UNIVERSITI PUTRA MALAYSIA

GRAPHENE OXIDE/ACRYLONITRILE BUTADIENE RUBBER NANOCOMPOSITES AND THEIR PHYSICOCHEMICAL PROPERTIES

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ITMA 2018 7

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By

NASSER ABD-ULLAH MOHAMMED

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

December 2017

DEDICATION

بسم الله الرحمن الرحيم

"*Taught man that which he knew not (alalak-Quran) (العلق) عَلَمَ الإِنْسانَ ما لَم يَعلَمْ*"

Upon Allah we are rely, every challenging work needs self-efforts as well as guidance of elders especially those who were very close to our heart. Whose affection, love, encouragement and prays of day and night make me able to get such success and honor and the reason of what I become today.

My humble effort I dedicate to my sweet and loving

Father and Mother

To my sisters, my brothers, my wife, my children, and

to all who taught me in my life.

I am really grateful to all of you. You have been my inspiration, and my soul mates.

Nasser, 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment
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December 2017

Chairman : Associate Professor Suraya Abdul Rashid, PhD
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Studies on the problems pertaining to the rubber industry include looking for ways to address the problem of early deformation mainly due to the weakness in the mechanical and thermal properties of the rubber. Therefore, seeking for alternative fillers (carbonic filler) with desired characteristics such as graphite derivatives is significant for improving the rubber products performance. It is also worth mentioning that in the National Graphene Action Plan 2020, Malaysia plans to invest in graphene for the rubber industry in addition to the other various industrial applications, thus this work is timely.

However, there are some challenges related to the homogeneity of the dispersion of graphene derivatives into dry rubber. Therefore, investigating the compatibility of the solvents to reduce agglomeration of fillers in the rubber matrix is important. Also, gaining substantial improvement in the crosslinking density of the rubber structure and thermal stability are strongly desirable to enhance the rubber performance.

In this study, graphene oxide (GO) was the candidate filler (prepared by the Hummer's method), exfoliated in aqueous solution. The selected matrix was acrylonitrile butadiene rubber (NBR) which is using for producing various parts in the automobile industry. Acetone was the suitable organic solvent for NBR dissolution and compatible with GO suspension. Unvulcanised GO/NBR nanocomposite was prepared as a first objective to verify the level of distribution GO sheets into NBR. Another aim was to investigate the crosslinking formation before vulcanisation treatment. The results showed that tensile strength was increased to 81.2% compared to the unfilled NBR. The improvement is attributed to the ability of

GO networks to restrict the mobility of the NBR molecular chains before vulcanisation treatment. This result could be used effectively in the applications of thermal adhesives.

Vulcanised GO/NBR nanocomposite was prepared by combining effective techniques as a new and facile method. The influence of GO on vulcanised GO/NBR nanocomposite properties with different filler contents of GO (0.2 to 2.4 phr - part per hundred rubbers) was investigated as the second objective. The results showed improvement in the mechanical and thermal properties at 1.2 phr of GO compared to unfilled vulcanised NBR.

For comparison, a commercial filler of carbon black (CB) reinforced vulcanised NBR was fabricated in order to study the possibility of replacing it with GO/NBR nanocomposite. Graphene nanoplatelets (GNP) were also used to prepare vulcanised GNP/NBR nanocomposite for another comparison of using a different type of graphite derivative. The comparisons as the third objective were performed at 1.2 phr of GO (the percolation threshold) without chemical functionalisation. The morphology analysis, identification of functional groups, and cure characteristics of the different nanocomposites were studied.

Based on the filer contents effect, the tensile strength was increased significantly at 1.2 phr in the vulcanised GO/NBR, up to ~149% compared to the unfilled vulcanised NBR. Moreover, based on the filler type, the improvement in GO/NBR nanocomposite was better than those of the vulcanised CB/NBR and GNP/NBR nanocomposites of about 69% and 29.5% respectively. These results were confirmed by the enhancement in the crosslinking density of 38%, 17% and 29% respectively. However, the thermal stability and the glass transition temperatures have the same levels of improvement.

Finally, it is concluded that the desired characteristics of GO and the high level of GO dispersion in a polar elastomer such as NBR matrix, have essential roles in the enhancement of the GO/NBR nanocomposite properties.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

NANOKOMPOSIT GRAFENA OKSIDA / AKRILONITRIL BUTADIENA GETAH DAN SIFAT KIMIK FIZIK MEREKA

Oleh

NASSER ABD-ULLAH MOHAMMED

Disember 2017

Pengerusi : Profesor Madya Suraya Abdul Rashid, PhD
Fakulti : Institut Teknologi Maju

Kajian mengenai masalah berkaitan dengan industri getah termasuklah mencari cara untuk meningkatkan prestasi produk getah. Pencarian pengisi alternatif dengan ciri yang dikehendaki seperti grafit menggalakkan penggunaannya dalam matriks getah pada kandungan yang rendah. Oleh itu, dalam Pelan Tindakan Grafene Nasional 2020, Malaysia merancang untuk melabur di dalam grafit untuk industri getah dan digunakan dalam pelbagai aplikasi industri.

Walan bagaimanapun, terdapat beberapa cabaran yang berkaitan dengan homogenisasi pengagihan graphena derivatif ke dalam getah kering. Oleh itu, pencocokan yang baik dari pelarut memberikan kurang pengumpulan pengisi ke dalam matriks getah adalah penting pada peringkat pertama.

Dalam kajian ini, grafena oksida (GO) telah disediakan menggunakan kaedah Hummer dan dikelupas menggunakan teknik pensonikan ultra dalam larutan akueus. Kemudian, ia disebarkan kedalm getah akrilonitril butadiena (NBR). Pemilihan pelarut yang sesuai telah dipertimbangkan semasa menggunakan kaedah pencampuran larutan. Seterusnya, kajian sifat nanokomposit GO/ NBR sebelum rawatan pemvulkanan telah dilakukan sebagai tujuan pertama. Juga, nanokomposit GO/NBR tervulkan disediakan dengan menggabungkan teknik yang berkesan. Kemudian, sifat mekanikal dan untuk lima kandungan (0.2 hingga 2.4) bgs (bahagian getah seratus) diselidiki sebagai objektif kedua. Sebagai perbandingan, karbon hitam (CB) yang diperkuat NBR tervulkan dibikin yang akan menggantikan GO / NBR pada masa hadapan kerana hasil buangan CB dan ciri-cirinya yang rendah. Tambahan pula, grafena nanoplatelet (GNP) digunakan untuk menyediakan nanokomposit GNP / NBR tervulkan bagi membandingkannya sebagai derivatif

grafit yang lain. Perbandingan telah dilakukan pada 1.2 bgs GO (kandungan ambang perkolasi) dengan tiada fungsi kimia. Penilaian ini termasuk analisis morfologi, memperkenalkan kumpulan berfungsi, dan ciri-ciri reologi.

Keputusan GO / NBR tidak tervulkan menunjukkan bahawa tegasan tegangan meningkat kepada 81.2% dan modulus pada kawasan anjal meningkat kepada 238% berbanding NBR yang tak diisi. Peningkatan ini disebabkan oleh keupayaan rangkaian GO untuk menyekat pergerakan rantaian molekul NBR tanpa rawatan pemvulkanan. Hasilnya penting untuk mengesahkan keseragaman penyebaran GO dalam NBR yang boleh digunakan dengan berkesan dalam aplikasi perekat.

Berdasarkan kesan kandungan pengisi, kekuatan tegangan meningkat dengan ketara pada 1.2 bgs paut GO kepada GO / NBR yang lebih kepadatan ~149% daripada NBR tervulkan yang tidak terisi. Selain itu, berdasarkan jenis pengisi peningkatan nanokomposit GO/NBR kenaikan itu lebih baik daripada nanokomposit CB / NBR dan GNP / NBR yang lebih mempunyai 69% dan 29.5%masing-masing. Keputusan ini disahkan oleh nilai pengurangan nisbah bengkak dan peningkatan dalam kepadatan paut silang kepada masing-masing 38%, 17% dan 29%. Kestabilan haba dan suhu peralihan kaca juga mempunyai tahap peningkatan yang sama.

Akhirnya, kekonduksian elektrik GO sangat rendah berbanding pengisi yang lain.

Akhirhya, dapat disimpulkan itu dari hasil-hasil ini bahawa ciri-ciri GO yang baik dan yang diperlukan tinggi serta keseragaman penyebaran GO dalam matriks NBR mempunyai peranan penting dalam meningkatkan sifat nanokomposit GO / NBR Penambahbaikan.

ACKNOWLEDGEMENTS

First and foremost, thanks, ALLAH (ﷲ)(SWT) for his mercy which has given me the opportunity and supports me to complete this thesis.

I would like to thank my advisor, Associate Professor Dr Suraya Abdul Rashid, for her interesting proposal and valuable guidance during my study in the Institute of Advanced Technology – UPM University. Her willingness to let me work independently and her help in critically evaluating my results have been enhanced my knowledge in searching skills. I would also like to thank my committee members Professor Dr Robiah Yunus, Dr Noorkhairunnisa Mazlan and Dr Umer Rashid, for providing me helpful advice.

I have been truly fortunate to meet and learn from many exceptional people during my study at Universiti Putra Malaysia UPM, Agency Nuclear Malaysia ANM, Universiti Kebangsaan Malaysia UKM and Malaysian Rubber Board (Lembaga Getah Malaysia LGM). Among them, I wish to express gratitude to Dr Chantara, Dr Intan, Dr Young, Mr Kamarul Arifin, Mr Abdullah and Mr Ali Wani for the great help to me over the providing advises and materials. I am thankful to the staff of Chemistry department, especially to Associate Professor Dr NoorAzowa and Dr Chieng Buong in Faculty of Science - for the consultations and the tests providing.

I deeply appreciate the love and support of my extended parents (Mrs S. Al-Esawi and Major General Lawyer Mr Abdullah Al-Saedi) and my dears; my uncle Dr Abd-Ulrzzaq Al-Esawi (Symbol of will), my brothers and my sisters. I could never express how grateful I am to have you as role models. Thank you for shaping me into who I am today and for always standing beside me in my endeavours. Most of all, I thank my wife (Mrs K. Al-Hashimi) and my children (Warrd, Reem, Mohammed and Deema). I have been able to reach this goal because you have been there for me through each and every challenge. This thesis is our accomplishment.

Finally, I would like to express my gratitude to the Ministry of Higher Education and Scientific Research of my first country Iraq and University of Technology- Applied Science Department.

Nasser, December 2017, Malaysia.

I certify that a Thesis Examination Committee has met on 15 December 2017 to conduct the final examination of Nasser Abd-Ullah Mohammed on his thesis entitled "Graphene Oxide/Acrylonitrile Butadiene Rubber Nanocomposites and their Physicochemical Properties" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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ASTM	American Society for Testing and Material
BR	Butadiene Rubber
CB	Carbon Black
CB/NBR	Carbon black reinforced nitrile butadiene rubber nanocomposite
CNFs	Carbon NanoFillers
CNTs	Carbon NanoTubes
CR	Chloroprene Rubber
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Differential Thermal Gravimetric
EG	Expanded Graphitic
EPDM	Ethylene Propylene Diene Monomer
FEF	Fast Extrusion Furnace
FTIR	Fourier -Transform Infrared Spectroscopy
GIA	Global Industry Analysts
GNP	Graphite Nanoplatelets
GNP/NBR	Graphene nanoplatelets reinforced acrylonitrile butadiene rubber nanocomposite
GO	Graphene Oxide
GO/NBR	Graphene oxide reinforced acrylonitrile butadiene rubber nanocomposite
GR	Graphite
HAF	High abrasion furnace
HXNBR	Hydrogenated carboxylated nitrile butadiene rubber
ISO	International Standards Organisation

MWCNTs	Multiwall carbon nanotubes
NBR	Nitrile Butadiene Rubber
NR	Natural Rubber
PNCs	Polymer Nanocomposites
PU	Polyurethane rubber
RGO	Reduced graphene oxide
RPM	Revolution per minutes
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
SiR,	Silicon Rubber
SWCNTs	Single wall carbon nanotubes
TEGO	Thermally exfoliated graphene oxide
TEM	Transmission electron microscopy
TGA	Thermogravimetric Analysis
VPR	Vinyl Pyridine Rubber
XNBR	Carboxylated nitrile rubber
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The technological classification of polymers divides them into three main types; thermoplastic, thermoset, and elastomer (rubber). The first type can be formed by heating (melting) and the second type can be prepared by adding chemicals such as hardeners to the polymer (Carraher Jr, 2010). However, rubbers have a complex preparation process compared to other polymers in which their curing is performed chemically and physically. They have divided into thermoplastic and thermoset elastomers also. Numerous polymers have been developed including ones with high mechanical, thermal and other physical properties when they are prepared in blends or composite forms(Sperling, 2005; Visakh et al., 2013).

Polymeric composites are prepared by the dispersion of the reinforcement materials, such as fibres or particulates of various kinds of fillers, into the polymer matrix. In the 1940s, polymeric composites were used for military applications and in varied fields such as construction and automobiles, so they became alternative materials. This is due to their desired combination characteristics involving the polymer matrix and the filler (Bergmann & Andrade, 2011; Carraher Jr, 2010; McWilliams, 2006). Generally, the type, size, and the aspect ratio of the filler affect the properties of the polymer composites. Therefore, any improvement represents the results of the interaction between the polymer's matrices and the filler's properties at the interfacial region. Consequently, different types of composites have been developed by modifying the structures and the technical preparation (Das et al., 2010; Deepalekshmi et al., 2013; Ponnamma et al., 2013).

A new class of polymeric composite materials, called polymer nanocomposites (PNCs), has been developed; their reinforcement phases have dimensions in the nanometer scale. The start of PNCs was in 1990 when Toyota used nano clay reinforced Nylon-6 in some parts of their automobiles, to enhance the mechanical, thermal and barrier properties (Nguyen & Baird, 2006). Since then, interest has increased in both the academic and industrial circles in developing polymer nanocomposites with different matrices and diverse types of nanofillers (Mensah et al., 2014). Nano-scale fillers with a range of 1-100nm at least in one dimension, such as layered silicates, carbon nanotubes (CNTs), carbon nanofillers (CNFs), and exfoliated graphite derivatives, etc., are dispersed in most polymers types including elastomers (Deepalekshmi et al., 2013). Based on their dimensional morphology, nanofillers can have iso-dimensional elongated or particle shape. When only one dimension is in the nanometer range, then the layered structures have a thickness of a few nanometers and length, e.g. clays of layered silicates and layered graphite flakes (Kodal & Ozkoc, 2013).

The main advantage of using a nanofiller in conventional composites is the light weight (low contents). Also, the large surface area contact increases the interface of the polymeric matrix with the nanofiller. Thus, it enhances the mechanical strength and the thermal stability, in addition to the other physical characteristics (Kang et al., 2014; Preetha et al., 2013). Reinforcement of nanocomposite elastomers by a nanofiller depends on the interfacial adhesion between the elastomer and the nanoparticles. Hence, homogenous distribution of the nanofiller in the polymer matrix is one of the challenges that determine the optimal properties of nanocomposites. However, the disadvantages caused by using nanoparticles are the increase in viscosity, dispersion difficulties (Agglomerations) and some environmental impacts (Kodal & Ozkoc, 2013; Zeng et al., 2015).

Early research on polymer nanocomposites concerned the development of nano clay filled thermoplastic and thermoset systems. Then, research expanded into elastomers in which the nanofillers used were those such as nano-silica and carbon. Currently, the rubber nanocomposite is being developed in the area of nanomaterials as it has low weight and is an alternative material with high properties compared to the neat elastomer. Therefore, nanocomposite rubber finds application in automobiles, aerospace, coatings, electronics, biotechnology, and healthcare (Deepalekshmi et al., 2013). The last report by Global Industry Analysts (GIA) mentioned that the global market for nanocomposites was projected to reach 1.5 billion pounds by the year 2017. In Malaysia, the National Graphene Action Plan 2020, (Rahim, 2016) reported that Malaysia has taken important steps in the use of graphene in nanomaterials to develop the industry and support employment opportunities via collaboration with local universities and developed countries.

In rubber nanocomposites, fillers such as clays and carbon black are used to improve the rubber properties for extensive applications. The most common application is tyres and parts of the automobile industry in which numerous researchers were and still are attempting to increase the strength, abrasion resistance and thermal resistance with low weight and processing. Carbonic and inorganic fillers with the vulcanization materials, such as zinc oxide, sulfur, and other standards fillers etc., are modifying the material to enhance its mechanical and thermal properties. The literature on rubber nanocomposites has shown that the incorporation of nano clay in rubbers, both natural rubber (NR) and synthetic rubbers such as styrene butadiene rubber (SBR), nitrile rubber (NBR), chloroprene rubber (CR) and ethylene propylene diene monomer (EPDM) rubber etc., enhances the mechanical and other properties (Deepalekshmi et al., 2013; Kodal & Ozkoc, 2013). Still, a few works on rubbers based on using nanofillers such as nano silicate, (CNTs) and graphite have been carried out in recent years (Bergmann & Andrade, 2011; Thomas & Stephen, 2010).

Also, there are several methods and modified techniques for preparing elastomer nanocomposites such as latex blending, solution mixing, direct mixing and in-situ polymerisation (Kang et al., 2014; Wu et al., 2013). These methodologies have their own advantages and limitations; these will be explained later. Most of the reported literature on elastomer nanocomposites involves using solution mixing techniques, either using latex rubber or dissolution dry rubbers in suitable solvents(Choi et al., 2005; Kang et al., 2014; Mensah et al., 2015). The process is followed by evaporating the solvent, and mastication with the vulcanisation additives. Finally, rheological curing and standard moulding conditions should be performed to obtain the nanocomposite rubber as in most previous works (Bai et al., 2011; Tarantili, 2013).

An important aspect of elastomeric nanocomposites development is to achieve a good grouping of properties; the performance of the polymeric composites depends on factors including formulation, the dispersion homogeneity of the filler in the matrix, the adhesion between the filler and the polymeric matrix and degree of crosslinking. Moreover, thermal stability and glass transition under a range of temperatures exchange influences with the mechanical strength in rubber nanocomposites. Some studies noted in the literature have reported on the mechanical, electrical, thermal and other physicochemical properties of NBR reinforced by nanoclay (Balachandran & Bhagawan, 2012; Dick, 2014). Although the effects of nano clay content and treatment on the properties of various rubbers have been investigated, studies on other types of nanofiller such as graphite derivatives are still under research in the academic field and research centers. Also, various challenges need to be addressed, such as the dispersion level of the nanoparticles in the elastomers, optimise the characteristics and the availability of nano graphitic fillers in bulk at low cost (Malas & Das, 2015; Mao et al., 2013).

1.2 Problem Statement

Rubber is an important material in various industrial applications but it doesn’t have the ability to withstand high mechanical and thermal effects without reinforcement. Therefore, it has been strengthened by many types of available and necessary fillers to improve its properties. The technological reinforcement of rubbers involves overcoming obstacles of the rubber composites preparation by using effective and compatible fillers. However, various problems such as mechanical deformation and thermal decomposition tend to emerged after a period of time.

The characteristics of rubber also play an important role in selecting it for use in various applications with acceptable performance. For example, synthetic rubber such as acrylonitrile Butadiene Rubber (NBR) is considered as a backbone in rubber used in the automobile industry. However, there are some challenges related to improving its resistance to the swelling due to the solvents and oils. Also, although the vulcanisation treatment is used with some fillers for enhancing NBR structure, the mechanical properties are still affected by the types of filler (Deepalekshmi et al., 2013).

Fillers such as carbon black (CB), silica and other clays are still the main fillers in rubber composites and used with relatively high weight percentages. Currently, CB faces several challenges since it is derived from crude oil and generates excessive wastes. Also, the functional groups on its surfaces, such as phenol, carboxylic acids, and lactones showed incomplete interaction with the rubber matrix. Moreover, the tendency of CB particles to aggregate is mostly expected, which reduces its solidity in terms of low crosslinking density in the elastomer chains. Therefore, finding new oleo chemical independent fillers, such as graphite derivatives, have received increasing attention for the replacement of CB (Mao et al., 2013; Sperling, 2005). This is due to their high characteristics and performance as reported (Li et al., 2012). Furthermore, their thicknesses, which are less than 10 nm, make them an extremely efficient structural reinforcement in the elastomers.

Other carbon-based nanofillers such as carbon nanotubes CNTs and expanded graphitic (EG) derivatives in nanocomposite rubber exhibit outstanding properties at low loading of the filler compared with CB and unfilled rubber compounds (Bai et al., 2011; Xie et al., 2005). Some research studied the characteristics of graphite derivatives and their influences on the polymers generally and elastomers properties in specific.

Graphene Oxide (GO) is a promising nanomaterial that is commonly prepared by the chemical oxidation of graphite. However, there are some problems facing the preparation process, such as the agglomeration of the GO sheets in the rubber matrix. The agglomerates can be one of the causes of the micro-defects in the rubber composites, or they reduce the cross-linking between the NBR chains. This is attributed to the incomplete exfoliation of the GO sheets, also due to the heterogeneous dispersion of GO in the rubber nanocomposite.

It is worth mentioning that the direct mixing technique does not provide a homogeneous dispersion of nanofiller into the rubber matrix as reported by several researches (Fryczkowski et al., 2013; Gudarzi & Sharif, 2012; She et al., 2014; Wang; et al., 2013). Therefore, dissolution of dry NBR in a suitable solvent with compatible viscosity makes the solution mixing method more effective method. The further critical issue should be investigated, is the compatibility between the GO suspension and the rubber solution.

Even though Graphite Nanoplatelets (GNP) is distinct graphitic nanofiller with high surface area, its characteristics is dissimilar compared to GO and CB. In this case, the comparison among the properties of GO/NBR, GNP/NBR and CB/NBR nanocomposites are required. This investigation could provide necessary information about the differences in the properties between two different groups of carbonic fillers.

Regarding the thermal properties, early thermal decomposition is a common problem facing rubber in high-temperature environments in hoses and seals applications. Therefore, dispersion of GO in the GO/NBR nanocomposites could improve the thermal stability. Accordingly, enhancement of the cross-linking density can increase the glass transition temperature T_g at low specific contents having an essential influence on the storage modulus and the weight residue for the rubber nanocomposite, compared with the unfilled NBR (Malas & Das, 2015; Wang et al., 2012).

This research is an important contribution for studying the possibility of using graphite derivatives in the rubber industry. Thus, it has not yet been used commercially, because it is still under academic and research work. Based on the recent reports, Malaysia has an interest in developing the technology of using graphite derivatives in the industry and in the rubber manufacturing in specific (Ali et al., 2017). This is one of the main justifications to set this proposal.

1.3 Hypothesis of the Study

Graphene possesses high physical and chemical characteristics. This encourages the study of improving the mechanical and thermal properties of rubber composites reinforced by one of the graphite derivatives. Thus, to search the possibility of replacing carbon black was hypothesised as in the following;

A few amount of graphene oxide (between 0.2 to 1.2 phr) can reinforced effectively a synthetic rubber such as NBR. The improvement in the mechanical properties is attributed to the presence of the functional group of oxygen on the GO surfaces. Also, the increase of the cross-linking of the rubber chains should increase the tensile strength of the GO/NBR nanocomposite.

The large surface area of GO sheets contributes to increase the interfacial interaction between NBR and GO. This characteristic reduces the swelling ratio when the GO/NBR nanocomposite is placed in the oil or solvents medium, thus its enhancing the crosslinking density of the composite.

High thermal capacity of GO and its ability to restrict the rubber chains mobility can increase the thermal stability of the GO/NBR nanocomposite. Furthermore, the increase in the glass transition temperature is attributed to the increment in the storage modulus. This result led to increase the resistance of the rubber nanocomposite to the thermal decomposition.

1.4 Objectives of the Study

The present study was undertaken to explore the potential of GO-reinforced NBR in the preparation of unvulcanised and vulcanised GO/NBR rubber nanocomposites. Also, it aimed to compare the characteristics of the vulcanised GO/NBR nanocomposite with the other carbonic/NBR nanocomposites. The salient objectives of the current research were:

1.4.1 To investigate the effectiveness of the dispersion of GO into NBR (dry) via the preparation of an unvulcanised GO/NBR rubber nanocomposite. Also, to characterise unvulcanised GO/NBR nanocomposites and their mechanical properties for different contents of GO.

1.4.2 To investigate the influence of GO on the mechanical strength and thermal stability of the vulcanized GO/NBR rubber nanocomposite at different low contents of GO compared to unfilled NBR.

1.4.3 To determine the variances in the characteristics and properties between the vulcanised GO/NBR nanocomposite and other rubber nanocomposites of NBR reinforced by CB and GNP at the optimal contents of GO.

1.5 Scope and Limitation of the Study

The scope of this study focuses on investigating the influence of the desired characteristics of GO on the physicochemical properties of GO/NBR nanocomposite. Therefore, unvulcanised and vulcanised GO/NBR rubber nanocomposites were prepared and characterized. This research covers experimental work based on the objectives, so the scope is summarized as follows;

1. Unvulcanised GO/NBR nanocomposites were prepared with five different contents of GO. Suitable NBR solution was prepared via selection the compatible solvent based on the ability of dissolution NBR and its viscosity. The parameters of the sonication process were adjusted in order to exfoliate the GO in a compatible aqueous solution. The mixing process and the qualitative of the coagulant mixture were monitored. Finally, the verification of the homogeneity was observed by characterising the GO/NBR nanocomposites using XRD, FTIR and SEM analysis. Also, by testing the tensile strength and the electrical conductivity at different contents of GO. The purpose was to verify the evidence of the functional groups role in the interfacial interaction between the GO sheets and the NBR chains. The expected findings could approve the effectiveness of using the product for coating and adhesives applications as a novel work.

2. Vulcanised GO/NBR nanocomposites preparation were performed for five different contents of GO as the second objective. This is for studying the influence of GO on the cure characteristics of the composites compared to unfilled NBR at an optimal temperature and time. The enhancement in the maximum torque and the curing time at 90% of torque were determine at optimal content of GO too. This test was essential to support the crosslinking forming interpretation and the curing time .

   Furthermore, analysing the vulcanised GO/NBR nanocomposites crosslinking density by swelling test, the tensile strength properties by tensile stress-strain test, and the storage modulus and loss energy using the DMA tests in the range of temperatures between -50 to +50 ºC were performed. The results were supported by the morphology observation analysis of the SEM micrograph for the fractured surfaces of the tensile test samples .

In the same context, the thermal decomposition behaviour of the unfilled NBR and the GO/NBR nanocomposites, were studied based on TGA and DTG analysis. The temperature equivalent to the initial thermal degradation temperature (T onset) at percolation threshold of GO contents was significant for analysing the thermal/mechanical properties. Also, the heat flow capacity provided needed information about T_g using DSC tests at the same five contents of GO in the vulcanised GO/NBR nanocomposites. Finally, from the electrical properties test of this rubber nanocomposite, high electrical resistance of GO in the nanocomposites was approved.

3. Influence of dispersion different types of carbonic filler in NBR matrix was determined in this study. Therefore, two different groups of filler of carbon black (CB)-N550 and graphene nanoplatelets (GNP)-C750 were used. The variances in the characteristics and properties between the vulcanised GO/NBR nanocomposite (which was mentioned above at 2) and other rubber nanocomposites of CB/NBR and GNP/NBR at the optimal contents of GO were studied.

In this part of the scope, as a novel work, the study involved analysing and comparing the mechanical and thermal properties in order to determine the variances in the enhancement due to using different fillers. Morphology, non-functionalisation, cure characteristics, and swelling ratio reduction of the graphitic rubber nanocomposites provide essential indications. This is concerning the expected improvement in the tensile strength, elasticity modulus, storage modulus, and the hardness property better than the carbon black base rubber composite.

Correspondently, their thermal properties were influenced also by optimal filler contents. The thermal decomposition, stability, and Glass transition temperatures provide further evidence of the level of the filler dispersion (agglomerations and aggregations) in the NBR matrix. Also, analysis can interpret the variances built on the structure, size, shape and the surface interaction of the fillers as concluded .

The electrical conductivity of the rubber nanocomposites was tested for GNP, CB, and GR reinforced NBR. As these fillers were not functionalised, the low impedance against the electrical charges in the rubber composites is expected.

The limitations of the study are to improve the mechanical and thermal properties of vulcanised NBR and reduce the weight. In the conclusion, the study mainly aimed to obtain high performance of rubber parts of automobiles, aerospace, and miscellaneous applications in the industry.

1.6 Outline of the Thesis

The thesis consists of five chapters, and the contents of each chapter are as outlined below:

Chapter 1 includes an introduction which presents a brief background of the field of elastomeric composites materials focusing on filler types and the nanosize effect. Also, the chapter highlights the research problem statements, the hypothesis, the research objectives and the scopes of the thesis.

Chapter 2 reviews the available literature concerning the fundamentals of polymeric composites. Also, information is given about NBR, the types of fillers available in general and graphene more specifically, and the preparation methods. In the characterisation section, the rheological curing and the crosslinking density, in addition to the morphology, are demonstrated in this chapter along with the main physicochemical properties.

Chapter 3 covers the materials which were used and the methodology. Also, the chapter includes GO exfoliation and dispersion into NBR. The preparation steps of unvulcanised (GO/NBR) nanocomposites with different contents of GO are showed. The vulcanization treatment of GO/NBR nanocomposite followed by the cure characteristics is displayed. For comparison, there is the preparation of another two rubber nanocomposites which were CB/NBR and GNP/NBR. The characterisation and properties of the rubber nanocomposites are demonstrated using the techniques of the rheometer, FTIR, XRD, SEM, the swelling test, tensile tests, DMA, hardness tests, TGA-DTG, DSC, and the electrical conductivity using two techniques.

Chapter 4 represents the results and discussions of all the tests including the data, the graphs, and the results. In the first section, the unvulcanised GO/NBR nanocomposite preparation includes the dissolution of NBR and the exfoliation of GO. The dispersion of the GO into the NBR is demonstrated and discussed. Then, there is a verification of the dispersion process by testing the characteristics and properties of the unvulcanised GO/NBR nanocomposite at different contents of GO.

The second section in this chapter is related to a discussion of the effect of the filler content on the vulcanised GO/NBR nanocomposites. The following characteristics are assessed: the cure characteristics, the morphology using (SEM, XRD, FTIR), the crosslinking density, the mechanical properties (tensile strength, storage modulus, loss modulus and loss energy (tan δ)), and the hardness property. Also, the thermal properties are determined, including the thermal stability (TGA-DTG) and the glass transition temperature T_g using DSC tests. In addition, the electrical conductivity property was studied.

The third section is related to the comparison of the previous section in this chapter involving vulcanised GO/NBR nanocomposites, with the other rubber nanocomposites which are filled with GNP and CB.

Chapter 5 includes the conclusions which were achieved and the suggested opportunities for future studies. These involve the essential conclusions of preparation and characterisation of unvulcanised GO/NBR nanocomposites. Also, the vulcanised GO/NBR nanocomposite characteristics and properties are displayed. Then, the main variances between the properties of the vulcanised GO/NBR, GNP/NBR, and CB/NBR nanocomposites are listed. Finally, future works and recommendations are suggested.

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