

SYNTHESIS AND CHARACTERIZATION OF HYDROXYL TERMINATED
LIQUID EPOXIDIZED NATURAL RUBBER GRAFTED GRAPHENE OXIDE

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ABSTRACT

Hydroxyl terminated liquid epoxidized natural rubber (HTLENR) was synthesized via an oxidative degradation of liquid epoxidized natural rubber (LENR) in the presence of cobalt acetylacetonate as an oxidizing agent. The subsequent treatment was conducted using sodium borohydride as a reducing agent for the formation of hydroxyl group. In order to obtain a low molecular weight of HTLENR, the reaction times were varied for 1 h, 4 h, 7 h, 10 h, and 24 h. Gel permeation chromatography was used to determine the molecular weight of HTLENR. The lowest molecular weight was achieved after 24 h reaction where M_w and M_n were 21869 g/mol and 3233g/mol, respectively. However, HTLENR prepared for 10 h reaction time with M_w and M_n of 37545 g/mol and 3879 g/mol, respectively was chosen as an optimum parameter for further reaction due to the economic factor as well as based on the highest rate of chain scission. The molecular structure of HTLENR was analyzed using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR). The appearance of broad peak around 3250 - 3550 cm^{-1} in FTIR spectrum after the reaction confirmed the existence of OH group in the prepared HTLENR and the peak intensity increased as the reaction time increased. The NMR analysis confirmed the highest hydroxyl content was achieved at 10 h reaction with the amount of approximately 7.56%. HTLENRs with different graphene oxide (GO) loadings (1%, 5% and 10% w/w) were produced by grafting reaction. The FTIR analysis showed a broad peak of OH in HTLENR-g-GO at higher amount of GO loading. Meanwhile, the differential scanning calorimetric analysis revealed the increase of glass transition temperature as the amount of GO in the HTLENR-g-GO increased. Thermal stabilities of HTLENRs were analyzed by thermogravimetric analysis which showed that at 1 wt% and 5 wt% of GO loadings give a higher decomposition temperature compared to the 10 wt% GO loading. Degree of grafting was calculated to be 40.56% at 5 wt% of GO loading and remained almost constant at 10% of GO loading. Based on the result obtained, it can be concluded that HTLENR was successfully produced with the optimum degree of grafting at 5 wt% GO loading.

ABSTRAK

Cecair getah asli terepoksida terminal hidroksil (HTLENR) telah disintesis melalui penguraian beroksida menggunakan cecair getah asli epoksida (LENR) dengan kobalt asetil asetonat sebagai satu agen pengoksida. Rawatan seterusnya dilakukan dengan menggunakan natrium borohidrida sebagai satu agen penurunan untuk pembentukan kumpulan hidroksil. Untuk mendapatkan berat molekul HTLENR yang rendah, masa tindak balas di pelbagaikan pada 1 jam, 4 jam, 7 jam, 10 jam dan 24 jam. Kromatografi penyerapan gel digunakan untuk menentukan berat molekul HTLENR. Berat molekul terendah dicapai selepas tindak balas 24 jam di mana M_w dan M_n masing-masing adalah 21869 g/mol dan 3233 g/mol. Walau bagaimanapun, HTLENR yang disediakan selama 10 jam masa tindakbalas dimana M_w dan M_n masing-masing adalah 37545 g/mol dan 3879 g/mol dipilih sebagai parameter optima untuk reaksi selanjutnya disebabkan oleh faktor ekonomi dan kadar pemotongan rantai HTLENR yang lebih tinggi. Struktur molekul HTLENR dianalisis menggunakan jelmaan inframerah Fourier (FTIR) dan resonan magnetik nuklear (NMR). Kemunculan puncak lebar sekitar 3250-3550 cm^{-1} di dalam spektrum mengesahkan kewujudan kumpulan OH di dalam HTLENR dan puncak keamatan bertambah apabila masa tindakbalas meningkat. Pengiraan kadar hidroksil di dalam HTLENR menggunakan NMR analisis mengesahkan bahawa masa tindakbalas pada 10 jam memberikan kandungan hidroksil tertinggi iaitu 7.56%. HTLENR gabungan grafena oksida (GO) pada kadar yang berbeza (1%, 5% dan 10% w / w) dihasilkan melalui tindakbalas cangkuk. Analisis FTIR menunjukkan puncak OH yang lebih luas di HTLENR-g-GO pada jumlah GO yang lebih tinggi. Sementara itu, analisis dari pengimbasan perbezaan calorimetri menunjukkan suhu peralihan kaca semakin meningkat apabila jumlah GO yang digunakan di dalam tindakbalas HTLENR-g-GO meningkat. Kestabilan haba HTLENR dianalisis oleh analisis termogravimetrik menunjukkan 1 wt% dan 5 wt% daripada kandungan GO memberikan suhu penguraian yang lebih tinggi berbanding 10 wt% GO. Darjah pengcangkukan dikira 40.56% pada 5 wt% GO dan peratusan mulai hampir sama pada 10 wt% kandungan GO. Berdasarkan keputusan yang diperolehi, dapat disimpulkan bahawa HTLENR berjaya dihasilkan dengan darjah pengcangkukan optimum GO pada 5 wt% kandungan GO.

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LIST OF ABBREVIATIONS

NR	-	Natural Rubber
ENR	-	Epoxidized Natural Rubber
LR	-	Liquid Rubber
LSR	-	Liquid Synthetic Rubber
LNR	-	Liquid Natural Rubber
LENR	-	Liquid Epoxidized Natural Rubber
TLR	-	Telechelic Liquid Rubber
TLNR	-	Telechelic Liquid Natural Rubber
CTNR	-	Carboxyl Terminated Liquid Rubber
HTNR	-	Hydroxyl Terminated Liquid Rubber
HLNR	-	Hydroxyl Liquid Natural Rubber
HTENR	-	Hydroxyl Terminated Epoxidized Natural Rubber
HTLENR	-	Hydroxyl Terminated Liquid Epoxidized Natural Rubber
CTBN	-	Carboxyl-terminated butadiene
CTPB	-	Carboxyl Terminated Polybutadiene
ATNBR	-	Amine Terminated Acrylonitrile Butadiene
HTPB	-	Hydroxyl-terminated polybutadiene
ETBN	-	Epoxy-terminated butadiene
ATBN	-	Amine-terminated butadiene
BR	-	Butadiene Rubber
SBR	-	Styrene Butadiene Rubber
NBR	-	Nitrile Butadiene Rubber
CB	-	Carbon Black
GO	-	Graphene Oxide
rGO	-	Reduced Graphene Oxide
CNT	-	Carbon Nanotube
SWCNT	-	Single Walled Carbon Nanotube
MWCNT	-	Multiwalled Carbon Nanotube
FET	-	Field Effect Transistor
NMP	-	N-Methyl-2-Pyrrolidinone

UPR	-	Unsaturated Polyester Resin
NaBH ₄	-	Sodium Borohydride
MgSO ₄	-	Magnesium Sulphate
H ₂ SO ₄	-	Sulphuric Acid
CAA	-	Cobalt Acetyl Acetonate
FAA	-	Ferric Acetyl Acetonate
H ₂ O ₂	-	Hydrogen Peroxide
HNO ₃	-	Nitric Acid
KClO ₃	-	Potassium Chlorate
KMnO ₄	-	Potassium Permanganate
H ₃ PO ₄	-	Phosphoric Acid
Na ₂ WO ₄	-	Sodium Tungstate
CH ₃ COOH	-	Acetic Acid
FE(II)	-	Iron
DMF	-	Dimethyl Formamide
PE	-	Polyester
PCL	-	Poly(ϵ -caprolactone)
PAA	-	Poly(acrylicacid)
TSH	-	P-toluenesulfonyl
DGEBA	-	Bisphenol-A diglycidyl ether
THF	-	Tetrahydrofuran
GPC	-	Gel Permeation Chromatography
FTIR	-	Fourier Transform Infrared
NMR	-	Nuclear Magnetic Resonance
DSC	-	Differential Scanning Calorimetry
TGA	-	Thermogravimetric Analysis
CVD	-	Chemical Vapour Deposition
GNR	-	Organic Synthesis of Graphene Nanoribbons
SEM	-	Scanning Electron Microscopic
UV	-	Ultraviolet

LIST OF SYMBOLS

g	-	Gram
mol	-	Mole
cm	-	Centimetre
nm	-	Nanometre
m ² /g	-	Meter square per gram
V	-	Voltage
s	-	Second
cm ² /Vs	-	Centimetre square per Voltage
W	-	Watt
m	-	Metre
m ²	-	Metre square
K	-	Kelvin
Wm/K	-	Watt meter per Kelvin
°C	-	Degree Celsius
mL	-	Millilitre
h	-	Hour
Min	-	Minutes
M _w	-	Weight Average Molecular Weight
M _n	-	Number Average Molecular Weight
T _g	-	Glass Transition Temperature
TPa	-	Terapascal
MPa	-	Megapascal
GPa	-	Gigapascal
S/m	-	Siemens per meter
DG	-	Degree of grafting
wt%	-	Weight percent

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Liquid rubber (LR) is another form of rubber having low molecular weight (M_w) of below 20000 g/mol that are used in various applications such as automotive, structural, medical as well as aerospace (Das *et al.*, 2015). LR is advantageous for the production of various products due to the ease of processing and less energy requirement in comparison to the high molecular weight rubber. LR can be either liquid natural rubber (LNR) or liquid synthetic rubber (LSR). Even though the researches on LNR has started much earlier, the progress is much slower than LSR (Nor & Ebdon, 1998). To date, various LSR products have been commercially available such as carboxyl-terminated butadiene (CTBN), hydroxyl-terminated polybutadiene (HTPB), vinyl-terminated butadiene-acrylonitrile which are widely used as toughening agents and binders (Kargarzadeh *et al.*, 2015). Currently, LNR on the other hand, has gained significant interest due to the current issue concerning the renewability and natural resources. Kargarzadeh *et al.* (2015) reported the use of LNR and liquid epoxidized natural rubber (LENR) as excellent toughening agent for unsaturated polyester resin. LNR can be obtained from various methods of degradation of NR either using mechanical (Gelling and Porter, 1988), oxidative (Nor and Ebdon, 1998) or photo degradation (Ravindran *et al.*, 1988).

The aforementioned methods for the production of LNR has led to the formation of inconsistent types of reactive terminal groups. The presence of these inconsistent terminal groups has resulted in the rubber vulcanizates with poor

mechanical properties owing to the presence of a high proportion of elastically inactive chain ends which limits the application of LNR. Telechelic liquid rubber (TLR) is a modified form of LR which contains consistent and specific functional groups at the chain end thus lowering the percentage of elastically inactive chain ends. The presence of this specific reactive terminal groups enabled higher chain extension and crosslinking of the LR. Hydroxyl and carboxyl are among the most reported reactive terminal group. Preparation, procedure and type of reagents are crucial parameters in determining the type of reactive terminal groups for that particular TLR (Nor and Ebdon, 1998). For instance, hydroxylated NR is very reactive due to the hydroxyl groups in its polymer chain. Therefore, hydroxylated NR can acts as intermediates for other reaction such as grafting reaction, esterification and so on (Azhar *et al.*, 2017).

Various telechelic LNR (TLNR) have been reported so far. Research on the use of natural rubber based binder for propellant rocket, hydroxyl TLNR (HTLNR) as replacement for hydroxyl-terminated polybutadiene (HTPB), which is a commercial synthetic liquid rubber was conducted extensively due to the low cost and green technology by HTLNR (Baharulrazi *et al.*, 2015; Shuhadah, 2016). The preparation of telechelic rubber from epoxidized natural rubber (ENR) was conducted in 2016 (Shuhadah, 2016). The use of ENR was expected to have better functionalization due to the presence of epoxy groups in the starting material.

Addition of filler is one of the methods that has been established to enhance the properties of rubber. Various reinforcing fillers such as fillers in the form of fine particles like carbon black, silica or calcium carbonate have been added into NR/elastomers for the enhancement of the rubber especially in terms of strength and stiffness (Donnet, 1998). According to López-Manchado *et al.* (2004), the incorporation of carbon based-fillers such as carbon nanotube have significantly improve the properties of rubber nanocomposites. López-Manchado *et al.* (2004) stated that a strong filler-matrix interaction was observed with increase of the storage modulus as well as a noticeable shift of the glass transition temperature (T_g) towards higher temperatures. Graphene, the newest member of the carbon family has received significant interest in the field of nanocomposites due to its exceptional physical

properties such as its unusual structural characteristics and electronic flexibility (Geim and Novoselov, 2007; Neto *et al.*, 2009), superlative mechanical strength (Lee *et al.*, 2008) and good thermal conductivity (Balandin *et al.*, 2008). However, pristine graphene is too hydrophobic and unable to form homogeneous polymer composites.

Therefore, graphene oxide (GO) which is an oxidized form of graphene, provides better alternative due to the presence of various oxygen functional groups and is expected to provide better interaction with reactive groups from telechelic LNR. GO is considered as a promising precursor to produce graphene-based materials due to the wide-ranging selection of functional groups that allowed for further functionalization (Che Man *et al.*, 2013). The incorporation of GO into various matrix can be done via solution mixing (Zhao *et al.*, 2010), melt blending (Berki *et al.*, 2017) and in situ polymerization (Potts *et al.*, 2011). The first two methods are usually favoured due to the simple process. Chemical modification on the other hand enable the interaction of filler and polymer matrices. Chemical modification such as hydrogenation, oxidation, hydroxylation and grafting are possible option to modify LNR or LENR. Thus in this research, synthesis of hydroxyl terminated liquid epoxidized natural rubber (HTLENR) and HTLENR grafted with GO has been prepared. Currently, research on the preparation and characterization of graphene/liquid natural rubber nanocomposite has yet to be reported. The formation of grafting is expected to ensure a good adhesion between GO and HTLENR matrix as well to enhance the properties of the prepared nanocomposite.

1.2 Problem Statement

Despite the advantages of LNR in comparison to NR, the applications of LNR is still limited due to the presence of unsaturated structure in the backbone as discuss previously (Berry and Morell, 1974). Thus, the transformation of LNR to telechelic LNR (TLNR) that bearing consistent reactive terminal end group is paramount which

help to reduce the unsaturated chain in LNR or in other liquid rubbers. TLNR such as hydroxyl terminated natural rubber (HTNR) and carboxyl terminated liquid rubber (CTLR) which capable of further chain extension reaction have been studied by various researchers (Nor and Ebdon, 1998; Shuhadah, 2016). To date, the presence of epoxy groups in LENR has been reported to possess better functionalization compared to HTNR and CTNR and shows good potential for the preparation of telechelic LENR (TLENR). However, the studies on the synthesis and properties of HTENR is still new. Shuhadah (2016) reported the synthesis of HTENR via oxidative degradation by using an ENR as a raw material. From this research, the M_n produced was still high which around 34000 g/mol. Getting lower M_n (~below 20000 g/mol) is crucial in preparation of telechelic liquid rubber to ensure high functionality of the reactive chain.

Thus, in this research, LENR was used as a starting material to produce HTLENR via oxidative degradation in the presence of oxidizing agent and ethanol as solvent. LENR was chosen due to the lower molecular weight as well as the presence of epoxide group which is expected to enhance the functionalization process. The molecular weight for HTLENR produced was also expected to be lower than previous research which use ENR as starting material (Shuhadah, 2016). Subsequently, graphene oxide (GO) was grafted onto the backbone of the prepared HTLENR to get the substantial improvements in properties of the composite. To date, GO as a filler help to form a good dispersion and interaction in rubber matrix. Based on literature search, grafting of GO onto HTLENR or telechelic natural rubber has yet to be reported. TLNR plays an important role due to reactive end chain that can be a precursor for synthesis of new composites. With addition of GO, this work might provide a new insight for performance of rubber nanocomposite for further engineering application in field of automotive, green energy and electronics.

1.3 Research Objective

The aim of this research was to synthesize HTLENR with low molecular weight in the range of 10000 g/mol and afterward perform grafting reaction with GO in order to enhance the performance of the liquid rubber. The research objectives are as below:

- (a) To determine the effect of various reaction time on molecular weight of HTLENR prepared by LENR via oxidative degradation.
- (b) To characterize the HTLENR obtained and propose the mechanism of the HTLENR.
- (c) To perform grafting reaction of HTLENR with GO and investigate the thermal stability of HTLENR-g-GO.

1.4 Scope of Study

There are three scopes that was identified in this research in order to achieve the objectives:

- (a) Depolymerisation of LENR by oxidation method to obtain lower molecular weight of liquid rubber (HTLENR). This depolymerization occur in the presence of ethanol as a solvent as well as cobalt acetyl acetonate (CAA) as oxidizing agent. Subsequently, sodium borohydride (NaBH_4) was added to ensure the formation of hydroxyl group. The reaction time was varied in order to study the effect of reaction parameters on the reduction of molecular weight.

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