MECHANICAL AND THERMAL PROPERTIES OF THERMALLY CONDUCTIVE FILLERS FILLED POLYPROPYLENE COMPOSITES

NURULIZZATI BT MOHD SHUKRI

UNIVERSITI SAINS MALAYSIA

2012

MECHANICAL AND THERMAL PROPERTIES OF THERMALLY CONDUCTIVE FILLERS FILLED POLYPROPYLENE COMPOSITES

By

NURULIZZATI BT MOHD SHUKRI

Thesis submitted in fulfillment of the requirements

for the Degree of

Master of Science

December 2012

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles "Mechanical and Thermal Properties of Thermally Conductive Fillers Filled Polypropylene Composites". 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: Nurulizzati Bt Mohd Shukri

Signature:

Date:

Witness by,

Main Supervisor: Prof. Dr. Ir. Mariatti Bt Jaafar @ Mustapha

Signature:

Date:

ACKNOWLEDGEMENT

In the name of ALLAH, Most Gracious, Most Merciful, All praise is due to ALLAH, peace and blessings of ALLAH be upon our prophet Muhammad S.A.W, I would like to address my gratitude to all those who have helped me throughout my MSc project in School Materials and Mineral Resources Engineering, Universiti Sains Malaysia. Especially, to my beloved husband, Ahmad Rahimi Ali, my daughter Nurul Damia Yasmine and all my family, for their unconditional love, encouragements and prayers which have given strength to keep moving.

My special thanks and appreciation to my supervisor, Prof. Dr. Ir. Mariatti Jaafar @ Mustapha. Her wide knowledge and logical thinking have been of great value for me. Her understanding, encouragement and personal guidance have provided a good basis for the present thesis. I wish to express my warm and sincere thanks to Dean of School Materials and Mineral Resource Engineering, Universiti Sains Malaysia, Prof. Dr. Ahmad Fauzi Mohd. Noor.

I would also like to thank the technician and staff for their assistance especially Mr. Mohammad, Mr. Sofi, Mr. Shahril, Mr. Segaran, Mr. Faizal, Mr. Rashid, Mr. Khairi, Mr. Suhaimi, and Mr Kemuridan. They are willing to help students in conducting experiment in lab. They had also taught me a lot of technical knowledge. My appreciation extends to my special friend, Nor Fadhilah Ibrahim for her patience and kindness in helping me during my hard time. I also would like to thank all my friend in postgraduate studies including, Hamizah, Dr. Mahani, Azliyana, Madihah, Shazlin, Hidayah, Nuraya, Kong Siew Mui, Hamidah, Safuan and others for their friendship and for helping me in all the possible way.

Thank you all.

TABLE OF CONTENT

CHAPTER 3: MATERIALS AND METHOD

List of Tables

List of Figures

List of Main Symbols

T_g	-	Glass transition temperature
$T_{d\%}$	-	Maximum thermal degradation temperature
X_{50}	-	Mean particle size
Mpa	-	Mega-Pascal
Ppm	-	Part per million
Vol. %	-	Volume percent
°C	-	Temperature
µm	-	Micro-meter
W/m.K	-	Watts/meter.Kelvin
%	-	Percent
Rpm	-	Rotation per minutes
H	-	Hour
Mm	-	Millimeter
Ml	-	Milliliter
Δt	-	Change in the temperature
Nm	-	Nanometer
J/Kg	-	Joule/Kilogram

List of Abbreviations

ASTM	-	America Standard for Testing Materials
MWNT	-	Multiwall carbon nanotube
DWNT	-	Doublewall carbon nanotube
SD	-	Synthetic diamond
BN	-	Boron nitride
Cu	-	Copper
MFI	-	Melt flow index
TGA	-	Thermo gravimetric analysis
DTG	-	Derivative thermo gravimetric
CTE	-	Coefficient of Thermal Expansion
DMA	-	Dynamic mechanical analysis
PP	-	Polypropylene
LDPE	-	Low density polyethylene
HDPE	-	High density polyethylene
PMMA	-	Poly (methyl methacrylate)
BM	-	Planetary ball milling
TRM	-	Two roll mill
AIN	-	Aluminium nitride
Si_3N_4	-	Silicon nitride
CB	-	Carbon black
ADHM	-	Additive rule of hybrid mixture
SEM	-	Scanning electron Microscope

SIFAT-SIFAT MEKANIKAL DAN TERMA BAGI KOMPOSIT POLIPROPILENA TERISI PENGISI KONDUKTIF TERMA

ABSTRAK

Kajian ini telah dijalankan untuk menyiasat kesan pelbagai pengisi seperti tiub nano karbon (MWNT), berlian sintetik (SD), boron nitrida (BN) dan tembaga (Cu) pada sifat-sifat komposit polipropilena (PP). Komposit ini dihasilkan dengan menggunakan kaedah pengisar berpenggulung dua dengan isipadu pengisi antara 1 hingga 4%. Hasil kajian mendapati bahawa PP/SD, PP/BN dan PP/Cu menunjukkan kekuatan tegangan maksimum pada 2 % isipadu pengisi dan corak menurun selepas isipadu itu. Mikroskop elektron imbasan (SEM) telah digunakan untuk memeriksa struktur patah, dan ia diperhatikan bahawa gumpulan bertambah dengan pertambahan pengisi. Kekonduksian terma, kestabilan terma, pekali pengembangan terma (CTE) dan modulus simpanan telah bertambah baik dengan pertambahan pengisi. Antara keempat-empat pengisi, MWNT menunjukkan potensi yang baik dalam meningkatkan sifat terma komposit PP. Dalam siri kedua, kesan ke atas sifat komposit PP terisi pengisi hybrid MWNT/SD dan MWNT/BN telah dikaji dan dibandingkan dengan komposit berpengisi tunggal. Hasil kajian menunjukkan bahawa komposit hibrid meningkatkan kekonduksian terma, kestabilan terma, pekali pengembangan terma dan modulus simpanan. Walau bagaimanapun, peningkatan ini mempunyai kelemahan di mana sifat tegangan dan lenturan komposit hibrid menjadi lebih rendah daripada komposit berpengisi tunggal. Dalam siri ketiga, penambahbaikan ke atas adunan dijalankan dengan menggunakan dua kaedah pengadunan; pengisar bebola planet dan pengisar berpenggulung dua. Peningkatan dalam kekuatan, kekakuan, kekonduksian terma dan modulus simpanan dapat diperhatikan dalam system ini. Walau bagaimanapun, kestabilan terma telah didapati berkurangan apabila dua kaedah pengadunan ini digunakan dalam proses fabrikasi.

MECHANICAL AND THERMAL PROPERTIES OF THERMALLY CONDUCTIVE FILLERS FILLED POLYPROPYLENE COMPOSITES

ABSTRACT

The current study was carried out to investigate the effect of various fillers for example (such as) carbon nanotube (MWNT), synthetic diamond (SD), boron nitride (BN) and copper (Cu) on the properties of polypropylene (PP) composites. This composite was compounded using two roll mill mixing method and the filler content was loaded from 1 to 4 volume %. It was observed that the PP/SD, PP/BN and PP/Cu exhibited maximum tensile strength at 2 volume % and a reduction trend can be observed after 2 volume %. Scanning electron microscopy (SEM) was used to examine the fractured structure of the composites, and it was observed that agglomeration increased as the filler loading increased. Thermal conductivity, thermal stability, coefficient of thermal expansion (CTE) and storage modulus of the composites were improved by addition of fillers in PP. Among these four fillers, MWNT showed greater potential in improving thermal properties of PP composites. In the second series, the effects of hybrid filler (MWNT/SD and MWNT/BN) in PP composites were studied. The results showed that the thermal conductivity, thermal stability, coefficient of thermal expansion and storage modulus of the hybrid composites were improved if compared to single fillers composites. However, the tensile and flexural properties of hybrid composites were noted to be lower than the single composites. In the third series, the improvements in the compounding were carried out by using two compounding methods; planetary ball mill and two roll mill. Enhancement in strength, stiffness, thermal conductivity and storage modulus of the composites has been observed in this system. Nevertheless, the thermal stability was found to be reduced as the two compounding methods were used in the fabrication process.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, the concept of polymer composites has been extended to the electronic application. In electronic application, effective heat dissipitation is crucial to enhance the performance and reliability of the electronic devices such as thermal conductance in circuit board, heat exchanger, heat sink, appliances and machinery. For most modern microelectronic devices, cooling is restricted by a low thermal conductivity of the polymeric packaging material (i.e., 0.10–0.25 W/m.K) as compared to commonly used metal or ceramic materials. Therefore, as the power density becoming larger and larger, the molding plastics encapsulate is required to have a high thermal conductivity to dissipate the huge accumulated heat and a low dielectric constant to avoid signal propagation delay (Zhou *et al.,* 2009).

Among the most versatile polymer matrices, polyolefins such as polypropylene (PP) is the most widely used thermoplastics in food packaging, automobile and other industrial sectors. Its well-balanced physical, mechanical properties, easy processability at a relatively low cost, high thermal stability and resistance to corrosion makes them an excellent material (Prashantha *et al.,* 2009; Bikiaris *et al.,* 2008). However, despite all these advantages, there is also drawback in its application. Their low thermal conductivity, resulting from the polymer matrix (which is a good thermal insulator), is a major drawback for reaching high power density levels. In fact, the current going across the filled polymer induces power dissipation by the joule effect, which leads to an important thermal gradient within the material and, in the long run, can damage the device due to unacceptable stresses (Droval *et al.,* 2008).

The addition of thermally conductive fillers in PP and other thermoplastic composites is mainly governed by price-performance relationships. Apart from reducing the price of final material, thermally conductive filler can also help to improve the thermal properties especially thermal conductivity, shrinkage of the molding and stiffness, which are principle limitations for bulk thermoplastics (Luyt *et al.,* 2009). Researchers have incorporated materials with high thermal conductivity into polymer to improve the thermal conductivity of the composites. In order to increase thermal conductivity of the composites, heat resistance at the filler-matrix interface need to be minimized. This resistance results from phonon scattering process. Adding thermal conductive filler with a high aspect ratio such as carbon nanotube, carbon fiber and nanowire, can easily form network structure and increase the thermal conductivity (Teng *et al.,* 2011; Kumlutas *et al.,* 2006). Such single composites cannot meet the requirement for thermal conductive nor need very high filler loading (up to 70 vol. %) to achieve the necessary thermal conductivity at expense of processing problem (Cui *et al.,* 2011).

Preparation of nanofiller in thermoplastic polymer composites (PC) by melt-compounding technique is very popular because it implies the use of conventional polymer processing equipments and generating moderate production costs (Perrin-Sarazin *et al.,* 2009). However, one of the most important drawbacks lies in the fact that nanoparticles such as CNT show a great tendency to establish strong van der Waals force which caused strong agglomeration phenomena. Hence, when mixed with polymer matrices, CNTs tend to segregate in tight bundles, precluding their effective distribution in composites. Homogeneous dispersion and distribution of nanofiller particles in polymer matrix is very important for improvement of mechanical properties of PC. In other word, the potential problem in preparation of PCs is poor dispersion and distribution of nanoparticles in polymer matrix. Generally, agglomeration is highly dependent on dispersion of particles in a matrix, i.e. increase in the degree of particle dispersion results in decreasing particles agglomeration. On the other hand, distribution indicates how uniformly the primary particles or their agglomerates are distributed through the composites. Suitable strategies are strictly required to improve the PC compatibility and dispersibility and to achieve the formation of homogeneous polymer based composites with improved polymer-filler interfacial adhesion (Perrin-Sarazin *et al.,* 2009).

A new alternative method for the preparation of composites materials relies on solid-state mixing at room temperature, which ought to involve an efficient mixing of two or more species by mechanical milling. Mechanical milling and mechanical alloying refers to high energy ball milling technique employed to process solid state single or multiple phase materials, respectively (Cavalieri *et al.,* 2002). It is an effective unconventional technique currently used in inorganic material synthesis and processing. Structural modification and mechanochemical activation, leading to great changes in their surface and contact between molecular solid is promoted (Sorrentino *et al.,* 2005; Perrin-Sarazin *et al.,* 2009; Gorrasi *et al.,* 2011). The undeniable advantage of these processes is that they are solvent free and are easy to scale up (Ambrogi *et al.,* 2012).

1.2 Problem statement

Most of applications in electronic industry require high thermal conductivity materials to dissipate the huge heat to avoid propagation signal delay. Polymers such as polyethylene (PE), polypropylene (PP) and polyamide (PA) are limited in this application due to the low thermal conductivity. These polymers will face failure at an early stage of the application. In order to increase the thermal conductivity of these polymers, addition of metal or ceramic fillers to the polymers is commonly been used. Fillers such as boron nitride, aluminum nitride, silicon nitride, alumina, silicon carbide, silica, synthetic diamond, and copper powder are widely employed for this purpose. Such single composites cannot meet the requirement for thermal conductive nor need very high filler loading (up to 70 vol. %) to achieve the necessary thermal conductivity at expense of processing problem. Hence, researchers are constantly developing new ways of reducing such problems and the common approaches that been used is by using nanofiller and combining two fillers or also known as hybrid. Application of nanofiller will reduce the filler loading amount due to high surface area, which is able to increase the interaction between filler-filler and filler-matrix interaction. Hybrids composites can achieve a balance between properties as compared to single reinforced composites. Conventional mixing techniques such as injection molding, extruder and internal mixer reported to be inefficient in mixing a nano size fillers (Zhou *et al.,* 2007**)**. Thus, different method such as high energy planetary ball milling (BM) is commonly been used to mix the nanofiller with polymer such as PP, PEEK, PMMA composites (Zhang *et al.,* 2008, Melo *et al.,* 2008, Joni *et al.,* 2010; Kang *et al.,* 2010; Hedayati *et al.,* 2011**)**. This method is widely used for metal and ceramic processing with fine microstructure (Sorrentino *et al.,* 2005; Melo *et al.,* 2008). The results show that BM method is powerful dispersion method to facilitate homogenous filler distribution and reduces the number of defects and entanglements. Thus improve properties of the polymer composites (Lu *et al.,* 2004; Hussain *et al.,* 2006). In this study, the combination effect of thermal conductive nanofillers and milling processing method was investigated.

1.3 Objectives of the study

The main objectives of the research are:

1. To investigate the effect of various high thermal conductive fillers (multiwall carbon nanotube, synthetic diamond, boron nitride and copper) and filler loading (1 to 4 volume %) on the properties of polypropylene composites.
2. To study the effect of hybrid fillers on the mechanical and thermal properties of polypropylene composites.
3. To study the effect of improvement in compounding by using planetary ball mill and two roll mill on the properties of polypropylene composites.

1.4 Organization of thesis

This thesis consists of five chapters as listed below.

Chapter 1: Gives some background of research topic, problem statement, objectives, and the general arrangement of the thesis.

Chapter 2: Provides the literature review on thermoplastic composites, thermally conductive fillers, factors affecting the thermally conductive composites, effects of hybrid composites on the mechanical and thermal properties and their applications. The literature review which was carried out is related to previous published works.

Chapter 3: Presents the material used, experimental procedures and characterization methods involved in the study.

Chapter 4: Reports on the characterization of thermally conductive fillers used. Based on results obtained in the study of single fillers, types of hybrid fillers and their composition have been investigated. The third section reports on the effect of improvement in compounding by using planetary ball mill and two roll mill methods. The physical, mechanical and thermal properties of the composites were investigated and compared.

Chapter 5: Concludes on the overall work as well as suggestions for the future work to complement this research.

1.5 Scope of study

The scope of this study includes investigation on the properties of four different types of fillers which are multiwall carbon nanotube (MWNT), synthetic diamond (SD), boron nitride (BN) and copper (Cu) filled polypropylene (PP) composites. Two roll mill method was used as a compounding process and properties such as tensile test, flexural test, thermal conductivity, thermal stability, coefficient thermal expansion and dynamic mechanical analysis were measured. Hybridization between MWNT/SD and MWNT/BN at compounding ratio of 1/3, 2/2 and 3/1 and the properties were characterized and analysis. In the last part, planetary ball mill and two roll mill methods were used to prepare MWNT/SD composites and the properties of this compound were investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

Composites are multiphase materials in which the different phases are artificially blended to attain properties that individual component alone cannot be attained. Generally, composites materials are made up of filler (one or more) in the particular matrix (Reddy, 2009). The matrices can be polymer matrix, metal matrix or ceramic matrix. Generally, polymer and metal are used as a matrix material because of some ductility is desirable; for ceramic, the reinforcing component is added to improve fracture toughness. The matrix phase serves several functions such as to bind the fillers together and acts as the medium by which an externally applied stress is transmitted and distributed to the fillers and only a very small proportion of an applied load is sustained by the matrix phase. The second function of the matrix is to protect the individual fillers from surface damage as a result of mechanical abrasion or chemical reactions with the environment. Finally, the matrix separates the fillers and by virtue of its relative softness and plasticity, prevents the propagation of brittle cracks from filler to filler, which could result in catastrophic failure (Callister, 2000).

Comparable to metal matrix and ceramic matrix, polymer matrix is widely used because polymer is the cheapest types of matrix, easy and better to process because of its low density materials. There are two typical polymer matrices which are thermoset and thermoplastic. The thermoplastic matrices was account for about 185 billion pounds per year or about 70% of the total worldwide plastic's industry production for the large volume and low cost commodity resins such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC) (Peters, 2004; Xanthos, 2005).

Filler can be defined according to American Society for Testing and Materials (ASTM) standard D-883, as relatively inert material added to a plastic to modify its strength, performance, working properties, or other qualities or to lower costs (Charles, 2007). Filler are used in polymers for variety of reasons: cost reduction, improve processing, density control, optical effect, thermal conductivity, control of thermal expansion, electrical, magnetic properties, flame retardancy and improved mechanical properties (Luyt *et al.*, 2006). There are three general types of fillers which are structural particulates and fiber as shown in Figure 2.1 and Figure 2.2.

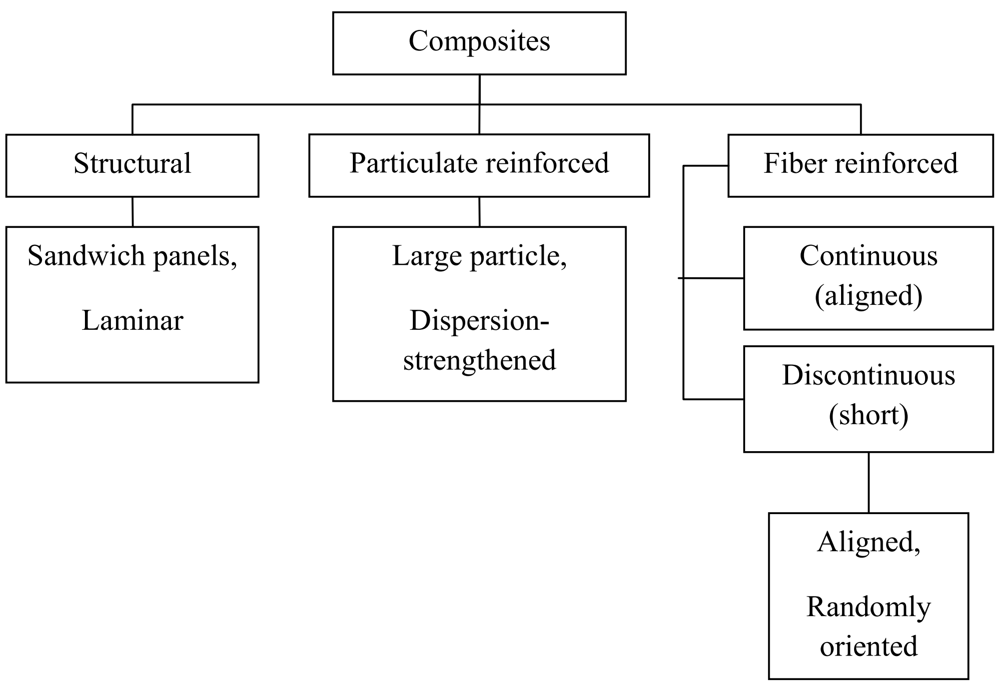

Figure 2.1: Classification scheme for the various composite types (Callister, 2003).

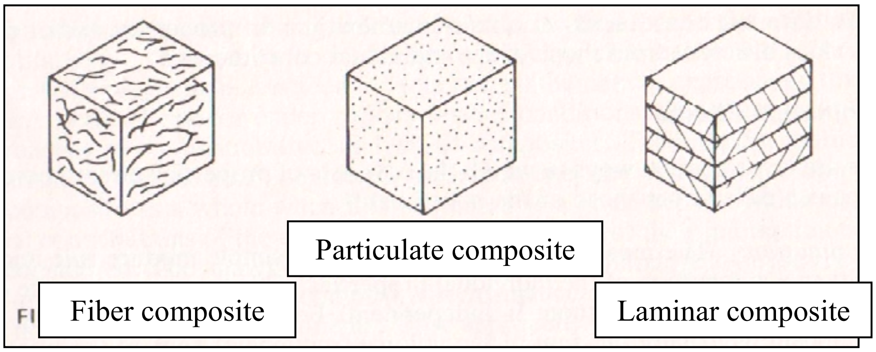

Figure 2.2: Class of composites (Schwartz, 1992).

Structural consist of simple binding together of different layers of materials such as papers, wood, sandwich panel and laminar. Fibrous filler is a fiber with an aspect ratio of at least 150:1. While, the particulates filler consist of reinforcing material being dispersed throughout the resin. The reinforcing material in particulate composites is more bulky and can be of many shapes and relative sizes. The incorporation of particulate fillers into polymer matrices is a well known technique to improve or modify some properties of neat polymer and used in very large quantities in all kinds of application (Charles, 2007).

One of the groups in particulate filler is thermally conductive. It is important in technological applications and constitutes an ongoing topic of tremendous commercial interest. It is well known that a conductive polymer composites consisting an insulating polymer matrix and conductive fillers in order to cope the thermal management issues. The thermal management issue has become a critical issue to achieve the sustained device performance and life time (Naficy and Garmabi, 2007; Dey and Tripathi, 2010; Gu *et al.*, 2009). The relatively high thermal conductive polymer composites were required to reduce heat buildup and also needed for fast signal propagation (Kumlutas and Tavman, 2006; Xie *et al.*, 2004).

2.2 Factor determining the properties of particulate filled polymer composites

Particulate filled polymer composites have a long history. Nevertheless, the basic information has yet to be established. This is largely due to the way in which the technology has developed, with different filler and polymer combinations tending to be developed to meet the specific demands of various industries (Moczo and Pukanszky, 2008). Investigations on the polymer properties containing various kinds of fillers have been widely reported (Jerebek *et al.,* 2010; Verbeek *et al.,* 2003). Generally failure properties such as tensile strength of this particulate composite are basically determined by the properties of the constituent phase (filler and matrix), composition and interfacial interaction (Jerebek *et al.,* 2010).

2.2.1 Constituent properties

Both of matrix and the filler exist as two separate constituent that do not combine chemically to any significant extent. In most composites, the matrix provides the framework and the filler provides the desired engineering or functional properties. Although the matrix usually makes up the bulk of the composites, the filler material is often used to such a large extend that it become the dominant material and makes a significant contribution to the overall strength and structure of the composites. In order to obtain the optimum properties in filled composites the two materials must be compatible and not react in a way that would degrade or destroy their inherent properties (Schwartz, 1992).

2.2.2 Composition

The properties of particulate filled thermoplastic depend strongly on the composition. The goal of the use of using fillers in polymer is either to decrease cost or to improve properties such as stiffness, dimension stability and thermal conductivity. These goals require the introduction of the largest possible amount of filler into the polymer, but the improvement of the targeted property may be accompanied by the deterioration of the others (Moczo and Pukanszky, 2008). Zhou *et al.* (2007) stated that the filler content should be under a desired level in order to avoid the deteriorating physical properties of the composites. In their study, the increasing of BN/HDPE volume fraction resulted in increasing the thermal conductivity. However, the stress at break was reduced begin at 30 vol. % of filler loading. Deformability, yield strain and elongation at break always decrease with increasing filler content.

2.2.3 Interfacial interactions

The quality of adhesion at the interface is of crucial importance for the behavior of particulate composites. The adhesion strength at the interface determines the load transfer between the components and affected the composites strength. However, tensile modulus is not affected by this parameter. In fact, tensile modulus is related to filler concentration and thus introduced to mechanical restraint (Metin *et al.,* 2004; Fu *et al.,* 2008). Particle-particle interactions induce aggregation and particle-matrix leads to the development of an interphase with properties different from those of both components (Pukanszky, 2000). The presences of aggregates are reported to induce the stress concentrators in MWNT/PP composites (Prashantha *et al.,* 2009).

2.3 Filler characteristics and their effect on composites properties

Generally, the effectiveness of reinforcing conductive fillers in composites is inversely proportional to the size and directly proportional to the aspect ratio of the filler. Moreover, the geometry of the particle is an important factor in achieving the maximum properties of the composites. The greater the surface to volume ratio of the filler, the greater will be the effectiveness of the filler (Reddy, 2009, Boudenne *et al.,* 2005). Qingzhong (2004) and Lazarenko *et al.* (2009) also reported that the polymer composite predominantly depends on the filler properties such as conductivity, the particle shape and size, and the volume fraction and nature of particle distribution. Besides, they found that the larger the concentration of the filler and the ability to form chain in the polymer matrix were induced better thermal properties of polymer composites (Qingzhong, 2004; Lazarenko *et al.,* 2009; Liang *et al.,* 2007).

2.3.1 Particle size and distribution

The mechanical properties of polymer composites containing uncoated fillers are determined mainly by their particle characteristic. Large particle drastically alter, usually deteriorate, the deformation and failure characteristics of composites. The volume in which stress concentration is effective is said to increase with particle size (Moczo and Pukanszky, 2008). Tang and Mariatti (2009) reported that the different particle size of graphite and nickel coated graphite filled HDPE has influenced the mechanical properties of the composites. However, modulus is not very affected by particle size. It is markedly improved by adding micro or nano-particles to a polymer matrix since hard particle have higher stiffness values than the matrix (Fu *et al.,* 2008).

On the other hand, Boudenne *et al.* (2005) and Jung *et al.* (2010) reported that, boron nitride (BN) and copper (Cu) nanoparticles filled HDPE and PP, respectively, resulted to better thermal conductivity and thermal stability compared to micro-size for both of fillers. This is due to the easier construction of thermal path in nanocomposites compared to micro composites. Moreover, small particle size is able to absorb and form thicker conductive paths to reduce the interfacial phonon scattering between matrix and fillers. The decreasing interfacial phonon scattering, resulted in increasing thermal conductivity and decreasing thermal expansion of the composites (Lee *et al.,* 2006; Yung *et al.,* 2006).

2.3.2 Specific surface area

The specific surface area of fillers is closely related to the particle size distribution and also has direct impact on composites properties (Moczo and Pukanszky, 2008). The high specific surface area is creating a great amount of interphase in a composite and a strong interaction between the fillers and the matrix (Lin *et al.,* 2010; Wu *et al.,* 2002). However, the drawback from high surface area is high tendency to form relatively large agglomerations and non-homogeneous dispersion within polymers especially in occurred in carbon nanotube (CNT) (Seyhan *et al.,* 2009). In addition, Tait *et al.* (2011) reported that the exfoliated graphite nanoplatelets possess high surface area and tend to aggregate which maybe the reason for the reduction in strength with addition of exfoliated graphite nanoplatelets.

2.3.3 Particle shape and aspect ratio

Particle shape is important in determine the stiffness, tensile strength, melt flow of the polymer composites. It can be determined by the genesis of the filler, by its chemistry, crystal structure and processing undergone (Rothon, 2003). Fillers for polymers exhibit in fact a stunning variety of chemical natures, particle sizes and shapes. Essentially three basic shapes can be distinguished: either spheres, or plaques (disks, lamellas) or rods (needles, fibers), as illustrated in Figure 2.3. Such basic shapes can be further combined to result in quite complex geometrical objects to which specific (reinforcing) properties can be associated (Leblanc, 2010). Usually the particle shapes were discussed in term of aspect ratio. The aspect ratio can be defined as long dimension to short dimension of the particles. It can vary from 1 for spherical particles to several 100 or more for fibers. Referring to Figure 2.4 where the effect of aspect ratio on network formation can be observed. Each of filler particles occupy 20 area percent with randomly assigned position and orientations, but their aspect ratio is different from each other. At aspect ratio of 1 (a), network formation is very short order and most particles are not in contact with another filler particles. When aspect ratio is increased up to 64 (Figure 2.4), the particle are joined into an effective network that contains multiple conduction path (Singh, 2002).

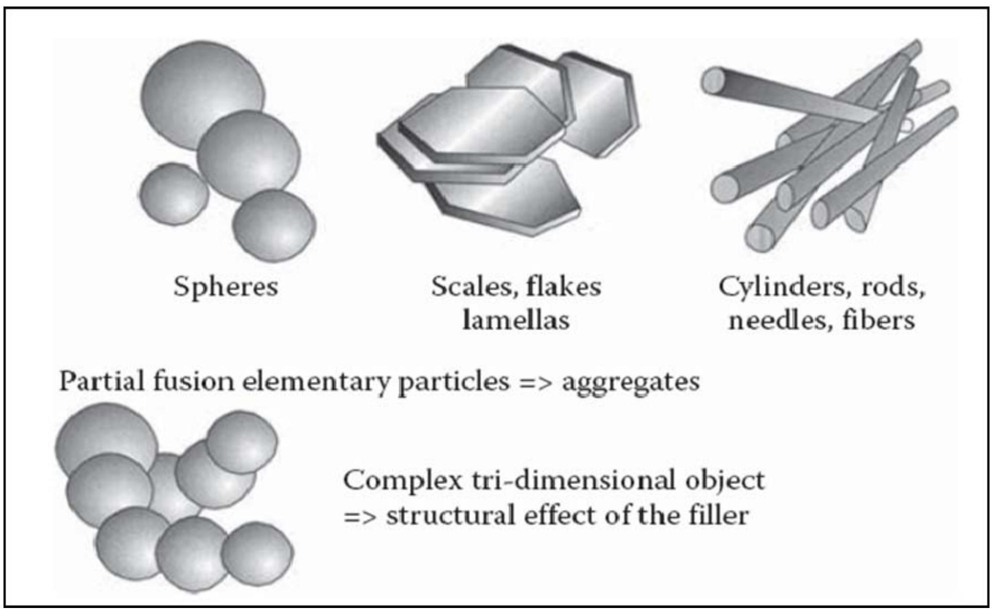

Figure 2.3: Filler basic shape and structure (Leblanc, 2010).

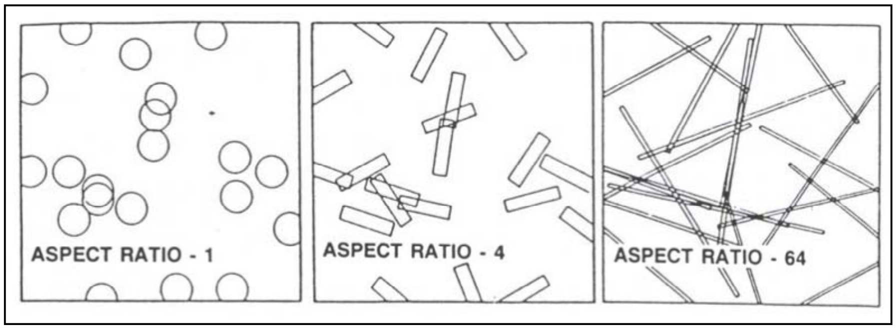

Figure 2.4: The effect of filler aspect ratio on network formation (Singh, 2002).

Debelak and Lafdi (2007) reported on the flake graphite with different surface area embedded in epoxy composites. The results showed that the filler with larger surface area increase the thermal conductivity and lowering the coefficient thermal expansion. This is because the surface area-to-volume ratio increases as the flake size gets larger. Similar observation was reported by Nurazreena *et al.* (2006) where flaky aluminum shape gives advantages rather than irregular dendritic copper and spherical iron in improving tensile properties and conductivity due to large surface area per unit volume, which subsequently impart better metal-to-metal contact. Whereas, Tekce *et al.* (2007) observed copper in fiber shape exhibited better excellent thermal conductivity than sphere and plates filled polyamide composites due to non-geometric fibrous. In addition, platelet and polygon gives by alumina, diamond and boron nitride can form better contact among the filler particles compared to the spherical shape present by silica filler. The non-spherical shapes have larger contact area and can conduct heat more efficient by than the spherical filler. However, the spherical shape were adequate to give superior thermal conductivity compared to the cubic particle shape due to better interaction even at lower filler concentrations (Lee and Yu, 2005; Kumlutas and Tavman, 2006).

2.3.4 Filler concentration

Concentration of filler in composites may vary over a wide range. At low filler concentration, too little filler is present to form a conductive network; that is, very few of the particles are nearly or actually in contact with other conductive particles. As a result, the conductive path includes many large gaps between filler particles, where conduction across the highly resistive matrix resin is necessary (Singh, 2002). Pezzotti *et al.* (2000), Xie *et al.* (2004) and He *et al.* (2007) reported that the addition of AIN/PS, AIN/PI and SI_3N_4/PS respectively, shows increasing of thermal conductivity as increase filler fraction. Homoegohar *et al.* (2006) reported that the tensile strength and flexural strength was sharply increased at lower filler content maximum up to 10% and after which the strength decreases. However, the tensile modulus was directly proportional to the filler loading. Addition of 20 % filler had increased up to 50 % tensile modulus.

Typically higher than 20 % by volume is generally required bringing the above-stated negatively effects of the fillers into play. This would detrimentally affect some important properties of the matrix polymers such as processability, appearance, density and ageing performance of mechanical properties (Wu *et al.,* 2002). Nurazreena *et al.* (2006) reported that tensile strength of aluminum, copper and iron embedded in HDPE shows decreasing trend with increasing filler loading. In tensile modulus, increasing trend was obtained with increasing filler loading for any types of fillers. Zerbarjad *et al.* (2004) reported the reduction in yield strength after addition of $CaCO_3$ into PP composites.

2.3.5 Filler property

Highly conductive metals such as silver will be more effective fillers than less conductive metals such as stainless steel (Singh, 2002; Weidenfeller *et al,*. 2004). Study by Lee *et al.* (2006) reported that BN can form conductive network at lower volume content compared to AIN, wollastonite, SiC whisker. This occurs due to the greater thermal conductivity value and thus, leads to better thermal conductivity of the BN filled HDPE composites. Table 2.1 summarizes the thermal conductive value of various conductive fillers.

Table 2.1: Typical properties of various thermally conductive fillers (Hnatek, 2002).

Material Metals	Thermal conductivity (W/m.K)	Material Insulators	Thermal conductivity (W/m.K)
Silver	430	Diamond	2000
Copper	400	Aluminum nitride	230
Gold	297	Beryllia (BeO)	210
Copper–tungsten	248	Alumina (Al_2O_3)	20
Aluminum	230	Glass ceramic	5
Molybdenum	140	Alumina	20
Nickel	92	Polyimide (PI)	0.002
Solder (SnPb)	57	Epoxy glass (PC board)	0.003
Steel	50	Polystyrene	0.15
Lead	40	Polypropylene	0.24
Stainless steel	29	u-Polyester	0.2

2.4 Thermal conductive fillers

Generally, thermal conductive fillers used to transfer heat by conduction involved in the use of a heat sink to dissipate heat from an electronic package, the heating of an object on a hot plate, the operation of a heat exchanger, the melting of ice on an airport runway by resistance heating, the heating of a cooking pan on an electric range, and in numerous industrial processes that involve heating or cooling. Effective transfer of heat by conduction requires matrices of high thermal conductivity. The conductive filler that normally been applied in polymer includes metals, diamond, carbon, graphite and ceramics (Lobo, 2003).

2.4.1 Multiwall carbon nanotube (MWNT)

MWNT which was discovered by Iijima in 1991 generated huge activity in most areas of science and engineering due to their unprecedented physical and chemical properties. Most of the researcher takes advantage of high thermal conductivity (~2000 W/m.K), high aspect ratio (1000:1), light weight and extraordinary mechanical properties make MWNT potentially attractive materials to produce conductive and reinforcing polymer composites (Xu *et al.,* 2006; Coleman *et al.,* 2006; Zhou *et al.,* 2007). Furthermore, the aspect ratio of the filler is a more important parameter dictating the thermal conductivity of a composite. Fillers with large aspect ratios easily form the bridges between them, known as conductive network. The formation of random bridges or networks from conductive fillers facilitates phonon transfer leading to high thermal conductivities (Yang and Gu, 2010).

Prashantha *et al.* (2009) and Razavi-Nouri *et al.* (2009) reported that the MWNT filled thermoplastic composites system increased the yield stress, tensile modulus and flexural properties of the polymer. While, Xu *et al.* (2006) reported that the increasing in thermal conductivity and crystallization, thermal stability and lowering coefficient of thermal expansion with addition of the filler loading of MWNT filled poly (vivylidene fluoride). However, problem rise from high aspect ratio is carbon nanotube easily tends to distribute non-uniformly in polymers due to the aggregation of the nanotubes as a result of the van der Waals interactions between individual tubes (Hussain *et al.,* 2006; Zheming *et al.,* 2010). Consistent dispersion of reinforcing material throughout the matrix leads to consistent load transfer from matrix to particle.

2.4.2 Synthetic diamond (SD)

SD was discovered in the early 1960s in the former Soviet Union. It is types of carbon materials existed in nature and meets the requirement of reinforcing filler (Osswald *et al.,* 2006). SD has high thermal conductivity (up to 2,000 W/m.K) and occupies a prominent place among the materials which offer developing high-efficiency heat sinks for semiconductor lasers, high-frequency, high power transistors, optical amplifiers, power LEDs and integrated circuits (Kidalov *et al.,* 2009).

Few works have been reported on the application of SD in thermoplastic composites. Shenderova *et al.* (2007) studied different concentration of SD filled in polyimide (PI) and poly (methyl methacrylate) (PMMA), results increasing thermal stability of the polymer composites. In addition, SD filled PI and PMMA also exhibits excellent in mechanical properties. Zhao *et al.* (2010) stated that increased of tensile strength up to 3 wt. %, afterwards reduced with filler loading filled poly (lactic acid) (PLA) composites. Lower SD content gives better dispersion in this system. The comparison between SD and other fillers such as silica, boron nitride, silicon nitride and alumina were studied by Lee and Yu, (2005). They reported at lower filler content, BN give the maximum thermal conductivity, but at higher filler loading, SD seems leading in thermal conductivity.

2.4.3 Boron nitride (BN)

BN was first synthesized by W.H.Balmain from boric acid and calcium cyanide in 1842 (Eichler and Lesniak, 2008). BN is a ceramic material that is isoelectronic with carbon, exist in multiple allotropic forms. It is analogues for graphite and commonly referred to as “white graphite”. BN containing boron and nitrogen compound in the layer structure (Raman, 2008). BN possesses high thermal conductivity (up to 300 W/m.K). It was light weight, soft and lubricious material that can be compounded into plastic with minimal impact on processing equipment (Zhou *et al.,* 2007). This is due to the weak van der Waals force, which enables the layers to slide against each other. BN fillers outperform many other ceramic types of filler in improving thermal conductivity of polymer matrices (Ng *et al.,* 2005). Moreover, this versatile material is now used in a number of applications such as metallization, the metal industry, cosmetic and thermal management (Eichler and Lesniak, 2008).

BN reinforced thermoplastic composites was reported to have better thermal stability and thermal conductivity (Ng *et al.,* 2005; Zhou *et al.,* 2007; Jung *et al.,* 2010). Effect on agglomeration of BN in thermoplastic matrices would lead to decrease in thermal conductivity of the polymer composites. In term of mechanical properties, stress at break showed an increasing trend up to 30 vol. % and tend to decrease after that. At higher BN loading, the composites were slightly brittle caused it to break easily (Jung *et al.,* 2010; Zhou *et al.,* 2007; Ng *et al.,* 2005).

2.4.4 Copper (Cu)

The primitive people first discovered the red metal, which is Cu has been serving us. While, Cu ores found in the United States contain approximately 1 % Cu in the form of copper sulfide. Cu is a very useful material. It has excellent electrical and thermal conductivity properties, is malleable and machinable, but has low mechanical properties. Applications such as heat exchangers, condensers, and other heat transfer devices take advantage of the high thermal conductivity of Cu (Schweitzer, 2006).

Cu filled thermoplastic composites were easily fabricated to various shape using internal mixer, extrusion and injection molding (Nurazreena *et al.,* 2006). Aside from inducing insulator to conductor transition, addition of metal fillers in polymer matrix appreciably improve the thermal properties of the composites. There are various metal fillers that have been widely used in conductive polymer composites such as Al, Ag, Ni, Au, Fe, Zn and Cu (Na *et al.,* 2010). Among them, Cu exhibits greater thermal conductivity value.

Effects of Cu in thermoplastic composites were widely reviewed. Luyt *et al.* (2006) reported on the Cu filled low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). Both matrices show increasing in thermal conductivity at the same filler loading. Cu filled LLDPE give higher reading. The reason is LLDPE have lower amorphous phase that is possible to have agglomeration in that system. Thus, more conductive path is able to form. In thermal stability, the anomalous was occurred where with increasing filler loading, the lower thermal stability was obtained in both matrices due to high heat capacities of Cu (0.39 J/Kg) and leads to the preferably absorbed the heat. Sofian *et al.* (2001) reported on the comparison of Cu, Fe, Zn and bronze filled high density polyethylene. At low metal filler, ineffectively improving thermal conductivity of metal fillers had been observed. It was associated to the existence of a discontinuous structure which were effected the heat transfer through the polymer matrix. While, different geometry of Cu filler filled polyamide were reported by Tekce *et al.* (2007). They observed that the composites with different Cu geometry increasing filler loading over that of the neat polymer, with the obvious trend shown by fiber, plates and spherical geometry.

2.5 Hybrid conductive composites

Hybrid composites are composed of two or more fillers whether same or different fillers in a single matrix to achieve a balance between properties of single filler reinforced composites. Usually a combination of two fillers proves to be useful in practice as it leads to achieve a balance between properties of single fiber reinforced composites (Gwon *et al.,* 2010; Himani and Purnima, 2010). There are a few types of hybrid composites with different types of reinforcement such as fiber/fiber hybrid, fiber/inorganic hybrid, inorganic/inorganic hybrid and organic/inorganic hybrid (Nurdina, 2009). Hybridization could also be used as a means of increasing the cost effectiveness of this type of material. Hybrid composites have been considered for a variety of applications, and hybridization can be carried out on many levels, ranging from intimate blending fiber within plies, through alternating ply to skin/core constructions. One example of the use of hybrid composites for mechanical performance reasons is in the construction of helicopter blades. Helicopter blades are often hybrid construction of glass and carbon fiber, a combination necessary to provide the required levels of stiffness, fatigue resistance and damage tolerance (Bleay and Humberstone, 1999). In addition, there are wide range applications of using hybrid concept such as in structural, flame retardant and also dental (Koo, 2006).

Marcq *et al.* (2011) stated that combination of micro and nanofiller is one of the new ways to improve conductivity. A high surface area of double wall carbon nanotubes (DWCNTs) were associated intermolecular van der Waals forces between DWCNTs leads to their arrangement in bundles and bundles agglomeration compared to multiwall carbon nanotube (MWNTs) which are more shorter and thus, well dispersed in MWNTs/micro-scale silver filled epoxy composites. Lin *et al.*

(2012) reported on different size of hybrid filler between nanoparticles ZrO_2 and microsize of short carbon fiber loaded in polyetheretherketone (PEEK), resulting good in tensile properties and wear resistance. The tensile strength and tensile modulus show improvement indicating the presence of synergetic effect of ZrO_2 and short carbon fiber on enhancement of mechanical properties.

In general, the hybrid composites system by employing carbon nanotube into other fillers such as boron nitride, synthetic diamond, carbon black, silica, aluminum and glass ceramic results in an effective method to form conductive network or conductive bridge. The thermal conductivity properties of hybrid fillers shows up to 50 % enhancement from single composites (Cui *et al.,* 2011; Teng *et al.,* 2011; Mukhopadhyay *et al,.* 2011; Socher *et al.,* 2011; Kang *et al.,* 2010). On the other hand, new designing way of hybrid micro size of silicon carbide in nano size of MWNT gives the advance to unite in improving the thermal conductivity of the composites (Zhou *et al.,* 2010).

Furthermore, the thermal conductivity property of filler also influenced the composites. The hybrid between Al with Si_3N_4 shows increasing in thermal conductivity compared to Al with wollastonite filled HDPE composites. The enhancement was induced by the higher thermal conductivity of Si_3N_4 shows in comparison with wollastonite. Thermal conductivity of wollostonite and silicon nitride are 2.5 and 85 W/m-K at 30 °C, respectively (Lee *et al.,* 2006).

Besides, thermal conductivity of hybrid BN with carbon black (CB) and carbon fiber (CF) demonstrated different results. BN and CB show increasing in thermal conductivity up to maximum loading. Whereas, hybridization between BN and CF decreased in thermal conductivity as compared to single filler composites.

This means that the addition of carbon fiber does not help in the formation of a filler network. This might be attributed to the low aspect ratio of CF after extrusion and the orientation effect induced by injection molding. However, in mechanical properties, BN/CF hybrid shows more stiff and tough which indicates BN and CF have the synergetic reinforcing and toughening effects (Ng *et al.,* 2004; Okamoto *et al.,* 2003). The enhancement in impact strength and tensile strength were proposed by Mirmohseni and Zavareh, (2010) in hybridization between epoxy, poly (acrylonitrile-co-butadiene-co-styrene) (ABS), clay and TiO_2. The obtained results indicated that the combination of materials would generate synergistic effect on impact and tensile strength of the epoxy polymer. In addition, although the SEM micrographs were observed little agglomerations, it is reported that TiO_2 and ABS still can act as crack stoppers.

2.6 Fabrication methods of particulate conductive composites

Fabrication method is the key to attain a good composites design with a manufacturing process that can operate with minimum problems. The goals of composites manufacturing process are able to: achieve a consistent product, minimize voids and reduce the residual stress (Peter, 2000). During the fabrication method of particulate filler and matrix, mixing must occur in two fundamental mechanisms which were dispersive mixing and distribution mixing. The dispersive mixing must overcome the different viscosity, surface energy, chemical compatibility, melting temperature. It is focused on short range blending of the compound. The distributive mixing depends on the types of equipment used (Meronek, 2007; Pukanszky, 2000). There are a few equipment for fabrication methods of the thermoplastic composites such as injection molding, extruder,