OPTIMISATION AND CHARACTERISATION OF FUNCTIONALISED GRAPHENE NANOPLATELETS FILLED NR/EPDM NANOCOMPOSITES

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MAZLIN AIDA BINTI MAHAMOOD

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

I declare that this thesis entitled "Optimisation and Characterisation of Functionalised Graphene Nanoplatelets Filled NR/EPDM Nanocomposites" 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 : ………………………................

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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 Science in Manufacturing Engineering.

Signature	:	………………………..............
Supervisor's Name	:	Dr. Noraiham Mohamad ………………………..............
Date	:	………………………..............

DEDICATION

To God, who gave me the life, strength and the guidance, to my beloved family, husband, mama, abah, abang, kakak dan adik-adik, thank you for giving me full encouragement and love. To my respective supervisor and lecturer, thank you for the lesson and knowledge. To all my friends and every person involved, your support is very well appreciated

ABSTRACT

Nowadays, polymer nanocomposites have attracted great interest due to their outstanding improvements in material properties as compared to neat polymers or conventional composites. This research is to prepare and characterise the Natural Rubber (NR) / Ethylene Propylene Diene Monomer (EPDM) filled Graphene Nanoplatelets (GNPs) nanocomposites for mechanical and thermal performance compared than unfilled NR/EPDM blend. The stage 1 of the research is to improve the miscibility between NR and EPDM rubber phases by using MAH grafted EPM compatibiliser. NR/EPDM blends were compounded using a Haake internal mixer and vulcanised by a semi-EV curing system in accordance to ASTM D3192. The response surface methodology (RSM) by Design Expert 6.0.10 software was used to optimize an internal mixer processing parameters and amount of MAH grafted EPM compatibiliser towards the maximum tensile strength (TS). The optimum mixing parameters was mixing temperature of 110°C, rotor speed of 40 rpm, mixing period of 5 mins and 5 phr amount of MAH grafted EPM compatibiliser with the highest repeatability and R^2 value of ~99.00%. The stage 2 of the research was focusing on the graphene nanoplatelets surface treatment by the non-covalent methods using polyethyleneimines (PEI) in an ethanol: distilled water medium (75:25). The physical adsorption of PEI on GNPs by non-covalent treatment was proposed as a possible interaction mechanism. During the stage 3 of this research, the effects of GNPs surface treatment and loading (0.25-5.00 wt. %) to the processability, mechanical, physical, thermal and morphological properties of the nanocomposites were studied. The surface treatment of GNPs enhanced the filler-matrices interaction in the NR/EPDM blend nanocomposites. The nanocomposites with 3.00 wt. % PEI-treated GNPs possessed outstanding mechanical properties compared to the unfilled blends and filled samples without treatment (tensile strength of 27.78 MPa, 19.65 MPa and 23.34 MPa; resepectively). The results were supported with thermal and dynamic analyses. At the last stage of the study, the superior thermal conductivity of 0.6220 $Wm^{-1}K^{-1}$ from the thermal conductivity analysis (TCA), showed that the NR/EPDM blends filled with 3.00 wt. % PEI-treated GNPs exhibited an enhancement in the heat dissipation and thermal-mechanical properties in comparison to the unfilled NR/EPDM blend. In overall, NR/EPDM filled GNPs nanocomposite that was prepared through the combination of an optimized melt-blending processing parameters and amount of MAH compatibiliser with addition of PEI-treated GNPs is able to provide a maximum effects of improved mechanical and thermal properties which is beneficial for the suggested application of rubber component in an automotive engine mount.

ABSTRAK

Pada masa kini, nanokomposit polimer telah menarik perhatian ramai disebabkan oleh prestasi amat cemerlang sifat-sifat bahan ini jika dibandingkan dengan polimer tulen atau komposit konvensional. Penyelidikan ini bertujuan menyediakan dan mencirikan sifat mekanik dan terma nanokomposit adunan getah asli (NR) / etilena propilena diena (EPDM) berpengisi kepingan nano zarah grafin (GNPs). Peringkat pertama penyelidikan dimulakan dengan percubaan menyelesaikan isu ketidaklarutcampuran dan ketidakserasian antara fasa getah NR dan EPDM, melalui penggunaan penserasi MAH grafted EPM. Adunan NR/EPDM telah disebatikan dengan menggunakan peralatan pencampur dalaman Haake dan divulkan secara sistem pematangan separa-EV, berdasarkan ASTM D3192. Metodologi permukaan sambutan (RSM) dari perisian Design Expert 6.0.10 telah digunakan, bagi pengoptimuman parameter pemprosesan dan amaun penserasi MAH grafted EPM, terhadap sifat kekuatan tegangan (TS) yang maksimum. Sambutan yang optimum telah diperolehi dari parameter pencampuran NR/EPDM; 110°C suhu pencampuran, 40 rpm kelajuan rotor, 5 minit tempoh pengadunan dan 5 phr amaun penserasi MAH grafted EPM, dengan kebolehulangan yang tinggi dan nilai R^2 sebanyak ~99.00%. Peringkat kedua penyelidikan telah memfokus kepada rawatan permukaan pengisi kepingan nano-zarah grafin secara bukan kovalen, dengan kehadiran polietilenaimina (PEI) dalam medium etanol-air suling (75:25). Mekanisma penjerapan fizikal secara interaksi sterik bukan kovalen GNPs-PEI, telah dicadangkan sebagai mekanisma tindak balas. Pada peringkat ketiga kajian, kesan rawatan permukaan GNPs dan penambahan pengisi yang berbeza (0.25-5.00 bt. %) terhadap kebolehprosesan, sifat mekanik, fizik, terma dan morfologi nanokomposit adalah diselidiki. Rawatan permukaan yang dijalankan keatas GNPs, telah meningkatkan interaksi antara matriks-pengisi dalam nanokomposit adunan getah NR/EPDM. Nanokomposit dengan 3.00 bt. % PEI-terawat GNPs menunjukkan sifat-sifat mekanik yang lebih baik berbanding adunan tidak berpengisi dan adunan berpengisi tidak terawat yang lain (kekuatan tegangan sebanyak 27.78 MPa, 19.65 MPa and 23.34 MPa; masing-masing). Keputusan kajian disokong dengan analisa terma dan dinamik. Pada peringkat terakhir ujikaji, keboleh aliran haba sebanyak 0.6220 $Wm^{-1}K^{-1}$ menunjukkan adunan NR/EPDM dengan 3.00 bt. % PEI-terawat GNPs, telah menunjukkan sifat termal-mekanik yang sangat baik berbanding adunan NR/EPDM tidak berpengisi. Keseluruhannya, penyediaan nanokomposit adunan getah NR/EPDM dengan GNPs menggunakan kombinasi parameter proses penyebatian lebur dan amaun penserasi MAH grafted EPM yang betul, dengan amaun penambahan PEI-terawat GNPs yang optimum, adalah berupaya memberikan kesan sinergistik yang maksimum keatas peningkatan sifat mekanik dan ketahanan haba, yang dilihat sangat berfaedah bagi aplikasi komponen getah pencagak enjin kenderaan automotif sebagaimana yang dicadangkan.

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LIST OF ABBREVIATIONS AND SYMBOLS

°C	-	Degree celsius
2D	-	Two dimensional
6PPD	-	*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine
ANOVA	-	Analysis of variance
ASTM	-	American standard testing of materials
ATR-FTIR	-	Attenuated total reflactance-FTIR
CNF	-	Carbon nanofiber
CNTs	-	Carbon nanotubes
CO_2	-	Carbon dioxide
CRI	-	Cure rate index
DCP	-	Dicumyl peroxide
DMA	-	Dynamic mechanical analysis
DSC	-	Differential scanning calorimetry
DTG	-	Derivative thermal gravimetry
E'	-	Storage modulus
E''	-	Loss modulus
EB	-	Elongation at break
EPDM	-	Ethylene propylene diene monomer
EPM	-	Ethylene propylene copolymer
FEA	-	Finite element analysis
FESEM	-	Field emission scanning electron microscopy
FWHM	-	Full width at half maximum
GNPs	-	Graphene nanoplatelets
GPa	-	Gigapascal
M100	-	Modulus at 100% elongation
M300	-	Modulus at 300% elongation
M500	-	Modulus at 500% elongation
MAH	-	Maleic anhydride
MBTS	-	2,20-dithiobis(benzothiazole)

M_c	-	Average molecular weight between crosslink
MH-ML	-	Torque difference
MH	-	Maximum torque
ML	-	Minimum torque
MMT	-	Montmorillonite
Mn	-	Average number molecule
Mw	-	Average weight molecule
nm	-	Nanometer
NR	-	Natural rubber
NR/EPDM	-	Natural rubber/ ethylene propylene diene monomer
OH	-	Hidroxyl
PEI	-	Polyethyleneimine
PEI-treated GNPs	-	GNPs treated with polyethyleneimine
phr	-	Per hundred rubber
PVA	-	Polyvinyl acetate
RSM	-	Response surface methodology
TMTD	-	Tetramethylthiuramdisulfide
Qm	-	Weight increase
υ_o	-	Molar volume of toluene
υ_r	-	Volume fraction of rubber in swollen sample
χ	-	Interaction constant characteristic between rubber and toluene
ρ	-	Density
x	-	Multiply to
/	-	Divide to
=	-	Equal to
%	-	Percent

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The emergence of nanomaterials in the area of polymer science and technology have caused nanosized materials to be widely employed in advanced composite systems (Arroyo et al., 2007; Sookyung et al., 2014). The dimension of one of the constituent phase in the composites sometimes can be between 1 to 100 nm, and under these atomic dimensions that particular phase has properties rather different from those of the same material in the bulk form and are referred to as ‗‗nanocomposite‘‘ (Olad, 2011).

Polymer nanocomposites are a type of composite system consisting of two main components; a polymeric matrix material (thermoplastics, thermosets or elastomers) and a nanoscale reinforcing material (nanoparticle) (Koo, 2006). This new class of composite materials have shown enhancement in mechanical properties, thermal stability, chemical resistance, gas permeability and electrical conductivity (Mortensen, 2007; Wu et al., 2013). The property enhancements of polymer nanocomposites are possible with several factors i.e. preparation methods, morphology of the polymer nanocomposites which are dependent on the surface chemistry of each component, type of polymers, as well as characteristics of polymer matrix such as crystallinity, molecular weight and polymer chemistry (Lee et al., 2005). In addition, polymer nanocomposites intend to overcome the drawbacks of polymers through reinforcing effects of the nanofillers while maintaining the natural advantages of the main polymer matrix.