ABSTRAK

Pengubahsuaian permukaan kovalen *Multi-Walled Carbon Nanotubes (MWCNTs)* terhadap kesan ke atas sifat haba dan mekanikal epoksi yang diisi MWCNTs nanokomposit dilaporkan dalam kajian ini. Epoksi DGEBA dan pengisi MWCNTs telah digunakan sebagai matriks dan tetulang sebagai peningkatan kepada polimer epoksi. Prestasi epoxy yang diisi MWCNTs tidak dirawat dan dirawat dibandingkan dan dinilai dalam kerja-kerja ini. MWCNTs yang mempunyai ciri-ciri permukaan lengai yang cenderung untuk menggumpal perlu diubah suai untuk menurunkan kelikatan epoksi disebabkan penyebaran yang baik oleh pengisi MWCNTs di dalam matriks. Kimia *Amino Propyl Triethoxy Silane (APTS)* telah digunakan sebagai medium untuk rawatan kovalen kerana ia adalah satu pendekatan rawatan yang mudah. Penilaian rawatan permukaan seperti Analisis Fourier Infra Merah (FTIR) dan spektroskopi Raman telah dilakukan untuk mengesahkan lagi kejayaan rawatan kovalen yang telah dilakukan keatas permukaan MWCNTs. Sampel nanokomposit yang mempunyai berat MWCNTs yang berlainan seperti 0.00 wt.%, 0.25 wt.%, 0.50 wt.%, 0.75 wt.%, 1.00 wt.% dan 3.00 wt.% telah diuji dengan menggunakan pelbagai ujian mekanikal dan haba iaitu ujian tegangan, ujian lenturan, ujian kesan, analisis TGA dan analisis DSC. Dari segi ujian mekanikal, hasil ujian tegangan dan ujian lenturan menunjukkan peningkatan untuk epoksi / MWCNTs dirawat dengan peningkatan sebanyak 38.69% dan 58.48% berbanding komposit MWCNTs yang tidak dirawat. Ujian fizikal yang termasuk adalah ujian kepadatan dan ujian penyerapan air. Keputusan eksperimen menunjukkan bahawa sifat haba dan mekanikal meningkat dengan ketara disebabkan rawatan kovalen yang dilakukan ke atas permukaan MWCNTs. Pemerhatian yang dijalankan melalui Pengimbas Mikroskopi Elektron (SEM) terhadap permukaan patah menunjukkan bahawa adanya peningkatan kepada ciri-ciri nanokomposit dan penyebaran oleh pengisi serta interaksi antara matriks dan pengisi adalah saling berkaitan disebabakan oleh kejayaan rawatan kovalen keatas MWCNTs.

ABSTRACT

The covalent surface modification of Multi-Walled Carbon Nanotubes (MWCNTs) towards the effect on thermal and mechanical properties of epoxy filled MWCNTs nanocomposites were reported in this research. DGEBA epoxy and MWCNTs filler were respectively used as a matrix and reinforcement in developing enhancement into the epoxy polymer. The performances of epoxy filled untreated and treated MWCNTs were compared and evaluated in this works. The MWCNTs which have an inert surface characteristic are tend to agglomerate and need to be modified in lowering their viscosity of epoxy due to good dispersion of MWCNTs fillers within the matrices. Amino Propyl Triethoxy Silane (APTS) chemical was used as a medium for covalent functionalization utilizing a simplified treatment approaches. Surface treatment evaluation was done by performing a Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy to further confirm the success of the covalent functionalization performed to the MWCNTs surfaces. The nanocomposites samples with 0.00 wt.%, 0.25 wt.%, 0.50 wt.%, 0.75 wt%, 1.00 wt.% and 3.00 wt.% of MWCNTs loadings were tested by using various mechanical and thermal testing which are tensile test, flexural test, impact test, TGA and DSC analysis. In term of mechanical testing, tensile and flexural testing result shows the improvement for epoxy/treated MWCNTs with 38.69% and 58.48% increament compared to the composite filled untreated/MWCNTs. Physical testing included are the density test and water absorption test. The experimental results shows that the thermal and mechanical properties were significantly improved due to the covalent treatment onto the MWCNTs surfaces. Scanning electron microscopy (SEM) observations on the fractured surfaces shows that the properties improvement in the nanocomposites and filler dispersion as well as the matrix-filler interaction is directly interrelated with the success of covalent functionalization of MWCNTs.

DEDICATION

I dedicate this report to my supervisor, Dr. Jeefferie bin Abd Razak, thank you for being a guider during this final year project. Thank you for your cooperation and help in the success of this report. Thanks also to my beloved parents and siblings for being a pillar of strength for me when I was weak and also to my friends, that always be a good listener when I have a problem or lack of confident.

Finally, I dedicate this report to my examiners, Prof Dr. Qumrul Ahsan and Dr. Mohd Shahadan for being my correctors, and also like to dedicate this report to all my respectable lecturers.

ACKNOWLEDGEMENT

IN THE NAME OF ALLAH

THAT MOST GRACIOUS AND MOST MERCIFUL

On this occasion, I want to take this opportunity to give a big thank to my supervisor Dr. Jeefferie bin Abd Razak for his helps and provides good guidance to me and shares his knowledge and experience during my research. He also helps me resolving many of the problems encountered throughout this work.

I want to give a big appreciation and special thanks to the Assistant Engineer, Mr. Azhar Shah, Mr. Mohd Radhuan, Mr. Muhammad Helmi, Mr. Mohd Farihan and Mr. Hairulhisham for their continuous help, cooperation and guidance in making the completion of my research success.

Not forget to my family and friends. Thank you for their support during my research, and always be a good listener when I have a problem or lack of confident. Special thanks to both of my parents for their prayer to the successfulness of my life and education. To all my friends, many thanks for the true friendships bloomed and hope all of us can be more succeed in the future. Last but not least, thank you to anyone that involved directly or indirectly in help me to complete the final report.

Thank you.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

APTS - Amino-Propyl Triethoxy Silane
ASTM - American Society for Testing and Materials
CNT - Carbon Nanotubes
CVD - Chemical Vapor Deposition
DGEBA - Diglycidyl Ether of Bisphenol A
DGEBF - Diglycidyl Ether of Bisphenol F
DSC - Differential Scanning Calorimetry
DWCNT - Double Walled Carbon Nanotube
FESEM - Field-Emission Scanning Electron Microscopy
FTIR - Fourier Transform Infrared Spectroscopy
HiPco - High-Pressure Carbon Monoxide
HCl - Hydrochloric acid
HMPA - Hexydro-4-methylphthalic anhydride
Hz - Hertz
MEKP - Methyl Ethyl Ketone Peroxide
MWCNT - Multi Walled Carbon Nanotubes
PMC - Polymer Matrix Composite
SEM - Scanning Electron Microscope
SiC - Silicon Carbide
SOP - Standard Operating Procedure
SWCNT - Single Walled Carbon Nanotubes
TEM - Transmission Electron Microscopy
TGMDA - Tetraglycidyl Methylene Diamiline
TGPAP - Triglycidyl P-Amino-Phenol
TiO_2 - Titanium Oxide
wt% - Weight percentage

ZrO_2	-	Zirconium dioxide
°C	-	Degree Celsius
kN	-	Kilo Newton
mm	-	Milimeter
nm	-	Nanometer
rpm	-	Revolutions per minute
µm	-	Micrometer
π	-	Pi

CHAPTER 1

INTRODUCTION

1.1 Background of study

Polymer matrix composite (PMC) has been described as the combination of polymer resin and reinforcement filler. There are many materials related to PMC including epoxy as a base matrix. Epoxy resin is a generic name for compounds that have two or more oxirane rings which are epoxy groups in one molecule, and are cured three-dimensionally by a suitable curing agent. Long time ago, condensation of epoxides and amines was first discovered by Schlack in 1938. As stated by Kaynak (2002), the usage of epoxy was expanded in 1946 and commonly used in industries afterwards. Nowadays, epoxy resins are commonly used in wide range of applications like in the fiberglass and composite industries, similar as polyester resin. However, epoxy resin has their limitation and drawbacks in terms of their brittleness that are not suitable for some applications, especially for high performance engineering purposes.

The purpose of this research is to enhance the thermal and mechanical properties of epoxy nanocomposites, through covalent surface modification strategy of multi-walled carbon nanotubes (MWCNTs) filler. In this research, diglycidyl ether of bisphenol (DGEBA) epoxy was used as a matrix. The DGEBA epoxy was chosen than DGEBF epoxy because of widely used applications especially in the polymer field. DGEBA epoxy has a molecular mass of 340.42 g.mol^{-1} and density of 1.16 g/mL at 25ºC. The price of DGEBA epoxy is \$65 for 25g, while DGEBF epoxy has a molecular mass of

312.36 and price of $125 for 1g. Both DGEBA and DGEBF must be placed in the refrigerator or under inert environment to maintain the condition and properties of the epoxy resin. According to the characteristics comparison between the DGEBA and DGEBF, it is show that DGEBA epoxy more cheap and easy to handle than DGEBF.

Due to advance in industrial research nowadays, many improvements have been made to the epoxy resin characteristic. As mentioned above, this research is to enhance the mechanical, thermal and structural properties of epoxy nanocomposites for high performance application. Hence, one way to improve the mechanical strength behavior of epoxy, is by performing the surface modification of filler toward their reinforcement strategy. For example, carbon nanotubes that are added to the epoxy resin matrix. Carbon nanotubes were divided into three major types which are single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). The MWCNTs was used in this research as reinforcement materials because of several factors whereby the bulk synthesis is easy and chance of defect appear is very less. Then, the MWCNTs were treated by using covalent treatment method before being mixed with the epoxy resin in order to observe their viscosity, dispersion and interaction between the epoxy and carbon nanotubes. Later, mechanical and thermal properties of the epoxy nanocomposites were observed by conducting appropriate testing and surface morphological observation via Scanning Electron Microscopy (SEM). This study is crucially important to explore the potential of MWCNTs surface modification towards enhancing the thermal-mechanical behavior of epoxy based nanocomposites.

1.2 Problem statement

Up till now, the study on mechanism of interaction between the epoxy matrix and MWCNTs in the complex nanocomposites systems is still scarce. This research provides a kick start to explore related interaction phenomenon between the matrix-filler, as to understand the thermo-mechanical properties of epoxy nanocomposites and the fundamental knowledge about the nanofiller reinforcement in the thermoset nanocomposites system. In order to enhance the mechanical and thermal properties of epoxy resin, there are several possible modification need to be done into the nanofiller. Incorporating MWCNTs nanofiller into the epoxy matrix resin is not as easy as just mixing it. There are several difficulty may arise during the effort of combining epoxy resin with MWCNTs nanofiller. One of them is the viscosity issue for epoxy resin. The viscosity of the epoxy resin may increase due to the agglomeration of MWCNTs. The untreated MWCNTs were easily to form agglomeration because of their inert characteristic.

Besides, MWCNTs are easy to entangle due to dimensional effect and high aspect ratio. The higher content addition of MWCNTs also can cause higher viscosity of the carbon nanotubes/epoxy of uncured resin mixture that may further worsen the dispersion of filler in the matrix. As a consequence the epoxy resin was not able to fully wetting into the surface of MWCNTs filler. The phenomenon of bad dispersion also can cause defects in epoxy composites after cured. Besides, worse dispersion condition of carbon nanotubes in the polymer matrix is due to the *van der Waals* interaction among carbon nanotubes which further caused agglomeration and bundles formation between the tubes. After that, it is about interaction between matrix and reinforcement filler. The epoxy resin as matrix phase do not have good interaction with the MWCNTs surface. This is because the untreated surface of MWCNTs has low ability to attract into the epoxy solution due to lack of functional group to promote the matrix-filler interaction. Hence, functionalization into MWCNTs filler was required to improve the dispersion and interfacial interaction between the MWCNTs within the epoxy resin.

The execution of polymer nanocomposites was determined by three factors which are volume fraction, matrix type and dispersion between filler and their matrix interface. Therefore, there is an urgent need to improve the polymer-filler interface bonding in order to enhance the interaction between MWCNTs and epoxy resin. To improve interface interaction between MWCNTs and epoxy resin, a procedure known as surface modification by chemical method which is called as covalent method was often used. Amino-functionalized carbon nanotubes exhibit higher surface energy and have much better wettability with epoxy resin. Therefore, the covalent treatments have been conducted in this research in order to solve the above-mentioned problems.

1.3 Objectives

The main objectives of this research are:

1. To modify MWCNTs surfaces by covalent treatment approach and to characterize the untreated and treated MWCNTs via FTIR and Raman spectroscopy method
2. To investigate the effects of MWCNTs surface modification towards the improvement of thermal and mechanical properties for epoxy filled MWCNTs nanocomposites
3. To evaluate the matrix-filler interaction mechanism of epoxy filled MWCNTs nanocomposites based on their fractured-surface morphological observation

1.4 Scope

In this research, epoxy resin were used as a matrix and carbon nanotubes as a reinforcement. The DGEBA epoxy with hardener and MWCNTs with 0.00 wt%, 0.25 wt%, 0.50 wt%, 0.75 wt%, 1.00 wt% and 3.00 wt% were used as matrix and reinforcement in this research. The epoxy-filled MWCNTs were prepared via mechanical-stirring method involving casting and vacuum molding. This method was chosen than the other method because of its simplicity, lower cost, safe operation and faster manufacturing cycle. Then, the MWCNTs were treated by covalent treatment in order to observe their interaction between epoxy and the surface of carbon nanotubes.

Apart from that, the mechanical properties of epoxy nanocomposites were tested by using the tensile test, flexural test and impact test. The tensile test was performed by applying a force using uniaxial load to measure the applied load and the elongation of the samples. Flexural test was applied in order to observe the stiffness and how good the samples resist to the bending while impact test was executed to determine the absorbed energy by a material during the occurrence of fracture. For tensile test, the fractured specimen was cut and mounted before performing the surface morphological observation by SEM. The mounted sample was gold coated to eliminate or reduce the charging effects during the observation.

The FTIR and Raman Spectroscopy were used to analyze the chemical functionalization between the MWCNTs and APTS as well as to further confirmed the success of covalent surface modification that performed into MWCNTs. The thermal properties evaluation were performed by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to analyze the thermal characteristic of produced nanocomposites. Towards the end, the efficiency of surface modification on MWCNTs that affecting the end results of nanocomposites behavior will be thoroughly evaluated by comparing each performance tested that involving the mechanical and thermal tests.

1.5 Rationale of Research

The rationales of research are detailed as follows:

1. To gain new knowledge about MWCNTs/epoxy nanocomposites by carrying out some related testing and characterization.
2. Develop more information and also understand about the role of MWCNTs when embedding to the epoxy resin and compare the strength between untreated and covalent functionalized MWCNTs as to improve the thermal and mechanical properties epoxy nanocomposites.
3. Higher strength of composite product would be developed from this research by embedding treated MWCNTs into epoxy resin as to enhance their thermal and mechanical properties.

1.6 Thesis organization

This research is organized into several sub-topic and chapters. The introduction part had started with the Chapter One that provides the concise background of the research, problem statement, objectives, thesis scope and also thesis organization. Chapter Two briefly discussed about the literature review of the research including related theories and investigations of the epoxy, carbon nanotubes, mechanical properties and thermal properties by the previous researcher. All these information are important to understand the thermal and mechanical properties of epoxy nanocomposites filled with modified carbon nanotubes. Chapter Three presents on how the research was conducted, method chosen and the characterization used. The flowchart of overall research methodology from beginning until the end, was also included in this chapter. Results and discussion obtained from the research are includes in Chapter Four. All of the results or figures from the testing and characterization were placed and comprehensively discussed in this chapter. Lastly, this research was concluded at the Chapter Five. Entire discussion about the introduction until the results and discussion parts will be concluded and summarized in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Epoxy as matrix

In polymer, epoxy thermosetting resin can be used to coat and cured the end products. However, in polymer matrix composites, epoxies are commonly used as matrices to bind the reinforcements as well as to transfer load during their actual service (Kim et al., 1994). There are several types of epoxy in polymer such as bisphenol-A type which is commonly used epoxy, bisphenol-F type and novolac (John, 1999). There are many other types of epoxy but, most are not suitable to a wide variety of applications. Besides, to convert epoxy resin to epoxy plastic, a reaction with suitable substance is required which is called hardener. The examples of epoxy hardener are amines, amides, acid anhydrides, imidazoles, boron trifluoride complexes, phenol, mercaptans and metal oxides (Curt, 2004). In this research, the diglycidyl ether of bisphenol-A was used as matrices and methyl ethyl ketone peroxide (MEKP) was used as hardener that disperse with MWCNTs in order to improve the thermo-mechanical properties of basic epoxy resin system. Epoxy resins are compound that contains of more than one epoxide group and the commercial epoxy resins contained aliphatic, cycloaliphatic or aromatic backbones. The most important intermediate for epoxy resins is the diglycidyl ether of bisphenol that derived from a highly reactive compound of epichlorohydrin. The base chemical structure of epoxy resin is the three-membered ring consists of one oxygen atom and two carbon atoms as depicted in the following Figure 2.1 (Curt, 2004; Maureen, 2012).

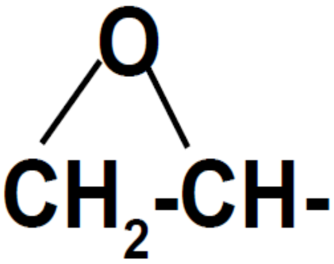

Figure 2.1: Base chemical structure of epoxy group (Curt, 2004)

Phenolic glycidyl ethers are formed by the condensation reaction between epichlorohydrin and a phenol group. The structure of pure DGEBA shown in Figure 2.2 is the first commercial epoxy resin that most widely used, today. DGEBA was used in this research because of their good properties in comparison with other thermosetting materials (Maureen, 2012).

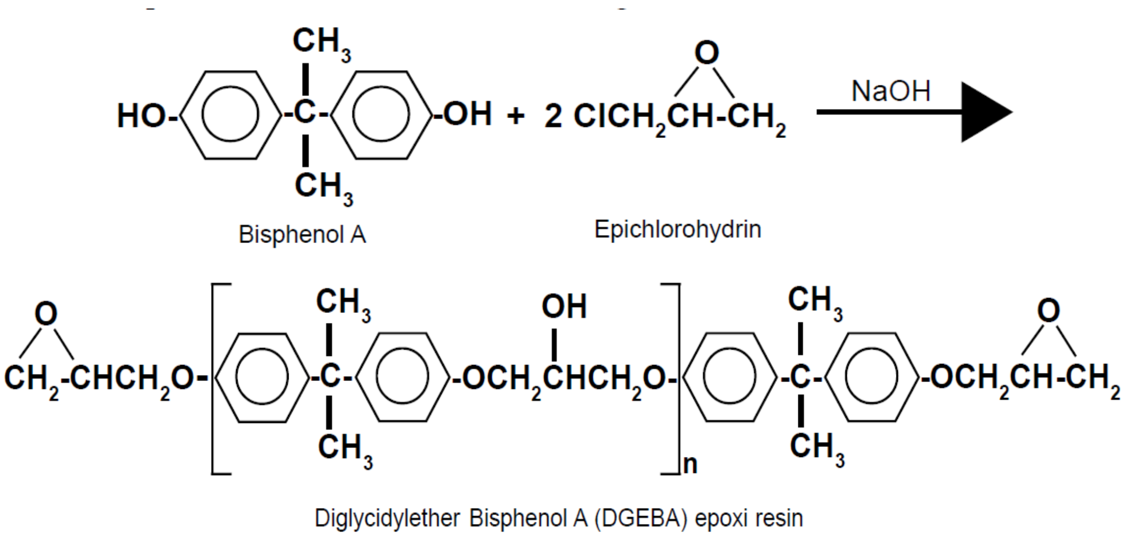

Figure 2.2: Chemical structure of Diglycidylether of Bisphenol A epoxy resin (Curt, 2004)

Another type of phenolic epoxy resin is diglycidyl ether of bisphenol-F. This material has a lower viscosity than DGEBA. Otherwise, phenol and cresol novolacs are another two types of aromatic glycidyl ethers as shown in Figure 2.3 (Maureen, 2012).

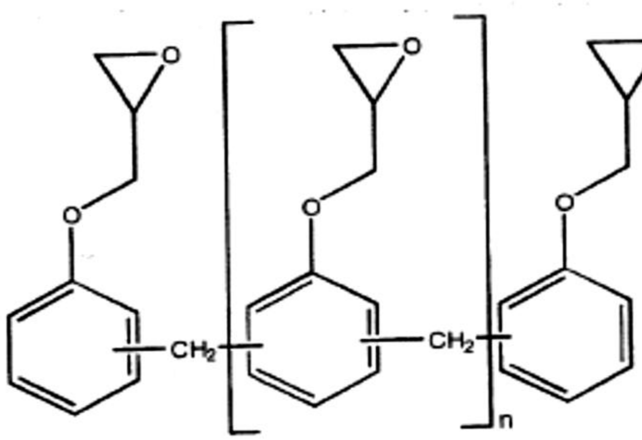

Figure 2.3: Chemical structure of Phenol novolac contains a methyl group on each benzene ring (Maureen, 2012)

Glycidyl amines are formed by reacting epichlorohydrin with an amine and the most important resin include is tetraglycidyl methylene diamiline (TGMDA). Another glycidyl amine which is triglycidyl p-amino-phenol (TGPAP), consist of three epoxy groups attached to a single benzene ring as depicted in the Figure 2.4 (Maureen, 2012).

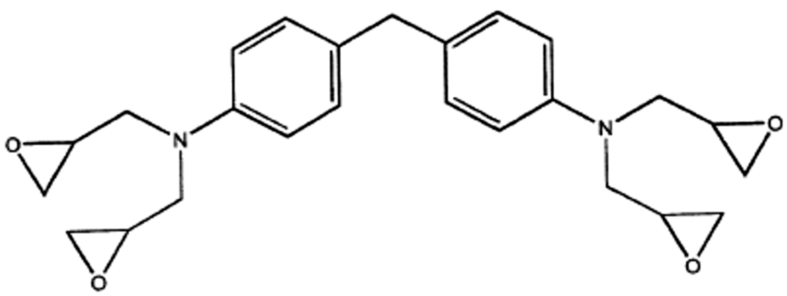

Figure 2.4: Chemical structure of Tetraglycidyl Methylene Dianiline (Maureen, 2012)