SYNTHESIS AND CHARACTERIZATION OF HYDROXYL TERMINATED NATURAL RUBBER-GRAFTED GRAPHENE OXIDE

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ABSTRACT

Hydroxyl terminated natural rubber (HTNR) was prepared from deproteinized natural rubber (DPNR) via oxidative degradation method in toluene at 80 ℃, in the presence of cobalt (II) acetyl acetonate (CAA) as oxidizing agent and sodium borohydride ($NaBH_4$) as reducing agent. Gel Permeation Chromatography (GPC) analysis revealed the molecular weight (MW) of the obtained HTNR were 69 000 g/mol (Mn) and 244 000 g/mol (Mw), respectively; while Fourier Transform Infrared (FTIR) analysis confirmed the presence of hydroxyl groups in the prepared HTNR. Subsequently, graphene oxide (GO) was grafted onto HTNR structure for the improvement of thermal property using tetrahydrofuran (THF) as solvent with GO loading of 5 and 10 wt%. The degree of crosslinking was determined based on the residue analysis from thermal gravimetry analysis (TGA) and revealed almost no grafting occurs for HTNR-g-GO of 5 wt% GO while HTNR-g-GO for 10 wt% GO resulted in 8.5 % grafting. FTIR analysis of both samples show consistent finding with the degree of crosslinking where the intensity of hydroxyl and epoxide peaks for HTNR-g-GO (10 wt%) was higher compared to HTNR-g-GO (5 wt%). Meanwhile, differential scanning calorimetry (DSC) analysis showed an improved thermal stability of the prepared HTNR-g-GO in comparison to the HTNR and DPNR sample. In conclusion, the addition of GO into HTNR via grafting process can be an effective method for the preparation of nanocomposite with enhance properties.

ABSTRAK

Getah asli berterminal hidroksil (HTNR) dihasilkan daripada getah asli ternyahprotein (DPNR) dalam toluena melalui degradasi oksidatif pada suhu 80 ℃, di hadapan kobalt (II) asetil asetonate (CAA) sebagai ejen pengoksidaan dan sodium borohiderat ($NaBH_4$) sebagai ejen pengurangan. Analisis Kromatografi Kebolehtelapan Gel (GPC) mendedahkan berat molekul (MW) daripada HTNR yang diperolehi adalah 69 000 g/mol (Mn) dan 244 000 g/mol (Mw), masing-masing; sementara Analisis Inframerah Jelmaan Fourier (FTIR) mengesahkan kehadiran kumpulan hidroksil dalam HTNR yang disediakan. Selepas itu, grafin oksida (GO) telah dicangkukkan ke dalam struktur HTNR untuk penambahbaikan sifat terma menggunakan tetrahidrofuran (THF) sebagai pelarut dengan pemuatan GO 5 dan 10 wt%. Darjah sambung silang ditentukan berdasarkan analisis residu dari termogravimetrik (TGA) dan mendedahkan hampir tidak ada cantuman terjadi untuk HTNR-g-GO (5 wt%) sementara HTNR-g-GO untuk 10 wt% GO menghasilkan 8.5% cantuman. Analisis FTIR bagi kedua-dua sampel menunjukkan penemuan yang konsisten dengan darjah sambung silang dimana intensiti puncak hidroksil dan epoksida untuk HTNR-g-GO (10 wt%) adalah lebih tinggi berbanding dengan HTNR-g-GO (5 wt%). Sementara itu, analisis kalorimeter pengimbas pembezaan (DSC) menunjukkan kestabilan terma yang lebih baik daripada HTNR-g-GO yang disediakan berbanding dengan sampel HTNR dan DPNR. Sebagai kesimpulan, penambahan GO ke HTNR melalui proses cangkukkan boleh menjadi kaedah yang berkesan untuk penyediaan nanokomposit dengan sifat-sifat yang lebih baik.

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LIST OF ABBREVIATIONS

AN	-	Acrylonitrile
CAA	-	Cobalt acetylacetonate
CNT	-	Carbon nanotube
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
CTNR	-	Carboxyl terminated natural rubber
DPNR	-	Deproteinized natural rubber
DSC	-	Differential scanning calorimetry
FTIR	-	Fourier transform infrared
GMA	-	Glycidyl methacrylate
GNPs	-	Graphene nanoplatelets
GO	-	Graphene oxide
GO/SBR	-	Graphene oxide/Styrene butadiene rubber
GPC	-	Gel Permeation Chromatography
GRGs	-	General rubber goods
HEA	-	2-hydroxyethylacrylate
HEC	-	2-hydroxyethylcinnamate
HNO_3	-	formic nitric acid
HNT	-	Halloysite nanotube
HNT-g XNBR	-	Halloysite nanotube grafted carboxylated nitrile butadiene rubber
HTLNR	-	High telechelic liquid natural rubber
HTENR	-	Hydroxyl terminated epoxidized natural rubber
HTNR	-	Hydroxyl terminated natural rubber
HTNR-g-GO	-	Hydroxyl terminated natural rubber grafted Graphene oxide
HTPB	-	Hydroxyl terminated polybutadiene
H_2O	-	Water

H_2O_2	-	Hydrogen peroxide
H_3PO_4	-	Phosphoric acid
H_2SO_4	-	Sulphuric acid
IPNs	-	Interpenetrating networks
IR	-	Infrared spectrum
ITO	-	Indium trioxide
KBr	-	Potassium bromide
$KClO_3$	-	Potassium chlorate
$KMnO_4$	-	Potassium permanganate
$K_2S_2O_8$	-	Potassium persulfate
LED	-	Light emitting diodes
LNR	-	Liquid natural rubber
LNR-6	-	Liquid natural rubber-6
MA	-	Maleic anhydride
MMA	-	Methyl methacrylate
Mn	-	Number average molecular weight
MRB	-	Malaysian rubber board
Mw	-	Weight average molecular weight
MW	-	Molecular weight
MWCNT	-	Multi-walled carbon nanotube
$NaBH_4$	-	Sodium borohydride
$NaNO_3$	-	Sodium nitrate
NBR	-	Nitrile butadiene rubber
NO_2	-	Nitrogen dioxide
NR	-	Natural rubber
NR-g-GMA	-	Natural rubber grafted Glycidyl methacrylate
NR/LLDPE	-	Natural rubber/ Linear low density polyethylene
N_2O_4	-	Dinitrogen tetraoxide
OLED	-	Organic light emiting diode
PA-6	-	Polyamide-6
PDI	-	Polydispersities
PLA-NR	-	Poly(lactic acid)-Natural rubber
PMMA	-	Poly(methyl methacrylate)
PS	-	Polystyrene

P_2O_5	-	Phosphorus pentoxide
SBR	-	Styrene butadiene rubber
SEM	-	Scanning emission microscopy
TCE	-	Transparent conducting
TCLNR	-	Telechelic chlorinated liquid natural rubber
TELNR	-	Telechelic epoxidized liquid natural rubber
T_g	-	Glass transition temperature
TGA	-	Thermogravimetric analysis
THF	-	Tetrahydrofuran
TLNR	-	Telechelic liquid natural rubber
TLSR	-	Telechelic liquid synthetic rubber
TPEs	-	Thermoplastic elastomers
TPNRs	-	Thermoplastic natural rubbers
UV	-	Ultraviolet
VPR	-	Vinyl pyride rubber
XNBR	-	Carboxylated nitrile butadiene rubber

LIST OF SYMBOLS

%	-	Percent
%wt	-	Weight percent
℃	-	Degree Celsius
℃/min	-	Degree Celsius per minute
cm^2/V s	-	Square centimeter per volume second
cm^{-1}	-	Per centimeter
m^2/g	-	Square meter per gram
g/mol	-	Gram per mol
g/cm^3	-	Gram per cubic centimetre
μm	-	Micrometer
μl	-	Microliter
g	-	Gram
h	-	Hour
mg	-	Milligram
mL	-	Milliliter
mL/minute	-	Milliliter per minute
nm	-	Nanometer
GPa	-	Gigapascal
MPA	-	Megapascal
TPa	-	Terapascal
pH	-	Potential of hydrogen
phr	-	Parts per hundred rubbers
rpm	-	Rotation per minute
W/m K	-	Watt per meter kelvin
w/v	-	Weight per volume
v/v	-	Volume per volume
et al.	-	And other

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Natural rubber (NR) is a renewable polymeric material, which is produced by *Hevea brasiliensis trees*. NR includes 94% polyisoprene in nearly 100% cis 1,4 polyisporene. Southeast Asian region is the world's most important plantation area for rubber. Thailand, Indonesia and Malaysia are three main producers with total production indicating 75% of the global output (Krungsi Research, 2016). NR is broadly used in the production of tires and general rubber goods (GRGs) such as rubber hose, bumper, anti-vibration rubber, and conveyer belt. Samsuri (2010) reported that, automotive industry is the most of natural rubber manufacture.

Moreover, NR is an important material with unique characteristics such as good strength, elasticity, flexible, resilience and abrasion resistance. However, the application of natural rubber is limited as it can be easily degraded by ozone, exposure to light, oxidation and owing to the presence of C = C in polyisoprene chain. Therefore, many researchers have concentrated on chemical modification of natural rubber to provide added value to NR.

Chemically modified natural rubber has been developed widely to obtain new functional polymeric materials. Hence, it opens many potentials to improve the properties of natural rubber such as gas permeability, resistance to oil or fire resistance. Several modifications had been done to modify natural rubber, including cyclisation, epoxidation, halogenation, hydroboration, hydrogenation and maleinization (Broosse J.C. *et al*., 2000; Heijden J.V.D, 2002). One of breakthrough in this area of research is liquid natural rubber (LNR), which is depolymerised natural rubber, containing a shorter polymeric chain. It is well recognized by its stickiness, but it has excellent crosslinking reactivity with molecular weight (Mw) lower than 10^5 (Heijden J.V.D, 2002). Several methods exist to manufacture liquid natural rubber such as mechanochemical peptization, thermal, photolysis, mechanical and redox method. Another benefit of liquid natural rubber is that the material can enhance processability of natural rubber, since LNR can act as adhesive, sealing agent, compatibilizer, plasticizer, viscosity modifier and caulking agent (Azhar *et al*., 2016). Recently, LNR is employed in the reaction rather than natural rubber because of easily dissolved in non-polar solvents, low molecular weight, contain reactive terminal groups and easy to process (Kebir *et al*., 2005). However, due to the presence of high proportion of elastic inactive chain, telechelic liquid natural rubber (TLNR) has often been suggested.

TLNR is a modified LNR with shorter polymeric chains (less than 10 000 g/mol) and contains several reactive terminal groups. A popular example of TLNR is hydroxyl terminated natural rubber (HTNR). There are few methods to construct HTNR such as depolymerization of DPNR by redox degradation, photochemical degradation, ozonolysis degradation, and oxidative degradation. Baharulrazi *et al*. (2015) reported that oxidative degradation is the most desirable method in order to obtain a low molecular weight of HTNR. In addition, it was found that the oxidative degradation can yield HTNR with reactive terminated functional group (Giang *et al*., 2016).

Hydroxyl terminated natural rubber is produced by deproteinized natural rubber (DPNR) as a raw material. DPNR is a purified form of natural rubber (NR) with very low nitrogen and ash contents. HTNR is suitable for further chain extension and crosslinking, also it is useable as compatibilizer, adhesives, vulcanizing mixtures for golf ball and tires. HTNR also has big potential in replacing imported binder that is hydroxyl terminated polybutadiene (HTPB) (Onn *et al*., 2014). In addition, more valuable product can be created by modifying HTNR which contain hydroxyl groups (chain extension reaction) and has low molecular weight lead to easy processing.

Chemical modification through addition of reinforcing filler into rubber matrix to improve its properties has been an important field of investigation in rubber industry. To name a few, this includes graphene (Papageorgiou *et al*., 2015), carbon black (Grundfest *et al*., 1994), graphene oxide (Mao *et al*., 2013), carbon nanotubes (Bokobza *et al*., 2012), multi-walled carbon nanotubes (MWCNT) (Ali *et al*., 2014).

Recently, the use of graphene as reinforcing filler has been widely reported due to its outstanding properties such as has high surface area, high tensile strength, superior electrical conductivity, high electron mobility, large aspect ratio, flexibility and thermal conductivity (Kuilla *et al*., 2010). However, graphene is not always the best selection due to its high manufacturing cost, difficulty for dispersion, lack functional groups and hydrophobic.

Recently much attention has been devoted to graphene oxide, the oxidation product of graphene. Graphene oxide (GO) has good dispersibility in water and other organic solvents due to the presence of the oxygen functionalities. Graphene oxide can be used as a filler for various polymer matrixes to increase mechanical and thermal properties. The function of graphene oxide is electrical insulator because of the disturbance of its sp^2 bonding networks (Papageorgiou *et al*., 2015). GO sheets have apparent thickness of 1 nm and lateral size up to tens of micrometers. It gives GO sheets very large surface area (Kim *et al*., 2010). GO can be produced from Hummers or Brodie technique.

Paran *et al*. (2016) reported that the carboxylated nitrile butadiene rubber (XNBR)-grafted halloysite nanotubes (HNTs) effectively improve morphology and mechanical properties of the PA6/ NBR TPEs by direct melt mixing method. Rosli, N. A *et al*. (2016) reported that the addition of liquid natural rubber (LNR) significantly improved the tensile and impact strength of poly(lactic acid)-natural rubber (PLA-NR) by melt blending. Recently, Quan *et al*. (2018) studied that the effect of graphene nanoplatelets (GNP) on the mechanical properties, fracture toughness and lap shear strength of rubber-modified epoxy adhesive. The result showed that the addition of GNP had no effect on the glass transition temperature. The tensile modulus increased due to the addition of 0.1% GNP with not subsequent enchance observed for higher GNP loading. The tensile strength was unaffected by the addition small amount of GNP. A systematic decrease in lap shear strength was determined due to the addition of GNP.

The addition of reinforcing filler into the natural rubber matrix is generally through melt mixing, mixing solution as well as chemical modification. Melt mixing is a preparation method chosen by industry because it combines low cost and speed (J. Wu *et al*., 2013). The advantages of this method can be used for both polar and non-polar elastomers (K.K. Sadasivuni *et al*., 2014). While mixing solution is the most commonly used in academic studies for the production of natural rubber matrix because the filler can be used and incorporated in the matrix without significant processing (S.K. Kumar *et al*., 2013). Nevertheless, both melt and mixing solution methods are associated with aggregation of filler within the composite structure which is detrimental to the properties of the material.

Chemical modification, on the other hand, enables the interaction of filler and polymer matrices by both non-covalent and covalent bonding. Non-covalent bonding involves the intercalation of monomer between the layers of GNPs, thus producing well-dispersed filler in the polymer matrix. The example of chemical modification is grafting. Grafting is one of the most important technique. The advantages using this method are better compatibility between filler and polymer matrix. Therefore, in this research grafting method have been used to get good interfacial between GO and HTNR thus increase thermal properties of HTNR.

1.2 Problem Statement

Natural rubber is high molecular weight cis 1,4 polyisoprene that is main renewable material applied in many applications especially in manufacturing tires.

Natural rubber has excellent dynamic properties, tensile strength, tear strength and elongation properties. However, due to the presence of C=C in polyisoprene chain, natural rubber has less toughness, difficult to process, poorer ageing properties and easily degraded by ozone. Therefore, chemical modification of natural rubber was achieved to improve the properties of natural rubber.

Liquid natural rubber is modified natural rubber having similar structure as natural rubber with low molecular weight and shorter polymer chain. Nor and Ebdon, (1998) stated that, liquid natural rubber can flow at room temperature that makes easy to mix and cheaper to process than natural rubber. Several methods can be used to produce liquid natural rubber such as mechanochemical peptization, thermal, photolysis, mechanical and redox method. However, due to the presence of high proportion of elastic inactive chain end on LNR, it is better to used Telechelic Liquid Natural Rubber (TLNR).

Telechelic liquid natural rubber (TLNR) is another type of liquid natural rubber with lower molecular weight and contain functional groups. Example of TLNR are hydroxyl terminated natural rubber (HTNR) and carboxyl terminated natural rubber (CTNR). However, HTNR is more effective than CTNR because HTNR is lower molecular weight than CTNR (Ibrahim *et al.,* 2014). HTNR is modified liquid natural rubber which contains hydroxyl functional groups. Method used to produce HTNR are photochemical degradation, redox degradation, ozonolysis degradation and oxidative degradation. Based on (Baharulrazi *et al.*, 2015; Giang *et al.*, 2016), oxidative degradation is the best method to produce hydroxyl terminated natural rubber with low molecular weight and contain hydroxyl functional groups.

To date various reinforcing fillers have been incorporated into NR/elastomers in order to provide the enhancement in strength and toughness. Reinforcing fillers such as carbon black, carbon nanotube, silica and montmorillonite have been reported to improve the mechanical properties of rubber nanocomposites. Based on Paran *et al*. (2016) reported that XNBR grafted HNTs can improve the morphology and mechanical properties of PA6/NBR TPEs by direct melt mixing method.

However, there is no research have been reported on the addition of reinforcing filler in to liquid natural rubber.

In this research, graphene oxide (GO), the oxidation product of graphene will be inserted into hydroxyl terminated natural rubber (HTNR) backbone via grafting method. HTNR is one type of telechelic liquid natural rubber with hydroxyl groups as a dominant. The prepared material HTNR-grafted-GO will be served as novel material with improved strength and toughness. To date graphene/NR nanocomposite prepared using reactive liquid rubber has yet to be reported. The formation of grafting will ensure a good adhesion/interfacial between GO and NR matrix thus enhance the properties of the prepared nanocomposite.

1.3 Objectives

The objectives of this research are:

1. To synthesis hydroxyl terminated natural rubber (HTNR) from DPNR via oxidative degradation method.

2. To characterise the prepared HTNR and HTNR-grafted-GO in terms of molecular weight, grafting percentage and thermal properties.

1.4 Scope of Study

In order to achieved the objective, there are three scopes have that been identified in this research:

1. HTNR from DPNR will be synthesised using oxidative degradation method at 80 ℃ in the presence of cobalt (II) acetyl acetonate (CAA) (5%

w/w) as oxidizing agent, sodium borohydride ($NaBH_4$) for reduction process, and ethanol (10% v/v).

2. The grafting of graphene oxide (GO) into HTNR will be conducted using tetrahydrofuran (THF) as the solvent and the solution will be stirred at room temperature for 24 h.

3. The percentage of graphene oxide was for 5% and 10% by weight of HTNR in order to obtain better thermal properties.

4. FTIR, DSC, GPC, and TGA are used to characterise the HTNR and HTNR-g-GO. FTIR is used to recognize the functional groups which present in the HTNR and HTNR-g- GO structure. The molecular weight of the prepared HTNR will be determined using GPC. DSC analysis is used to measure the glass transition temperature of the HTNR before and after the grafting. Finally, TGA is used to measure the stability of HTNR and HTNR-g-GO as a function of temperature or time.

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