UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

SYNTHESIS AND PHYSICO-MECHANICAL ANALYSIS OF GRAPHENE NANOPLATELETS (GNPs) FILLED NATURAL RUBBER/ETHYLENE PROPYLENE DIENE MONOMER (NR/EPDM) FOR VIBRATION RESISTANCE

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A thesis submitted
in fulfilment of the requirements for the degree of Master of Science
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DECLARATION

I declare that this thesis entitled "Synthesis and Physico-Mechanical Analysis of Graphene Nanoplatelets (GNPs) filled Natural Rubber/Ethylene Propylene Diene Monomer (NR/EPDM) for Vibration Resistance" is the results 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 : Juliana Bte Yaakub

Date : 27th October 2014

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 Science in Manufacturing Engineering.

Signature :……………………………………………………...

Supervisor Name :Dr. Noraiham Binti Mohamad

Date :27^{th} October 2014

ABSTRACT

In recent years, polymer nanocomposites have attracted great interest due to their remarkable improvements in materials properties when compared with virgin polymer or conventional micro and macro-composites. This research is an effort to explore the potential of graphene nanoplatelets (GNPs) filled natural rubber/ethylene-propylene-diene rubber (NR/EPDM) as mount rubber based on their physico-mechanical and vibration damping properties. At stage 1, the effects of compatibilizer and processing parameters on the properties of NR/EPDM (70: 30 phr) blends were studied. The blends were prepared by melt compounding using Haake Internal Mixer. Using Response Surface Methodology (RSM) of two-level full factorial, the effects of epoxidized natural rubber, ENR-50 contents (-1:5 phr; +1:10 phr), mixing temperature (-1:50 °C; +1:110 °C), rotor speed (-1:40 rpm; +1: 80 rpm) and mixing time (-1:5 min; +1:9 min) in NR/EPDM blends were evaluated. Cure characteristics and tensile properties were selected as the responses. The coefficient of determination, R2 values above 0.90 were accurate to represent the actual system. The findings were further supported by swelling behaviour, thermal and morphological characteristics. At stage 2, a facile method for surface treatment of GNPs was demonstrated. In stage 3 and 4, the effects of unfunctionalized and functionalized GNPs loading (0, 0.25, 0.50, 1, 3 and 5 wt%) on cure characteristics, physico-mechanical, structural, vibration, thermal properties of the composites as well as on their morphologies were studied. The studies were carried out through Monsanto rheometer analysis, tensile test, swelling test, X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), vibration test, dynamic mechanical analysis (DMA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The GNPs show good compatibility with NR/EPDM matrix due to their improvement observed in cure characteristics, tensile properties and crosslink density compared with unfilled vulcanized NR/EPDM. It was in line with the observation on structural and chemical properties of GNPs dispersed in NR/EPDM matrix. XRD and FTIR pattern have provided sufficient explanation regarding the state of dispersion of GNPs filled NR/EPDM matrix. The morphology of the unfunctionalized and functionalized GNPs in the NR/EPDM matrix revealed uniform distribution of GNPs up to 3 wt% loading, whereas, GNPs agglomerates were observed at 5 wt%. The vibration test via free vibration test had proven the potential of GNPs filled NR/EPDM as mount rubber in which their amplitude decays faster than the vulcanized NR/EPDM. The storage modulus, loss modulus and tan δ showed good agreement with the vibrational damping behaviours. TEM analysis revealed the existence of intercalated and exfoliated structure of GNPs which resulted in improved vibration damping characteristics and mechanical properties. In overall, GNPs filled NR/EPDM are capable to absorb vibrational energy particularly for a mount rubber.

ABSTRAK

Dalam tahun-tahun kebelakangan ini, nanokomposit polimer telah menarik minat yang besar kerana peningkatan yang luar biasa dalam sifat bahan tersebut berbanding polimer dara atau komposit konvensional makro maupun mikro. Kajian ini merupakan satu usaha untuk meneroka potensi adunan getah asli/ etilena-propilena-diena getah (NR/EPDM) yang diisi grafin nano platelet (GNPs) sebagai getah pemegang enjin berdasarkan sifat fiziko-mekanikal dan ciri-ciri redaman getaran mereka. Pada peringkat 1 penyelidikan, kesan penserasi dan parameter pemprosesan terhadap NR/EPDM (70:30 bahagian per seratus getah) dikaji. Adunan dilaksanakan melalui kaedah penyebatian lebur menggunakan pencampur dalaman Haake. Menggunakan faktoran aras dua Metodologi Permukaan Sambutan (RSM), kesan kehadiran getah asli terpoksida, ENR-50 (-1:5 phr; +1:10 phr), suhu pencampuran (-1:50°C; +1:110°C), kelajuan pemutar (-1:40 rpm; 1:80rpm), dan masa pencampuran (-1:5min; +1:9min) dalam adunan NR/EPDM telah dinilai. Ciri matang dan sifat tegangan telah dipilih sebagai tindak balas. Nilai pekali penentuan, R2 yang melebihi 0.90 adalah tepat untuk mewakili sistem sebenar. Penemuan ini kemudiannya telah disokong oleh kelakuan pembengkakan, ciri terma dan morfologi. Dalam peringkat 2, kaedah mudah telah dibangunkan untuk memberi rawatan permukaan pada permukaan GNPs. Dalam peringkat 3 dan 4, kesan pembebanan pengisi GNPs yang difungsikan dan tidak difungsikan (0, 0.25, 0.50, 1, 3 dan 5 wt%) terhadap ciri matang, sifat fiziko-mekanikal, struktur, getaran, terma dan morfologi dikaji. Kajian tersebut dijalankan melalui analisis meter alir Monsanto, ujian tegangan, ujian getaran, ujian pembengkakan, pembelauan sinar-X (XRD), penjelmaan Fourier infra-merah (FTIR), analisis mekanik dinamik (DMA), kemikroskopan elektron imbasan (SEM) dan kemikroskopan transmisi elektron (TEM). Pengisi GNPs menunjukkan keserasian yang baik dengan matrik NR/EPDM ekoran peningkatan ciri matang, sifat tegangan dan rintangan pembengkakan berbanding NR/EPDM tanpa pengisi. Corak ujian XRD dan FTIR telah menyediakan penjelasan yang mencukupi mengenai keadaan serakan GNPs dalam matriks NR/EPDM. Morfologi GNPs yang difungsikan dan tidak difungsikan didalam matrik NR/EPDM mempamerkan taburan pengisi seragam sehingga 3 wt% GNPs, manakala penggumpalan diperhatikan pada bebanan pengisi sebanyak 5 wt%. Sementara itu, ujian getaran telah membuktikan bahawa NR/EPDM yang diisi GNPs memberi kesan positif kepada sifat redaman getaran yang mana amplitud getaran merudum lebih cepat daripada NR/EPDM tanpa pengisi. Modulus penyimpanan, modulus kehilangan dan tan δ menunjukkan keputusan yang berhubung baik dengan ujian redaman getaran. TEM analisis mendedahkan wujudnya struktur interkalasi dan eksfoliasi daripada GNPs yang menyebabkan penambahbaikan ciri-ciri getaran redaman dan sifat-sifat mekanik. Keseluruhannya, NR/EPDM yang diisi GNPs berupaya menyerap tenaga berkaitan dengan getaran terutamanya untuk getah pemegang enjin.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
ASTM	-	American standard testing method
BS	-	British standard
C	-	Carbon
CH	-	Hydrocarbon
CNTs	-	Carbon nanotubes
COOH	-	Carboxylic group
CV	-	Conventional vulcanization
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
DMTA	-	Dynamic mechanical thermal analysis
e.g	-	Example
ENB	-	Ethylidene norbornene
et. at.	-	and others
etc	-	Et cetera
i.e	-	In example
FTIR	-	Fourier transform infrared spectroscopy
GNPs	-	Graphene nanoplatelets
GO	-	Graphene oxide
LGM	-	Lembaga getah Malaysia
MAH	-	Maleic anhydride
Mc	-	Molecular weight between crosslink
MBTS	-	2,20-dithiobis (benzothiazole)
M_H	-	Maximum torque

M_L	-	Minimum torque
M_H-M_L	-	Torque difference
M_{100}	-	Modulus at 100% elongation
M_{300}	-	Modulus at 300% elongation
MWNT	-	Multi-walled carbon nanotube
NR	-	Natural rubber
NVH	-	Noise, vibration and harshness
OH	-	Hydroxyl group
Phr	-	Parts per hundred rubber
PNCs	-	Polymer nanocomposites
Qm	-	Weight increase of the NR/EPDM blends in toluene
R2	-	Constant of determination
R&D	-	Research and development
RSM	-	Response surface methodology
SEM	-	Scanning electron microscopy
SWNT	-	Single-walled carbon nanotube
Tg	-	Glass transition temperature
Ts	-	Tensile strength
T_2	-	Scorch time
T_{90}	-	Cure time
Tm	-	Melting temperature
TMTD	-	Tetramethylthiuram disulfide
TEM	-	Transmission electron microscopy
TOR	-	Trans-polyoctenylene rubber
UTM	-	Universal testing machine
Vc	-	Crosslink density
Vr	-	Volume fraction of the swollen rubber
Vs	-	Molar volume of the solvent (toluene)
XRD	-	X-ray diffraction
W_0	-	Initial mass of samples before the immersion in toluene
W_1	-	Mass of samples after the swelling
Wt%	-	Weight percent
6PPD	-	dN-(1,3-Dimethylbutyl)-N'-phenyl-p phenylenediamine

LIST OF UNITS

^{o}C	-	Celsius
m/s	-	Meter per second
%	-	Percentage
min	-	Minute
kg	-	Kilogram
mm	-	Millimeter
µm	-	Micrometer
s	-	Second
nm	-	Nanometer
g	-	Gram
Hz	-	Hertz

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2. **Juliana Yaakub**, Noraiham Mohamad, Jeefferie Abd Razak, Kok-Tee Lau, Mohd Edeerozey Abd Manaf, Mohammed Iqbal Shueb, “Stable Dispersion of Graphene Nanoplatelets (GNPs) in Different Types of Solvents and Facile Method for Surface Modification GNPs with Chitosan”, 2014, Publication in Applied Mechanics and Materials.
3. **Juliana Yaakub**, Noraiham Mohamad, Jeefferie Abd Razak , Zanariah Jano, Mohammed Iqbal Shueb, “Cure Characteristics, Swelling Behavior and Morphology of Graphene Nanoplatelets (GNPs) Filled NR/EPDM Composites”, 2014, Publication in American-Eurasian Journal of Sustainable Agriculture (AEJSA).
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International Conferences

1. **ICPRC 2014**

Juliana Yaakub, Noraiham Mohamad, Jeefferie Abd Razak , Zanariah Jano , Mohammed Iqbal Shueb, "Cure Characteristics, Swelling Behaviour and Morphological Properties of Graphene Nanoplatelets (GNPs) Filled NR/EPDM Composites", International Conference on Plastics, Rubber and Composites (ICPRC 2014), Langkawi, Malaysia, 20-21 June 2014 (Oral presentation).

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Juliana Yaakub, Noraiham Mohamad, Jeefferie Abd Razak, Kok-Tee Lau, Mohd Edeerozey Abd Manaf, Mohammed Iqbal Shueb, "Stable Dispersion of Graphene Nanoplatelets (GNPs) in Different Types of Solvents and Facile Method for Surface Modification GNPs with Chitosan" International Conference on Design and Concurrent Engineering (iDECON 2014), Avillion Legacy Hotel, Melaka, Malaysia, 22 - 23 Sept. 2014 (Oral presentation).

CHAPTER 1

INTRODUCTION

1.1 Introduction

Polymer nanocomposites are at the forefront of advanced materials applications, where the incorporation of dispersed nanofillers into a polymer matrix provides materials with tailored and controlled properties without compromising the processing ease of the host polymer (Balazs et al., 2006; Winey et al., 2007; Chatterjee et al., 2013). Extensive studies have shown that even at a very low level of nanofiller loading, the material offers significant improvement in mechanical strength and stiffness which are not inherent in pure polymers or conventional composites (Rafiee et al., 2009; Zaman et al., 2011; Araby et al., 2013). To date, however, scarce attention has been given on the vibration damping potential of rubber nanocomposites despite being a significant area as they affect the safety as well as overall system performance and reliability of the materials (Liao et al., 1994; Khan et al., 2011). Therefore, it is necessary to study the vibration damping characteristics with a goal to develop polymer nanocomposites that not only show excellent mechanical properties but also possess good in vibration damping capability.

Vibration is a repetitive motion of objects in alternately opposite directions from its position of equilibrium when that equilibrium has been disturbed (Jones, 2001). A variety of machinery, structures and dynamic systems are prone to vibratory motions. The undesirable vibrations in a structural system can lead to unpleasant motions, noise and dynamic stress that can lead to increase fatigue life of the structural components which 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.

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.

Natural rubber (NR) is a unique and versatile material that has been used successfully in various engineering applications for 150 years and remains the important elastomer especially for springs and mountings components (Sethu, 2009). It is frequently applied in shock and vibration isolators applications due to its excellent damping properties and it occupies high resilience, high tensile, fatigue resistance, tear properties and low cost (Schaefer, 2002). Besides that, NR is the elastomer of choice for the majority of applications requiring high resilience and level of cyclic flexing. However, NR exhibit poor resistance to heat and ozone that makes it not suitable for numerous applications that