

**MULTIWALL CARBON NANOTUBE (MWCNT),  
MWCNT/CARBON BLACK (CB) AND MWCNT/SILICA  
HYBRID FILLERS FILLED NATURAL RUBBER  
NANOCOMPOSITES**

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**UNIVERSITI SAINS MALAYSIA  
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AND MWCNT/SILICA HYBRID FILLERS FILLED NATURAL RUBBER  
NANOCOMPOSITES**

**by**

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**Thesis submitted in fulfillment of the requirement  
for the degree of  
Master of Science  
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## DECLARATION

I declare that the content presented in this dissertation is my own work which was done at University Sains Malaysia unless informed otherwise. The dissertation has not been previously submitted for any other degree.

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## LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
CB	Carbon black
CB/MWCNT	Carbon nanotube to multiwall carbon nanotube ratio
CBS	N-cyclohexyl-2-benzothiazole sulfonamide
CNT	Carbon nanotubes
Eb	Elongation at break
FTFT	Fatigue to Failure Tester
FTIR	Fourier transforms infrared spectroscopy
IPPD	N-isopropyl-N'-phenyl-paraphenylenediamine
ISO	International Organization for Standardization
MDR	Moving Die Rheometer
MWCNT	Multiwall carbon nanotubes
NR	Natural Rubber
PHR	Part per Hundred Rubber
RRIM	Rubber Research Institute of Malaysia
Si69	Bis-(3-triethoxysilylpropyl) tetrasulfane
SMR L	Standard Malaysian Rubber Light
SMR	Standard Malaysian Rubber
SWCNT	Single wall carbon nanotubes
TGA	Thermo gravimetric analysis



## LIST OF SYMBOLS

M100	Modulus at 100% elongation
M300	Modulus at 300% elongation
M <sub>H</sub>	Maximum Torque
Q <sub>f</sub> /Q <sub>g</sub>	Rubber-filler interaction
T <sub>90</sub>	Optimum Vulcanization Time
T <sub>s2</sub>	Scorch Time

**KARBON NANOTIUB BERBILANG DINDING (MWCNT), MWCNT/HITAM  
KARBON (CB) DAN MWCNT/SILIKA PENGISI HIBRID TERISI  
NANOKOMPOSIT GETAH ASLI**

**ABSTRAK**

Karbon nanotub berbilang dinding (MWCNT) merupakan salah satu bahan penguat yang istimewa. Ianya digunakan sebagai bahan pengisi di dalam komposit polimer kerana sifat mekaniknya yang unik dan mempunyai nisbah luas permukaan per isipadu yang tinggi. MWCNT ini ditambah di dalam komposit polimer untuk mendapatkan peningkatan yang tinggi ke atas sifat fizikal dan mekanik sebatian getah. Dalam kajian ini, pengaruh pengisi MWCNTs secara tunggal dan hibrid terhadap sifat-sifat pematangan, sifat tensil, hayat fatig, morfologi, analisis gravimetik terma (TGA) dan interaksi getah-pengisi ( $Q_f/Q_g$ ) nanokomposit NR/MWCNT telah dijalankan. Bagi Hibrid nanokomposit NR/MWCNT, pengisi hitam karbon (NR/CB/MWCNT) dan silika (NR/silica/MWCNT) telah digunakan, manakala bagi pengisi MWCNTs yang digunakan secara tunggal, kesan penggunaan Si69 dan kaedah pencampuran secara larutan telah dikaji. Keputusan menunjukkan masa skoj dan pematangan berkurang dengan peningkatan pembebanan MWCNTs bagi setiap nanokomposit NR/MWCNT yang menggunakan MWCNTs secara tunggal ataupun secara hibrid. Modulus tensil nanokomposit NR/MWCNT meningkat dengan peningkatan pembebanan MWCNTs tetapi kekuatan tensil, pemanjangan takat putus dan hayat fatig berkurang. SEM menunjukkan terdapat banyak pengelompokan pengisi MWCNTs di dalam matrik getah asli. Dengan

menggunakan Si69 dan kaedah pencampuran larutan, pengisi MWCNTs terserak dengan baik di dalam matrik getah asli dan sifat-sifat tesil dan hayat fatig dapat ditingkatkan. Bagi hibrid pengisi hitam karbon (NR/CB/MWCNT) kekuatan tensil yang optimum dapat dicapai pada 29.5 phr CB/0.5 phr MWCNTs, manakala bagi pengisi hibrid silika (NR/silica/MWCNT) kekuatan tensil yang optimum adalah pada 29 phr silika/1 phr MWCNTs. Peningkatan pembebanan MWCNTs yang seterusnya dalam nisbah pembebanan hibrid menyebabkan kekuatan tensil, pemanjangan takat putus dan hayat fatig berkurang, tetapi modulus tensil dan interaksi getah-pengisi ( $Q_f/Q_g$ ) meningkat. Keputusan SEM menunjukkan terdapat penyerakan pengisi dan interaksi antara pengisi hybrid dengan matrik getah asli yang baik pada 29.5/0.5 CB/MWCNT dan 29/1 silika/MWCNT. Peningkatan pembebanan MWCNTs yang seterusnya dalam nisbah pembebanan hibrid menyebabkan pengelompokan MWCNTs menjadi dominan dan ini mengurangkan kesan penguatan MWCNTs.

**MULTIWALL CARBON NANOTUBE (MWCNT), MWCNT/CARBON BLACK  
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**ABSTRACT**

Carbon nanotubes are an intriguing reinforcement for polymers because of their unique mechanical properties and extremely large surface area per unit volume. These MWCNTs are added in order to get a substantial improvement in the physical and mechanical properties of the rubber compound. In these present studies, MWCNTs are added as a filler in natural rubber (NR) matrix. The effect of single and hybrid MWCNTs loading on cure characteristics, tensile properties, fatigue life, morphology, thermal gravimetric analysis (TGA) and rubber-filler interaction ( $Q_f/Q_g$ ) of NR/MWCNT nanocomposites were investigated. For the hybrid NR/MWCNT nanocomposites, carbon black (NR/CB/MWCNT) and silica (NR/silica/MWCNT) were used as hybrid fillers and for the single NR/MWCNT nanocomposites, the effect of Si69, and different mixing method i.e mechanical and solution mixing was studied. The results show that scorch and cure time decrease with increasing MWCNTs loading for all single and hybrid MWCNTs loading. The tensile modulus increase with increasing MWCNTs loading but decrease in tensile strength, fatigue life and elongation at break. The SEM results show there is a lot of agglomeration of MWCNTs occurred. Using solution mixing method and Si69 as a coupling agent, the MWCNTs are well dispersed in the natural rubber matrix and the tensile properties and fatigue life of NR/MWCNT were enhanced. For NR/CB/MWCNT hybrid nanocomposites, the optimum tensile strength was achieved at 29.5 phr CB/0.5 phr

MWCNTs loading ratio while for NR/silica/MWCNT, the optimum tensile strength is 29 phr silica/1 phr MWCNTs loading ratio. As the MWCNTs loading increased in hybrid loading ratio, the tensile strength, elongation at break and fatigue life are decrease, however the tensile modulus and rubber filler interaction ( $Q_f/Q_g$ ) value increased. The SEM results show a good dispersion and better interaction between hybrid filler with natural rubber matrix at 29.5/0.5 CB/MWCNT loading ratio and 29/1 silica/MWCNT loading ratio. As MWCNTs loading ratio increased the agglomeration of MWCNT became dominant and reduced the reinforcing effect of MWCNTs.

## CHAPTER 1: INTRODUCTION

### 1.1 Introduction

Rubber is one of the most extensively used products, ranging from household to industrial product. Since the discovery of vulcanization process by Charles Goodyear, rubber technologies have developed rapidly. One of the weaknesses of the neat rubber is that it has low strength and modulus (Bokobza, 2007; Frogley et al., 2003). Therefore an additional reinforcing phase is necessary to enhance the properties of rubber. Generally carbon black, calcium carbonate, zinc oxide, magnesium oxide, talc, mica and silicates (Iijima, 1991; Ismail and Freakley, 1996; Shanmugaraj et al., 2007) are mostly used for rubbers, but the full reinforcing effects of these fillers are depends on several parameter including the size of the particles, aspect ratios, degree dispersion and orientation in the matrix and the degree of adhesion with the polymer chains.

By incorporating nanofillers into rubber as the reinforcing filler, it is expected that the properties of the rubber will even better because a small size of nanoparticles could increase the corresponding surface area and allowing achieving the required mechanical properties at low filler loading (Sui et al., 2005). Unlike traditional non-active fillers, mainly used for cost reduction, nanofillers are performance-enhancing. They can be used in relatively small amounts (5 - 10%) in order to provide substantial improvements in physical and other properties. Nano sized particles (diameter ca. 40nm) can form a very fine and homogenous distributed network in the polymer matrix. As compared to micron size filler particles the nano size filler particles are able to occupy substantially greater

number of sites in the polymer matrix. The significant increase in specific surface area of filler particles contributes to the enhanced physical property of the polymer matrix.

Carbon nanotubes (CNT) is one of the most common nanofiller that have been attracted a great deal from all over the world since the first discovery by Iijima (2002). Carbon nanotubes are allotropes of carbon and belong to fullerene structural family. As the name indicates, nanotubes are cylindrical in shape with at least one end capped with a hemisphere of the buckyball structure; it is spherical in shape. In nanotubes, the diameters are in the order of a few nanometers, however, they are millimeters or even centimeters long. Therefore these nanotubes possess a high aspect ratio, thereby imparting high strength to the polymer with a small weight percent. With the unique properties such as high mechanical strength, electrical and thermal conductivity, carbon nanotubes has been destined to be one of the great nanoreinforcement (Shanmugharaj et al., 2007).

Many research efforts have been directed towards producing CNT/polymer composites for functional and structural applications (Coleman et al., 2006; Schadler, 2003). However, even after a decade of research, the full potential of employing CNTs as reinforcements has been severely limited because of the difficulties associated with dispersion of entangled CNTs during processing and poor interfacial interaction between CNTs and polymer matrix. The nature of dispersion problem for CNTs is rather different from other conventional fillers, such as spherical particles and carbon fibers, because CNTs are characteristic of small diameter in nanometer scale with high aspect ratio ( $>1000$ ) and thus extremely large surface area. In addition, the commercialized CNTs are supplied in the form of heavily entangled bundles, resulting in inherent difficulties in dispersion.

Based on studies(Coleman et al., 2006; Kim and Kim, 2006; Thess et al., 1996), the dispersion of CNTs is not only a geometrical problem, dealing with the length and size of the CNTs, but also relates to a method on how to separate individual CNTs from CNTs agglomerates and stabilize them in polymer matrix to avoid secondary agglomeration. Researchers have employed different techniques to attain optimum dispersion of nanotubes in the polymer matrix including (i) solution mixing,(Pham et al., 2003) (ii) sonication (Xie et al., 2004), (iii) coagulation (Du et al., 2003), (iv) melt compounding (Dondero and Gorga, 2006; Ham et al., 2006; Kim and Kim, 2006; Yu et al., 2005), (v) in situ emulsion polymerization (Ham et al., 2006; Yu et al., 2005), (vi) the use of surfactants (Gong et al., 2000) and (vii) chemical functionalization of carbon nanotubes (Ramanathan et al., 2005; Wu et al., 2005).

The performance of a CNT/polymer nanocomposite depends on the dispersion of CNTs in the matrix and interfacial interactions between the CNTs and the polymer. However, the carbon atoms on CNTs walls are chemically stable because of the aromatic nature of the bond. As a result, the reinforcing CNTs are inert and can interact with the surrounding matrix mainly through van der Waals interactions, unable to provide an efficient load transfer across the CNT/matrix interface. Good interfacial adhesion between CNTs and rubber is essential to enhance the property of NR/MWCNT nanocomposites. In order to achieve this, some modification need to be done on MWCNTs surfaces so that the interaction between CNTs and rubber could be improved. Many modification techniques that have been studied like plasma, thermal, laser treatment and acid treatment (Bokobza, 2007). However such complicated high cost preparation procedures would reduce the practicability and repeatability of these studies (Bokobza, 2007).



Chemical modification of carbon nanotubes is the best technique to get more homogenous dispersion through covalent and noncovalent attachments of functional groups in nanotube with matrix. Among the different functionalization methods electrochemical modification and surface initiated in situ polymerization are the appreciable means for the preparation of nanotubes reinforced polymers with maximum properties (Gong et al., 2000).

But despite a poor dispersion, CNTs have been shown to impart to a rubbery matrix, a higher level of reinforcement than that provided by any previously existing filler such as carbon black (CB), silanized silica, clay fibers, or layered silicates. A method of incorporating simultaneously CNTs and another type of filler could be of interest on account of possible synergistic effects that could arise between the two different fillers. Through a combination of benefits of each type of filler, these hybrid composites could potentially exhibit improved characteristics with regard to single-filler materials. On the other hand, diluting expensive CNTs with a cheaper reinforcing component, without compromising the mechanical properties of the resulting material, would have an economic impact as that will reduce the cost of the nanotube-based composite (Bokobza et al., 2008). This approach was used by Leong et al. (2004) who showed that the introduction of CaCO<sub>3</sub> into a talc-filled polypropylene, in addition to making the composite cheaper, had the unique advantage of synergistically increasing the overall impact strength of the hybrid composite. Low-density polyethylene was filled with CB and carbon fibers in order to move the percolation threshold to reduced filler content (Di et al., 2003). The authors reported that the incorporation of carbon fibers into polyethylene/CB composites provides long conductive pathways to bridge uncontacted CB aggregates.

The excellent mechanical properties of CNTs combined with unique transport properties along with other multi-functional characteristics render a huge potential for structural and functional applications of CNT/polymer nanocomposites. Although numerous studies have dedicated to the development of CNT/polymer nanocomposites for various purposes, their applications in real products are still in their early stage of realization (Bokobza et al., 2008). In this study, the effect of different mixing method, multiwall carbon nanotubes (MWCNT) loading, treated MWCNTs, carbon black (CB)/MWCNT and silica/MWCNT hybrid fillers on the properties of natural rubber nanocomposites was investigated.

## **1.2 Objectives**

This present work aims to use the unique properties of MWCNTs in natural rubber compounds. There are little works has been done in order to investigate the potential of MWCNTs in natural rubber as a filler. The main objectives of this work are:

1. To study the effect of the MWCNTs loading and mixing methods on cure characteristics, tensile properties, fatigue life, morphology and rubber-filler interaction of multiwall carbon nanotube filled natural rubber nanocomposites.
2. To investigate the effects of MWCNTs treated with Bis-(3-triethoxysilylpropyl) tetrasulfane, (Si69) on cure characteristics, tensile properties, fatigue life, morphology and rubber-filler interaction of multiwall carbon nanotube filled natural rubber nanocomposites
3. To study the effects of CB/MWCNT hybrid loading ratio on properties on cure characteristics, tensile properties, fatigue life, morphology and rubber-filler

interaction of multiwall carbon nanotube/carbon black filled natural rubber nanocomposites

4. To study the effects of silica/MWCNT hybrid loading ratio on properties on cure characteristics, tensile properties, fatigue life, morphology and rubber-filler interaction of multiwall carbon nanotube/silica filled natural rubber nanocomposites

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Nanotechnology

#### 2.1.1 An overview of nanotechnology

Microtechnology has changed our lives dramatically. The most striking impact is apparent in computer technology, which is essential for today's industry, and also for our individual life styles. Apart from microelectronics, microtechnology influences many other areas. The size of typical structures that is accessible is in the sub-micrometer range, which is at the limits of optical resolution and barely visible with a light microscope. This is about 1/1000 smaller than structures resolvable by the naked eye, but still 1000 times larger than an atom. Today's developments are addressing the size range below these dimensions. Because a typical structure size is in the nanometer range, the methods and techniques are defined as nanotechnology (Köhler and Fritzsche, 2007).

Nanotechnology is the study and control of matter at dimensions of roughly 1 to 100 nanometers (nm), where unique phenomena enable novel applications (Koo, 2006). Nanotechnology is also the design, fabrication and application of nanostructures or nanomaterials. The excitement surrounding nanoscale science and technology gives us unique opportunities to develop revolutionary materials. Nanoscale science and technology is a young field that encompasses nearly every discipline of science and engineering. Nanoscale is a magical point on the dimensional scale: Structures in nanoscale (called nanostructures) are considered at the borderline of the smallest of human-made devices and the largest molecules of living systems (Mansoori, 2005). Our ability to control and manipulate nanostructures will make it possible to exploit new physical, biological and

chemical properties of systems that are intermediate in size, between single atoms, molecules and bulk materials (Bhattacharya et al., 2008). There are many specific reasons why nanoscale has become so important some of which are as the following (Roco et al., 2000):

- A key lecture of biological entities is the systematic organization of matter on the nanoscale. Developments in nanoscience and nanotechnology would allow us to place man-made nanoscale things inside living cells. It would also make it possible to make new materials using the self-assembly features of nature. This certainly will be a powerful combination of biology with materials science.
- Nanoscale components have very high surface to volume ratio, making them ideal for use in composite materials, reacting systems, drug delivery, and chemical energy storage (such as hydrogen and natural gas).
- Macroscopic systems made up of nanostructures can have much higher density than those made up of microstructures. They can also be better conductors of electricity. This can result in new electronic device concepts, smaller and faster circuits, more sophisticated functions, and greatly reduced power consumption simultaneously by controlling nanostructure interactions and complexity.

Nanotechnology is entering into all aspects of science and technology including, but not limited to, aerospace, agriculture bioengineering, biology, energy, the environment, materials, manufacturing, medicine, military science and technology. It is truly an atomic and molecular manufacturing approach for building chemically and physically stable structures one atom or one molecule at a time (Mansoori, 2005). Presently some of the

active nanotechnology research areas include nanolithography, nanodevices, nanorobotics, nanocomputers, nanopowders, nanostructured catalysts and nanoporous materials, molecular manufacturing, diamondoids, carbon nanotube and fullerene products, nanolayers, molecular nanotechnology, nanomedicine, nanobiology, organic nanostructures to name a few. The above mentioned technologies, and more, stand to be improved vastly as the methods of nanotechnology develop. Such methods include the possibility to control the arrangement of atoms inside a particular molecule and, as a result, the ability to organize and control matter simultaneously on several length scales. The developing concepts of nanotechnology seem persistent and broad. It is expected to influence every area of science and technology, in ways that are clearly unpredictable.

Nanotechnology will also help solve other technology and science problems. For example, we are just now starting to realize the benefits that nanostructuring can bring to (Roco et al., 2000):

- (a) wear-resistant tires made by combining nanoscale particles of inorganic clays with polymers as well as other nanoparticle reinforced materials
- (b) greatly improved printing brought about by nanoscale particles that have the best properties of both dyes and pigments as well as advanced ink jet systems
- (c) vastly improved new generation of lasers, magnetic disk heads, nanolayers with selective optical barriers and systems on a chip made by controlling layer thickness to better than a nanometer
- (d) design of advanced chemical and bio-detectors

- (e) nanoparticles to be used in medicine with vastly advanced drug delivery and drug targeting capabilities,
- (f) chemical-mechanical polishing with nanoparticle slurries, hard coatings and high hardness cutting tools

### **2.1.2 Polymer nanocomposites**

Nanomaterials can be classified into nanostructured materials and nanophase/nanoparticle materials. The nanometer size covers a wide range, from 1 nm to as large as 100 to 200 nm. The introduction of inorganic nanoparticles as additives into polymer systems has resulted in polymer nanocomposites (PNs) exhibiting multifunctional, high-performance polymer characteristics further than what traditional filled polymeric materials possess (Koo, 2006). Nanocomposite technology is applicable to a wide range of polymers from thermoplastics and thermosets to elastomers. Two decades ago, researchers from Toyota Central Research and Development produced a new group of polymer~clay complexes or composites, which was aptly called polymer- layered silicate nanocomposites or polymer nanocomposites. Today, there is a variety of nanofillers used in nanocomposites. Cost and availability continue to change as the field is relatively new and several of these fillers are still being developed. The most common types of fillers are natural clays (mined, refined and treated), synthetic clays, nanostructured silicas, nanoceramics, nanocalcium carbonates and nanotubes (carbon based) (Bhattacharya et al., 2008).

The development of these new materials will allow the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergies between materials, that only occur when the length scale of morphology and the

fundamental physics associated with a property coincide, i.e., on the nanoscale level. Multifunctional features attributable to polymer nanocomposites consist of improved (Collister, 2001):

- Efficient reinforcement with minimal loss in ductility and impact strength
- Thermal endurance
- Flame retardance
- Improved liquid and gas barrier properties
- Improved abrasion resistance
- Reduced shrinkage and residual loss
- Altered electrical, electronic and optical properties

Through control/alteration of the additives at the nanoscale level, one is able to maximize property enhancement of selected polymer systems to meet or exceed the requirements of current military, aerospace, and commercial applications. (Koo, 2006)

In the past few years, polymer nanocomposites have aroused widespread interest because of the small particle size and surface activity of nanoparticles, allowing the required properties to be achieved at low filler loadings (Pinnavaia and Beall, 2000; Sinha Ray and Okamoto, 2003; Utracki, 2004). So, a nanocomposite is a nanostructured material consisting of a homogenous dispersion of nanoparticles inside a polymer matrix. Because of their nanometer filler size, nanocomposites show unique properties typically not shared by their more conventional microcomposite counterparts and therefore, offer new technology and business opportunities (Bhattacharya et al., 2008). The main feature of a



nanoparticle is that it has at least one dimension in the nanometric range. Among these nanometer-scale reinforcing particles, layered silicates and organoclay are the most commonly used nanoparticles for the production of polymer nanocomposites.

Structurally, polymer/clay complexes can be classified as either nanocomposites or (conventional composites). The classification depends on the nature and interaction of the components as well as on the preparation method. The nature and interaction of the components refers to the type of silicate material, the organic material used to render the hydrophilic silicates organophilic, and the nature of the polymer matrix. The preparation technique pertains to mechanical factors that facilitate the penetration or intercalation of polymer chains into the layers of silicate. Ultimately, this may lead to exfoliation, i.e., delamination of silicates into individual layers. These mechanical factors include the mechanical shear or extension employed, residence time and type of mixer. Depending on these factors, three morphologies are possible: phase-separated, intercalated, and exfoliated (Alexandre and Dubois, 2000). "Phase-separated" refers to composites that maintain immiscibility between the polymer and the inorganic filler.

The exfoliated structure facilitates maximum reinforcement due to the large surface area of contact with the matrix. This represents the significant difference between nanocomposites and the conventional composites (microcomposites). There are numerous reports that the enhancement of properties imparted by the well-dispersed and distributed silicate layers can be achieved with only a small weight fraction of these fillers. The properties that show enhancement include:

- Mechanical properties, e. g. strength, modulus and dimensional stability
- Retardation of gases. water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

### **2.1.3 Current status, trend and future perspective.**

Recently, polymer nanocomposites are steadily growing and dominating the world of science and technology due to their peculiar and fascinating properties as well as their unique applications in commercial sectors. The interest in polymer nanocomposites is due to the major improvements in mechanical properties, gas barrier properties, thermal stability, fire retardancy and other areas. There are many factors that affect the polymer nanocomposites properties such as (Koo, 2006);

- Synthesis method such as melt compounding, solvent blending, in-situ polymerization and emulsion polymerization
- Polymer nanocomposite morphology
- Types of nanoparticles and their surface treatments
- Polymer matrix such as crystallinity, molecular weight, polymer chemistry and whether thermoplastic or thermosetting

The demand for high-performance and low cost polymer composites poses new challenges for materials scientists. Nanoclays, nanoceramic particles and carbon nanotubes with their nanometer size, large surface area, high mechanical strength and stiffness have been shown to be effective reinforcement materials for the polymer nanocomposites.

The flexibility in selecting appropriate nano building blocks allows one to design novel materials properties and to optimize them for each desired application. Structural and morphological changes in the polymers induced by nanomaterials could lead to significant enhancement in several aspects of their mechanical properties. Understanding the synthesis–structure–property relationship of nanocomposites is vital for the development of advanced polymer nanocomposites with enhanced mechanical strength, stiffness and toughness for structural engineering applications (Tjong, 2006).

Although the potential for the commercial application of nanocomposites is enormous, the actual application has been occurring at a very slow pace. In many instances, the performance of the developed nanocomposites did not meet the expectations, e. g., not very significant increase in their useful properties or drop in mechanical or optical properties. While it has been shown that the modulus or stiffness of thermoplastics can be increased by adding very small amounts of clay, in many cases it comes with the disadvantage of decreasing strength. Addition of clay to polymers, such as nylon-6 and EVA, increases the gas barrier properties but their optical properties may be compromised. Performance not yet meeting expectations may not be due to any inherent flaws in the concept of nanocomposite technology (Bhattacharya et al., 2008). It is rather clue to the fact that the developments in this new area are still in their infant stage. The production of

nanocomposite is very system-specific. The understanding of the chemistry of filler modification, the physics and thermodynamics of filler dispersion, and the interplay of filler-polymer at the interphase is crucial to the development of customized nanocomposites (Bhattacharya et al., 2008).

## **2.2 Carbon Nanotubes**

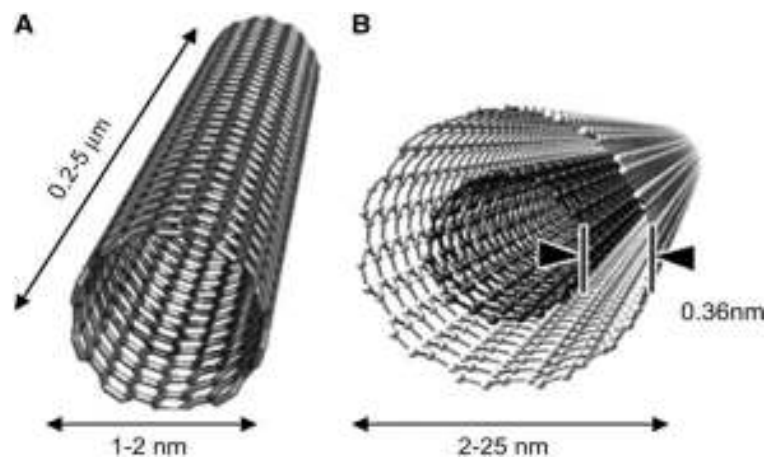
### **2.2.1 Structure and properties**

Carbon nanotubes (CNT) were first discovered in 1991 by Sumio Iijima. It is a completely new type of carbon fibre which comprises coaxial cylinders or graphite sheets, which range from 2 to 50 sheets (Yamabe, 1995). These tubes consist of rolled up hexagons, 10,000 times thinner than a human hair. Carbon nanotube can be classified into two types, single wall carbon nanotube (SWCNT) and multiwall carbon nanotubes (MWCNT). The first observations Sumio made (Burstein, 2003) were of multi-walled nanotubes, and after two years later the single wall nanotubes were observed. Iijima along with Ichihashi (1993) used carbon electrodes with a small amount of iron and filled the chamber around the carbon arc with methane and argon gas which yielded the single wall carbon nanotube. Single wall nanotubes are basically a single fullerene molecule that has been stretched out so their length is a million times its diameter (Dresselhaus et al., 1995). Donald Bethune and colleagues also observed the single wall carbon nanotube during the same time (Bethune et al., 1993).

After several years, Yamabe (1995) have found a way to produce the bundles of single wall carbon nanotubes for a first time. Nowadays carbon nanotubes vigorously produced using various technique including arc discharge (Ajayan, 1999; Liu and Gao, 2005), laser

ablation (Chiang et al., 2001; Soundarrajan et al., 2002), high pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD) (Dai, 2002; Resasco et al., 2002). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

A single-walled carbon nanotube (SWCNT) is one such cylinder, while multiwall tubes (MWCNT) consist of many nested cylinders whose successive radii differ by roughly the interlayer spacing of graphite (Figure 2.1). They have a tendency to form in bundles which are parallel in contact and consist of tens to hundreds of nanotubes (Zhao et al., 2002). Depending on how the graphene walls of the nanotube are rolled together they can result in an arm chair, zig zag or chiral shapes (Figure 2.2).



**Figure 2.1:** Conceptual diagram of single-walled carbon nanotube (SWCNT) (A) and multiwalled carbon nanotube (MWCNT) (B) delivery systems showing typical dimensions of length, width, and separation distance between graphene layers in MWCNTs (Gogotsi, 2006)

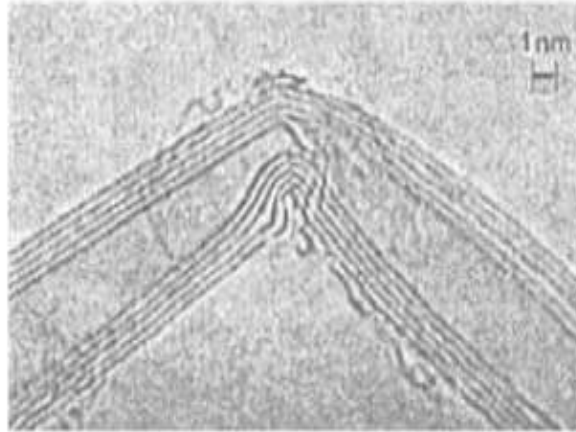


carbon nanotubes have the highest Young's modulus of all different types of composite tubes (Salvetat-Delmotte and Rubio, 2002).

**Table 2.1:** Mechanical properties of carbon nanotube (Yamabe, 1995)

Material	Young Modulus (GPa)	Tensile strength (GPa)	Density (g/cm <sup>3</sup> )
Single wall nanotube	1054	150	
Multi wall nanotube	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

The strength of the carbon-carbon bond gives rise to the extreme interest in the mechanical properties of nanotubes. Theoretically, they should be stiffer and stronger than any known substance. Both single and multi wall carbon nanotubes, are expected to have large bending due to high in-plane tensile strength of graphite. The simulations conducted by Dresselhaus and colleagues indicate it can be twisted, elongated, or bent into circles but then still regain their original shape [Figure 2.3] (Dresselhaus et al., 1995). Some other properties are discussed in Table 2.2.



**Figure 2.3:** TEM micrograph and computer simulation of nanotube buckling (Dresselhaus et al., 1995)

**Table 2.2:** Some other properties of carbon nanotubes (Meyyappan, 2005)

Properties	function
Electrical	Electron confinement along the tube circumference makes a defect-free nanotube either semiconducting or metallic with quantized conductance whereas pentagons and heptagons will generate localized states
Optical and optoelectric	Direct band gap and one-dimensional band structure make nanotubes ideal for optical applications with wavelength ranging possibly from 300 to 3000 nm
Thermal and thermoelectric	Inherited from graphite, nanotubes have the highest thermal conductivity while the quantum effect shows up at low temperature



### **2.2.2 Carbon nanotubes in rubber nanocomposites.**

Rubber/carbon nanotubes nanocomposites have been a particular interest for the past few years due to high modulus, aspect ratio and excellent thermal and electrical properties of carbon nanotube. The first reported study on CNT/SBR compounds was carried out by Chen and Song (2004). They analyzed the effects of different contents of MWCNTs on the performance and microstructure of the SBR composites processing in an open roll mill at room temperature. MWCNTs were modified by refluxing in a HNO<sub>3</sub> solution before blending with SBR rubber. The authors observed a gradual increase of the mechanical properties, tensile and tear strength, shore hardness and abrasion with increasing the MWCNTs content. The performances of MWCNT/SBR compounds were better than those of carbon black (N330)/SBR composites. The authors suggest the likely application of carbon nanotubes for tires with rolling hysteresis and decreased fatigue loss.

Bokobza, demonstrated the intrinsic potential of multiwalled carbon nanotubes (MWCNTs) as reinforcing filler in elastomer matrices, in particular, styrene-butadiene copolymers. Despite a poor dispersion detected by transmission electron microscopy and atomic force microscopy, sensible improvements in the mechanical and electrical properties of SBR matrix by the addition of MWCNTs were observed. The incorporation of 1 phr of carbon nanotubes increases the tensile modulus and strength of the compound, approximately 45% and 70%, respectively. Compared to carbon black (CB), small filler loading of carbon nanotubes is required to reach the same performances due to a stronger interfacial adhesion between the polymer and the nanotubes. So, quite similar hysteresis

curves are obtained when SBR is filled with 10 phr of MWCNTs or 5 phr of CB (Bokobza and Kolodziej, 2006).

However, the authors observed that the carbon nanotubes are able to form a critical concentration of conduction (continuous interconnecting filler network) at a small filler loading: 2-4 phr of MWCNTs are required, against 30-40 phr for CB. By the addition of 2 and 4 phr of MWCNTs, the conductivity of the composite increases by five orders of magnitude, reflecting the formation of a percolation network. However, the aggregation of MWCNTs yields a conductive material at a higher volume fraction than that expected from individually well dispersed carbon nanotubes. The authors studied the variations in resistivity under uniaxial deformations of up to 200%. They observed a gradual increase in the resistivity of the compound with strain applied. When second stretch was conducted after total unloading of the sample, the resistivity slightly decreased and when the strain reached the maximum value of the first stretching, the two curves coincided, that is, the sample was now in the same state as it was in the first stretching. The authors studied the changes in the resistivity under uniaxial extension by atomic force microscopy observations of stretched composites. They observed an increase of the roughness of the sample with strain and the filler structures align in the direction of strain. The structure became more slender under deformation, with a loss of contacts between aggregates and an increase in the resistivity (Bokobza and El Bounia, 2008).

De Falco et al. (2007) developed an easy technique to fabricate cured styrene-butadiene rubber/ multiwalled carbon nanotube composites. The compounds were prepared by dissolving the SBR in toluene in a ratio of 25 ml g<sup>-1</sup>, then adding the filler. Previously dispersed in ethanol by sonication, and then drying. Afterwards, the other components, N-

t-butyl-2-benzothiazole sulfonamide (TBBS) and sulfur were added as a cure system and then the system was stirred and put to evaporate for 4 days as films in Petri capsules until constant weight before the cure. This procedure successfully obtained a homogeneous dispersion of the filler into the elastomer matrix without agglomeration. The incorporation of a small quantity of multiwalled carbon nanotubes (0.66 wt%) led to a sensibly increase of the mechanical properties when compared with pristine SBR compound or CB-filled SBR. The authors attributed this higher reinforcing effect to the higher aspect ratio in the MWCNTs compared with CB (around 500 times) and the better interface between the two phases in the case of SBR/MWCNT composites.

Zhao et al. (2002) found that by adding 0.25 wt% of SWCNTs, the modulus of the SWCNT/NR composite prepared with toluene as a solvent increased about 20% compared to the pure NR material. They attributed this improvement to the formation of additional sources of entangle SWCNTs or physical crosslinks in the network in presence of carbon nanotubes. These extra crosslinks play an important role at the beginning of the deformation increasing the modulus. At higher deformations, some of the physical crosslinks may dissipate when polymer chains slide on the carbon nanotubes. In addition, comparing the crosslink densities of the NR and SWCNT/NR samples calculated from mechanical and Raman spectroscopy measurements, the authors observed that SWCNTs can be used as Raman sensors to evaluate the crosslinking process of rubbery materials. The D' peak of SWCNT's was shifted upwards as the extent of vulcanization is increased by increasing the amount of sulfur. Therefore, they concluded that, Raman spectroscopy could be used to determine the degree of crosslinking in rubbery materials (Zhao et al., 2002).

In order to improve the adhesion between carbon nanotubes and natural rubber at the interface, carbon nanotubes have been superficially modified. Sui et al. (2008) observed that after being treated with acid and ball milling, CNTs dispersed well in the rubber matrix and interfacial interaction between them was improved. The vulcanization times, scorch and optimum cure time decreased and the maximum torque increased after adding acid treated and ball milled CNTs into natural rubber (NR). By adding the treated CNTs, comprehensive performance of the resulting nanocomposites achieved a considerable increase compared to neat natural rubber and carbon black/natural rubber composites.

### **2.2.3 Modification of carbon nanotube**

Due to their exceptional mechanical, thermal and electrical properties, in addition to their low density with respect to the class of organic and inorganic tubes, carbon nanotubes (CNTs) are extremely promising for the development of high performance nanostructured materials. Since their discovery in 1991 the research in this exciting field has been in continuous evolution. With most of the research focused on the assessment of the CNT properties and the development of advanced structural composites based on CNTs (Iijima and Ichihashi, 1993). However, the incorporation of nanotubes is not a trivial task mainly if a good dispersion is mandatory to maximize the advantage of nanotube reinforcement. As deposited CNTs can be dispersed in common solvents by sonication, but they precipitate when this treatment is switched off. In order to overcome this problem, it was demonstrated the possibility to functionalized the CNTs.

Chemical modification is not a new tool to enhance the compatibility between reinforcements and matrix, in as much as chemical attack and graft have been used in

natural fibers, synthetic fibers and particles (Wu et al., 2008). However the carbon nanotube nanocomposite field is very recently and chemical functionalization offers an important tool in order to improve interface and reach the amazing properties that carbon nanotubes can provide. Moreover although different researches have taken pan in this field, it is needed to understand the possible interactions in order to control and to improve the interface between carbon nanotubes and polymer matrix. The recent results in chemical modification of carbon nanotubes to incorporate these materials to polymer are promising and could be the way to form strong and functional new advanced materials. It has been proposed that by inserting a functional group on to the surface of CNTs using oxidation process, the CNT-polymer composites “link” can be improve. Jia et al. (1999) suggested that the initiator opens the  $\pi$  bonds found in CNTs and, in this way, CNTs take part in the polymerization. However have been signed on that although opening  $\pi$  bonds in CNTs to join them with other chemical groups has been proposed, oxidation provides more possibilities to bond the nanotubes with the matrix, due to reactive chemical groups such as carboxyl (COOH) and carbonyl (C=O) which are found on the tip and on the wall surface.

Other recent paper (Gojny et al., 2003) have shown that carboxyl-terminated carbon nanotubes treated with amines and incorporated to epoxy matrix have better interaction than those that were not treated chemically, showing an important improvement in the interface links between these two materials. In this study TEM pull out test were developed showing a better interaction due to chemical groups on CNTs surface. Other authors have developed in situ functionalized MWNTS (f-MWCNTs) in phenoxy composites by melt mixing with 1-(aminopropyl) imidazole (Goh et al., 2003). In this research the composites

with more than 4.8 wt % show higher storage modulus than the polymer matrix, however the behavior in high temperature is not common in these materials, in as much as f-MWCNTs lie to increase the modulus when normally the polymer matrix lie to flow. In this research the modulus at high temperature is diminished with the incorporation of in situ functionalized nanotubes. Liu L. and D. Wagner (2005) recently produce two carbon nanotubes polymer nanocomposites developed with two types of epoxy resins using functionalized MWNT (f-MWNT) and MWNTs. f-MWNTs consisted of carboxyl terminated nanotubes. Viscosity was a determined point in the synthesis of these composites, in as much as better dispersion was reached in rubbery epoxy resin than in glassy epoxy. However in both cases functionalized carbon nanotube nanocomposites present better tensile modulus than those produced with MWNTS and the only resins, using 1 wt % of nanotubes. In addition very good impact properties were reached when functionalized nanotubes were incorporated into epoxy resin.

### **2.3 NATURAL RUBBER**

Natural rubber has been known to the inhabitants of South America for centuries. Christopher Columbus is considered to be the first European to discover it, during his second voyage in 1493-6. By the end of eighteen century, rubber became very popular in the western. During that time, Europe and America were using few tons of rubber per year. However the productions of rubber products were restricted due to the difficulty of processing the rubber. Moreover, natural rubber tends to turned sticky in hot weather and stiffened in the cold (Morton, 1987).