



**Faculty of Manufacturing Engineering**

**CHEMICALLY MODIFIED GRAPHENE  
NANOPLATELETS-THERMOSET ADHESIVE  
THROUGH ULTRASONICATION ASSISTED MIXING  
FOR NATURAL RUBBER ALUMINIUM BONDING**

**Mazatul Nadia binti Mohd Zafri**

**Master of Engineering in Manufacturing Engineering**

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**CHEMICALLY MODIFIED GRAPHENE NANOPATELETS  
-THERMOSET ADHESIVE THROUGH ULTRASONICATION  
ASSISTED MIXING FOR  
NATURAL RUBBER-ALUMINIUM BONDING**

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**A thesis submitted  
in fulfillment of the requirements for the degree of Master of Engineering  
in Manufacturing Engineering**

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**UNIVERSITI TEKNIKAL MALAYSIA MELAKA**

**2019**

## DECLARATION

I declare that this thesis entitle “Chemically Modified Graphene Nanoplatelets Thermoset Adhesive Through Ultrasonication Assisted Mixing for Natural Rubber-Aluminium Bonding is the result of my own research except as cited in the reference. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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26<sup>th</sup> August 2019

Date :.....

## APPROVAL

I hereby declare that I have read this thesis and in my opinion, this thesis is sufficient in terms of scope and quality for the award of Master of Engineering in Manufacturing Engineering.

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26<sup>th</sup> August 2019

Date :.....

## **DEDICATION**

*Dedicated to my beloved mother, Maslina Ismail, my supportive father, a man like no other, Mohd Zafri Mohd Nor, my loving fiancé, Khairul Firdaus Zaiful Hakim and all my friends.*

## ABSTRACT

Passive engine mount is an integrated system of rubber and metal which help to reduce noise, vibration and harshness to an automotive system. In recent years, there are increasing demands in the use of aluminium alloy (Al alloy) to replace steel in the engine mount components due to their lightweight properties. Owing to its high strength and sustainability, natural rubber (NR) is also widely used for the same application. It also own low market price. However, the technology development on rubber to aluminium bonding is still infancy. The existing adhesive used is very expensive due to the utilization of primer and insufficient to provide strength required for the component. Therefore, this study is a preliminary effort to explore the potential of graphene nanoplatelets (GNPs) filled epoxy as an adhesive to bond natural rubber-aluminium alloy without any utilization of primer. In this study, the effect of treated GNPs loading at 0%, 0.5%, 3%, and 7% wt on the bonding strength of the epoxy/GNPs adhesive to bond NR composites-Al alloy was investigated. Firstly, the GNPs were chemically treated via ultrasonication method prior the addition of epoxy to form the adhesive. Then, the epoxy/GNPs adhesive was applied on the pre-etched aluminium alloy before placing in a mould for vulcanization bonding. The NR composites-Al alloy was bonded with the prepared epoxy/GNPs adhesive under the temperature of 140°C, 100 kg/cm<sup>2</sup> for 10 minutes using hot press machine. Then, the samples were subjected to peel test

using UTM machine at the crosshead speed of 50mm/min in accordance to ASTM D429 at room temperature to determine the bonding strength. The findings were further supported by thermal, structural, compositional and morphological analyses using Different Scanning Calorimetry (DSC), X-ray diffractometry (XRD), fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) techniques. The epoxy/GNPs adhesive is proven to improve the bonding strength between NR composites-Al alloy for up to 200% compared to the control sample (epoxy without treated GNPs). The highest bonding strength was observed in epoxy/3-GNPs for the value of 44 N compared to 16 N for the control sample. This is due to the uniform distribution of GNPs and good interaction between epoxy/GNPs with the Al alloy surface. This finding is significant for the engine mount manufacturer to improve their current technology or existing recipe for the rubber-aluminium bonding in their product manufacturing.

## ABSTRAK

Pencagak enjin pasif adalah sistem bersepadu yang mengabungkan bahan getah dan logam yang membantu mengurangkan bunyi bising, getaran dan kekasaran bagi sistem automotif. Kebelakangan ini, terdapat permintaan yang semakin meningkat dalam penggunaan aloi aluminium (Al aloi) bagi menggantikan keluli sebagai komponen enjin kerana sifatnya yang ringan. Manakala, getah asli (NR) pula digunakan secara meluas disebabkan kekuatan bandingan yang tinggi dan kelestariannya, di samping harga pasaran yang rendah. Namun begitu, pembangunan teknologi lekatan getah kepada aluminium adalah masih di peringkat awal. Perekat sedia ada yang digunakan adalah sangat mahal kerana penggunaan primer dan tidak mencukupi untuk memberikan kekuatan yang diperlukan bagi komponen tersebut. Oleh itu, kajian ini adalah usaha awal untuk meneroka potensi epoksi terisi grafin nanokepingan (GNP) sebagai perekat untuk mengikat getah asli- aloi aluminium tanpa penggunaan primer. Dalam kajian ini, kesan pembebanan GNP pada 0%, 0.5%, 3%, dan 7% wt pada kekuatan ikatan perekat epoksi/GNP untuk ikatan komposit NR- aloi Al diselidiki. Pertama, GNP dirawat kimia melalui kaedah ultrasonik sebelum penambahan epoksi untuk penghasilan perekat. Perekat Komposit NR-aloi Al diikat dengan perekat epoksi / GNP di bawah suhu 140°C, tekanan 100 kg/cm<sup>2</sup> selama 10 minit menggunakan mesin penekan panas. Kemudian, sampel dikenakan uji kopekan menggunakan mesin UTM pada halaju kepala rentas



50mm / min mengikut ASTM D429 pada suhu bilik untuk menentukan kekuatan ikatan. Penemuan ini disokong lagi oleh analisis termal, struktur, komposisi dan morfologi menggunakan Kalorimeter Pengimbasan Kebezaan (DSC), Pembelauan sinar-X (XRD), transformasi empatier spektroskopi inframerah (FTIR) dan teknik mikroskopi pengimbasan elektron (SEM). Perekat epoxy / GNP terbukti dapat meningkatkan kekuatan ikatan antara komposit NR-Al aloi sehingga 200% berbanding dengan sampel kawalan (epoksi tanpa GNP yang dirawat). Kekuatan ikatan tertinggi diperhatikan dalam epoksi / 3-GNPs untuk nilai 44 N berbanding 16 N untuk sampel kawalan. Ini disebabkan oleh pengagihan seragam GNP dan interaksi yang baik antara epoksi / GNP dengan permukaan aloi Al. Penemuan ini penting bagi pengeluar gunung enjin untuk meningkatkan teknologi semasa atau resipi sedia ada bagi ikatan getah-aluminium dalam pembuatan produk mereka.

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## **LIST OF ABBREVIATIONS**

AL	Aluminium
ASTM	American Society for Testing and Materials
CNT	Carbon Nanotubes
DSC	Differential scanning calorimetric
FTIR	Fourier Transform Infrared
GNPs	Graphene Nanoplatelets
MWCNTs	Multi walled carbon nanotubes
NR	Natural Rubber
SEM	Scanning electron microscope
XRD	X-Ray Diffraction

# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

Engine mounts rubbers are commonly used to provide vibration attenuation in isolating the vibration source (Ooi et al., 2010). They play an important role in the efficient functioning of automobile systems. Generally, these engine mounts have great effects on the noise and vibration harshness (NVH) characteristics in automobiles (Svaricek et al., 2004). Deficiency of engine mounting vehicles could lead to excessive engine vibrations and eventual damage to the gear box components (Yu et al., 1999). In addition, without the engine mount rubber, the passengers and the driver of the vehicle might be uncomfortable due to the vibration from the engine and road excitations (Darsivan and Martono, 2006). Hence, a study of dynamic damping measurement of the engine mount rubber is important in order to provide the information of dynamic damping characteristic under real operation condition as it act as a damper to damp the vibration and noise created by the engine.

Rubbery materials are usually subjected to physical and chemical property changes due to aging, whether they are in service or in storage. In the rubber industry, it is usually necessary to evaluate the aging resistance of automobile components such as the engine mount, tires, and seals, but this might take several years for a complete process

to be observed in real service. Moreover, because of considerable variations in the conditions in terms of location and seasonal variations, it is very difficult to evaluate changes due to degradation in a natural rubber compound in absolute terms. Under real service conditions, engine mounts are exposed to a combination of factors including oxygen, heat, various liquids, and dynamic motion. In addition, the rubber engine mount dynamic performance changes with operation time. Although this variation may not shift the resonance frequencies of the isolator that significantly, their change in performance does lead to more vibration energy being transferred into the vehicle. As a result, this variation is harmful to the overall vehicle and to the ride comfort, and therefore is of interest to the designer (Ageing of a polymeric engine mount investigated using digital image correlation). Thermal ageing is one of the main ageing mechanisms for an engine mount (Ageing of a polymeric engine mount investigated using digital image correlation).

In this case, the prolong efficiency of engine mounting and service life is highly depending on thermal dissipation capacity of the entire mount's system; rubber, metal, rubber-metal bonding. In this project, a new graphene nanoplatelets modified adhesive to bond Natural rubber composites (NR) and Al-alloy via vulcanization bonding process will be investigated. The presence of graphene nanoplatelets (GNPs) is hypothesized to improve the efficiency and service life of a rubber engine mount. It creates the channel for heat to be dissipated out from the rubber without acting as the stress concentrator and prevent the accumulation of static charge. The bonding strength of NR composites-Al alloy using GNPs modified thermoset adhesive produced significant bonding strength for stress and energy transfer through and out of the system. This will significantly enhance vibration insulator properties as well as increase the ageing resistance.

Graphene is a single-atom-thick sheet of  $sp^2$  bonded carbon atoms comes with high specific area, mechanical, electrical, thermal, and chemical stability properties (Choi et al., 2010). With estimated Young's modulus of 1 Tpa and ultimate strength of 130 Gpa, graphene was labelled as —the strongest material ever. Graphene platelets are electrically conductive of 6000 S/cm and thermally conductive of  $5 \times 10^3$  W/mK at room temperature (Kim et al., 2010). Large specific surface area of the platelets is up to 2630  $m^2/g$  (Peigney et al., 2001 cited in Choi et al., 2010) due to the platelets consist of very fine graphene of 0.34 nm in thickness and  $\sim 1 \mu m$  in the lateral dimension (Sadasivuni et al., 2014). inevitably cost industries in maintenance, repair, and replacement (Gu et al., 2014). Thus, vibration damping has become a priority research area in a number of industries including car, aerospace, and sports equipment manufacturing; from point of view of both fundamental research and practical requirements in the field of suppressing vibration and noise.

In this project, a modified thermoset adhesive (Epoxy/GNPs matrix adhesive) will be used to bond the Natural Rubber composite with the Al alloy via the vulcanization method for the engine-mount rubber application. Epoxy-based adhesives find vital applications (Higgins, A., 2000) in automotive, aeronautics, electronics and packaging industries due to their excellent mechanical properties (Banea, M.D. & Silva, L.F.M.D., 2009). Epoxy-based thermosets can be identify by high strength, excellent adhesion to numerous metallic and nonmetallic substrates, possess small shrinkage during and after cure, and high resistance to chemicals and extreme temperatures (Hu, P. et al., 2013).

## 1.2 Problem Statement

Weight reduction is particularly important because average vehicle weight is expected to increase since the automobile industry will continue to market new models with increased luxury, convenience, performance, and safety as demanded by their customers. If this is to be achieved, there will have to be a radical increase in the use of lightweight materials such as aluminium alloys. An important fact is that the weight reduction has a ripple effect on fuel efficiency. For example, weight reduction enables the manufacturer to develop the same vehicle performance with a smaller engine, and such a smaller engine enables the use of smaller transmission and a smaller fuel tank. The use of lightweight materials can help reduce vehicle weight and improve fuel economy. The pressure for weight reduction has driven a gradual decrease in the amount of steel and cast iron used in vehicles and the corresponding increase in the amount of alternative materials, especially aluminium. [Miller et al., 2014; Hirsch, 2009].

Together with the evolution towards lighter vehicle, reduction of engine vibration and the dynamic forces transmitting from engine to the automotive body structure has always been an important part of automotive body structure has always been an important part of automotive research. Automobile engineers face the task of creating a mechanism to absorb these vibrations and provide a smooth ride. The usage of motor mounts is the best solution for dampening the effects of vibrations and oscillations. For automotive, there are various engine mounts available in the market; passive engine mount and active engine mount. Despite the advancement in the design and increased in system complexity, rubber engine mount maintains its popularity for its functionality, compactness, simplicity, maintenance free as well as cost effective



[Ramachandran et al., 2018]. Moving forward with technology on rubber engine mount as well as industrial demand in using the lightweight material for the automotive application, the technology advancement on the bonding or joining system is still infancy. The commonly used joining method for engine mounting system are fasteners and adhesive. Nowadays, automotive industry prefer the adhesive joining method as it meets the light weight principle which is best suited with the current demand. However, commonly used adhesive bonding system is not enough to provide the bonding strength needed. In addition, it also consumes a lot of money due to the utilization of primer. Therefore in order to overcome these problems, a preliminary study was conducted on a new adhesive formulation. Graphene nanoplatelets (GNP) were introduced into a rubber-modified epoxy adhesive in order to simultaneously improve the bulk mechanical properties, fracture toughness and single joint lap shear strength of the adhesive. According to (Quan, Carolan, Rouge, Murphy, & Ivankovic, 2018) the Young's modulus of the rubber-metal system was observed to increase marginally from 2.46 GPa to 2.56 GPa upon the addition of 0.1 wt.% GNPs. Therefore in order to improve the bonding strength of the joining system, GNPs was incorporated into the adhesive formulation. Moreover, the adhesive formulation used was an epoxy based adhesive. Epoxy-based adhesives are one of the most generally used adhesives, for joining metals and fiber reinforced polymer composites (Jia, et al., 2016). Epoxy-based thermosets can also be identify by high strength, excellent adhesion to numerous metallic and nonmetallic substrates, possess small shrinkage during and after cure, and high resistance to chemicals and extreme temperatures (Hu, et al., 2013) which explains the used of this adhesive formulation in this study.