FABRICATION AND PROPERTIES OF ELECTROMAGNETIC INTERFERENCES SHIELDING EPOXY COMPOSITES FOR ELECTRONIC PACKAGING APPLICATION

by

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LIST OF SYMBOLS

σ	Electrical conductivity
ε	Dielectric permittivity
ε'	Dielectric constant
ε''	Dielectric loss
ε_0	Permittivity of air
δ	Skin depth
μ	Magnetic permeability
μ_r	Relative permeability
γ	propagation constants
ω	Electromagnetic wavelength
$tg\delta_c$	Conductance loss tangent
C_{60}	Fullerene
ξ	Zetapotential
μ_E	Electrophoretic mobility
η	Viscosity of medium
d(H)	Hydrodynamic diameter
D	Translational diffusion coefficient
k	Boltzmann's constant
T	Absolute temperature
ρ_v	Volume resistivity
d	Main electrode diameter

t	Sample thickness
Rv	Volume resistance
E_i	Incident electric field
E_t	Transmitted electric field
f	frequency
R	Reflectance
A	Absorbance
T	Transmittance
I_D/I_G	Intensity ratio of D band and G band in Raman Spectroscopy
SE_R	Reflection loss
SE_A	Absorption loss
SE_M	Multiple internal reflection loss
Z_o	Impedance of the free space

LIST OF ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
CNT	Carbon nanotubes
CNF	Carbon nanofiber
DC	Direct current
DI	Deionized
ECal	Electronic calibration
EVA	Ethylene-vinyl acetate
EM	Electromagnetic
EMI	Electromagnetic Interferences
FTIR	Fourier transform infra-red
FESEM	Field emission scanning Electron Microscope
F-MWCNTs	Functionalized MWCNTs
LCP	Liquid Crystal Polymers
MnZn ferrite	Manganese Zinc Ferrite
MWCNTs	Multiwalled carbon nanotubes
NEMP	High-power electromagnetic pulse
PAN	Polyaniline
PET	Polyethylene terephthalate
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PTT	Poly (trimethylene terephthalate)
PU	Polyurethane
SE	Shielding Effectiveness

SWCNTs	Single-walled carbon nanotubes
TETA	Triethylenetetramine
XRD	X-ray Diffractometer
XPS	X-ray photoelectron spectroscopy
XANES	X-ray absorption near edge structure

FABRIKASI DAN SIFAT-SIFAT KOMPOSIT EPOKSI PENGHADANG GANGGUAN ELEKTROMAGNETIK UNTUK APLIKASI PEMBUNGKUSAN ELEKTRONIK

ABSTRAK

Pembangunan pesat peranti rangkaian tanpa wayar telah membawa masalah serius dalam pencemaran elektromagnet. Tujuan utama kajian ini adalah menghasilkan komposit penghadang gangguan elektromagnetik (EMI) yang berkesan untuk aplikasi pembungkusan elektronik. Dalam kajian ini, komposit epoksi penghadang EMI telah dihasilkan dengan menambah tiub-nano karbon berdinding ganda (MWCNTs) dan ferit zink mangan (ferit MnZn) dalam epoksi. MWCNTs telah difungsionalisasi dengan asid nitrik pekat dalam pelbagai masa tindak balas. MWCNTs dengan 2 jam rawatan fungsionalisasi menunjukkan peningkatan dalam kestabilan koloid, penyebaran dalam epoksi, kekonduksian elektrik, sifat dielektrik dan keberkesanan penghadangan EMI berbanding dengan MWCNTs asli. Ini disebabkan oleh kehadiran kumpulan berfungsi oksigenik yang ditambah ke permukaan tiub-nano karbon seperti yang diperhatikan dalam spektrum spektroskopi inframerah transformasi Fourier. Walau bagaimanapun, sifat-sifat komposite MWNCTs/ epoksi berkurang bagi rawatan yang lebih daripada 2 jam disebabkan kerosakan struktur seperti yang disahkan dengan spektroskopi Raman. Dalam bahagian kedua kajian, ferit MnZn telah disintesiskan melalui kaedah gel-sitrat dengan pelbagai suhu pengkalsinan. Didapati bahawa peningkatan suhu pengkalsinan akan meningkatkan ketulenan fasa dan saiz zarah ferit MnZn. Ferit MnZn yang dikalsinasi dalam suhu 1000 °C menunjukan ketulenan fasa yang tertinggi dengan purata saiz zarah 856.4 nm. Dalam kajian komposit epoksi MWCNTs /ferit MnZn, nisbah pengisian 3:1 menunjukkan nilai tertinggi dalam keberkesanan penghadangan EMI dan mekanisme penghadangn adalah dikuasai oleh penyerapan. Selain itu, didapati prestasi komposit penghadang EMI telah dapat dipertingkatkan dengan peningkatan kandungan pengisi dan ketebalan komposit. Prestasi komposit dengan 2.0 mm, 4.0 vol.% kandungan pengisi dengan gunaan lapisan belakang yang konduktif diadapati setanding dengan gasket/pad penghadang EMI komersial. Komposit epoksi penghadang EMI yang dihasikan dalam kajian ini berupaya menghasilkan keberkesanan maksimum penghadang EMI sebanyak 65 dB pada 9GHz.

FABRICATION AND PROPERTIES OF ELECTROMAGNETIC INTERFERENCES SHIELDING EPOXY COMPOSITES FOR ELECTRONIC PACKAGING APPLICATION

ABSTRACT

Rapid development in wireless commination devices was lead to seriousness in electromagnetic pollution. The main aim of this study is develop an effective electromagnetic interferences (EMI) shielding composites for electronic packaging application. In the present study, an EMI shielding epoxy composites have been fabricated by incorporated both multiwalled carbon nanotubes (MWCNTs) and manganese zinc ferrites (MnZn ferrites) in epoxy matrix. MWCNTs was functionalized with concentrated nitric acid with various functionalization reaction time. MWCNTs with 2 hours functionalization treatment shows enhancement in colloidal suspension stability, dispersion, electrical conductivity, dielectric properties and EMI shielding effectiveness (SE) as compared with pristine MWCNTs. This is due to presence of oxygenic functional groups on the surface of nanotube as observed within Fourier transform infra-red spectroscopic spectra. However, the properties of functionalized MWNCTs/ epoxy composites decrease for more than 2 hours treatment due to extensive damage of its structure as verified with Raman spectroscopy. In the second part of the study, MnZn ferrite was synthesized via citrate gel method with various calcination temperature. It is found that as the calcination temperature increases, the higher phase purity and larger particle size of MnZn ferrite were obtained. MnZn ferrite nanoparticle calcinated at 1000 °C exhibited the highest phase purity with average particle size of 856.4 nm. In the study of functionalized MWCNTs/ MnZn ferrite epoxy composite, fillers ratio of 3:1 showed the highest EMI SE and the shielding mechanism of the composite was dominated by absorption. It is observed that the EMI shielding effectiveness of composites were increased with the filler loading and composites thickness. It is also found that the EMI shielding performance of 2.0 mm fabricated composite, with the filler loading of 4.0 vol.% and applied of conductive back-layer, was comparable with commercial EMI shielding gaskets/pads. Maximum SE of 65 dB at 9 GHz was obtained for the EMI shielding polymer composites produced in the present study.

CHAPTER 1

INTRODUCTION

1.1 Overview

Nowadays, a serious new pollution problem known as the electromagnetic interference (EMI) has been created from the widely use of electronic devices and instruments in the commercial, industrial, healthcare, and defense sectors. High power of EMI can bring disturbance or malfunction of electric devices or instruments in power system, communication, automotive, healthcare and etc., which induces significant losses in time, energy, resources, and money (Im *et al.*, 2011). The EMI problem is significantly increasing due to the interference of wireless devices with digital devices and the increasing sensitivity of electronic devices since currently most of the electronic gadgets are looking for wireless and higher chip speeds (Paul, 2006). Thus, an effective method of shielding the unwanted electromagnetic wave is highly demanding.

Generally, electromagnetic interference shielding is depending to the reflection or absorption of electromagnetic radiation by a material, which served as a shield or barrier against the penetration of the electromagnetic wave through the shield (Chung, 2006). The important factors in determining the efficiency of EMI shielding are the geometric configuration and the thickness of the shield and its materials properties, typically characterized by the values of conductivity, (σ), permeability, (μ), and permittivity, (ε) (Steffan *et al.*, 2007).

The integration of EMI shielding into electronic packaging is most common method used in any electronic devices. A variety of materials and method of EMI shielding have been intensely studied and implemented into various level enclosures, gasketing, cable and connector shielding, bounding and grounding, and integral assembling. The most basic principle of shielding housing and enclosure is to install a Faraday cage around an electronic devices. In early day, the enclosures and shielding housing is commonly made of metal sheet and foil such as coppers, aluminium, silver, nickel, and stainless steel due to its excellent electrical conductivity (Geetha *et al.*, 2009). However, metals are heavy, tend to corrode, and hard to process in corners and tips (Sudha *et al.*, 2010). Thus, better candidate like conductive polymer composites was introduced into electronic packaging application because they are much lower in density and easy to shape by molding. The extensive study on conductive polymer composites was done by many researchers for the last few years. Numerous types of fillers such as carbon, aluminum, nickel, stainless steel, precious metal (gold, silver, and platinum) are introduced into elastomers for EMI shielding gaskets and in epoxy adhesive for mounting electronic components (Geetha *et al.*, 2009).

The effectiveness of EMI shielding of composite materials are depend on conductive fillers size. Smaller unit size of conductive filler is more effective than conductive filler with a larger unit size due to skin effect. Thus, fillers with nano in size such as carbon nanotubes (Li *et al.*, 2006b), graphene (Al-Hartomy *et al.*, 2012) and ferrite nanoparticles (Gairola *et al.*, 2010) are getting acceptance owing to their superior physical and chemical properties. However, there are some drawbacks such as electromagnetic wave tend to reflect rather absorb and low efficiency of EMI shielding of metallic magnetic fillers at high frequency when either one type of nanofillers was introduced into polymer composites (He *et al.*, 2014). Recently, a new strategy of shielding EMI was implemented by introduced both dielectric and magnetic lossy nanofillers into composites for much effective electromagnetic interference absorption in a broad frequency range with controllable permittivity and permeability of composites. For example carbon nanofibers (CNFs) and NiFe particles added into epoxy matrix and Nanoiron decorated carbon nanotubes added into polypropylene (PP) matrix have indicated an enhanced electromagnetic interference absorption (Park *et al.*, 2009; He *et al.*, 2014).

1.2 Problem Statement

Electromagnetic interference shielding are getting more and more challenging due to rapid expending usage of miniaturized devices and mobile telecommunication system. The ability of electronic packaging to shield EMI from surrounding and internally is greater demanding. Therefore, the purpose on this study is urging to develop a much effective EMI shielding composites for electronic packaging.

Highly conductive polymer composites have low impedance. Thus, successful reflected back incoming electrically dominant wave because of the impedance mismatch. However, electronic devices within the shield may mutually interfere and once EMI enter the shield, tends to traps within until they are absorbed (Grimes and Grimes, 1993). Hence, the focus point of this study is to improve the absorption loss in EMI shielding composite. In order to be effective in EMI absorption, its need to satisfy the impedance matching condition first, where the magnetic permeability value much closed to electric permittivity value of the shielding material (Gama *et al.*, 2011).

Based on others recent study, application of both dielectric and magnetic lossy fillers into composites significantly improve the absorption of EMI. Therefore, in this study both carbon nanotubes and manganese zinc ferrite are the suitable candidates for the dielectric and magnetic lossy fillers for EMI shielding polymer composites, since carbon nanotubes inherent excellent dielectric properties and manganese zinc ferrites ($Mn_{1-x}Zn_xFe_2O_4$) possess fascinating magnetic and electromagnetic properties (Cao *et al.*, 2012; Li *et al.*, 2006b; Zhang *et al.*, 2009; Song *et al.*, 2010).

Pristine MWCNTs is unlikely to disperse homogenously in epoxy matrix due to inherent bundling or entangling nature of MWCNTs (Kim *et al.*, 2012). With certain degree of functionalization with nitric acid, oxygenic functional groups presence on the surface of MWCNTs and enhanced the dispersion of MWCNTs in polymer matrix. However, excessive oxidation would damage the structure of MWCNTs and suffered loss in desired properties such as electrical conductivity and permittivity (Kitamura *et al.*, 2011). Therefore, effect of functionalization reaction time on dispersion, electrical and dielectric properties, and EMI shielding effectiveness are important to be studied.

There are various parameters governed the properties of ferrite such as calcination temperature and duration, type and amount of dopant, particle size, phase homogeneity and etc. The most important factors that control the magnetic properties of ferrite are particle size, particle size distribution and phase formation (Shirsath *et al.*, 2011). Therefore, the study on effect of calcination temperature on phase formation and particle size are essential, in order to synthesize the MnZn ferrite with good magnetic properties.

Two type of fillers were added into epoxy matrix to fabricate an EMI shielding composite. The fillers ratio have to be optimized in order to ensure both complex permittivity and complex permeability of composites are almost the same, which able to maximize absorption of EMI (Tong, 2008). Besides, the amount of fillers and thickness of the composites are the key parameters that affecting the performance of EMI shielding of composite. Therefore, the effect of fillers ratio, filler loading, and thickness on EMI shielding effectiveness of composite were studied in this research. This goal is to fabricate an effective EMI shielding composites for electronic packaging application, which is comparable with commercialized EMI shielding gaskets/pads.

1.3 Objectives

Recently, rapid development in various electronic and communication devices using the electromagnetic (EM) wave lead to seriousness in electromagnetic pollution. The task to ensure electronic packaging is able to shield the electromagnetic interference from the surrounding and mutual interference among the system is becoming more challenging. The main objective of this study is to develop an effective EMI shielding composites in electronic application by incorporated functionalized MWCNTs and manganese zinc ferrite into epoxy matrix.

Specific objectives of the present study are as follow,

1) To study the effect of functionalization reaction time on nanotubes dispersability and structural, electrical and dielectric properties, and EMI shielding performance of functionalized MWCNTs epoxy composites.
2) To synthesize manganese zinc ferrite nanoparticle via citrate gel route and study the effect of calcination temperature on purity, microstructure morphology, and particle size of manganese zinc ferrite.
3) To evaluate the effect of fillers ratio, filler loading and composite thickness on EMI shielding effectiveness of functionalized MWCNTs/ manganese zinc ferrite epoxy composite.
4) To compare the performance of EMI shielding on fabricated functionalized MWCNTs/ manganese zinc ferrite epoxy composite and commercial EMI shielding gaskets/ pads.

1.4 Thesis Organization

The main purpose of this study was to develop an effective EMI shielding composites for electronic packaging application. This study was divided into three main stages. First stage is functionalized MWCNTs by chemical oxidation with concentrated nitric acid. The mixture of MWCNTs and concentrated nitric acid (65%) was heated under reflux for designated reaction time (2Hr, 4Hr, 6Hr, 12Hr, and 24Hr). The effect of functionalization reaction time on dispersability, structural, electrical and dielectric properties, and EMI shielding performance at frequency range 7 GHz to 12 GHz of functionalized MWCNTs epoxy composite were evaluated to determine the suitable reaction time.

Second stage is synthesis process of manganese zinc ferrite nanoparticle via citrate gel method. Precursors and citric acid was stirred under heat to form sol and further heating to form gel. Dry gel was calcined with different temperature (800 °C, 900 °C and 1000 °C) to form ferrite nanoparticles. The effect of calcination temperature on purity, microstructure morphology and particle size of manganese zinc ferrite nanoparticle were studied and decided a suitable calcination temperature. The final stage of this study was fabricated an epoxy composites with functionalized MWCNTs and synthesized manganese zinc ferrite nanoparticle. The effect of fillers ratio, fillers loading and composites thickness on EMI shielding effectiveness on MWCNTs/MnZn ferrite epoxy composites were evaluated and determined the most effective EMI shielding composites. The comparison between commercialized EMI shielding gaskets/ pads and fabricated EMI shielding composites was done as conclusive study.