

**PREPARATION AND CHARACTERIZATION OF
GRAPHENE FILLED EPOXY THIN FILM
NANOCOMPOSITE FOR ELECTRONIC
APPLICATIONS**

ZAID AWS ALI GHALEB

**UNIVERSITI SAINS MALAYSIA
2016**

**PREPARATION AND CHARACTERIZATION OF GRAPHENE
FILLED EPOXY THIN FILM NANOCOMPOSITE FOR
ELECTRONIC APPLICATIONS**

by

ZAID AWS ALI GHALEB

Thesis submitted in fulfillment of the requirements

for the degree of

Doctor of Philosophy

August 2016

DECLARATION

I hereby declare that I have conducted, completed the research work and written the thesis entitles **“PREPARATION AND CHARACTERIZATION OF GRAPHENE FILLED EPOXY THIN FILM NANOCOMPOSITE FOR ELECTRONIC APPLICATIONS”**. 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 of University.

Name of Student: Zaid Aws Ali Ghaleb

Signature

Date: 9 August 2016

Witness by

Supervisor: Prof. Dr. Ir. Mariatti Jaafar

Signature

Date: 9 August 2016

Co-supervisor: Assoc. Prof. Dr. Zulkifli Mohamad Ariff

Signature

Date: 9 August 2016

ACKNOWLEDGEMENTS

First and foremost, I would like to express my unreserved gratitude and praises to Almighty Allah for His generous blessing and grace bestowed upon me during this research work.

Next to this, I would like to express my heartiest appreciation and deepest sincere gratitude to my main supervisor Prof. Dr. Ir. Mariatti Jaafar for her valuable advice, assistance, encouragement, and constant dedication during my period of study. Sincere thanks are accorded to my co-supervisor, Assoc. Prof. Dr. Zulkifli Mohamad Ariff for the discussions and his patience and providing invaluable suggestions and recommendations.

Special thanks to the Dean, Prof. Dr. Zuhailawati Hussain and all the staff in School of Materials and Mineral Resources Engineering USM for their co-operation and help. I would like to put forward my gratitude to the technical staffs namely En. Mokhtar, En. Mohammad Hassan, En. Rashid, En. Faizal, En. Azam, En. Azrul, En. Khairi and all the numerous people whose names have not been mentioned.

Special thanks and acknowledged to the Ministry of Education Malaysia (MOE) for the Malaysian International Scholarship (MIS) that made this research possible.

Finally, a very special thank and deepest gratefulness to my parents, brother, sister and friends for their love, motivation, encouragement and continued support.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	ix
LIST OF FIGURES	xi
LIST OF SYMBOLS	xix
LIST OF ABBREVIATIONS	xxii
ABSTRAK	xxv
ABSTRACT	xxvii
CHAPTER ONE: INTRODUCTION	
1.1 Background	1
1.2 Problem statement	3
1.3 Objectives	6
1.4 Thesis outline	7
CHAPTER TWO: LITERATURE REVIEW	
2.1 Introduction to electronic packaging	9
2.1.1 Overview	9
2.1.2 Electrically conductive adhesives	11
2.1.3 Electrically conductive adhesives categories	13
2.2 Polymer binders for ECAs	15
2.2.1 Introduction	15
2.2.2 Epoxy resin	17

2.3	Nanofillers for ECAs	21
2.3.1	Graphene	22
2.3.2	Carbon nanotubes	24
2.4	Characterization and properties of graphene	26
2.4.1	Characterization	26
2.4.1.1	Optical imaging of graphene layers	27
2.4.1.2	Transmission electron microscopy	27
2.4.1.3	Raman spectroscopy	29
2.4.2	Properties	31
2.5	Preparation methods of graphene/polymer composite	34
2.5.1	Ultrasonication	34
2.5.2	Solution blending	35
2.5.3	Melt mixing	36
2.5.4	In situ intercalative polymerization	37
2.6	Thin film fabrication methods	38
2.7	Factors influence the properties of graphene/polymer composite	40
2.7.1	Effect of graphene volume fraction	40
2.7.2	Effect of addition of MWCNTs as a secondary filler	42
2.7.3	Effect of polymer type	44
2.7.4	Effect of preparation methods	46
2.7.5	Effect of graphene surface treatment	47
2.7.6	Effect of graphene characteristics	50
2.7.7	Other factors	51

CHAPTER THREE: MATERIALS AND METHODS

3.1	Materials	53
3.1.1	Epoxy resin and curing agent	53
3.1.2	Fillers	54
3.1.2.1	Graphene nanopowder	54
3.1.2.2	Multi-walled carbon nanotubes	54
3.1.3	Dispersion solvent	55
3.1.4	Coupling agent	56
3.1.5	Other chemicals	56
3.2	Sample preparation	57
3.2.1	Stage 1: The effect of sonication time and filler loading	57
3.2.2	Stage 2: The effect of chloroform as dispersion solution	58
3.2.3	Stage 3: The effect of amine coupling agent on the GNP filled epoxy composites	59
3.2.4	Stage 4: The effect of GNP-MWCNT hybrid in epoxy composites	61
3.2.5	Stage 5: Preparation and properties of GNP-MWCNT hybrid epoxy (Epolam 2015) composites	62
3.3	Characterizations	64
3.3.1	Fourier transform infrared spectroscopy	64
3.3.2	Raman spectroscopy	64
3.3.3	Atomic force microscopy	64
3.3.4	Tensile properties	65
3.3.5	Electrical conductivity	65
3.3.6	Morphology studies	66

3.3.6.1	Transmission electron microscopy	66
3.3.6.2	Field emissin scanning electron microscopy	66
3.3.7	Thermal properties	67
3.3.7.1	Differential scanning calorimetry	67
3.3.7.2	Dynamic mechanical analysis	67

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	The effect of sonication time and filler loading	68
4.1.1	Characterization of particulate fillers	68
4.1.2	Tensile properties	70
4.1.3	Dispersion analysis of GNP/epoxy thin film nanocomposites	75
4.1.4	Fracture surface morphology of unfilled epoxy, GNP/epoxy and MWCNT/epoxy thin film nanocomposites	77
4.1.5	Electrical conductivity	81
4.2	The effect of dispersion solution and filler loading	83
4.2.1	Fourier transform infrared spectroscopy analysis	84
4.2.2	Raman spectroscopy analysis	85
4.2.3	Morphology of GNP/epoxy and ch-GNP/epoxy thin film nanocomposites	86
4.2.4	Tensile properties	90
4.2.5	Fracture surface morphology of GNP/epoxy and ch-GNP/epoxy thin film nanocomposites	95
4.2.6	Electrical conductivity	98
4.2.7	Thermal properties	100
4.3	The effect of amine coupling agent on the GNP filled epoxy composites	102

4.3.1	Fourier transform infrared spectroscopy analysis	103
4.3.2	Raman spectroscopy analysis	105
4.3.3	Morphology of m-GNP nanofillers	107
4.3.4	Atomic force microscopy of GNP and m-GNP nanofillers	108
4.3.5	Tensile properties	110
4.3.6	Fracture surface morphology of m-GNP/epoxy thin film nanocomposites	114
4.3.7	Electrical conductivity	116
4.3.8	Dynamic mechanical analysis	118
4.4	The effect of GNP-MWCNT hybrid in epoxy composites	123
4.4.1	Morphology of GNP-MWCNT/epoxy hybrid thin film nanocomposites	124
4.4.2	Tensile properties	127
4.4.3	Fracture surface morphology of GNP-MWCNT/epoxy hybrid composites	131
4.4.4	Electrical conductivity	133
4.5	The effect of GNP-MWCNT hybrid in epoxy-Epolam 2015 composites	137
4.5.1	Morphology of GNP-MWCNT/epoxy-Epolam hybrid thin film nanocomposites	137
4.5.2	Tensile properties	140
4.5.3	Fracture surface morphology of GNP-MWCNT/epoxy-Epolam hybrid composites	144
4.5.4	Electrical conductivity	147
4.5.5	Thermal properties	148

**CHAPTER FIVE: CONCLUSIONS AND SUGGESTIONS FOR FUTURE
WORKS**

5.1	Conclusions	151
5.2	Suggestions for future works	154

REFERENCES	155
-------------------	-----

APPENDICES

LIST OF PUBLICATIONS AND CONFERENCES

LIST OF TABLES

		Page
Table 2.1	Conductive adhesives compared with solder (Li and Wong, 2006)	12
Table 2.2	Comparison of the properties of different types of curing agents for epoxy (Ratna, 2009)	20
Table 2.3	Mechanical properties of graphene	32
Table 2.4	Comparison of thin film fabrication methods (Foo <i>et al.</i> , 2011)	39
Table 3.1	Typical properties of D.E.R. TM 332 epoxy resin, Polyetheramine D230, Epolam 2015 resin and Epolam 2015 hardener as supplied by manufacturer	54
Table 3.2	General properties of GNP and MWCNTs. Skyspring Nanomaterials, Inc. data sheet and Yeoh <i>et al.</i> (2009)	55
Table 3.3	The properties of chloroform as supplied by manufacturer	55
Table 3.4	The properties of ethylenediamine as supplied by manufacturer	56
Table 3.5	Sample codes corresponding to the composition of the epoxy hybrid composite containing 0.5 vol% carbon nanofillers of different GNP/MWCNT amounts	61
Table 4.1	Average length and width of GNP as supplied by manufacturer, GNP/epoxy and ch-GNP/epoxy composites measured by TEM imaging and analysis	88
Table 4.2	Glass transition temperatures (T_g) of unfilled epoxy, GNP/epoxy and ch-GNP/epoxy nanocomposites	101

Table 4.3	Glass transition temperature (T_g) of unfilled epoxy, GNP/epoxy and m-GNP/epoxy composites	122
Table 4.4	Comparison of tensile strength, tensile modulus, electrical conductivity and percolation threshold values of unfilled epoxy and different epoxy composites systems	136
Table 4.5	Glass transition temperatures (T_g) of epoxy-DER, epoxy-Epolam, GNP-MWCNT/epoxy-DER hybrid composites and GNP-MWCNT/epoxy-Epolam hybrid composite	149

LIST OF FIGURES

		Page
Figure 1.1	Levels of electronic packaging (Lau, 1994)	2
Figure 2.1	Schematic illustrations of (a) isotropically conductive adhesive (ICA), (b) anisotropically conductive adhesives (ACA) and (c) non-conductive adhesives (NCA) (Rongwei et al., 2010)	13
Figure 2.2	A typical percolation curve showing the abrupt increase in conductivity at the percolation threshold (Li and Wong, 2006)	14
Figure 2.3	Epoxide group of epoxy resin	17
Figure 2.4	Reaction of epichlorohydrin and bisphenol A for preparation of DGEBA	18
Figure 2.5	Mechanism of curing of epoxy resins by amine	19
Figure 2.6	Graphene (top left) is a honeycomb lattice of carbon atoms. Graphite (top right) can be viewed as a stack of graphene layers. Carbon nanotubes are rolled-up cylinders of graphene (bottom left). Fullerenes (C ₆₀) are molecules consisting of wrapped graphene through the introduction of pentagons on the hexagonal lattice (Kuilla <i>et al.</i> , 2010)	23
Figure 2.7	Typical Raman spectra for a single-layer graphene sample and bulk graphite using a 532 nm excitation laser. The spectra are offset vertically for clarity. Graphene can be identified by the position and shape of its G (1580 cm ⁻¹) and 2D (2700 cm ⁻¹) peaks (Childres <i>et al.</i> , 2013)	30

Figure 2.8	Triangular sublattices of graphene. Each atom in one sublattice (A) has 3 nearest neighbors in sublattice (B) and vice-versa (Cooper <i>et al.</i> , 2012)	32
Figure 2.9	Cluster structure of carbon filler primary particle agglomerates (left), arrangement of these cluster below (middle) and at (right) percolation concentration (Pionteck and Wypych, 2007).	42
Figure 2.10	Flexural modulus ratio (a) and flexural strength ratio (b) of epoxy composites with a fixed concentration of 0.1 wt%; electrical conductivities (c) of MWCNTs, GNP and MWCNTs-GNP (0.8:0.2) epoxy composites as a function of the filler content and electrical conductivity (d) of epoxy composite with different MWCNTs-GNP ratios at constant overall concentrations of 0.8 wt% and 4 wt% (Yue <i>et al.</i> , 2014).	43
Figure 2.11	Chemical functionalization of graphene using amidation reaction (Xu <i>et al.</i> , 2009)	49
Figure 3.1	Chemical structure of ethylenediamine	56
Figure 3.2	Schematic of the fabrication of (a) GNP/epoxy and (b) ch-GNP/epoxy nanocomposites	59
Figure 3.3	Schematic of the procedures used in this study for the chemical treatment of GNP	60
Figure 3.5	Flow chart showing the overview of the present study	63
Figure 4.1	TEM images of (a) GNPs and (b) MWCNTs (at magnification of 10 kx for (a) and 5 kx for insert image, and	69

80 kx for (b) and 40 kx for insert image)

Figure 4.2	Stress-strain curves of unfilled epoxy and epoxy thin film nanocomposites with different fillers loading and sonication time	70
Figure 4.3	Tensile properties of unfilled epoxy and epoxy thin film nanocomposites with different fillers loading and sonication time: (a) tensile strength, (b) tensile modulus and (c) elongation at break	72
Figure 4.4	Optical micrographs of 0.2 vol% of GNP/epoxy thin film nanocomposites: (a) GNP 10 minutes, (b) GNP 20 minutes and (c) GNP 30 minutes	76
Figure 4.5	SEM images on tensile fracture surface of the unfilled epoxy thin film (at magnification of 500 kx for a and 1000 kx for b)	78
Figure 4.6	SEM images on tensile fracture surface of 1 vol% of GNP/epoxy thin film nanocomposites produced at 20 minutes sonication time (at magnification of 500 kx for a, c and 1000 kx for b, d)	78
Figure 4.7	SEM images on tensile fracture surface of 1 vol% of GNP/epoxy thin film nanocomposites produced at 30 minutes sonication time (at magnification of 500 kx for a, c and 1000 kx for b, d)	79
Figure 4.8	SEM images on tensile fracture surface of 1 vol% of MWCNT/epoxy thin film nanocomposites produced at 20 minutes sonication time (at magnification of 500 kx for a, and 1000 kx for b)	80

Figure 4.9	Electrical conductivity of unfilled epoxy and epoxy thin film nanocomposites with different fillers loading and sonication time	81
Figure 4.10	FTIR spectra of GNP/epoxy and ch-GNP/epoxy nanocomposites	84
Figure 4.11	Raman spectra of GNP and ch-GNP nanofillers	85
Figure 4.12	TEM images of 0.2 vol% GNP/epoxy composites (at magnification of 7 kx for a and b, 20 kx for c and 30 kx for d)	87
Figure 4.13	TEM images of 0.2 vol% ch-GNP/epoxy composites (at magnification of 7 kx for a and b, 20 kx for c and 30 kx for d)	89
Figure 4.14	Stress-strain curves of unfilled epoxy, GNP/epoxy, and ch-GNP/epoxy thin film nanocomposites with different fillers loading	90
Figure 4.15	Tensile properties of unfilled epoxy, GNP/epoxy, and ch-GNP/epoxy thin film nanocomposites with different fillers loading: (a) tensile strength, (b) tensile modulus and (c) elongation at break.	92
Figure 4.16	SEM images of tensile fracture surface: (a) cross section of 0.2 vol% of GNP in epoxy thin film, (b), (c), (d), (e), (f) and (g) 0.2 vol% of GNP in epoxy composites (magnification of 100 x used for (a) and 200 kx used for (b), (e), (f) and 500 kx used for (c) and 1000 kx used for (d) and (g))	96
Figure 4.17	SEM images of tensile fracture surface: (a) cross section of	97

0.2 vol% of ch-GNP in epoxy thin film, (b), (c), (d), (e), (f) and (g) 0.2 vol% of ch-GNP in epoxy composites (magnification of 100 x used for (a) and 200 kx used for (b), (e), (f) and 500 kx used for (c) and 1000 kx used for (d) and (g))

Figure 4.18	Electrical conductivity of GNP/epoxy and ch-GNP/epoxy composites at different fillers loading	98
Figure 4.19	DSC thermograms recorded during the second heating at the rate of 10°C min ⁻¹ for unfilled epoxy, GNP/epoxy and ch-GNP/epoxy nanocomposites	101
Figure 4.20	FTIR spectra's of (a) raw GNPs; (b) GNP-COOH; (c) GNP-COCL and (d) GNP-NH ₂	105
Figure 4.21	Raman spectra of GNP and m-GNP nanofillers	106
Figure 4.22	TEM images of m-GNP (at magnification of 5 kx for a, 7 kx for b, 10 kx for c and 15 kx for d)	108
Figure 4.23	AFM topography images of (a) GNP and (b) m-GNP deposited onto a mica substrate	109
Figure 4.24	Stress-strain curves of unfilled epoxy, GNP/epoxy, and m-GNP/epoxy thin film nanocomposites with different fillers loading	110
Figure 4.25	Tensile properties of unfilled epoxy, GNP/epoxy, and m-GNP/epoxy thin film nanocomposites with different fillers loading: (a) tensile strength, (b) tensile modulus and (c) elongation at break	112

Figure 4.26	SEM images of tensile fracture surface: (a) cross section of 0.2 vol% of m-GNP in epoxy thin film, (b), (c), (d), (e), (f) and (g) 0.2 vol% of m-GNP in epoxy composites (magnification of 100 x used for a and 200 kx used for b, c, f and magnification of 500 kx used for d, e, g)	115
Figure 4.27	Electrical conductivity of GNP/epoxy and m-GNP/epoxy composites at different fillers loading	117
Figure 4.28	Plot of storage modulus for unfilled epoxy, GNP/epoxy, and m-GNP/epoxy thin film nanocomposites with different fillers loading	119
Figure 4.29	Plot of tan delta for unfilled epoxy, GNP/epoxy, and m-GNP/epoxy thin film nanocomposites with different fillers loading	121
Figure 4.30	TEM images of epoxy hybrid composites in various proportions of GNP to MWCNT: (a) and (b) 0.1:0.4; (c) and (d) 0.25:0.25; (e) and (f) 0.4:0.1 (at magnification of 15 kx for a, c and e and 38 kx for b, d and f)	125
Figure 4.31	Schematic diagram of GNP-MWCNT/epoxy hybrid composites in various proportions of GNP to MWCNT: (a) 0.1:0.4; (b) 0.25:0.25; (c) 0.4:0.1	126
Figure 4.32	Stress-strain curves for the unfilled epoxy and their composites with the same content (0.5 vol%) of GNPs, MWCNTs and selected GNP-MWCNT hybrids	128
Figure 4.33	Tensile properties of unfilled epoxy and their composites with the same content (0.5 vol%) of GNPs, MWCNTs and GNP-MWCNT hybrids: (a) tensile strength, (b) tensile	129

modulus and (c) elongation at break

Figure 4.34	SEM images on tensile fracture surface of the epoxy hybrid composites in various proportions of GNP to MWCNT: (a), (b), (c) and (d) GNP:MWCNT (0.1:0.4); (e), (f), (g) and (h) GNP:MWCNT (0.4:0.1) (at magnification of 200 kx for a, e, 500 kx for b, f and 1000 kx for c, d, g and h)	132
Figure 4.35	Electrical conductivity of 0.5 vol% GNP-MWCNT/epoxy hybrids composites as function of GNP:MWCNT ratio	134
Figure 4.36	TEM images of 0.5 vol% GNP-MWCNT/epoxy-Epolam (0.1:0.4) hybrid composites (at magnification of 7 kx for a, b and 15 kx for c and 38 kx for d, e, f)	139
Figure 4.37	Stress-strain curves for the epoxy-DER, epoxy-Epolam, GNP-MWCNT/epoxy-DER hybrid and GNP-MWCNT/epoxy-Epolam hybrid composite	141
Figure 4.38	Tensile properties of epoxy-DER, epoxy-Epolam, 0.5 vol% GNP-MWCNT/epoxy-DER (0.1:0.4) hybrid composites and 0.5 vol% GNP-MWCNT/epoxy-Epolam (0.1:0.4) hybrid composite: (a) tensile strength, (b) tensile modulus and (c) elongation at break.	142
Figure 4.39	SEM images on tensile fracture surface of the 0.5 vol% of GNP-MWCNT/epoxy-Epolam hybrid composites (at magnification of 200 kx for a, b, 500 kx for c, d and 1000 kx for e, f).	145
Figure 4.40	SEM images of the residues from a burned GNP-MWCNT/epoxy thin film nanocomposites: (a), (b) and (c) epoxy-Epolam (0.1:0.4) hybrid nanocomposite; (d), (e) and	146

(f) epoxy-DER (0.4:0.1) hybrid nanocomposite (at magnification of 1000 kx for a and d, 2000 kx for b and e and 3000 kx for c and f).

Figure 4.41 Electrical conductivity of epoxy-DER, epoxy-Epolam, GNP-MWCNT/epoxy-DER hybrid composite and GNP-MWCNT/epoxy-Epolam hybrid composite. 147

Figure 4.42 DSC thermograms recorded during the second heating at the rate of $10^{\circ}\text{C min}^{-1}$ for epoxy-DER, epoxy-Epolam, GNP-MWCNT/epoxy-DER hybrid composites and GNP-MWCNT/epoxy-Epolam hybrid composite 149

LIST OF SYMBOLS

$^{\circ}\text{C}$	Degree Celsius
T_m	Melting temperature
Ω	Ohm
cm	Centimeter
m	Meter
W/mK	Watts per meter kelvin
psi	Pounds force per square inch
mil	Military
μm	Micrometer
T_g	Glass transition temperature
wt%	Weight percentage
vol%	Volume percentage
nm	Nanometers
GPa	Giga pascal
S/m	Siemens per meter
2-D	Two dimensional
3-D	Three dimensional
\AA	Angstrom
kV	Kilovolt
m^2/g	Square meter per gram
E	Young's modulus
σ_{ts}	Tensile strength
TPa	Terapascal

kHz	kilohertz
E	Amount of energy
P	Power
t	Time
mm	Millimeter
phr	Parts per hundred
mPa.s	Milli pascal second
g/ml	Gram per milliliter
g/l	Gram per liter
V_f	Volume fraction
ρ_f	Density of filler
ρ_m	Density of matrix
M_f	Weight of filler
M_t	Total weight of composite
rpm	Revolutions per minute
g/cm^3	Gram per cubic centimeter
mW	Milliwatts
kN	Kilo newton
V	Volt
R_v	Volume resistance
ρ	Electrical resistivity
σ	Electrical conductivity
d	Diameter of the sensor
T	Thickness of the sample
R	Resistance

E'	Storage modulus
δ	Tan delta

LIST OF ABBREVIATIONS

ACA	Anisotropically conductive adhesives
ACF	Anisotropically conductive film
AFM	Atomic force microscopy
Ag	Silver
ASTM	American society for testing and materials
Au	Gold
BADGE	Bisphenol-A diglycidylether
BGA	Ball grid array
Bi	Bismuth
CNTs	Carbon nanotubes
COF	Chip on flex
COG	Chip on glass
CSP	Chip scale package
Cu	Copper
CVD	Chemical vapor deposition
DC	Direct current
DGEBA	Diglycidyl ether of bisphenol A
DMA	Differential mechanical analysis
DMF	Dimethyl formamide
DSC	Differential scanning calorimetry
DWCNT	Double-walled carbon nanotubes
ECAs	Electrically conductive adhesives
Et ₃ N	Triethylamine