

# **POLYMER NANOCOMPOSITES**

*Crystallization, Reinforcement and Conductivity through SWNTs*

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*under the*

**Faculty of Technology**

*by*

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**December 2006**

## Certificate

Certified that, the thesis entitled '**POLYMER NANOCOMPOSITES: Crystallization, Reinforcement and Conductivity through SWNTs**' submitted to Cochin University of Science and Technology under the Faculty of Technology, by Mr. Anoop Anand K, is an authentic record of the original research carried out by him under my supervision and guidance. The thesis has fulfilled all the requirements as per regulations and no part of the results embodied has been submitted to any other institution for any other degree/diploma.

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20<sup>th</sup> Dec 2006




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## Declaration

I hereby declare that, the thesis entitled '**POLYMER NANOCOMPOSITES: Crystallization, Reinforcement and Conductivity through SWNTs**' submitted to Cochin University of Science and Technology, under the Faculty of Technology, is based on the original research carried out by me under the supervision of Dr. Rani Joseph, Professor, Dept. of Polymer Science and Rubber Technology, and further, no part of the results presented has been submitted to any other institution for any other degree/diploma.

Cochin  
20<sup>th</sup> Dec 2006



Anoop Anand K

...to the one who always treasured my life, for her unstinted support,  
unconditional love and care

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## Preface

Carbon nanotubes (CNTs) have been widely considered as attractive candidates for use as fillers in composite materials due to their distinctly superior mechanical, thermal, electrical and electronic properties. The CNT can be thought of as the ultimate carbon fiber with breaking strengths reported as high as 200 GPa, and elastic moduli in the 1 TPa range. This, coupled with their enormous surface area per gram and large aspect ratios, has triggered a revolution in using CNTs as a reinforcing phase for polymer matrices.

The current research investigates the possibility of using single walled carbon nanotubes (SWNTs) as filler in polymers to impart several properties to the matrix polymer. SWNTs in a polymer matrix like poly(ethylene terephthalate) induce nucleation in its melt crystallization, provide effective reinforcement and impart electrical conductivity. We adopt a simple melt compounding technique for incorporating the nanotubes into the polymer matrix. For attaining a better dispersion of the filler, an ultrasound assisted dissolution-evaporation method has also been tried. The resulting enhancement in the materials properties indicates an improved disentanglement of the nanotube ropes, which in turn provides effective matrix-filler interaction. PET-SWNT nanocomposite fibers prepared through melt spinning followed by subsequent drawing are also found to have significantly higher mechanical properties as compared to pristine PET fiber.

SWNTs also find applications in composites based on elastomers such as natural rubber as they can impart electrical conductivity with simultaneous improvement in the mechanical properties.

This thesis is divided into seven chapters:

Chapter 1 presents a concise introduction to the subject. Carbon nanotubes, their synthesis, growth mechanism, structure, properties and applications are briefly reviewed. The state-of-art research in polymer-carbon nanotube nanocomposites is discussed. The principal objectives of the work are mentioned at the end of the chapter.

Chapter 2 deals with the preparation and crystallization characteristics of nanocomposites of poly(ethylene terephthalate) and single walled carbon nanotubes. The composites have been prepared by a simple melt compounding technique and their crystallization characteristics have been investigated using differential scanning calorimetry and wide angle X-ray diffraction analysis.

Chapter 3 includes the evaluation of mechanical properties of PET-SWNT nanocomposites. The viscoelastic characteristics of the nanocomposites are presented here. Thermal and dimensional stability as well as electrical conducting properties are also investigated.

Chapter 4 presents the method of preparing nanocomposites through ultrasound assisted dissolution-evaporation. Crystallization, mechanical, dynamic mechanical, thermal and electrical properties of these nanocomposite samples are studied.

Chapter 5 comprises the fabrication of PET-SWNT nanocomposite fibers through melt spinning. The effect of fiber formation conditions on the development of their mechanical properties is studied.

Chapter 6 deals with the preparation and characterization of nanocomposites based on natural rubber with carbon nanotubes. The nanotubes have been incorporated into the elastomer matrix through conventional mill mixing as well as latex stage mixing. The mechanical, electrical, thermal and ageing characteristics of NR-SWNT nanocomposites are presented in this chapter.

Chapter 7 presents summary and conclusions of the investigations.



# Chapter 1

## General introduction

Our ability to engineer novel structures has led to unprecedented opportunities in materials design. It has fueled rapid development in nanoscience and nanotechnology for the past one decade leading to the creation of new materials with interesting nanoscale features. In the framework of this rapid development, the domain of nanocomposite materials is attracting more and more researchers; both academic and industrial. The field of nanocomposites involves the study of multiphase materials where at least one of the constituent phases has at least one dimension of the order of nanometers.<sup>1</sup> The use of these nanoscale fillers to augment the properties of polymers has provided a radical alternative to conventional composites and modified polymers. The promise of nanocomposites lies in their multifunctionality, the possibility of realising unique combinations of properties unachievable with traditional materials.

The current research aims to investigate the possibility of use of carbon nanotubes for fabricating polymer-based nanocomposites and thereby imparting several properties to the matrix polymer. In this chapter, a concise introduction to the subject is presented. Carbon nanotubes, their synthesis, growth mechanism, structure, properties and applications are briefly reviewed. The state-of-art research in polymer-carbon nanotube nanocomposites is also discussed. An outline of the principal objectives of the work is given at the end of the chapter.

### 1.1 Carbon nanotubes

The ground breaking discovery of carbon nanotubes (CNTs), in 1991 followed by the realisation of their amazing properties led scientists all over the world to focus their research efforts on these fascinating structures. Carbon nanotubes (also known as bucky tubes) are long thin cylinders of carbon that are unique for their size, shape, and

remarkable physical and electrical properties.<sup>2-5</sup> They can be thought of as layers of the conventional graphite structure rolled up into a cylinder such that the lattice of carbon atoms remains continuous around the circumference. Their name is derived from their size, since the diameter of a nanotube is of the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several micrometres in length.

The number of carbon shells in CNTs varies from one to as many as fifty, the former being single walled carbon nanotubes- SWNTs and the latter, multi walled carbon nanotubes- MWNTs. These intriguing structures have sparked much excitement in recent years and a large amount of research has been dedicated to their understanding.<sup>6-8</sup> They are potentially useful in a wide variety of applications in nanotechnology, electronics, optics, and other fields of materials science.<sup>9-14</sup>

### 1.1.1 The discovery

The discovery of carbon nanotubes dates back to the 1985-legendary sequence of experiments by Harry Kroto, of the University of Sussex, and Richard Smalley, of Rice University, Houston.<sup>15,16</sup> During the vaporisation of graphite, Kroto and Smalley were struck by a surprising outcome: in the distribution of the resulted gas-phase carbon cluster, detected by mass spectroscopy,  $C_{60}$  was by far the most dominant species. Later they realised that a *closed* cluster containing precisely 60 carbon atoms would have a structure of unique stability and symmetry, as shown in figure 1.1. Although they had no direct evidence to support this structure, subsequent work has proved them correct. The discovery of  $C_{60}$  published in *Nature* in November 1985, had an impact, which extended the way beyond the confines of academic chemical physics, and marked the beginning of a new era in carbon science.<sup>17,18</sup>

In the beginning, however, the progress was slow mainly because of the small quantity of  $C_{60}$  produced in the Kroto-Smalley experiments. Eventually, more than a laboratory curiosity, the bulk production of  $C_{60}$  was achieved by a technique developed by Wolfgang Krätschmer of the Max Planck Institute at Heidelberg, and Donald Huffman of the University of Arizona. They used a simple carbon arc to vaporize graphite

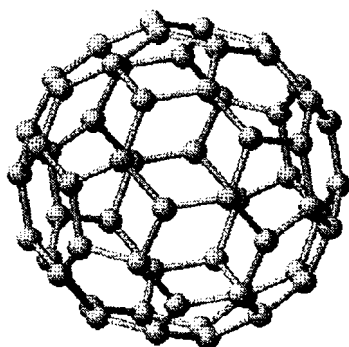


Fig. 1.1  $C_{60}$ : Buckminster Fullerene

in an atmosphere of helium and collected the soot, which settled on the walls of the vessel. Dispersing the soot in benzene produced a red solution, which could be dried down to produce beautiful plate like crystals of ‘fullerite’: 90 %,  $C_{60}$  and 10 %,  $C_{70}$ . This report appeared in *Nature* in 1990.<sup>19</sup>

Sumio Iijima of the NEC laboratories in Japan, was fascinated by the Krätschmer-Huffman *Nature* paper, and decided to embark on a detailed study of the soot produced by their technique. The initial High-Resolution Transmission Electron Microscopic (HRTEM) studies were disappointing: the soot collected from the walls of the arc-evaporation vessel appeared almost completely amorphous, with little obvious long-range structures.

Eventually, Iijima turned his attention to the hard cylindrical deposit, which formed on the graphite cathode after arc evaporation. This cathodic soot contained a whole range of novel graphitic structures, the most striking of which were hollow fibers, finer and more perfect than any previously seen. Iijima’s beautiful images of carbon nanotubes, shown first at a meeting at Richmond, Virginia in October 1991, and published in *Nature* a month later (figure 1.2).<sup>20</sup>

### **1.1.2.1 Arc discharge**

The carbon arc discharge method, initially used for producing C<sub>60</sub> fullerenes, is the most common and perhaps the easiest way to produce carbon nanotubes as it is rather simple to undertake. However, it is a technique that produces a mixture of components and requires separating nanotubes from the soot and the catalytic metals present in the crude product.

This method creates nanotubes through arc-vaporisation of two carbon rods placed end to end, separated by approximately 1 mm, in an enclosure that is usually filled with an inert gas (He, Ar) at low pressure (between 50 and 700 mbar). Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen.<sup>21</sup> A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vaporises one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode.<sup>22</sup>

Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs, which is shown in figure 1.3. Two distinct methods of synthesis can be performed with the arc discharge apparatus. If SWNTs are preferable, the anode has to be doped with metal catalyst, such as Fe, Co, Ni, Y or Mo. A lot of elements and mixtures of elements have been tested by various authors and it is noted that the results vary a lot, even though they use the same elements.<sup>23</sup> This is not surprising as the experimental conditions differ. The quantity and quality of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, kind of gas, the current and system geometry. Usually the diameter is in the range of 1.2-1.4 nm.

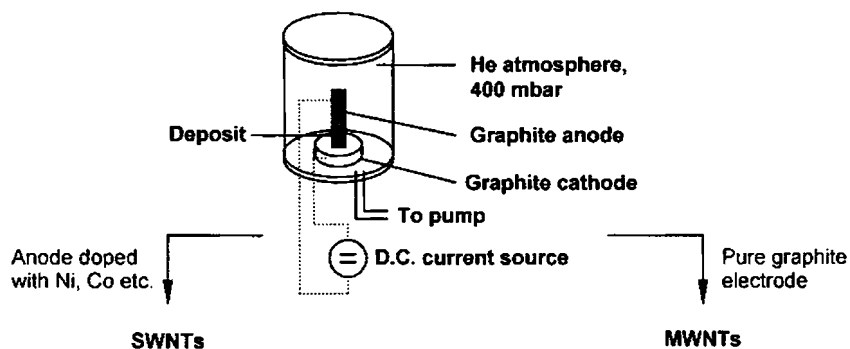


Fig. 1.3 Experimental set-up of an arc discharge process

### 1.1.2.2 Laser ablation

In 1995, Smalley's group at Rice University reported the synthesis of carbon nanotubes by laser vaporisation (figure 1.4).<sup>24</sup> A pulsed, or continuous laser is used to vaporise a graphite target in an oven at 1200 °C. The oven is filled with He or Ar gas in order to keep the pressure at 500 Torr. A very hot vapour plume forms, then expands and cools rapidly. As the vaporised species cool, small carbon molecules and atoms quickly condense to form larger clusters, possibly including fullerenes. The catalysts also begin to condense, but more slowly at first, and attach to carbon clusters and prevent their closing into cage structures.<sup>25</sup> Catalysts may even open cage structures when they attach to them. From these initial clusters, tubular molecules grow into single walled carbon nanotubes until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become that much coated with a carbon layer that they cannot absorb more and the nanotubes stop growing. The SWNTs formed are bundled together by van der Waals forces.

Laser ablation is almost similar to arc discharge, since the optimum background gas and catalyst mix is the same as in the arc discharge process. This might be due to very similar reaction conditions needed, and the reactions probably occur with the same mechanism. The condensates obtained by laser ablation are normally contaminated

### 1.1.2.3 Chemical vapour deposition

Chemical vapour deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to gaseous carbon source. Commonly used gaseous carbon sources include CH<sub>4</sub>, CO and C<sub>2</sub>H<sub>2</sub>. The energy is used to ‘crack’ the molecule into reactive atomic carbon. Then the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. Excellent alignment, as well as positional control on nanometer scale, can be achieved by using CVD.<sup>27,28</sup> Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow single rather than multi walled nanotubes.<sup>29</sup>

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotubes. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Ammonia may be used as the etchant.<sup>30</sup> Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900 °C ranges.<sup>31</sup> Typical yields of CVD are approximately 30 %. In the last decennia, different techniques for the carbon nanotubes synthesis with CVD have been developed, such as plasma enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, vapour phase growth, aero gel-supported CVD and laser-assisted CVD.

### 1.1.2.4 CoMoCat process

In this method, SWNTs are grown by CO disproportionation at 700-950 °C. The technique is based on a unique Co-Mo catalyst formulation that inhibits the sintering of Co particles and therefore inhibits the formation of undesired forms of carbon that lower the selectivity.

labelled 'tip-growth'. Depending on the size of the catalyst particles, SWNTs or MWNTs are grown. In arc discharge, if no catalyst is present in the graphite electrode, MWNTs will be grown on the C<sub>2</sub> particles that are formed in the plasma.

### **1.1.3 Structure and properties**

#### **1.1.3.1 Structure of carbon nanotubes**

It is the chemical genius of carbon that it can bond in different ways to create structures with entirely different properties. Graphite and diamond, the two bulk solid phases of pure carbon, bear testimony to this. The mystery lies in the different hybridisation that carbon atoms can assume. The four valence electrons in carbon, when shared equally (sp<sup>3</sup> hybridised), create isotropically strong diamond. But when only three are shared covalently between neighbours in a plane and the fourth is allowed to be delocalised among all atoms, the resulting material is graphite. The latter (sp<sup>2</sup>) type of bonding builds a layered structure with strong in-plane bonds and weak out-of-plane bonding of the van der Waals type. Graphite, hence, is weak normal to its planes and is considered as a soft material due to its ability to slide along the planes. The story of fullerenes and nanotubes belongs to the architecture of sp<sup>2</sup> bonded carbon and the subtlety of a certain group of topological defects that can create unique, closed shell structures out of planar graphite sheets.<sup>38</sup>

Graphite is the thermodynamically stable bulk phase of carbon upto very high temperatures under normal ranges of pressure (diamond is only kinetically stable). It is now well known that this is not the case when there are only a finite number of carbon atoms. Simply speaking, this has to do with the high density of dangling bond atoms when the size of the graphite crystallites becomes small (say, nanosize). At small sizes, the structure does well energetically by closing onto itself and removing all the dangling bonds. Preliminary experiments done in the mid 1980s, which served as the precursor to the fullerene discovery, suggested that when the number of carbon atoms is smaller than a few hundred, the structures formed correspond to linear chains, rings, and closed shells.<sup>39</sup> The latter, called fullerenes, are closed shell all

carbon molecules with an even number of atoms (starting at  $C_{28}$ ) and  $sp^2$  bonding between adjacent atoms.

To form curved structures (such as fullerenes) from a planar fragment of hexagonal graphite lattice, certain topological defects have to be included in the structure. To produce a convex structure, positive curvature has to be introduced into the planar hexagonal graphite lattice. This is done by creating pentagons. It is a curious consequence of the Euler's principle that one needs exactly 12 pentagons to provide the topological curvature necessary to completely close the hexagonal lattice; hence, in  $C_{60}$  and all the other fullerenes ( $C_{2n}$  has  $(n-10)$  hexagons) there are many hexagons but only 12 pentagons. The rule of pentagon numbers will hold, however big the closed structure may be created out of hexagons and pentagons. One can thus imagine that a greatly elongated fullerene can be produced with exactly 12 pentagons and millions of hexagons. This would correspond to a carbon nanotube.<sup>40</sup>

The structure of a single walled carbon nanotube (SWNT) can be conceptualized by wrapping a one-atom-thick layer of graphite (called graphene) into a seamless cylinder and when concentric cylinders, one inside the other are present, they are referred to as multi walled carbon nanotubes (MWNTs).<sup>41</sup> Most SWNTs have a diameter of close to 1 nm, with a tube length that can be many thousands of times larger (figure 1.8). SWNTs with length upto orders of centimeters have been produced.



### 1.1.3.2 Mechanical, electrical and thermal properties of carbon nanotubes

Carbon nanotubes are one of the strongest materials known to man, both in terms of tensile strength and elastic modulus.<sup>42</sup> The strength results from the covalent  $sp^2$  bonds formed between the individual carbon atoms. In 2000, a nanotube was tested to have a tensile strength of 63 GPa. In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa. CNTs also have very high elastic modulus, of the order of 1 TPa.<sup>43</sup> Since carbon nanotubes have a low density for a solid of 1.3-1.4  $g/cm^3$ , its specific strength is the best of known materials.

Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5 % and can increase till the maximum strain the tube undergoes before fracture by releasing strain energy. CNTs are not nearly as strong under compression. Due to their hollow structure, they tend to undergo buckling when placed under compressive, torsional or bending stress.

Multi walled carbon nanotubes, multiple concentric nanotubes precisely nested within one another, exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. This property has already been utilized to create the world's smallest rotational motor and a nanorheostat.

Due to the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given  $(n,m)$  nanotube, if  $2n + m = 3q$  (where  $q$  is an integer), then the nanotube is metallic, otherwise the nanotube is a semiconductor. Thus all armchair ( $n=m$ ) nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting. In theory, metallic nanotubes can have an electrical current density more than 1,000 times stronger than metals such as silver and copper.

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as ‘ballistic conduction’, but good insulators laterally to the tube axis.

### **1.1.3.3 Defects in nanotubes**

As with any material, the existence of defects affects the nanotube properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by upto 85 %.<sup>44</sup> Another well-known form of defect that occurs in carbon nanotubes is the Stone Wales defect, which creates a pentagon and heptagon pair by rearrangement of the bonds. Due to the almost one-dimensional structure of CNTs, the tensile strength of the tube is dependent on the weakest segment of it in a similar manner to a chain, where a defect in a single link diminishes the strength of the entire chain.

The nanotube’s electrical properties are also affected by the presence of defects. A common result is the lowered conductivity through the defective region of the tube. Some defect formation in armchair-type tubes (which are metallic) can cause the region surrounding that defect to become semiconducting. Furthermore, single monoatomic vacancies induce magnetic properties. The thermal properties of the nanotubes are also heavily affected by defects.

### **1.1.4 Nanotube research**

The method for producing nanotubes described by Iijima in 1991 gave relatively poor yields, making further research into their structure and properties difficult. A significant advance came in July 1992 when Thomas Ebbesen and Pulickel Ajayan made a serendipitous discovery of preparing nanotubes in gram quantities.<sup>45</sup> Further research made the availability of nanotubes in bulk quantities possible, which in turn gave an enormous boost to the pace of nanotube research worldwide.<sup>46</sup>

One area, which attracted early interest, was the idea of using carbon nanotubes as ‘molecular containers’.<sup>47</sup> A landmark in this field was the demonstration by Ajayan

and Iijima that nanotubes could be filled with molten lead and thus be used as molds for 'nanowires'.<sup>48</sup> Subsequently more controlled methods for opening and filling nanotubes have been developed, enabling a wide range of materials, including biological ones, to be placed inside. The resulting opened or filled tubes might have fascinating properties, with possible applications in catalysis, or as biological sensors. Filled carbon nanoparticles may also have important applications in areas as diverse as magnetic recording and nuclear medicine.

Perhaps the largest volume of research into nanotubes has been devoted to their electronic properties. A short time after the publication of Iijima's 1991 letter in *Nature*, two other papers appeared on the electronic structure of carbon nanotubes.<sup>49,50</sup> Noriaki Hamada and colleagues from Iijima's laboratory in Tsukuba carried out band structure calculations on narrow tubes and demonstrated that the electronic properties are a function of both tube structure and diameter. These remarkable predictions stimulated a great deal of interest, but attempts to determine the electronic properties of nanotubes experimentally presented great difficulties. Since 1996, however, experimental measurements have been carried out on individual nanotubes, to confirm the theoretical predictions. The results have prompted speculation that nanotubes might become components of the future nanoelectronic devices.

SWNTs are the most likely candidates for miniaturizing electronics past the microelectromechanical scale that is currently the basis of modern electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors. One useful application of SWNTs is in the development of intramolecular field effect transistors (FETs).

A variety of other possible applications of nanotubes are currently of exciting interest. For example, transparent and electrically conductive films of carbon nanotubes have been developed to replace indium tin oxide (ITO) in LCDs, touch screens, and photovoltaic devices. Carbon nanotube films are substantially more mechanically robust than ITO films, making them ideal for high reliability touch screens and flexible displays. A number of groups are exploring the idea of using nanotubes as tip for





























































































































































































































































