UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

SWELLING AND THERMAL EFFECTS ON MECHANICAL PROPERTIES OF NR/EPDM FILLED GRAPHENE NANOPLATELETS FOR ENGINE MOUNTING

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Master of Science in Manufacturing Engineering

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

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202□

DECLARATION

I declare that this thesis entitled "Swelling and Thermal Effects on Mechanical Properties of NR/EPDM filled Graphene Nanoplatelets for Engine Mounting" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ……………………………

Name : KHAIRU ILWANI BINTI KARIM

Date : 3 JANUARY 2022

APPROVAL

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

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Date : 3 JANUARY 2022

DEDICATION

To my beloved late father Karim Kechik. To his words of inspiration and encouragement in the pursuit of excellence, still linger on. To my beloved mother, who always stood behind me and knew I would succeed. Thanks for all you did. This work is dedicated to them.

ABSTRACT

Nowadays, rubber blend nanocomposites have fascinated most researchers to be utilized in engine mounting. Graphene nanoplatelets (GNPs) have been known to have outstanding properties in physical, mechanical, electrical and thermal. In some applications, structures and components may be subjected to harsh service conditions such as high heat, liquid and dynamic stress. This research is aimed to explore the swelling and thermal effects on the physical and mechanical properties of NR/EPDM filled graphene nanoplatelets (GNPs) for engine mounting. In Stage 1, the effect of the thermal cycle on the tensile properties of NR/EPDM blends and NR/EPDM nanocomposites were studied. The NR/EPDM blends and NR/EPDM nanocomposites were prepared through melt compounding. Then, both materials were subjected to a thermal cycle before their tensile properties were measured. In Stage 2, both NR/EPDM blends and NR/EPDM nanocomposites were subjected to oil immersion in three types of oil medium; brake oil, gear oil and engine oil to assess their effects on the tensile properties. In Stage 3, the oil-immersed composites were subjected to dynamic loading to determine the fatigue life cycles due to more critical tensile properties under swelling media. Finally, the findings were further supported by swelling behaviour and compositional (FTIR), structural (XRD), thermal (DMTA) and morphological characteristics (SEM). Thermally affected NR/EPDM nanocomposites showed higher performance under tensile stress at the thermal cycles of 60°C and 120°C if compared to NR/EPDM blend. The tensile strength and modulus of elongation at 100% and 300% for nanocomposites were consistently 30-60% higher than NR/EPDM blend due to reinforcing effects of GNPs and their good interaction with the matrix which supported by the higher crosslink density in NR/EPDM nanocomposites. The declination in tensile properties with the increased thermal cycle was due to the chain embrittlement effect and in line with the increase in amorphous phases showing by the broadening of XRD spectra. Furthermore, the NR/EPDM nanocomposites exhibited better performance under the effect of swelling media in comparison with NR/EPDM blends. The immersion in gear and engine oil caused a major deterioration to both materials and caused sudden drops in tensile properties. The increment in elongation at break once immersed in oils was due to the softening effect of the rubber chains and re-distribution of GNPs sheets observed in XRD and FTIR analyses. The morphological analysis also verified that the swelling process caused the formation of wrinkles and cracking on both rubber surfaces, which appears to reduce in NR/EPDM nanocomposites. The swollen NR/EPDM blend and nanocomposites were further tested under fatigue stress. The unswollen and swollen nanocomposites exhibited higher resistance towards dynamic stress with maximum fatigue life higher than the blends about 10^5 cycles. The morphological analysis illustrates a more wrenching pattern on the fatigue fracture of the NR/EPDM nanocomposites. This has proven that the NR/EPDM nanocomposites can withstand thermal cycles, oils and fluctuating stress better than NR/EPDM blend and showed higher potential to be utilized as engine mounting material.

KESAN PENGAMPULAN DAN HABA PADA SIFAT MEKANIKAL NR/EPDM TERISI NANOKEPINGAN GRAFIN UNTUK PENCAGAK ENJIN

ABSTRAK

Kini, nanokomposit adunan getah telah menarik minat ramai penyelidik untuk digunakan dalam pencagak enjin. Grafin nanokepingan (GNPs) telah diketahui mempunyai ciri-ciri luar biasa dalam fizikal, mekanikal, elektrik dan haba. Dalam beberapa aplikasi, struktur dan komponen berkemungkinan terdedah kepada keadaan perkhidmatan yang teruk seperti haba, cecair dan tegasan beban dinamik. Kajian ini bertujuan untuk mengkaji dan membandingkan kesan pengampulan minyak dan haba pada sifat fizikal dan mekanikal adunan NR/EPDM dan NR/EPDM nanokomposit terisi GNPs untuk pencagak enjin. Dalam Tahap 1, kesan kitaran terma pada sifat tegangan adunan dan nanokomposit dikaji. Adunan dan nanokomposit disediakan melalui penyebatian lebur. Kemudian kedua-duanya dikenakan kitaran terma sebelum diuji untuk penentuan sifat tegangan. Dalam Tahap 2, adunan dan nanokomposit NR/EPDM direndam dalam tiga jenis medium minyak; minyak brek, minyak gear dan minyak enjin untuk menilai kesannya terhadap sifat tegangan. Dalam Tahap 3, komposit terendam minyak dikenakan beban dinamik untuk menentukan kitaran hayat lesu kerana sifat tegangan yang lebih kritikal dibawah pengaruh medium pengampulan. Akhirnya, penemuan disokong lanjut dengan tingkah laku pengampulan dan ciri-ciri komposisi (FTIR), struktur (XRD), haba (DMTA) dan morfologi (SEM). Nanokomposit NR/EPDM yang terjejas teruk menunjukkan prestasi yang lebih tinggi di bawah tegasan tegangan pada kitaran haba 60 °C dan 120 °C jika dibandingkan dengan adunan NR/EPDM. Kekuatan tegangan dan modulus pemanjangan pada 100% dan 300% untuk nanokomposit secara konsisten adalah 30-60% lebih tinggi daripada kekuatan adunan disebabkan oleh kesan penetulangan GNPs dan interaksi yang baik dengan matriks dan disokong oleh ketumpatan paut silang yang lebih tinggi dalam nanokomposit. Pengurangan sifat tegangan dengan kenaikan kitaran haba disebabkan oleh kesan perapuhan rantaian dan ia selaras dengan peningkatan fasa amorfus yang ditunjukkan oleh pelandaian spektra XRD. Selain itu, nanokomposit mempamerkan prestasi yang lebih baik di bawah pengaruh media pengampulan berbanding adunan. Rendaman dalam minyak gear dan enjin menyebabkan kemerosotan utama kepada kedua-dua bahan dan menyebabkan penurunan mendadak dalam sifat tegangan. Peningkatan pemanjangan pada takat putus setelah direndam dalam minyak adalah disebabkan oleh kesan pelembutan rantaian getah dan penaburan semula kepingan GNP yang turut diperhatikan dalam analisa XRD dan FTIR. Analisis morfologi mengesahkan proses pengampulan menyebabkan pembentukan keriput dan keretakan pada permukaan getah, yang kelihatan lebih berkurang pada nanokomposit. Adunan dan nanokomposit yang terampul diuji dengan lebih lanjut di bawah tekanan lesu. Nanokomposit yang terampul dan tidak terampul mempamerkan ketahanan yang lebih tinggi terhadap tegasan dinamik dengan hayat lesu maksimum yang lebih tinggi daripada adunan kira-kira 10^5 kitaran. Analisis morfologi menggambarkan corak perengkuh yang lebih teruk pada patah lesu bagi nanokomposit. Ini telah membuktikan bahawa nanokomposit NR/EPDM boleh menahan kitaran haba, minyak dan tekanan turun naik yang lebih baik daripada adunan NR/EPDM dan menunjukkan potensi yang lebih tinggi untuk digunakan sebagai bahan pencagak enjin.

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LIST OF ABBREVIATIONS AND SYMBOLS

ASTM	-	American standard testing method
DMTA	-	Dynamic mechanical thermal analysis
DSC	-	Differential scanning calorimetry
E_B	-	Elongation at break
ENR	-	Epoxidized natural rubber
ENR-50	-	Natural rubber having 50% of epoxidation
EPDM	-	Ethylene propylene diene monomer
FTIR	-	Fourier transform infrared spectroscopy
GNP	-	Graphene nanoplatelets
LGM	-	Lembaga Getah Malaysia
MBTS	-	2,20-dithiobis (benzothiazole)
M_H	-	Maximum torque
M_L	-	Minimum torque
M_L-M_H	-	Torque difference
M_{100}	-	Modulus at 100% elongation
M_{300}	-	Modulus at 300% elongation
NR	-	Natural rubber
OM	-	Optical microscope
Phr	-	Parts per hundred rubber
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis

TMTD	-	Tetramethylthiuram disulphide
V_c	-	Crosslink density
V_r	-	Volume fraction of the swollen rubber
V_s	-	Molar volume of the solvent (toluene)
XRD	-	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background

Engine mounts are a critical component in passenger cars. Its function is to isolate the vibration from an engine to the car body (Ooi and Ripin, 2014). They are two categories of engine mount; passive engine mount and active engine mount. Mostly passive engine mount is made from elastomeric materials either, natural or synthetic rubber or the blend of the rubber. These elastic mounts were first introduced in the 1930s using rubber-based components, being small in size and relatively cheap (Yu et al., 2001). Together with engine mounts, these materials are widely used for various automotive parts such as shock absorbers, rubber tires, seals, gaskets, lining, etc. The superior property of cured elastomer is the ability to undergo stretching to a large extent and resume its original shape when force is removed. It absorbs considerable energy during the deformation (Hofmann, 1990). According to Samad and Ali (2010), the engine mount is preferred to avoid direct metal-to-metal contact between the engine and the car body. Elastomer material is used to produce engine mountings due to their ability to possess outstanding shock-absorbing characteristics and ability to exhibit crystallization when stretched (Alipour et al., 2013).

In recent years, researchers and developers have made efforts focusing on improving engine mounting technology to achieve better vibration isolation, smooth vehicle movement, and noise reduction with good compression set and aging properties (Rashid et al., 2008). Material development is a significant contributor to the improvement of engine mounting.

New kinds of elastomers that permit specification of the amount of damping have been developed. Polymer materials or derivatives, especially elastomers, can be designed to withstand higher engine compartment temperatures. For this purpose, the optimization of formulation and processing techniques is crucial. The designed elastomers should provide specific dynamic properties that can sustain the varying vehicle environments over a certain period (Vahdati and Saunders, 2002). The effects of strain amplitude, repeat cycling, and temperatures are among important parameters in evaluating an engine mounting elastomer's potential. There are several elastomer systems available for engine mounting, such as natural rubber (NR), natural rubber/polybutadiene rubber (NR/BR) blend, nitrile rubber/ poly(methyl methacrylate) (NBR/PMMA), polyurethane (PU), epoxidized natural rubber/neoprene (ENR/CR) blend and ethylene-propylene-diene-monomer (EPDM)/nylon 6 blend (Peng et al., 2015).

A rubber blend is a combination of two or more dissimilar rubbers which useful to improve specific properties that are not inherent in a single rubber. It is also to combine each rubber type's dominant properties to develop new material for some specific properties (Sahakaro et al., 2011). The properties of any blend are functions of the adhesion between the components. While most of the blends are thermodynamically incompatible, many have been found to have technological importance (Bhowmick and Chakraborty, 1989). The chemical and physical blending of two or more polymers was a useful technique for preparing materials with properties lacking in the component polymers (Bartczak and Galeski, 2014). The properties of any blend are functions of the adhesion between the components. While most of the blends are thermodynamically incompatible, many have been found to have technological importance (Bhowmick and Chakraborty, 1989).

Natural rubber (NR) can exhibit crystallization when stretched. Stress-induced crystallization can be used to increase modulus and resistance to deformation, preventing the propagation of defects. In contrast, ethylene propylene diene monomer (EPDM) rubber has saturated hydrocarbon backbones, which usually impart good weathering oxidation and chemical resistance (Costa and Nunes, 1994). The vulcanized NR/EPDM systems have been extensively studied due to their superior performances in tires and other demanding applications (Nabil et al., 2012). Significant improvements in heat and ozone resistance (Motaung et al., 2011), chemical resistance, and reduction in compression set (Alipour et al., 2013) of NR/EPDM blends have attracted researchers to explore further and improvise the NR/EPDM compounds formulation.

Multiple studies have been conducted on elastomer-filled carbon black for engine mounting. Carbon black is a famous material in industrial rubber products as a commercial reinforcing filler and is extensively used when high strength is essentials (Nabil et al., 2012). The main uses of carbon black are as a reinforcing agent in rubber-based goods, such as tires, tubes, conveyer belts, cables, and engine mounting. The addition of carbon black can affect all phases of a rubber factory's operation and the end products' performance characteristics due to its unique properties, which can produce strong interactions with any rubber, from tire components to industrial rubber products (Ramesan, 2005). As a practical guide, an increase in a carbon black aggregate size or structure will improve cut growth and fatigue resistance. Carbon black also has higher tensile strength, tear strength, modulus, and abrasion resistance when compounded with rubber (Choi et al., 2003). However, the most considerable hindrance of carbon black as advanced industrial filler is their limitation in dispersion and distribution in viscous polymer matrices. Their surface properties increase the tendency for aggregations and agglomerations during processing and limit the further improvement of the composites' physical and mechanical properties. The use of high loading carbon black increases the stickiness that is unfavorable in processing and reduces the