MECHANICAL AND THERMAL PROPERTIES OF NANOPARTICLES FILLED SILICONE RUBBER COMPOSITES

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MECHANICAL AND THERMAL PROPERTIES OF NANOPARTICLES FILLED SILICONE RUBBER COMPOSITES

by

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DECLARATION

I declare that the contents presented in this thesis are my own original research work which was done in Universiti Sains Malaysia. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to literature, and acknowledgement of collaborative research and discussions. This thesis has not been submitted for any other degree.

Signature:
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Date: 12nd July 2012

In my capacity as main supervisor of the candidate's thesis, I certify that the above statements are true to the best of my knowledge.

Signature:
Name: Associate Professor Ir. Dr. Mariatti Jaafar @ Mustapha
Date: 12nd July 2012

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LIST OF ABBREVIATIONS

AlN	Aluminium nitride
Al_2O_3	Aluminium oxide
BET	Brunauer-Emmett-Teller
BN	Boron nitride
CNT	Carbon nanotube
CTE	Coefficient of thermal expansion
CVD	Chemical vapour deposition
DEA	Dielectric analysis
HCR	Heat-cured silicone rubber
HDPE	High density polyethylene
HIPSN	Hot isostatically pressed silicon nitride
HPSN	Hot-pressed silicon nitride
MWCNT	Multiwalled carbon naotube
ND	Nanodiamond
ND1	Synthetic diamond in 100 nm
ND2	Synthetic diamond in 200 nm
PE	Polyethylene
PI	Polyimide
PMMA	Poly(methyl methacrylate)
RBSN	Reaction bonded silicon nitride
RTV-1	One-component RTV rubbers
RTV-2	Two-component RTV rubbers
RTV rubbers	Room-temperature vulcanization silicone rubbers
SD	Synthetic diamond

SEM	Scanning Electron Microscope
SiC	Silicon carbide
SN	Silicon nitride
SSN	Sintered silicon nitride
SWCNT	Single-wall carbon nanotube
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
TIM	Thermal interface material
TNT	Trinitrotoluene
TPS	Transient Plane Source
UTM	Universal Testing Machine
ZnO	Zinc oxide

LIST OF SYMBOLS

B	Boron
CH_2=CH	Vinyl
CH_3	Methyl
C_6H_5	Phenyl
N	Nitrogen
Si	Silicon
T_5	Temperature at 5 % weight loss
T_{20}	Temperature at 20 % weight loss
wt. %	Weight %
vol. %	Volume %
ε’	Dielectric constant
ε’’	Dielectric loss

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SIFAT-SIFAT MEKANIKAL DAN TERMA KOMPOSIT ELASTOMER SILIKON TERISI PARTIKEL NANO

ABSTRAK

Pada peringkat pertama kajian ini, tiga jenis pengisi partikel nano iaitu nitrida boron (BN), nitrida silikon (SN) dan berlian nano (ND) telah digunakan untuk menghasilkan komposit elastomer silikon. Antara tiga jenis pengisi yang dikaji, ND merupakan pengisi yang terbaik dalam mempertingkatkan kekonduksian terma, kekuatan tensil dan terikan pada patah bagi komposit elastomer silikon. Justeru itu, ND dipilih sebagai pengisi pada peringkat seterusnya. Pada peringkat kedua, komposit pengisi hibrid dihasilkan dengan menggabungkan pengisi yang sama jenis tetapi dengan saiz dan bentuk yang berlainan pada nisbah pengisi yang berbeza. Pengisi-pengisi itu merupakan berlian sintetik (SDs) yang dinamakan sebagai ND (4-15 nm), ND1 (100 nm) dan ND2 (200nm). ND mempamerkan bentuk sfera manakala ND1 dan ND2 mempamerkan bentuk tidak sekata. Keputusan ujian menunjukkan bahawa komposit hibrid ND/ND2 menunjukkan prestasi yang lebih baik daripada komposit hibrid ND/ND1 dalam kekonduksian terma, kestabilan terma dan kekuatan tensil. Pada peringkat ketiga, nanotiub karbon dinding berbilang (MWCNT) dengan pembebanan pengisi yang berbeza telah ditambahkan ke dalam komposit hibrid ND/ND2 dengan pengisi nisbah 1/3. Penambahan 0.5 isipadu % MWCNT ke dalam komposit ND/ND2 telah meningkatkan kestabilan terma komposit pengisi hibrid sebanyak 19 %. Selain itu, penambahan MWCNT juga meningkatkan pemalar dielektrik komposit ND/ND2 dengan ketara. Walau bagaimanapun, kehilangan dielektrik bagi komposit hibrid MWCNT/ND/ND2 yang tinggi pada pembebanan pengisi 0.5 isipadu % hingga 1.0 isipadu % menjadikannya tidak sesuai diaplikasikan sebagai bahan antara muka terma. Kesan MWCNT ke atas kestabilan terma dan sifat-

sifat tensil adalah kecil dan boleh diabaikan. Justeru itu, gabungan komposit hibrid yang terbaik dalam kajian ini dan sesuai diaplikasikan dalam bidang mikroelektronik sebagai bahan antara muka terma adalah 0.25 isipadu % MWCNT terisi komposit ND/ND2.

MECHANICAL AND THERMAL PROPERTIES OF NANOPARTICLES FILLED SILICONE RUBBER COMPOSITES

ABSTRACT

In the first stage of current study, three types of nano fillers which are boron nitride (BN), silicon nitride (SN) and nanodiamond (ND) have been used to fabricate silicone rubber composites. Among the three fillers studied, ND has emerged as the best filler in enhancing the thermal conductivity, tensile strength and strain at break of silicone rubber composites. Therefore, ND was chosen as filler in the next stage of research. In the second stage, hybrid filler composites were fabricated by combining same type of filler with different sizes and shapes at different filler ratio. The fillers are nanodiamonds (NDs) which denoted as ND (4-15 nm), ND1 (100 nm) and ND2 (200nm). ND exhibits spherical shape while ND1 and ND2 exhibit irregular shape. All the testing results showed that hybrid ND/ND2 composite presented better performance in thermal conductivity, thermal stability and tensile strength than hybrid ND/ND1 composites. In the third stage, different loading of multiwalled carbon nanotubes (MWCNT) also added into the hybrid ND/ND2 composites at filler ratio of 1/3. Incorporation of 0.5 vol. % of MWCNT into ND/ND2 composites has increased 19 % thermal conductivity of hybrid fillers composites. Moreover, addition of MWCNT also increased the dielectric constant of ND/ND2 composites significantly. However, the dielectric loss of hybrid MWCNT/ND/ND2 composites is high at the filler loading of 0.5 vol. % to 1.0 vol. % which is not suitable to be applied as thermal interface material (TIM). The effects of MWCNT on thermal stability and tensile properties are small and negligible. Therefore, the best combination of hybrid composite in this study that can be applied as TIM in microelectronic field is 0.25 vol. % of MWCNT filled ND/ND2 composites.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Silicone rubber or polydimethylsiloxane (PDMS) is a member of siloxane family and is one of the most important types of high-temperature resistance synthetic rubbers with superior thermal stability, low-temperature toughness and electrical insulating properties. Therefore, silicone rubber has been extensively used in the industry as electrical-insulating products, sealing products, etc (Wang et al., 1998). However, unfilled silicone rubbers usually have low mechanical, electrical and thermal conductive properties. That is why silicone rubbers are often used as a polymer matrix for preparation of thermally conductive composites which are stable in a wide range of temperature and have good weather and chemical resistance properties (Mu et al., 2007). Silicone rubber often combined with fillers such as fumed and precipitated silica (SiO_2), aluminium nitride (AlN), aluminium oxide (Al_2O_3), boron nitride (BN), nanodiamond (ND), silicon nitride (SN) and zinc oxide (ZnO) to improve the required properties (Noll, 1968; Chojnowski et al., 1993; Han et al., 2008).

In recent years, there have been a lot of researches on enhancing the thermal properties of silicone rubber-based composites. One of the reasons is to fulfill the needs for development of advanced microprocessors. Development of advanced microprocessors has resulted in continuous reduction in device size and increment in speed as well as power density. Therefore, thermal management becomes a challenge as the miniaturization of electronic device. Performance and reliability of microelectronic devices greatly depends on the heat dissipation of the device since the premature component failure can be caused by heat generated by the microprocessor (He, 2002). The heat for a device is dissipated from heat source to heat sink and then to the outer environment. However, the interface between heat source and heat sink may comprise point contacts at asperities and air pockets due to imperfect or rough mating surface for both devices. This lead to heat is either conducted through the physical contact points or transmitted through air gaps. Since air is a poor conductor of heat, thermal interface material (TIM) is employed between the heat source and heat sink to reduce thermal contact resistance and provide effective heat conduction. Therefore, it is vital to improve the thermal conductivity of interface material in order to improve the performance of microelectronic devices (Shaikh et al., 2007; Sartre and Lallemand, 2001).

A superior TIM should possess high thermal conductivity and can be easily deformed by small contact pressure so that all the uneven areas of imperfect mating surfaces can be contacted. Furthermore, better tensile strength is also needed for TIM to prevent electrical shorting from device to heat sink. (Zhou et al., 2008). Most TIM, except pure metals, is composed of a polymer matrix filled with thermally conductive but electrically insulating particles like ceramic (Gwinn and Webb, 2003). Silicone rubber-based composites are gaining attention in new applications, like elastomeric thermal pads and electronic packaging materials, due to the improved thermal properties of the composites. The advantages of elastomeric thermal pads are easy handling, able to absorb tolerance variances in assemblies and can be compressed to 25% of their total thickness (Zhou et al., 2007).

Advancement in nanotechnology that attracted many researches to incorporate particles in nano or micron size with better thermal properties into silicone rubber has been developed in order to fabricate TIM with better thermal performance. Research by Mu et al. (2007) on thermal conductivity of silicone rubber composites filled with micron size ZnO fillers concluded that thermal conductivity of silicone rubber increased with the volume content of ZnO. Kemaloglu et al. (2010) focused on the properties of thermally conductive micro and nano size of BN reinforced silicon rubber composites. It was reported that micro and nano size BN filled silicon rubber composites provided higher tensile modulus, hardness, thermal conductivity and reduced tensile strength, strain at break and coefficient of thermal expansion (CTE). Since both silicone rubber and thermally conductive particles have their own unique and excellent properties, it is believed that by combining these materials can lead to a very attractive and multifunctional composite that can find extensive applications in electronic packaging especially as a TIM (Zhou et al., 2007).

Thermally conductive fillers in polymer composites play an important role in conduction of heat for the purpose of heating or cooling. ND has emerged as a very attractive material in microelectronic field because it has very high thermal conductivity (2000 W/mK). ND which is chemically and mechanically stable can withstand high composite processing temperatures too (Shenderova et al., 2007; Chung, 2001). For instance, Shenderova et al. (2007) in their study on ND filled polyimide (PI), poly(methyl methacrylate) (PMMA) and PDMS composites revealed that addition of 1-2% mass of ND particles into the matrices has improved the thermal stability, thermal conductivity and adhesion of the composites. Furthermore, research on thermal properties of composites filled with different fillers by Han et al. (2008) also found out that incorporation of 5 – 45 vol. % of BN, alumina, synthetic diamond, silicon carbide and SN into epoxy resin has increased the thermal conductivity of the epoxy composites. In their research, BN is the best material in enhancing the thermal conductivity of the epoxy composites. With all the results mentioned, it proves that inclusion of thermally conductive particles can improve the thermal conductivity of polymer composites.

Hybrid fillers composite systems are gaining more attention nowadays because most of the published data showed convincing results on the improved properties of such systems (Zhou et al., 2008a; Sanada et al., 2009). Extensive research works have been done on investigating the properties of hybrid fillers composite systems. According to Lee et al. (2006), studies on the thermal conductivity of high density polyethylene (HDPE) composites filled with hybrid fillers showed that the use of hybrid AlN and SiC fillers was found to be effective in improving thermal conductivity of the composites. Zhou et al. (2010) explored on improving the thermal conductivity of epoxy composites with hybrid multiwalled carbon naotubes (MWCNTs)/micro-SiC fillers. The highest thermal conductivity which is 24.3 times higher than that of the epoxy was recorded by hybridization of 5 wt. % MWCNTs and 55 wt. % micro-SiC in epoxy resin.

1.2 Problem Statement

Silicone rubber TIM with better thermal conductivity is needed to solve the thermal management issue in the design of computer and telecommunication systems. IC designers and manufacturers are always seeking solutions to overcome the heat generated problems resulted from the growing of complexity and power level in semiconductor devices. In order to manage this escalated need for heat dissipation, packaging industry has improved through the use of more thermally efficient TIM which promotes heat transfer within a package. Therefore, TIM with better tensile strength and thermal properties is always the target to be achieved by researchers in order to tackle the heat dissipation problems in electronic industry (Dean and Pinter, 1999). The thermal conductivity of polymeric TIMs basically does not exceed about 5 W/mK and is normally less than about 1 W/mK (Tong, 2011).

Other than that, dielectric strength is also an important electrical property in a typical assembly where TIM is used. TIM with low dielectric constant is needed for fast signal propagation for electronic devices. Generally, the dielectric constant range for TIM is around 2.5 to 6.5 (Xu et al., 2001). Mechanical properties like tensile strength and strain at break for TIM play a role in avoiding electrical shorting from the device to the heat sink. Devices with larger surface areas will need TIM with better tensile strength and strain at break to conform to the interface than smaller devices. The tensile strength range for TIM to be applied in electronic field is around 1 to 8 MPa according to the end application (Zhou et al., 2008).

It is undeniable that silicone rubber possesses certain preferable properties that made it used heavily in the industry like good electrical properties, optical clarity, chemical resistance, etc. However, there are not many applications of the silicone rubber used in the unfilled state especially in microelectronic field as TIM. One of the reasons is unfilled silicone rubber usually has poor thermal conductivity (0.165 W/mK). Therefore, fillers always play a vital role in reinforcing the elastomer to achieve better mechanical or thermal properties to suit the application needs in electronic industry (Mu et al., 2007; Demir et al., 2005). In previous studies, many different types of fillers in different size and shape with certain volume contents have been used to produce silicone rubber composites to improve the thermal conductivity of silicone rubber such as BN, AIN, SN, ZnO, etc so that the silicone rubber composites can be applied as TIM to solve the thermal management issues (Dolmatov, 2007; Maitra et al., 2009).

ND in nanometer size produced by detonation process are getting more and more attention in the industry due to the unique characteristics of diamond such as superior hardness, thermal conductivity (2000 W/mK), magnetic and optical properties. There were extensive researches in recent years on ND in the fields of composite coating, grinding, polishing, plating, medicine and biology, etc (Zou et al., 2009; Dolmatov, 2007). However, there are very few works on incorporation of ND into elastomer to improve the thermal properties of the composites so that it can be applied in microelectronic field. Maitra et al. (2009) and Monteiro et al. (2007) only focused on the enhancement of mechanical properties of ND filled polymer composites while other works more on ND characterization.

Other than the thermal conductivity of the fillers, the effects of filler size, orientation and content on thermal performance of the composites have been addressed by many researchers too. Zhang et al. (2011) demonstrated the effects of filler size and content on the thermal conductivity and mechanical properties of Al_2O_3/HDPE composites. Results showed that thermal conductivity and tensile strength of the composites increase with the decrease of particle size. Furthermore, Zhou et al. (2007a) investigated the effects of content and particle size of BN fillers on the thermal conductivity and mechanical property of silicone rubber. The results indicated that composites with hybrid BN fillers in three different particle sizes shows better thermal conductivity if compared with the single filler composites at the same filler content. Since most of the published data displayed that mechanical or thermal properties of the hybrid composite systems were better than that of single filler composite systems (Zhang et al., 2011; Sanada et al., 2009; Lee et al., 2006), hybrid composite systems has been adopted in the current study by reinforcing silicone rubber with hybrid ND and CNTs in order to produce an elastomeric thermal pad.

1.3 Research Objectives

The objectives of the current study are as follow:

1. To compare the physical, mechanical and thermal properties of nanodiamond (ND), boron nitride (BN) and silicon nitride (SN) filled silicone rubber composites with filler loadings from 0.5 vol. % to 2.0 vol. %.
2. To study the effects of different particle sizes and shapes of ND towards the physical, mechanical and thermal properties of hybrid ND filled silicone rubber composites.
3. To compare the properties of hybrid composites which consist of different sizes and shapes ND and MWCNTs fillers at filler loading of 2.0 vol. %.

1.4 Organization of Thesis

This thesis consists of five chapters. Chapter 1 introduces the properties of silicone rubber and thermally conductive fillers in general. A simple introduction on the thermal management issues caused by the rapid development of advanced microprocessors in microelectronic field has been discussed. This chapter also includes the problem statement and objectives of the current research. Chapter 2 is about literature review on silicone rubber, ND, MWCNT, BN and SN. This chapter also discusses about the processing and properties of particulate-filled polymer composites. Chapter 3 records the materials and chemicals involve in this research alongside with their respective properties. Chapter 3 also includes the research methodology, the experimental procedures to fabricate composites and the methods to characterize the composites. Chapter 4 discusses the results of characterization in detail, which is separated into four parts. The first part is made up of the characterization of as-received fillers; the second part compares the properties of ND, BN and SN filled silicone rubber composites with different filler loading (0, 0.5, 1.0, 1.5 and 2.0 vol. %); the third part discusses the effects of different particle size and shape of ND particles towards the properties of hybrid ND/silicone rubber composites while the last part discusses the properties of hybrid fillers filled silicone rubber composites. At last, Chapter 5 summarizes and concludes the overall research. The recommendations for future studies also included in this chapter.

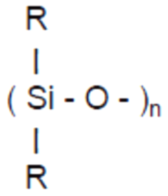
CHAPTER 2

LITERATURE REVIEW

2.1 Silicones

Silicones are a family of synthetic polymers which referred to polymers with the main chain consists of repeating –Si–O– units together with predominantly organic side groups. The basic repeating unit of silicone polymer is $(R_2SiO)_n$ as shown in Figure 2.1 is known as "siloxane", where R is organic side groups. In general, there will be one or more side groups attached to silicon atoms, like phenol (C_6H_5), methyl (CH_3) or vinyl $(CH_2{=}CH)$ units. These groups affect the properties of silicone polymers such as solvent resistance, lubricity and reactivity with organic chemicals and polymers. The bond angle of Si–O–Si bond is 134° which is unlike the C–C–C bond angle seen in the other polymers with tetrahedral angle (109°). Therefore, siloxane chains are very flexible, resulting very low viscosities when compared with other rubbers. Furthermore, silicones also exhibits high heat resistance and chemical stability because of the bond energies of the Si–O–Si bond is much higher than that of the C–C–C bonds (Kothandaraman, 2008).

Silicone polymers are available in different forms like fluids, greases, rubbers and resins. Rubber is a tough elastic polymeric substance made from the latex of a tropical plant or synthetically while conductive rubber is deliberately rendered electrically conductive by the inclusion in the unvulcanized mix of certain types of carbon black. Silicones have found many and diverse applications in the fields of rubbers, resins, lubricants, insulators, medicines, etc. due to their good thermal stability, water repellency, anti-adhesive characteristics and constancy of properties over a wide range of temperature. In general, silicone composites produced with silicone resins show outstanding long-term thermal stability at temperatures around 300°C and excellent moisture resistance and electrical properties (Chanda and Roy, 2009; Schweitzer, 2000).



$$(\mathrm{SiR_2} - \mathrm{O} -)_n$$

Figure 2.1: The basic repeating unit of siloxane, $(R_2SiO)_n$ (Kothandaraman, 2008).

2.1.1 Silicone Rubber

Silicone rubbers or silicone elastomers, also known as polysiloxanes, are inorganic synthetic elastic substances which contain linear silicone polymers crosslinked in a 3-dimensional network. Normally, fillers which act as reinforcing agent or additive are incorporated in this network for certain mechanical, chemical or physical properties (Jerschow, 2002). The silicone rubber inherits the unique properties of silicone mentioned in Section 2.1 due to the “silicone-oxygen” molecular structure. However, silicone rubbers have negligible tensile strength, poor tear resistance and abrasion resistance. The tensile strength of a crosslinked and nonreinforced high-molecular weight silicone rubber is in the range of about 49 psi. This tensile strength value is too low to fulfill most application requirements of silicone rubber in the industry. Therefore, silicone rubbers are always reinforced by reinforcing fillers like fumed silica to improve their tensile strength in order to meet the requirements of end applications (Harper, 2002; Schweitzer, 2000; Katz and Milewski, 1987).

Silicone rubbers mainly can be classified into two categories which are room-temperature vulcanization silicone rubbers (RTV rubbers) and heat-cured silicone rubbers (HCRs), depending on whether cross-linking is accomplished at ambient or elevated temperature. RTV rubbers are low-molecular-weight liquid silicones with reactive end groups. In general, RTV rubbers can be separated into two classes which are one-component RTV rubbers (RTV-1) and two-component RTV rubbers (RTV-2). RTV-1 consists of an air-tight package containing silanol-terminated polysiloxane, cross-linking agent and catalyst while RTV-2 system involve separate packages for the polysiloxane and cross-linking agent. On the other hand, HCRs typically are compounded with catalyst, colour and additives mixed and milled into siloxane polymers. Normally, HCRs are applied in molded parts for high-temperature service or in applications that utilize their chemical and weathering resistance (Chanda and Roy, 2009; Sancaktar, 2011).

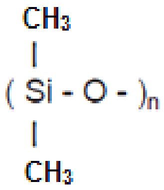
The vulcanization of RTV rubbers can be classified into two categories, which are condensation cure and addition cure. Condensation cure of silicone rubber can be moisture dependent or moisture independent. For moisture condensation cure system, atmospheric moisture is utilized for hydrolysis reactions that lead to crosslinking of the polymer chains. Hence, curing rate is depending on the rate of moisture diffusion into the rubber. Moisture independent condensation cure involves direct condensation reactions between polymers with different functional groups. This cure system offers silicone rubbers with fast rate of deep section cure at both room and elevated temperature. In general, addition cure always happen in two-component systems. Addition cure are done by adding polyfunctional silicon hydride crosslinker to a vynil containing silicone polymer with a complex of platinum as catalyst. Sometimes, palladium, rhodium and ruthenium are used as catalyst too. This curing system is used where deep section cures are needed in a confined space because there are no volatile by-products (Sweet, 1979; Morton, 1987).

2.1.2 Polydimethylsiloxane

Polydimethylsiloxane (PDMS) which contains methyl groups as the substituents on the siloxane backbone is by far the most common silicone polymer that has been most widely studied. 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 monomer, $SiO(CH_3)_2$ of PDMS is exhibited in Figure 2.2. The flexibility of PDMS is contributed by the inorganic siloxane backbone while a very low surface energy is imparted by the methyl groups. This leads to a glass-transition temperature of less than -120°C and consequently quite a wide range of application temperatures, from below -40°C to above 150°C. In addition, the degradation of PDMS can be up to 300°C. Thus, PDMS finds electrical and non electrical applications like they have been used in the insulation of electrical equipment and for laminating printed circuit boards (Leblanc, 2010).

Other than that, properties that have made PDMS a very important inorganic polymer from a commercial point of view include its very high hydrophobicity, high thermal stability, non-toxicity and high gas permeability. As a consequence, the applications of PDMS are in extremely diverse areas which include areas such as high-temperature insulators, antifoam applications, biotransplants, drug-delivery systems, flexible elastomers and many more. As drawbacks, PDMS is characterized by very poor tensile strength so it requires addition of reinforcing additives to improve the mechanical properties to meet the requirement of the final application.

PDMS as written above is depicted with a linear backbone. However, all the applications stated above are not achieved by such a linear polymer alone but by its many modifications. Normally, PDMS is used in crosslinked form after being reinforced with fillers in many elastomeric applications. Crosslinks are formed between different polysilaxane chains as a consequence of intermolecular Si–O–Si linkages or $Si–CH_2CH_2–Si$ links (Chandrasekhar, 2005).



$$\begin{array}{l} \quad CH_3 \\ \quad | \\ (\,Si - O -\,)_n \\ \quad | \\ \quad CH_3 \end{array}$$

Figure 2.2: The basic repeating unit of PDMS, $[SiO(CH_3)_2]_n$ (Chandrasekhar, 2005).

2.2 Introduction to Particulate Fillers

Nowadays, particulate fillers have played an important role in the development of commercial uses for polymers. At first, fillers were seen as cheap diluents. However, their ability to beneficially modify many properties of polymers soon to be realized so they are used for many purposes today. Therefore, particulate filler can be defined as a solid compounding material, usually in finely divided form, which may be added in relatively high proportions to a polymer for technical or economic reasons. In addition, particulate fillers are also considered as solid additives that differ from the matrices with respect to their composition and structure.

There are many reasons for using particulate fillers in polymer matrices. One of the reasons of using fillers is lowering the cost. Final product cost will be reduced when incorporation of fillers into the polymer reduces the resin content. Furthermore, fillers provide a reduction of shrinkage during curing of a thermoset system or a thermoplastic resin. This reduced shrinkage can prevent warpage or cracking that may happen in the case of large molded parts. In general, thermal conductivity of mineral fillers is in the order of ten times greater than the thermal conductivity of polymer. Hence, the filled polymer displays a higher thermal conductivity than the unfilled resin. This provides faster dissipation of localized hot spots which may cause thermal decomposition of a polymer or failure of a sensitive electronic component adjacent to the polymer. A common effect of most inorganic fillers in polymer system is reducing the mold shrinkage and thermal expansion. Other reasons for using fillers in polymer system include improved processing, density control, optical effects, electrical properties, magnetic properties, flame retardancy and improved mechanical properties (Katz, 1998; Rothon, 2001).

In rubber industry, particulate fillers can be classified as reinforcing and non-reinforcing, depending on whether or not they improve the performance characteristics of the final product. For non-reinforcing fillers or so-called inactive fillers, they result small increases in viscosity of the compound, cause deterioration of the mechanical properties of the vulcanizate and do not show any reinforcing action. Hence, they are usually called extenders which are used to reduce the production cost of rubber goods. Generally, powder minerals like calcium carbonates, china clay, and barium sulphate, are used as non-reinforcing fillers. On the other hand, reinforcing fillers or active fillers are able to enhance the performance characteristics such as the tensile strength, modulus, etc. of the composite. In addition, reinforcement in vulcanized elastomers can be concluded as the simultaneous improve in stiffness and resistance to fracture by the incorporation of filler. Particulates like carbon blacks and silica are the most widely used reinforcing fillers in the rubber industry.

Apart from that, there is one new type of filler which has emerged to challenge the domination of traditional fillers such as carbon blacks and silica in the rubber industry. They are new-generation nano scaled fillers. Examples of nanoscaled fillers are layered silicates, carbon nanotubes, carbon nanofibers, exfoliated graphite, etc. Nanoscaled fillers dispersed as a reinforcing phase in elastomer matrix has became a relatively new form of useful materials. These composites show a change in structure and composition over a nanometer length scale and possess remarkable property improvements if compared with the unfilled polymer or conventional micron-sized composites (Kim et al., 2011).

2.3 Synthetic Diamond

Diamond has grown increasingly important in science and technology due to its extreme hardness, chemical inertness, high thermal conductivities, wide optical transparency and other unique properties. However, the supply of naturally occurring diamond is limited, uncertain and far below demand. This has fuelled efforts to synthesize diamond in the laboratory. Experiments on the production of synthetic diamond (SD) or nanoscale diamond crystallites have already been carried out in the late 1950s and early 1960s by DeCarli and Jamieson. They discovered that tiny diamond crystallites could be gained from the action of a shock wave on graphitic material. This shock wave procedure was patented in the 1960s. From that time on, DuPont Corp. has been producing about 2 million karat of SD in this manner per year. Around 1963, the basic principle of detonation synthesis to fabricate SD was discovered by Russian scientists Volkov and Danilenko. They found out that the soot provided by the detonation of carbonaceous explosives bore diamond. However, these results were remained unpublished due to their military relevance. In early

1980s, the first plant for an industrial scale production of nanodiamond (ND) in an output of several tons per year has been established. This is beneficial to the researchers who study on SD because SD can be available in sufficient amounts at reasonable prices. Nowadays, there are big plants exist, for instance, in Russia, Ukraine, China, Germany, the USA and Japan (Krueger, 2010).

Today, several methods are available to fabricate nanoscale diamond particles. The simplest technique is the milling of larger synthetic or natural microndiamonds and separation of the smaller fraction by centrifugation. Another method is circular shockwaves transformation of graphitic material into diamond crystallites. Ignition of an explosive which cause the propagation of a circular shockwave that compresses the driving tube is applied in this method. Thus, sp^2 carbon material is transformed into sintered ND particles in the process. There is also another technique called detonation synthesis which is for bulk-scale production of ND. This technique which involves a mixture of trinitrotoluene (TNT), hexogen and octogen, synthesizes a novel class of nanomaterials with unique surface properties. During the explosion, pressure may reach 20 GPa for a duration of a fraction of one micro second and temperature could exceed 3000°C. The lack of oxygen in the combustion of the explosive led to a large amount of diamond particles in the soot residue. The soot residue also contains various impurities such as metal and concrete debris from the reaction chamber and a significant amount of nondiamond carbon. Chemical Vapour Deposition (CVD) techniques have been developed to fabricate diamond at low pressure and low temperature conditions from gas phase precursors which are some carbon containing gas (CH_4, C_2H_2) diluted in hydrogen. CVD refers to the process where solid materials are formed from the gas phase at proper temperature and pressure. The main attraction of CVD diamond is its film form where new applications like coatings or optical mirrors are possible.

Diamond which is carbon in the most concentrated form, involves sp^3 hybridization of the valence electrons in carbon to form chemical bonds. Each carbon atom in diamond shares all four of its available electrons with adjacent carbon atoms. This forms a tetrahedral unit with 1.54 Å in length. The shared electron-pair bonding forms covalent bond which is responsible for the many superlative properties of diamond. Equal angles of 109°28' formed by the covalent bond separating each carbon atoms. The repeating structural unit of diamond consists of eight atoms and displays the face-centered cubic structure as shown in Figure 2.3 (Nor et al., 2011; Dua, 2004).

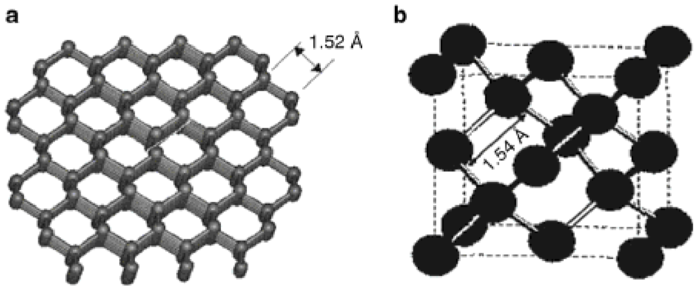


Figure 2.3: (a) Diamond lattice. (b) Face-centered cubic structure of diamond (Nor et al., 2011).

Milled synthetic microdiamond particles display pronounced facets while shockwave and detonation diamond usually possess rather rounded shapes without pronounced facets. The detonation ND has the smallest particle sizes among particulate SD which is ranging from 4 to 5 nm. Normally, an individual grain with 4 nm in width consists of about 7200 carbon atoms and there is about 1100 atoms are situated on the surface. Oxygen-containing groups such as chemical functional groups (hydroxyl, carboxylic, lactones, ketones and ethers) and graphitic material are exist on the surface of diamond particle as shown in Figure 2.4. Thus, dispersal of detonation diamond can be challenging due to the tendency to aggregate via interparticle bonding. On the other hand, most micron diamonds are fabricated by breaking large diamond grains of poor quality. The breaking of diamond can be done by stamping, compression, impact, shear and attrition. Impact and shear always produce micron diamonds in irregular shape (Yeap and Loh, 2009).

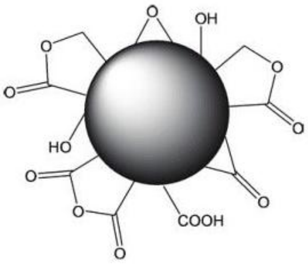


Figure 2.4: The detonation ND surface is covered with a variety of functional groups (Yeap and Loh, 2009).

SDs are widely used in biomedical application due to its non-toxic property. ND particles have been considered as a vehicle for gene and drug delivery. In addition, microdispersed sintered ND is served as a stationary phase in high-performance liquid chromatography. Furthermore, SD powder which is one of the hardest man-made abrasives is used in a variety of grinding and polishing application in diverse industries. ND with its high thermal conductivity (around 2000 W/mK) is an ideal material of choice for certain electronic applications like three dimensional and hybrid circuit packages, power laser diodes and multichip modules. Diamond thermal greases which are formulated with ND powder and silicone fluids have been applied as base oil to provide superior thermal conductivity for heat dissipation purposes in electronic field (Sung and Lin, 2010).

2.4 Carbon Nanotubes

Carbon nanotubes (CNTs) have becoming remarkable objects that look set to revolutionize the technology landscape in the near future after the discovery by Iijima in the early 1990s. Since then, tones of researches in different field such as mechanics, optics and electronics have focused on both the fundamental physical properties and on the potential applications of CNTs. The expectations surrounding CNTs are quite high especially in electronic field. Nanotube-based technologies have been recognized as the best solution for further miniaturization of microchips when many believes that current techniques for miniaturizing microchips are about to reach their lowest limits. Apart from that, CNTs are good candidates for the design of composite materials. A few weight percent of CNTs that embedded in polymer matrices are able to enhance the conductivity, either electrical or thermal, and mechanical resistance of the materials. Another application of CNTs which possess high thermal conductivity is to improve the flame retardancy of polymers. This is due to the fact that polymers are less thermally stable than nanotubes and nanotubes are flammable at high temperature (Bhushan, 2006).

In general, single-wall carbon nanotubes (SWCNTs) are the fundamental form of CNTs. A SWCNT is a single hexagonal layer of graphene sheet of nanometer scale diameter that has been rolled up to form a seamless hollow cylinder and capped by hemispherical ends. There are three types of SWCNTs which are armchair nanotubes, zig-zag nanotubes and chiral nanotubes as shown in Figure 2.5a. The term ‘armchair’ and ‘zigzag’ refer to the arrangement of hexagons around the circumference while ‘chiral’ is referred to hexagons that are arranged helically around the tube axis. Armchair and zig-zag nanotubes possess planes of symmetry both parallel and perpendicular to the nanotube axis while chiral nanotubes do not.

All armchair nanotubes are metallic whereas only 1/3 of the chiral nanotubes have metallic character. On the contrary, a multiwalled carbon nanotube (MWCNT) is a stack of graphene sheets rolled up into concentric cylinders as shown in Figure 2.5b. The wall of each MWCNT layer is parallel to the central axis. They have a diameter between 2 and 100 nm (Iqbal and Goyal, 2010).

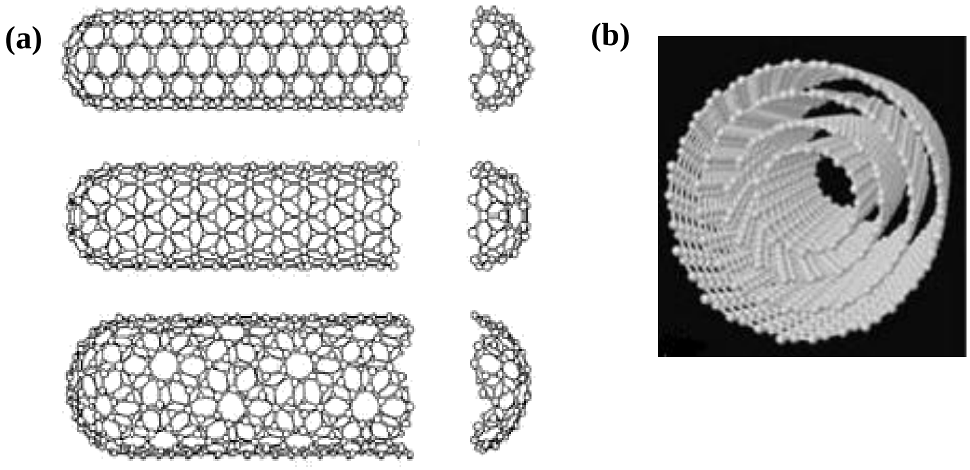


Figure 2.5: (a) Armchair (top); zigzag (middle) and chiral SWCNTs. (b) Structure of MWCNT (Iqbal and Goyal, 2010; Grady,2011).

CNTs are unique because of the particularly strong covalent bonding between the carbons of the curved graphene sheet, which is stronger than in diamond. This can be proved by the difference in C–C bond lengths for CNT and diamond, which are 0.142 and 0.154 nm respectively. This strong bonding makes both SWCNTs and MWCNTs particularly stable against deformations. The tensile strength for SWCNTs was measured as ~45 GPa. Ideal or defect-free MWCNTs are also expected to have high tensile strength too. The flexural modulus of ideal MWCNTs should logically better than that of SWCNTs due to the increasing number of walls. Traditionally, carbon-based materials have been a material class that exhibits very high thermal conductivity. Thus, high thermal conductivity is expected in CNTs with even stronger sp^2 bonds than the sp^3 bonds in diamond. In addition, other characteristics of CNT include inertness, high aspect ratio, low mass density, large surface area and versatile electronic behavior likes high electron conductivity (Bhushan, 2006; Grady, 2011).

2.5 Boron Nitride

Boron nitride (BN) is a synthetic product and not found in nature. BN is constructed by boron (B) and nitrogen (N) atoms. B and N from group III and V in the Periodic Table of Elements are neighbours of carbon in group IV. Hence, BN is expected to form similar covalent structures to the carbon allotropes due to the B–N bonds and C–C bonds are isoelectronic. As a result, BN exists in various crystalline forms like hexagonal phase (h-BN), cubic phase (c-BN), rhombohedral phase (r-BN) and wurtzite phase (w-BN).

H-BN which crystallizes similar to graphite in a hexagonal sheet layered structure is the most stable and softest among BN polymorphs. The atomic planes are formed by hexagonal rings with strong covalent bonds (α-bonding) between B and N atoms in the rings. Weak Van der Waals bonding (π-bonding) exists between the atomic planes. The atomic planes are stacked on top of each other without any horizontal displacement. Since N has higher electronegativity, the π-electron is located at the nitrogen. Therefore, h-BN is an electrical insulator and its colour is white. On the other hand, c-BN exhibits similar crystallite form to the diamond lattice so B and N atoms are tetrahedrally coordinated. B and N atoms display sp^3 hybridization in this arrangement. Thus, c-BN shows high hardness, high thermal conductivity and electrically insulative property. BN is able to form a superhard hexagonal phase in wurtzite type (w-BN). This modification is a high pressure phase.

The r-BN structure is similar to the h-BN and is formed during conversion of c-BN to h-BN. All of these four crystallite forms are shown in Figure 2.6 below (Haubner et al., 2002; Lee et al., 2009).

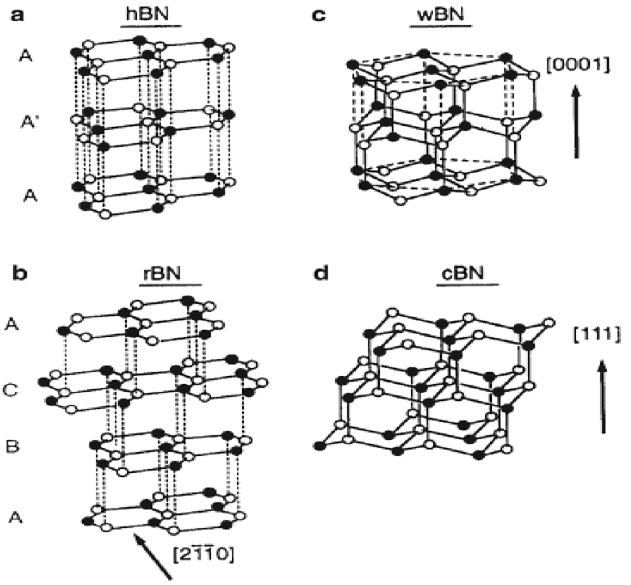


Figure 2.6: Graphical representations of (a) h-BN, (b) r-BN, (c) w-BN and (d) c-BN phases (Lee et al., 2009).

2.6 Silicon Nitride

Silicon nitrides (SNs) are a range of advanced engineering ceramic material with predominantly covalent bonding. SN is formed with each silicon (Si) atom is bonded to four N atoms and each N atom is bonded to three Si atoms as shown in Figure 2.7. This has resulted to a strong network in SN. Thus, SN has been characterized by high strength, fracture toughness, hardness, creep resistance and excellent chemical and thermal stability. All of these superior properties have led to the development of SN in the industry as engine components, bearings and cutting tools. Four different grades of SNs are available commercially resulted from different methods of fabrication which governs their resulting properties and applications. There are reaction bonded SN (RBSN), hot-pressed SN (HPSN), sintered SN (SSN) and hot isostatically pressed SN (HIPSN).

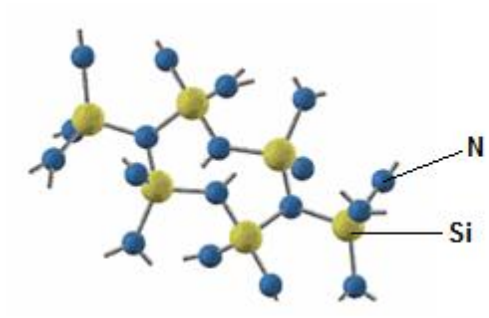


Figure 2.7: Structure of SN (Oxtoby et al., 2007).

RBSN is a high-purity grade of SN gained from direct nitriding of compacted silicon powder. RBSN shows superior thermal shock resistance and excellent corrosion resistance to molten nonferrous metals, especially aluminium metal. HPSN is made by adding a flux to a fine SN powder and then pressing the powder in a graphite die by applying both heat and pressure using sintering aids. The resultant body is fully dense with excellent mechanical properties. Applications of HPSN tend to be simple shapes as the preparation of finished components requires expensive machining by utilizing diamond grinding. Apart from that, SSN consists of a family of fully dense materials which can be fabricated in cost-effective and complex net shape. SSN has the best combination of properties which makes it the leading technical ceramic for structural applications like automotive engine parts, bearings and ceramic armor. HIPSN is gained by glass-encapsulated parts that are placed in an autoclave with heat and pressure applied. Although there is a slight decrease in strength, a great enhancement in reliability can be observed (Cardarelli, 2008).

2.7 Particulate-filled Silicone Rubber Composites

Elastomeric composites are gaining attention widely in the industry due to their light weight, design flexibility and processability. Particulate filled elastomers are the most commonly used classes among them. Nowadays, the term ‘filler’ in rubber technology is no longer implied as a material to save cost for the expensive rubber but it is known as a material with the ability to modify the properties of the rubber. Modern-day fillers can change one or more of the following properties:

- improve surface characteristics and dimensional stability;
- change thermal, magnetic and electrical properties;
- improve mechanical properties, durability and rheology;
- affect chemical reactivity, biodegradability, etc.

Therefore, incorporation of micron- or nano-sized inorganic filler particles in elastomer has been the standard practice in the composite industry (Kim et al., 2011).

2.7.1 Properties of Particulate-filled Silicone Rubber Composites

2.7.1.1 Mechanical Properties

In practical application, silicone rubbers are often reinforced with particulate fillers to improve the physical and mechanical properties. The mechanical properties of silicone rubber composites normally are characterized by their tensile strength, strain at break, tensile modulus and hardness. Generally, tensile strength increases with decreasing particle size and filler loading. It also can be enhanced by filler with higher aspect ratio. For example, rod-like particles show higher reinforcing effect on tensile strength due to the increasing interaction bonding between the polymer and the filler particle surface. Furthermore, modulus and hardness of silicone rubber composites increase with filler loading and decreasing particle size. Tear strength and impact strength can be enhanced by low loading of fillers with high aspect ratio while compressive strength is promoted by high loading of particles with low aspect ratio (Otterstedt and Brandreth, 1998).