UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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PROPERTIES OF CHEMICALLY MODIFIED GRAPHENE THROUGH THERMAL, COMPOSITIONAL AND MORPHOLOGICAL ANALYSIS

This report submitted in accordance with requirement of the UniversitiTeknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Material) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UniversitI Teknikal Malaysia Melaka (UTeM) as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material). The member of the supervisory committee is as follow:

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ABSTRAK

Objektif utama kajian ini adalah melaksanakan modifikasi dan fungsionalisasi permukaan (penyalutan polimer) pada *Graphene Nanoplatelet* (GNP) dengan menggunakan bahan termoplastik melalui kaedah pencampuran larutan. *Graphene* telah digunakan secara meluas kerana prestasinya yang baik dan merupakan pengisi baru yang berpotensi untuk komposit polime rfungsian. Pengaruh modifikasi kimia pada taburan GNP dikaji melalui pemerhatian visual dan analisis kemikroskopan electron penghantaran (TEM). Kesan fungsionalisasi permukaan (formulasi& proses) terhadap sifat termal dan komposisi GNP termodifikasi dengan sifat-sifat dan kebolehcampuran bererti disokong oleh analisis melalui spektroskopi penjelmaan Fourier infra-merah (FTIR) dan permeteran kalori pengimbasan kebezaan (DSC). Modifikasi permukaan GNP memerlukan sonikasi di dalam larutan kloroform selama 1 jam untuk mendapatkan pencampuran seragam yang optimum. Penyalutan bahan polimer pada permukaan *graphene* yang telah dimodifikasi menunjukkan nisbah 1:4 memberikan tindak balas bukan kovalen yang terbaik. Setelah itu, komposit NR/EPDM di tetulang GNP-terfungsi dihasilkan untuk menunjukkan keserasian GNP-terfungsi dengan monomer getah NR / EPDM yang tinggi. Keputusan ini disokong oleh perincian dan analisis morfologi menggunakan kemikroskopan elektronimbasan (SEM) dan dapat disimpulkan bahawa propilena menunjukkan keserasian kimia terbaik dengan serakan *graphene* yang paling baik di dalam matriks NR / EPDM.

ABSTRACT

The main objective of this research is to perform surface modification or functionalization (polymer encapsulation) on graphene nanoplatelet (GNP) using thermoplastic material via solution mixing method. Graphene have been extensively used because of their excellent performance and is a new class of promising filler for functional polymer composites. The influence of the chemical modification on the graphene nanoplatelet dispersion was investigated by visual observation and Transmission Electron Microcopy (TEM) analysis. The effect of surface functionalization variables (formulation & process) to the thermal and compositional properties of modified graphene nanoplatelet with significant miscibility and properties were supported by Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetric (DSC). Surface modification of GNP requires sonication in chloroform for 1 hour to achieve the optimum uniform mixture. The encapsulation of polymeric materials with on modified graphene at ratio of 1:4 showed the best non-covalent reaction..Then, the NR/EPDM reinforced functionalized-GNP was prepared to show the high compatibility of functionalized-GNP with NR/EPDM rubber monomer. The results were supported by characterization and morphological analysis using Scanning Electron Microscopy (SEM) and it can be concluded that propylene monomer showed the best compatibility with high degree dispersion of graphene in NR/EPDM matrix.

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Thank you very much.

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LIST OF ABBREVIATIONS

CCG	-	Chemically converted graphene
CO-890	-	Polyoxyethylene (40) nonylphenyl ether
CTE	-	Coefficient of thermal expansion
DSC	-	Differential Scanning Calorimetric
EPDM	-	Ethylene propylene diene monomer
FTIR	-	Fourier Transform Infrared Spectroscopy
GNP	-	GrapheneNanoplatelet
KOH	-	Potassium hydroxide
NR	-	Natural rubber
PE	-	Polyethylene
PP	-	Polypropylene
SEM	-	Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy
THF	-	Tetrahydrofuran
TS	-	Tensile strength
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

^{o}C	-	Celsius
ms^{-1}	-	meter per second
%	-	percentage
kW	-	kilo watt
min	-	minute
kg	-	kilogram
mm	-	millimeter
µm	-	micrometer
s	-	second
nm	-	nanometer
g	-	gram
Hz	-	hertz
MPa	-	mega pascal

CHAPTER 1

INTRODUCTION

1.0 Background

Nanotechnology is utilized in various fields where the applications range anywhere from engineering to cosmetics. The leading attribute of this technology is the size that makes it so feasible to use in many different fields. The nanosize of the materials provides certain advantages like high surface area and low surface defects in the material, thus improving the material properties. For example in composites nanotechnology can be used in the filler material to increase the composite strength and to decrease the composite weight. Graphene is potential nanofiller that can dramatically improve the properties of polymer based composites at a very low loading and it has been attracting great interest due to its unique structure and properties. Moreover, polymer composites can be easily processed and fabricated into intricately shaped components with excellent preservation of the structure and properties of graphene using various processing methods. This is very important to make full use of the outstanding properties of graphene.

Graphene is a one-atom-thick planar sheet of sp 2 –bonded carbon atoms arranged in a hexagonal lattice with the basic structural unit of some carbon allotropes, including graphite, carbon nanotubes and fullerenes. It is believed to be the "thinnest and strongest material in the universe" and predicted to have remarkable physical and chemical properties (Jinhong *et al.*, 2012). Graphene, as nanofiller, may be preferred over other conventional nanofiller owing to high surface area, aspect ratio, tensile strength (TS), thermal conductivity and electrical conductivity, EMI shielding ability, flexibility, transparency, and low thermal expansion (CTE). Furthermore, graphene has high conductivity and provides higher reinforcement than carbon nanotubes, low viscosity and non-toxicity (Stankovich., *et al.,* 2006).

The incorporation of graphene into the compound materials can provide them with the unique functions of graphene. Hereby a lot of graphene modified materials with enhanced performance are investigated and applied in different fields. In the automotive industry application, the incorporation of graphene as a nanofiller into NR/EPDM blend will produce thermally and electrically conductive on NR/EPDM composites that can help dissipate heat from the engine and prevent the accumulation of static charge.Natural rubber (NR) is widely used in shock and vibration isolators applications such as automotive engine mounts because of its high resilience (elasticity), high tensile, fatigue resistance, tear properties and low cost. In contrast, ethylene propylene diene monomer (EPDM) has excellent resistance to heat, oxidation and ozone, as well as to oils and chemicals, including ethylene glycol. NR/EPDM blend may provide a kind of rubber-rubber mixture, which may become technologically important as it combines the excellent outdoor properties of EPDM with the good elastic and dynamic properties of NR. In addition, the mixture of NR/EPDM with graphene will give good thermal conductivity also plays a vital role in improving the service life of engine mounts and could reduce costs and environmental impact.

Compared with CNT, graphene has a higher surface-to-volume ratio because of the inaccessibility of the inner nanotube surface to polymer molecules. This makes graphene potentially more favorable for improving the properties of polymer matrices, such as the mechanical electrical, thermal, and microwave absorption properties. More importantly, graphene is much cheaper than CNT, because it can be easily derived from a graphite precursor in large quantity. Therefore, graphene as a low cost alternative to CNT in nanocomposites is highly expected.

1.2 Problem Statement

Graphene has been touted as the "miracle material" of the 21st Century. The ‘‘thinnest’’ known material, graphene exhibits excellent electrical conductivity, mechanical flexibility, optical transparency, thermal conductivity, and low coefficient of thermal expansion (CTE) behavior (Kuila *et al.*, 2012). It has been widely used as nanofiller in the preparation of polymer nanocomposites materials. However, the preparation of homogeneous graphene-polymer composites entails some difficulties. To achieve high-performance of polymer nanocomposites, homogeneous dispersion of graphene nanoplatelet in the polymer hosts and proper interfacial interactions between the nanoplatelet and the surrounding matrix must be considered.

The main problem is, the nature of graphene itself is not compatible with the organic polymer matrix and the individual sheets tend to restack to form graphite through π–π stacking or tend to form irreversible agglomerates to their large specific surface area and the Van der Waals interactions between the interlayer of graphene, which lowers its effectiveness as a nanofiller for property improvements. Aggregation can be reduced by the attachment of other small molecules or polymers to the graphene sheets. Therefore, the prevention of aggregation was of particular importance for graphene sheets because most of their unique properties were only associated with individual graphene and keeping them well separated was required in the preparation and processing of graphene. To make the more easily dispersible in liquids, it is necessary to physically or chemically attach certain molecules or functional groups to their smooth sidewalls without significantly changing the nanomaterial desirable properties. In recent years, some modification has been used for obtaining graphene dispersion in aqueous media by functionalizing graphene surfaces.

The significant of the graphene has attracted so many attentions to be used in automotive industry. One of the possible utilization is graphene as filler for material of engine mounting. The graphene will tend to develop high shock absorption, thermally conductive, with optimum mechanical performance and service environment resistance of NR/EPDM filled graphene composites. Thus, the chosen of the polymeric material such as Polypropylene and Polyethylene in this research is to show the high compatibility of propylene and ethylene monomer of NR/EPDM with the dispersion of graphene.

The processing of graphene with polymeric material involves choosing a proper blending method to reach a satisfactory dispersion of the nanofiller throughout the polymeric matrix. The three main methods of processing polymer encapsulated of graphene are in situ polymerization, solution mixing and melt blending. In situ polymerization is efficient method to uniformly disperse graphene and provide strong interaction between the graphene and polymer matrix. Generally, graphene is mixed with monomers or pre-polymers and then graphene/polymer composites with uniform dispersion and improved properties can be obtained by polymerizing the monomers or pre-polymers but the polymerization process is usually accompanied by a viscosity increase that hinders manipulation and limits load fraction. While, method is melt blending which is a versatile and commonly used method to fabricate polymeric materials, especially for thermoplastic polymers. However, this technique is that it may cause graphene buckling and even rolling or shortening due to the strong shear forces, thus reducing their aspect ratios, which is not favorable for achieving a low percolation threshold and high conductivity of the composites. For solution mixing method, graphene is generally dispersed in a solvent and then mixed with a polymer solution by mechanical mixing, magnetic agitation, or high-energy sonication. Subsequently, a composite can be obtained by vaporizing the solvent. This method is considered an effective means to prepare composites with uniform graphene dispersion. Hence, my research will be proceed with the solution mixing method due the polymeric materials to encapsulated with graphene are ideal choice because of their ease of fabrication by a low-cost room-temperature fabrication process.

Therefore, my research will focus on complicates efforts to utilize the surface functionalization on graphene, as well as in practical applications which require preparation of uniform mixtures of graphene with different organic, inorganic solvent and dispersion of polymeric materials with modified graphene by using solution mixing method.

1.3 Objectives

- To perform surface functionalization (polymer encapsulation) on graphene nanoplatelet using thermoplastic material via solution mixing method.
- To study the effect of surface functionalization variables (formulation & process) to the thermal and compositional properties of modified graphene nanoplatelet
- To study the morphological properties of NR/EPDM based rubber composite incorporated with modified graphene nanoplatelet.

1.4 Scope

This research will focus on properties of chemically modified graphene through thermal, compositional and morphological analysis via solution mixing method. The properties of pure graphene were compared with the chemically modified graphene. The findings were supported by the characterization and analysis on the thermal, compositional and morphological analysis of the sample are observed using Differential Scanning Calorimetric (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microcopy (TEM) and Scanning Electron Microscopy (SEM).

1.5 Chapter Overview

This research is divided into five chapters that describe the analytical and experimental research performed. The First Chapter is an introduction to the study that brief about objectives, problem statement, significant of study and the thesis overview. Chapter Two present the literature review that relates to the theories on graphene and previous investigations on the issues and current method to be the chemically modified graphene. The important element that included in this chapter is about the materials and processing involved and also related experimental testing. Chapter Three, provides details explanations on the methodology used for overall research work, raw materials, characterization of the materials, samples preparation and procedure property analysis and testing. In Chapter Four, the result of the characterization and analysis on the properties for the chemically modified graphene were explained in details. The Chapter 5 summarizes major findings and offers some concluding remarks. The recommendation for future project also has been included in this Chapter 5.