THE EFFECT OF SURFACE MODIFICATION OF MULTI-WALLED CARBON NANOTUBES ON PROPERTIES OF SILICONE RUBBER COMPOSITES

CHUA TZE PING

UNIVERSITI SAINS MALAYSIA

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THE EFFECT OF SURFACE MODIFICATION OF MULTI-WALLED CARBON NANOTUBES ON PROPERTIES OF SILICONE RUBBER COMPOSITES

by

CHUA TZE PING

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TABLES OF CONTENTS

CHAPTER 1 – INTRODUCTION

CHAPTER 2 – LITERATURE REVIEW

CHAPTER 3 – MATERIALS AND METHODS

CHAPTER 4 – RESULTS AND DISCUSSION

CHAPTER 5 – CONCLUSION AND RECOMMENDATION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

3APTES	3-aminopropyltriethoxysilane
ASTM	American Society for Testing and Materials
CNTs	Carbon nanotubes
CTE	Coefficient of thermal expansion
D-MWNTs	Dipheny-lcarbinol modified multi-walled carbon nanotubes
DMA	Dynamic mechanical analyzer
EDS	Energy dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared
M100	Modulus at 100% elongation
MWNTs	Multi-walled carbon nanotubes
PDMS	Polydimethylsiloxane
SD-MWNTs	Silanized diphenylcarbinol modified multi-walled carbon nanotubes
SEM	Scanning electron microscope
Si	Silicon
SWNTs	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
TMA	Thermomechanical analyzer
TGA	Thermogravimetric analysis
TIM	Thermal Interface Materials
U-MWNTs	Unmodified multi-walled carbon nanotubes
UV-vis	Ultraviolet visible

LIST OF SYMBOLS

Co	Cobalt
I_v	Resultant current
m_f	Weight of filler
m_m	Weight of matrix
Mo	Molybdenum
m_T	Total weight of mixture
ρ_f	Density of filler
ρ_v	Volume resistivity
R_v	Volume resistance
V_f	Filler volume fraction
V_v	Voltage potential
σ	Electrical conductivity
Si	Silicon
T_g	Glass transition temperature

LIST OF APPENDICES

LIST OF PUBLICATIONS AND SEMINARS

Journals

		Page
1	Chua, T P; Mariatti, M; Azizan A and Rashid A A. (2009) Surface functionalization of multi-walled carbon nanotubes via electron reduction of benzophenone by potassium metal. Journal of Alloys and Compounds, 480, p.534-536. *(Impact Factor: 1.510)*	131
2	Chua, T P; Mariatti, M; Azizan A and Rashid A A. (2010) Effects of surface-functionalized multi-walled carbon nanotubes on the properties of poly(dimethyl siloxane) nanocomposites. Composites Science and Technology, 70, p.671-677. *(Impact Factor: 2.533)*	132

Seminars

1	Chua, T P; Mariatti, M; Azizan A, Rashid A A and Sim, L C. (2008) Electrical and tensile properties of multi-walled carbon nanotubes filled polydimethylsiloxane nanocomposites. In: 8th National Symposium on Polymeric Materials, 26th-27th November 2008, Penang. Malaysia. P24, p.65.	133
2	Chua, T P; Mariatti, M; Azizan A and Rashid A A. (2009) Thermal properties of functionalized multi-walled carbon nanotube/poly(dimethylsiloxane) nanocomposites. In: 11th International Conference on Electronic Materials and Packaging (EMAP), 1st-3rd December 2009, Penang. Malaysia: IEEE-CPMT. p.60	134

KESAN PENGUBAHSUAIAN PERMUKAAN NANOTIUB KARBON DINDING BERBILANG KE ATAS SIFAT KOMPOSIT GETAH SILIKON

ABSTRAK

Dalam kajian ini, getah silikon jenis poli(dimetilsiloksana) dipilih sebagai matriks untuk penyediaan bahan terma antara muka (TIM) kerana ia senang diproses, lengai kepada serangan bahan kimia, tidak toksik dan mempunyai kestabilan terma yang tinggi. Dua jenis nanotiub karbon dinding berbilang (MWNTs), iaitu diubahsuai oleh kumpulan difenilkabinol (D-MWNTs) dan D-MWNTs dirawat oleh silana (SD-MWNTs) dihasilkan dengan rawatan kimia. D-MWNTs dihasilkan dengan penurunan satu elektron benzofenon oleh logam kalium dan SD-MWNTs dihasilkan dengan merawat D-MWNTs dengan 3-aminotrietoksisilana (3APTES). Raman dan UV-vis spectroskopi mendedahkan kehadiran sisi dinding kovalen bagi sampel D-MWNTs. Analisis spektroskopi inframerah jelmaan fourier (FTIR) dan spektroskopi penyerakan tenaga (EDS) digunakan untuk mengesahkan kehadiran difenil-kabinol dan silana atas permukaan D-MWNTs and SD-MWNTs. Mikroskopi elektron penghantaran (TEM) menunjukkan sisi dinding bagi D-MWNTs dan SD-MWNTs diselaputi oleh lapisan yang tidak seragam. Kajian terhadap aplikasi MWNTs yang telah diubahsuai; D-MWNTs dan SD-MWNTs dalam matriks PDMS menunjukkan cantuman molekul silana ke atas D-MWNTs, ini meningkatkan penyerakan MWNTs dalam matriks PDMS, ini seterusnya meningkatkan sifat terma, mekanikal dan mekanikal dinamik jika berbandingkan dengan komposit yang terisi U-MWNTs. Secara am, dengan penambahan 1.5 % isipadu SD-MWNTs dalam matriks PDMS, kekonduksian haba meningkat masing-masing sebanyak 123% dan 41% berbanding dengan PDMS tulen dan komposit dengan 1.5 % isipadu U-MWNT/PDMS. Secara ringkasnya, peningkatan interaksi antara pengisi dan matriks meningkatkan kestabilan haba, modulus simpanan dan kekuatan tensil bagi komposit MWNTs dimodifikasi dalam matriks PDMS.

THE EFFECT OF SURFACE MODIFICATION OF MULTI-WALLED CARBON NANOTUBES ON PROPERTIES OF SILICONE RUBBER COMPOSITES

ABSTRACT

In the present study, silicone rubber type poly(dimethylsiloxane) (PDMS) was chosen as a matrix for Thermal Interface Materials (TIM) due to its ease of processing, inert to chemical attack, non-toxic and high thermal stability. Two types of modified multi-walled carbon nanotubes (MWNTs), which are diphenylcarbinol modified MWNTs (D-MWNTs) and silanized diphenylcarbinol modified MWNTs (SD-MWNTs) were produced by chemically treatment. D-MWNTs were prepared by one electron reduction of benzophenone by potassium metal and SD-MWNTs were prepared by treated D-WMNTs with 3-aminopropyltriethoxysilane (3APTES). Raman and UV-vis spectroscopies reveal the presence of covalent sidewall functionalization for sample D-MWNTs. Fourier transform infrared spectroscopy (FTIR) and energy dispersion spectroscopy (EDS) analysis confirmed the presence of diphenyl-carbinol and silane on the surface of the D-MWNTs and SD-MWNTs. Transmission electron microscopy (TEM) indicates that the side wall of the D-MWNTs and SD-MWNTs are covered by non-uniform layer. Studies on the application of modified MWNTs; D-MWNTs and SD-MWNTs in PDMS matrix show that the grafting of silane molecules onto D-MWNTs improves the dispersion of MWNTs in PDMS matrix; this subsequently enhances the thermal, mechanical and dynamic mechanical properties as compared to composites containing U-MWNTs. In general, with the application of 1.5 vol.% SD-MWNTs in PDMS matrix, thermal conductivity increase 123% and 41% compared to neat PDMS and

1.5 vol.% U-MWNT/PDMS composites, respectively. In short, improvement in thermal stability, storage modulus and tensile strength of modified MWNTs in PDMS matrix are due to an increase interaction between the fillers and the matrix.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Today, electronic products tend to be miniaturized, light weighted and multi-functional. This will make the heat generation occurring inside the devices has become more serious. So, thermal management is widely recognized to be an important aspect of computer design, with device performance being significantly affected by temperature. By increasing power densities and decreasing transistor dimensions in electronic devices are hallmarks of modern computer chips. Both trends are increasing the heat generated within the chip and surrounding packaging (Schelling et al., 2005). Heat dissipation is the most critical problem that limits the performance, power, reliability and further miniaturization of electronic devices (Grujiric et al., 2005; Shaikh et al., 2007). Thermal management of multi-functional electronic devices is very important for packaging of the products. Ineffective dissipation of the thermal energy, as a small difference in the operating temperature difference in the order of 10-15 ^{o}C could result in a twofold reduction in the lifespan of the device (Viswanath et al., 2000). Recent studies show that the carbon nanotubes (CNTs) polymer composites has excellent conductive properties and is one of materials which can be used for production of miniature electronic devices managing heat transfer (Song and Youn, 2006).

Polymers such as plastic and elastomer are used in the electronic packaging materials as electrical insulator and have extremely low thermal conductivity compared to ceramic and metallic materials. Therefore, polymer materials are necessarily to be filled with high thermal conductivity fillers to enhance the thermal conductivity capability. A thermal interface material (TIM) is the materials used in the electronic packaging which was effectively worked as heat conduction to dissipate heat from electronic devices (Prasher, 2006). There are various form of TIM such as thermal greases (He, 2005), elastomeric thermal pads (Mu and Feng, 2007), and phase change materials (Nayak et al., 2006). Elastomeric thermal pads are TIM which most widely used in cooling electronic devices. Poly(dimethylsiloxane) is an organosilicone compound and also known as silicone rubber. It is the most widely used silicone rubber in electronic packaging field. Its unique properties including low chemical reactivity, usability over wide temperature range (from -100 ^{o}C up to +100 ^{o}C), highly flexibility, resistance to ozone, and essentially non-toxic nature (Lötters et al., 1997).

1.2 Problem Statement

Since the discovery of carbon nanotubes (CNTs) in 1991 by Ijima (Ijima, 1991), and the realization of CNTs unique physical properties, including mechanical, thermal and electrical, these properties have been extensively investigated by researchers in various fields such as chemistry, physics, materials science and electrical engineering (Kang et al., 2006). These properties make them attractive for applications in many scientific and technological fields such as electronic structure (Star et al., 2003) and polymer composites (Frogley et al., 2003). CNTs are considered to be the ideal thermal conductive agent because of the thermal conductivity itself. Thermal conductivity of single-walled CNTs (SWNTs) is 6000 Wm^{-1} K^{-1} and multi-walled CNTs (MWNTs) is 3000 Wm^{-1} K^{-1} (Mamunya et al., 2008). The electrical percolation threshold was reported achieving the conductivity of 2 Sm^{-1} with 1.0 wt.% CNTs in epoxy matrices (Andrews and Weisenberger, 2004). According to the previous reports, by introducing small amounts of CNTs, electrical, mechanical and thermal properties of composites can be improved (Sandler et al., 2003; Allaoui et al., 2002; Kim et al., 2008).

However, some limitations still exist in fabricated CNT-polymer composites. For examples, the tendency of CNTs to aggregates and form much bigger agglomerate due to the high van der Waals forces of attraction (Fiedler et al., 2006) is one major problem. Beside, atomically smooth non-reactive surface of nanotubes built of rolled graphere sheets and lack in interfacial bonding between nanotubes and polymer matrix (Shen et al., 2007). This is major challenge to disperse CNTs and obtained good adhesion between CNTs and the polymer matrix.

Recent reports on the chemical compatibility and dissolution properties of CNTs have promoted interest in developing surface modifications of CNTs (Singh et al., 2006; Kim et al., 2007). The chemical modification of CNTs not only can improve the dispersion capability of CNTs in solvents and composites, but also can enhance the compatibility of CNTs with the composite matrix. It is commonly agreed that the surface modified CNTs with functional groups that are structurally similar to the polymer should have good compatibility and would lead to much better nanocomposites (Men et al., 2008). It has been reported that acid treatment of CNT could introduce carboxylic groups on the surface of CNTs and helps to improve the surface contact with polymer matrix (Yuen et al., 2007). Other possible surface modification treatments include laser ablation (Kokai et al., 2005) and plasma (Chou et al., 2008). Recent work reported on the chemical modification of MWNTs using silane coupling agents showed an improved of the properties of the polymer composites compared to unmodified MWNTs filled polymer composites (Ma et al., 2006; Zhou et al., 2008). Based on the literature studies, it is observed that most of the previous works are focused on the modification process of the MWNTs, only a few reports studied on the modification of CNT and their application as filler in polymer matrix.

The present studies focus on the surface modification of MWNTs, using one electron reduction of benzophenone by potassium metal and silanization using 3-aminopropyltriethoxysilane. Silane treatment is chosen in the present study due to possibility of 3APTES to form local siloxane-type environment at the surface of MWNTs, which is believed to promote the compatibility with the surrounding silicone rubber (PDMS). The characterizations of unmodified and functionalized MWNTs are carried out by FTIR, Raman, UV-vis, EDS and TEM. The functionalized MWNTs are then applied into the PDMS matrix and the properties were measured.

1.3 Research Objectives

Objectives of the present study are as follow:

1. To modify the surface of MWNTs with diphenyl-carbinol groups and silanization to diphenyl-carbinol-functional groups and to characterize the properties of the surface modified MWNTs
2. To compare the properties of unmodified and surface modified MWNTs (D-MWNTs) and (SD-MWNTs) in poly(dimethylsiloxane) matrix.

1.4 Scope of Research Project

In this study, two types of chemical surface modification for MWNTs, namely one electron reduction of benzophenone by potassium metal and silane functionalization by using 3-aminopropyltriethoxysilane (3APTES) are used. The samples are refered as unmodified MWNTs (U-MWNTs), diphenyl-carbinol-functionalized MWNTs (D-MWNTs) and silanized D-MWNTs (SD-MWNTs). Samples of 0.5, 1.0, 1.5, and 2.0 vol.% (with respect to the PDMS) of unmodified MWNTs (U-MWNTs) and 0.5, 1.0, and 1.5 vol.% of D-MWNTs and SD-MWNTs ware prepared, filler dispersion in the PDMS matrix are observed using optical microscope. Electrical percolation threshold for each of the fillers with their respective matrix is studied. Neat PDMS is also prepared using the same procedure for comparison purposes.

Various characterization techniques are employed to determine the optimum materials properties such as DMA, TMA, TGA, thermal conductivity analyzer and etc. Overall, the characterization tools used can be divided into thermal, chemical, morphology, mechanical, electrical tools.

1.5 Organization of Thesis

This thesis consists of five chapters. In the first chapter, a brief introduction on thermal performance challenges faced by the microelectronics industries was described. This chapter also includes some of the problem statements currently for CNTs. Next, the specific and measurable objectives of the present study are described, followed by the scope of the research work.

Chapter 2 consist literature review on various type of chemical surface modification for MWNTs and type of dispersion methods which will affect the MWNTs/PDMS composites properties.

Chapter 3 begins with a full list of materials and chemical used in this research alongside with their respective materials properties. Then, preparation procedures for surface modification of MWNTs and fabrication of MWNT/PDMS composites are described. Materials characterizations used in the present study have been described in this chapter.

Chapter 4 describes and discusses the characterization results of MWNTs after surface modification and MWNT/PDMS composites in details. Overall, Chapter 4 is subdivided into two parts, with the first part describing the chemical, morphology and thermal result for surface modified MWNTs, which includes FTIR, thermal stability, Raman spectra and MWNTs morphology. Second part, describes the thermal, mechanical and electrical of MWNTs/PDMS composite, which include its thermal stability, CTE, storage modulus, tan delta, tensile strength, elongation at break. Also studied in the second part is the thermal and electrical conductivity of the MWNTs/PDMS composites.

Finally, in Chapter 5, the conclusions from this research are listed down along side with recommendations for future studies in this related field.

CHAPTER 2

LITERATURE REVIEW

2.1 Silicone Rubber

The first organosilicon compound was discovered in year 1863 by Charles Friedel and James Crafts, which is tetraethylsilane by reaction of tetrachlorosilane with diethylzinc (Lynch, 1978). Silicone rubbers are semi-inorganic polymers (polyorganosilanes) (Ebnesajjad, 2008) and also classified as organosilicon compounds It also contains "backbone" silicon-oxygen linkages as seen in Figure 2.1, which is the same bond that found in quartz, glass and sand. Silicone rubbers can be in fluid, elastomeric, or resinous, depending on the types or organic groups on the silicone atoms and the extent of cross-linkage between polymer chains (Ebnesajjad, 2008).

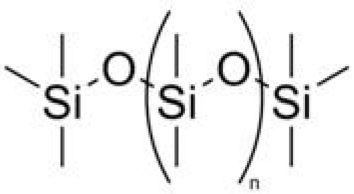


Figure 2.1: Silicon-Oxygen bond (Wikipedia, 2009)

Silicone rubbers are formed via repeated alternating silicon to oxygen atoms and contain no unsaturation in their backbone (Lynch, 1978). Unsaturation or double bond in an organic polymer backbone (Figure 2.2) is an area of chemical activity where vulcanization can occur. At the same time, this area is prone to degradation by ultra-violet (UV), ozone, corona, heat and others ageing factor (Morton, 1999 & Sam, 2007). Without unsaturation in the silicone rubbers backbone, the rubber remain flexible despite the exposure to high or low temperatures, weather, moisture, oxygen, ozone, or UV radiation (Ebnesajjad, 2008).

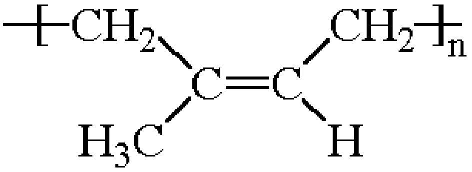


Figure 2.2: Chemical structure of cis 1,4- polyisoprene (Macrogalleria, 2010)

Their applications are numerous and varied. Silicone rubber are applied where organic materials (based on carbon) can not withstand exposure to the environmental conditions, superior reliability is required, or their durability gives them economic advantages (Ebnesajjad, 2008).

Compare to other organic rubbers, silicone rubber has a very low tensile strength. For this reason, care is needed in designing products to withstand even low imposed loads. However, silicone rubbers offer good resistance to extreme temperatures, being able to operate normally from -55°C to 300°C. The silicone rubbers own their high heat stability from the strong silicon-oxygen-silicon bonds (Lynch, 1978). At the extreme temperatures, the tensile strength, elongation, tear strength and compression set can be far superior to conventional rubbers although still relative low to other materials (Ebnesajjad, 2008).

Silicone rubber is classified into two categories namely, room temperature vulcanizing (RTV) and high temperature vulcanizing (HTV) silicone rubber. RTV silicone rubber is supplied in either liquid or paste form and is based on polymers of intermediate molecular weight and viscosities. Polymer viscosity for RTV was in the range of 0.1-20 Pascal sec (Pa.s) and chain length (number of SiO_2 units) lower than 800. RTV silicone rubber is available in two types, namely one part and two parts. The curing reaction of one part silicone rubber is the condensation cure type, which cured when exposed to moisture. On the other hand, the two part silicone rubber consists of one part of resins and the other part consist catalyst which is used to initiate cross-linking. HTV silicone rubbers are mainly so-called solid silicone rubbers. They have a very high viscosity in the uncured state and appear as solids. Unlike RTV silicone rubber, HTV silicone rubber is based on high molecular weight polymer gums with corresponding molecular weights between 500,000 to 1,000,000. Polymer viscosity of HTV silicone rubber is 20,000 Pa.s and chain length (number of SiO_2 units) 6000 (Jerschow, 2001).

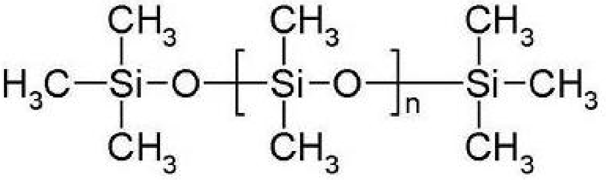
Silicone rubbers system vary significantly in their physical properties as a result of the degree of cross-linkage and the type of radical (R) within the monomer molecule. In the regard, the chief radicals are methyl, phenyl and vinyl group (Ebnesajjad, 2008).

2.1.1 Poly(dimethylsiloxane)

Poly(dimethylsiloxane) (PDMS) occasionally call dimethicone is a common silicone rubber and is the most widely used silicon-based organic polymer (Lau et al., 1998). These silicon-based organic polymers are typically the most cost-effective to produce and generally yield good physical properties in silicone elastomers and gels. The chemical formula for PDMS is $(CH_3)_3SiO[SiO(CH_3)_2]_nSi(CH_3)_3$, where n is the number of repeating monomer

$[SiO(CH_3)_2]$ units. The PDMS is manufactured in multiple viscosities, ranging from a thin pourable liquid (when n is very low), to a thick rubbery semi-solid (when n is very high) (Lynch, 1978). It consists of methyl side groups on silicon-oxygen-silicon-oxygen chains as seen in Figure 2.3. It is optically clear, and is generally considered to be inert, non-toxic and non-flammable.

PDMS is very flexible due to large bond angles and bond lengths when compared to those found in more basic polymers such as polyethylene. For example, a C-C backbone unit has a bond length of 1.54 Å and a bond angle of 112˚, whereas the polysiloxane backbone unit Si-O has a bond length of 1.63 Å and a bond angle of 130˚. The polysiloxane backbone differs greatly from the basic polyethylene backbone, yielding a much more flexible polymer. Due the bond lengths are longer, PDMS can easily change the conformation, forming a flexible material (Silicone rubber, 2009).



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Figure 2.3: Chemical structure of polydimethylsiloxane (DowCorning, 2009)

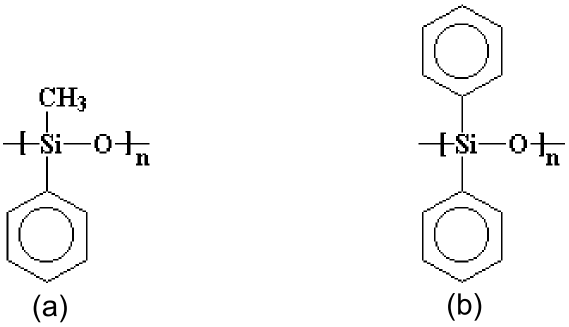
Synthesis of silicone rubber is quite amazing due to the fact that one of its precursors is silicone metal. The process is briefly described as (Lynch, 1978): sand or silica is reduced to the elemental form of silicon, Si. After that, Si is mechanically ground and reacted with methyl chloride in the presence of copper, Cu at 300°C. This results in the combination of methyl chlorosilanes (mono, di and tri).

Dimethylschlorosilane is separated out via distillation. Dimethylchlorosilanes are hydrolyzed to form silanols that rapidly condense to form linear siloxanes and cyclic. These linear siloxanes are exposed to potassium hydroxide, KOH to form cyclic dimethyl tetramer (D4). D4 is polymerized in the presence of strong base like KOH where the ring opens for chain formation. Inhibitors are used to terminate the process.

During the polymerization, this reaction release potentially hazardous hydrogen chloride gas (Lynch, 1978). So for medical uses, process is developed where the chlorine atoms in the silane precursor are replaced with acetate groups, so that the reaction product of the final curing process is nontoxic acetic acid (vinegar). As a side effect, the curing process is also much slower in this case.

2.1.2 Phenylsilicone

Phenyl silicone system contains diphenyldimethylpolysiloxane copolymers. The steric hindrance of the large phenyl groups significantly prohibits high concentrations of diphenyl units on the polymer chain. The phenyl functionality also boosts the refractive index of the polymers and silicone systems that use these polymers. Silicone polymers with diphenyl functionality are used for biophotonic applications where higher-refractive-index materials can be used to create a thin lens (e.g., intraocular lenses). Devices with several layers of diphenyl elastomer systems may be created to control the release rates of certain drugs. Figure 2.4 shows a typical structure for a methyl phenyl silicone.



(a) (b)

Figure 2.4: Type or phenylsilicone structure: (a): Polymethylephenylsiloxane and (b) Polydiphenylsiloxane (Thermosetting Resins, 2009).

2.1.3 Flourosilicone

Fluorosilicone are based on trifluoropropylmethylpolysiloxane polymers and are used for applications that require fuel or hydrocarbon resistance. Flourosilicones are a unique family of elastomers that can survive where most conventional materials fail, including applications such as jet fuel exposure, gasoline/diesel exposure, engine oils and most solvents and chemicals and only has little effect on physical properties, causing only slight swelling. The trifluoropropyl group contributes a slight polarity to the polymer, resulting in swell resistance to gasoline and jet fuels (Silastic®, 2000). However, polar solvents such as methyl ethyl ketone and methyl isobutyl ketone—may significantly affect fluorosilicones. Although some fluorosilicones contain 100% trifluoropropylmethylpolysiloxane repeating units, other systems contain a combination of the fluorosiloxane units and dimethyl units to form a copolymer. Adjusting the amount of trifluoropropylmethylsiloxane units in the polymerization phase provides optimal performance in specific applications (MDDI, 2009). Figure 2.5 shows a typical structure for a fluorosilicone. Flourosilicone rubber products are used in many industries, from automotive and aerospace to chemical and petroleum manufacturing (Silastic®, 2000).

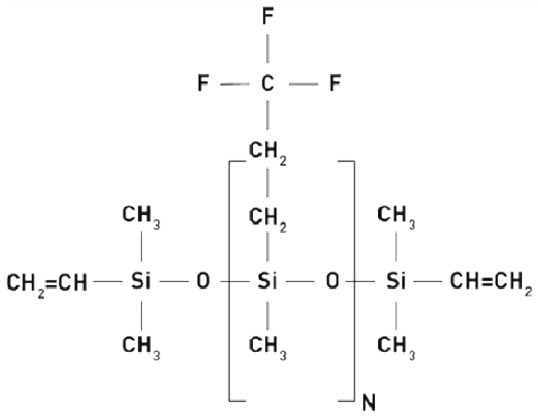


Figure 2.5: Typical structure for a methyl flourosilicone (MDDI, 2009)

2.2 Cure Systems for Silicone Rubber

Cure system of silicone rubber is very important to achieve a good balance of tack, adhesion, cohesive strength and mechanical properties. Cure in the crosslinking mechanism that builds viscosity and give silicone their desired properties. There are two primary cure mechanisms for silicone rubber. Peroxide-cure system also known as free radical cure is typically silicone resin and polymer dispersed in solvent used with peroxide curing agent. Platinum-cure systems also known as addition cure system is typically silicone resin, polymer and crosslinker dispersed in solvent plus a platinum catalyst.

2.2.1 Peroxide-Cure System

This system is the oldest crosslinking chemistry used for silicones. The catalyst most typically used with silicone rubber is organic peroxide. Different organic peroxides decompose (become reactive) at different temperature and different rates (Lynch, 1978). The catalyst most typically used with silicone rubber is benzyl peroxide (Facts, 2005), because it can be used to vulcanize all types of silicone and fluorosilicone compound at low temperature (Lynch, 1978). Cure is a two-step process that requires the use of multi-zone oven to remove the solvent before curing the silicone rubber. Table 2.1 lists a number of peroxide curing agents along with their properties, application and commercial names.

Peroxide cure employs a free-radical cure mechanism which is shown in Figure 2.6. The chemistry utilized free radicals which is generated by organic peroxide that decomposed at elevated temperatures (Malczewski et al., 2003) and radicals will capture hydrogen atoms from methyl groups of adjacent linear molecules, thus causing crosslinking reaction (Lynch, 1978). Peroxide-cure will produce by-products.

$$R^{\cdot} + CH_2 = CH - Si \equiv \rightarrow R - CH_2 - CH^{\cdot} - Si \equiv$$

$$\begin{aligned} & RCH_2 - CH^{\cdot} - Si \equiv + CH_3 - Si \equiv \\ & \quad \rightarrow RCH_2 - CH_2 - Si \equiv + \equiv Si - CH_2^{\cdot} \end{aligned}$$

$$\begin{aligned} & \equiv Si - CH_2^{\cdot} + CH_2 = CH - Si \equiv \\ & \quad \rightarrow \equiv Si - CH_2 - CH_2 - CH^{\cdot} - Si \equiv \end{aligned}$$

$$\begin{aligned} & \equiv Si - CH_2 - CH_2 - CH^{\cdot} - Si \equiv + \equiv Si - CH_3 \\ & \quad \rightarrow \equiv Si - CH_2 - CH_2 - CH_2 - Si \equiv + \equiv Si - CH_2^{\cdot} \end{aligned}$$

$$2 \equiv Si - CH_2^{\cdot} \rightarrow \equiv Si - CH_2 - CH_2 - Si \equiv$$

Figure 2.6: Schematic illustration of silicone crosslinking using radical (Malczewski et al., 2003)

Table 2.1: Organic peroxide curing agents for silicone rubber compounds (Lynch, 1978).

Peroxide	**Commercial Grade**	**Form**	**Active Conc.**	**% Active Oxygen**	**Recommended Use**	**General Cure Temp. (^{o}F)**
2,4-Cl_2 Benzoyl Peroxide	Cadox TS (50)^3 Luperco CST ^{2}	Paste Paste	50% 50%	2.1	Hot Air vulcanization	220-250
Benzoyl Peroxide	Cadox BSG^3 Uperco AST^2 Cadox 99^3 (200 Mesh)	Paste Paste Powder**	50% 50% 99%	 3.15 6.3	Molding, Steam, CV Molding, Steam, CV Molding, Steam, CV,solution coating	240-280
Dicumyl Peroxide*	DiCup 40C^1 DiCup R^1	Powder Crystalline	40% 99%	2.4 5.9	Thick section and carbon black stocks, CV	320-340
2,5-bis(*t*-butyl peroxy)* 2,5-Dimethyl hexane	Varox* Luperco 101 XL^2 Lupersol 101^2 Varox (Liquid)^5	Powder Powder Liquid Liquid	50% 50% 95% 95%	 5.5 11.0	 Bonding Thick section and carbon black	320-350
t-Butyl perbenzoate	Same^2	Liquid	100%	7.8	General for high activation – sponge temperature	290-310
Ditertiary butyl* peroxiode	Same^{2,7} CW-2015^6	Liquid Powder	100% 15%	10.6 1.6	Thick section and carbon black	340-360
Cumyl,*t*-Butyl peroxide* α,α-‘-bis(*t*-Butyl peroxy) diisopropyl benene	Trigonox T Vul-Cup 40KE^1 Perkadox 14/40	Liquid Powder Powder	95% 40% 40%	7.2 3.8	Molding, Steam, CV Molding, Steam, CV	300-340 340
1,1 di-*t*-Butyl peroxy* 3,3,5-trimethyl cyclohexane	Trigonox 29/40	Powder	40%	4.2	Molding, Steam, CV	275-325
t-Butylperoxy* Isopropyl carbonate	B.P.I.C.^{4}	Liquid	100%	9.1	Molding and CV	280-300

*Normally limited to use with vinyl-containing base polymer

**Use powder, not paste, for self-bonding stocks

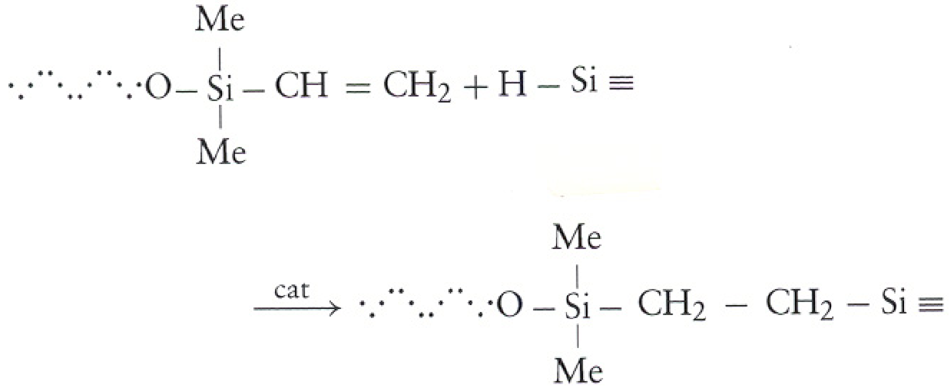
Manufacturers:

[1] Hercules Inc. [2] Lucidol Div., Pennwalt Corp. [3] Noury Chemical Corp. [4] PPG Industries [5] R.T. Vanderbilt [6] Harwick Standard Chemicals [7] Shell Chemical Corp.

Courtesy, Silicone Products Dept., General Electric.

2.2.2 Platinum-cure System

Platinum (Pt) cure required the use of platinum catalyst to develop silicone rubber properties. This process is also known as additional cure system. Changing the catalyst level has little impact on the cured silicone rubber properties (Facts, 2005). Cure is a one-step process where silicone rubber can be cured in vented, continuous oven at temperature as low as 80°C (Facts, 2005). Pt-cure mechanism is shown in Figure 2.7 has no by-products. However, Pt-cure catalyst costs are higher than for peroxide-sure system, which may be reflected in product prices (Malczewski et al., 2003). Cure systems comparison between Pt-cured system and peroxide-cured system are shown in Table 2.2 and typical physical properties for different cured systems are shown in Table 2.3.



$$\cdots O-\overset{Me}{\underset{Me}{Si}}-CH=CH_2+H-Si\equiv \xrightarrow{cat} \cdots O-\overset{Me}{\underset{Me}{Si}}-CH_2-CH_2-Si\equiv$$

Figure 2.7: Schematic illustration of silicone crosslinking by addition (Malczewski et al., 2003)

Table 2.2: Cure system comparison (Facts, 2005)

Peroxide cure	Platinum cure
Very good high-temperature properties	Good high-temperature properties
Peroxide catalyst not easily poisoned	Platinum catalyst easily poisoned
Properties can be modified by manipulatuing peroxide level	Properties cannot be modified by manipulating platinum level
Good tack and adhesion	Superior tack and adhesion
Often required priming	May not required priming
Must be cured at high temperature	Can be cured at low temperatures
Requires multi-zone oven	Can be cured in single-zone oven

Table 2.3: Comparison of typical physical properties representative Silastic® Peroxide[a]-cured and Pt-cured[b] Elastomer (Malczewski et al., 2003)

Property	**Units**	**35-Durometer Elastomer**		**50-Durometer Elastomer**		**65-Durometer Elastomer**	
		Pt-cured	**Peroxide-cured**	**Pt-cured**	**Peroxide-cured**	**Pt-cured**	**Peroxide-cured**
Tensile Strength	**MPa**	9.84	8.21	10.16	9.41	7.94	7.59
Elongation	**%**	1171	971	903	596	890	590
Modulus at 200%	**MPa**	1.11	0.97	2.14	2.50	2.82	3.07
Tear Strength (die B)	**kN/m**	36.6	24.5	45.9	35.9	45.5	42.2

[a]Catalyzed with 2,4 dichlorobenzyl peroxide, 1% w/w. Post-cured 2 hours at 177°C
[b]Cured at 116°C for 10 minutes, no post-cure.

2.3 Carbon Nanotubes

In 1985, an unplanned experiment discover a new molecule make purely of carbon which known as ‘Buckyballs’ and these molecules comprise sixty carbon atoms arranged in soccer ball shape. What was discovered was not just a single new molecule, but an infinite class of new molecules of fullerenes. Each fullerene (C_{60}, C_{70} and C_{82} as shown in Figure 2.8) possesses the essential characteristic of being a pure carbon cage (Colbert, 2003). The fullerene molecule exists in discrete molecular form and consists of hollow spherical cluster of sixty carbon atom. Each molecule is composed of groups of carbon atoms that are bonded to one another to form hexagons and pentagonal geometry configurations (Sumanth, 2004; Thostenson et al., 2001).

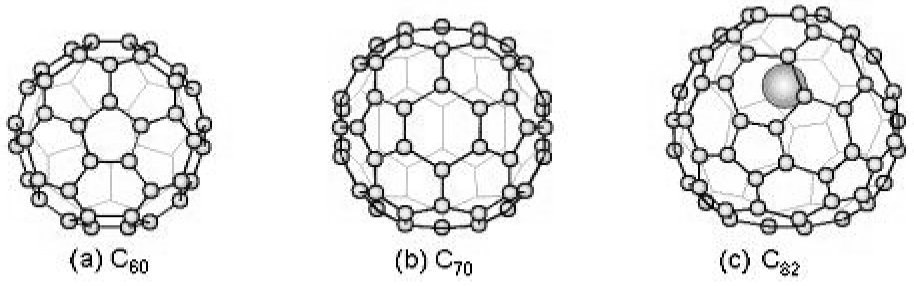


Figure 2.8: Types of fullerene: (a) C_{60}, (b) C_{70} and (c) C_{82} (Maruyama, 2009)

Carbon nanotubes are long cylinders of 3-coordinated carbon, slightly pyramidalized by curvature from the pure sp^2 hybridadization of graphene, toward the diamond like sp^3. A perfect tube is capped at both ends by hemi-fullerenes, leaving no dangling bonds (Gogotsi, 2006) as shown in Figure 2.9. Nanotubes have been constructed with length-to-diameter ratio of up to 28,000,000:1 (Zheng et al., 2004), which is significantly larger than any other material.

Figure 2.9: Carbon nanotube with both end capped by hemi-fullerenes (Friedrich *et al.*, 2005).

Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Structures comprising only one cylinder are termed single-walled carbon nanotubes (SWNTs), whereas multiwalled nanotubes (MWNTs) contain two or more concentric graphene cylinders (Grobert, 2007) which as shown in Figure 2.10.

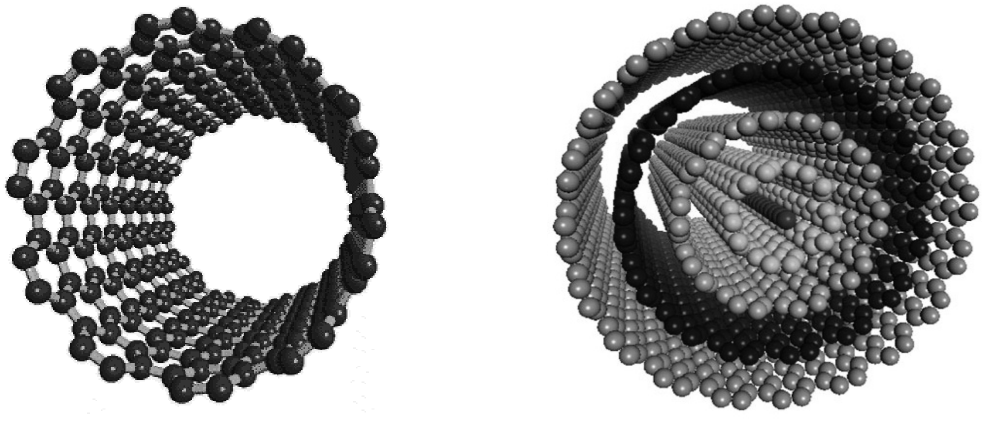

(a) (b)

Figure 2.10: Image of SWNT with one tube (Richter and subbaswamy, 2009) and image of MWNT with concentric tube (Physics, 2009)

Since the discovery of CNTs, there have been different techniques in producing them. The different methods to synthesize CNTs include arc-discharge (Wang et al., 2006; Zeng et al., 1998), laser ablation (Zhang et al., 1997; Kusaba and Tsunawaki, 2006) and chemical vapor deposition from hydrocarbon (Finnie et al., 2006; Andrew et al., 2006). In 1991, Iijima (Hsieh et al., 2006) first observed MWNTs through the electric arc discharge method (Dai, 2002). Laser ablation technique was reported by Iijima et al. (Colbert, 2003) in year 1993. During the synthesis of CNTs, impurities in the form of catalyst particles, amorphous carbon and non tubular fullerenes are also produced such that the nanotubes have to be purified to eliminate them. The electric arc discharge technique generally involves the use of two high purity graphite rods as the anode and cathode, the rods are brought together under helium atmosphere and the voltage is applied until a stable arc is achieved. The materials then deposits on the cathode to form a build up consisting of an outside shell of focused material and softer fibrous core containing nanotubes and other carbon particles (Shi et al., 2000; Zhao and Liu, 2004).

In laser ablation technique, laser is used to vaporize a graphite target held in a controlled atmosphere oven at temperature near 1200°C then condensed materials are then collected on a water cooled target. Both arc discharge and laser ablation techniques produce small quantities of CNTs with a lot of impurities (Lv et al., 2005; Zhang et al., 1997). Gas phase techniques are developed to overcome these limitations. Chemical vapor deposition (CVD) from hydrocarbons is a gas phase technique that utilizes hydrocarbon gases as the carbon source for production of CNTs. The CNTs are formed by the decomposition of carbon containing gas, the hydrocarbons pyrolize readily on surfaces when they are heated above 600°C - 700°C. This is continuous process as the carbon source is continuously replaced by flowing gas (Andrew et al., 2006).

These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. These exceptional properties of carbon nanotubes have been investigated for devices such as field-emission displays, scanning probe microscopy tips, and microelectronic devices (Thostenson et al., 2001).

2.3.1 Single-walled Carbon Nanotubes

Single-walled Carbon Nanotubes (SWNTs) are capped at each end, for example, by the two hemispheres of C_{60}, connected by a straight segment of tube, with only hexagonal units in its structure. Originally called 'buckytubes', they are now more commonly referred to as single-wall carbon nanotubes (SWNT) (Colbert, 2003). SWNT can be conceptualized as seamless cylinders rolled up from graphene rectangles as shown in Figure 2.11 or as cylindrical isomers of large fullerenes (Gogotsi, 2006). Most SWNTs have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer.

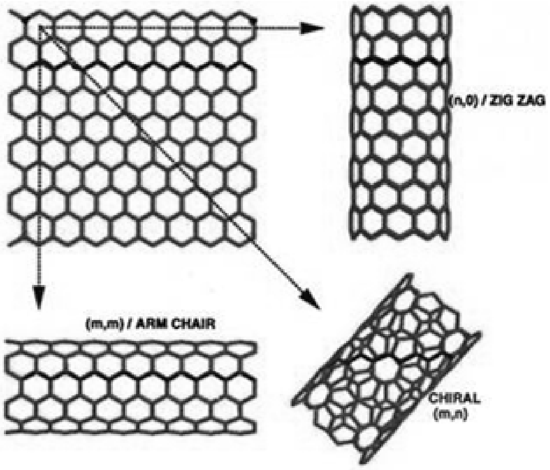


Figure 2.11: Schematic representation of the relation between nanotubes and graphenes (Ke, 2009).

Ideal SWNTs are classified according to three possible crystallographic configurations; zigzag, armchair, and chiral, depending on how the graphene sheet is rolled up. In the zigzag conformation, two opposite C-C bonds of each hexagon are parallel to the tube axis, whereas in the armchair conformation the C-C bonds are perpendicular to the axis. In all other arrangements, the opposite C-C bonds lie at an angle to the tube axis, resulting in a so-called helical nanotube that is chiral (Grobert, 2007). However, it can also be divided into three categories, including metal, narrow-gap semiconductor and moderate-gap semiconductor for its electronic property, based on graphene rolling direction (Hsieh et al., 2006) which shown in Figure 2.10. SWNTs properties are strongly dependent on their structure, e.g. for typical diameters, all armchair SWNTs and one-third of all zigzag nanotubes are metallic, the rest are semiconducting (Grobert, 2007).

SWNTs have unique properties, by rolling a graphene sheet to form a SWNT; the total energy of the nanotube is increased by the strain energy associated with the curvature of the nanotube, the strain energy increases with decreasing nanotube diameter. SWNTs have a tensile modulus that ranges from 270 GPa to 1 TPa and a tensile strength ranging from 11 to 200 GPa which is 10 to 100 times higher than the strongest steel at a fraction of the weight (Li et al., 2000; Lu, 1997). SWNTs have a very low density of ~1.3 g/cm^3, this is because of the hollow structure of SWNTs. SWNTs also exhibit exceptional thermal and electrical properties. SWNTs are thermally stable up to 2800ºC in vacuum. SWNTs thermal conductivity can be as high as 5000-8000 W/mK and is many times as high as that of diamond (900-2320 W/mK); these high values are due to the large phonon mean free paths present in SWNTs, the fact that their electric-current carrying capacity is 1000 times higher than that of copper wires (Thostenson et al., 2001). SWNTs have excellent mechanical and electrochemical properties. Incorporating SWNT into polymers at high loadings is difficult. SWNT have a wall one atom thick and diameters typically 1.4 nm but range 0.3–2 nm, are 200 nm length; grown by catalyzed chemical vapor deposition (CVD), cost purified is ~$500/g (Kang et al., 2006).

2.3.2 Multi-walled Carbon Nanotube

In 1991, the carbon nanotubes were successfully synthesized by Dr. Sumio Iijima, a Japanese electron microscope investigator in the fundamental research laboratory of NEC Company. They were found in the form of needlelike, hollow and multi-layered structures as shown in Figure 2.12 at the negative plate while being synthesized by the arc discharge method (Hsieh et al., 2006). MWNTs are essentially concentric single walled tubes, where each individual tube can have different chirality (Thostenson et al., 2001).There are two models which can be used to describe the structures of MWNTs. In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, e.g. a diameter 8 nm SWNT within a larger diameter 10 nm SWNT. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper (Gogotsi, 2006).

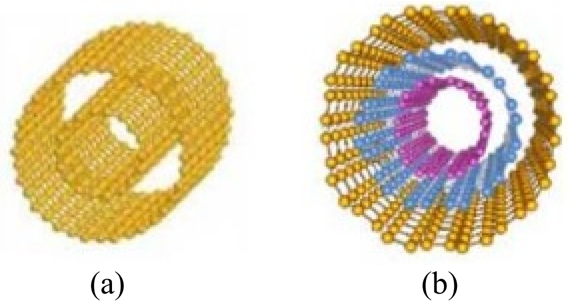

(a) (b)

Figure 2.12: Schematic representation two MWNTs consisting of (a) two and (b) three concentric graphene shells (Study, 2009)

The double walls CNT are a variation of MWNTs (Kang et al., 2006). Double-walled carbon nanotubes (DWNTs) must be emphasized here because they combine very similar morphology and properties as compared to SWNT, while improving significantly their resistance to chemicals. This is especially important when functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of DWNT or MWNTs, only the outer wall is modified.

The MWNTs do not have as high or varied properties, but are easier to process because of their large diameter of 10–50 nm, and 1–50 µm length, grown by CVD; also bamboo MWNT 20–40 nm diameter, 1–20 µm length, internal closeouts, ~$150/g. The double walls CNT are a variation of MWNT. Their diameters is 2–4 nm, 1–50 µm length, grown by CVD of methane over cobalt nanoparticles supported on porous MgO nanoparticles (Kang et al., 2006). The MWNTs broke in the outermost layer ("sword-in-sheath" failure), and the tensile strength of this layer ranged from 11 to 63 GPa for the set of 19 MWNTs that are loaded. Analysis of the stress-strain curves for individual MWNTs indicate that the Young's modulus (E) of the outermost layer varies from 270 to 950 GPa (Yu et al., 2000). MWNTs thermal conductivity can be as high as 5000-8000 W/mK.

CNTs can be embedded into polymers to make light weight composites with exceptional properties for structural applications. The conductivity and dielectric properties of the polymers can be improved by the addition of CNTs in the polymers. Embedding SWNTs in the polymers increases the toughness of the polymer and at the same time does not change ductility. SWNTs show exceptional mechanical, electrical, and thermal properties that can be exploited as reinforcements for composite structures, in the case of MWNTs very weak van der Walls forces exist to link the individual graphene shells together, allowing the inner shells to rotate and slide freely. But the SWNTs prices are relatively higher than MWNTs. For this reason, MWNTs are desired for investigations of the structure/property relationships in CNTs/polymers composite. MWNTs can be functionalized to enhance its properties in CNT/polymers composites.

2.4 Composites Fabrication with Improved Material Properties

Several processing methods are available for producing CNT-polymer composites based on the polymer being used. For example, the most common solution processing method is unsuitable for polymers that are insoluble. For thermoplastic polymer, melt processing method is a common alternative. For thermosetting polymers such as epoxy, a hardener is used for curing. For insoluble and thermally unstable polymers, chemical processing is often used, which involves *in-situ* polymerization or covalent functionalization of CNTs with polymer molecules. Various CNTs-polymer composites have been fabricated to improve the material properties such as electrical conductivity, mechanical strength, radiation detection, optical activity, etc.

2.4.1 Electrically Conductive Composites

Many researchers have tried to incorporate CNTs in polymer matrix to tailor electrical properties which suitable for different applications such as for electronic goods, semiconductor components and circuit board, because different applications normally require specific levels of conductivity. For protection against electrostatic discharge, a low level of conductivity (i.e. high level of resistivity ranging from 10^4 – 10^8 ohm/cm) is enough whereas to protect against electromagnetic interference as well as to prevent the emission of interfering radiation, resistivity of $\leq 10^4$ ohm/cm is needed.

Niu et al. (2008) revealed two methods used for the preparation of mechanically strong yet electrically conductive polyvinylidene fluoride, (PVDF-CNT) composites. In solution methods, PVDS first dissolved in a solvent such as