

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING  
UNIVERSITI SAINS MALAYSIA

ALIGNING OF CARBON NANOTUBES WITH AN EXTERNAL ELECTRIC FIELD  
TO IMPROVE THERMAL CONDUCTIVITY OF POLYDIMETHYLSILOXANE  
NANOCOMPOSITES INTERFACE MATERIAL

BY

MIMI SYAHIRA BINTI MASRAFF

Supervisor: Prof. Dr. Zulkifli bin Ahmad

Dissertation submitted in partial fulfillment of the requirements for the degree of  
Bachelor of Engineering with Honours  
(Polymer Engineering)

Universiti Sains Malaysia

**JUNE 2018**

## DECLARATION

I hereby declared that I have conducted, completed and research work and written the dissertation entitled “Aligning of carbon nanotubes with an external electric field to improve thermal conductivity of polydimethylsiloxane nanocomposites interface material”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Name of Student: Mimi Syahira binti Masraff

Signature:

Date: 25 June 2018

Witness by

Supervisor: Prof. Dr. Zulkifli bin Ahmad

Signature:

Date: 25 June 2018

## **ACKNOWLEDGEMENTS**

I would like to thank my supervisor Prof. Dr. Zulkifli bin Ahmad for giving me the opportunity to conduct my final year project under his supervision. I really appreciated his guidance and mentorship throughout the duration of the project. He had always been there for me no matter how tough the situation might be and he always willing to share priceless knowledge and experiences with me. Without his supervision, this research work is impossible to be completed.

I would like to thank all the technical staffs in School of Materials and Mineral Resources Engineering for helping me with my research whenever I needed. They were always very helpful with their effort to teach and assist me on how to handle equipment and tools available in the laboratory. I would like to especially thanks Penchem Technologies Sdn Bhd for allow me to use their equipment to complete my testing. My subsequent gratitude also goes to Final Year Project Monitoring Committee for continuously guiding me in conducting my final year project.

I would like to thank and dedicate this thesis to my parents. Without their continuous love, encouragement, and advices, I would not have completed this thesis project. I would like to thank my siblings for keeping me entertained with their company.

Last but not least, I thank Allah SWT for His countless blessings, guidance and help.

## TABLE OF CONTENTS

<b>Contents</b>	<b>Page</b>
DECLARATION	ii
ACKNOWLEDGEMENTS	iii
CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF SYMBOLS	x
LIST OF ABBREVIATIONS	xi
ABSTRAK	xii
ABSTRACT	xiii
 <b>CHAPTER 1: INTRODUCTION</b>	
1 PREAMBLE	1
1.1 Problem Statement	6
1.2 Thesis Objectives	8
1.3 Thesis Outline	9
 <b>CHAPTER 2: LITERATURE SURVEY AND THEORETICAL BACKGROUND</b>	
2 INTRODUCTION	11
2.1 Thermal Management and Electronic Packaging	12
2.2 Materials for Electronic Packaging	14

2.2.1	Thermally Conductive Polymeric Composites	16
2.2.2	Polymer composites embedded with carbon-based fillers	20
2.3	Aligning Carbon Nanotubes to Improve Multifunctional Properties of PDMS Nanocomposites	24
2.3.1	Composites with aligned Polymer Fibers	26
2.4	Material	28
2.4.1	Material Selection	28
2.4.2	Matrix Materials	29
2.4.3	Filler Materials	33

## **CHAPTER 3 METHODOLOGY**

3	INTRODUCTION	37
3.1	Experimental	37
3.1.1	Materials	37
3.2	Methodology	39
3.2.1	CNT/PDMS nanocomposites fabrication	40
3.3	Condensation Polymerization of Polydimethylsiloxane	41
3.3.1	One-part RTV system	41
3.3.2	Two-part RTV Systems	42
3.4	Sample Characterization	42
3.4.1	Fourier transform infra-red spectroscopy	43
3.4.2	FESEM	43
3.4.3	Thermal conductivity	43
3.4.4	Thermal Mechanical Analysis (TMA)	43

## **CHAPTER 4: RESULTS AND DISCUSSION**

4	INTRODUCTION	45
4.1	Fourier Transform Infra-red Spectroscopy	45
4.2	Glass Transition Temperature	48
4.3	Coefficient of Thermal Expansion	53
4.4	Thermal Conductivity	56
 <b>CHAPTER 5: CONCLUSION</b>		
5	SUMMARY	65
5.1	Recommendations	67

## LIST OF TABLES

Table 2.1 Thermal Conductivity of some Polymers .....	19
Table 2.2 Thermal Conductivity of some Fillers .....	19
Table 2.3 Silicon and carbon bond rotational energy barriers (Liaubau, 1985, Stark et. al., 1982 and Myshlyaeva et. al., 1974) .....	31
Table 2.4 Comparison of silicon, carbon and oxygen radii (Noll, 1968 and Brook, 2000) .....	32
Table 3.1 The properties of materials used to produce CNT/PDMS composite .....	38
Table 3.2 Formulation of CNT-PDMS composites .....	40
Table 4.1 CTE comparisons at temperature below and above the $T_g$ . All values were extracted from the slopes in quasi-equilibrium cooling curves. ....	54

## LIST OF FIGURES

Figure 1.1 Conduction through TIM Filling Gap .....	2
Figure 1.2 Polymer Based Thermal Interface Material (TIM) in Various Form.....	3
Figure 1.3 Schematic diagrams for a) randomly oriented and b) aligned composite particles.....	8
Figure 2.1 Schematic diagram of an electronic packaging.....	15
Figure 2.2 Reaction scheme for platinum catalyzed PDMS curing.....	30
Figure 2.3 Schematic for SWNT and MWNT .....	34
Figure 4.2 $T_g$ of non voltage-assist CNT/PDMS composite and voltage-assist CNT/PDMS composites at varied degree.....	49
Figure 4.3 Schematic diagram of the relative microscale motions between nanofillers and the PDMS matrix .....	50
Figure 4.4 SEM micrographs of CNT/PDMS composite with 12.75 wt.% SWNTs at 5000X (a) 10 V (b) 20 V and (c) 30V.....	52
Figure 4.5 CTE of non voltage-assist CNT/PDMS composite and voltage-assist CNT/PDMS composites at varied degree.....	54
Figure 4.6 Change in thermal conductivity for non voltage-assist CNT/PDMS composite and varied voltage-assist CNT/PDMS composite.....	57
Figure 4.7 SEM images of non voltage-assist CNT/PDMS composites under 10000X	59
Figure 4.8 SEM images of 10 V voltage-assist CNT/PDMS composites under 10000X .....	59
Figure 4.9 SEM images of 20 V voltage-assist CNT/PDMS composites under 10000X .....	60

Figure 4.10 SEM images of 30 V voltage-assist CNT/PDMS composites under 10000X .....	60
Figure 4.11 Schematics images of polymer fibers in CNT/PDMS composites at different degree of CNTs dispersion and alignment a) no voltage-current b) 10V c) 20V d) 30V .....	61
Figure 4.12 Schematic of fillers forming conductive pathway in polymer matrix.....	63

## LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius
cm <sup>-1</sup>	Centimeter
g/L	Gram per Liter
g/mol	Gram per mol
mL	Millimeter
mm	Milimeter
Ppm/K	Part per million per Kelvin
s	Second
T <sub>g</sub>	Glass Transition Temperature
T <sub>m</sub>	Melting Temperature
W/mK	Watts per meter Kelvin
μL	Microleter

## LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflectance Fourier Transform Analysis
CNT	Carbon Nanotube
CNT/PDMS	Carbon Nanotube/Polydimethylsiloxane Composite
CPU	Control Processing Unit
MEMS	Microelectromechanical Systems
MMC	Metal Matrix Composite
PDMS	Polydimethylsiloxane
PMC	Polymer Matrix Composite
SEM	Scanning Electron Microscopy
TIM	Thermal Interface Material
TMA	Thermal Mechanical Analysis
VGCF	Vapor Grown Carbon Fiber

**MENJAJARKAN ZARAH-ZARAH KOMPOSIT DENGAN MEDAN  
ELEKTRIK LUARAN UNTUK MENINGKATKAN KONDUKSI TERMA  
BAHAN RUANG HUBUNG KAIT DARI POLIDIMETILSILOKSANA (PDMS)**

**ABSTRAK**

Kemajuan dalam industri semikonduktor mendorong kepada penghasilan komponen elektronik dengan peminiaturan dan peningkatan kapasiti kuasa yang akan mengakibatkan masalah pengurusan haba. Sebagai gerakbalas kepada perubahan ini, pencarian bahan pelbagai fungsi dengan keupayaan untuk mengalirkan haba yang efektif dan kekonduksian elektrik yang boleh disesuaikan menjadi semakin penting. Kajian ini mengkaji tentang kesan daya elektrik luaran dalam menjajarkan karbon nanotub untuk membina dan mencirikan polimer komposit dengan keupayaan untuk mengalirkan haba. Komposit CNT/PDMS telah disediakan dan daya elektrik luaran pada tahap berbeza telah diperkenalkan semasa proses pematangan untuk menggalakkan penjajaran karbon nanotub. Kemungkinan peningkatan konduksi elektrik dan haba dengan pengenalan daya elektrik luaran dan jajaran karbon nanotub telah diselidik. Ciri-ciri komposit juga telah diselidik merangkumi sifat fizikal, terma dan elektrik untuk memenuhi keperluan penggunaan bahan ini sebagai bungkusan elektronik. Keputusan eksperimen mendedahkan bahawa komposit yang telah disediakan menunjukkan sifat anisotropi dengan peningkatan konduksi elektrik dan haba yang sangat ketara pada arah daya elektrik.

**ALIGNING OF COMPOSITE PARTICLES WITH AN EXTERNAL ELECTRIC  
FIELD TO IMPROVE THERMAL CONDUCTIVITY OF  
POLYDIMETHYLSILOXANE (PDMS) THERMAL INTERFACE MATERIAL**

**ABSTRACT**

Advancements in the semiconductor industry have led to the miniaturization of components and increased power densities, resulting in thermal management issues. In response to this shift, finding multifunctional materials with excellent thermal conductivity and tailored electrical properties are becoming increasingly important. For this research thesis, the effect of an external electric field on aligning of carbon nanotubes was studied to develop and characterize thermally conductive polymer composites. A CNT/PDMS composite was prepared and an external electric field at various degrees was introduced during the curing to promote the carbon nanotubes alignment. The possibility of improving the thermal conductivity by introducing and aligning polymer fibers in the composites was investigated. The composites were characterized with respect to their physical, thermal, and electrical properties to propose possibilities of application in the electronic packaging industries. Experimental results reveal that the resulting nanocomposites exhibit anisotropic properties with significantly improved electrical and thermal conductivities in the alignment direction.

# CHAPTER 1

## INTRODUCTION

### 1 Preamble

At present, the density of electronic components is continuously increases with the ongoing miniaturization of electronic devices and products, as does the applied power. Miniaturization leads to advancements in wireless communications and portable systems such as smartphones, laptops, pocket calculators and electronic watches. In advance technology, reducing size and space requirements enhance the performance of nanotechnology and microelectromechanical systems (MEMS) specifically for military and aerospace applications (Ramsden, 2012). However, the high power density compacted in a component results in rapid heat generation. Overheating is one of the major challenges stood in the way of creating microelectronics. This typically caused by electrical loss. Leaked current locally warm the material and provide the passage of greater current and greater localized warming of material, leading to the failure of material (Seeber, 1998). Therefore, it is crucial to dissipate heat away from the components as soon as possible in order to keep their temperature below critical values and avert device from permanent damage.

Many approaches have been made in order to keep the temperature of an electronic component below its critical values and protect the device from permanent damage. Heat sink is one of the most conventional approaches used for thermal management of an electronic device. Typically, a heat sink is attached to a surface of semiconductor device, such as a central processing unit (CPU), so that heat is transferred from the semiconductor device to ambient air via the heat sink. When attaching the heat sink to the semiconductor device, respective surfaces of the device and heat sink are brought

into intimate contact with each other. However, as much as 99% of the respective surfaces are separated from each other by a layer of interstitial air, no matter how precisely the heat sink and the semiconductor device are manufactured. Therefore, thermal interface material is used to eliminate air gaps between the heat source and heat sink to improve heat flow (G.-L. Chen & Charles Leu, 2005). Fig. 1.1 shows conduction through thermal interface material (TIM) filling gap.

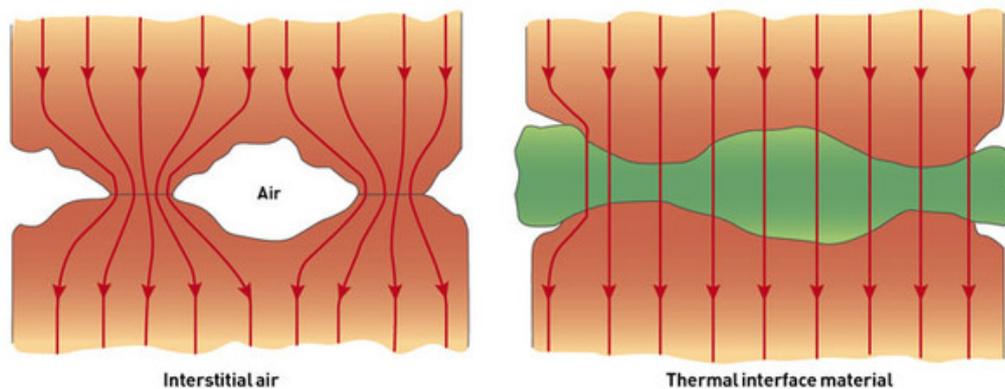


Figure 1.1 Conduction through TIM Filling Gap

Thermal interface materials (TIMs) are widely used in the electronics industry, and especially in microelectronic devices, to reduce the thermal resistance and facilitate heat transfer to the heat sink, by filling the air gap between the two surfaces and increasing their overall heat transfer capability. For that reason, improving the performance of TIM has been the focus of much attention. Most TIMs are polymer-based composites filled with heat conducting fillers. A thermal-interface material may presence in the form of thermal grease, thermal films and thermal pads. Few examples of thermal interface materials are shown in Fig. 1.2.

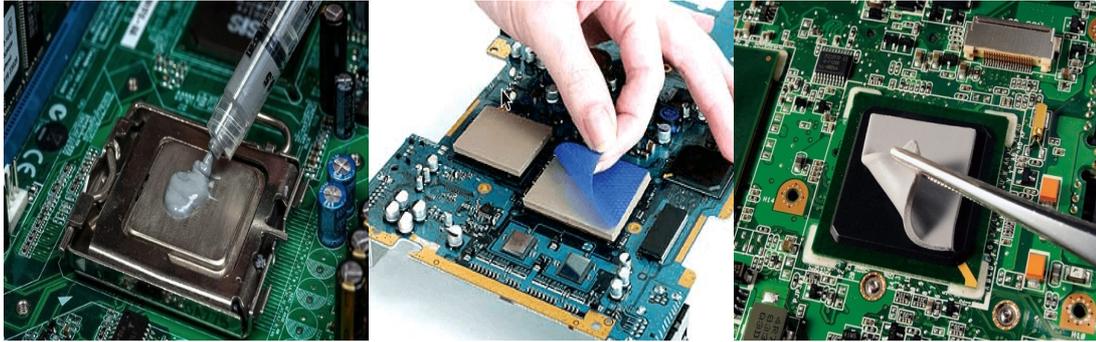


Figure 1.2 Polymer Based Thermal Interface Material (TIM) in Various Form

Nanocomposite is a class of multi-component material in which one of the phases is dispersed in second one in nanometer range. Conventional fillers in polymers have often been used to reduce cost or improve material properties required for particular applications. Ceramic fillers such as silica or alumina are typically used to reduce cost and increase the stiffness in epoxy resins. The drawback is however that addition of such rigid particles further reduces the ductility in the already brittle epoxy. Soft particles, such as rubber, on the other hand can be used to toughen the epoxy matrix but they consequently reduce the stiffness. The outstanding properties of carbon nanotubes, graphene nanoplatelets (few layers of graphene) and graphene can be exploited by inclusion of such nanofillers into a matrix to form nanocomposites. Several polymer matrices may be used along with these carbon nanofillers to synthesize interesting composites which is the primary focus of this present work. There are several methods for manufacturing polymer nanocomposites but the ability to disperse nanofillers is a critical factor for tuning their properties (Maxwell, 1873).

In polymeric composite TIM, metallic particles can serve as fillers to promote heat transfer due to their high intrinsic thermal conductivity, typically  $k=200-400$  W/mK. Over the past decades, different polymer families have been examined to improve heat transfer. One of the first experiments on the thermal conductance of metal-polymer

joints was done by Fletcher and Miller in the 1970s. Different types of elastomers with and without metallic or oxide fillers were investigated, indicating decreases in joint resistance with these fillers. Fletcher et al. also studied the effect of additives in TIM formulation using polyethylene. Later, Ochterbeck et al. investigated the decrease in thermal joint resistance using polyamide films combined with paraffin, diamond, and metallic foils. They concluded that the hardness of the fillers was the most important parameter determining the efficiency of the interface materials. The thermal conductivity of most of these materials was found to be independent of the testing temperature used (10-100 °C). Parihar and Wright conducted an experimental investigation on the contact resistance of stainless steel and silicone rubber. Since the thermal conductivity of the rubber was largely temperature-dependent, the contact joint resistance was also a function of temperature in this case. Many polymers such as polyethylene, polypropylene, poly(vinyl chloride), Teflon, Delrin, and Nylon were also tested by Marmira et al.<sup>19</sup> Marotta et al.<sup>20</sup> reported that some commercial elastomeric gaskets and graphite-based materials displayed less dependence of the thermal contact resistance on contact pressure. Recently, Kim et al. studied the thermal joint conductance of low density polyethylene and polyester. There has been a wide range of investigations on TIM and the improvement of heat transfer, and further details on this topic can be found in reviews by Yovanovich and Prasher.

Common fillers include aluminum oxide (alumina), boron nitride, aluminum nitride, and magnesium oxide. Metal fillers, such as silver, can be used where electrical isolation is not needed (Tong, 2011). Improving the structural and functional properties of polymers and polymeric composites has been recognized as a key to dramatically increase their wide applications. Carbon nanotubes (CNTs) show great promise as a nanofiller in polymer composites due to its unique mechanical, electrical and thermal

properties. CNTs have excellent mechanical properties, in particular high stiffness and axial strength due to their seamless cylindrical graphitic structure (Treacy, Ebbesen, & Gibson, 1996). Moisala, Li, Kinloch, and Windle (2005) recently developed epoxy/CNTs nanocomposites with remarkably enhanced thermal conductivities as a function of the filler content. However, the property improvements achieved so far using CNTs are still much lower than the theoretical predictions. Such factors include the degree of dispersion and exfoliation, and critically, the orientation of the nanoplatelets. Different approaches have been reported for orienting carbon nanofillers, based mainly on employing mechanical stretching, an electric field and a magnetic field (Vajtai, 2013). The use of an electric field has been reported to align carbon nanotubes and graphene nanoflakes to improve the electrical conductivity and mechanical properties of polymer nanocomposites (Gupta, Rajput, Singla, Kumar, & Lahiri, 2016a; Wang, Zhang, & Chen, 2007; Wu et al., 2015).

Polydimethylsiloxane (PDMS) is an ideal material to serve as a thermal interface material. PDMS is a viscoelastic material with highly tunable mechanical properties. PDMS is also hydrophobic and will not swell in the presence of moisture. However, their extremely low thermal conductivity greatly limits their applications that demand good dissipation of heat.

In this context, the design and fabrication of a thermal interface material with 1) relatively low mass density; 2) coefficient of thermal expansion similar to metals; and 3) higher thermal conductivities than most polymers needed. This material would serve as a mean to promote heat dissipation as well as to reduce the weight of the electronic devices.

## 1.1 Problem Statement

In order to tailor the aforementioned multifunctional properties of the material, one potential direction is to develop composite materials that possess combined properties of two or more materials. Composite materials have traditionally been used for structural applications. Currently, ongoing research is being conducted on multifunctional composites that can be used in thermal management and electronic packaging applications. For these applications, high thermal conductivity is the most important objective when selecting materials. Most metal matrix composites (MMCs) such as carbon fiber-reinforced aluminum or copper, silicon carbide particle-reinforced aluminum, and diamond particle-reinforced aluminum do not show substantial improvement in thermal conductivity. There are exceptions, such as, vapor grown carbon fiber (VGCF) reinforced aluminum matrix composite exhibited a thermal conductivity as high as 642 W/mK with a density of 2.44 g/cc. However, a very common disadvantage of all MMCs, including VGCF reinforced aluminum, is that they are electrically conductive, which may not be suitable for many electronic packaging applications due to the possibility of having short-circuits. Research has also been conducted on a second type of composites, which are polymer matrix composites (PMCs), where polymers are embedded with fillers. PMCs have a number of advantages, including their low mass-density and the ability to be injection molded into complex shapes with tight tolerances, eliminating the need for further machining that are often required with metal-cast parts. Due to their multifunctionality, which includes enhanced thermal conductivity and mechanical properties, these composites are gaining traction in a number of markets such as aerospace, automotive, microelectronics, and thermal management industries. These multifunctional polymeric composites may result in materials for electronic packaging having high thermal conductivities, coefficient of

thermal expansion similar to that of metals, light weight, high strength, increased reliability, and good manufacturability. Carbon nanotubes (CNTs) show great promise as a nanofiller in polymer composites due to its unique mechanical, electrical and thermal properties.

Alignment of CNTs during processing has attracted much interest in improving thermal conductivity of composites. The good dispersion and alignment of the nanotubes along with good adhesion with polymers are key factors for thermal conductivity enhancements. Ghose et al. processed EVA/MWCNT samples with significant alignment and observed thermal conductivity parallel to alignment in aligned sample higher than in the unaligned one, suggesting successfully heat conduction along aligned CNTs. Moreover, addition of isotropic Al nanofiller was helpful to reduce the conductive difference in the axial and the transverse directions, likely acting as a bridging agent between aligned conductive pathways. Kim et al. proved that the alignment of CNTs was possibly derived from dragged shear force during the optimized milling process. Alignment of 5 wt.% CNTs in ethylene propylene diene rubber (EPDM) matrix (0.28 W/m·K) resulted in obvious improvements in thermal conductivities (0.70 W/m·K).

As for this research, we want to understand the effects of an external electric field on aligning the CNTs since good dispersion and alignment of CNTs significantly enhances the thermal conductivity of a composite. Since nanofiller dispersion and alignment are the key issue governing the properties of the composite, an alternative is needed to be employed to fabricate samples ensuring good nanofiller dispersion in the polymer matrix. Fig. 1.3 illustrates the schematic drawing of randomly oriented and aligned CNTs within the polymer matrix. Application of external electric field during curing was expected to align the CNTs and improve degree of dispersion, thus creating

thermally conductive pathways and enhance thermal conductivity of CNT/PDMS composites.

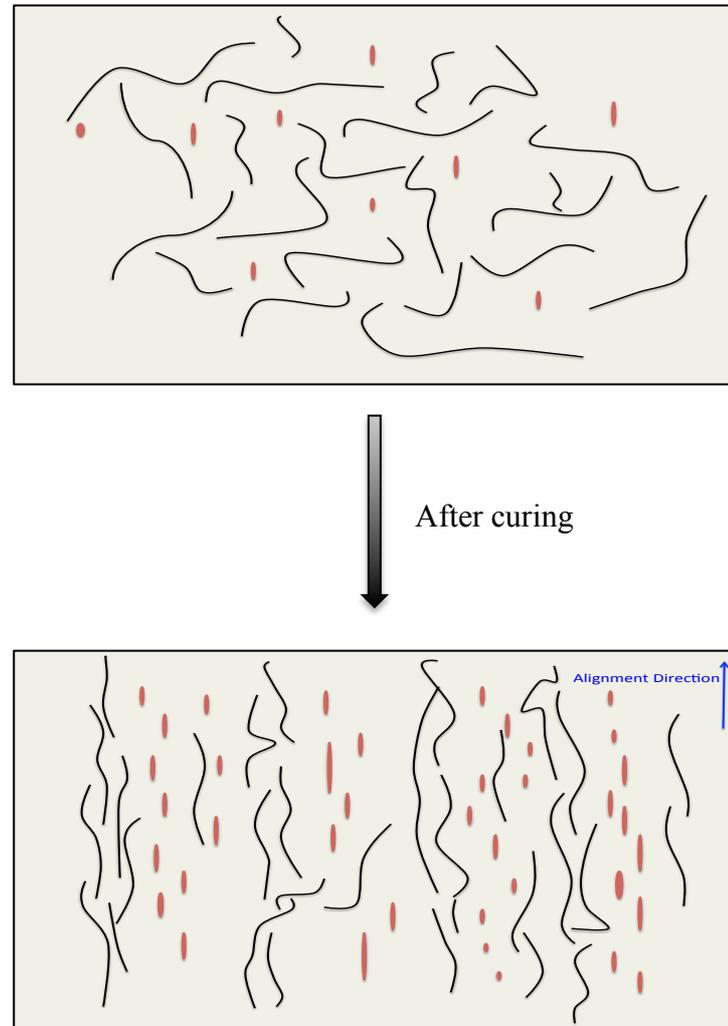


Figure 1.3 Schematic diagrams for a) randomly oriented and b) aligned composite particles

## 1.2 Thesis Objectives

For thermal management specific application, thermal interface material, materials should fulfill several desired properties such as lightweight, easy to process and should have tailored electrical conductivity. Polymers suit best for these desired properties, however, they have poor thermal conductivity, which is the fundamental property

required for thermal interface material. It is well known that the properties of a polymer can be altered accordingly to our desire. One of the methods is by having a composite consists of two or more materials. For thermal interface materials, conductive fillers may be incorporated with the polymer matrix to obtain all the multifunctional properties mentioned above.

For this research project, several hypotheses were evaluated with the aim to improve the effective thermal conductivity of the multifunctional composite material while keeping intrinsic properties of the polymer matrix. The main objectives of this research project are summarized as follows:

- 1) To study the effect of external electric field at various degrees, i.e., 0 V, 10V, 20 V and 30 V on aligning CNTs within the PDMS matrix to improve thermal conductivity of CNT/PDMS composites.
- 2) To fabricate and characterize thermally conductive polymer composites with the maximum possible thermal conductivity ( $k$ ), i.e., exceed 0.25 W/mK ( $k$  for neat PDMS) while keeping all the other intrinsic properties of a polymer.

### **1.3 Thesis Outline**

This thesis focuses on the synthesis and the characterization of CNT/PDMS composites, their application as components in thermal interface materials (TIM) to improve the thermal conductivity. A background and literature review is presented in Chapter 2 on the following topics: thermal management and electronic packaging, materials for electronic packaging and thermally conductive polymer composite. Chapter three focuses on the fabrication of CNT/PDMS composites interface material using PDMS as the base resin and CNTs as the conductive fillers. The characterization of the

composites by different methods is then discussed. Chapter four is a discussion on the properties of CNT/PDMS composites and reporting their thermal conductivity compares with commercial materials. Chapter five summarizes the conclusions drawn from this research and some recommendations for future work.

## CHAPTER 2

### LITERATURE SURVEY AND THEORETICAL BACKGROUND

#### 2 Introduction

Since 1930's, polymers have made outstanding advances in the markets of metals, wood, glass, paper, leather, and vulcanized rubber that were regularly used in most household goods and industrial components as well as creating new markets of their own. The main reason behind the widespread use of polymers is their unique set of properties such as toughness, lightweight, low cost, and ease of processing and fabrication. Even though polymers are not the panacea of industry's material problems, their unique set of properties have made them one of the important classes of materials finding their way into widespread use in the electronic industries.

The most common application of polymers in electrical and electronic devices is as semiconductor packaging, which put a semiconductor chip enclosed or encapsulated to ensure environmental protection, and it provides for a reliable means of interconnection to the next level of integration. Specifically, a semiconductor package should protect the chip from mechanical stresses, environmental stresses, and electrostatic discharge during handling and mounting onto a printed circuit board and beyond. The package must also meet the chip's various performance requirements, encompassing the physical, mechanical, electrical and thermal. Finally, the package must meet specifications for quality and reliability as well as be a cost effective solution toward the final product. The continuing improvements in the multifunctional properties of polymers over the years have made them even more important to the electrical industry by extending their useful range (A. Chen & Lo, 2012).

## **2.1 Thermal Management and Electronic Packaging**

Moore's Law, the famous prediction that states that the number of transistors on a chip will double about every two years, has held for four decades. The emerging three-dimensional (3D) chip architecture (Sun, Chen, Dong, & Jin Ouyang, 2011) has offered a new opportunity to continue the complementary metal-oxide-semiconductor (CMOS) performance trends for the next decade. It not only serves as a promising solution to mitigate the interconnect problem in modern microprocessor designs, but also enable much higher memory bandwidth for future 3D microprocessors.

Recent progress in the fabrication of high-aspect-ratio vertical interconnects, called through-silicon vias (TSVs) (Au et al., 2012), have opened new avenues for high density area array interconnects between stacked processor and memory chips. Through the integration of a very large System on a Chip (SoC) in multiple tiers, the average distance between system components is reduced, leading to improved performance. However, the surging performance and functions on a chip has come with a hidden cost, which is heat. The continuous increase in component densities being packed onto a chip requires more power to run it. A large portion of that power turns into heat, leading to the fast heat up of the chips, if not properly cooled. Overheating results in hardware failure reducing chips' reliability, potentially leading to computer crashes, mangled files, graphical glitches, and even permanent damage. In other words, the future of 3D Integrated Circuits crucially hinges on the development of practical solutions for heat removal.

As it is known, the trend in packaging electronic systems and subsystems has been to reduce size and increase performance. Higher levels of integration in semi-conductors and the increased usage of hybrids and multichip modules (MCMs) are some examples.

System-in- Package (SiP) and few chip package (FCP) are also examples of high-density multichip packaging. The placement of more functions in a smaller package has an inevitable result of higher heat densities, which requires that high priority be given to thermal management in their design to maintain system performance and reliability. As clock rates increase every year, the power dissipated in the semiconductors during switching is increasing at a linear rate proportional to frequency.

$$P = \frac{cv^2}{2} f \quad \text{-----} \quad 2.1$$

where,

$C$  = input capacitance in farads

$V$  = peak-to-peak voltage swing of signal in volts

$f$  = switching frequency in hertz

If the values of input capacitance and voltage swing had remained the same while the clock frequency increased, the amount of power dissipated would have grown in a linear rate and would be unmanageable. Fortunately, reduced input capacitance for each new generation of semiconductors and continuous reduction of voltage swings, which are directly tied to logic power supply voltages, from the classic 5.0 V to a forecasted value of less than 1 V have aided the thermal management of electronic devices. An ASIC process such as IBM's 0.10  $\mu\text{m}$  Cu-11 using a 1.8 V supply has a heat dissipation of 0.009  $\mu\text{W}/\text{MHz}/\text{gate}$ . An older 0.55  $\mu\text{m}$  process using a 5.0 V supply from Texas Instruments has a dissipation of 0.42  $\mu\text{W}/\text{MHz}/\text{gate}$ .

Electrical parameters such as gain, leakages, offset, or forward drop of an active device are changed if the temperature is increased. Most circuit simulations incorporate the variations in electrical parameters due to temperature change. It is estimated that

leakage currents in circuits often double every 10°C. If the temperature of an active device increases too much, it will exceed the manufacturer's specifications and usually fail. Therefore, it is desired to have the temperature of electronic components below their critical value to avoid any permanent damages. Since there is a need of high performance and small size of electronic components, installation of separate heat sinks is not an option anymore. It is desired that the entire packaging of electronic devices be made out of composite materials that can simultaneously provide signal distribution, heat dissipation, package protection, and power distribution. In other words, this prompts the need to develop advanced monolithic and composite materials that are tailored to meet the specific requirements of the electronic packaging or other heat management solutions.

## **2.2 Materials for Electronic Packaging**

Electronic packaging comprises of the housing, their interconnections, encapsulants as well heat sinks or other cooling components. It serves as the housing of the integrated circuit chips (dies), the interconnections that provides circuit path from Si Chip to motherboard and outside world for signal transmission, power, and ground, the encapsulations for protecting the chips and interconnections from moisture, chlorides and other species during its service life, the heat sinks or other cooling components needed to manage heat generated by the chips, the power supply and the housing for electromagnetic interference (EMI) shielding (Chung, 1995).

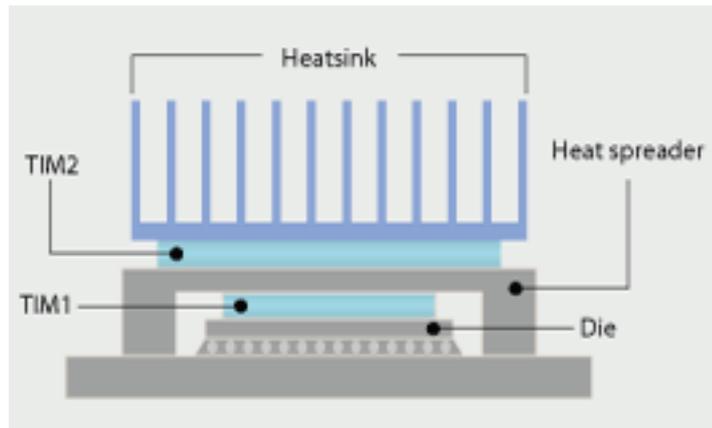


Figure 2.1 Schematic diagram of an electronic packaging

Materials used for each different level of packaging or packaging architecture varied accordingly for effective performance over time. The level of packaging or packaging architecture is classified into zeroth, first, second, third, fourth and fifth levels of packaging. The chip, component, printed wiring board, and assembly level packaging referred to as the zeroth, first, second and third levels of packaging, respectively. Meanwhile, the fourth and fifth level of packaging being the electronic module formation by the integration of the back panel and power supply with an outer housing and the system formation by integration of electronic modules (Pecht et al., 2017).

Many new developments have been reported on the applications of polymers as an electronic component. Along with the continuous developments, many new types of polymeric materials have been introduced and commercialized. Many of these newer polymers have unique combinations of electrical, optical, thermal, chemical and physical properties over the traditional materials they replaced. Examples of such polymers include intrinsically conducting polymers, those that emit light or exhibit dielectric properties, photoresists as well as polymers exhibiting non-linear optical properties (Goosey, 2000).

Recently, increasing packaging density, increasing reliability requirements, stringent weight restrictions for airborne and other systems as well as cost constraints are the key trend in the electronic industry. To meet the needs arising these issues, it is desirable for packaging materials to have these attributes such as low, tailor able coefficient of thermal expansion, high thermal conductivity, excellent thermal oxidative resistance, low cost and low density for weight-critical systems. Conventional materials do not satisfy all these requirements. One approach to meet these needs is to create new composite materials with properties tailored specifically for electronic packaging.

The electronic packaging industry has been making use of composite material, defined as a material consisting of two or more constituents, each of which maintains distinct properties and regions. Traditionally, polymer-matrix composites, in the form of glass fiber reinforced polymer (GFRP) printed circuit boards (PCB) are well-established packaging materials. At present, new composites, commonly known as *advanced composites* have been developed in recent years. Ultrahigh modulus carbon (graphite) fibers and silicon carbide particles are the key reinforcements to leading matrix materials such as aluminum, copper and epoxy. These reinforcements have the important advantages of high production volume, higher thermal conductivities and low cost (Chung, 1995).

### **2.2.1 Thermally Conductive Polymeric Composites**

Polymers have found their usage in almost every application and industry ranging from automotive to medical. However, they all lack in their ability to conduct heat, a fundamental property requirement for electronic packaging application. For example, when use as heat sinks in electric or electronic systems, composites with a thermal conductivity approximately from 1 to 30 W/m.K are required. Polymers often lack in

areas where superior mechanical, thermal and electrical properties are desired. To overcome this obstacle, polymers are filled with particles that enable them to fulfill the application-specific requirements while keeping their low density, ease of processing and low cost.

Nanocomposite is a class of multi-component material in which one of the phases is dispersed in second one in nanometer range. Conventional fillers in polymers have often been used to reduce cost or improve material properties required for particular applications. Ceramic fillers such as silica or alumina are typically used to reduce cost and increase the stiffness in epoxy resins. The drawback is however that addition of such rigid particles further reduces the ductility in the already brittle epoxy. Soft particles, such as rubber, on the other hand can be used to toughen the epoxy matrix but they consequently reduce the stiffness. The outstanding properties of carbon nanotubes, graphene nanoplatelets (few layers of graphene) and graphene can be exploited by inclusion of such nanofillers into a matrix to form nanocomposites. Several polymer matrices may be used along with these carbon nanofillers to synthesize interesting composites which is the primary focus of this present work. There are several methods for manufacturing polymer nanocomposites but the ability to disperse nanofillers is a critical factor for tuning their properties. Such composites find a wide palette of potential applications ranging from bicycle frames, badminton rackets to micro/nano devices, nanopackaging, smart materials, sensors and actuators among many others. Bionanocomposites used for applications such as tissue engineering and load-bearing composites for bone reconstruction are of significant interest. The most important factor driving the use of nanocomposites for mechanical reinforcement in industrial scales is the reduction in weight to its mechanical performance ratio as compared to their metallic counterparts. Major applications of nanocomposites are found in aerospace

industry as critical components in aircraft. Recently launched Boeing 787 Dreamliner is manufactured with 80 vol% composites, featuring an unique light weight construction with 50 % carbon and glass fiber reinforced materials. The average fuel savings of all CNT-reinforced aircrafts is about 10 % along with improved physical and structural properties. Another important application is in the form of conducting films and coatings for devices like displays, touch screens etc. Enhanced electrical conductivity coupled with mechanical strength, optical and thermal properties is the key for such new-age applications (Lu & Xu, 1997).

In this context, thermally conductive polymer matrix composites are used increasingly for thermal management of electronic packaging system. The polymer matrix includes both thermosetting and thermoplastic types. Meanwhile, different kinds of fillers or reinforcements especially nanoparticulate fillers such as vapor grown carbon fiber (VGCF), carbon foam, carbon nanotube, carbides, nitrides and carbon nitrides have been extensively studied to achieve desirable thermal conductivity, mechanical strength, hardness, corrosion and wear resistance (Tong, 2011). Table 1 and 2 display the thermal conductivities of some polymers and fillers.

Table 2.1 Thermal Conductivity of some Polymers

<b>Material</b>	<b>Thermal Conductivity at 25 °C [W/m.K]</b>
Polyimide (PI)	0.11
Polydimethylsiloxane (PDMS)	0.25
Epoxy Resin	0.19

Table 2.2 Thermal Conductivity of some Fillers

<b>Material</b>	<b>Thermal Conductivity at 25 °C [W/m.K]</b>
Graphite	100-400 (on plane)
Carbon black	6-174
Carbon nanotubes	2000-6000
Silver	450
Nickel	158
Boron nitride	250~300
Aluminum nitride	200

As of examples, polyurethane composites filled with alumina or carbon fibers have improved thermal conductivities up to 50 times over the pure polyurethane. The thermal conductivities for both polymer composites with alumina and carbon fibers increase with increasing volume fraction of the fillers. The thermal conductivity for 20 vol. % of PU/Al<sub>2</sub>O<sub>3</sub> is five times that of pure PU, meanwhile the increase in thermal conductivity is up to 50 times for the PU/CF system (Lu & Xu, 1997).

Various inorganic fillers such as aluminum nitride (AlN), wollastonite, silicon carbide whisker (SiC) and boron nitride (BN) also have significantly enhanced the thermal conductivity of polymer composites. Different shape and size of these inorganic fillers

as well surface treatments of fillers affected the performance of the fillers. The thermal conductivity of HDPE filled with AlN-wollastonite and AlN-SiC hybrid fillers was remarkably increased (Lee, Park, Kim, Lee, & Yoon, 2006).

Choi and Kim (2013) prepared thermally conductive polymer composites filled with single or combination of aluminum nitride and aluminum oxide hybrid fillers with various sizes. The maximum thermal conductivities for composites filled with large-sized aluminum nitride and small-sized aluminum oxide particle, and the other composites filled with large-sized aluminum oxide and small-sized aluminum nitride were 3.402 W/mK and 2.842W/mK, respectively. The use of these hybrid fillers was found to be effective for increasing the thermal conductivity due to the enhanced connectivity offered by the structuring filler.

Previous studies revealed that the thermal conductivities ( $k$ ) of a polymer could be effectively enhanced with incorporation of various conductive fillers but the possible  $k$  of polymer matrix composites (PMCs) is still, not as high as those of other advanced materials, such as metal matrix composites or ceramic matrix composites. However, they have a number of advantages, including ease of fabrication, low density and for some materials, relatively low material costs. Therefore, a technological breakthrough that allows fabrication of PMCs with dramatic improvements in  $k$ , without the compromise of electrical insulating property of polymers, will be vital to the technological advancement in the field of heat management for electrical and electronic devices.

### **2.2.2 Polymer composites embedded with carbon-based fillers**

Metal matrix composites (MMC) such as carbon fiber-reinforced aluminum or copper, silicon carbide particle-reinforced aluminum, and diamond particle-reinforced

aluminum do not show substantial improvement in thermal conductivity. However, vapor grown carbon fiber (VGCF) reinforced aluminum matrix composite exhibited a thermal conductivity as high as 642 W/mK with a density of 2.44 g/cc. A common disadvantage of all MMCs is that they are electrically conductive, which may not be suitable for many electronic packaging applications. Research has also been conducted on a second type of composites i.e. polymer matrix composite (PMC) where polymers are embedded with fillers. Micro- and Nano- sized carbon fillers, including multi-walled carbon nanotubes (MWNTs), carbon fibers (CFs), and graphene nanoplatelets (GNPs) have been embedded in polymers to develop multifunctional polymer composites. Carbon filler-reinforced polymer composites have a number of advantages, including their low density and the ability to be injection molded into complex shapes with tight tolerances, eliminating the need for further machining that are often required with metal-cast parts. Together with the added multifunctionality, such as enhanced thermal conductivity as well as mechanical properties, these composites are gaining traction in a number of markets such as aerospace, automotive, and microelectronics industries for thermal management and electronic packaging applications. These multifunctional polymeric composites may result in materials for electronic packaging having high thermal conductivities, coefficient of thermal expansion similar to that of metals, light weight, high strength, increased reliability, and, above all, good manufacturability. The commonly used reinforcing carbon-based fillers in these composites are Multi Walled Carbon Nanotubes (MWNTs), Carbon Fibers (CF) and Graphene Nanoplatelets (GNPs) because of their extremely good mechanical, thermal and electrical properties.

### 2.2.2.1 CNT-based nanocomposites preparation methods

The formations of micro or nano scale structure greatly affect the bulk properties of composite materials. This varies accordingly to the processing steps. A brief review on CNT-based composites preparation methods is given here, including solution mixing, melt blending, and in situ polymerization.

One of the most commonly used techniques for preparing CNT based polymer–matrix composites is *solution mixing*. Three major steps involve in solution mixing: 1) dispersing CNTs in a suitable solvent, mixing with the polymer solution, and recovering the composite by precipitating or casting a film (Safadi, Andrews, & Grulke, 2001). Rather than simple stirring, high power ultrasonication is more preferable to make metastable suspensions of CNT or CNT/polymer mixtures in order to tackle the difficulties in dispersing the pristine CNTs (Paredes & Burghard, 2004). In addition, functionalized, heat or acid treated CNTs (Sagar et al., 2015) are often used to get well dispersed CNTs in polymer matrix. By solution mixing method, many polymer/CNT composites were successfully prepared, including polyacrylonitrile/SWCNT, poly(methyl methacrylate)/SWCNT], poly(ethylene oxide)/MWCNT, poly(L-lactic acid)/MWCNT, chitosan/MWCNT. However, the solution mixing approach requires appropriate solvent selection, as it is applicable only to polymers that freely dissolve in solvents suitable to obtain a relatively stable suspension of CNTs.

*In-situ Polymerization* involves dispersion of nanotubes in monomer then followed by polymerization. The initial dispersion of the nanotubes in the mixture of solvent and monomer and consequently in the composites can be achieved with functionalized CNTs as in solution blending. Furthermore, in-situ polymerization methods enable covalent bonding between functionalized nanotubes and the polymer matrix using

various chemical reactions. A few examples are mentioned here. The composites of polyimides/MWCNTs were obtained by the reaction of 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA). The composites of polyaniline/MWCNT (acid treated) were synthesized by chemical oxidative polymerization. The composites of polypyrrole/MWCNT were prepared by in-situ inverse microemulsion and in-situ chemical polymerization.

*Melt Blending* is a convenient method to produce CNTs based nanocomposites owing to its cost effectiveness, fast production and environmental benefits, this being a solvent-free process. Melt blending uses high temperature and high shear forces to disperse nanotubes in a thermoplastic polymer matrix, using conventional equipment used for industrial polymer processing. End-grafted macromolecules as compatibilizers and coupling agents are often used to enhance dispersion. Melt-blending approach was reported for all the main polymer types, including polyolefines (PE, PP), polyamides, polyesters (PET, PBT and others), polyurethane, polystyrene, etc. However, compared with solution mixing, melt blending is generally less effective at dispersing nanotubes in polymers and limited to lower concentrations due to the high viscosities of the composites at higher nanotubes loadings.

Recently, masterbatches or thermoplastic polymers containing high loading of CNTs (typically 15-20 wt.%) have been widely used in the melt preparation of CNT based polymer nanocomposites. For industrial applications of melt mixing extrusion technique, as compared to direct nanotube incorporation, masterbatch dilution is more favorable since it reduce dispersion difficulties, offers a dust-free environment thus no safety-risk concerns, and ease of handling. The state of CNTs dispersion within the diluted composites is influenced by the state of CNT dispersion in the masterbatches,

processing conditions and compatibility between CNTs and polymer matrix. Instead of the thermal conductivity of CNT based nanocomposites prepared from CNT masterbatch, the rheological and electrical properties have been paid much attention to.

### **2.3 Aligning Carbon Nanotubes to Improve Multifunctional Properties of PDMS Nanocomposites**

Chain orientation is a phenomenon unique to polymers. The one-dimensional nature of the linear polymer chain makes it possible to obtain strongly anisotropic properties. The anisotropy arises when molecules are aligned along a common direction. The intrinsic properties of a polymer chain are strongly directional dependent (Gedde, 1999). By aligning the CNTs in the polymer matrix, the multifunctional properties of the composite can be improved.

CNTs can be aligned before or after embedded into the composite matrix. At present, different new approaches have been reported for orienting carbon nanofillers, based mainly on employing mechanical stretching, an electric field and a magnetic field. An electric field can be applied to a CNT suspension to assemble, rearrange and orient the CNTs. Furthermore, strong magnetic field can be applied to magnetically align CNTs in polymer composites. However, very high magnetic fields are usually required (Tong, 2011). Mechanical stretching which employs the drawing force to orient the nanotubes in the composites is also used to align the CNTs in polymer composites (Vajtai, 2013).

On the other hand, the use of an electric field has been reported to carbon nanotubes, carbon nanofibers and carbon black to improve the electrical conductivity, thermal conductivity and mechanical properties of polymer nanocomposites. For example, the effect of aligned graphite nanosheets had been reported by (Wang et al., 2007).