UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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NANO HYBRID OF MWCNTs/GNPs FILLED EPOXY NANOCOMPOSITES FOR STRUCTURAL APPLICATION

This report is submitted in accordance with requirement University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory committee is as follow:

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ABSTRAK

Bahan-bahan nano karbon seperti nanotube karbon (CNTs) dan nanoplatelets graphene (GNPs) mempunyai ciri-ciri yang membanggakan dari segi sifat mekanikal, fizikal, dan haba mereka. Sifat-sifat intrinsik dan ekstrinsik yang terkumpul oleh CNTs dan GNPs menjadikan mereka sebagai pengisi yang ideal dan sesuai untuk penyediaan nano komposit polimer yang digunakan dalam aplikasi kejuruteraan maju pada masa kini. Oleh itu, dalam kajian ini, nano komposit epoksi yang disediakan mengandungi sistem tetulang hibrid MWCNTs-GNPs. Sistem epoksi nano komposit telah diisi dengan komposisi MWCNTs, GNPs dan MWCNTs / GNPs menggunakan kaedah adunan sebati oleh pengadunan secara automatik dengan kaedah pengawetan yang betul dalam ketuhar vakum yang dipanaskan. Kesan sinergi hybrid MWCNTs / GNPs nano komposit telah dinilai dengan membandingkan ciri-ciri mekanikal, fizikal dan haba yang dialami antara epoxy tulen dan pengisi tunggal bertetulang nano komposit daripada epoksi / MWCNTs dan epoksi / GNPs pada nisbah 1.00 wt.% daripada beban pengisi. Pemerhatian morfologi melalui Mikroskop Imbasan Elektron (SEM) pada permukaan sampel yang patah telah dikaitkan lagi dengan ciri-ciri yang dilihat adalah akibat daripada nano komposit yang dihasilkan. Kekuatan tegangan dan kekuatan lenturan hibrid MWCNTs/ GNPs yang dipenuhi nano komposit epoksi telah meningkat kira-kira 7.65% dan 7.24% berbanding daripada epoksi tulen. Selain itu, hibrid MWCNTs/ GNPs nano komposit mengalami peningkatan kestabilan haba seperti yang ditunjukkan oleh nilai Tg dimana berlakunya peningkatan sehingga 60 ° C (daripada analisis DSC), suhu permulaan degradasi yang lebih tinggi dan baki kandungan sisa sebanyak 15% (daripada analisis TGA) dimana merupakan paling tinggi berbanding daripada epoxy tulen, epoksi / 1.00 wt.% MWCNTs dan epoksi / 1.00 wt.% GNPs nano komposit. Pemerhatian oleh SEM telah mendedahkan bahawa sistem hibrid MWCNTs / GNPs bertetulang komposit epoksi memiliki interaksi matriks pengisi baik kerana permukaan matriks yang dihasilkan adalah kasar dan ikatan serat diantara matriks-matriks yang boleh membawa kepada fenomena matriks retak dimana dapat meningkatkan banyak sifat-sifat ujian prestasi sistem epoksi seperti yang dilaporkan oleh kebanyakkan penyelidikan. Secara keseluruhannya, kajian ini telah mendapati bahawa dengan menggabungkan MWCNTs dan GNPs nanofiller dengan nisbah 1.00wt.% / 1.00wt.% berkemungkinan boleh memberikan prestasi yang hebat dan juga boleh dipercayai untuk digunakan pada aplikasi struktur maju.

ABSTRACT

Carbon nanomaterials such as carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) exhibit superior performance in term of their mechanical, physical, and thermal properties. Outstanding intrinsic and extrinsic properties of the CNTs and GNPs make them as an ideal fillers for polymer nanocomposites application that used in advanced engineering applications. Hence, in this research, a novel class of epoxy nanocomposites has been developed containing a hybrid reinforcement systems of MWCNTs-GNPs. The epoxy filled MWCNTs, GNPs and MWCNTs/GNPs nanocomposites system were prepared by using a simplified solution casting method with proper curing in the vacuum heated oven. The synergistic effects of MWCNTs/GNPs nanoreinforcements were evaluated by comparing their physical, mechanical and thermal performances with pure epoxy and the single filler reinforced nanocomposites of Epoxy/MWCNTs and Epoxy/GNPs at 1.00 wt. % of nanofiller loadings. The morphological observation through Scanning Electron Microscope (SEM) on the fracture surfaces of the samples were correlated further with the resulted properties of produced nanocomposites. The tensile strength and flexural strength of hybrid MWCNTs/GNPs filled epoxy nanocomposites had increased about 7.65 % and 7.24% as compared than neat epoxy. Besides, the hybrid MWCNTs/GNPs filled epoxy nanocomposites experienced enhanced thermal stability as indicated by enhanced *Tg* value of up to 60°C (from DSC analysis), higher degradation onset temperature and higher residue content of 15% (from TGA analysis) which are the highest compared than pure epoxy, Epoxy/1.00 wt.% MWCNTs and Epoxy/1.00 wt.% GNPs nanocomposites. Fractured surface morphologies observation by SEM had revealed that the hybrid MWCNTs/GNPs reinforced epoxy composite system possessed good matrix-filler interaction due to rougher matrix surfaces, matrix yielding, and matrix-fiber de-bonding which lead into matrix cracking phenomena that improves many of the properties testing in this reported research. In overall, this research had found that by combining the MWCNTs and GNPs nanofiller at 1.00wt. %/1.00wt. % of loading ratio are possible to provide such a promising and reliable performance that applicable for advanced structural applications.

DEDICATION

Dedicated to;

My beloved parents, Abd Rashid Bin Yusuff and Zainoon Binti Abdullah and my appreciated siblings,
My great supervisor, DR Jeffeerie Bin Abd Razak
My special friend, Mohd Haizal Bin Ahmad Azani
My precious friends wherever where they are,
Thank you for your supports, guidance and helps whether directly and indirectly giving me moral support, cooperation, encouragement and also understanding.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscope
ASTM	-	American society for testing and materials
CNT	-	Carbon nanotubes
CVD	-	Chemical vapour deposition
DETA	-	Diethylene triamine
DMA	-	Dynami c mechanical analysis
DSC	-	Differential scanning calorimetric
DWCNTs	-	Double walled carbon nanotubes
MWCNTs	-	Multi walled carbon nanotubes
RTM	-	Resin transfer moulding
SEM	-	Scanning electron microscope
SOP	-	Standard Operation Procedure
SWCNTs	-	Single walled carbon nanotubes
TGA	-	Thermogravimetric analysis
VARTM	-	Vacuum-assisted resin transfer moulding
IFSS	-	Interfacial shear strength
GNPs	-	Graphene nanoplatelets

LIST OF SYMBOLS

cm	-	Centimetre
m	-	Metre
%	-	Percent
g/cm^3	-	Grams per centimetre cube
wt. %	-	Weight percent
mm	-	Millimetre
MPa	-	Mega Pascal
GPa	-	Giga Pascal
°C	-	Degree Celsius
TPa	-	Tera Pascal
W/mK	-	Watt per metre per Kelvin
K	-	Kelvin
nm	-	Nanometer
kg.cm3	-	Kilogram centimetre cube
phr	-	Part per hundred resin
τ_{ISS}	-	Interfacial shear strength
kg	-	Kilograms
mm/min.	-	Millimetre per minute
rpm	-	Revolution per minute
kN	-	Kilo newton
W	-	Sample width
y	-	Geometry correction factor
B	-	Sample thickness
K_{IC}	-	Fracture toughness
m	-	Mass
v	-	Volume
°C/min	-	Degree celsius per minute
N_2	-	Nitrogen gas
Hz	-	Hertz

CHAPTER 1
INTRODUCTION

1.1 Background of study

Epoxy resin can be described as a broad class of thermosetting polymers in which the primary cross linking occurs through the reaction of an epoxide group. In general, according to Boyle, (2010) an epoxy resin has identified as a molecule containing a three-membered ring, consisting of one oxygen atom and two carbon atoms. Besides, epoxy resin is classified as a high class of thermosetting polymers that commonly used in civil engineering applications and in the cultural heritage conservation, due to their advanced chemical and mechanical properties, as repairing materials, adhesives, coatings, and matrices for composites (Alamri *et al.*, 2012). However, epoxy resin are limited in their usage because of the brittleness behaviour with poor strength and toughness characteristic (Zaman *et al.*, 2011).

In order to enhance the performance of epoxy resin, various types of fillers inclusions were introduced as the reinforcement agent into the epoxy based composites system. According to Lorenzo *et al.*, (2009) the reinforcing filler were verified to overcome these problems since the properties of epoxy resin in term of their mechanical properties, electrical, optical and thermal properties was changed, later after the incorporation strategy.

There are many functional filler were incorporated to the epoxy resin for the specific reason. Usually carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) are the most popularly explored nanomaterials, since both of these carbon nanomaterials derivative were offering abundant promising and outstanding benefits towards improving the epoxy resin matrix end performances. For example, by adding carbon nanofiller such as CNTs and GNPs, into the epoxy resin will give good advantages in the resulted composites that exhibiting improved thermal, electrical and mechanical properties relative to those of the neat polymer matrix (Chang *et al.*, 2015).

CNTs are known as seamless cylindrical for their structure that formed by wrapping graphene sheets with carbon atoms (Zakaria *et al.*, 2014). Mazoc *et al.* (2012) state that CNTs are tubular structure that composed of curvy graphene sheets with diameter up to several tens of nanometers with typical length up to several micrometers. According to Li *et al.* (2013), the mechanical and electrical properties of the polymer composites can be improved by adding of CNTs owing to their high elastic modulus as well as excellent thermal and electrical conductivity. Next, GNPs is an atomic layer thick and two dimensional graphitic system that has been identified as considerable research interest, due to its excellent electronic and mechanic properties as prescribed by its unique structure. Lately, GNPs was becoming more attractive since it can produce an impressive enhancement in the resulted composites properties even at a very low filler content addition. Besides, GNPs sheet is considered to be a kind of good thermal conductive filler or additive for thermal engineering application, since its layered structure are able to form the effective pathway for heat transfer (Song *et al.*, 2013). GNPs also becoming a very promising filler for polymers composites application since it has large specific surface area, high aspect ratio, and extraordinary electrical and thermal conductivities characteristics (Zhang *et al.*, 2012).

However, the incorporation of nano-filler into epoxy resin matrices remains a very challenging task up to now. The major obstacle in producing good performance nanocomposites are the difficulty in achieving their good nano-filler dispersion in the polymer matrix. The nano-filler tend to agglomerate and entangle due to van der Waals attractions. Another obstacle is the processing difficulties that induced by the increase of epoxy resin viscosity due to the nano-fillers incorporations.

In this research, the nano-filler of MWCNTs and GNPs were hybridized as combined nano filler system for the epoxy matrix resin. The potential of filler hybridization were evaluated based on the effects of loading ratio between the MWCNTs and GNPs toward the structural performance of epoxy nanocomposites. It was expected that, by determining the correct ratio of MWCNTs and GNPs hybrid ratio, will be producing a great synergistic effects for the resulted structural and thermal properties of epoxy based nanocomposites.

1.2 Problem Statement

Epoxy resin is a cross-linked polymer that are widely used as a matrix for advanced engineering composites. This is due to their good stiffness, specific strength, dimensional stability and chemical resistance behaviour. Hence, epoxy have various wide application such as adhesives, composites laminates, coatings and etc (Alamri, 2012). However, epoxy resin was being unable to meet some of the customer demands due to their main drawback which is generally brittle that restrict their structural applications for many advanced engineering purposes.

Nanocomposites technology gives interesting and challenging alternative for modification of polymer matrix properties. There are a lot of advantages of nanocomposites over conventional composites which includes their mechanical, electrical, thermal, barrier and chemical properties such as increased tensile strength, improved heat deflection temperature, flame retardant, etc (Chang *et al.*, 2015). Another advantage of nanocomposites is that the strength, shrinkage, warpage, viscosity and optical properties of the polymer matrix are not significantly affected. The enhanced properties are attributed to the structure and morphology of the nanocomposite, as they (clays/polymer) contain organically treated clays such as hectorite, montmorillonite, and synthetic mica as well as nanotubes (carbon nanotubes, halloysite nanotubes). These nanomaterials have a large aspect ratio (1000:1) and each one is approximately 1 nm thick and hundreds or thousands of these layers are stacked together with weak van der Waals forces to form a clay particle, resulting in subsequent exfoliation in which the individual layers are peeled apart and then dispersed throughout the polymer matrix. The excellent degree of exfoliation, which resulting in smaller particle sizes and provides greater surface area to interact with the host polymer, results in improved performance. The properties of nanocomposites usually depends on the shape and size of particles. Besides that, ratio of variable, degree of dispersion, orientation of nanoscale second phase, efficient load transfer from particles to matrix and physical or chemical interactions of the particles with the host matrix also effects the properties of nanocomposites. When the size of particles changed from macro size to nano size, the surface area per unit volume drastically increases and their physical properties also change. The large surface-to-volume ratio of the nanoscale inclusions plays a vital role in improving the properties of nanocomposites. It is thought that many of the characteristics of nanocomposites are determined by the interfacial interactions. High aspect ratio particles provide extremely large interfacial area between the particles and the host material and are expected to lead to a strong reinforcement at low filler content (Yue *et al.*, 2014).

Hence, nano-carbon filler were introduced to reinforce the performance of epoxy resin. Ramkumar *et al.*, (2010) studied that the stiffness and flexural fatigue life was improved as the polymer matrix composites were incorporated with the nanoclay. In addition, some researcher used hybrid fillers in order to have a perfect potential of both fillers. Usually, nanoscale carbon-based fillers which included carbon nanotubes, graphene, carbon nanofiber, and carbon black are commonly used to enhance the performance of nanocomposites. Previously the carbon based nanomaterials was always being used in the single form. Different types of carbon nanomaterials derivative, gives different effects for the resulted properties of nanocomposites. Considering the benefits of as-mentioned carbon nanomaterials, therefore the exploration and investigation between their potential on hybridization of two or more types of carbon nanofiller is further seek, due to the promising synergistic effects that could be gained from this efforts. This initiative has been applied to increase the structural and mechanical properties, thermal stability, and electrical conductivity of polymer nanocomposites. Of all the carbon based nanofiller, GNPs and CNTs perhaps the newest combination and has grabbed wide attention since the performance of the epoxy was tremendously increased by adding of these two carbon based nanofiller into the thermoset epoxy system.

The uses of graphene sheet as thermal filler to increase the thermal conductivity of nanocomposites systems for the thermal applications has been reported. Besides, by applying CNTs with different nanoparticles combination as hybrid fillers were proved to improve the fatigue behaviour, mechanical and electrical properties of reinforced composites. Boger *et al.* (2010) used silica and MWCNTs hybrid nanoparticles to increase the high cycle fatigue life of epoxy laminates and finally found that the life was increased by several orders of magnitude in the number of load cycles.

However, the incorporation of CNTs and GNPs into the thermosetting nanocomposites remains challenging, since they are difficult in achieving their good dispersion in the matrix, because they tend to agglomerate and entangle due to cumulative van de Waals forces. In addition, a strong interfacial interaction is required to obtain efficient load transfer from matrix to hybrid nanofiller. Thus, the poor dispersion and weak interfacial bonding can limit the reinforcing effectiveness by hybrid nanofiller as their tendency to deteriorate the composite properties becoming more intense.

Until now, limited research are available to study the effect of MWCNTs/GNPs as hybrid filler in the epoxy nanocomposites system for the structural application. Hence, this research is conducted to understand the synergistic effect of hybrid filler MWCNTs/GNPs into the epoxy thermoset nanocomposites system.

1.3 Objectives

The main objective of this research is to study the structural behaviour and the morphological properties of the MWCNTs/GNPs filled epoxy nanocomposites. In order to fulfil the stated main objective, the following minor objectives were focused as below:

I. To prepare hybrid epoxy nanocomposites filled MWCNTs/GNPs by using a specified solution casting method

II. To determine the thermal and structural properties of epoxy nanocomposites filled MWCNTs/GNPs by using various type of mechanical and physical as well as thermal analysis

III. To evaluate the fracture surface morphology of epoxy nanocomposites filled MWCNTs/GNPs, epoxy/MWCNTs, epoxy/GNPs by using a scanning electron microscope (SEM) observation

1.4 Scope of study

This research is focusing on the preparation and characterization of nano hybrid MWCNTs/GNPs filled epoxy nanocomposites for the structural application. MWCNTs/GNPs filled epoxy nanocomposites were prepared by using the solution casting method. Different composition ratio of MWCNTs/GNPs were mixed with epoxy nanocomposites to determine an ideal ratio of filler combination that was suitable for the structural application. The product of epoxy nanocomposites were characterized in terms of their thermal and mechanical properties. Various type of mechanical testing, physical testing and thermal analysis were manipulated to differentiate the characteristics of epoxy nanocomposites. The mechanical and physical analysis were included the tensile, flexural, and impact testing as well as the fracture toughness determination followed by water absorption testing and density and void content. While for the thermal analysis was included the thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). As for microstructure and fractograph analysis, the scanning electron microscope (SEM) will be used to evaluate the fracture surface morphology. Towards the end, the relationship between the structural behaviour of epoxy/MWCNTs-GNPs hybrid nanocomposites with the effects of MWCNTs/GNPs hybrid ratio, will be evaluated based through the morphological analysis as observed through SEM and their resulted mechanical, physical and thermal properties.

1.5 Thesis Organization

There are five (5) chapters in this report. Chapter 1 is the introduction of the research. This chapter consists of background, problem statement, objectives of the report, scope of the thesis and overall chapter review in brief. Chapter 2 is the literature review. This chapter presents the published literatures that are relevant to the particular topic of this research, demonstrating the information of any previous work and awareness of related theories and discussions. Critical comparison and comment that lead into the gap for this research is reported in this chapter. Chapter 3 is the methodology of the research. This chapter discusses the review of the methodology carried out in order to produce the desired product or outcome of the project. Chapter 4 is about the data analysis and discussion on it. All the data gained and collected from various testing will be discussed in this part. These will include the mechanical properties, thermal properties and physical properties, as well as morphological observation. Finally the thesis was ended-up by the conclusion part, which included in the chapter 5. In this chapter, all the discussion will be concluded and critically summarized based on the as stated and aimed objectives for this research.

CHAPTER 2
LITERATURE REVIEW

2.0 Introduction

This chapter is an overview for preparation and characterization of the multi-walled carbon nanotubes, graphene, MWCNTs/ GNPs filled epoxy nanocomposites. Therefore the extensive review on the material properties and their constituent were discussed in this chapter. Besides, the basic overview of MWCNTs and other related nanocomposite material systems were also explained. Furthermore, various type of mechanical, physical and thermal analysis were described to differentiate the characteristic of the epoxy nanocomposites. Towards the end, the relationship between the structural behaviour of epoxy/MWCNTs-GNPs nanocomposites with the effect of MWCNTs/GNPs hybrid ratio and filler loading are also discussed by the evaluation of morphological analysis as observed through scanning electron microscope (SEM).

2.1 Nanocomposites

Nanocomposites are broadly classified as a class of materials in which one or more phases with nanoscale dimensions are embedded in the matrix of metal, ceramic or polymer. Introduction of nanoscale reinforcing fillers into the polymeric composite formulation have attracted considerable attention, recently. The purpose of adding the nanoscale second phase to the polymer matrix is to create the synergistic effects between the various constituents of nanomaterials. Hence, improves the properties of nanocomposites in terms of their mechanical, thermal and electrical properties (Shokrieh *et al.*, 2014). According to Noohafanita *et al.* (2014), the changes in reinforcement size of nanocomposites from micro-meter to nanometer scale represents new boundaries in material science. In fact, different type of nanomaterials derivatives also gives different effect to the resulted properties of nanocomposites such as electrical, optical, and thermal properties. Besides, the properties of composites product were also depended on the interaction between the matrix and filler. Therefore preparing a good