X-BAND FREQUENCY ELECTROMAGNETIC INTERFERENCE SHIELDING AND MECHANICAL PROPERTIES OF DUAL FUNCTIONALIZATION MULTI-WALLED CARBON NANOTUBE (MWCNT) EPOXY POLYMER NANOCOMPOSITES

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by

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LIST OF SYMBOLS

λ	Wavelength
r	Distance from source
MHz	Megahertz
GHz	Gigahertz
kHz	kilohertz
R	Reflection
A	Absorption
H	Magnetic field
E	Electric Field
wt%	weight fraction
vol%	volume fraction
dB	decibel
°C	Temperature
Fe	Iron
Ni	Nickel
Al_2O_3	Aluminium oxide
Al	Alumina
DI	Distilled water

δ	Skin depth
SE_R	Reflection loss
SE_A	Absorption loss
SE_M	Multiple internal reflection loss
ω	angular frequency
μ	relative magnetic permeability
σ	electrical conductivity
ε_0	permittivity of free space
t	thickness
ε’	dielectric constant/real permittivity
ε”	dielectric loss/imaginary permittivity
ε_r	relative complex permittivity
μ_r	relative permeability
SA/V	surface area-to-volume
nm	nanometre
S/m	Siemens per metre
°	degree
Co	Cobalt
bi-MNP	bimetallic nanoparticle
Cu	copper

Pt	platinum
Pd	palladium
Mo	molybdenum
Cr	chromium
COOH	carboxyl group
C-CI	carbon chloride
CONH	amide group
NH_2	amine group
OH	hydroxyl group
φ_c	percolation threshold
pS/cm	picoSiemens per centimetre
T_g	glass-transition temperature
mΩ	milli Ohms
s	second
min	minute
mm	millimetre
NaOH	Sodium hydroxide
$Ni(NO_3)_2 6H_2O$	nickel nitrate hexahydrate
$C_{10}H_{10}Fe$	Ferrocene
g/mol	gram per mole

mol	mole
C_2H_5OH	ethanol
°C/min	flow rate
Ar	Argon
W	Watt
g	gram
ml	millilitre
θ	theta/angle of incidence
N	load
$\tan \delta_\varepsilon$	dielectric loss tangent
GPa	GigaPascal
MPa	MegaPascal

LIST OF ABBREVIATIONS

EMI	Electromagnetic Interference
SE	Shielding Effectiveness
CNT	Carbon nanotube
EM	Electromagnetic
SWCNT	Single walled Carbon Nanotube
MWCNT	Multi walled Carbon Nanotube
SDS	Sodium Dodecylsulfate
DCM	Dichloromethane
DMF	Dimethylyformamide
TCVD	Thermal Chemical Vapor Deposition
MIR	Multilple Internal Reflection
MWS	Maxwell-Wagner-Sillars
CB	Carbon black
PANI	Polyaniline
PCL	poly (ε –caprolactone)
PU	Polyurethane
PVDF	Polyvinylidene fluoride
PP	polypropylene

PPy	polypyrrole
Triton X-100	octyl phenolethoxylate
DTAB	dodecyl tri-methyl amoniumbromide
CBT	cyclic butyl terephthalate
SLS	sodium lauryl sulfate
CPC	Conductive polymer composite
DGEBA	bisphenol A
PMMA	Poly(methyl methacrylate)
CTAB	cetyltrimethylammonium bromide
AC	alternating currents
TMD	trimethylhexamethylenediamine
XRD	x-ray diffraction
FTIR	Fourier-transform infrared spectroscopy
EDX	energy dispersive x-ray
FESEM	field emission scanning electron microscope
HRTEM	high-resolution transmission electron microscope
RBM	radial breathing mode
FWHM	full-width half maximum
EVA	ethylene-vinyl acetate,
NBR	acrylonitrile-butadiene copolymer

SBR	styrene-butadiene rubber
ABS	acrylonitrile butadiene styrene
SEBS	styrene-ethylene-butylene-styrene
PEDOT	poly (3,4- ethylenedioxythiophene)
PE	polyethylene
PS	polystyrene
PDMS	polydimethylsiloxane
PC	polycarbonate
UHMWPE	ultrahigh-molecular-weight polyethylene
EMA	ethylene methyl acrylate
PTT	polytrimethylene terephthalate
PLLA	Poly(L-lactide)
PRS	Pristine
DF-CNT	Surfactant functionalization CNT

FREKUENSI X-BAND PEMERISAIAN GANGGUAN ELEKTROMAGNET DAN SIFAT MEKANIK RANGKAP DUAAN MWCNT POLIMER NANOKOMPOSIT

ABSTRAK

Perkembangan sistem elektronik dan alat telekomunikasi gigahertz yang meluas di sektor awam dan ketenteraan telah menyebabkan pencemaran elektromagnetik yang serius, di mana ia boleh mempengaruhi pengoperasian alat elektronik dan menimbulkan masalah kesihatan kepada orang ramai. Penyelesaian bahan pelindung gangguan elektromagnetik (EMI) yang berkesan dalam pelbagai aplikasi adalah merupakan pencarian aktif. Penyelidikan ini secara eksperimental meneliti prestasi pelindung EMI, dan sifat mekanik komposit bertetulang epoksi tiub nano karbon (CNT). CNT disintesis menggunakan pemangkin dwi yang terdiri daripada nikel dan ferocenne melalui pemendapan wap kimia (CVD) pada suhu antara 600 hingga 900°C. Komposit dihasilkan melalui pemprosesan larutan dan pengacuan diperkuat dengan CNT yang difungsikan melalui pengfungsian surfaktan (DF-CNT), yang kemudian dibandingkan dengan CNT yang asli (PRS-CNT). CNT yang disintesis mempunyai ukuran antara 19 - 24 nm dan 48.36% berat karbon mengikut analisis medan pancaran mikroskop imbasan electron pancaran medan (FESEM), mikroskop pemancaran elektron resolusi tinggi (HRTEM), dan serakan tenaga sinar-x (EDX), sementara pembelauan sinar-x (XRD) mendedahkan fasa karbon. CNT yang disintesis pada suhu 800°C memperlihatkan kualiti karbon yang terbaik yang didepositkan, disebabkan oleh penyusunan semula menjadi kepingan graphene yang mempunyai penghabluran tinggi dengan diameter CNT paling rendah setelah pengfungsian. DF-CNT mempunyai ukuran antara 15.1 hingga 23.4 nm dan 90.6 - 94.5 wt% dengan purata pengurangan ukuran sebanyak 21.55% dan menunjukkan ketulenan dan penghabluran tertinggi dengan I_D/I_G antara 1.06 - 1.25 menunjukkan fungsionalisasi surfaktan telah menghasilkan kualiti CNT terbaik dengan kadar kerosakan dan bahan asing selain karbon yang minimum. Epoksi yang diperkuat dengan komposit DF-CNT (EP/DF-CNT) menunjukkan sifat EMI, termal, elektrik, kekerasan, dielektrik dan mekanikal yang lebih tinggi daripada epoksi bertetulang CNT yang asli. Peningkatan ini dikaitkan dengan kerosakan dan pengagregatan dinding CNT yang kurang dengan peningkatan kumpulan fungsi yang sangat beroksigen yang menyebabkan dispersi CNT-epoksi yang sekata. Komposit epoksi yang diperkuat dengan DF-CNT mampu meningkatkan kekuatan tegangan dan modulus hingga 19% dan 69%, kekuatan lenturan dan modulus sebanyak 57% dan 62%, kekuatan mampatan dan modulus sebanyak 56% dan 41%, keberkesanan pelindung EMI (EMI SE) sebanyak 42.3%, kekonduksian terma sebanyak 27%, kekerasan sebanyak 53% dan kekonduksian elektrik sebanyak 27% jika dibandingkan dengan CNT yang asli. Penyelidikan ini menyediakan kaedah pengfungsian yang senang dan sesuai untuk menghasilkan komposit epoksi bertetulang CNT diperkasa dengan pelbagai fungsi dengan prestasi pelindung EMI yang sangat baik yang mungkin dapat diterapkan dalam industri elektronik dan aeroangkasa.

Kata Kunci-komponen; karbon nanotiub (CNT); surfaktan-pengfungsian CNT (DF-CNT); polimer nanokomposit; Gelombang radiasi elektromagnetik (EM); Gangguan elektromagnetik (EMI); Perisai EMI; Sifat mekanikal

X-BAND FREQUENCY ELECTROMAGNETIC INTERFERENCE SHIELDING AND MECHANICAL PROPERTIES OF SUAL FUNCTIONALIZATION MWCNT POLYMER NANOCOMPOSITES

ABSTRACT

The wide development of gigahertz electronic systems and telecommunication devices in civilian and military sectors have brought severe electromagnetic pollution, which may affect the operation of the electronic device and pose a health issue to the public. The effective electromagnetic interference (EMI) shielding material solutions in a wide range of applications are active quest. This research experimentally investigated the EMI shielding performance, and mechanical properties of the carbon nanotubes (CNTs) epoxy reinforced composites. The CNTs were synthesized using dual catalyst consist of nickel and ferrocene via chemical vapor deposition (CVD) at a temperature ranging between 600 to 900^{o}C. The composites were manufactured via solution processing and casting reinforced with CNT that were functionalized via surfactant (DF-CNT) functionalization, which then compared with pristine CNT (PRS-CNT). As synthesized CNT had the size between 19 – 24 nm and 48.36 wt% of carbon according to field emission scanning electron microscope (FESEM), high-resolution transmission electron microscope (HRTEM), and energy dispersive x-ray (EDX), while x-ray diffraction (XRD) revealed the existence of carbon phase. CNT synthesized at 800°C displayed the best quality of carbon deposited, which attributed to the restructuring into high crystalline graphene sheets with the smallest CNT diameter after functionalization. DF-CNT had the size between 15.1 to 23.4 nm and 90.6 – 94.5 wt% with average size reduction of 21.55% and displayed highest purity and crystallinity with I_D/I_G ranging 1.06 - 1.25 suggesting surfactant functionalization had produced the best quality of CNT with minimal defects and impurities. Epoxy reinforced with DF-CNT (EP/DF-CNT) composite showed higher EMI, thermal, electrical, hardness, dielectric and mechanical properties than PRS-CNT reinforced epoxy. This increment is associated with the less minimal CNT wall damage and agglomeration with highly oxygenated functional groups which enable homogeneous dispersion of CNT-epoxy. It was demonstrated that the DF-CNT filled epoxy composites are capable of increasing tensile strength and modulus by up to 19% and 69%, flexural strength and modulus of 57% and 62%, compressive strength and modulus of 56% and 41%, EMI shielding effectiveness (EMI SE) of 42.3%, thermal conductivity of 27%, hardness of 53% and electrical conductivity of 27% when compared to a PRS-CNT. This research provides a feasible functionalization way to produce multifunctional CNT reinforced epoxy composite with excellent EMI shielding performance that is possible to be applied in the electronics and aerospace industries.

Keywords-component; carbon nanotube (CNT); surfactant-functionalised CNT (DF-CNT); polymer nanocomposites; Electromagnetic (EM) wave radiation; Electromagnetic interference (EMI); EMI shielding; Mechanical properties

CHAPTER 1

1.1 INTRODUCTION

In recent years, electromagnetic (EM) wave radiation in the gigahertz (GHz) range has been considered an alarming danger for information technologies, defence safety technologies, commercial appliances and biological systems. When these EM waves interfere with the input signal of the electronic devices, a special type of electrical contamination is generated in the surrounding environment known as electromagnetic interference (EMI). EMI is a sort of noise or electronic disruption generated by EM waves that ruin or impede the efficiency of neighbouring electronic components or gadgets. In places like hospitals with a large number of equipment that produce EM radiations, it is vital to attain EM compatibility between equipment to ensure the proper functioning of critical lifesaving systems and ensure the operators of machinery are safe (Boyle, 2006). In Europe, special guidelines for protecting children and other vulnerable groups from EMI exposure and occupational laws aimed at protecting pregnant women and people with medical implants in the workforce have been enforced (Hansson Mild et al., 2009, Gajšek et al., 2013). Other instance where the disturbance of EMI may be detrimental includes a power transmission line, sensors, communication units, batteries, remote sensing tools, televisions, the payload of rockets, computers, mobile phones, transformers, medical devices, military and commercial plane, space systems and units of spacecraft which are positioned externally (Aljunid et al., 2018). Therefore, developing light-weight and economical EMI shielding is vital in order to mitigate EMI pollution. EMI shielding is the best strategy to protect the environment and the well-being of living creatures from the harmful effects of EM waves. The EM waves will be reflected or absorbed using a compromising shield,either magnetic-based materials or conductive-based materials.

Polymers provide several advantages over metals and ceramics as they can be easily shaped using silicon mould and hot-press compression. Due to this, it is possible to prepare a variety of formulations and configurations as well as polymer exhibits substantially lighter materials than metallic materials (Saini et al., 2009, Theilmann et al., 2013). Despite that, their processability is hindered by extensive delocalization of π-electrons, and they suffer from contraction, swelling, softening and cracking, which gives a deleterious effect to their electrical and mechanical behaviour. Inducing second phase materials or fillers can enhance these properties. Polymer reinforcement using fillers such as organic or inorganic materials is common in the fabrication of current polymer composites. Conventional composites consist of micrometre particles, platelets or fibres as fillers in polymer composites have been investigated widely for EMI application. For instance, carbon fibres and carbon black reinforced thermosetting resin. Polymer reinforced with micrometre fillers displays enhancement in hardness; however, its tensile properties deteriorate due to stress concentration caused by a high content amount of filler that contradicts a high content amount of filler that contradicts the practical necessity of smart thin EMI SE materials. Besides that, a small aspect ratio of micrometre filler exhibits poor network bonding formation between filler and polymer, which worsen the electrical and thermal conductivity (Thomassin et al., 2008). To produce an active electromagnetic shield with improved properties for polymer nanocomposites fillers, such as metal and carbon nanostructures, are introduced. The term ‘nanocomposites’ has been comprehensively acknowledged, constituting a large group of materials comprising structures in the nanometre range between 1-100 nm. The properties of the nanocomposites have attracted the attention of researchers for EMI application due to the size of the structure, which can exhibit extraordinary strength, electrical and thermal properties that contrast from those of the bulk matrix (Arjmand &Sundararaj, 2015). Polymer nanocomposites are hybrid organic-inorganic materials that are formed by incorporating a small amount of nanofiller dispersed at a molecular level in the polymer matrix. The uniform dispersion of nanofillers can eventually lead to a large interfacial area between the constituents of the nanocomposites. The reinforcing effect of filler is directly influenced by nature and type of nanofillers, properties of the polymer matrix, concentration of polymer and filler, particle aspect ratio, size, orientation and distribution (Bagotia, 2018). Most of the EMI nanocomposite research was initially focused on metallic nanofillers of different shapes; spheres, rods, tubes, and wires due to their exceptional electrical, thermal, and mechanical properties. However, they have encountered problems such as high reflectivity, susceptible to corrosion and uneconomical processing. Nanocarbons such as carbon nanotube (CNT) soon gained the attention with its exceptional properties like lower-weight fraction and more conductive composites could be obtained (Joshi et al., 2013, Micheli et al., 2014). CNTs are considered as seamless cylinders formed by atoms made up of carbon which are covalently bonded with one another via sp^2 hybridization resulting in wrapping the graphene sheets. These allotropes can be formed into single walled CNT (SWCNT), and multi walled CNT (MWCNT) and the variation in their diameter can significantly vary their electrical properties. CNT aspect ratio (100-5000) has a significant impact on EMI shielding. CNTs are considered as ultimate carbon fibres due to ultra-high-strength (20-100 GPa) and modulus (~1000 GPa), the ultimate strain of 12%, exceptional electrical conductivity (10^7 S/cm) and thermal properties (>200 W/mK). In order to make the entire cross-section of a filler to be active in shielding, the dimensions of the conductive filler need to be less than the length of incident radiation penetration. Therefore, CNTs are suitable to shield in the GHz range as they are good conductors at high frequencies (Ameer &Gul, 2016). Hence, CNTs are a promising selection designed for the production of effective EMI shielding composites. Epoxy resin is a crosslinked polymer consist of more than one epoxy group or oxirane ring found on their molecular structure. Epoxy resins are primarily valuable for aerospace fields due to their excellent adhesion, resistance towards chemical, corrosion, and toughness. Epoxy resins subjected as conventional thermosetting matrices illustrate prominent features with exceptional mechanical behaviour, economical and simple fabrication for higher structural composites. Nonetheless; epoxy resin's principle drawback may be due to its inherent brittleness and poor electrical conductivity, which is the main intrinsic property required for excellent EMI shielding. The performance of epoxy resin can usually be improved by incorporating a different sort of particulate filler and fibrous reinforcement (Phan et al., 2016). Subsequently, a few exploration efforts are now dedicated to the epoxy matrices reinforcement incorporated with CNT as CNT is viewed to be a principle strengthening material.

In achieving the desired properties for EMI shielding of epoxy/CNT composites, a most important prerequisite is to have a low percolation threshold of CNT with well-ordered alignment and consistent dispersion throughout the polymer matrix as well as increment in the interface properties. There is a certain threshold value at which the filler forms a continuous path in a polymer composite and conductivity increments sharply. A region that is under dynamic research in aerospace is the enhancement of electrical behaviour of composite fabricated from epoxy resin and CNTs (Saini &Aror, 2012). The electrical conductivity of the composite is dependent on the conductive network formation amongst epoxy matrix and CNT. Hence, chemical modification or CNT functionalization may expand the interaction with polymer through better dispersion and interfacial adhesion of the CNT. Functionalization on CNT will create defect sites either on the wall or the tube's end cap by introducing functional groups like carbonyl, hydroxyl, and carboxyl groups (Islam Rubel et al., 2019). Chemical modification using organic or surfactant treatment has shown to be very effective in increasing the reactivity of CNT with polymer matrix with improved wetting or adhesion characteristics and reduced CNT agglomeration. The presence of functional groups induces a better interface, resulting in an improved load transfer from the matrix to the reinforcement (Yun et al., 2010). Surface active molecules using surfactants, for instance, sodium dodecylsulfate (SDS), dichloromethane (DCM) and dimethylyformamide (DMF) induced on CNT molecules manage to decrease the aggregative tendency of CNTs with the presence of p-stacking interactions of benzene rings, causing high dispersive capability of CNTs in a polymer matrix (Khan et al., 2016). Thus, enhanced properties of composites are relied upon to be accomplished by using organic solvent functionalized CNT in the epoxy composite.

1.2 PROBLEM STATEMENT

In early years, EMI related issues apparently reduced via Faraday’s cage mechanism whereby blocking external electric fields (charge or radiation) by an enclosure made up of conductive materials like metal such as nickel, iron, cobalt, steel) due to high electrical conductivity and good permeability (Conecici et al., 2017). Despite using metals, the EM contamination is not entirely wiped out or attenuated as EM signals are generally reflected at the surface of the metal, protecting the environment only beyond the shield. Also, metals are mostly heavy, corrosive, low flexibility and difficult to process, in addition to high production cost. (Sankaran et al., 2018). Significant research efforts have been established for the development of polymeric materials to bypass the limitations of metallic EMI shielding material. Polymer-based materials are advantageous over the metal-based shielding as the former has the ability to shield EM waves via dominant absorption shielding. This is highly preferable in military applications like camouflage and stealth technology. However, polymers do not possess high electrical conductivity like metal, which is a drawback in developing them for EMI shield. To impart electrical conductivity within polymers, fillers like CNT possessing high electrical conductivity can be added and at the same time enhance the electrical property. They also can improve the thermal and mechanical properties of the composites. It is important to consider the thermal and mechanical properties of the composites. When absorption plays a dominant role for EMI shielding, the absorbed energy of an EM wave is transformed into thermal energy, which could increase the temperature of an absorbing medium, e.g., a polymer composite, excessively. Thus, it is vital to dissipate the absorbed thermal effectively by increasing the thermal conductivity of the polymer composite. Otherwise, the inherently low thermal conductivity of the polymer composite may result in an unwanted excessive temperature increase and consequently degrade the performance and long-term durability of shielded devices (Kim et al., 2020, Arief et al., 2017, Li et al., 2018b). In addition, the mechanical properties have to be considered as the shielding material need to be able to withstand the load bearing capacity; therefore it requires a high amount of strength in the designed material. To address this issue, our study is aimed at dissipating the heat energy generated and mechanical properties improvement by adding fillers like CNT, which possess high thermal conductivity and mechanical properties.

An ideal EMI shielding should be lightweight, with high EMI shielding effectiveness, excellent at broad bandwidth, have tuneable reflection frequency and possess a multi-functionality. However, in utilizing the amazing properties of CNTs, there are major drawbacks that have to be taken into consideration. Imparting the intrinsic properties of the CNTs are seen as a huge challenge for researchers due to the difficulty to disperse CNT in the epoxy matrix. CNTs regarded as quasi 1D nanomaterials, which usually exist in the form of flexible fibre-like or rod-like character due to large aspect ratio, high surface area and intrinsic van der Waals force of attraction. This will lead to difficulty in dispersing CNT in polymer medium and as well as in various solvents due to agglomeration of these tubes caused by weak intermolecular forces called van der Waals force. Poor dispersion of the CNTs will significantly diminish reinforcement efficiency due to CNT slippage. Relatively weak Van der Waal's bonding among the concentric layers decreases the load-bearing capacity of CNTs resulting in CNT slippage (Tang et al., 2004) (Debelak & Lafdi, 2007). The performance of reinforced composite can deteriorate as a result of the formation of micro-voids and defects in the epoxy composites (Yasmin, 2004). Agglomeration of CNTs affects the size (diameter/length) and distributions of filler materials/particles and overall is likely to reduce the aspect ratio. Thus, this situation causes the bundle formation of CNTs fibre, which creates defects such as lumps and aggregates in the produced composites, thereby reducing the mechanical properties which are essential in EMI shielding material.

A large number of research has been performed to raise the dispersion of CNT in the polymer matrix. Previous studies had focused mainly on the processing issues and paid less attention to the filler design aspect. The growth of CNT under various temperature has been reported in several publications; however, it has not been studied extensively on the relationship between growth temperature on influencing the role of CNT diameter variance in EMI properties. Therefore, our research has highlighted the influence of the diameter by varying the synthesizing temperature of the CNT, which plays a major role in terms of channelling the mobile charge carriers across the fibres in the composite, thus influencing primarily on the electrical and EMI shielding effectiveness. Besides, functionalization of CNTs is highlighted in this research as it is very important to improve their degrees of reactivity and homogenous dispersion by introducing specific functional groups that will be attached onto the side or ends of the CNTs. The surface of CNTs clusters is highly tortuous; thus, chemical functionalization concentrate on the surface treatment to the CNT structure to enhance their chemical interaction with the polymer matrix, and it has improved the dispersion of CNT. Highly concentrated acid solutions are often used to assist in the shortening process by increasing the number of defect sites making the CNT samples in an oxidised state, promoting better bonding with epoxy. However, the chemical functionalization method involving strong alkali and acid often creates structural defect that deteriorates the intrinsic properties of CNT. Therefore, by regulating the CNT diameter during synthesizing and the method of functionalization could probably solve the problems mentioned above.

1.3 SCOPE OF STUDY

In this work, CNTs were synthesized using thermal chemical vapor deposition (TCVD) that only required a short processing period. Five different samples were prepared. Firstly, CNT was synthesized at a varying temperature of 600-900°C in 40 minutes. The untreated samples were soaked, washed and sonicated with the combination of dichloromethane (DCM) and dimethylyformamide (DMF) to obtain functionalized DF-CNTs (treated samples). Finally, the incorporation of DF-CNTs in epoxy resin composites was prepared via solution processing and casting, which will be compared with pristine CNT (PRS-CNT) epoxy composite at fixed filler content, 5 wt%. Besides that, the functionalized CNT also used for composite fabrication, which determines the best intermolecular bonding that can provide higher shielding effectiveness.

The morphological, microstructural, EMI, dielectric behaviour, electrical and thermal conductivity and mechanical properties were conducted on all samples. Instruments such as higher resolution transmission electron microscope (HRTEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) spectrometer and energy-dispersive X-ray (EDX) were utilized. Fourier transform infrared (FTIR) and Raman spectroscopy were conducted to examine optical features such as FTIR and Raman characteristics. The interaction between the samples and electromagnetic field for exploring their reflection, transmission and complex permittivity over an X-band frequency range had also been examined using a vector network analyser (VNA). The complex permittivity measurement in the dielectric study involved dielectric constant (ε') and dielectric loss factor (ε"). Electrical and thermal conductivity were performed on each composite. Mechanical properties such as tensile, flexural and compression were also examined on the composites. The obtained morphological, microstructural and elemental studies were then related to each other and correlated with EMI results.

1.4 OBJECTIVES OF STUDY

The core objectives of this research as follows:

1) To determine the physical properties, morphological structure and degree of DF-CNT distribution in epoxy polymer compared to those of the pristine CNT epoxy polymer.
2) To evaluate the EMI shielding, dielectric, electrical and thermal conductivity properties of DF-CNT epoxy polymer nanocomposites and compare to the EMI requirement property (of > 20 dB EMI shielding effectiveness and 10^{-2} S/m electrical conductivity).
3) To investigate the mechanical (tensile, flexural and compression) properties of DF-CNT/epoxy polymer nanocomposites.

1.5 THESIS OVERVIEW

This thesis is divided into five chapters that describe the theoretical, analytical and experimental research performed. The first chapter is an introduction to the field of the research study. In this chapter, a few points are highlighted: field of study, the problem statement of the research carried out, the scope of works, objectives of the study and benefits of the research, as well as an overview of the thesis. Chapter two presents the literature review that relates the theories on composites and previous investigations and experiments to the CNTs, which utilized CNTs as their filler reinforcements for EMI shielding application. Previous studies on individual processing parameters towards the effects of CNT composite qualities are also critically reviewed. Chapter three described the material properties, process flow for the synthesis of CNTs and fabrication of the CNT-epoxy composites. The research flow, raw materials, procedural of the research works, and experimental testing involved were described in detail. In chapter four, the effects of processing parameters consist of CNT growth using dual catalyst and variation in growth temperature and polymer-filler interaction when surfactant CNT functionalization utilized are analysed. Relations between processing parameters and factors that affect composites quality are discussed. In chapter five, the findings in chapter 4 are summarised, and recommendations for future research work are stated.

CHAPTER 2

LITERATURE REVIEW

2.1 ELECTROMAGNETIC RADIATED FIELD

The universe comprises 70% of vacuum energy and 26% exotic dark matter, the residual 4% and 0.005% covered by common matter (for example, planets, stars, asteroids) and radiation (light, X-rays, cosmic and gamma rays) (Bahcall, 2015). The definition of EM radiation is transferring or propagating energy through space-time, carrying an EM radiant energy. Electromagnetic radiation is a radiated form of energy as it can transport energy as electromagnetic waves while propagating through a vacuum. It comprises of two oscillating criteria, electric field (E) and magnetic field (H), which are perpendicular to one another and to the direction of wave propagation, as illustrated in Figure 2.1. Electromagnetic radiation such as gamma rays, X-rays, ultraviolet radiation, visible light, infrared radiation, microwaves and radio waves are known as electromagnetic spectrums. Figure 2.2 illustrates the EM spectrum used to describe different types of EM energy according to their frequencies and wavelengths. The EM spectrum arrays from lower energy waves like radio waves and microwaves to higher energy waves like X-rays and gamma rays (Kajihara et al., 2011). Low-intensity radiation (internal EMI) and high-intensity radiation field (external EMI) are the two major types of EMI that affect an aerospace system (Mishra et al., 2018). The terms "near-field", "transition zone" and "far-field" depend on the distance between the electromagnetic radiating source and shielding enclosure. Both EM sources and receiver are closer to one another in the near-field interference, whereas, in the far-field interference, the source and receiver both are further from one another. Near-field interference depends on capacitive coupling mechanism, small electric dipole and conductive, which cause electric and magnetic field of an electromagnetic wave to interact with high and low impedance based circuits. The wave impedance (H/E) declines (inversely proportional) with increasing distance from the source (Rodriguez-Fortuno et al., 2013, Ginzburg et al., 2014, Kajihara et al., 2011). As for far-field interference, is based on fundamental electromagnetic coupling mechanism and small current loop whereby wave impedance (H/E) increases (directly proportional) with increasing distance from the source. As shown in Figure 2.2, the region within the distance $r > \lambda/2\pi$ is the far field while the distance $r < \lambda/2\pi$ is the near field.

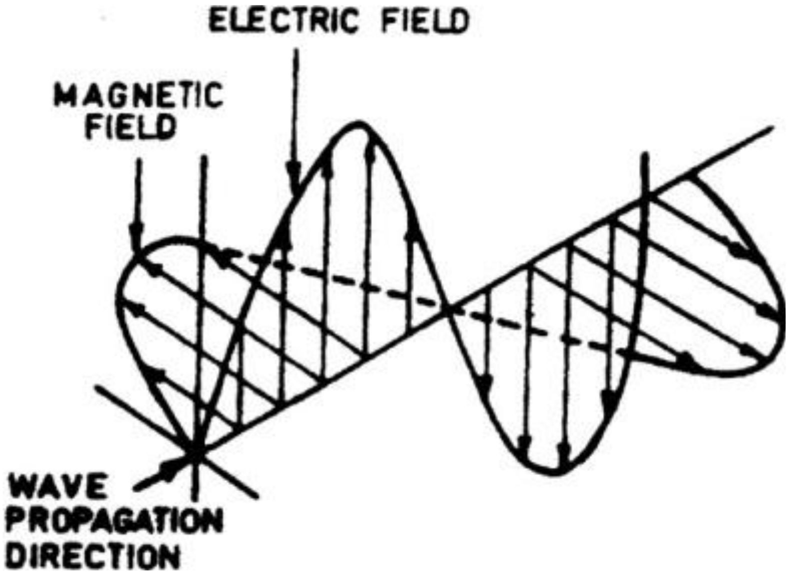

Figure 2.1: Electromagnetic radiation vector (Kimura, 2017)

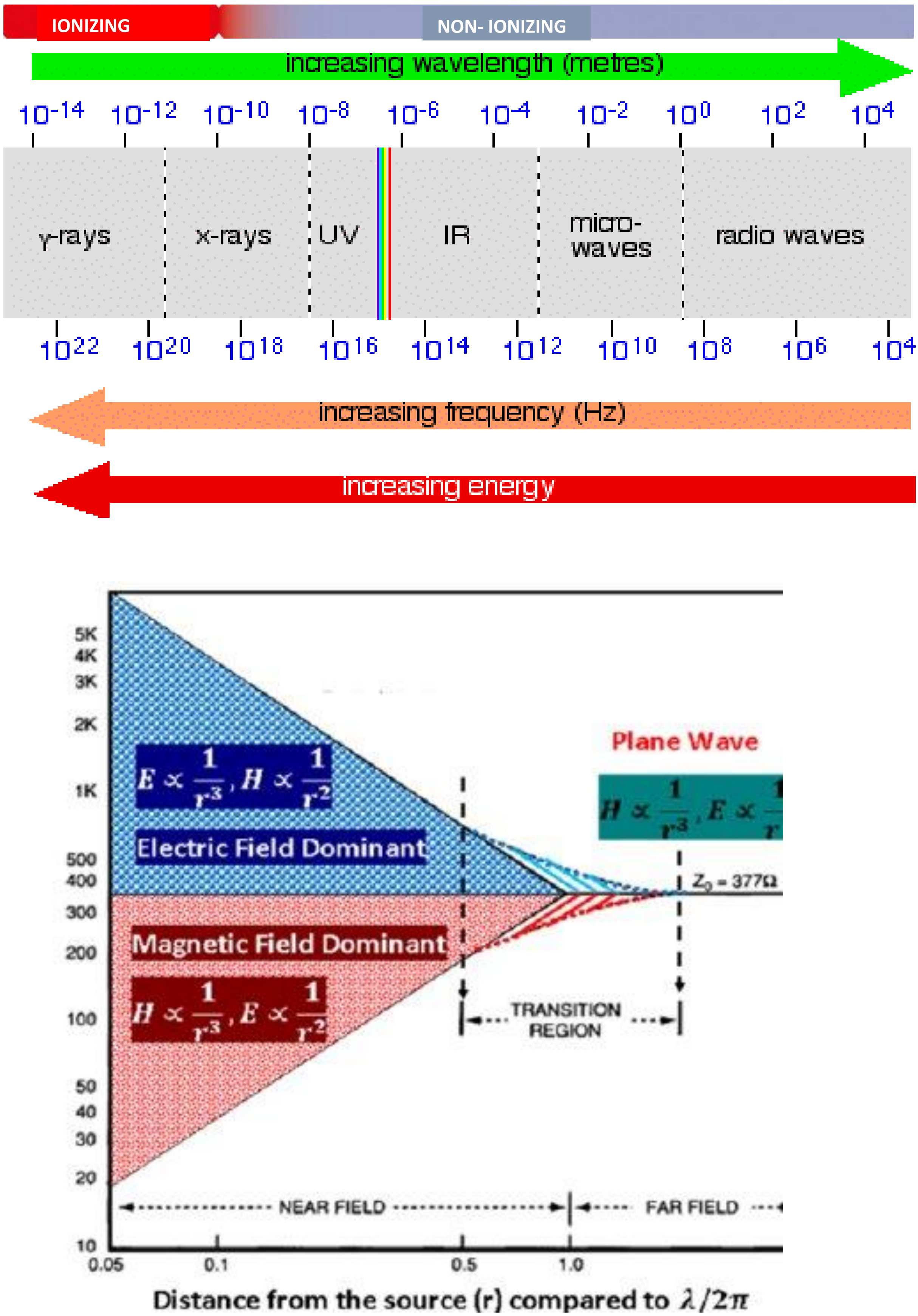

Figure 2.2: EM spectrum and Wave impedance in far field and near field (Kajihara et al., 2011)

2.1.1 LOW INTENSITY RADIATED FIELD

Low intensity radiated fields are created from electronic devices such as blue tooth devices, laptops, mobile phones and wireless accessories. The operating frequency range is from 30 MHz to 5 GHz. The frequency produced by these electronic gadgets matches or adjacent to the frequency spectrum of communication and navigation systems. Despite that, the signal of communication and navigation systems will be distorted, which eventually cause these distorted signals induced by the EMI of both frequencies (Das et al., 2001, Ahmad et al., 1992, Davenport, 1981).

2.1.2 HIGH INTENSITY RADIATED FIELD

Natural events such as lightning strikes and solar flares and humankind activities mostly generate high-intensity radiated fields. The capability and the lifespan of equipment parts have deteriorated. Lightning carries a current of approximately a hundred thousand amperes and a high range of electromagnetic fields. Materials that are less conductive than aluminium in components of military and commercial aircraft can be damaged by lightning. (A Dasa, 2008, Roh et al., 2008). Other than that, lightning strikes can ruin aircraft interior parts due to a rise in temperature to above room temperature triggered by resistive heating, which finally damages the aircraft materials. Thus, EMI shielding composite materials ought to be formed for EMI and lightning protection. Varied strategies have been studied to produce EMI shielding material in order to obtain the desired performance from devices under the lightning strike and EMI environments (Cheng et al., 2001, Ramachandran &Vigneswaran, 2009).

2.1.3 CLASSIFICATION OF ELECTROMAGNETIC INTERFERENCE

Article 1.166 of the International Telecommunication Union's (ITU) Radio Regulations (RR) define EMI as the effect of unwanted energy due to one or a combination of emissions, radiations, or inductions upon reception in a radio-communication system manifested by performance degradation, misinterpretation, or loss of information that could be extracted in the absence of unwanted energy with mathematical simplicity. Table 2.1 provides information about communication tools in accordance with their working frequency range. EMI can be categorized into binary classifications (Ganesh, 2014):

1) Narrowband EMI (narrow bandwidth)
2) Broadband EMI (wide bandwidth)

Table 2.1: Communication devices and related frequency range

Category	**Frequency**	**Name**	**Application**	**References**
Radio frequency	30-300 kHz	VLF-LF	Marine communication	(I.A. MOLDOVAN1, 2010)
Microwaves	300 MHz to 1 GHz	UHF	Telecommunication, microwave oven, mobile phones	(Hazmin Sabri et al., 2019)
Microwave frequency bands	1-2 GHz	L Band	Mobile phones, wireless LAN, radars, GPS	(Rajabi &Aksoy, 2019)
Microwave frequency bands short wave	2-4 GHz	S Band	Bluetooth	(Samsuzzaman et al., 2014)
Microwave frequency bands	4-8 GHz	C Band	Satellite communication, cordless telephone, Wi-Fi	(Monti-Guarnieri et al., 2017)
Microwave frequency bands	8-12 GHz	X Band	Satellite communication	(Hirako et al., 2018)
Microwave frequency bands	12-18 GHz	Ku Band	Satellite communication	(Shrestha &Choi, 2019)
Microwave frequency bands	18-27 GHz	K Band	Satellite communication	(Rahman &Robertson, 2018)
Microwave frequency bands	27-40 GHz	Ka Band	Satellite communication	(Hasan &Bianchi, 2016)
Microwave frequency bands	40-75 GHz	V Band	Military and R&D	(Takizawa &Hashimoto, 1999)

Microwave frequency bands	75-110 GHz	W Band	Military and R&D	(Hamed et al., 2018)

2.1.4 EMI SHIELDING THEORY

Based on Lorentz force law, electrons in the shield interact with the incident EM wave and induce an electromagnetic field when an EM wave is incident/propagate on the surface of the shield. The induced field direction is opposite to the direction of the incident EM waves which causes a decrease in the power of the incident EM wave (Kogut, 2018). Shielding is the process whereby a certain level of attenuation is extended using a strategically designed EM shield. The term electromagnetic shielding effectiveness (SE) is defined as the capability of an EMI shielding material in attenuating EM signal. For efficient shielding action, the shield must possess either mobile charge carriers (electrons or holes) or electric and/or magnetic dipoles which interact with the electric (E) and magnetic (H) vectors of incident EM radiation. Accordingly, for the value of 10 dB EMI SE means that 10% of incident energy has penetrated and 20 dB means only 1% of incident energy has penetrated. It depends on EMI attenuation, frequency, the distance of shield from the source, thickness of the shield and the type of shield material (Surendra Loya1, 2016). The higher frequency of the microwave would have more effective EMI SE if the thickness of the material were constant (Huang et al., 2009). Three mechanisms are involved in a complete shielding; multiple internal reflections (MIR), reflection (R), absorption (A) contribute towards overall attenuation with SE_R, SE_A and SE_M, respectively as per Figure 2.3. Part of the incident radiation is reflected from the front surface of the shield, some part is absorbed within the shield material, and another part is reflected from the shield rear surface to the front, where it can aid or hinder the effectiveness of the shield depending on phase relationship with the incident wave (Nanni et al., 2009). Therefore, as per Equation 1, the total shielding effectiveness of a shielding material (SE) equals to the sum of the absorption loss (SE_A, reflection loss (SE_R) and the correction factor to account for multiple reflections loss (SE_M) in thin shields and shall be neglected if the thickness of the shield is more than the skin depth of the shield.

$$SE_{dB} = SE_R + SE_A + SE_M = 20 \log \left[\frac{E_i}{E_t} \right] = 20 \log \left[\frac{H_i}{H_t} \right] \quad \text{Equation 1}$$

Whereby E_i and H_i are incident electric field and magnetic field respectively whereas E_t and H_t are transmitted electric field and magnetic field, respectively.

Reflection (R) of radiation is defined depending on the presence of free mobile charge carriers (electrons) in the shield material. These mobile charges carriers generate impedance mismatch resulting in the reflection of a large part of the incident wave (Chen et al., 2015). The higher the mobile charge carriers in the shield, the higher the capacity to attenuate the EM wave through reflection and absorption mechanisms. Absorption (A) depends on the thickness of shield materials (Hazmin Sabri et al., 2019). As the thickness of the shield increases, the absorption is higher. In the situation where the shield has inadequate free electrons, a portion of the wave is transmitted and reaches the opposite face of the shield (shield-to-air interface) and is reflected into the shield (Joshi et al., 2015). This reflected wave generated from the second interface is most likely a portion of the reflection mechanism. Multiple reflections (MIR) can be ignored if the shield's thickness is greater than the shield's skin depth based on Schelkunoff's theory. It can be ignored in the case of very high frequencies (~ GHz or high) or a thick absorbing shield, a condition when $|SE_A| \geq 10$ dB so that the amplitude is negligible by the time the wave reaches the 2nd boundary (Wang et al., 2009). Skin depth (δ) is defined as the distance up to which the intensity of EM drops to $1/e$ of its original strength (e is the Euler's number and $1/e$

= 0.37 or 37%) (Eddib &Chung, 2017, Kim et al., 2012). SE_M is also omitted when SE_A is more than 10 dB (Wang et al., 2009, Al-Saleh &Sundararaj, 2009).

The δ of a good conductor (when σ >> 2πωε$_0$) is express as per in Equation *2* (Farukh et al., 2015b):

$$\delta = \sqrt{\frac{1}{\pi\omega\mu\sigma}} \qquad \text{Equation 2}$$

where μ is the relative magnetic permeability of shielding material, ω is the frequency, ε_0 is the permittivity of free space (8.854 × 10^{-12} F/m)., σ is the electrical conductivity of shielding material. The δ will vary inversely proportional to magnetic permeability, electrical conductivity and frequency, implying an increment in magnetic permeability, electrical conductivity and frequency. Skin effect is particularly essential at low frequencies, whereby fields experience are more probably predominantly magnetic with lower wave impedance than 377 Ω (Singh et al., 2015, Ahmad et al., 2018). Wave impedances are mainly attributedto the reflection mechanism whereby reflection of the signals from a mismatch between the wave impedances for the signal propagating into the air and the absorbing material, respectively. Wave impedance is proportional to the inverse of the dielectric constant of the medium. The reduction in reflection of EM waves in CPCs is mainly due to the lower impedance mismatch of CPCs due to the dominant role of absorption through dissipation of electromagnetic energy through multiple networks of conductive fillers.

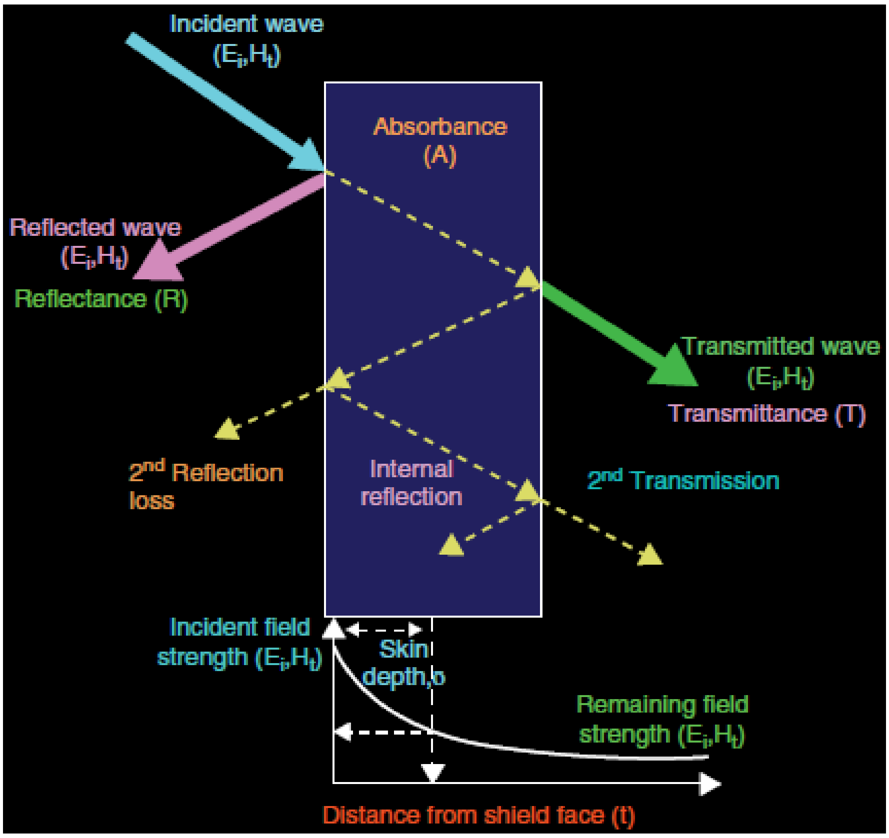

Figure 2.3: Fundamental mechanism of EMI shielding (Al-Saleh &Sundararaj, 2009)

2.1.5 ABSORPTION LOSS (SE_A)

Absorption loss(SE_A), is a function of the physical characteristics of the shield and independent on the type of source field. Therefore, $SE_A$is similar for all three waves (electric, magnetic and plane wave). The amplitude decreases exponentially, as in Figure 2.3, when an electromagnetic wave passes through a medium. SE_Aoccurs because currents induced in the medium produce ohmic losses and heating of the material. Absorption in conductive nanocomposites originates from Ohmic loss and polarization loss. Ohmic loss comes from the dissipation of energy by nomadic charges through conduction, hopping, and tunneling mechanisms, whereas polarization loss derives from the reorientation of electric dipoles in each half cycle of the electromagnetic wave. The energy dissipation by Ohmic loss is represented by the imaginary permittivity (Liu et al., 2007b, Ansari &Akhtar, 2016).

The absorption term SE_A is given as in Equation 3

$$SE_A(\text{dB}) = -20\frac{t}{\delta}\log_{10}e = -8.68\frac{t}{\delta} = -8.68t\left(\sqrt{\frac{\sigma_T\ \mu_r\ \omega}{2}}\right)$$

Equation 3

where *t* is shield thickness. Based on the above expression, SE_A is directly proportional to the square root of relative permeability (μ_r) and conductivity (σ_T) and angular frequency (ω). Absorption loss increases with increasing frequency for a given material. A good material will have high conductivity and adequate thickness, to achieve the required number of skin depths at the lowest frequency of concern (Zhang et al., 2015).

2.1.6 REFLECTION LOSS (SE_R)

The reflection loss is related to the relative mismatch between the incident wave and the surface impedance of the shield. Hence, the reflection term SE_R under planar wave can be expressed as Equation 4

$$SE_R(\text{dB}) = -10\log_{10}\left[\frac{\sigma_T}{16\ \varepsilon_0\omega\mu_r}\right]$$

Equation 4

Based on the expression above, SE_R directly proportional to σ_T and inversely proportional to μ_r . For a given material, SE_R decreases with increasing frequency (Liu et al., 2007b, Nayak et al., 2012).

2.1.7 PROPERTIES GOVERNING EMI SHIELDING MECHANISM

EMI shielding mechanism of an EMI shielding material should have certain characteristics to mitigate the EMI shielding problems. Firstly, the dielectric (relative complex permittivity, $\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$). The real parts ε'_r indicate the charge storage, whereas the imaginary parts ε''_r indicate dielectric loss during interaction with EM waves. The amount of losses is calculated from the tangent of dielectric loss ($\tan\delta_{\varepsilon} = \frac{\varepsilon''_r}{\varepsilon'_r}$) (Cheng et al., 2017, Wang et al., 2018). The dielectric constant of polymer composites mainly depends on the number of micro-capacitors and the polarization centres. Micro-capacitors are derived from the nanofiller-polymer-nanofiller arrangements in the polymer composites, whereas the polarization centres are formed from the defects in the nanofiller structure. Nanofillers attached to the polymer matrix act as electrodes filled with a non-conducting or insulating polymeric material. Polarization centres and the number of micro-capacitors reach the maximum at higher filler loading. The thickness of the dielectric barrier decreases, and the number of micro-capacitors increases due to higher filler concentration (Al-Saleh et al., 2013).

Dielectric loses energy through two main mechanisms knows as dielectric loss parameter (ε''); in conduction loss, a flow of charge through the material causing energy dissipation. The dielectric loss is influenced by orientational, ionic, interfacial and electronic polarization (Kao, 2004, Langhe &Ponting, 2016). The ionic and orientational polarization is ascribed to the bound charges in the material. Dielectric loss frequently occurs due to the movement of charges in the alternating magnetic field as polarization switches direction. Interfacial polarization generating from space charges that mount up owning to the difference in the electrical conductivity/dielectric constant at the interface of two different materials based on Maxwell-Wagner-Sillars (MWS) theory (Van Beek, 1960). Enhanced dielectric permittivity of composite materials can enhance dielectric loss contribution because of conductivity mismatch between insulating matrix and conductive fillers. As a result of this electrical conductivity discrepancy amid filler and matrix, composite materials may possess accumulated charges and polarization at their interfaces.

Therefore, polymer composite materials with a high dielectric value could be a good EM wave absorbers. EMI SE is also influenced by the radiation frequency and thickness, whereby in accordance with Equation 3, SE_A increases with the increase of radiation frequency and thickness. Other key parameters for shielding are the size and aspect ratio of fillers and nanomaterials can provide better electrical, magnetic and mechanical properties. For instance, a large area of graphene sheets comprising with high aspect ratio can decrease inter-sheet contact resistance, which provides higher electrical conductivity of large area graphene thin film as compared to small aspect ratio (small size graphene sheets) thin film. Therefore, several factors can influence EMI SE, including electrical conductivity, size of filler, dielectric permittivity and thickness of the shielding materials. However electrical conductivity and dielectric properties are the crucial aspect for effective shielding materials. In the last six years, the number of publications recorded in Scopus associated with EMI shows an increasing trend by 78%, indicating the significance in the advancement of EMI shielding material (Aal et al., 2008).

2.2 METALS FOR EMI SHIELDING

Metals have been witnessed as the best electrical conductors, which are capable of reflecting, absorbing and transmiting EM waves. Plastics, rubbers as well as fabrics are insulators and transparent to the EM waves. Metals have exceptional electrical conductivity and thermal conductivity; therefore, metal enclosures or shields have been utilized to block the penetration of GHz range frequency EM waves. The most common metal utilized for shield construction is mumetal which consists of high permeability alloy consisting of iron (Fe, 14%), copper (Cu, 5%), chromium (Cr, 1.5%) and nickel (Ni, 79.5%). Silver (Ag), Al, Ni, brass, metalized plastics, and conductive carbon/graphite particles or fibers are few other metals used as shielding materials. However, there are few limitations imposed by such metals; for instance, stainless steel is acknowledged for high density, and Al suffers from low impact resistance. Regardless of their good EMI SE, EM pollution has not been completely eliminated or mitigated as EM signals are almost entirely reflected at the surface of the metal, which protects the environment only beyond the shield. Besides that, metals used for EMI shielding are inconvenient in terms of weight and flexibility as today's electronic devices have become faster, smaller and lighter. They are easily exposed to corrosion which forms inter-modulation issues as a result of the formation of rusty bolt effect of non-linearity. EMI shields developed from two different metals are susceptible to galvanic corrosion resulting in non-linearity and by this means to degrade the total EMI SE of the metallic shield (Geetha et al., 2009, Sankaran et al., 2018).

2.3 POLYMER COMPOSITES FOR EMI SHIELDING

Inorganic/polymer hybrid materials have been gaining increasing research attention because of their outstanding lightweight, stability, flexibility, efficient absorption and ease of manufacturing. The main conditions for efficient EMI shielding material are lightweight and highly electrical conductive for practical applications, specifically in automobiles, aerospace, and portable electronic device. The reinforcement of polymer composite upon the addition of electrically conducting nanofillers will enhance high electrical conductivity and, consequently, can be utilized as an effective shielding materials. Carbonaceous fillers are recognized widely due to outstanding electrical conductivity, which is essential for shielding material.