pyrolysis at 900 °C in spectra A, B, C and D.
Figure 3.11: Raman spectra of pristine SWNTs, SWNTs-CH$_2$CH$_2$COOH, SWNTs-CH$_2$CH$_2$CH$_2$COOH and SWNTs-CH$_2$CH$_2$COOH after pyrolysis at 900 °C are shown in spectrum A, B, C and D.
The significant $\sim 1300$ cm$^{-1}$ peak, sp3 carbon stretching, at spectrum B and C is the diagnostic feature for functionalized SWNTs. Further more, this peak became weakened in Spectrum D indicating the pyrolysis removes the functional groups and return the sp3 carbon to sp2 carbon. To study the reaction process, 50mg SWNTs were dispersed in 50 ml ODCB and heated at 90–100 °C. 1 grams of glutaric acid peroxide was added to the solution each day, Raman spectra of the reactants were collected every other day and are shown in Figure 3.12. Clearly the $\sim 1300$ cm$^{-1}$ peak was gradually enhanced during the course of reaction.

UV/Vis spectra were also collected from pristine SWNTs, SWNTs-CH$_2$CH$_2$COOH and SWNTs-CH$_2$CH$_2$CH$_2$COOH in 1% Sodium dodecyl Sulfate (SDS) water solution and are shown in Figure 3.13, traces A, B and C respectively. Clearly the van Hove transitions from 200 nm to 1400 nm wavelength were lost after the sidewall attachment, in agreement with previous functionalization studies.$^{20,24,25}$

Although SWNTs are featureless in the infrared spectrum because the non polar and symmetric carbon-carbon bond is IR inactive, FTIR is still a useful technique to study the sidewall functional groups of SWNTs.
Figure 3.12: A: Pristine SWNTs B: After 2 days C: After 6 days D: After 10 days
Figure 3.13: UV/Vis spectra of A: Pristine SWNTs; B: SWNTs-CH₂CH₂COOH C: SWNTs-CH₂CH₂CH₂COOH
Figure 3.14 FTIR spectra of

A: SWNTs-CH$_2$CH$_2$COOH, B: SWNTs-CH$_2$CH$_2$CONHCH$_2$CH$_2$NH$_2$,

C: SWNTs-CH$_2$CH$_2$CH$_2$CONH\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\end{array}
\]

D: SWNTs-CH$_2$CH$_2$CH$_2$CONH

\[
\begin{array}{c}
\text{C}_2\text{H}_5 \\
\text{C}_2\text{H}_5 \\
\text{NH}_2
\end{array}
\]
Spectrum A in Figure 3.14 shows the FTIR spectrum from the acid functionalized SWNTs. The 2912 cm⁻¹ peak can be assigned to carbon-hydrogen bond stretching, and 1708 cm⁻¹ peak is a very reasonable peak for an acid carbonyl. Spectrum B, collected from a SWNTs/amide compound (SWNTs-CH₂CH₂CONHCH₂CH₂NH₂), shows a 3284 cm⁻¹ peak that can be assigned to nitrogen-hydrogen stretching. It also shows that carbon-hydrogen signal at 2912 cm⁻¹ are slightly increased and as expected, the carbonyl peak shifts to lower frequency because of the formation of the amide. Spectrum C was collected from another SWNTs/amide compound:

![Chemical Structure](image)

As expected, the carbon-hydrogen stretching is greatly enhanced. The carbonyl peak was found split and one band shifts to 1626 cm⁻¹. This compound was used as a part of curing agents in epoxy composites and the study will be discussed in details in next chapter. Spectrum D was collected from the third SWNTs/amide compound made using Scheme 3.9:
As Scheme 3.9 shows, this compound was made by using SWNTs-CH$_2$CH$_2$CH$_2$COCl to react with diethyltoluenediamine at 120 °C. The spectrum shows significant aliphatic carbon hydrogen stretching between 2800 and 3050 cm$^{-1}$, and these absorbances could hardly be observed when reaction proceeded at room temperature. This could be due to the lower reactivity of aromatic amines.

TGA/MS data were very useful in analyzing the functionalized SWNTs. The TGA plot in Figure 3.15 shows that when the temperature was close to 170 °C it started losing weight and approximately 25% weight loss happened during the pyrolysis process. It is worth mentioning that the alkylated
Figure 3.15: TGA Plot of pyrolysis of SWNTs-CH2CH2COOH in argon to 800 °C
Figure 3.16: Mass spectrometry of the pyrolysis of SWNTs-CH$_2$CH$_2$COOH in argon atmosphere.
SWNTs lost weight at about the same temperature and phenylated SWNTs started the weight loss at ~250 °C. If we assume all the 25% weight losses are due to the loss of the functional groups, approximately there is one functional group (CH₂CH₂COOH) versus every 20 carbon atoms of the SWNTs. The online Mass Spectrometry data also offer very useful information and are shown in Figure 3.17. The evolution curves were obtained for the parent ion (m/z 73) of the detaching CH₂CH₂COOH, and fragment ions with the m/z 72 {CH₂CH₂COO}, m/z 45 {COOH}, m/z 44 {CO₂}, and m/z 29 {CH₃CH₂}. All the fragment ions were observed to peak at the same time (and evolution temperature) as the evolution curve for the parent ion which indicates that all fragments originate from the same parent (molecular) ion.

Figure 3.17 shows a typical TEM image of the SWNT amide derivative specimen placed on a lacey carbon-coated copper grid. This image shows that the covalent attachment of functional groups produces a “bumpy” sidewall morphology for the nanotubes. Zoomed image of an individual nanotube found in the same specimen (inset on Figure 3.17) indicates the attached long-chain moieties which tend to bend and stretch along the SWNT sidewalls.
Figure 3.17: TEM image of SWNTs-CH$_2$CH$_2$CONH$_2$$_6$$_{10}$CH$_2$C$_6$H$_{10}$NH$_2$
Solubility data (mg) for SWNT and SWNT-derivative.

<table>
<thead>
<tr>
<th>Solvent, 150 ml</th>
<th>Pristine SWNT</th>
<th>SWNT-{CH_2CH_2COOH}_x</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Dichlorobenzene</td>
<td>3.5</td>
<td>7.0</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>Not soluble</td>
<td>16.0</td>
</tr>
<tr>
<td>Water</td>
<td>Not soluble</td>
<td>15.2</td>
</tr>
<tr>
<td>1% NH_4OH in water</td>
<td>Not soluble</td>
<td>15.1</td>
</tr>
</tbody>
</table>
Figure 3.18: Solubility comparison of A: SWNTs and B: SWNTsCH$_2$CH$_2$COOH in isopropanol
The comparative quantitative estimation of the solvation of pristine SWNT and the SWNT derivative in several polar solvents was performed by the procedure described in section 3.2.6. The obtained solubility data are presented in the above table. They show that in comparison with the pristine nanotubes, the solubility of functionalized SWNTs (SWNTs-CH₂CH₂COOH) is significantly improved. Isopropanol was found to be the best solvent for SWNT-CH₂CH₂COOH. This has been exemplified by comparison with the pristine SWNT shown on the picture in Figure 3.18. At the same time, the observed solvation properties of the functionalized SWNTs prepared in the present work were not particularly sufficient for conducting the $^{13}$C NMR spectroscopy studies in the solution. Therefore, we have carried out these studies in the solid state.

Before this thesis, $^{13}$C NMR studies of functionalized SWNTs were rarely reported and were done by several research groups mostly on unfunctionalized SWNTs. These studies indicate that five different samples of SWNTs give an isotropic $^{13}$C NMR signal at δ 121-126 ppm,\textsuperscript{53, 54, 55, 56} while three different samples of MWNTs give a considerably broader $^{13}$C NMR signal at δ 121-130 ppm.\textsuperscript{57, 58, 59} Thus, the observation of an $^{13}$C NMR signal at δ 123 ppm for the purified HiPco SWNTs in our experiments is
Figure 3.19 $^{13}$C NMR of pristine and functionalized SWNTs
reasonable (Figure 3.19A). However, this signal is considerably narrower (half-height linewidth is only about 9 ppm) than those observed previously, which suggests that the purified HiPco SWNTs could be more uniform in composition (with respect to diameter, length, and chirality) or relatively fewer defects.

Functionalization with the \((\text{CH}_2)_n\text{COOH}\) moieties \((n = 2\) or \(3\)) creates different local environments on the nanotube and clearly broadens this signal (Figure 3.19 B and C). The peak maximum also appears to shift slightly upfield. The Raman and IR spectra of these compounds provide clear evidence for the attachment of aliphatic functionality to SWNT sidewalls, but the methylene groups give very weak signals at best in the MAS \(^{13}\text{C}\) NMR spectra. If the corresponding \(^1\text{H}\) NMR signal is very broad and shifted, decoupling may not be effective, since it would cause the methylene carbon signals to be severely broadened.

Functionalization also results in the appearance of a carbonyl signal at about \(\delta 172\) ppm, which is exceptionally shielded for a carboxylic acid.\(^60,61,62\) Such a \(^{13}\text{C}\) chemical shift is more typical of an ester or anhydride, but the IR absorption at 1708 cm\(^{-1}\) (Figure 3.14 A) is clearly more consistent with a carboxylic acid because an ester carbonyl is more likely to have an IR absorbance under 1650 cm\(^{-1}\). Furthermore, acid treatment, which would be
expected to hydrolyze an ester or anhydride, did not affect this IR peak. Not only is the carbonyl signal at δ 172 ppm exceptionally shielded, it also is much broader than the carboxyl signals in the CPMAS spectra of the precursor peroxides. Thus, the π-system of the nanotube itself appears to exert a significant shielding and broadening effect on the carbonyl carbon of the substituent.

There have been precedents for such an effect in solution state $^1$H and $^{19}$F NMR studies of functionalized nanotubes. $^1$H and $^{19}$F NMR have been used to see the interaction between the substituent and the SWNT. In the $^{19}$F NMR spectrum of the SWNT, bearing $n$-C$_8$F$_{17}$ substituents, the signals for the two CF$_2$ groups closest to the nanotube are broadened beyond detection. Broadening and shifting of resonances has also been observed for non-covalently functionalized nanotubes. The major interaction between the $n$-C$_{10}$H$_{21}$O-substituted poly(p-phenyleneethynylene) and SWNT is believed to be π-stacking; the methylene protons closest to the SWNT are broadened and shifted upfield by 0.5 ppm, while the phenylene protons are too broad to be detected.

Thus, it is not unreasonable to observe in the spectra of SWNTs-CH$_2$CH$_2$COOH and SWNTs-CH$_2$CH$_2$CH$_2$COOH the signals of the methylene carbons, which are even closer than the carbonyl carbon to the
nanotube, to shift even further upfield and broaden almost beyond detectability. For both of the samples, only very weak broad signals consistent with aliphatic carbon are centered at about δ 20 ppm.

Functionalization of the SWNTs with CH₂CH₂CONHCH₂CH₂NH₂ group has surprisingly little effect on the linewidth of the signal from the nanotube carbons in the spectrum of SWNT-CH₂CH₂CONHCH₂CH₂NH₂. The amide group produces a peak at δ 174 ppm. Signals from the methylene carbons are clearly stronger than in the spectra of SWNTsCH₂CH₂COOH and SWNTs-CH₂CH₂CH₂COOH. The increased intensity presumably results from the relatively remote NHCH₂CH₂NH₂ methylene carbons, whose signals appear upfield of their expected position in the ¹³C NMR spectrum.

3.4 Peroxide functionalization studies on C60 fullerene

In this thesis, peroxides were also used to functionalize C60 to compare with SWNTs. Functionalization of fullerene has been an attractive area and many studies were reported. For example, fluorination and further alkylation,⁶⁶, ⁶⁷ photoinduced electron transfer (PET) functionalization,⁶⁸ various types of cycloaddition such as [2 + 1], [2 + 3], and Diels-Alder reactions ⁶⁹, 1,3-dipolar cycloaddition reaction with thiocarbonyl ylide,⁷⁰
some other free radical addition reaction for C60 functionalization, photocycloaddition reactions, azomethine ylide cycloadditions, dihydrogenation by using BH₃ followed by hydrolysis, electrophilic additions of nitronium and many others. However, organic diacyl peroxides, a common free radical source, has not been thoroughly studied.

200 mg C60 were added to 100 ml dry toluene in a 200 ml flask and heated to 90 ~100 °C, 1 gram of lauryl peroxide, benzoyl peroxide and succinic acid peroxide were added to the flask for reaction. Approximately 2 hours after the peroxides were added, the purple C60/toluene solution was found to be dark brown. The reactions proceeded for 12 hours. After the reactions were finished, the solutions were filtered using a 0.2 μm pore-size Teflon membrane and large amounts of chloroform and carbon disulfide were used to flush to products. In the reaction using succinic acid peroxide, tetrahydroforan (THF) was also used to flush. Finally the reaction products were collected from the membrane and dried in a vacuum oven at 70 °C for more than 12 hours. Approximately 100~120 mg products were obtained eventually.

A variety of characterization techniques were used to study the functionalized C60 fullerenes including FTIR, solid state C NMR and the
Scheme 3.10

\[ \text{C}_{11}\text{H}_{23}\text{COOOOCC}_{11}\text{H}_{23} \rightarrow (\text{C}_{11}\text{H}_{23})_n \]

100\(^\circ\)C, - CO\(_2\)

Scheme 3.11

\[ \text{C}_6\text{H}_5\text{COOOOCC}_6\text{H}_5 \rightarrow (\text{C}_6\text{H}_5)_n \]

100\(^\circ\)C, - CO\(_2\)

Scheme 3.12

\[ (\text{HOOCCH}_2\text{CH}_2\text{COO})_2 \rightarrow (\text{CH}_2\text{CH}_2\text{COOH})_n \]

100\(^\circ\)C, - CO\(_2\)

\( n = 1, 2, 3, 4, 5, 6 \)
matrix assisted laser desorption/ionization (MALDI) technique Mass Spectrometry (MS).

The peroxide functionalization reactions are illustrated by Scheme 3.10, 3.11 and 3.12. It was also discovered that the radicals from the decomposition of the peroxides were readily attached to C60 molecules and up to six attachments were observed according to the MALDI MS spectrum shown in Figure 3.20. Figure 3.20 is the MALDI MS spectrum obtained from undecylated C60. It clearly shows the product is a mixture of monoundecylated, diundecylated, triundecylated, tetraundecylated, pentaundecylated and hexaundecylated C60 and the percentage decreases with the increasing attachment numbers. The solid-state $^{13}$C NMR spectra are shown in Figure 3.21, 3.22 and 3.23. Figure 3.21 shows the undecylated C60 $^{13}$C NMR spectrum. Clearly the C60 signal was greatly broadened and shifted to 147.4 chemical shifts from 142.7 chemical shifts, which is a significant shift. The signals which range from 16.2 to 44.4 chemical shifts are apparently from the long chain aliphatic carbons. The peak at 58.4 chemical shift is likely from the hydrogenated cage sp3 carbon of the C60 molecules, which means that the functional groups are not all attached to C60 in pairs, i.e. a functional group may be paired with a hydrogen. The
Figure 3.20: MALDI mass spectrum of undecylated C60
Figure 3.21: $^{13}$C NMR spectrum of undecylated C60
Chemical shifts

Figure 3.22: $^{13}$C NMR spectrum of phenylated C60
Figure 3.23: $^{13}$C NMR of C60-(CH$_2$CH$_2$COOH)$_n$ (n= 1,2,3,4,5,6)
broad band at \( \sim 85 \) chemical shifts can be assigned to the cage sp3 carbon of C60 connected with the functional group. Figure 3.22 shows the \(^{13}\text{C}\) NMR spectrum obtained from phenylated C60. Again, the C60 carbon was broaden and shifted to 147.1 chemical shift, and a new peak at 128.6 chemical shift are apparently belong to phenyl functional groups. The hump at 61.0 is from the hydrogenation of the cage C60 carbon and the 75.8 peak is from the cage sp3 carbon connected to the functional groups. Figure 3.23, obtained from C60-CH\(_2\)CH\(_2\)COOH\(_n\) (n= 1,2,3,4,5,6), also provides useful information. Clearly, the C60 peak shifts from 142 to 146.8 chemical shift and becomes broader because of the attachment of the functional groups. It is also reasonable to assign the 176.9 peak to the acid carbonyl carbon, although an aliphatic acid carbonyl carbon's \(^{13}\text{C}\) NMR signal normally shows an \( \sim 180 \) chemical shift. This shift may be due to the upshielding effect of C60 as observed in SWNTs functionalization. The 21.4 and 25.8 peaks are apparently methylene carbon signals.

FTIR spectra were all obtained from these three C60 derivatives compounds. Figure 3.24, the spectrum obtained from undecylated C60, shows significant two carbon-hydrogen peaks in the range of 2850 \( \sim 3000 \) cm\(^{-1}\) as expected. Figure 3.25, the spectrum taken from phenlyated C60, also shows dominating aromatic carbon hydrogen stretching between 3000 to
3100 cm\(^{-1}\). Figure 3.26, the spectrum taken of C60-CH\(_2\)CH\(_2\)COOH, shows a
dominating acid carbonyl peak at 1711 cm\(^{-1}\) as expected. Aliphatic carbon
hydrogen peaks between 2850 and 3000 cm\(^{-1}\) are also present in the
spectrum, a wide hump from 2600 to 3500 cm\(^{-1}\) is a typical acid hydroxide
peak.

The solubilities of these functionalized C60 were also studied and it
was discovered that undecylated C60 and phenylated C60’s solubility in
common solvents including chloroform, hexane, toluene is not improved
considerably compared with C60. The solubity of C60-CH\(_2\)CH\(_2\)COOH was
also investigated and the results are the following: 2.3 mg/20 ml in
water/ethanol (1:1) and 5.0 mg/20ml in THF.
Figure 3.24: FTIR spectrum of C60-(C_{11}H_{23})_n, n=1,2,3,4,5,6
Figure 3.25: FTIR spectrum of C60-(C₆H₅)n, n= 1, 2, 3, 4, 5, 6
Figure 3.26: FTIR spectrum of C60-(CH$_2$CH$_2$COOH)$_n$, $n = 1, 2, 3, 4, 5, 6$
3.5 Conclusions

Organic diacyl peroxides functionalizations of single wall carbon nanotubes (SWNTs) and C60 fullerene have been proven to be successful and effective methods. Compared with other free radical sources such as a diazonium salt radical source, organic diacyl peroxides are apparently more affordable and will be more appropriate for mass production of products.

Especially the succinic acid peroxide and glutaric acid peroxide functionalizations are particularly useful because they are terminated with the carboxylic acid moiety to the sidewalls of carbon nanotubes and C60 fullerene. Further, functionalization of the carboxylic groups in the nanotube side chains with terminal amines and diamines has been demonstrated. These types of sidewall functionalizations promise an improved solubility and processing for the nanotubes which enable their incorporation into polymer composite materials through chemical bonding to surrounding matrices via terminal functional groups. They also can provide sites for covalent attachment of biologically active moieties, peptides, aminoacids, proteins, oligonucleotides, to the nanotubes for drug delivery and biosensor applications.
Chapter 4 Epoxy/SWNTs Composites

4.1 Introductions

Single wall carbon nanotubes have been considered a useful material for developing nanotube reinforced composites because of their superior physical properties such as high strength and flexibility, outstanding thermal and electrical conductivity and relatively low density. In this thesis, epoxy/SWNTs polymer composites are investigated because they are critically important materials used in aircraft, space exploration vehicles, electronics and many other applications. It has been believed that epoxy/SWNTs composites are promising materials with high strength, lightweight and multifunctional features.

However, epoxy/SWNTs composites should not be made by simply mixing epoxy and SWNTs together without chemical bonding between them. Previous studies have shown that using pristine nanotubes in epoxy had not shown any improvements in mechanical properties. Thus it is clear that the interfacial bonding between nanotubes and polymer and the ability to disperse the nanotubes homogeneously throughout the polymer matrix will be critically important to make use of the excellent physical properties of nanotubes for structural composite applications.
Theoretically, only with chemical bonding between SWNTs and polymer chain molecules, can the external tensile load be effectively transferred from the matrix to the SWNTs through the interfacial shear stress. Some previous studies showed mechanical improvements of several thermoplastic polymers where interfacial interaction between polymer and SWNTs might exist. Some other studies showed poor load transfer ability because of the lack of interfacial bondings between pristine nanotubes and epoxy matrix. Theoretical simulation and calculations strongly suggest that with no chemical bonding, the fiber/matrix adhesion comes from van der Waal's and electrostatic interactions and other minor factors.

In the previously published studies, a variety of nanotube composite studies to achieve different goals were reported. For example: PVA-carbon nanotube composite films, carbon-nanotube-epoxy composites with Ultra-low electrical percolation threshold, polymer-grafted single-wall nanotube composites prepared via a single-step debundling/polymerization scheme, carbon nanotube/teflon composites for electrochemical sensors and biosensor applications, carbon nanotubes polyaniline composites, fluorinated single wall nanotube/polyethylene composites for multifunctional radiation protection, carbon nanotubes with polystyrene composites, multiwalled carbon nanotubes (MWNT)-reinforced epoxy
composite thin films prepared by a microfabrication process,\textsuperscript{95} carbon nanotube-amorphous diamond thin-film composites synthesized by pulsed laser deposition (PLD),\textsuperscript{96} carbon nanotube/polyelectrolyte composites for actuator material applications.\textsuperscript{97}

Single wall carbon nanotubes need sidewall or end functionalization for possibility of bonding with matrix. Sidewall and end functionalization are both mentioned in the earlier chapters of this thesis.\textsuperscript{19, 20, 21, 22, 23, 24, 25, 26} These functionalizations enable the attachment of various functional groups to SWNTs which may offer chemical bonding opportunities with polymer molecules for making SWNTs/polymer.

In this chapter, SWNTs were functionalized by using organic diacyl peroxide reaction to attach functional groups not only at the sidewall of SWNTs to create bonding opportunity but also use HNO$_3$/H$_2$SO$_4$ treatment to create end functional groups to fully incorporate SWNTs into epoxy composites. Previously, the SWNTs were functionalized by concentrated HNO$_3$/H$_2$SO$_4$ followed by fluorination before being incorporated into epoxy polymer to achieve up to 18\% tensile strength improvement with only 1\% addition of SWNTs.\textsuperscript{98} In this thesis, this integration of SWNTs and epoxy method provided more effective load transfer through robust chemical bonding, thus ultimately make full use of SWNTs to achieve mechanical
properties enhancement of composites. Considerable improvement of mechanical properties with only 1 wt % addition was demonstrated due to improved dispersion and interaction.

4.2 Fabrications of Epoxy/SWNTs Composites

4.2.1 Functionalization of SWNTs

SWNTs were functionalized with succinic acid peroxide as described in Chapter 3 to prepare SWNTs-CH$_2$CH$_2$COOH (scheme 3.5). In addition, concentrated HNO$_3$/H$_2$SO$_4$ treated SWNTs were also functionalized with succinic acid peroxide by using the same approach to create COOH groups not only at the tip end but also at the sidewall.$^{22, 23}$ After the SWNTs-CH$_2$CH$_2$COOH samples were made, they were further reacted with 4,4'$'$-methylene(bisecyclohexaneamine) as shown in Scheme 3.8. Thus SWNTs were attached by amine terminated functional groups and could be used as a part of curing agents in epoxy composites. The functionalized SWNTs were characterized by using the method described in chapter 3 and their FTIR spectra were shown in Figure 4.1 and the SEM image of the amino-SWNTs is shown in Figure 4.2.
Figure 4.1: ATR-IR spectra of the SWNT derivatives produced by reactions with diamines:
A: SWNTs-CH₂CH₂COOH;
B: SWNTs-CH₂CH₂CONH(C₆H₁₀CH₂C₆H₁₀NH₂;
C: Cut/ SWNTs-CH₂CH₂CONH(C₆H₁₀CH₂C₆H₁₀NH₂
Figure 4.2: SEM image of Amino-SWNTs
4.2.2 Preparation of epoxy/SWNTs composites

The functionalized SWNTs were weighed and dispersed in DMF (2 mg/mL) by sonication for 5 minutes by using a high-power CUP-HORN ultrasonic processor and then for 1 hour in an ultrasonic bath (40 kHz). Thereafter, the weighed epoxy resin was added, and the solution was stirred for 30 min. DMF was evaporated at 100 °C in a vacuum chamber. The SWNT/epoxy blend was prepared by stirring for 5 minutes with a high-shear mixing homogenizer to achieve homogeneity. A 100:26 ratio of EPI-CURE W curing agent was added, and further stirring was performed with a high-shear mixer. The blend was degassed for 5 h in a vacuum oven and then cast into an aluminum mould. The curing cycle was 2 hours at 100°C under a pressure of 0.3 Mpa followed by another 2 hours at 160°C. During mixing, an air release agent, BYK-A 555, was added to reduce porosity. Epoxy/SWNTs composites were prepared using a various percentages of both pristine BuckyPearl SWNTs and functionalized SWNTs. Eight dog-bone-shaped specimens were cut and polished for the tensile testing. Following the same procedure described above, a control sample from pure epoxy resin was also prepared and tested for comparison. The chemical reactions are illustrated
Scheme 4.1

\[ \text{Diagram showing chemical structure} \]

\[ X = \begin{array}{c}
\text{Chemical structure} \\
\end{array} \]
by scheme 4.1. In these reactions, nanotubes are integrated easily into the epoxy structure via reaction with the epoxy groups, becoming integral part of the matrix instead of separate fillers. These direct chemical bonds provide strong interfacial shear stress and effective load transfer, which will be shown in the next section of this chapter.

After the epoxy/SWNTs composites were prepared (Figure 4.3), microscopic analyses, tensile properties analysis and Dynamic Mechanical Analysis were performed. The results are discussed in the following section.

4.3 Mechanical testing results and discussions

The prepared epoxy/SWNTs composite and neat epoxy samples are shown in Figure 4.3. The neat epoxy sample is yellow, and the epoxy/SWNTs sample is completely black although it contains only 1% SWNTs.

Figure 4.4 shows the SEM image of the fracture surfaces of epoxy/SWNTs composites samples. This image shows dispersion of the SWNT bundles in the epoxy matrix. As the image shows, broken bundles of SWNTs were shown on the fracture surface, they were not pulled out of the
Figure 4.3: Pictures of neat epoxy(A) and SWNTs reinforced epoxy(B)
Figure 4.4: SEM image of fracture surface of nanotube epoxy composites
epoxy structure, but still embedded and held in the matrix. This evidence strongly suggests strong interfacial chemical bonding between epoxy polymer molecules and SWNTs to transfer stress load during tension. Interconnections between SWNTs through epoxy molecules could result in network of SWNTs, *i.e.* SWNT bundles were crosslinked. Crosslinking of SWNTs helps to prevent the sliding of nanotubes bundles, but the drawback is that it increases the difficulty of unroping of nanotubes and homogenous dispersion.

**Tensile Properties improvement**

Because of the superior mechanical properties of SWNTs, the SWNTs reinforced epoxy composites, improved mechanical properties of epoxy/SWNTs composites are desired. A series of tensile tests were carried out to investigate the direct impact of functionalized nanotube on the mechanical properties including tensile strength, Young’s modulus and strain to failure. As expected, epoxy composites with one weight percent of functionalized SWNTs addition showed excellent improvement of the mechanical properties. The results are shown in Figure 4.5, where curve 1, 2, 3 and 4 were obtained from neat epoxy sample, epoxy reinforced with 1% pristine SWNTs, epoxy reinforced with 1% functionalized SWNTs (as
Figure 4.5: Stress test results: 1 pure epoxy; 2 1 wt% pristine SWNTs; 3 1 wt% amino-SWNTs; 4 4 wt% amino-SWNTs
shown by scheme 4.1) and epoxy reinforced with 4% functionalized SWNTs. The curve 2 shows that without chemical bonding between SWNTs and epoxy matrix, the tensile strength did not improve but decrease because SWNTs could only be considered impurity inside and there is no load transfer. Comparing curve 1, curve 2 and curve 3 also shows the advantage of functionalized SWNTs in composites. The tensile strength at break point increased from 83 MPa to 104 MPa, 25% higher than neat EPON 862 epoxy, and a 30% increase compared with a pristine nanotube/epoxy system. The Young’s modulus had more than 30% improvement from 1 wt% functionalized SWNTs reinforced epoxy. Furthermore, as shown in curve 4, for 4 wt% loading composites, up to 70% improvement in Young’s modulus was obtained but there was no further improvement on break strength. We believed that was due to significant viscosity increase when more SWNTs were used in the blend, which led to dispersion difficulty during curing process. The experimental results also show that nanotubes epoxy composites exhibited an increased strain to failure up to 8.5%, a 30% of improvement compared to relatively brittle neat epoxy. This outstanding elongation in SWNT reinforced composites was from SWNT’s outstanding sotropic strain to failure (20%). This property is crucial to improve the fracture toughness of epoxies since the usefulness of epoxy in composites
applications is sometimes limited by their brittle nature. Although various toughening methods have been used to increase toughness like rubber modified epoxy, but unfortunately they also damaged other mechanical strengths. ⁹⁹ But in the case of functionalized SWNTs refined epoxy, with chemical bonding between the SWNTs and epoxy matrix, SWNTs were proven to not only effectively increase strain to failure, but also increase fracture toughness and impact resistance. The epoxy/SWNTs composite samples made with SWNTs with or without HNO₃/H₂SO₄ treatment before peroxide functionalization were found having similar performances.

**Dynamical Mechanical Properties**

Dynamic Mechanical Analysis (DMA) was also used to study the mechanical properties of epoxy/SWNTs composites. Dynamic behavior of a polymer material refers to the temperature-dependent properties of polymer materials, such as the storage modulus E’ in this study. ¹⁰⁰ It reflects the amount of energy stored in the composites as elastic energy when the sample is bent, which is affected by the existence of the filler. The measurement results are shown in Figure 4.6, where curve 1 was obtained from neat epoxy, curve 2 and 3 were obtained from epoxy composites reinforced with
Figure 4.6: DMA test results of: 1. epoxy; 2. 1 wt% SWNTs; 3. 4 wt% pristine SWNTs; 4. 1 wt% amino-SWNTs; 5. 4 wt% amino-SWNTs
1% and 4% pristine SWNTs, curve 4 and 5 were obtained from epoxy composites reinforced with 1% and 4% amino-functionalized SWNTs obtained from Scheme 4.1. The composites of epoxy with amino-functionalized SWNTs show dramatically increased storage moduli compared with the neat epoxy and the composites with pristine nanotubes. Specifically, the storage modulus at room temperature (25°C) increased from 3.4GPa for pure epoxy to 6.4 GPa for composites with a higher loading of 4 wt% amino-SWNTs, which almost doubled the value of the storage modulus. These experimental results clearly show that significant mechanical property improvement was obtained by adding functionalized nanotubes.

4.4 Conclusions

Obviously, the strength, modulus and strain improvements originate from the effective load transfer between SWNTs and the epoxy matrix. It is the strong interfacial covalent bonding that makes the load transfer possible. Furthermore, it is also observed that nanotube composites failed before reaching the yield points during tensile testing, suggesting more room for further improvement. As a comparison, use of pristine SWNTs for composites has very limited reinforcement role because of lack of interfacial bonding, i.e., load transfer ability.
Chapter 5 Conclusions: Funcionalization is the pathway for SWNTs Uses

Single wall carbon nanotubes (SWNTs) is a unique material with plausible chemical and physical properties. A wide range of applications have been proposed, some prototypes were realized and many additional investigations of their properties, applications are under way.

This thesis is focused on the chemistry of single wall carbon nanotube derivatives, including their preparations, characterizations and applications, such as flororonanotubes as cathode materials in a lithium battery and functionalized single wall carbon nanotube reinforced epoxy composites. Specifically:

Fluorinated derivatives of single wall carbon nanotubes (SWNTs) could be made by using SWNTs to react with elemental fluorine directly, the stoichiometry could be controlled by adjusting the reaction temperature; similar to graphite fluoride (CFx), the fluorinated derivatives of SWNTs could be used as a cathode material in a lithium battery and a higher voltage (~0.7V) was obtained. According to thermochemistry calculations, it was concluded that the higher output voltage originates from the less negative heat of formation of fluorinated SWNTs compared with CFx. The lower power density is due to its lesser fluorine content. Furthermore, the oxidative
properties and thermal stability were also investigated in this thesis. It was found that fluorinated SWNTs have unique chemical reactivity, they could function as a weak oxidizer and react with a series of binary metal compounds at room temperature or elevated temperatures.

This thesis has also studied functionalization of SWNTs with organic diacyl peroxide including lauryl peroxide, benzoyl peroxide, succinic acid peroxide and glutaric acid peroxide. Upon heating, these peroxides readily decompose and produced a variety of radicals. These radicals were found attaching to the sidewall of SWNTs through an addition process. The sidewall functionalized SWNTs have improved solubilities and also create more chemical reaction opportunities to SWNTs. A parallel study with C60 fullerene was also performed and a various characterizations confirmed the structures of the products.

By using peroxides functionalization, alkyl carboxylic acid groups could be attached to the SWNT sidewall. These derivatives could further react with thionyl chloride and diamines to form terminal amine functional groups at SWNT sidewall. This compound, used as a part of curing agent in EPON 862 epoxy polymer, greatly improves the stress, strain, and storage modulus and other mechanical properties. By using this method, a fully integrated nanotube epoxy composite materials for structural application was
developed. Single wall carbon nanotubes play a reinforcement role in the epoxy matrix. Mechanical testing results demonstrated the effectiveness of the significant mechanical properties enhancement through such integration of functionalized single-walled nanotubes into epoxy system. Furthermore, the techniques for developing a fully integrated nanotubes epoxy composite by functionalization can be extended to other polymer systems.
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