THERMAL-INDUCED AND THERMO-OXIDATIVE DEPOLYMERIZATION OF NATURAL RUBBER AND ITS EPOXIDIZED DERIVATIVES

by

Bashir Betar

Thesis submitted in fulfillment of the requirements of the degree of

Master of Science

June 2015

Special Dedication

This thesis is especially dedicated to:

My parents who are infinitely precious to me.

My father, my mother, my brother, my sister who have filled my life with joy and happiness.

Assoc. Prof Dr Mas Rosemal Hakim Bin Mas Haris

To whom I am deeply grateful.

ACKNOWLEDGEMENT

I would like to take this opportunity to wish to express my gratitude to people who have helped and guided me throughout the completion of my master thesis.

First of all I would like to express my sincere gratitude to my principal supervisor Associate Prof Dr Mas Rosemal Haris Bin Mas Hakim for guiding me and giving me endless support, advice and encouragement throughout my research.

My sincere appreciation also goes to Gunasunduri Raju, Luqman Idrees for their advice and for assisting in various ways in my laboratory work.

I would like to thank all the staff of School of Chemistry for their continuous help and support, and Ministry of Science & Innovation (MOSTI) for providing the financial supports: Research University (RU) grants no. 100/PKIMIA/814124 and FRGS 203/PKIMIA/6711183.

Last but not least, I would like to express my appreciation to all my family members and friends for their spiritual support, perseverance and encouragement.

This thesis is heartily dedicated to my parents for their material and support in all aspects of my life.

Finally, I thank God for His mercy and blessing on me.

TABLE OF CONTENTS

Page

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: MATERIALS AND RESEARCH METHODOLOGY

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 5: CONCLUSION

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

$CDCl_3$	deuterated chloroform
D_2O	deuterated water
ppm	parts per million
TMS	tetramethylsilane
C1	depolymerization under condition-1
C2	depolymerization under condition-2
C3	depolymerization under condition-3
^{o}C	degree Celsius
NR	natural rubber
ENR25	25 mole percent Epoxidized natural rubber
ENR50	50 mole percent Epoxidized natural rubber
KOH	potassium hydroxide
TGA	thermogravimetric analysis
DTG	derivative thermogravimetry
FT-IR	fourier transforms infrared
NMR	nuclear magnetic resonance
GPC	gel permeation chromatography
THF	tetrahydrofuran
g	gram
hr	hour
$\overline{M_w}$	weight average molecular weight
$\overline{M_w}^{\,std}$	standardized value of $\overline{M_w}$

min	minute
WSRD-K^+	water soluble rubber derivative complex with potassium ions
BDE	bond dissociation energy

PEMDEPOLIMERAN GETAH ASLI DAN TERBITAN TEREPOKSIDANYA SECARA TERARUH-TERMA DAN TERMO-OKSIDAAN

ABSTRAK

Pemdepolimeran getah asli (NR) dan terbitan terepoksidanya, ENR25 dan ENR50 (NR dengan kandungan epoksi, masing-masing, dalam lingkungan 25% dan 50%) secara teraruh-terma telah dilaksanakan pada 200 ^{o}C dalam keadaan: (1) tekanan ambien (760 mm Hg) di mana $[O_2] \approx 20.95\%$, tekanan rendah (85 mm Hg) di mana $[O_2] \approx 2.34\%$, dan tekanan ambien (760 mm Hg) tetapi sampel-sampl dimasukkan dalam bekas-bekas tertutup yang mengandungi $[O_2] \approx 100\%$. Getah-getah permulaan dan yang telah dipemdepolimerkan (diasingkan pada jarak masa 1, 2, 4, 8, 12 dan 16 jam) dipercirikan dengan menggunakan kaedah (i) Kromatografi Penyerapan Gel (GPC), (ii) Penentuan kandungan gel, (iii) Spektroskopi Resonans Magnetik Nukleus Transformasi Fourier Proton (^{1}H FT-NMR), (iv) spektroskopi Inframerah Transformasi Fourier (FT-IR) dan (v) analysis termogravimetri (TGA). Data GPC pemdepolimeran NR berlaku dengan lebih pantas daripada pemdepolimeran ENR25 yang pula berlaku dengan lebih pantas daripada pemdepolimeran ENR50. Kandungan gel purata bagi NR, ENR25 dan didapati meningkat dengan peningkatan jarak masa pemdepolimeran. Kepekatan molekul oksigen yang lebih tinggi menyebabkan pembentukan gel yang lebih tinggi dalam jarak masa pemdepolimeran yang singkat. Keputusan anlisis spektra ^{1}H NMR menunjukkan bahwa kandungan epoksi ENR25 dan ENR50 yang telah mengalami pemdepolimeran adalah sama secara praktikal dengan kandungan epoksi ENR25 dan ENR50 yang belum mengalami pemdepolimeran. Analisis kuantitatif proton aldehid dilakukan keatas getah-getah yang telah dipemdepolimerkan dengan kedua-dua kaedah FT-NMR and FT-IR bagi meningkatkan kefahaman tentang mekanisme pemdepolimeran NR dan terbitan terepoksidanya. Keputusan TGA menunjukkan tiada perubahan ketara antara kestabilan getah-getah permulaan dan yang telah mengalami pemdepolimeran. Pemdepolimeran NR, ENR25 dan ENR50 dicadangkan berlaku melalui pemutusan rangkaian ikatan karbon-karbon alilik bagi unit isoprena atau unit isoprena terepoksida secara teraruh-terma. Seterusnya, tindak balas radikal-radikal alkil dengan molekul-molekul oksigen akan akhirnya menghasilkan kumpulan hidroksil dan aldehid sebagai kumpulan penghujung. Pembentukan gel (bahan yang tidak terlarut) adalah ekoran daripada tindak balas sambungsilang antara radikal-radikal polimer yang terhasil selepas proses pemutusan rangkaian. ENR50 yang telah dipemdepolimerkan dan yang mempunyai $\overline{M_w} = 44777$ g mol^{-1} telah digunakan sebagai contoh untuk penyediaan terbitan getah terlarut air. Produk inovatif ini dicirikan dengan spektroskopi ^{1}H dan ^{13}C NMR pada suhu yang berlainan dan D_2O digunakan sebagai pelarut.

THERMAL-INDUCED AND THERMO-OXIDATIVE DEPOLYMERIZATION OF NATURAL RUBBER AND ITS EPOXIDIZED DERIVATIVES

ABSTRACT

Thermal-induced depolymerization of natural rubber (NR) and its epoxidized derivatives, ENR25 and ENR50 (NR with epoxy content of approximately 25% and 50%, respectively) was conducted at 200 °C under the following conditions: (1) ambient pressure (760 mm Hg) whereby $[O_2] \approx 20.95\%$, (2) reduced pressure (85 mm Hg) whereby $[O_2] \approx 20.95\%$, and (3) ambient pressure (760 mm Hg) but samples were placed inside sealed containers whereby the initial $[O_2] \approx 100\%$. The starting and depolymerized rubbers (isolated at 1, 2, 4, 8, 12 and 16 hr time intervals) were characterized by means of (i) Gel Permeation Chromatography (GPC), (ii) Gel content determination, (iii) Proton Fourier Transformed Nuclear Magnetic Resonance (^{1}H FT-NMR) spectroscopy, (iv) Fourier Transformed Infrared (FT-IR) spectroscopy and (v) Thermo Gravimetric Analysis (TGA). GPC data reveals that NR depolymerized faster than ENR25 which in turn depolymerized faster than ENR50. The average gel content of NR, ENR25 and ENR50 is found to increase with the increase in depolymerization time interval. Higher concentration of oxygen molecules resulted in higher formation of gel in shorter depolymerization time interval. ^{1}H NMR spectral analysis reveals that the epoxy content of depolymerized ENR25 and ENR50 is practically the same as that of the undepolymerized ENR25 and ENR50, respectively. Quantitative analyses of aldehyde protons of the depolymerized rubbers using both FT-NMR and FT-IR techniques were performed as a means to gain further insights on the mechanism of depolymerization of NR and its epoxidized derivatives. TGA results show insignificant difference in the thermal stability of the starting and depolymerized rubbers affirming the notion that the general molecular structures of the aforesaid materials are similar. The depolymerization of NR, ENR25 and ENR50 is proposed to proceed via thermal-induced chain scission of the carbon-carbon allylic bond of isoprene or epoxidized isoprene units. Subsequently, the reaction of the resulting alkyl radicals with oxygen molecules result in the formation of hydroxyl and aldehyde as end groups. The formation of gel (insoluble materials) was the result of crosslinking reactions between polymeric radicals produced after chain scission. Depolymerized ENR50 with $\overline{M_w}$ of 44777 g·mol^{-1} was used as an example to successfully prepare a water-soluble rubber derivative. This innovative product is characterized by means of variable temperature ^{1}H and ^{13}C NMR spectroscopy with the use of D_2O as solvent.

CHAPTER 1:

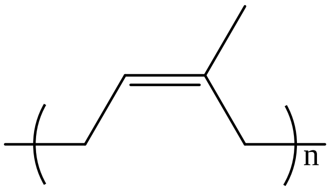
INTRODUCTION

1.1 General Introduction

Natural rubber (NR) that has found numerous uses in our current everyday life is obtained from *Hevea Brasiliensis* tree in latex form which typically composed of the substances shown in Table 1.1 (Hourston and Tabe, 1996). The chemical constituent of the dry natural rubber is 99 % *cis*-1,4-polyisoprene (Figure 1.1).

Table 1.1: Typical composition of latex from *Hevea Brassilinies*

Content	**%**
dry natural rubber	36
protein	1.6
inositols-carbohydrates	1.5
neutral lipid	1
phospholipids	0.6
salt (mainly K,P and Mg)	0.5
amino acids and N-bases	0.3
water	58.5

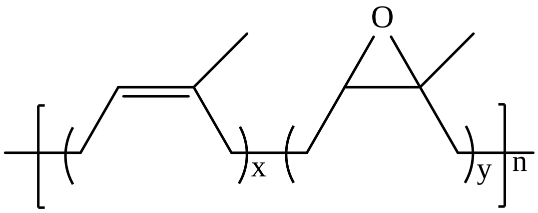


n = repeating unit

Figure 1.1: A simplified structure of *cis*-1,4-polyisoprene

Due to its unsaturated bond and non-polar character, NR has some drawbacks such as poor resistance to oxidation, weathering and a wide range of organic solvents (Brosse *et al*., 2000, Varaporn Tanrattanakul *et al.,* 2002). To overcome these disadvantages, chemical modifications of NR have been extensively carried out to produce derivatives such as chlorinated natural rubber (Pande, *et al.,* 1956), hydrogenated natural rubber (Tangthongkul, *et al.,* 2005), maleate natural rubber (Carone *et al*., 2000; Nakason *et al*., 2006), and epoxidized natural rubber (Gelling, *et al*., 1991, Ramesh and De, 1993; Mohanty *et al*., 1996; Nakason *et al*., 2004)

Epoxidized natural rubber (ENR) shows improved solvent resistance and gas permeation properties compared to that of NR (Chuayjuljit *et al*., 2005). A simplified structure of ENR is depicted in Figure 1.2 (Mas and Raju, 2014). The epoxy group is distributed randomly on the polymer backbone (Saito et al., 2007). Commercially, ENR is available in two grades designated as ENR25 and ENR50 which refer to NR with epoxy content of approximately 25% and 50%, respectively.



n = repeating unit
x = isoprene unit
y = epoxidized isoprene unit
Epoxy content = ([y]/([x] + [y])100%

Figure 1.2: A simplified structure of an ENR

Depolymerization is a reverse process of polymerization. It reduces the chain length of a polymer or copolymer after an initiation step (bond cleavage or dissociation step) into oligomers or mixture of oligomers during the propagation step and before reaching equilibrium or termination step. On the other hand, degradation is usually accompanied by total destruction of a polymeric material (Li and Koenig, 2005) resulting in undesirable changes in the useful properties of the material (Hatada et al., 1996). However, often in the literature there is confusion in the use of the terms depolymerization and degradation. It should be clear that depolymerization reduces chain length which is reflected by decrease in weight average molecular weight ($\overline{M_w}$) but the original structure of a depolymerized polymer or copolymer should remain quite similar to that of the corresponding starting or undepolymerized material. NR and its epoxidized derivatives degrade at temperature range 300 - 500 ^{o}C with a rapid degradation at about 400 ^{o}C (Golub and Gargiulo, 1972; Li, *et al.*, 1998; Chen and Qian, 2002).

Depolymerized ENR can be obtained after epoxidation and/or after depolymerization of a given NR. An outline for the formation of depolymerized NR and ENR is shown in Figure 1.3.

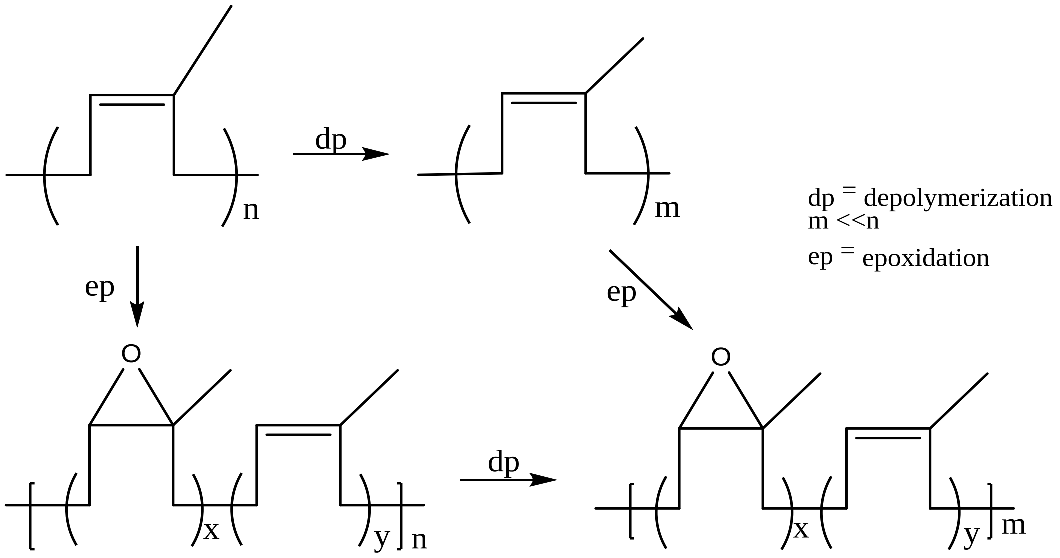


Figure 1.3: A general route for the formation of depolymerized NR and ENR

Both NR and its epoxidized derivatives can be depolymerized by chemical-induced and thermal-induced methods. Chemical-induced depolymerization has been widely explored and generally involves the use of NR or its epoxidized derivatives in latex form with hydrogen peroxide and sodium nitrite (Keith and Peter, 1990), sodium chlorite and hydrogen peroxide (Sidek and Zainul, 1991), tetrahdrofuran (Seung and In-Kwon, 1998) and periodic acid (Phinyocheep *et al.*, 2005). The thermal-induced depolymerization is comparatively less studied and involves heating of NR or its epoxidized derivatives in solid form inside a heat chamber, for example an oven. Low molecular weight rubbers which sometimes referred as liquid natural rubber and liquid epoxidized natural rubber have been used widely for adhesives, pressure sensitive adhesives and sealing materials due to their good adhesive properties and excellent crosslinking reactivity (Tangpakdee, et al., 1998). Furthermore, they can be easily processed with less energy compared to undepolymerized rubbers. Depolymerized NR and its epoxidized derivatives can also be used to prepare innovative products such as water-soluble rubber derivatives which can be used for cleaning water containing very fine, unfilterable particulates like smoke residue, carbon or wood dust, or finely dispersed liquid such as oil droplets or undesired pigmentation in a very simple and cost effective manner (Mas, 2004; Mas, 2007).

1.2 Problem statements

Chemical-induced depolymerization of NR and its epoxidized derivatives involves the use of the polymers in latex form and various chemicals (including hydrogen peroxide, appropriate stabilizers and organic acids and/or sodium salts). Trained personnels are required to handle the hazadous chemicals and the work-up steps to obtain the final solvent-free depolymerized NR or its epoxidized derivatives with desired $\overline{M_w}$ are quite time consuming. Furthermore, the present of side reaction products and impurities such as metal salt (sodium nitrite) imbeded in the depolymerized NR or its epoxidized derivatives are unavoidable and difficult to be removed.

Thermal-induced depolymerization of NR and its epoxidized derivatives, on the other hand, involves only the use of the polymers in solid form (commonly referred to as neat form) inside a heat chamber. By merely controlling or setting the temperature at appropriate value, i.e., below the beginning of degradation (300 ^{o}C) but high enough to evaporate any low boiling solvent or water molecules and to initiate chain scission may result in the production of cleaner depolymerized NR or its epoxidized derivatives which are highly desired especially for the preparation of water-soluble rubber derivatives.

A survey of the literature reveals that report pertaining to the study of thermal-induced depolymerization NR and its epoxidized derivatives under similar experimental conditions is, to date, non-existent. Thus, it is of interest to study and establish the relative rate of thermal-induced depolymerization of NR and its epoxidized derivatives.

1.3 Research Objectives

1. To depolymerize NR, ENR25 and ENR50 at 200 °C under:

(i) ambient pressure

(ii) reduced pressure

(iii) ambient pressure but with initial high oxygen concentration,

and characterize by means of (i) Gel Permeation Chromatography (GPC), (ii) Gel content determination, (iii) Proton Fourier Transformed Nuclear Magnetic Resonance (^{1}H FT-NMR) spectroscopy, (iv) Fourier Transformed Infrared (FT-IR) spectroscopy and (v) Thermogravimetric Analysis (TGA).

2. To prepare an example of water-soluble rubber derivative and characterize it by means of ^{1}H and ^{13}C NMR spectroscopic technique using D_2O as solvent.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural rubber

Natural rubber (NR) is an agriculture commodity and one of the main income in several countries such as Malaysia, Thailand and Indonesia. NR has the advantage to be a renewable material with excellent physical properties such as excellent flexibility, and resistance to tear. (Nakason, *et al.*, 2004) NR is used to produce over 40,000 products, including medical devices, surgical gloves, aircraft tires and countless engineering and consumer products. In addition, NR has very high molecular weight and can be altered to yield other derivatives that find usage in numerous applications like anticorrosive, binders, coatings and process aids.

However, NR has some drawbacks, such as low sensitivity to some chemicals and solvents, flame resistance, and poor ozone resistance. This is due to its unsaturated bond chain structure and non-polar character, which can cause some limitation in variety of applications. (Brosse *et al*., 2000)

Therefore, several modifications of NR have been accomplished in different ways to improve various properties such as epoxidized natural rubber (Ramesh and De, 1993; Mohanty *et al*., 1996 and Nakason *et al*., 2004), maleate natural rubber (MNR)

(Carone *et al*., 2000 and Nakason *et al*., 2006), hydrogenated rubber (Tangthongkul, *et al.,* 2005) and chlorinated rubber. (Pande, *et al.,* 1956)

Slandered Malaysian Rubber (SMR) is Malaysian-made commercialized product since 1965. SMR is a type of natural rubber has been examined for its usability and quality in packing, grading, tape and labelling, electricity, oil and air resistance, etc. Many grades are existed in, such as SMR5, SMR 20, SMR 10, SMR CV, SMR LV, etc., supplying a wide range grads to market for various applications. The SMR grade is mainly determined by its cleanliness or maximum dirt content, the bigger the number of SMR, the lower quality and lower rubbery performance of rubber.

2.2 Epoxidation of natural rubber

Epoxidized natural rubber (ENR) is a derivative of NR produced by chemical modification. ENR has some properties different from NR through epoxidation. These properties are the ability to strain crystallize, elevated T_g values and higher solubility parameter. The polarity of ENR increases with increases of epoxy content. As such, at high epoxy content, ENR becomes more resistant to hydrocarbon materials and less resistant to polar solvents. Therefore, ENR has been widely used for various rubber goods, such as high-damping engineering mounts, acoustic devices, and adhesives. (Baker & Gelling, 1987)

In epoxidation process, epoxides were introduced to the backbone double bonds of NR, which were altered into using an organic peracid (Figure 2.1). NR can be epoxidized *in situ* in the latex form, using organic peracids derived from acetic or formic acids. (Gelling, 1991)

^{13}C NMR of the ENR has shown that epoxidation are distributed randomly with one, two and three adjacent epoxide groups present at levels consistent with those predicted.

$$\mathbf{HCOOH + H_2O_2 \rightleftharpoons HCOOOH + H_2O}$$

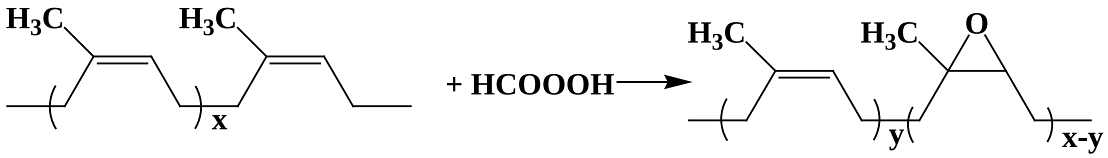


Figure 2.1: Epoxidation of natural rubber

In 1990, Roy*, et al.,* reported a studies on the epoxidation of NR. Epoxidation of NR with in-situ formed performic acid with and without acetic acid at room temperature were studied. Various side reaction products were detected in ^{1}H-NMR and FT-IR analysis. The study was able to achieve only up to 65% of epoxy contents.

ENR was prepared with different amount of hydrogen peroxide and thermal study has been done. (Heping *et al.*, 1999) It was found that ENRs can be prepared by controlling the experimental conditions. However, the kinetics of forming ENRs was studied and it was found to be second order reaction. The thermal stability was increased by the epoxy content of ENR based on TGA results.

2.3 Depolymerization and degradation of NR and ENR

2.3.1 Metathesis degradation

Metathesis degradation of NR has been studied. (Arisol *et al.*, 1988 and Korshak *et al.*, 1982). Arisol reported metathesis degradation of NR using WC_{16}- $(CH_3)_4Sn$ catalyst system. It was found that the reaction reduces the molecular weight of NR and the degraded material is more soluble compared to NR. The properties of NR would also affected by various times and temperatures. Low molecular weight material were analyzed using GC. Thermal properties had showed some changes in the structure also occurred.

2.3.2 Ozonolysis degradation

Ozonolysis was discovered by Murray & Story in 19767. Wide applications were found and substantial interest for the problems related to the low stability of 1,4-cis-polyisoprene ozone ageing.

Ozonolysis of natural rubber was reported previously. (Anachkov, *et al.*, 2000) This reaction was conducted in chloroform solution. FT-IR and FT-NMR studies showed a formation of a new products which are aldehyde, ketone and ozonides. Proposed mechanism was suggested as well.

2.3.3 Radiation degradation

Radiation degradation of ENR has been studied by using NMR and FT-IR to observe the change in structure when expose ENR to high energy. The samples were gamma irradiated under vacuum and air. It was found that the resulting irradiated samples are not soluble in solvents due to crosslinking, therefor solid-state NMR was used. It was found that the mechanism involves ring opening of the epoxy groups. Moreover, the cross-linked product yield was found to be higher in vacuum condition compared to that of under ambient condition. (Perera, 2000)

2.3.4 Chemical depolymerization

Keith and Peter in 1990s have patented method for reducing the molecular weight of rubber in latex by using chemicals in order to depolymerize of NR and ENR by using hydrogen peroxide and sodium nitrite. The order of adding hydrogen peroxide and sodium nitrite is not critical. Starting from NR latex, with pH adjusted to 6.0 and with reduced concentrations of hydrogen peroxide (2.2 to 2.5 ml of 50 wt 7.) and sodium nitrite (1.4 to 1.5g). At the completion of the reaction, the pH was raised to 8.6 with aqueous sodium hydroxide. Also the effect of varying the ratio of hydrogen peroxide to sodium nitrite was illustrated. Formic acid was used to reduce the alkalinity of the latex prior to reaction.

The production method involved depolymerising NR latex to the desired and controlled molecular weight by a reduction-oxidation process has been developed by Sidek and Zainul in 1991.

Viz. sodium chlorite and hydrogen peroxide were used as depolymerization reagents. Firstly, NR was stabilized by using surfactant agent (teric acid) and the DRC set to be 20 %. The pH of the mixture was then adjusted to 4.5 with hydrochloric acid. Sodium chlorite solution and hydrogen peroxide were added gradually. The reactant mixture was then heated up to 70 °C for 1 day. The reaction was stopped by adding potassium hydroxide solution to pH 7. A scale up production has been studied as well. It found that LNR with $\overline{M_w}$ less than 10,000 could be produced.

The influence of temperature and reaction time in the degradation of NR latex has been reported. (Siti Zaleha *et al.*, 2007) Chemical thermal degradation of NR latex has been carried out to obtain low molecular weight of NR and ENR by varying the reaction time and temperatures. It was found that the rate of depolymerization depends on both temperature and reaction time. Sodium nitrite and hydrogen peroxide were used as depolymerization reagents. FT-IR spectra of the depolymerized materials show existing of both epoxy and hydroxyl groups, indicating that the carbon-carbon double bonds have undergone epoxidation and hydrolysis. Further confirmation of forming epoxy and hydroxyl groups was obtained from ^{1}H NMR.

Depolymerization of ENR is based on a reaction in which a chemical with reactive polar groups cleavage the active linkage in the polymer backbone. Periodic acid was used for chemical degradation of ENR. (Phinyocheep *et al.*, 2005) It was found that the depolymerization rate depends on the amount of the periodic acid used. The epoxy content determined by ^{1}H NMR of the samples after being depolymerized, shows that the epoxy content was almost the same after degradation. Moreover, there was no observation of forming a signal corresponding to side reactions such as formation of diol and furan. ^{13}C NMR has confirmed the existence of aldehyde and ketone function. A proposal mechanism of the degradation reaction of the unsaturated rubber by periodic acid, as it occurred at the double bond of the rubber.

An application for recycling of waste rubber tire, a chemical degradation of NR by using periodic acid was reported. (Faten *et al*., 2012) A detailed FT-NMR study has been done, it suggests that the cleavage occured in two-steps mechanism. In the first step, periodic acid (H_5IO_6) reacts with double bond to form an epoxide or a-glycol. While in the second step, the epoxide or glycol is cleaved by reaction with a second equivalent of H_5IO_6.

Seung and In-Kwon in 1998 has reported depolymerization of NR in supercritical tetrahdrofuran. The solution of NR and tetrahydrofuran was fed into the reactorusing high vaccum liquid pump and the temperature was raised to 300 ^{o}C. carbon- carbon double bond were attacked in this reaction by the radicals formed by tetrahdrofuran, and it converted to carbon-carbon single bond. As a result of the reaction, more than ten organic compounds were produced.

Depolymerization and epoxidation of NR was conducted by disolving NR in toluene, then acetic acid; sodium tungstate ($Na2WO_4 \cdot 2H_2O$) and hydrogen peroxide (H_2O_2) solution was added to NR solution at 60℃. (Jiang *et al*., 2009) By combining sodium tungstate with the geneally adopted acetic acid / hydrogen peroxide epoxidation system, natural rubber can be effectively oxidized to prepare telechelic epoxidized liquid natural rubber (TELNR).

2.3.5 Thermal degradation and depolymerization

Thermal depolymerization of NR was discovered in 1860s by G Williams, when NR (*cis*-1,4-polyisoprene) and gutta percha (*trans*-1,4-polyisoprene) were subjected to destructive distillation or pyrolysis. However, the mechanism of thermal oxidation of rubbers were developed in 1946 by Bolland and Gee. This free radical chain oxidation mechanism comprises of stages. The initiation step wherein the radicals are formed. The propagation step describes the reaction with oxygen, a chain branching reaction describes the decomposition of the formed hydroperoxides and the accumulation of radicals. The termination step describes the recombination of radicals.

A lot of attention has been paid to study the thermal degradation of NR by using TGA technique. (Golub and Gargiulo, 1972, Chen and Qian, 2002, Chen and Qian, 2003, Franco Cataldo, 2006 and Maria *et al*., 2006) These reports have studied the profile of the thermal behavior TGA for different type of rubber such as 1,4 polyisoprene, waste rubber, cis-1,4-polyisoprene, chlorinated natural rubber, NR in different compound formulations, and NR condoms. The experiments mainly conducted at TGA instrument under different gas flow such as oxygen or nitrogen, with different time intervals. The NRs samples after degradation were analyzed by using different techniques such as FT-IR, gas chromatography analysis and ^{1}H NMR. Different information were given after NR was being degraded. Some reports claimed that the degradation cleavage took place at the carbon-carbon single bonds, others claimed on the carbon-carbon double bonds.

Thermal degradation of ENR by using TGA instrument has been studied. (Li *et al*, 1997) The experiments were conducted under air and nitrogen gas. The study suggests that the thermal degradation of ENR occurred in one step, while the thermo-oxidative in multiple steps. That was because in thermo-oxidative the oxygen has played a role in the degradation process.

Oxidative and nonoxidative thermal degradation of vulcanized and unvulcanized NR was studied by Amerongen in 1955. Two methods were applied for investigation. The first method is an oxygen-free heating, wherein the experiment was conducted at 90 ^{o}C for 20 min, then mercury pressure was applied to remove the oxygen from the flask. After that, the flask was flushed three times with nitrogen gas and sealed. In the second method, different concentrations of oxygen were applied and the amount of oxygen was measured by gas volumenometry. The results suggests that the changes in rubber properties could be both thermal and oxidative. For unvulcanized NR, one of the changes in vulcanized rubber is the rate of reaction at temperatures between 80 to 140 ^{o}C, the oxidative degradation reaches almost to the same order as that of the thermal degradation in the absence of oxygen at temperatures higher by 60 to 100 ^{o}C.

Poll and Lee in 1994 have studied the thermal degradation of ENR by using FR-IR technique. The experiment was carried out in air oven under different temperatures 90, 120, and 160 ^{o}C for two hours at different interval times. This study suggests that the thermal oxidation of NR and ENR occurs on the carbon-carbon double bond, because of the oxidative products which are hydroperoxide, carboxylic acids, alcohols, ester and other carbonyl compounds. Moreover, the epoxide ring involves in the thermal oxidation as the oxidative products are similar to that found in NR.

2.4 Bond dissociation energy

Bond dissociation energy (BDE), is a measurement of the strength of a chemical bond. It is defined as the standard enthalpy change when a bond is cleaved. The bigger the bond energy, the stronger the bond. (John, 1999)

Bond energies are very different depending on the nature of the chemical groups to which the atoms belong. A few selected data are included in Table 2.1. The dissociation energies of the various bonds in the polymer determine the pathway of degradation or depolymerization. The process always begins with the cleavage of the weakest available bond or with an attack at this site, and the initiation step usually determines the further direction of the process. (Li and Koenig, 2005 and Gijsman, 2008).

Table 2.1: Bond Dissociation Energy (BDE) of some selected bonds

Type of bond	ΔHf298 kJ mol-	Reference
C─C allylic bond of methylene	334-339	Gijsman, 2008
C─H allylic bond adjacent to methylene	414	Li and Koenig, 2005
C─H allylic bond adjacent to methyl	435	Li and Koenig, 2005
O=O double bond of oxygen molecule	498	John, 1999
C=C double bond of alkene	614	John, 1999
C─O or O─C of oxirane	779	John, 1999

2.5 Instrumentation background

2.5.1 Gel permeation chromatography

Gel Permeation Chromatography (GPC), also referred to as size exclusion chromatography (SEC), is a separation technique where is a mixture are separated and sorted from one another based on size of the molecule when solvated in a solvent as a mobile phase, (Ocotore, 1998).

In GPC, the sample (dissolved in a solvent) inject onto the column, which is filled with a rigid and pours particles. Large molecules elute from the column first, followed by smaller molecules. It is an important tool for the analysis of polymers. The essential results are molecular weight ($\overline{M_w}$) data and Mw distribution curves, which are needed to characterize a polymer with regard to differences in properties. GPC, however, is the only techniques, which in addition yields the Mw distribution, (Andre Striegel, 2009).

Polymer molecular weight is quite important as many physical and mechanical properties rely on it. In General, polymer consists of repeating unites (monomers) chemically are bonded together as a long chains. All polymers are a mixture of unequal size chains. Therefore, the $\overline{M_w}$ of polymer is not a single value. Between different possible ways of determining averages, (Scheirs, 2000), one of them are the most useful, which is the weight average molecular weight and the number average molecular weight.

Weight average molecular weight Mw is defined by:

$$Mw = \frac{\sum M_i \, {N_i}^2}{\sum M_i N_i}$$

$\overline{M_w}$ takes into consideration that the molecular weight of a chain in determining contributions to the molecular weight average. The longer the chain, the more the chain contributes to $\overline{M_w}$.

Number average molecular weight Mn is the statistical average molecular weight of all the polymer chains in the sample, and is defined by:

$$Mn = \frac{\sum M_i \, N_i}{\sum N_i}$$

Where M_i is the molecular weight of the chain and $N_i$is the number of the chains of that molecular weight. M_n can be predicted by polymerization mechanisms and is measured by methods that determine the number of molecules in a sample of a giving weight.

The difference in the distributions can be quantified by comparing the polydispersity index (PDI). The PDI is a very important parameter in study of polymer because it gives an idea about the homogeneity of the polymer. It is used as a measure of the width of the molecular weight distribution of the polymer. It is defined by equation 4.1 as below:

$$\mathrm{PDI} = \frac{Mw}{Mn}$$

2.5.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is one of the most important characterization methods proves to be of great tools in structure elucidation which can be related to the chemist's comprehension of molecular structure. It determines the physical and chemical properties of atoms or the molecules. NMR relies on the phenomenon that nuclear magnetic resonance can provide detailed information about the microstructure, dynamics and reaction state.

Commonly, NMR spectroscopy is used by scientists to explore the properties of organic and inorganic molecules, although it is applicable to any kind of sample that contains nuclei possessing spin. The influence of NMR spectroscopy on the sciences has been intrinsic because of the range of information and the diversity of samples, including solutions and solids.

A drawback is that comparatively to other analysis techniques, large amount, about 2–50 mg, of a purified and cleaned material is required. Preferably, the sample should be dissolved in a deuterated solvent, because NMR analysis of solids requires an extra instruments to be equipped with NMR and may not give equally well-resolved spectra. Moreover, the time consuming for NMR spectroscopy analysis is relatively long. Better methods has existed to detect and quantified of impurities as NMR is inherently not very sensitive.

2.5.3 Fourier Transformed Infrared Spectroscopy

Fourier transformed infrared spectroscopy (FT-IR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a materials. FT-IR can use for quantitative and qualitative analysis for organic and inorganic compounds. FT-IR spectra analysis simultaneously provides spectral data in a wide spectral range. There are several infrared types have been used in the world, but the most common one is FT-IR. FT-IR thin film spectra can use for quantitative as FT-IR transmission (Valeri P. Tolstoy, 2003).

FT-IR recognizes chemical bonds in a molecule by producing an infrared absorption spectrum. A characteristic molecular fingerprint that can be used to screen and scan samples for many different components. FT-IR spectroscopy is an efficient analytical instrument for identifying functional groups and characterizing covalent bonding information, (Smith, 2011).

FT-IR was used in this work to detect the functional groups band before and after depolymerization and to quantitate calculation of microstructure content of polyisoprene, in particular for the aldehyde end group of the polymers chains after chain scission had taken place. FT-IR tools can be used by selecting the proper internal slandered peak which has moderate intensity, little interfering factors by other peaks or conditions, (Chen *et al*., 2013).

2.5.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique in which changes in physical and chemical properties of materials are measured as a function of temperature (or time) under a controlled atmosphere to measures weight changes in a material as a function. Thermogravimetric analysis (TGA) principle uses include measurement of a material's thermal stability, filler content in polymers, moisture and volatile solvents and the percent composition of components in a material. The measurement is usually carried out in air or in an inert gas, such as Argon or Helium, and the weight is verified as a function of increasing temperature, (Gabbott, 2008).

Materials characterization through analysis of characteristic studies of degradation mechanisms and reaction kinetics, determination of organic content in a sample, and determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints.

CHAPTER 3

MATERIAL AND METHODS

3.1 Chemicals and solvents

All the chemicals were obtained commercially (table 3.1) and used without further purification except for 1,4-dioxane which was dried with anhydrous magnesium sulphate. Natural rubber (NR, commercially available as SMR CV 20), epoxidized natural rubber with 25% epoxidation (ENR25), and epoxidized natural rubber with 50% epoxidation (ENR50) in dried (neat) form were supplied by Lembaga Getah Malaysia (LGM) Sungai Buluh, Malaysia. The $\overline{M_w}$ of the NR, ENR25 and ENR50 was determined using GPC to be 978377, 742310 and 653223 g mol^{-1}, respectively.

Table 3.1: List of chemicals

Chemicals	Brand
1,4-dioxane (AR)	R&M Chemicals
Anhydrous magnesium sulphate (M_w = 120.36 g/mole, AR)	R&M Chemicals
Potassium hydroxide pallet (M_w=56.11 g/mole, AR)	QREC
Sodium hydroxide pallet (M_w=39.997 g/mole, AR)	QREC
Chloroform (AR)	QREC
Xylene (AR)	Fisher
Deuterated chloroform 99.96 atom %D	Sigma-Aldrich
Deuterium oxide 99.9 atom %D	Sigma-Aldrich
Potassium bromide (FT-IR grade)	Sigma-Aldrich

3.2 Methodology

3.2.1 Condition-1: Depolymerization of NR, ENR25 and ENR50 under ambient pressure at 200 ^{o}C.

Ten samples of ENR50 (each weighing 1.00 g) were cut as small as possible (grain-size) with a stainless steel scissor and placed separately inside 15 ml glass vials. Each vial was then wrapped with aluminium foil and hung to a glass rod in a convection oven (Venticell 111). The temperature of the oven was raised to 200 ^{o}C while the pressure was maintained approximately at 760 mm Hg (ambient pressure). At time intervals 1, 2, 4, 8 and 12 hr, two samples were removed from the oven and cooled to room temperature in a desiccator. A sample of each interval time was set aside for gel content determination as described later in the text. For the other sample of each interval time, chloroform (10 ml x 3) was added and the content of each vial poured into a separate screw-cap glass bottle (50 ml size) which was left standing overnight to ensure complete dissolution of the rubber samples. The content of each screw-cap glass bottle was then suction-filtered using a 55 mm Whatman paper (Cat. No. 1001 055) placed inside a Buchner funnel. The resulting solutions were analysed by means of GPC, NMR, IR and TGA techniques as described below.