PREPARATION, CHARACTERIZATION AND PROPERTIES OF GRAPHENE FILLED EPOXY NANOCOMPOSITES PRODUCED USING COLLOIDAL POLYMERIZATION METHOD

by

MUHAMMAD HELMI BIN ABDUL KUDUS

Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy

APRIL 2018

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful

All praises to ALLAH for the strengths and His blessing in completing this thesis. Peace is upon Prophet Muhammad S.A.W, our beloved prophet whom his teaching makes us strongly believed that ALLAH is the only Hope in everything, and to ALLAH we must thanks. Million thanks to my father Haji Abdul Kudus bin Ahmad and my mother Hajjah Naimah bt Abdul Latiff for their endless prayers until now. I am deeply indebted to my supervisor, Prof. Dr Hazizan bin Md Akil, for his outstanding advice through years. Funds for this research were provided by Universiti Sains Malaysia (USM) through CREST and Cluster of Polymer Composites (CPC) Grant. A special thanks to Prof Dr Zuhailawati binti Hussain (Dean), Prof Dr Ir Mariatti bt Jaafar and Assoc. Prof Ahmad Badri bin Ismail from School of Materials and Mineral Resources for their helps and supports. Appreciation is expressed to my fellow researchers, especially Mr Razlan Zakaria, Dr Bisyrul Hafi Othman, Dr Shuhadah Saleh and Mr Mohd Hafiz Zamri for their valuable helps. I also would like to thank and appreciate to all supportive technicians for their advices and patience during the research. Lastly I would like to thank my sister Siti Noor Hayati Abdul Kudus, my wife Nuur Sa’adah Zakaria and my family for their support and encouragement. May ALLAH blesses and rewards all of your goodness as He said in the Quran:

“So whoever does an atom's weight of good will see it. And whoever does an atom's weight of evil will see it.” (Quran 99:7-8)

Thank you very much.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: CONCLUSION AND SUGGESTION FOR FUTURE WORKS

LIST OF PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CNT	Carbon Nanotubes
DGEBA	diglycidyl ether of bisphenol-A
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
Epoxy/oGNP^{colloidized}	oGNP filled epoxy nanocomposites via colloidization mixing sequence
Epoxy/oGNP^{conventional}	oGNP filled epoxy nanocomposites via conventional mixing sequence
FESEM	Field Emission Scanning Electron Microscopy
FR4	Commercial glass-reinforced epoxy composites for electronic circuit board application
FTIR	Fourier Transform Infrared
GF	Graphite Flakes
GNP	Graphene Nano Platelets
GNS	Graphene Nano Sheet
GO	Graphene Oxide
HRTEM	High-resolution transmission electron microscope
HGO	Hummer GO
HGO+	Hummer modified GO
IGO	Improved Hummer GO

OG	Oxidized Graphene
oGNP	Oxidized Graphene Nano Platelets
PCB	Printed Circuit Board
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TMD	Tetra Methylhexaethylene diamine
THF	Tetrahydrofuran
NMP	N-Methyl-2-pyrrolidone
WLR	Weight Loss Rate

LIST OF SYMBOLS

@	Alias
A	pre-exponential constant in the Arrhenius equation, an empirical relationship between temperature and rate coefficient
Br	Bromin
C	Carbon
COOH	Carboxyl
E_a	Activation Energy
Et	Ethyl ($–CH_2CH_3$)
EtO–CO	Ester
$f(\alpha)$	The differential expression of a kinetic model function
O	Oxygen
OH	Hydroxyl
Q	Ratio of the weight of solvent in swollen polymer and weight of polymer
R	Gas constant
T	Temperature
T_p	Absolute temperature at maximum weight loss rate
V	Volume fraction
wt %	Weight percentage
α	Conversion
β	Heating rate
ε	Dielectric constant
χ	Huggins epoxy-solvent interaction constant

PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT NANO EPOKSI TERISI GRAFIN YANG DIHASIL MENGGUNAKAN KAEDAH PEMPOLIMERAN KOLOID

ABSTRAK

Permasalahan yang selalu timbul semasa pembuatan epoksi terisi grafinkebanyakannya adalah penyebaran grafin, masalah pengagregatan semula dan pengurangan kepadatan sambung-silang. Satu turutan yang berbeza dalam penyediaan komposit epoksi dilakukan dengan mencampurkan platlet grafin teroksida (oGNP) dengan agen pematangan sebelum mencampurkannya dengan resin epoksi. Apabila oGNP dicampur dengan trimetilheksametilena diamina (TMD), tindak balas kondendsasi antara kumpulan hidroksil dan kumpulan amina menyebabkan pembentukan koloid TMD/oGNP. Koloid TMD/oGNP digunakan untuk mematangkan resin epoksi. Pengkoloidan akan menambah baik penyebaran grafin dan menghalang penggumpalan semula grafin dalam resin epoksi dan menyebabkan ketumpatan sambung silang lebih tinggi. Analisa termogravimetri (TGA) menunjukkan bahawa kestabilan terma sistem epoksi/oGNP bertambah baik, manakala kehadiran oGNP menjadikannya lebih stabil terhadap pelarut dari sudut peningkatan ketumpatan sambung silang. Keputusan menunjukkan bahawa turutan pencampuran TMD/oGNP dapat meningkatkan sifat-sifat akhir komposit epoksi berbanding kaedah konvensional untuk menghasilkan komposit nano epoksi terisi grafin. Kaedah konvensional merujuk kepada pembuatan komposit nano epoksi/grafin dengan mencampurkan grafin dengan resin epoksi sebelum menambah dalam agen pematangan. Komposit nano Epoksi/oGNP$^{\text{dikoloid}}$ menunjukkan ketumpatan sambung silang lebih tinggi daripada komposit nano Epoksi/oGNP$^{\text{konvensional}}$. Komposit nano

Epoksi/oGNP^{dikoloid} menunjukkan kekonduksian haba yang lebih tinggi daripada komposit nano Epoksi/oGNP^{konvensional} dengan kepekatan pengisi yang sama, selari dengan nilai ketumpatan sambung silang. Untuk Epoksi/oGNP^{konvensional}, di mana rangkaian amida antara karboksilik dan amina kumpulan telah agak dibentuk, ketumpatan sambung silang yang tinggi mempertingkatkan aliran haba melalui pengangkutan fonon. Menariknya, sifat-sifat dielektrik komposit nano epoksi juga menunjukkan hubungan langsung dengan ketumpatan sambung silang sebagai Epoksi/oGNP^{dikoloid} dengan memperolehi nilai pemalar dielektrik lebih tinggi daripada Epoksi/oGNP^{konvensional}. Rumusan daripada kajian menyatakan bahawa epoksi komposit nano terisi grafin yang dihasilkan melalui kaedah pempolimeran koloid meningkatkan sifat-sifat terma, sifat-sifat tensil dan sifat-sifat dielektrik berdasarkan peningkatan jumlah kepadatan sambung silang dan sebaran grafin yang lebih baik. Seterusnya analiss degradasi secara terma menggunakan kajian kinetic secara non-isoterma menunjukkan degradasi secara terma yang berlaku ke atas epoksi adalah mengikut mekanisma F1 dan Epoksi/oGNP^{dikoloid} mencapai jangkahayat degradasi secara terma yang paling tinggi.

PREPARATION, CHARACTERIZATION AND PROPERTIES OF GRAPHENE FILLED EPOXY NANOCOMPOSITES PRODUCED USING COLLOIDAL POLYMERIZATION METHOD

ABSTRACT

Common issues during fabrication of graphene filled epoxy mostly are dispersion of graphene, re-agglomeration problem and reduction of crosslink density. A different sequence of epoxy composite preparation was performed by mixing oxidized graphene platelets (oGNP) with a curing agent prior to mixing it with epoxy resin. When oGNP was mixed with trimethylhexamethylene diamine (TMD), the condensation reaction between the hydroxyl and amine groups resulted in the formation of a TMD/oGNP colloid. The TMD/oGNP colloid was used to cure epoxy resin. The colloidization eventually improved the dispersion and prevented re-agglomeration of graphene in the epoxy resin and resulted in higher crosslink density. A thermogravimetric analysis (TGA) showed that the thermal stability of the epoxy/oGNP system had improved, while the presence of the oGNP gave more stability to the solvent in terms of an increase in the crosslink density. These results showed that the TMD/oGNP colloid mixing sequence was able to enhance the properties of the epoxy composite compared to the conventional method of obtaining graphene filled epoxy nanocomposites. Conventional method refers to fabrication of epoxy/graphene nanocomposites by mixing the graphene into the epoxy resin prior to adding into the curing agent. Epoxy/oGNP^{colloidized} showed higher crosslink density than Epoxy/oGNP^{conventional} nanocomposite. Epoxy/oGNP^{colloidized} nanocomposites showed a higher thermal conductivity than an epoxy/oGNP^{conventional} nanocomposite with the same concentration of filler, which is parallel to the crosslink density result.

From the observation, in Epoxy/oGNP$^{\text{conventional}}$, where amide network between carboxylic and amine groups were relatively formed, a high crosslink density enhanced the thermal conductivity via phonon transport. Through the analysis, the dielectric properties of epoxy nanocomposites also showed direct relationship with crosslink density as Epoxy/oGNP$^{\text{colloidized}}$ obtained higher dielectric constant value than Epoxy/oGNP$^{\text{conventional}}$. The summary of the study concludes that fabrication of graphene filled epoxy nanocomposites via colloidal polymerization method, enhance the thermal properties, tensile properties and dielectric properties due to the increasing amount of crosslink density and better dispersion of graphene. Further thermal degradation analysis via non-isothermal kinetic study shows an F1 mechanism occurs for epoxy thermal degradation and the Epoxy/oGNP$^{\text{colloidized}}$ achieved the highest lifetime for thermal degradation.

CHAPTER ONE

INTRODUCTION

1.1 Background

Graphene nano-platelets (GNP) have received enormous attention over the years from scientists working in various technological fields and applications. It is claimed that GNP have better properties than those of carbon nanotubes (CNT) given their extremely high aspect ratio and surface area (Li *et al.*, 2005a; Li *et al.*, 2008; Yu *et al.*, 2008; Xu and Shi, 2011). GNP has increasingly become popular in electronic material studies (Min *et al.*, 2013; Ghaleb *et al.*, 2014) as well as in various polymer composite applications (Lee *et al.*, 2008b; Sun *et al.*, 2010; Chu *et al.*, 2012). Like CNT, GNP is associated with the carbon allotropes category, as it has the graphitic structure of carbon. In comparison with the hollow-wire structure of carbon nanotubes, the graphene nanoplatelets are small particles with a graphitic carbon structure with minimal thickness. The flake-shaped graphene nanoplatelets with their extreme aspect ratio, have also attracted the attention of researchers in various fields and applications.

Recently, the level of interest has intensified regarding graphene filled epoxy nanocomposites thanks to the versatility of epoxy (good chemical resistance, high modulus and satisfactory thermal stability)(Saeb *et al.*, 2013; Jin *et al.*, 2015). This is primarly due to the encouraging aspects of graphene (outstanding modulus (Lee *et al.*, 2008a), high electron mobility (Novoselov *et al.*, 2004), and thermal conductivity (Balandin *et al.*, 2008)) benefiting from the two-dimensional honeycomb structure of graphene consisting of sp^2 carbon atoms. It has also been reported that the use of graphene oxide (GO) in epoxy nanocomposites is more useful than graphene because of the presence of the reactive oxygen functional groups such as hydroxyl, epoxy, and carboxyl groups (Dreyer *et al.*, 2010; Zhu *et al.*, 2010). However, the dilemma of choosing between pristine (Yun *et al.*, 2011) and functionalized GO (Ganguli *et al.*, 2008; Bao *et al.*, 2011; Kim *et al.*, 2011; Timofeeva and Singh, 2014; Li *et al.*, 2017) to overcome the poor dispersion and exfoliation of the platelets in polymer resin, continues to be faced regarding epoxy/GO composites.

Other than the widespread use of GNP as reinforcement in epoxy composites, researchers are still unable to exploit the full potential of graphene in epoxy composites. The fabrication of graphene-filled epoxy composites share the same common problems as with other particulate filler reinforcements, such as poor dispersion and the high tendency of filler agglomeration occurring in the resin matrix. The GNP tend to agglomerate as the filler loading is increased (Li *et al.*, 2007; Chandrasekaran *et al.*, 2013; Li *et al.*, 2013; Tang *et al.*, 2013), due to the van der Waal forces (Stankovich *et al.*, 2007; Tang *et al.*, 2013). Many attempts have been made to minimise these issues, such as via the functionalization of the GNP (Kuila *et al.*, 2012; Haziqah and Rahman, 2013; Timofeeva and Singh, 2014; Ahmadi-Moghadam *et al.*, 2015), treating the GNP with ozone GNP (Li *et al.*, 2005a; Li *et al.*, 2007), and via intercalation via thermal and exfoliation methods (Biswas *et al.*, 2011; Chandrasekaran *et al.*, 2013). The result of these studies shows that the properties of the treated or functionalized GNP epoxy composites increased, and performed much better than the untreated GNP epoxy composites. Functionalized GNP is believed to enhance the mechanical properties of the composites by improving the interlocking count on the GNP surface (Li *et al.*, 2005b; Li *et al.*, 2005a).

However, the treated or functionalized GNP epoxy composites still face the problem of re-agglomeration of the GNP during processing. Even though the level of the re-agglomeration that occurs is not as high as the agglomeration of untreated GNP, it still shows that something must be undertaken to optimise the performance of GNP reinforcement. Inam and Peijs (2007) encountered this re-agglomeration problem early in their carbon nanotube (CNT)-filled epoxy composites and proposed adjusting the temperature, heating rate and viscosity to avoid re-agglomeration from occurring. In a separate study, Santos *et al.* (2016) reported that the functionalized GNP did not entirely prevent the agglomeration from occurring, but only delayed the re-agglomeration process. Rarely do scientists focus on the functionalization and combination of GNP with the mixing sequence (processing) to improve the dispersion and reduce agglomeration. To date, the conventional method of preparing the epoxy after the functionalization process is still being adopted.

From this point, three problems have been identified as being a common hindrance to achieving higher properties of graphene filled epoxy nanocomposites, namely poor dispersion of graphene, re-agglomeration of graphene and the reduction of crosslink density. Various studies have attempted to solve these problems. The reinforcement of epoxy with graphene-based fillers has been the subject of various reports, (Li *et al.*, 2005a; Yu *et al.*, 2007; Ganguli *et al.*, 2008; Martin-Gallego *et al.*, 2011; Min *et al.*, 2013; Shokrieh *et al.*, 2013). However, little has been learned concerning the explicit correlation that exists between graphene loading and crosslink formation.

To solve this problem, a straightforward and novel method, namely colloidal polymerization of oxidized graphene (oGNP) and diamine was introduced in this work. The colloidal polymerization is developed to solve poor dispersion, re-agglomeration and the reduction of the crosslink density applying a single novel approach. In the sense of crosslink density, colloidal polymerization provides additional crosslink among the graphene and epoxy matrix instead of giving restriction to the crosslinking process.

In this work, the graphene filled epoxy nanocomposites were fabricated via colloidal polymerization between oxidized GNP and diamine curing agent. The GNP was oxidized via acid oxidation to obtain a possible carboxylic group (-COOH) on the GNP surfaces. The oxidized GNP (oGNP) was mixed with the diamine curing agent before mixing with the epoxy resin, instead of after mixing it with the epoxy resin. The oGNP is expected to undergo a condensation reaction with the diamine curing agent, tetramethylhexadiamine (TMD), to form a colloidal mixture of oGNP/TMD for further use, in curing the diglycidyl ether of bisphenol A (DGEBA) epoxy resins. The colloidal polymerization approach is expected to solve poor dispersion, re-agglomeration and the reduction of the crosslink density, given that the current technique does not efficiently solve the raised problems. The properties of the nanocomposites were investigated accordingly. To further evaluate the extra formation of the crosslink density, non-isothermal degradation kinetic was performed to obtain the value of activation energy, E_a. The thermogravimetric analysis (TGA) data can be used to obtain the kinetic parameters which can subsequently be used to predict the lifespan of the polymer at different temperatures.

From previous experience, kinetic evaluation, based on single heating rate methods (isothermal), is not dependable and has encountered many problems. Moreover, thermal degradation of epoxy nanocomposites does not follow a single mechanism, because both the activation energy (E_a) and the pre-exponential factor (A) are not constant during the reaction. The non-isothermal data acquired by thermal analysis techniques could be used to provide a reasonably accurate description of the kinetics of degradation (Budrugeac and Segal, 2008). Hence, kinetic evaluation based on multiple heating rate methods (non-isothermal) is preferred and is more convenient to perform because it is not necessary to carry out a rapid temperature jump of the sample at the beginning. The Flynn Wall Ozawa, Kissinger and Coats-Redfern methods are among the simplest methods to obtain E_a from TGA data. In the thermal degradation process, high E_a is required to break the chemical bonds. Theoretically, the higher crosslink density of nanocomposites requires higher E_a to be thermally degraded. Moreover, the obtained E_a could also be used for predicting the lifetime of nanocomposites.

1.2 Problem Statements

Currently, epoxy-graphene based nanocomposites are widely used in various applications. GNP have been introduced to epoxy nanocomposites, proven to improve the stiffness, impact resistance, and hardness of the nanocomposites. However, the main problem associated with GNP as filler in the epoxy matrix is due to its poor dispersion, re-agglomeration and reduction of crosslink density. Even though various treatments and modification of GNP have been proposed to improve the level of dispersion, the problem still exists. Moreover, crosslink density is also reported to be reduced via graphene loading.

From a processing perspective, limited work has previously been undertaken towards optimising epoxy composites via fabrication methods. Almost all graphene-epoxy composites reported, were using conventional methods of the processing sequence, (i.e. mixing epoxy with graphene and promoting the dispersion of graphene before the addition of the diamine curing agent). The sequence of mixing in prepared epoxy-graphene is rarely studied. Most of the research on epoxy/functionalized graphene composites, studied functionalized graphene as this had always been utilised as an ‘assistant’ to the mixing process such as mechanical mixing, and sonication to ease the dispersion of graphene in an epoxy matrix. The introduced functional group eventually helped to minimise the level of graphene agglomeration occurring, and at the same time bring physical interlock and van der Waal bonding between the graphene and the epoxy polymer chain. The interlock would provide good interphase between the filler and matrix when the resin is later cured. However, the re-agglomeration factors were always ignored by most researchers given that they were using low viscosity resin, solvent processing, high-temperature curing and applying a longer curing duration.

This study utilises oxidized graphene as the primary mechanism for the dispersion parameters which alleviates re-agglomeration from occurring during the curing process. Graphene is easily dispersed in a low viscosity medium. Because of that, many studies on epoxy composite processing have used a solvent to reduce the viscosity of the epoxy. However, the re-agglomeration of the dispersed graphene will readily occur in a low viscosity medium. Even for non-solvent processing, the viscosity of the epoxy resin is reduced during the addition of a low viscosity curing agent. Moreover, for an elevated temperature curing epoxy system, the viscosity of the mixture drops again initiated by the rising temperature before crosslinking occurs. These low viscosity events give time to the dispersed graphene to be stacked again and to re-agglomerate. To date, the dispersion of graphene in epoxy studies have only focussed on the various types of functionalization on graphene to improve dispersion, and very little work has been concentrated on re-agglomeration. As a result, well-dispersed graphene without re-agglomeration remains a challenge to achieve and therefore, re-work on the conventional processing methods should be progressed given such limitations.

1.3 Research Objectives

The objectives of this study are:

1. To investigate the success of the simplified Hummers' method for the oxidation of graphene procedure using several characterization method such as Raman Spectroscopy, FTIR analysis and HRTEM;
2. To inspect the fabrication of graphene filled epoxy nanocomposites via colloidal polymerization mixing between oxidized graphene and a diamine curing agent, and propose the mechanism of chemical reaction that occurs during colloidal polymerization;
3. To compare the crosslink density of graphene filled epoxy nanocomposites with different fabrication sequences by using swelling test.
4. To compare tensile properties, thermal conductivity, thermal degradation, and dielectric properties of graphene filled epoxy nanocomposite fabricated via the colloidal polymerization method and conventional method;
5. To evaluate the effect of crosslink density and dispersion level of graphene on tensile properties, thermal conductivity, thermal degradation, and dielectric properties of graphene filled epoxy nanocomposite fabricated via both the colloidal polymerization method and the conventional method; and
6. To analyse the thermal stability, kinetic of thermal degradation and lifetime prediction on graphene filled epoxy nanocomposites and the effect of water uptake on dielectric properties of graphene filled epoxy nanocomposites.

1.4 Scope of Research

This study focuses on the novel processing technique of graphene filled epoxy nanocomposites preparation, with minimum agglomeration and good dispersion. A process called “colloidal polymerization” which has formed “colloidal suspension” between graphene and the curing agent was introduced to maintain the graphene dispersion after the sonication process, before the curing process. The assessment of the effectiveness of the newly-developed technique was carried out by correlating the dispersion with the associated properties using various characterization techniques including FTIR, TGA, crosslink density, tensile test and dielectric test.

This study however only investigates the effect of the independent variables (different mixing sequences and functionalization of graphene), the correlation between the fundamental properties (dispersion of graphene and crosslink density) to the physical and mechanical properties (chemical resistivity, tensile properties, thermal stability and dielectric properties), of epoxy nanocomposites without quantifying the degree of dispersion and the effect of filler loading. **Figure 1.1** illustrates the schematic representation of the relationship between the independent variables, fundamental properties and the physical/mechanical properties.

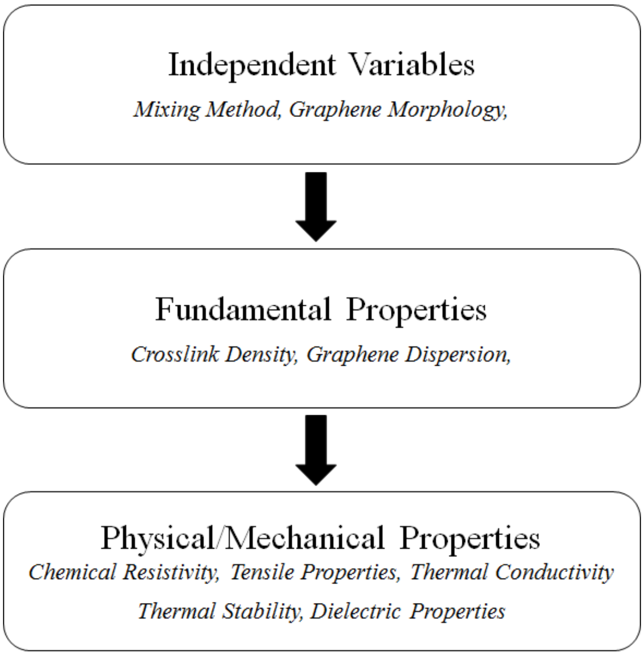

Figure 1.1: Schematic representation of the relationship between the independent variables, fundamental properties and the physical/mechanical properties

1.5 Thesis Organization

The structure of the thesis is presented as follows.

Chapter One: presents background of this study, problem statements, research objectives, scope of research and thesis organization.

Chapter Two: presents a literature review of prior studies which have investigated:

- Graphene filled epoxy nanocomposites;
- The graphene oxidation method;
- Fabrication challenges;
- Overcoming challenges; and
- The disadvantages of the conventional fabrication method.

This chapter also highlights the limitations of these studies for graphene filled epoxy nanocomposites to obtain better improvements in nanocomposite properties.

Chapter Three: presents the materials used and research methodology to examine the effect of colloidal polymerization on the fabrication of graphene filled epoxy nanocomposites. All parameters of fabrication were set, such as the resin/curing agent ratio, the filler weight percentage, mechanical mixing, curing temperature, and curing time. Different mixing sequences differentiated the three fabrication methods of the nanocomposites. The characterization and tests of all samples and specimens were conducted to analyse the relevancy of nanocomposite properties improvement via different mixing sequences.

Chapter Four: presents the results and discussion, detailing the process of graphene oxidation by acid, the condensation polymerization reaction between oxidized graphene and the diamine curing agent and the epoxy composite curing method. Further discussion in this chapter is centred on the tensile properties, thermal properties and dielectric properties which have a direct relationship with the morphology of graphene, dispersion of graphene and crosslink density.

Chapter Five: presents the overall conclusions based on the research along with suggestions for future investigation.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview

In this chapter, the progress and works on graphene filled epoxy composites are reviewed, regarding the works on oxidation and functionalization of graphene, fabrication of epoxy nanocomposites, achievements in properties enhancement and their applications. The main challenges in graphene filled polymer nanocomposites as well in epoxy nanocomposites is to obtain good dispersion level of graphene in matrix. In graphene filled epoxy nanocomposites, homogenous dispersion of graphene nanoplatelets (GNP) in epoxy matrix usually show improvement in thermal and tensile properties of the resulting nanocomposite. Several recent methods of processing have been reviewed in order to overcome the dispersion issues and divided into three categories; (i) mechanical dispersion, (ii) solvent/surfactant processing, and (iii) oxidation/functionalization of graphene. Graphene always dispersed mechanically in epoxy resin via mechanical stirrer and high frequency sonication while several peoples tend to use solvent processing to extend the ease of dispersion of graphene especially for high viscosity resin. The oxidation and functionalization of graphene aims surface modification and provide significant improvement of graphene dispersion which have led to optimum utilization of graphene performance as nanoscale particulate reinforcement. The nanocomposites show a major improvement in stiffness, impact resistance and hardness when compared with neat epoxy. Recent developments in functionalization of graphene have created new perspectives for achieving these goals. For future epoxy composites applications, the competitive edge will come from a technology that excels in tailoring epoxy properties, controlling fabrication process and in production plants toward maximizing product quality.

2.2 Progress in Graphene Filled Epoxy Nanocomposites

Products based on thermoset composites are used in a broad range of applications in automotive, electrical, and other industries. The future success of thermoset (new types or reinforced) rests upon continuous innovation to meet the demands in cost, quality and competition in properties with other polymer composites. The technical and business aspects of thermoset indicates a capacity for change, which will enable the thermosetting composites industry to overcome the challenges ahead. of all the thermoset composites currently known, epoxy composites have been extensively used in many industrial and technological applications as adhesives, constructions, coating and insulation or low dielectric materials for electric devices (Lee and Neville, 1967; Lubin, 2013) due to their good balance of properties such as low shrinkage after cure; excellent moisture, solvent and chemical resistance; superior electrical and mechanical properties; good adhesion to many substrates (Wang and Shieh, 1999).

Epoxy itself is known as a rigid thermosetting polymer. Among polymeric materials, it possess high mechanical properties such as tensile properties as well as flexural properties after cure depending on type of resin, and composition between resin and curing agent. Not only because of excellences in all mentioned aspects, the tailor-ability of their properties and ease of processing are also of the crucial factors that make epoxy has been chosen. The tailor-ability of epoxy properties could be done in various ways, such as modification of the resin (Ramos *et al.*, 2005; Tao *et al.*, 2007); selection of different curing agents (Nohales *et al.*, 2006; Tao *et al.*, 2007); and trading off ratio between resin and curing agent (d'Almeida and Monteiro, 1996; Grave *et al.*, 1998). Tao *et al.* (2007) showed their fluorinated epoxy (BGDF) would achieve about the same mechanical properties as unmodified commercial epoxy (BADGE) which cure with the same system, but having lower dielectric constant and water absorptions which attributed to the incorporation of CF_3 groups in the network structure of epoxy resins. d'Almeida and Monteiro (1996) has concluded in their work that the strong dependence of deformation behavior on the resin/hardener ratio, in compression of their DGEBA/TETA epoxy system cured at room temperature without any post cure treatment. Whereas the epoxy rich system would behave as brittle materials, and the amine rich system have a much larger deformation capacity.

The most common ways to tailor the properties of epoxy is by incorporating various types of filler for ones desired properties into optimized epoxy system. This ways of enhancement eventually has created the field of epoxy composites science and technological applications. Industries introduced various additives in epoxy since 1930s by mixing epoxy with fillers, extenders and plasticizers for stand-alone applications such as packaging, adhesives, and low-cost molded parts. By earlier 1940s – to 1950s, the epoxy composites become more use to mechanical and engineering application when the glass fiber reinforced epoxy composites dominated in aircraft fabrication. When boron and carbon fiber were introduced in 1960s, both surpass their predecessor as fiber reinforcement in polymer composites by their ease of processing and provide higher strength and stiffness. As the demands in space program and military declined in 1970s and 1980s, the price of carbon fiber and glass fiber increased. The need of lower cost of reinforcement for polymer composites, including epoxy composites, bring out the production of aramid fibers and graphite as reinforcements. Until the 1990s era, both academic and industrial studies started to extend the composite paradigm to smaller scales, from macro to nano-meter scales. Carbon nanotubes were taking over the popularity of nanoscale reinforcement materials in epoxy nanocomposites. By utilizing the type, morphology, size and surface chemistry of fillers, the properties of epoxy composites would be enhanced according to various needed applications; ranging from commodity to engineering use. The researches of epoxy composites recently has been extended to the use of nano-meter scale filler size and surface functionalization of fillers to optimize the interaction (interphase and interface) between matrix and filler. Whereas both interphase and interface are important factors of strengthening the composite.

Since the rise of graphene in 2004 (Geim and Novoselov, 2007), the world of material science and technology are continuously stimulated and still exploring the unique possibility of the single atom thickness of graphitic carbon nanoparticles in electrical, mechanical, thermal and optical applications. Including the field of polymer composites, especially for epoxy based nanocomposites, graphene have become remarkable material to be used as reinforcement. Owing to the extreme aspect ratio, which is higher that carbon nanotubes, graphene have brought tremendous attention in epoxy nanocomposites application to enhance the mechanical properties such as tensile, flexural, fracture toughness, compression etc. While graphitic structure or graphene would enhance the thermal, electrical and optical properties. In real time application of graphene reinforced epoxy nanocomposites, epoxy and graphene have been explored for applications such as electrostatic-dissipative, anti-corrosive, and electromagnetic interference (EMI) shielding, stealth composite coating and specifically for sensors (Tung *et al.*, 2016).

2.2.1 Chemical Properties

2.2.1 (a) Chemical Resistance

Epoxy is well known to have good chemical resistance to the most chemical and solvent. For that credit, the epoxy was used in various coating and adhesives applications to protect the devices from chemical corrosion. Incorporating graphene as reinforcement in epoxy has increase the chemical resistance of epoxy composites. Work by Zhang *et al.* (2015) showed corrosion resistance of zinc coated with graphene nano-sheet (GNS) filled epoxy resin with 0.7 wt% of GNS loading increase four times than zinc coated with neat epoxy. Graphene is a good inhibitor (Prasai *et al.*, 2012; Nayak *et al.*, 2013) and graphene distributed on epoxy resin matrix could form a good protective layer to act as a barrier to the penetration of solution. For these reasons, the GNS filled epoxy resin coating with good mechanical properties presented better corrosion resistance (Zhang *et al.*, 2015). Regardless of chemical corrosion, solvent swelling is also crucial for polymer including epoxy nanocomposites.

2.2.1 (b) Water Absorbance

Water absorption properties is a behavior of a material to attract water molecules from environment. Water absorption of epoxy resins is associated with the hydroxyl groups and tertiary amine formed in the curing process (Van Krevelen and Te Nijenhuis, 2009). The presence of hydroxyl groups and tertiary amines in epoxy resin attracts water molecules and form hydrogen bonding. The water absorption properties of epoxy basically varies on the degree of hydroxyl groups and tertiary amines. However, the amount of water molecules in epoxy resins not only because of water absorption. If the epoxy not fully cured, the polymerization between epoxy and curing agent could still occurs at certain elevated temperature which produce water as byproduct. Water absorption by epoxy resins has been extensively studied because of its impact on the structure properties of these resins. Unappropriated level of absorbed water will cause resins to swell and to produce “crazing” of the surface. The interaction between water and epoxy can reduce the glass transition temperature (T_g) and degrade the mechanical properties of epoxy (Li *et al.*, 2004). Regardless of affecting mechanical properties, water absorption properties directly affects dielectric properties. Although relation between water absorption and dielectric properties of graphene filled epoxy nanocomposites are less reported, the influence of water absorption on dielectric properties of epoxy/SiO_2 nanocomposites which was reported by Dayuan *et al.* (2015) can be used as reference. They reported that the water uptake will affect dielectric properties of the nanocomposites as the results that permittivity, capacitance and tan δ of pure epoxy were strongly affected by the water absorptions. In other words, the water absorption properties is crucial to epoxy nanocomposites which served in electronic devices application especially as insulating materials and electronic impedance control.

2.2.2 Tensile Properties

After the rise of graphene (Geim and Novoselov, 2007), graphene filled epoxy nanocomposite attracted tremendous studies to improve mechanical properties (Rafiee *et al.*, 2009; Zaman *et al.*, 2012; Feng *et al.*, 2013; Yang *et al.*, 2013; Meng *et al.*, 2014), thermal conductivity and dielectric properties of epoxy nanocomposites. In 2009, Rafiee *et al.* (2009) reported the Young’s modulus of the graphene filled epoxy nanocomposite was ~30% greater than the neat epoxy as compared to ~3% increase for single-walled carbon nanotubes. The tensile strength of the neat epoxy was enhanced by ~40% with graphene platelets compared to ~14% increment for multi-walled carbon nanotubes. Meanwhile Feng *et al.* (2013) worked on graphene reinforced spirocyclic phosphazene epoxy (SP-epoxy) shows the SP-epoxy/graphene nanocomposites at 1.0 vol % of graphene incorporation also exhibit more than a 25% increment in tensile modulus over the SP-epoxy thermoset. Further tensile properties improvement of graphene filled epoxy nanocomposites were studied via modification of graphene. The work of Yang *et al.* (2013) on 1 wt% hydrogen passivation graphene filled epoxy nanocomposite demonstrated 103.3% and 57.4% increase in elastic modulus compared to the control sample and the composite with the same amount of graphene. Same improvement of tensile properties by modified graphene (m-GnPs) filled at 1 vol% m-GnPs, where the Young's modulus of epoxy increases 8.6% higher than its peer unmodified graphene (GnPs) nanocomposite (Meng *et al.*, 2014). From their work, Meng *et al.* (2014) concluded that the improved dispersion of m-GnPs in epoxy matrix has produced more total specific surface area in a unit volume, which can avoid stress concentrations and enable stress transfer across interface under loading; and also the strong interface formed by covalent bonding effectively transfers stress between matrix and GnPs compare to interface debonding for unmodified graphene composite. The other works on graphene and modified graphene filled epoxy composites also resulted in enhancement of tensile properties especially tensile modulus with only below 5 wt% filler incorporation (Zaman *et al.*, 2012; Jiang *et al.*, 2014; Zaman *et al.*, 2014; Zhang *et al.*, 2014; Ahmadi-Moghadam *et al.*, 2015).

Almost every explanation about tensile properties limitation address the graphene agglomeration where it is a well-known issue in graphene filled epoxy nanocomposites. Most of the graphene synthesis methods produce agglomerated graphene (Singh *et al.*, 2011). As far mentioned, graphene tends to agglomerate due to intermolecular van der Waals cohesive forces (Zacharia *et al.*, 2004; Lee *et al.*, 2014). As a result, dispersing graphene in epoxy matrix is always challenging. The relationship between dispersion level and the nature of crack propagation is explained in the work of Atif *et al.* (2016). The crack propagation can be best barricaded by homogenously dispersed graphene. The summary of the works on graphene filled epoxy nanocomposites is depicted in **Table 2.1**.

Table 2.1 : Summary of the works on graphene filled epoxy nanocomposites

Year	**Filler**	**Increase in σ (%)**	**Increase in E (%)**	**References**
2015	Graphene nanoplatelete	38	14	(Ahmadi-Moghadam *et al.*, 2015)
2014	modified Graphene	18.8	42.2	(Jiang *et al.*, 2014)
2014	modified Graphene	-11.1	21.5	(Zaman *et al.*, 2014)
2014	modified Graphene	28	23.6	(Meng *et al.*, 2014)
2014	modified Graphene	46.2	31.7	(Zhang *et al.*, 2014)
2013	Graphene	31.8	34.1	(Feng *et al.*, 2013)
2012	modified Graphene	-0.23	0.267	(Zaman *et al.*, 2012)
2013	Graphene oxide	12.3	10	(Yang *et al.*, 2013)
2009	Graphene	41.8	29.8	(Rafiee *et al.*, 2009)

2.2.3 Thermal Properties

2.2.3 (a) Thermal Conductivity

Advanced electronic devices utilize special polymer matrix composites (PMC) instead of conventional ceramic materials. Polymer composites with high thermal conductivity is needed in science and technological application, especially in heat and thermal management in electronic devices. High thermal conductivity insulation materials required in electronic applications requiring heat dissipation effective as a heat sink, light emitting diode (LED) encapsulation and printed circuit board (PCB) in the electronic packaging. The nature of the polymer is good at insulation properties, but is less efficient in heat conductivity which can be overcome by adding additives that able to conduct heat. Relationship between polymer matrix and additives are essential to make more effective heat conduction.

In order to fabricate polymer composite with high thermal conductivity, various filler materials have been introduced to increase the effectiveness of thermal conductivity in polymer composites (Biercuk *et al.*, 2002; Hsieh and Chung, 2006; McGrath *et al.*, 2008; Zakaria *et al.*, 2014). Among various filler materials, graphene is widely chosen to reinforce polymer composites especially in the application of thermal conductivity. Graphene possesses extreme thermal conductivity (~ 5,300 W/mK) due to the phononic transport and nearly free electron state of its structure (Balandin *et al.*, 2008; Ghosh *et al.*, 2010; Balandin, 2011). Several studies on the potential use of graphene in polymer composites for thermal conductivity enhancement and thermal management (Yu *et al.*, 2008; Veca *et al.*, 2009b; Goyal and Balandin, 2012; Shahil and Balandin, 2012a; Shahil and Balandin, 2012b). Yu *et al.* (2007) reported a thermal conductivity of 6.44 W/mK from a polymer composite with about 25 vol % of graphene. The graphene layers prepared from acid treatment for intercalation of graphite and then exfoliated via thermal shock, provide excellent thermal increments when incorporated in an epoxy matrix. Graphene sometimes were used in hybrid with carbon nanotube (CNT) to obtain synergistic effect which enormously enhanced thermal conductivity by 700% (Yu *et al.*, 2008) as shown in **Figure 2.1**. The work of Ganguli *et al.* (2008) that dispersed a 20 wt% of silane-functionalized graphene oxide (GO) into epoxy resin, and showed thermal conductivity increase to 5.8 W/mK.

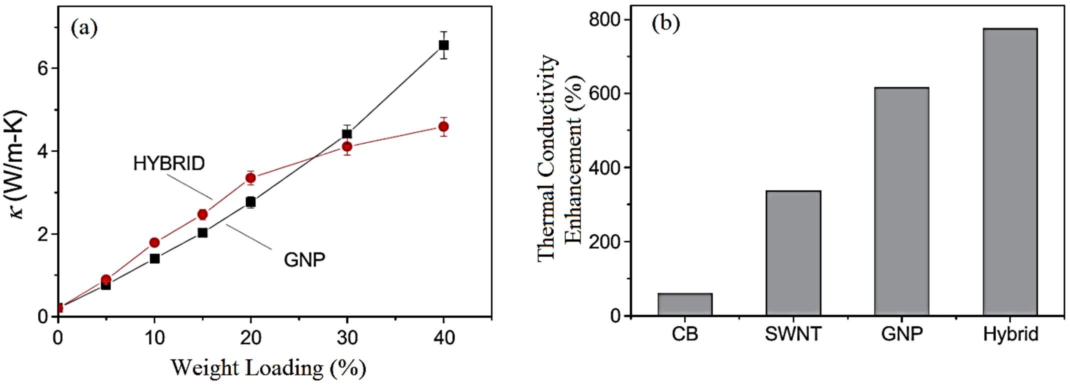

Figure 2.1: a) Thermal conductivity of epoxy composites with GNP-SWNT hybrid filler (red circles), GNP:SWNT (3:1) and GNP filler (black squares) as a function of the filler loading, and (b) thermal conductivity enhancement of epoxy compositesfor SWNT, GNP and GNP-SWNT hybrid filler at 10 wt % loading incomparison with carbon black (CB) (Yu et al., 2008).

However, the applicability of graphene is still limited due to its low dispersion, primarily caused by their tendency to aggregate as a result of van der Waals interactions between the surfaces. The highly cohesive van der Waals energy (5.9 kJ/mol) of non-oxidized graphene makes it impossible to form well dispersed graphene polymer composites (Zacharia *et al.*, 2004). The low dispersion of graphene makes it very difficult to prepare graphene polymer composites at high filler loading. Although graphene oxide that exfoliated from graphite could rise the dispersion issues, they experience significant losses in thermal conductivity even after reduction due to structural disorders and defects of the π-orbital structure during oxidation. (Hummers Jr and Offeman, 1958; Eda *et al.*, 2008). In order to resolve these problems, several approaches have been suggested for the fabrication of non-oxidized graphene (Viculis *et al.*, 2003; Kwon *et al.*, 2011; Wang *et al.*, 2011; Park *et al.*, 2012), such as the use of a graphite intercalation compound (GIC), and solvent exfoliation or surfactant-assisted exfoliation (Hernandez *et al.*, 2008; Lotya *et al.*, 2009; Lotya *et al.*, 2010). Still, the poor dispersion of the resultant graphene in polymer matrix should be improved to achieve better composite properties. This is quite trade-off between dispersion level and defect level of graphene. Despite of playing trade-off between dispersion level and defect level of graphene, thermal conductivity of polymeric materials can be enhanced by another route for achieving composites with high thermal conductivity (Kim *et al.*, 2015), especially in epoxy composites. In graphene filled epoxy composites, thermal conductivity can be further increased by improving interphase between filler and matrix via promoting covalent bond between graphene and epoxy matrix. **Table 2.2** shows the summary of the works on graphene filled epoxy nanocomposites with regards to thermal conductivity properties.

Table 2.2 : Summary of the works on graphene filled epoxy nanocomposites

Year	Filler	Filler Loading	Increase in Thermal Conductivity (W/m/K)	Increase in Thermal Conductivity (%)	References
2007	Thermally Oxidized GNP	20 vol %	6.44	-	(Yu *et al.*, 2007)
2008	Silane functionalized GO	20 wt %	5.8	-	(Ganguli *et al.*, 2008)
2008	Graphene/CNT hybrid	40 wt %	~ 4	700	(Yu *et al.*, 2008)
2011	Pyrene - functionalized Graphene	4 phr	1.91	16.4	(Teng *et al.*, 2011)
2013	Pyrene-functionalized graphene	10 wt%	1.53	86	(Song *et al.*, 2013)
2016	Graphene Oxide/CNT hybrid	30 wt%	1.698	800	(Gu *et al.*, 2016)
2017	Graphene	3 wt%	0.47	126.4	(Zakaria *et al.*, 2017)

In general, the aspects which is influencing thermal conductivity of graphene filled epoxy nanocomposites can be divided into three factors, i.e i) dispersion of graphene, ii) morphology of graphene, and iii) interface of graphene-epoxy (Pollack, 1969; Martin-Gallego *et al.*, 2011). These factors are very dependent to each other's in a complex relationship.

2.2.3 (b) Thermal Degradation

Polymeric materials are critical to high temperature environment. High temperature will always affect their chains mobility thus alter the properties of the material. While thermosetting polymer like epoxy materials require higher temperature to induce chain mobility as the epoxy chains were crosslinked during curing process. Differ than thermoplastic materials, epoxy and thermosetting materials did not melt upon heating. This polymer group tends to degrade and decompose into carbon char without melt. The degradation of epoxy composites were analyzed through kinetic study. It is already known from previous experience that kinetic analysis based on single heating rate methods (isothermal) is not dependable and encountered with many problems (Burnham, 2000; Vyazovkin, 2000). Therefore, the multiple heating rate methods (non-isothermal) like Flynn-Wall-Ozawa (Ozawa, 1965; Ozawa, 1970; Flynn, 1997), Kissinger (Kissinger, 1957), Coats-Redfern (Coats and Redfern, 1963; Coats and Redfern, 1964), MacCallum-Tanner (MacCallum and Tanner, 1970), Friedman (Friedman, 1964) and etc, are most preferred for the same reason. Non-isothermal runs found to be more convenient to carry out because it is not necessary to perform a sudden temperature jump of the sample at the beginning.

Less but not least, it should be much interesting to understand the structure-properties relationship which are governed by the mathematical description of the decomposition process of polymers in the solid state which are rely on three kinetic components; (1) two Arrhenius parameters, apparent activation energy (E_a) and pre-exponential factor (A); (2) the analytical expression describing the kinetic model, f(α); (3) the former parameter E_a is the most frequently used to discuss the thermal stability of these polymers. The kinetic degradation and glass transition as well as chain mobility which have been obtained from TGA can generate parameters, which can be subsequently used to deduce the lifetime of polymer at different temperatures. The thermal behavior of epoxy system has reported depend on the polymeric network crosslink density, functional group, types of curing agent (Ochi *et al.*, 1995), and filler properties (Zhou *et al.*, 2007; Jin and Park, 2012; Zakaria *et al.*, 2014).

2.2.4 Evaluation Thermal Degradation Kinetic

An optimal thermal degradation process depends on the understanding of the thermal degradation kinetics, thermal degradation mechanism, and an accurate modeling of thermal degradation process. This modeling process includes determining the mechanism and an appropriate kinetic equation in term of activation energy. An accurate model not only helps to predict the thermal degradation behavior, but also can be used to predict the lifetime of epoxy nanocomposites. The model can further be used to compare the degradation behavior of different epoxy nanocomposites fabrication methods and different filler architectures.

In this nanocomposites study, dynamic thermogravimetric methods have been used to calculate the thermal degradation kinetic parameters using three selected model; Flynn-Wall-Ozawa , Kissinger and Coats Redfern. The application of dynamic thermogravimetric methods holds great potential as a tool for deriving the mechanisms of physical and chemical processes that occur during polymer degradation (Doğan *et al.*, 2008). The kinetic for polymer degradation usually supposed that the conversion rates are proportional to the concentration of the reacted material. Hence, the rate of conversion, dα/dt can be expressed by the following basic rate equation (1).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\, f(\alpha) \qquad (1)$$

where and k(T) and f(α) are functions of temperature and conversion respectively. However, in cases of thermogravimetric analysis, the conversion of the reacted material (α) is represented as the ratio of actual mass loss at time (t) to the total mass loss at complete degradation process as shown in (2).

$$\alpha = \frac{M_o - M_t}{M_o - M_f} \qquad (2)$$

where M_o, M_t, and M_f, are the initial weight of sample, the weight of sample at time, and the final weight respectively, of the completely decomposed sample. The k value is modeled successfully by the Arrhenius equation (3);

$$\mathrm{k} = \mathrm{A}\exp - \frac{Ea}{RT} \qquad (3)$$

where A is the frequency factor, E_a is the apparent kinetic energy of the degradation reaction, R is the gas constant, and T is the absolute temperature. The *k* from (1) is expected to follow Arrhenius Equation. Thus, by substituting (3) into (1), one obtains (4);

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{Ea}{RT}\right)\mathrm{f}(\alpha) \qquad (4)$$

According to non-isothermal kinetic theory, thermal degradation data is generally performed by the following (9).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta\frac{d\alpha}{dT} = A\exp\left(-\frac{Ea}{RT}\right)\mathrm{f}(\alpha) \qquad (5)$$

where β=dT/dt is a constant heating rate. Rearranging equation (5) one can be simplified as equation (6).