PRODUCTION OF FUNCTIONALIZED LIQUID NATURAL RUBBER FROM LOW GRADE NATURAL RUBBER AS A PRECURSOR FOR SEMI-RIGID POLYURETHANE

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PRODUCTION OF FUNCTIONALIZED LIQUID NATURAL RUBBER FROM LOW GRADE NATURAL RUBBER AS A PRECURSOR FOR SEMI-RIGID POLYURETHANE

ABSTRACT

Functionalized liquid natural rubber (FLNR) derived from low grade natural rubber (NR) was synthesized by *in situ* redox method using hydrogen peroxide (H_2O_2) in the presence of sodium nitrite ($NaNO_2$). The formation of hydroxyl (OH) as a main functional group was confirmed by Fourier Transform Infrared (FTIR) spectroscopy with a peak at 3425 cm^{-1}. The Nuclear Magnetic Resonance (NMR) spectroscopy showed the presence of central and end OH groups in the FLNR. Response surface methodology (RSM) optimization was used to investigate the effect of varying feed parameters towards response of molecular weights and OH values. The response surface contours were constructed for modeling the relationship between processing factors and response output. The developed models showed that $NaNO_2$ was the main factor followed by H_2O_2 that influence the FLNR properties. Multi response optimization was done using Derringer's desirability function. The optimum conditions for minimizing average number molecular weight (M_n) and molecular weight distribution (MWD) while maximizing OH value were determined to be at low ratios of $NaNO_2/H_2O_2$ and high ratios of H_2O_2/isoprene unit. The predicted optimum response for M_n was around and less than 30,000 g/mol, polydispersity index (PDI) between 1.48 and 1.61 and OH value between 194 and 229 mg KOH/g. The optimization confirmation was done, and the minor error of percentage calculated from the predicted and observed responses was obtained. Gel Permeation Chromatography (GPC) was used to investigate of the reduction of molecular weight performance and OH autotitrator used to measure the OH values of FLNR. The selected optimum values of FLNR responses were used to produce a semi-rigid polyurethane (PU) precursor. The preparation of FLNR based semi-rigid PU was carried out by *one-shot* and two-*shot* methods. The urethane linkage formation was confirmed by FTIR with a peak at 3317 cm^{-1} due to -NH- and disappearance peak of the NCO at 2295 cm^{-1}. A rubber polyol chain length as soft segment has shown to have a major implication in the polymer products due to the high soft segment content compared to hard segment content in the semi-rigid PU formulation. The semi-rigid character of the PU with low polyol chain length and high soft phase domain favoured solubility in non-polar solvent (toluene and chloroform) and low polar solvent (THF). As for high polyol chain, it was insoluble in any solvent thus its high stability. The differences in glass transition temperatures (T_g) obtained indicated stronger interaction between hard and soft segment by both of *one-shot* and *two-shot* method. The thermal stability behaviour as determined by thermogravimetry analyzer (TGA) showed that the *two-shot* method had improved the semi-rigid PU performance either at low or high value of polyol chain length. Studies on the chemical stability, hydrolytic stability and soil test degradation behaviour were shown to be influenced by the high soft segment contents in semi-rigid PU composition.

Keywords: functionalized liquid natural rubber, hydroxylation, depolymerization, RSM and polyurethane.

PENGHASILAN CECAIR GETAH ASLI TERFUNGSI DARIPADA GETAH ASLI GRED RENDAH SEBAGAI ASAS UNTUK SEMI-TEGAR POLIURETENA

ABSTRAK

Getah asli cecair terfungsi (FLNR) yang diperolehi daripada getah asli (NR) gred rendah telah dihasilkan melalu kaedah redoks *in situ* menggunakan hidrogen peroksida (H_2O_2) dengan kehadiran natrium nitrit ($NaNO_2$). Pembentukan hidroksil (OH) sebagai kumpulan berfungsi utama telah disahkan oleh spektroskopi inframerah jelmaan fourier (FTIR) pada puncak 3425 cm^{-1}. Spektroskopi resonans magnetik nuklear (NMR) telah menunjukkan kehadiran kumpulan tengah OH dan kumpulan hujung dalam FLNR. Pengoptimuman *response surface methodology* (RSM) telah digunakan untuk mengkaji kesan pelbagai parameter suapan terhadap respon berat molekul dan nilai-nilai OH. Kontur *response surface* dibina untuk permodelan hubungan antara faktor-faktor pemprosesan dan *output* respon. Model yang dibangunkan menunjukkan bahawa $NaNO_2$ sebagai faktor utama diikuti H_2O_2 yang mempengaruhi sifat-sifat FLNR. Pengoptimuman multi respon telah dilakukan menggunakan fungsi *desirability* Derringer's. Kondisi optimum untuk meminimumkan berat molekul nombor purata (M_n) dan taburan berat molekul (MWD) manakala nilai OH maksimum telah ditentukan pada nisbah yang rendah bagi $NaNO_2/H_2O_2$ dan nisbah yang tinggi bagi H_2O_2/isoprena. Respon optimum yang diramalkan bagi M_n adalah dalam lingkungan kurang dari 30,000 g/mol, poliserakan (PDI) di antara 1.48 dan 1.61 dan nilai OH di antara194 dan 229 mg KOH/g. Pengesahan pengoptimuman yang telah dilakukan dan ralat kecil bagi peratusan yang telah dikira dari respon yang diramal dan dinilai telah diperolehi. Kromatografi penelapan gel (GPC) telah digunakan untuk mengkaji penurunan prestasi berat molekul dan pengukur *autotritator* OH digunakan untuk mengukur nilai OH bagi FLNR. Pemilihan nilai-nilai optimum bagi respon FLNR telah digunakan sebagai asas untuk menghasilkan semi-tegar poliuretena (PU). Penyediaan FLNR berasaskan semi-tegar PU dijalankan melalui teknik *one-shot* dan *two-shot*. Pembentukan ikatan uretena telah disahkan melalui FTIR pada puncak 3317 cm^{-1} berdasarkan -NH- dan kehilangan puncak NCO pada 2262 cm^{-1}. Getah poliol sebagai sebahagian segmen lembut telah menunjukkan implikasi major dalam produk polimer berdasarkan kandungan segmen lembut yang tinggi berbanding peratus kandungan segmen keras di dalam formula penyediaan semi-tegar PU. Ciri-ciri semi-tegar dengan panjang rantai poliol yang rendah dan domain fasa lembut yang tinggi menyukai kelarutan di dalam pelarut tidak polar (toluena dan klorofom) dan pelarut polar rendah (THF). Bagi rantai poliol yang tinggi, ia tidak melarut dalam mana-mana pelarut maka ia berkestabilan tinggi. Perbezaan dalam suhu peralihan kaca (T_g) telah menunjukkan kekuatan interaksi di antara segmen keras dan lembut adalah dari kedua-dua kaedah penyediaan *one-shot* dan *two-shot*. Kestabilan sifat terma yang diukur oleh penganalisa permeteran graviti haba (TGA) telah menunjukkan kaedah penyediaan *two-shot* telah memperbaiki prestasi semi-tegar PU sama ada pada nilai rendah dan nilai tinggi rantai poliol. Kajian keatas kestabilan kimia, kestabilan hidrolitik dan kelakuan ujian degradasi tanah terbukti dipengaruhi oleh kandungan segmen lembut yang tinggi dalam komposisi semi-tegar PU.

Kata kunci: Cecair getah asli terfungsi, hidroksilasi, pendepolimeran, RSM dan poliuretena.

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°C/min	Degree celsius per min
1,3-BDO	1,3-butanediol
1,4-BDO	1,4-butanediol
1,6-HDO	1,6-hexanediol
^{13}C	Carbon-13
^{1}H	Proton-1
2FI	Two-factor interactions
Adjusted R^2	Adjusted of coefficients of determination
AIBN	Azobis-iso-butyronitrile
Anhydrous $MgSO_4$	Anhydrous magnesium sulphate
ANOVA	Analysis of variance
ATR FT-IR	Attenuated total reflectance
BDO	Butanediol
BPO	Benzoyl peroxide
$CDCl_3$	Deuterated chloroform
CHDI	Cyclohexyl diisocyanate
COD	Cyclooctadiene
CTNR	Carboxy-terminated natural rubber
CV	Constant viscosity
D	Global desirability function
DBDTL	Dibutyltin dilaurate
DEA	Diethanolamine
DMF	Dimethyl formamide

DMSO	Dimethyl sulfoxide
DPNR	Deproteinized natural rubber
DRC	Dry rubber content
DSC	Differential scanning calorimetry
EG	Ethylene glycol
ELNR	Epoxidized liquid natural rubber
ENR	Epoxidized natural rubber
FLNR	Functionalized Liquid Natural Rubber
FT-IR	Fourier Transform Infrared
g	Gram
g/mole	Gram per mole
GP	General purpose
GPC	Gel permeation chromatography
$H_{12}MDI$	4,4-dicyclohexylmethane diisocyanate
H_2O_2	Hydrogen peroxide
H_5IO_6	Periodic acid
HCl	Hydrochloric acid
HDI	1,6-hexamethylene diisocyanate
HLNR	Hydroxylated liquid natural rubber
HTBD	Hydroxytelechelic butadiene
HTLNR	Hydroxylated telechelic liquid natural rubber
HTNR	Hydroxylated telechelic natural rubber
HTPB	Hydroxytelechelic polybutadiene
HTPI	Hydroxytelechelic cis-1,4-polyisoprene
I-IPDI	Isocyanurate of isophorone diisocyanate
IPDI	Isophorone diisocyanate

IPN	Interpenetrating polymer networks
$K_2S_2O_8$	Potassium persulfate
$KHC_8H_4O_4$	Potassium acid phthalate
LNR	Liquid natural rubber
M	Molar
MDI	Methylene diphenyl diisocyanate
mg	Milligram
mL	Milliliter
M_n	Number-average molecular weight
MOCA	4,4-methylenebis-2-chloroaniline
M_w	Weight-average molecular weight
N	Normality
NaCl	Sodium chloride
$NaNO_2$	Sodium nitrite
NaOH	Sodium hydroxide
NDI	1,5-Naphthalene diisocyanate
NMR	Nuclear Magnetic Resonance
NR	Natural rubber
NRL	Natural rubber latex
OH	Hydroxyl
OH value	Hydroxyl value
$Pb(OAc)_4$	Lead tetraacetate
pbw	Part by weight
PDI	Polydispersity index
PDMS	poly(dimethylsiloxane)
PHMO	poly(hexamethylene oxide)

Predicted R^2	Predicted of coefficients of determination
PRESS	Predicted residual sum of square
PU	Polyurethane
R^2	Coefficients of determination
ROMP	Ring opening metathesis polymerizations
RSM	Response Surface Methodology
Ru	Ruthenium
S/N ratio	Signal to noise ratio
Semi-rigid PU	Semi-rigid polyurethane
SMR	Standard Malaysian Rubber
$Sn(Oct)_2$	Stannous octoate
TDI	Toluene diisocyanate
TEA	Triethanolamine
T_g	Glass transition temperature
TGA	Thermogravimetry analyzer
T_gh	Glass transition temperature of hard segment
T_gs	Glass transition temperature of soft segment
THF	Tetrahydrofuran
TLNR	Telechelic liquid natural rubber
T_m	Melting temperature
T_mh	Melting temperature of hard segment
TODI	Bitoluene diisocyanate
TPU	Thermoplastic polyurethane
TSC	Total solid content
UV	Ultra-violet
w/v	Weight per volume

CHAPTER 1: INTRODUCTION

1.1 Background study

Polyurethane (PU) rubber is elastomeric PU that is derived from rubber polyol. This PU is composed of hard and soft segments arranged in the structure. This PU basically is the result of the reaction between diisocyanates and the chain extender, usually low molecular weight diols or diamines (Heiss, 1978; Mao, 1978). The soft segment is usually polyol, either hydroxy-terminated or amine-terminated polyester, polyether, polycarbonate and in special cases, polyolefin or hydrocarbon. Relatively few basic isocyanates (Burel et al., 2005a; Rogulska et al., 2007; Rogulska et al., 2006) and a range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of PU materials. Along with the wide different polyols (mostly with polyesters and polyethers backbone), hydroxytelechelic polydienes, such as polybutadienes based PUs (Auvray et al., 2003; Brosse et al., 2000; Davis & Koch, 1983; Graham & Shepard, 1981; Schafheutle et al., 2002; Schumann et al., 2000) and polyisoprene based PU (Grabowski, 1962; Sperling et al., 1998) are found to present particular interest both in industry and research development due to their physicochemical (physically and chemically changes such as solubility and stability) and mechanical properties (such as hardness, brittleness, elongation etc.).

The synthesis of functional polymers from renewable resources has attracted considerable attention because of their potential attributes as substitute to petrochemical derivatives (Lligadas et al., 2013; Nohra et al., 2013). Since natural rubber (NR) is a renewable source, it has become of particular interest for ongoing research to develop and refine its processing techniques to produce greater product varieties for the development of this industry. As a starting material, NR has a hydrocarbon structure that can be modified further to diversify its applications. One of the many derivatives of NR products is its depolymerization into functionalized liquid natural rubber (FLNR). These derivatives with low molecular weight ($M_n \leq 30{,}000$) are gaining high potential uses as new development products (Abdullah & Ahmad, 1992; Cenens & Hernandez, 1999; Dirckx et al., 1999). FLNR such as hydroxylated liquid natural rubber (HLNR), hydroxytelechelic liquid natural rubber (HTLNR) or telechelic liquid natural rubber (TLNR) represent a potential precursor of a very wide range of polymers. This type of NR is suitable for further chain extension and crosslinking, and has potential applications in making a variety of products based on NR (Nor & Ebdon, 1998). The chemical modifications of these materials (functionalized polydienes), are mainly focused on the oligomer characteristics which are strongly dependent on molecular weight distribution and the reaction conditions such as temperature, time, solvent nature, monomer ratios and stirring frequency (Knifton & Marquis, 1992).

However, one of the major factors impeding the use of FLNR obtained from depolymerized liquid NR is its high cost. While the average cost of NR from 1990 to 2015 was estimated at $0.63 USD per pound, depolymerized liquid NR has steadily increased from $3.50 to $4.00 USD per pound from 2011 to 2015. Currently, the world NR production is forecast to rise 4.3 percent annually to around 12 million tons per year (Fainleib et al., 2013); a certain amount of it is discarded in the producing countries during working operations (coagulation, washing, sheeting, etc.). These rejects could be a valuable source of depolymerized liquid NR, at a reasonable cost in comparison with petroleum-based isoprene derivatives, because in this case the cost of the starting substrate is practically zero. Therefore, in this current work, the low grade NR or low quality cup lump rubber was used as a starting material compared to the previous works that basically use the fresh rubber sources (Brosse et al., 2000; Burel et al., 2005a; Burel et al., 2005b). This low grade NR is rarely used and unfavorable in the rubber research field. Basically, this rubber material was chosen to be used for the big compounding products such as tyres, bridge bearings and any car components that normally use high molecular weight NR. The impurities and highest molecular weight of this material one the key issues especially when used as raw materials for niche products. This otherwise wasted leftover latex yield was selected because of its attractively low cost and ease of treatment for the reaction as well as having cleaner, more uniform and better aesthetic properties after processing compared to recycled rubber.

This current study will focus on the production and development of FLNR by *in situ* method that consists of hydroxylated group for use as precursor for semi-rigid PU. The *in situ* method was recommended as it is simple, easy and the cheapest method especially for industrial purposes. The advantage of this method is that the depolymerization and functionalization process was generated by *in situ*. The FLNR derived from NR is able to act as the reactive intermediate polyol. PU can be prepared by employing this FLNR polyol for the soft segment and aliphatic isocyanates (MDI) (Heiss, 1978; Mao, 1978; Ojha et al., 2009; Rogulska et al., 2007) with/without chain extender (1,4 butanediol) (Heiss, 1978; Mao, 1978) for the hard segment. The study on the formation of semi-rigid PU will be concentrated on the reaction conditions through two different methods of preparation i.e. *one-shot* and *two-shot* methods. Various stoichiometric ratios of isocyanate to hydroxyl groups ([NCO]/[OH] ratio) to identify the hard segment and soft segment compositions will be carried out. The reaction was also carried out in the presence of stannous octoate or tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) as a catalyst (Heiss, 1978; Mao, 1978). The preparation of semi-rigid PU is believed to have the character is between flexible and rigid PU. At the same time, it has enhanced properties that will overcome certain problems that were hindered in flexible and rigid PUs. Thus, to obtain better formulation for this semi-rigid PU, the optimized parameters is necessary that can fulfill the criteria of precursor (polyol) as starting material.

An attempt is made to investigate the priority parameters that are useful for these rubber materials that can act as starting material to develop useful rubber technology products such as FLNR. From the previous researches (Ibrahim et al., 2014; Kébir et al., 2005a), there are hardly any specifics discussion that is related to the optimization of *in situ* depolymerization and hydroxylation of FLNR as precursor for PU. The study by *in situ* method in FLNR preparation had been reported but frequently the discussion was directly focusing on the character and examination of the final products (Isa, 2011; Isa et al., 2007). The experimental design focusing on reaction time, temperature, or other variables have already been extensively studied (Isa, 2011; Kébir et al., 2005a). However, studies on the relationship of molar ratios of hydrogen peroxide (H_2O_2) and sodium nitrite ($NaNO_2$) as the reagents have been scarce until recently (Ibrahim & Mustafa, 2014). Although they have made significant characterization of their experimental responses using Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FT-IR), and identified a single optimum point with it, a statistical model describing the relationship between the molar ratios of the two reagents was not clearly elucidated.

In general, the step-wise experimental study approach for each of the parameters involved in the synthesis procedures is not only time consuming but also requires special attention in cases where there is a contribution of multiple parameters interacting simultaneously in the system. Therefore, an appropriate model can be of significant interest to simulate and predict the responses from the parameters involved in the synthesis process. Among the modeling approaches, the response surface methodology (RSM) is a powerful technique in optimizing the industrial process. In this study, the simultaneous depolymerization and hydroxylation of NR was done *in situ* using a $NaNO_2/H_2O_2$ system. The aim of the present work is to study the effect of varying the amounts of H_2O_2 and $NaNO_2$ in their action feed towards the resulting properties of molecular weight and formation of hydroxyl functionality of the synthesized FLNR. RSM is used for studying these variables for the depolymerization and hydroxylation process to predict the outcome of the molecular weight and OH content of FLNR. The RSM enables the prediction of the optimum parameters that useful for PU synthesis. The RSM study begins with a definition of a problem concerning which response is to be measured, how it is to be measured, which variables are to be explored. The experiment plan is then designed and followed by analysis of variance (ANOVA) (Idris et al., 2006).

Then, the synthesis of FLNR based semi-rigid PU film was performed by *one-shot* and two-*shot* technique. The characterization was examined and analyzed by Fourier transform infrared (FT-IR) and the molecular weight was identified using gel permeation chromatography (GPC). The interaction between soft and hard segment in semi-rigid PU was measured through solubility behaviour and could be determined via differential scanning calorimetry (DSC). The thermal stability of the semi-rigid PU was investigated by TGA. In addition, studies on chemical stability, hydrolytic stability and soil test degradation behaviour were done to justify the effect of hard and soft segment content on semi-rigid PU composition.

1.2 Problem statement

PU is normally produced from petroleum based materials. Polyols currently used in the production of urethanes are petrochemical, being generally derived from propylene or ethylene oxides. Polyester polyols and polyether polyols are the most common polyols used in urethane production. As petrochemicals are ultimately derived from petroleum, they are non-renewable resources. Besides the production of a polyol requires a great deal of energy, as oil must be drilled extracted from the ground, transported to refineries, refined, and otherwise processed to yield the polyol. These required efforts add to the cost of polyols and to the disadvantageous environmental effects of its production. Also, the price of polyols tends to be somewhat unpredictable and tends to be exhausted in the near future. Also, as the consuming public becomes more aware of environmental issue and exhaustive issue, there are distinct marketing disadvantages to petrochemical based products.

Consumer demand for “bio-based” or “green chemistry” products continues to grow. The term “bio-based’ or “green chemistry” polyols for this application is meant to be broadly interpreted to signify all polyols not derived exclusively from non-renewable resources. Thus, it would be most advantageous to replace polyester or polyether polyols, as used in the production of urethane foams or films and elastomers, with multipurpose application, renewable, less costly, and more environmentally friendly. Therefore, the natural resources derived from plants can replace the use of petroleum. The synthesis of semi-rigid PU rubber based on NR modification is one alternative to reduce the petroleum use.

NR has the hydrocarbon structure that can be used as the starting hydrocarbon chemicals to replace petroleum in any chemical reactions. This new development will be a cost-effective technique as we use waste natural crumb rubber in the PU modification. Many of the chemical modifications of rubber have dealt principally the synthetic rubbers because of the higher purity of the product. Previous researchers on FLNR study mostly focusing on latex concentrated, rubber sheet, crepe rubber and crumb rubber from field latex but in this study the raw material used is sourced from the unwanted portions of the latex tapping yield (low quality cup lump or low grade NR). The low grade NR sometimes give the unstable reaction process depending on the impurities but the *in situ* method known as the simplest and cheapest method of preparation. The difficulty work was faced to get the better condition on stability control of NR during conducting the reaction. The composition of each parameter especially reduction and hydroxylation agent should be control carefully. In addition, the reaction temperature, agitation rate and time of reaction must be considered during the synthesis to make sure the composition of reduction and hydroxylation agent was efficient to form the targeted FLNR. Because of that phenomenon, the related parameters on reaction control need to be studied to find out how this method (*in situ*) is useful in the FLNR synthesis. Then the optimum parameters were chosen to see how the performance of FLNR can act as semi-rigid PU precursors using RSM optimization and confirmation.

Semi-rigid PU either from segmented or nonsegmented PU has the various applications especially in various biomaterials or biomedical applications. PUs offer a broad range of physical properties and characteristics including high tensile and tear strengths, chemical and abrasion resistances, good processibility and protective barrier properties (Brosse et al., 2000; Burel et al., 2005a; Heiss, 1978; Mao, 1978; Rogulska et al., 2007; Rogulska et al., 2006). PU basically are segmented polymers comprising of hard segment and soft segment. The hard segments are formed from short-chain diols and diisocyanates and particularly affect the modulus, hardness and tear strength. Meanwhile the soft segments are composed of long chain diols and provide flexibility and low temperature resistance. The interactions between hard segments containing many hydrogen bonding and dipole-dipole interactions provide pseudo-crosslinked network structure between linear PU chains. The formation of semi-rigid type of PU will give the enhanced properties compared to flexible and rigid PU. The formulation and preparation of semi-rigid PU is commonly quiet difficult compared to flexible and rigid PU. By using the RSM optimization and confirmation on FLNR intermediate, semi-rigid PU had been prepared and produced.

1.3 Objectives of study

This study embarks on the following objectives:

- To synthesize functionalized liquid natural rubber (FLNR) with $M_n<30{,}000$ g/mol consisting of hydroxyl reactive groups (OH value is between 150 - 250 mg KOH/g) as intermediate polyols using *in situ* depolymerization and hydroxylation method.
- To optimize FLNR produced as a semi-rigid PU precursor based on response surface methodology (RSM) by analysis of variance (ANOVA).
- To determine the formulation and identify the thermal and stability properties of polyol rubber based semi-rigid PU film.

1.4 Scope of study

Chapter 1 describes the general introduction of PU elastomer and FLNR as the starting materials. The use of FLNR that basically consists with hydroxyl reactive groups as intermediate to produce PU is explained. Then, the research design of FLNR as precursors for semi-rigid PU product also is discussed by optimizing the parameters using response surface methodology (RSM). The problem statement is described as to the reason why the natural rubber gave good benefit to replace the petroleum sources as raw materials. Besides that, the reason for use of raw materials of natural rubber sources (low grade NR and the chosen method of reaction *in situ* compare *ex situ* method reaction is also explained. In this study, the gap in knowledge is the optimization method on parameter and application of modelling is rarely studied in the field of rubber. The objectives are proposed to the study.

Chapter 2 describes on literature review for FLNR and the process of preparation. The PUs based on NR derivatives are discussed including the preparation and application. The main discussion on PU is how to synthesize and what are the ingredients that involved in the formulation to produce either flexible, rigid or semi-rigid PU. The properties of PU is focused on the development of PU for biomaterial purposes which will be of advantage to the environment.

Chapter 3 describes the materials, procedure, subjects or participants and also statistical procedures that have been used for this study. This study is carried out in two stages. First stage is the synthesis of FLNR as precursors for the preparation of semi-rigid PU. The optimization was run using Response Surface Methodology by Design Expert Software. Second stage is the formulation of semi-rigid PU by *one-shot* and *two-shot* method. The overall samples were characterized by using the various instruments, such as GPC, autotitrator, FT-IR, NMR, DSC and TGA. Besides that, the other properties of samples were examined by exposure in different media.

Chapter 4 discusses the results on production of FLNR by degradation of NR and hydroxylation via *in situ* method and its characterization are GPC, OH value (OH value), FT-IR and NMR. The parameters on the production of FLNR had been optimized using RSM and analyzed by ANOVA. The prediction, confirmation and observation on molecular weight and OH value were generated and used for the formulation of semi-rigid PU based on FLNR.

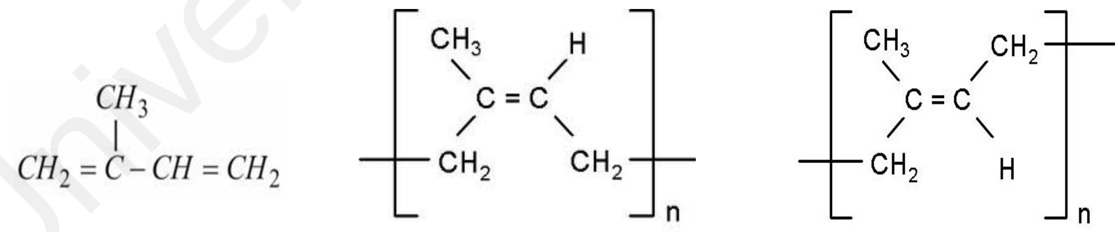
Chapter 5 discusses the semi-rigid PU film formulation by *one-shot* and *two-shot* techniques. The formation of semi-rigid PU was confirmed by FT-IR. The molecular weight by GPC, hardness test and density are also conducted to perceive the character of the semi-rigid PU. As for enhancement, the solubility test was done and this result could help as evidence on the effect of rubber polyol (FLNR) in the soft and hard segment of semi-rigid PU properties. Besides that, the measurement by DSC and TGA also investigate the effect of FLNR on thermal properties of semi-rigid PU. Other properties of these type of PU film was also performed, i.e. chemical stability, hydrolytic stability and soil test degradability.

Chapter 6 concludes of this FLNR based semi-rigid PU. The significance of RSM as useful optimization method in formulation of semi-rigid PU based on rubber polyol.

CHAPTER 2: LITERATURE REVIEW

2.1 Natural rubber

Natural rubber (NR) is a polymer in liquid form obtained from rubber tree and mostly found in tropical areas especially at North South Asia. Nowadays Asia especially Malaysia, Thailand and Indonesia are known as the main countries that produce NR. The main structure of NR molecule is hydrocarbon that consists of the C_5H_8 isoprene composition (Figure 2.1 (a)). NR basically is divided into two types which are cis-1,4-polyisoprene and trans-1,4-polyisoprene. Cis-1,4-polyisoprene (Figure 2.1(b)) is obtained from latex of *Hevea Brasilensis* tree and it has an irregular conformation in the solid state. It is also unable to crystallize under normal conditions and exists as an amorphous or rubbery material. In contrast, trans-1,4-polyisoprene (Figure 2.1 (c)) is produced from *Balata* (*Manikalkae* species) and *Gutta percha* (*Palagian* and *Payena* species). They have more regular structures compared to cis-1,4-polyisoprene and able to crystallize. They can crystallize under normal conditions and exist as hard rigid materials (Nor & Ebdon, 1998).



(a) (b) (c)

Figure 2.1: Chemical structure of (a) isoprene (b) cis -1,4-polyisoprene and (c) trans-1,4-polyisoprene

The raw material used to produce NR is a white milky fluid called latex taken from the latex cups of rubber trees. It can be categorized as field latex, scrap, soil lump and bowl lump. Chemically, natural rubber latex (NRL) consists of total solid content

(TSC) including dry rubber content (DRC), resins, proteins, ash, sugar and water. Even though the structure of NR is similar to synthetic cis-1,4-polyisoprene, the presence of various non-rubber components in this natural product, such as amino acids, proteins, carbohydrates, neutral and polar lipids, and inorganic substances ; can possibly modify its chemical reactivity and mechanical properties (Nor & Ebdon, 1998). Figure 2.2 shows different types of raw rubber processings and their usage in making various rubber products.

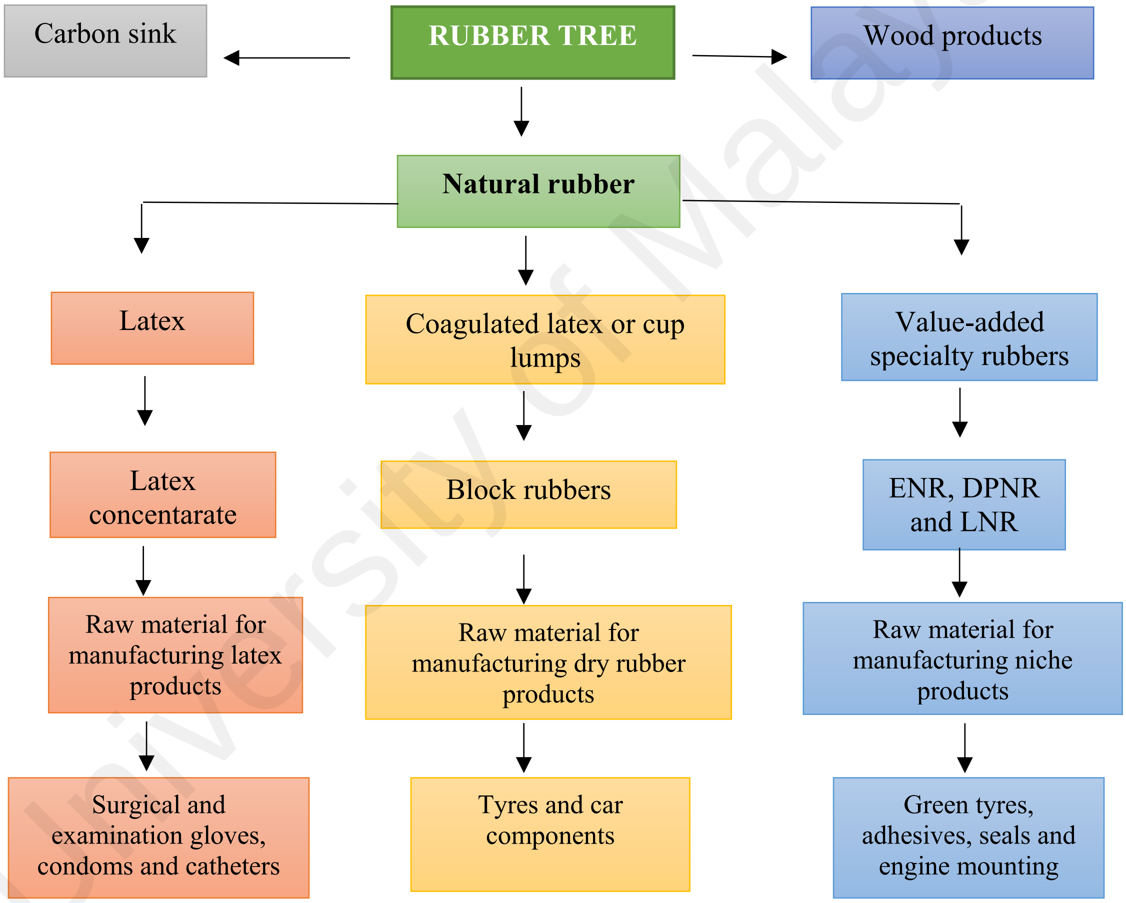


Figure 2.2: Schematic diagram of raw rubber processing and rubber products manufacturing

The product of NR can be broadly classified under two categories; dry and liquid rubber. Dry rubber refers to the grades, which are marketed in the dry form such as rubber sheet, crepe rubber and crumb rubber; whereas liquid rubber refers to the latex concentrate production. As shown in Figure 2.2, basically coagulated latex or cup lumps NR used as raw material for manufacturing of dry rubber products to produce high molecular weight end products such as tyres, car components etc.

In this work, natural crumb rubber from low quality cup lump was chosen because it is rarely used and basically known as “technical specification rubber” (Van et al., 2007). The benefits of this NR are that it is cleaner and uniform, has good appearance and easy to process. So, it is very useful to chemically modified as value-added specialty rubbers of raw material for manufacturing niche products in varieties applications especially for biomaterials purposes.

2.2 Liquid natural rubber

Liquid natural rubber (LNR) is defined as dry NR that can be poured, flow and pumped without inside medium such as solvent at room temperature. It also can be defined as material in NR form with the same microstructure having short polymer chain with low molecular weights about 10^5 g/mol. It can flow at room temperature and the mixing process in no longer a problem and may cost less. LNR has been commercialized and the first production on a small scale basis was by Hardman in 1923 (Sheard, 1972). Basically, the preparation of LNR involved the oxidative chain scission of the polyisoprene backbone. The technique of oxidation reaction or degradation of NR also developed year by year as renewable sources. The chemical degradation of NR is a straightforward method of creating functional liquid NR (FLNR) that can be used for additives such as compatibilizer and plasticizer (Abdullah & Ahmad, 1992; Ahmad & Abdullah, 1992; Ahmad et al., 1994; Dahlan et al., 2000; Dahlan et al., 2002a; Dahlan et al., 2002b; Dileep et al., 2003; Mounir et al., 2004; Nor & Ebdon, 1998), adhesives (Glennon, 1981, 1982; Nor & Ebdon, 1998; Thongnuanchan et al., 2007), coating (Dechant, 1991; Gupta et al., 1985; Nor & Ebdon, 1998; Phinyocheep & Duangthong, 2000; Woods, 1990), binders (Gupta et al., 1985), thermoset PU (Cavallaro et al., 1997; Nor & Ebdon, 1998) and interpenetrating polymer networks (IPN) (Baek and Kim, 2003; Merlin & Sivasankar, 2009; Nor & Ebdon, 1998; Sperling et al., 1998).

Nowadays, most of the researches on LNRs are focus on the development of new materials. LNR technology has entered a new era with the development of LNR bearing reactive terminal groups which are capable of being utilized in further chain extension reactions (Nor & Ebdon, 1998; Zhang et al., 2010). The inclusion of the specific functional groups acting as pendant groups at the chain ends are potentially reactive with the other reagents through chain extension reactions to be able to produce new polymer structures (Kébir et al., 2006; Kébir et al., 2005a; Kébir et al., 2007).

2.3 Functionalized liquid natural rubber

Functionalized Liquid Natural Rubber (FLNR) can be defined as low molecular weight NR having M_n of 10^2-10^4, approximately, and bearing reactive terminal groups capable of being used in further chain extension and crosslinking or entering into further polymerization (Nor & Ebdon, 1998). FLNR consists of isoprene units but is different from NR as it has reactive groups at the chain end and main chain, is donated by X and Y as shown in Figure 2.3 (a). This X and Y may, or, may not be similar. Previous study had reported that the average functionality of FLNR was the ranges of 1.9 to 2.8. The M_n values of FLNR was obtained from redox method between 3000 and 35000 g/mol and polydispersities between 1.70 and 1.97 (Nor & Ebdon, 1998; Pautrat & Marteau, 1974). Even though research on the production of FLNR has begun in the early 1970s but the commercial FLNR is still not widely available and used. Most of the research and investigation are those prepared in laboratory (Brosse et al., 2000).

One of the favorable FLNR is a telechelic liquid natural rubber (TLNR). The term of ‘telechelic’ refers to the low molecular polymers bearing two functional end groups. This term can also be applied to oligomers having two or more terminal groups (Brosse et al., 2000; Nor & Ebdon, 1998). The general chemical structure of TLNR is shown in Figure 2.3 (a) and (b) shows the hydroxylated telechelic natural rubber (HTNR) containing hydroxyl group as the terminal chain in the structure. There is also the probability of the hydroxylated liquid natural rubber (HLNR) containing hydroxyl groups at the centre of the chain besides at both terminals in the structure.

Figure 2.3: Chemical structures of (a) telechelic liquid natural rubber and (b) hydroxytelechelic liquid natural rubber

2.4 Synthesis method of functionalized liquid natural rubber

Fundamentally, the methods comprise of controlled depolymerization (degradation) and hydroxylation of the NR backbone through oxidation chain scissions by either chemical or photochemical procedures. The methods can be classified into five main categories, namely oxidative depolymerization in the presence of redox system, oxidative depolymerization by photochemical method, oxidative depolymerization at high temperatures and high pressures, oxidative and depolymerization by cleavage reagent specific to double bond and metathesis depolymerization or degradation. Each category has different approach either using *in situ* or *ex situ* techniques or modification on the final products.

2.4.1 Oxidative depolymerization in the presence of redox system

The depolymerization method employs an appropriate mixture of oxidizing and reducing agents or named as redox couple. The redox couple can cleave polymer chains with the appearance of reactive terminal groups on the resulting oligomers (Nor & Ebdon, 1998). The depolymerization uses oxidizing agent such as an organic peroxide, hydrogen peroxide (H_2O_2), atmospheric oxygen or ferric chloride-oxygen, coupled with reducing agent such as an aromatic hydrazine or sulphanilic acid or sodium borohydride can yield FLNR bearing phenylhydrazine, carbonyl or hydroxyl terminal groups, depending on the redox system.

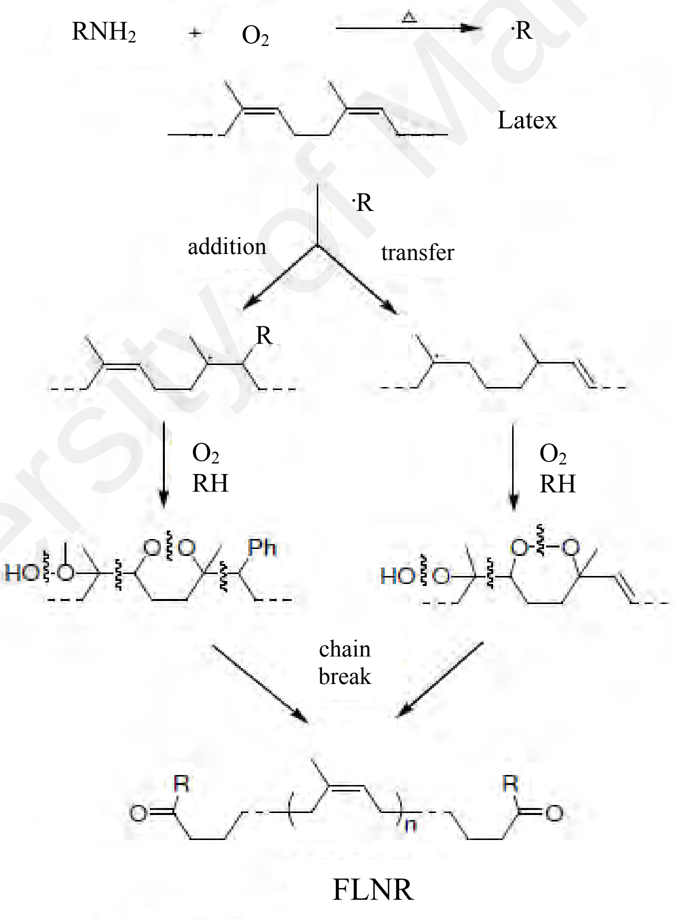


Figure 2.4: Depolymerization of natural rubber in the latex phase by combining atmospheric oxygen in the presence of phenylhydrazine at the carbon-carbon double bond

A phenylhydrazine-oxygen system had been developed by previous researchers producing FLNR with the targeted molecular weight but suffered from the use of toxic reagents and the difficulty to remove impurities which when leaving left a dark brown colour products. The reaction of the latex phase using phenylhydrazine as reducing agent and atmospheric oxygen as an oxidizing agent was more favored economically especially in the industrial scale (Nair et al., 1995; Sperling et al., 1998). The reaction mechanism of this system was shown in Figure 2.4.

Oxidative depolymerization reaction of deproteinized natural rubber (DPNR) using different initiators, azobis-iso-butyronitrile (AIBN), potassium persulfate ($K_2S_2O_8$) and benzoyl peroxide (BPO) in the presence of a carbonyl product such as acetone formaldehyde or propanal had also been reported (Tangpakdee et al., 1998). The finding of study demonstrated that $K_2S_2O_8$/propanal system was most effective for NR degradation at 60°C. The proposed mechanism brought forward is that the oxidation of chain is by radical initiator followed by the reaction of propanal with aldehyde end group. The obtained FLNR contains aldehyde and ketone groups as shown in Figure 2.5.

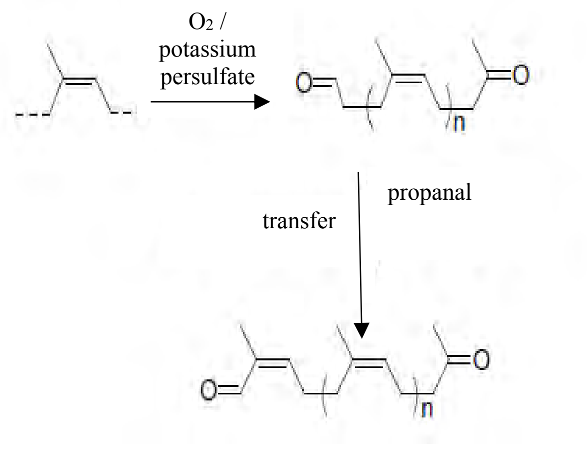


Figure 2.5: Depolymerization reaction of depolymerized natural rubber in the presence of potassium persulfate and propanal

The effect of H_2O_2 as oxidizing agent followed by $NaNO_2$ as reducing agent has also been reported. However, studies on the relationship of molar ratios of H_2O_2 and $NaNO_2$ as the reagents have been scarce until recently (Ibrahim et al., 2014; Ibrahim & Mustafa, 2014). Although characterization of the experimental responses using GPC, NMR and FT-IR, and identified a single optimum point with it, a statistical model describing the relationship between the molar ratios of the two reagents was not clearly elucidated.

2.4.2 Oxidative depolymerization by photochemical method

Control depolymerization of NR by photochemical chain scission for preparation of LNR was first discovered (Cunneen, 1974). The low molecular weight LNR was obtained by irradiated NR with ultra-violet (UV) light in presence of nitrobenzene as a photosentisizer to produce carboxy-terminated natural rubber (CTNR). Although the study of degradation of NR in solid state was revealed but no further development was made.

The controlled degradation of NR in solution was also studied previously by Ravindran et al., (1988) who found that sunlight is almost as effective as UV light in depolymerization of NR in toluene. However, the depolymerized NR structure was complicated by side reactions. The suggested mechanism of this study on development of hydroxyl (OH) bond as reactive group is shown in Figure 2.6.

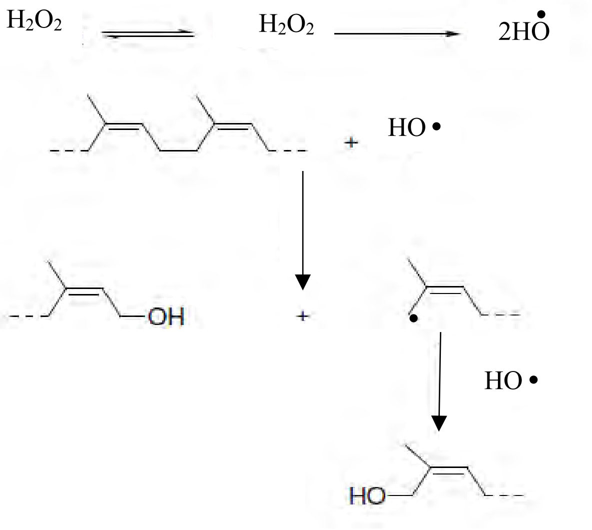


Figure 2.6: Depolymerization of cis-1,4-polyisoprene by hydrogen peroxide/ultraviolet radiation

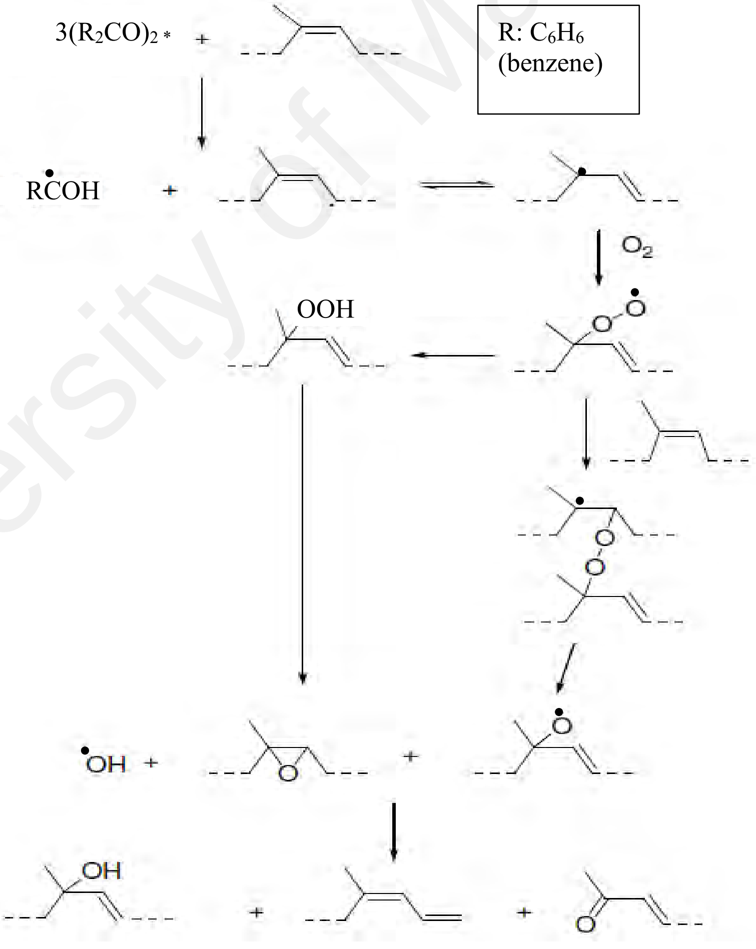


Figure 2.7: Depolymerization of cis-1,4-polyisoprene reaction by benzophenon/ultraviolet radiation

Later, the photochemical depolymerization method was revised (Nor & Ebdon, 1998). However, depolymerization of NR from fresh latex with 20% DRC (Dry Rubber Content) by sunlight and H_2O_2 lacked the information of other reagent types and functionality. In another case, NR was swelled in solution and depolymerized in the presence of benzophenone (photosentisizer) and exposing to sunlight for a day. FLNR with weight-average molecular weight (M_w) between 10,000 and 50,000 g/mol was obtained. The mechanism of the reaction believed to be involved in this method is given in Figure 2.7 in which there is chain scission and obtaining OH, hydroperoxide and ketone end groups are obtained (Nor & Ebdon, 1998)

Besides that, the depolymerization of DPNR latex with potassium persulfate ($K_2S_2O_8$) was studied. The incompletely controlled results showed that competitive reactions between epoxidation and cleavage reaction had occurred (Tangpakdee et al., 1998). In addition, the depolymerization of DPNR latex in the presence of periodic acid as reported by Phinyocheep et al. showed that the content of epoxide before and after depolymerization was approximately the same (Phinyocheep et al., 2005). Later, the modification of FLNR using periodic acid in depolymerization and functionalization was been done by Saetung et al. for use as potential PU precursors (Saetung et al., 2010).

2.4.3 Oxidative depolymerization at high temperatures and high pressures

In this method, the rubber solution of the masticated NR in toluene containing hydrogen peroxide (30-40%) was heated at 150°C in reactor at a pressure of 200-300 psi to yield HTNR having M_n less than 3000 g/mol. From the analytical data, the efficiency of functionalization of HTNR by this method was low. This situation happened because of the presence of side reactions. A mechanism of reaction that the appearance of hydroxylated groups has been proposed as shown in Figure 2.8.

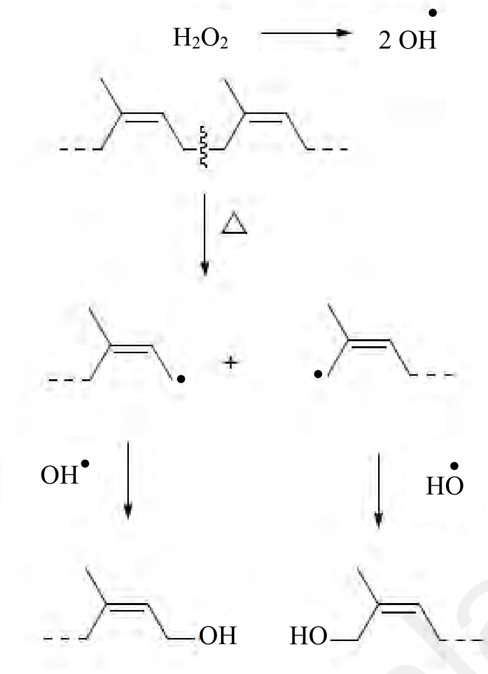


Figure 2.8: Depolymerization of cis-1,4-polyisoprene by hydrogen peroxide at high temperature and high pressure

The depolymerization reaction of FLNR was reported and found the existing of H_2O_2 at high temperature will form side reactions such as furanization and crosslinking (Zhang et al., 2010). They suggested that the depolymerization reaction is not advisable at temperatures more than 90°C.

2.4.4 Oxidative and depolymerization by cleavage reagent specific to double bond

2.4.4.1 Ozonolysis

The term of 'ozonolysis' refers to the cleavage of bonds by ozone leading to the formation of peroxy or non-peroxy products, whereas the term 'ozonization' refers purely to the process of treatment of a compound with ozone (Nor & Ebdon, 1998). Criegee had proposed the mechanism of ozone attack on C=C bonds of polydiene rubber backbones, causing chain scission and yielding various peroxidic products (Criegee, 1975) (Figure 2.9).

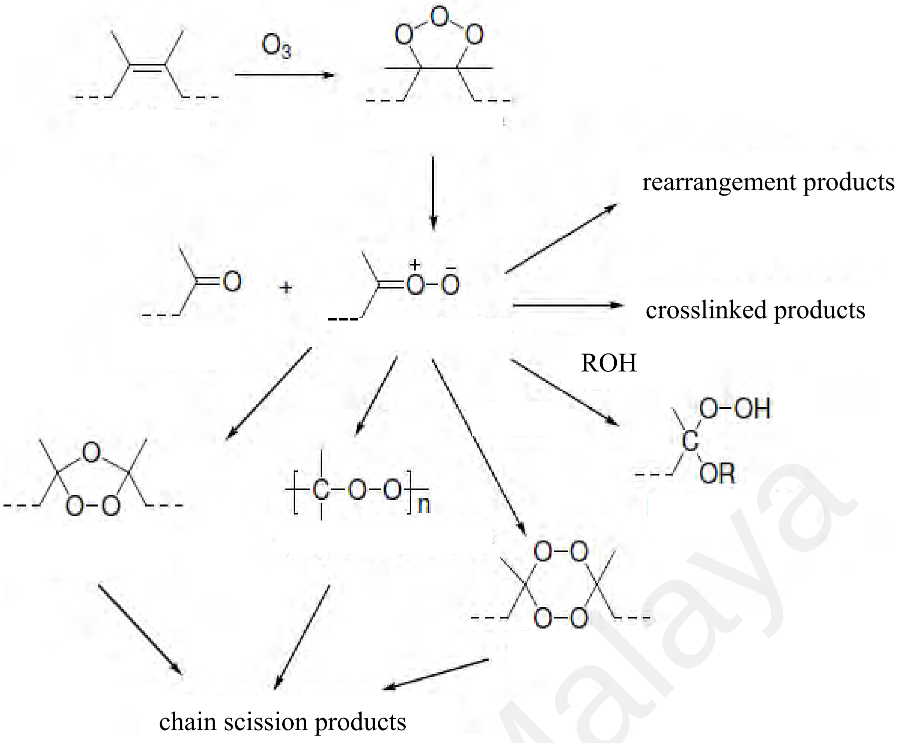


Figure 2.9: Mechanism reaction of ozone at double bond of polydienes

This depolymerization has resulted in a decrease of molecular weight and increase in species containing oxygenated functional group such as aldehyde, ketonee and peroxide.

Besides that, Tanaka et al. showed that controlled ozonolysis of trans- and cis-1,4-polyisoprene and 1,4-polybutadiene had resulted in selective chain scission and produces HTNRs and HTBDs having low repeating units with very narrow polydispersities (Tanaka et al., 1999). The ozonolysis of cis-1,4-polyisoprene in hexane at ice-bath temperature of about -3 to 0°C without further treatment has been shown to form telechelic oligomers bearing only ketone and carboxylic acid end groups with no oligomeric ozonides being identified (Montaudo et al., 1992) and Figure 2.10 represents the reaction mechanism as proposed by Anachkov et al. (Anachkov et al., 2000; Anachkov et al., 1985). It also reported that ozonolysis of cis-1,4-polyisoprene in carbon tetrachloride can lead to the basic ozonolysis products of ozonide, ketones and aldehydes.

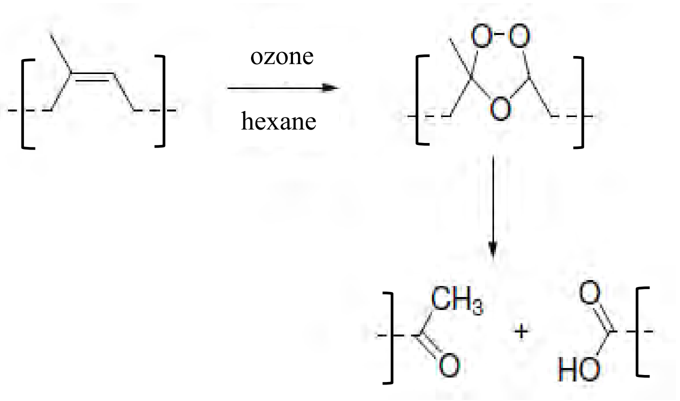


Figure 2.10: Proposed mechanism of ozonolysis of cis-1,4-polyisoprene in hexane

2.4.4.2 Cleavage by periodic acid or transition compounds

The bifunctional oligomers were developed by Guizard et al. using the specifically double bonds cleavage method. Ruthenium (Ru) tetraoxide was used in the presence of periodic acid (H_5IO_6) as co-oxidant. Chain scission was shown occur at unsaturated sites rather than randomly (Guizard & Cheradame, 1979, 1981). Further study reported that lead tetraacetate ($Pb(OAc)_4$) caused degradation of hydrolyzed epoxidized synthetic rubber faster than that of epoxidized synthetic rubber. H_5IO_6 could also be used to degrade NR and acid hydrolyzed NR. It is believed that the chain depolymerization of NR occurs in the presence of a few NR 1,2-diol units in the molecular chain (Burfield & Gan, 1977). Later, with the use of H_5IO_6 it was found that the epoxide content of starting rubber decreased from 25 to 8% after degradation reaction. The presence of aldehyde and ketone moieties, residual oxiranes, and secondary furanic and cyclic structures were shown by NMR spectrum (Reyx & Campistron, 1997).

Besides that, Gillier-Ritoit et al. (Gillier-Ritoit et al., 2003) investigated chain depolymerization of polyisoprene using H_5IO_6 in organic solvent similar to those of depolymerized epoxidized polyisoprenes. The depolymerized rubber contained aldehyde and ketone terminal ends, but the reaction was slower than in case of epoxidized polyisoprene. They found that in epoxidized polyisoprene, the H_5IO_6 cleavage of polymer chain could occurred have nearly instantaneously, whereas the H_5IO_6 cleavage of double bonds was a slow reaction process. They proposed two step mechanisms for the cleavage of the double bonds. Firstly, H_5IO_6 reacts with a double bond to give an epoxide and α-glycol. Secondly, the epoxide or α-glycol is cleaved by reacting with the second equivalent of H_5IO_6. The proposed mechanism of the reaction is shown in Figure 2.11.

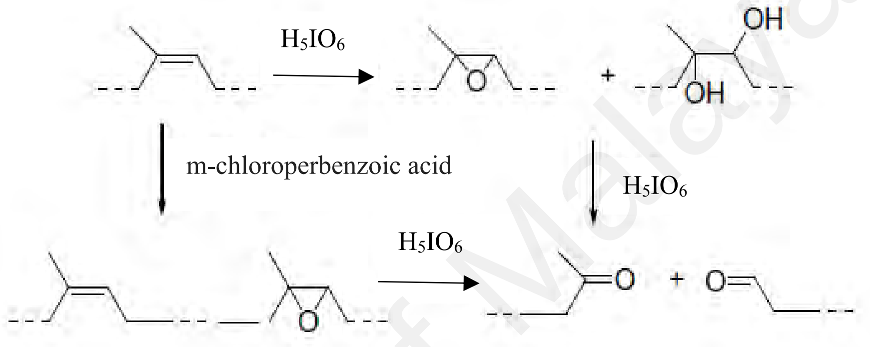


Figure 2.11: Depolymerization of cis-1,4-polyisoprene and epoxidized cis-1,4-polyisoprene using periodic acid

Mauler et al. investigated that degradation of cis-1,4-polyisoprene by using H_5IO_6/ultrasonic radiation (sonochemical degradation) was more efficient than the use of radiation or chemical degradation alone. The presence of ultrasound irradiation has accelerated the chemical degradation process leading to lower molecular weight products. Analysis on molecular weight data confirmed that in the case of sonochemical degradation the increase of temperature did not imply automatically an increase in the rate of the chemical process. The sonochemical reaction rate constant must be a function of parameters of both processes, ultrasonic and chemical degradation, as well as parameters which are the results of combination of the two processes though more study is needed for further understanding (Mauler et al., 1997).

The *in situ* method in the degradation of deproteinized epoxidized NR in latex phase had also been studied using H_5IO_6 (Phinyocheep et al., 2005). There was no observation of NMR signals corresponding to products of side reactions such as formation of diol and furan in the ENR samples, as previously mentioned. The epoxides and the new signals of carbonyl and hydroxyl functional groups were found and also a decrease in the molecular weight. Therefore, the reaction pathway was proposed (Guizard & Cheradame, 1981) as shown in the Figure 2.12.

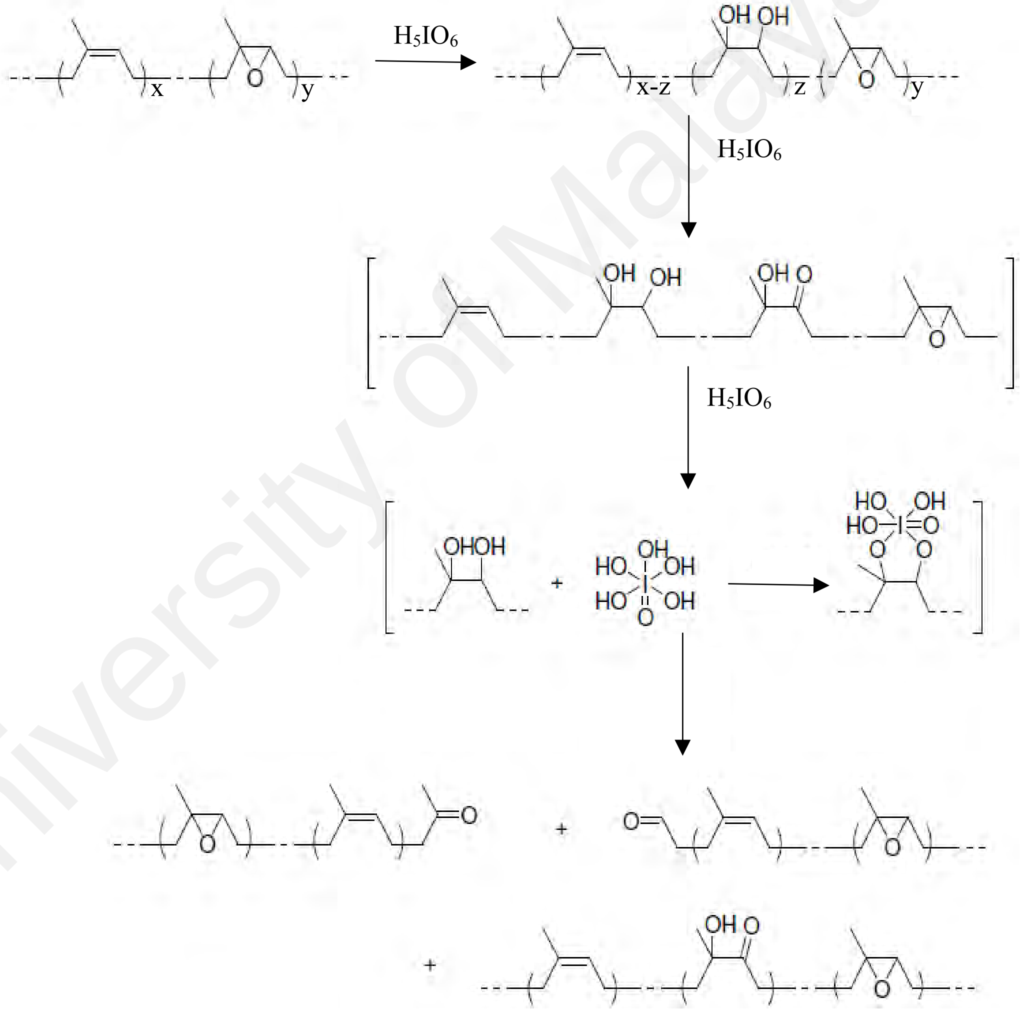


Figure 2.12: Proposed reaction pathway of oxidative degradation of epoxidized rubber by periodic acid

The methods of depolymerization and hydroxylation using H_5IO_6 is useful as a process of epoxidation formation and decreases the molecular weight of NR. Depolymerization reaction to get the product of low molecular weight liquid rubber functions with epoxide is normally carried out using periodic acid. This type of epoxidized liquid natural rubber (ELNR) product will be useful for coating application.

2.4.5 Metathesis depolymerization

The metathesis method is another approach for depolymerization of rubber to produce the reactive intermediate polyol. The polybutadiene was the first to be used in the study by metathesis depolymerization. Marmo et al. had described the mechanism on the synthesis of mass-exact telechelic polybutadiene oligomer by metathesis degradation of cis-1,4-butadiene using allylsilane monoene and alkyldienes complex catalyst (Marmo & Wagener, 1993). The mechanism was proposed whereby the first stage of reaction was through intermolecular cyclization of 1,4 polybutadiene, followed by macrocyclic butadiene cross-metathesis with functionalized monoene to form linear difunctional telechelic oligomer (Marmo & Wagener, 1995) (Figure 2.13).

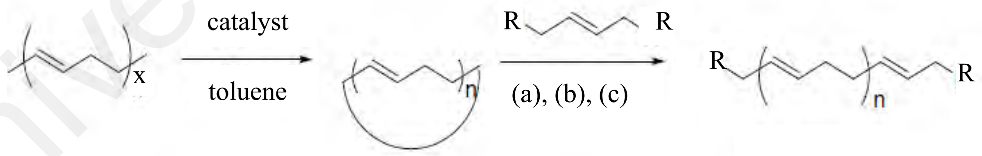


Figure 2.13: Depolymerization of cis-1,4-polybutadiene with diethyl 4-octene-1,8-dioate (a), bis(t-butyldimethylsilyl)-3-hexane-1,6-diol diether (b), and 2-butene-1,4-diylbis(phthalimide) (c)

The use of ruthenium (Ru) metathesis catalyst was studied by Hilmyer et. al for synthesis of end-functionalized polybutadiene (Hilmyer et al., 1997). Metathesis of olefin alcohols with Ru showed that side reactions may complicate the use of these materials as chain transfer agents in ring opening metathesis polymerizations (ROMP).

Further study of ROMP showed highly active Ru catalyst has allowed the preparation of bis(acetoxy)-terminated telechelic polybutadienes with molecular weights controllable up to 3.0 x 10^4 (Bielawski et al., 2001). The polymers obtained via the ROMP of cyclooctadiene (COD) in the presence of an acetoxy functionalized chain transfer agent using monomer/catalyst ratios, had molecular weight as high as 9.8 x 10^4. The acetoxy groups were easily cleaved with methanolic solutions of sodium hydroxide to afford high yields of hydroxytelechelic polybutadienes (HTPB).

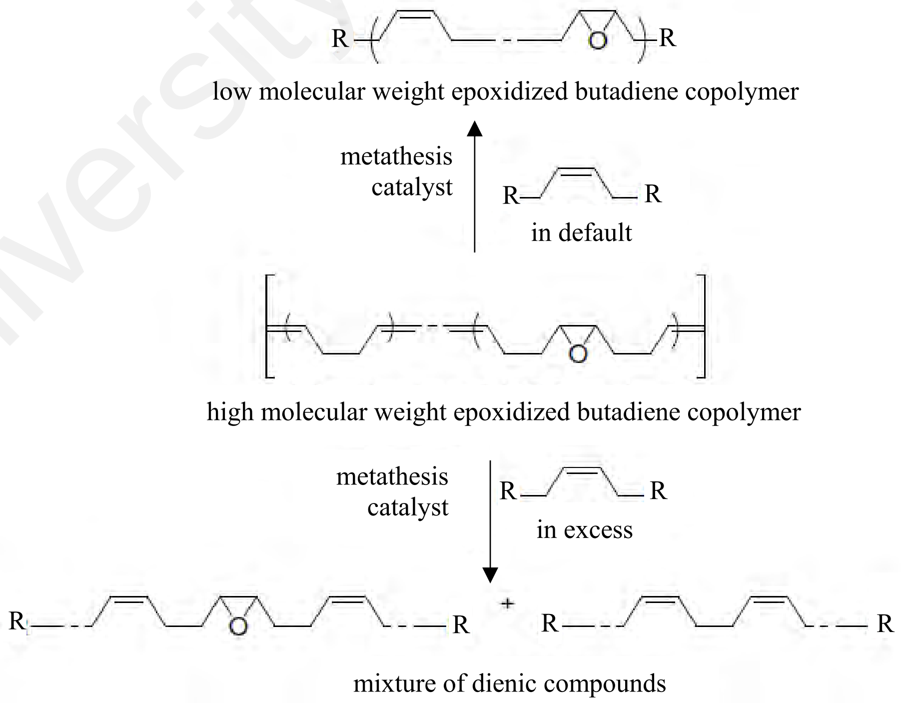


Figure 2.14: Mechanism of metathesis alkenolysis of partially epoxidized polybutadiene

Nevertheless, presently this technique is rarely used in the polyisoprene depolymerization. Metathesis introduces metathetic alkenolysis of partially epoxidized cis-1,4-polybutadiene using Grubbs' ruthenium benzylidene compound as catalyst and 4-octene as depolymerizing agent (Figure 2.14) and has been shown when the mole ratio of monomer unit to catalyst decreases, yield of oligomer increases linearly (Thanki et al., 2004).

In recent times, Solanky et al. developed a new approach on metathesis methodology in obtaining end-functionalized acetyloxy polyisoprene (Solanky et al., 2005). The second-generation Grubbs catalyst and chain transfer agent from cis-1,4-polyisoprene were used in this study. Oligomers of molecular weight were obtained in very good yields, while lower molecular weight was obtained in moderate yields. In this study, the telechelic natural rubber was obtained from deproteinized natural rubber in latex phase. But the molecular weight for this type of telechelic rubber achieved was only 38,000 g/mol. Figure 2.15 shows the mechanism of reaction of this study.

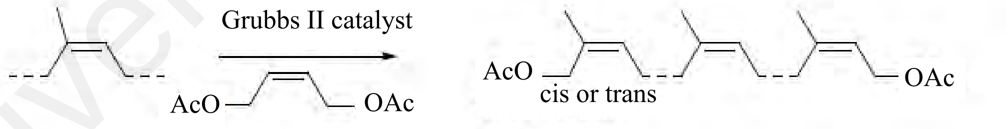


Figure 2.15: Mechanism of polyisoprene product by metathesis degradation

Even though some approaches on the metathesis techniques were done on functionalized diene rubber (etc. polybutadiene and polyisoprene) but they need further modification and development to get the appropriate molecular weight of rubber polyol as precursor in PU synthesis specifically if the solid rubber is used. Basically, the synthesis using the rubber in latex form as the starting materials by metathesis technique could be an alternative for a new technique for producing telechelic and/or functionalized diene rubber.

2.5 Functionalized liquid natural rubber as polyurethane precursor

The chemical modification of polymer is one of the first tools in macromolecular chemistry. The objectives behind chemical modification research are dual either to improve the behavior and the performance of a basic polymer or to prepare new materials for specific uses in area outside its traditional ones. By chemical modifications, specific functional groups chain ends will be potentially reactive with other reagents through chain extension reaction to form a new polymer structures (Kébir et al., 2005a; Kébir et al., 2005b).

Recently, the functional groups such as hydroxyl to form polyol from rubber based have strongly developed. Comparatively few basic isocyanates and a range of polyols of different molecular weights and functionalities are used to produce PU materials (Woods, 1990). Between the common polyols mostly used there are the polyester and polyether backbones, new hydroxytelechelic polydienes, specially, hydroxytelechelic polybutadiene are of particular interest in polymer industry and researches (Grabowski, 1962; Graham & Shepard, 1981; Schapman et al., 1998, 2001; Schapman et al., 2002). Polybutadiene based PUs widely used as solid propellants, explosives, adhesives, sealants, electric and electronic devices, high frequency acoustic and/or mechanical insulatings, elastic coatings, biocompatible medical devices. However, even though their uses are wide, microstructures and functionalities of these oligomers are uncontrollable due to their synthetic approach. For example, hydroxytelechelic polydienes are mainly synthesized by the classical radical polymerization leading to oligomer characteristics strongly depending to the reaction conditions (temperature, time, solvent nature, monomer ratios, stirring frequency) (Brosse et al., 2000). Telechelic polyisoprenes had been obtained through degradation of high molecular weight cis-1,4-polyisoprene with controlled microstructures and functionalities (Gillier-Ritoit et al., 2003; Kébir et al., 2006; Kébir et al., 2005a) for further reaction with isocyanate for the development of new PUs.

As mentioned before, the modification to form FLNR was reported by Saetung *et al*. (Saetung et al., 2010) and the novel HTNR-based PU foam was successfully prepared. The thermal properties were investigated, and the results indicated that the HTNR-based PU foam has good low temperature flexibility. The modification of PU based on semi-rigid type is not widely done because of the difficulty to get the appropriate value of equivalent weight. Meanwhile, as rigid PUs has been reported to suffer ageing performance and degradation behaviour, thermoset PUs exhibiting better hydrolytic, chemical and environmental resistances than rigid PU and also the high performance character of the isophorone diisocyanate based PUs with respect to their ageing conditions have been developed (Gopalakrishnan & Fernado, 2011).

2.6 Polyurethane

Polyurethanes (PU) are useful in a broad range industries and applications, including machinery transport, furnishings, textiles, paper-making, packaging, adhesives and sealants, and medicine (Lamba et al., 1997).The formation for the PU by polyaddition polymerization was firstly discovered by Otto Bayer of I.G. Farbenindustrie, Leverkusen, Germany in 1937. The PU was synthesized by Bayer via reaction between diamines and aliphatic diisocyanates and produced polyurea materials. This material being infusible and strongly hydrophilic could not compete with the polyamides, particularly in fiber applications. Further work using aliphatic diisocyanates and glycol produced material with properties that could be used in fibrous applications (Otto, 1966; Otto et al., 1965).

Synthesis of materials with high molecular weight glycols and aromatic diisocyanates had yielded the first PU elastomers.

In polyaddition polymerization, two- or polyfunctional OH or amino-group containing compounds are allowed to react with di- or polyisocynates (Cowie & Arrighi, 2007). Typically, PU forms as a reaction product of the polyaddition of di- or multifunctional isocyanates and di- or multifunctional alcohols, according to Scheme 2.1.

Scheme 2.1: Formation of polyurethane

In principle, important isocyanate hardeners used are difunctional isomers of toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). Meanwhile, the hydroxyl components basically used are from di- or multifunctional polyester or polyether polyols. The properties of the final PU polymer are based on the functionality, chain length, or molecular weight of the polyol molecules. Linear thermoplastic PU (TPU) are produced from difunctional components. The existing chain extenders (e.g., 1,4-butanediol) in difunctional components such as polyester or polyether based PU become inhomogeneous and separate into hard and soft domains as a consequence of strong intermolecular interactions (hydrogen bonding of urethane groups). For PU elastomer that is crosslinked to a low extent, the phase separation is avoided, and the bulk of that polymer is homogeneous. Depending on the amounts of water in the atmosphere or adsorbed on surfaces, its reaction with isocyanates may also be relevant for the chemistry of PUs, especially in thin films and coatings (Wehlack et al., 2007).

PU elastomers are diblock, flexible elastomers consisting of soft segment reinforced by condensation with a hard segment (diisocyanate). The phase separation morphology, in which the hard and soft phases are thermodynamically immiscible, promotes hydrogen bonding in the hard domain involving urethane C=O and N-H moieties on adjacent polymer chain segments (van Heumen et al., 1995). The elastomeric properties of the TPU vary with the number of variables, including soft segment molecular weight and hard segment concentration as a consequence of alteration in hydrogen bonding characteristics. The soft segment typically has low glass transition temperature (T_g) with low molecular weight. The hard segment usually has high T_g linked with a low molecular weight chain extender. PU is generally synthesized with chain extenders consisting of low molecular weight diols or diamines which produce additional urethane or urethane-urea segments respectively. The properties range from very brittle and hard materials to soft, tacky and viscous (Lamba et al., 1997).

2.6.1 Classification of polyurethane

Depending on the properties and the way in which it is used, PU can be categorized in two main types: foams and solid PU. There are many types of preparation methods which are differentiated according to the medium of preparation, sequence of adding the reactants and also according the to the type of cure.

2.6.1.1 Foamed polyurethane

There are three types of PU foams produced. Firstly, the low density flexible foams that are composed of lightly crosslinked (open-cells) for air to flow through the structure very easily. Secondly, the low density rigid foams that are highly crosslinked polymers with closed-cell structure useful for thermal insulation properties. Thirdly, high density flexible foams that have the huge applications in self-skinning foams and microcellular elastomer that are useful for moulded parts for upholstery and vehicle trim and foreshore soling (Dombrow, 1965; Woods, 1990).

2.6.1.2 Polyurethane elastomers

Most of PU elastomers (solid PU) have excellent abrasion resistance with good resistance to attack by oil, petrol and many common non-polar solvents. They may be tailored to meet the needs of specific applications as they may be soft or hard, high or low resilience, solid or cellular. Most of PU elastomers are based on segmented block copolymers having alternating soft and hard segments. The soft segments are polyester or polyether chains, the hard segments (rigid or stiff at ambient temperature) are the reaction products of a polyfunctional isocyanate and a diol or a diamine. In general, the fully-cured elastomers are tough, abrasion-resistant materials of high strength having good resistance to many solvents and chemicals (Dombrow, 1965; Woods, 1990).

In this study, the focus on the development of PU elastomer that is the semi-rigid PU. This type of PU was prepared as cast PU elastomer. In the previous research, the cast PU elastomer was made by mixing and pouring a degassed reactive liquid mixture into the mould. The product formed includes both linear and partially crosslinked materials. The linear cast PU elastomers are chemically and physically similar to TPU (Woods, 1990). The PU elastomeric behaviour involves highly flexible chains due to the low degree of intermolecular interaction and the presence of crosslinks. Physical crosslinking is capable obtained through hydrogen bonding and hard domain formation. Meanwhile chemical crosslinking is introduced through tri- or multifunctional elements and cannot be easily destroyed by thermal treatment except in some special cases of labile chemical groups, producing an irreversible network. It is a contrast as in the case with physical crosslinks. Therefore, physically crosslinked PUs allow multiple melting or dissolution of the material which is of great practical importance (Prisacariu, 2011). Basically, most of the researcher had produced semi-rigid PU in foam or film foam form compared to film form. It is because of easy processing and forming. The process and procedure for semi-rigid PU film cast is quite tedious because of the formulation that must be critically considered. Besides that, the procedure to develop a better appearance of the PU film requires the use of Teflon mould for easy film removal. Therefore, the composition of semi-rigid PU film with segmented approach must be well formulated.

2.6.2 Synthesis method of polyurethane

The PU microstructures and overall properties, especially physical and mechanical behaviours are strongly dependent on the synthesis method. PU polymerization contains features of both addition and condensation polymerizations. Although no small molecule is eliminated during polymerization, the reaction between the diol and the diisocyanate can be classified as a condensation polymerization. The polymerization kinetic more resembles that of condensation polymerization than addition polymerization. There are many types of preparation methods and all type of preparations are differentiated according to the medium of preparation, sequence of adding the reactants and also according the to the type of cure. Based on the various and many preparation methods, the reactants and also the type of cure, the PU can be modified according to the application. There are basically two methods in producing the PU namely *one-shot* method and pre-polymer or also known as *two-shot* method (Oertel & Abele, 1985; Prisacariu, 2011) .

2.6.2.1 *One-shot* method

The *one-shot* method also known as *one-step* synthesis route is the quickest and easiest of the manufacturing techniques. A functional or multifunctional liquid isocyanate and liquid diol are mixed in a mould and allowed to react as shown in Figure 2.16. A lightly crosslinked or network structure can be synthesized with careful selection of the precursors. Curing of material from *one-step* technique produces an elastomer.

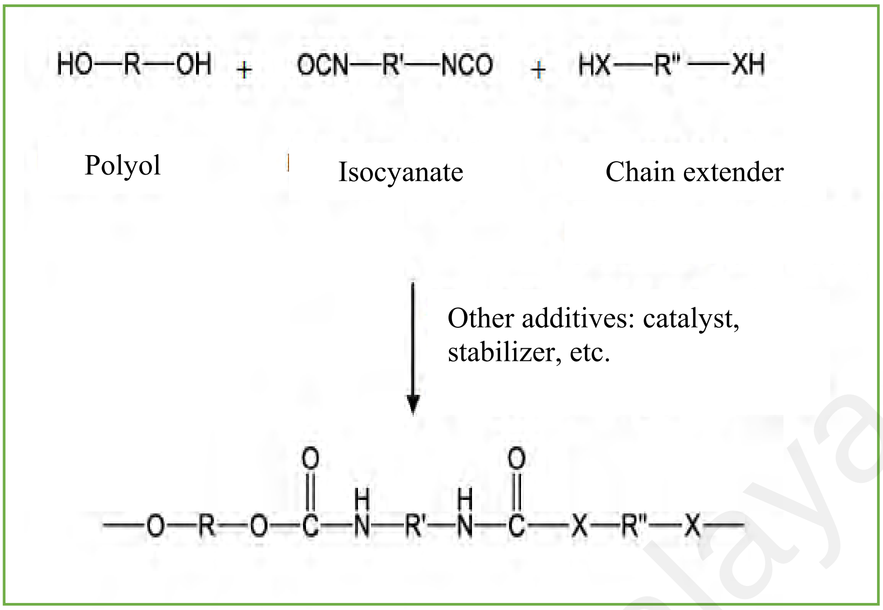


Figure 2.16: *One-shot* method of polyurethane synthesis

2.6.2.2 *Two-shot* method

In contrast to *one-shot* method, the *two-shot* method is commonly referred to as the pre-polymer method. Synthesis through more than *one-step* gives greater control over the chemistry of the reaction, influencing the structure, physical properties, reactivity and processability of the finished product. As the *two-shot* method is more controlled, it produces linear PU chains, fewer side reactions and polydispersity index (PDI) near to 2, which is an expected result of step-growth polymers (Prisacariu, 2011). The first step of the reaction involves synthesis of a pre-polymer from polyol (soft segment oligomer) in excess diisocyanate to produce an isocyanate terminated molecule. The prepolymer generally has a low molecular weight and is either a viscous liquid or a low melting solid. This is followed by chain extension with a short diol or some diamine chain extenders to form the hard segment and also to increase the overall molecular weight of the polymer (Figure 2.17). The reaction of the pre-polymer with a diol or diamine chain extender constitutes the second step, which produces a multiblock copolymer of the (AB)n type (Lamba et al., 1997).

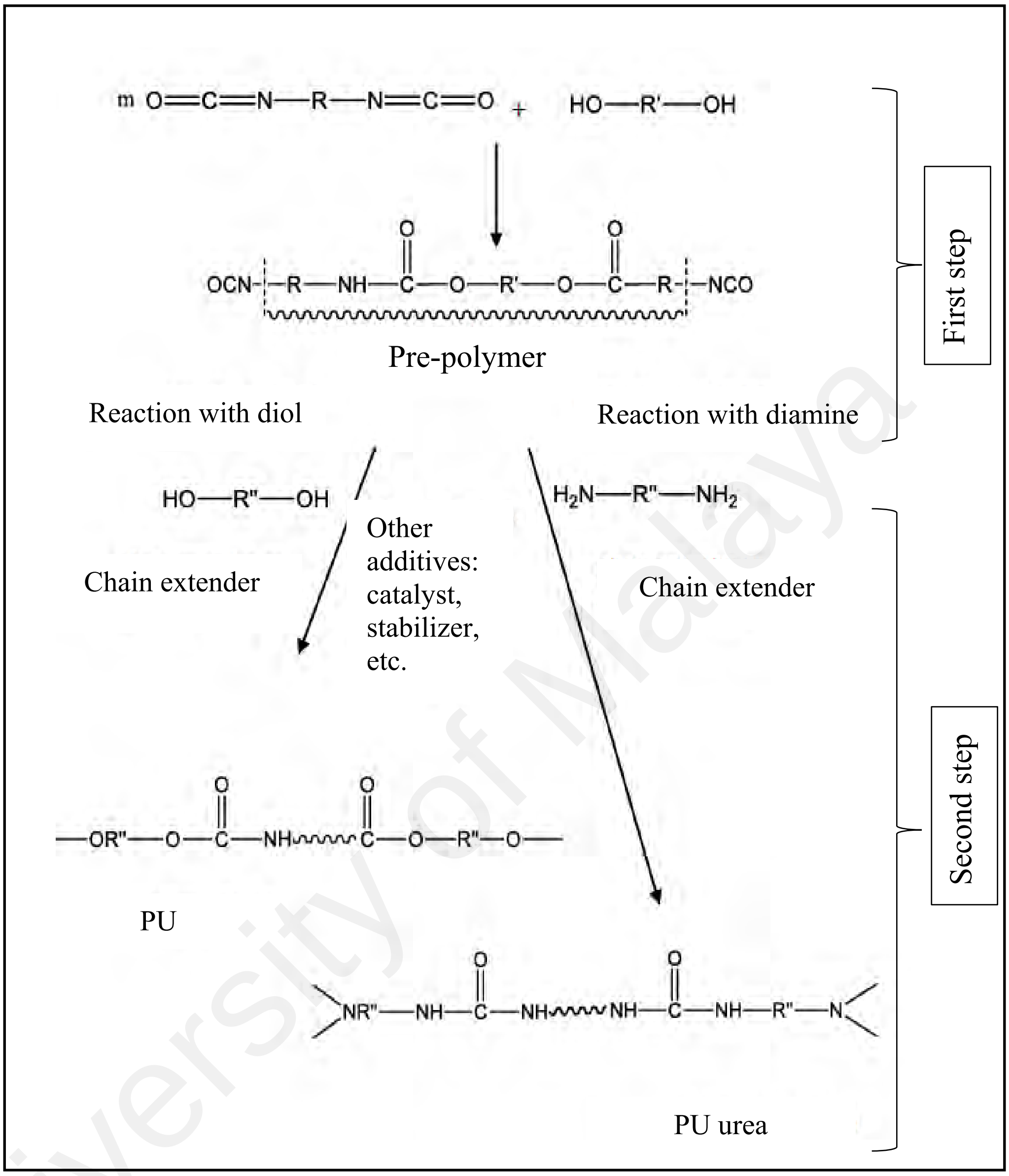


Figure 2.17: *Two-shot* method of polyurethane synthesis

PU structures obtained by the *two-step* procedure tend to be more regular than the corresponding polymers obtained via the *one-step* route. This is because the pre-polymer route caps the polyol with the diisocyanate and then connects these oligomers with the chain extenders. This provides a more regular hard–soft–hard–soft sequence than in the *one-step* synthesis route where the hard segment size distribution is narrower. The structural regularity may result in better mechanical properties since hard segments aggregate or crystallize much easier to form physical cross-linking points (Prisacariu, 2011).

2.6.3 Raw materials of polyurethane

PU is a linear polymer that has a molecular backbone containing carbamate groups ($-NHCO_2$) or called as urethane linkage. It is produced through an addition reaction between a diisocyanate and a polyol and rapidly yields high molecular weight material. PU commonly contains other functional groups in the molecule including ester, ether or urea groups. A variety of raw materials which include monomers, pre-polymers, catalyst, chain extenders and additives are used to produce PU.

The properties of PU are greatly influenced by the types of isocyanates and polyols used to make it long and flexible segments contributed by the polyol (especially rubber based) will give soft and elastic polymer. The amounts of crosslinking give either tough or rigid polymers. Long chains and low crosslinking give a polymer that is very stretchy, short chains with lots of crosslinks produce a hard polymer while long chains and intermediate crosslinking give a polymer useful for making foam. The crosslinking present in PU means that the polymer consists of a three-dimensional network and the molecular weight is very high. The choices available for the isocyanates and polyols, in addition to other additives and processing conditions allow PU to have the very wide range of properties that make them such widely used polymers.

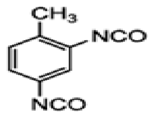
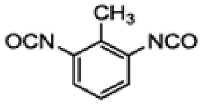
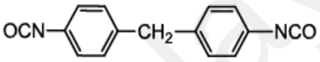
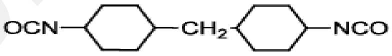
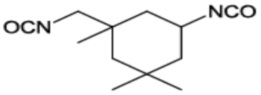
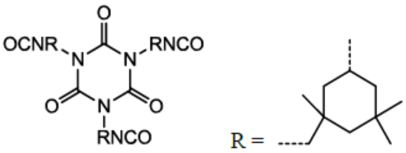
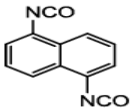
2.6.3.1 Isocyanates

Isocyanates are mainly elements of the hard segments of PUs. Molecules that contain two isocyanate groups (–NCO) are called diisocyanates. They react with compounds containing alcohol (hydroxyl groups) to produce PU. The following properties such as the ability of the PU to crystallize, microphase separation, modulus of elasticity, tensile strength and hardness will increase with increasing symmetry of the isocyanate. Both aliphatic and aromatic isocyanates can be used to synthesize PU. Aromatic diisocyanates and polymers made from them are unstable toward light and become yellow with time but the properties are similar to aliphatic isocyanates. PUs based on aliphatic isocyanates have greater light stability and possess increased resistance to hydrolysis and thermal degradation.

The improvement of the strength of PU is obtained from isocyanates with a more regular structure and an aromatic backbone structure. The presence of an aromatic isocyanate in the hard segment yields a stiffer polymer chain with higher melting point. The two most commonly used isocyanates are toluene diisocyanate (TDI) and 4,4'-diphenylmethylene diisocyanate (MDI). TDI is less expensive than MDI, but MDI has superior reactivity, and polymers based on MDI may possess better physical properties. MDI is crystallizable while 2,4-TDI does not crystallize in the solid state. Other aromatic diisocyanates can also result in high-performance polymers, such as naphthalene diisocyanate (NDI) and bitoluene diisocyanate (TODI), but at a higher cost than MDI based materials. The chemical structures of commonly used diisocyanates used in PU synthesis are shown in Table 2.1 (Lamba et al., 1997).

The influence of the structure and amount of different isocyanates in PU, based on hydroxyl telechelic cis-1,4-polyisoprene (HTPI), on mechanical behavior and thermal properties was studied (Kébir et al., 2006). They reported that the diisocyanate structure (TDI, MDI, $H_{12}MDI$) had no significant effect on the properties of the PU but only I-IPDI showed a different performance on the stiffness improvement at equivalent ratio of [NCO]/[OH] = 1.75.

Table 2.1: Isocyanates used for making polyurethane

Name	Structure
2,4- Toluene diisocyanate (TDI)	
2,6-Toluene diisocyanate (TDI)	
4,4-Methylenediphenyl diisocyanate (MDI)	
1,6-Hexamethylene diisocyanate (HDI)	$OCN-(CH_2)_6-NCO$
4,4-Dicyclohexylmethane diisocyanate (H_{12}MDI)	
Isophorone diisocyanate (IPDI)	
Isocyanurate of isophorone diisocyanate (I-IPDI)	
1,5-naphthalene diisocyanate (NDI)	

In this study, MDI was selected as a part of the hard segment content because of its major application in producing rigid PU. The soft segment from rubber polyol that has higher flexibility is believed able to combine with MDI to form semi-rigid PU in the presence of low percentage of chain extender to enhance the PU structure. Besides that, MDI has good adhesion properties that strengthen the PU structure (Smith et al., 2005).

2.6.3.2 Polyols

The materials that have significant role in the PU structure are polyols. The polyol flexible segment is believed to contribute to flexibility of PU products and are responsible for certain properties such as the high elongation at break, low temperature resistance and low T_g. The structure of polyol is an important factor in determining the properties of PU. Each polyol has its own specialty in terms of physical and mechanical properties of PU products. In production of PU, traditionally, it has been produced by polyester and polyether soft segments. PUs synthesized from polyesters possess relatively good physical properties; however, they are susceptible to hydrolytic cleavage of the ester linkage. Meanwhile, polyether-based PUs exhibit a relative high resistance to hydrolytic cleavage, when compared with polyester urethanes, and are favoured for used in applications where hydrolytic stability is required. In addition, the ether bond (C−O) bond in the polyether soft segment and the ester (CO−O) bond in the polyester are capable of hydrogen bonding with the urethane linkages (NH−CO) in the hard domain, influencing the degree of microphase segregation. Polyesters are generally stronger hydrogen bond acceptors than polyethers. These general observations are dependent upon the crystallinity or ordering of the soft segment, which is a function of molecular weight. Thus, polyester PU is stiffer and have higher strength than the polyether PU with a better resistance to high temperature, solvents and oxidation. Polyether polyols give higher resilience with good hydrolysis resistance.

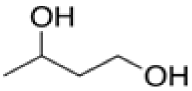
The polydiene based PU, the HTPB has also been proposed as PU precursors (Hepburn, 1992). This type of polyol has also been used for special types of PU elastomers where products of low water absorption and sensitivity are required. In general, the mechanical strength of this class of PUs is lower than that of their polyester and polyether analogues with the advantage of giving the PUs a very low T_g and hence temperature flexibility. The study on PU network from commercial hydrogenated hydroxy-terminated polyisoprene (EPOL®, Atofina) was prepared by Burel *et al*. (Burel et al., 2005a). Moreover, Kébir et al. had synthesized PU successfully with NR backbone and they are able to control and modulate PUs structure to obtain lower or higher thermal-mechanical properties than one of commercial polydiene based PU (Kébir et al., 2006; Kébir et al., 2005a).

In this current work, focus has been made to produce semi-rigid PU. This type of PU is similar to TPU formation but using polyols of different molecular weight (refer to M_n and MWD) and OH value (refer to equivalent weight). TPU basically use very low M_n with moderate OH values (depends on types of flexible and semi-rigid PU) and functionality of 2. Thus, the study of this semi-rigid PU containing polyols of moderate M_n (less than 30,000 g/mol) with OH value in range 190 – 250 mg KOH/g are suggested and prepared. The idea was proposed from previous research that used polyol from butanediol as precursor with M_n in the range of 500 – 20,000 g/mol (Cenens & Hernandez, 1999).

2.6.3.3 Chain extender

Chain extenders are low molecular weight hydroxyl or amine terminated compounds that play an important role in polymer morphology. The choice of chain extender and diisocyanate determines the characteristics of the hard segment and to a large extent the physical properties of PU. The most important chain extenders are linear diols such as ethylene glycol, 1,3-butanediol 1,4-butanediol and 1,6-hexanediol (Table 2.2).

Table 2.2: Diol chain extenders

Name	Structure
Ethylene glycol (EG)	
1,3-butanediol (1,3-BDO)	
1,4-butanediol (1,4-BDO)	
1,6-hexanediol (1,6-HDO)	

The influence of chain extenders especially on thermal properties of PUs based on hydroxytelechelic polyisoprene with toluene diisocyanates has shown that the thermal stability depends on the nature of the chain extender: PU (tetraethylene glycol) < PU (n-alcanediol) < PU (glycol) < PU (1,4- diphenyl dimethanol) using the 1,4-BDO as chain extender (Kébir et al., 2006). The chain extender, BDO provides a good balance between hardness and low temperature flexibility with MDI systems. Compared to other chain extenders, BDO combines the best attributes of hydroxyl reactivity, linearity and overall system compatibility to result in the proper crystallinity required in the PU hard segment. Also, the BDO/MDI systems provide lower exposure hazard than MOCA/TDI system. MOCA is also known as 4,4-methylenebis-2-chloroaniline is a hindered aromatic primary diamine. It contains the chlorine atoms inside the structure and OSHA has identified this type of chemical as suspected human carcinogen (Demarest, 2014). BDO is useful as a chain extender for thermoplastic urethane elastomer. It yields crystalline urethane domains which readily melt and flow at elevated temperatures but phase-separates at ambient temperatures in order to yield tough elastomeric networks. In addition, cast urethane elastomers continue to be the major end use of BDO because of its overall consistency and reliability.

Besides that, the study on the effect of the chain extender length on the structure of MDI/diol hard segments has shown that BDO and longer diol chain extenders (up to octandiol) produce PUs with properties that depend on whether the diol has an *even* or *odd* number of methylene (CH_2) groups. The even diol polymers adopt the lowest energy fully extended conformations that allow hydrogen bonding in both directions perpendicular to the chain axis. Such hydrogen bonding network would not be possible for the odd diol polymers in the extended conformation because they adopt contracted, higher energy conformations. Both the *odd* and *even* diol polymers adopt staggered chain structures with triclinic unit cells, but the even diol polymers have a high crystalline order (Prisacariu, 2011).

Previous study has also reported that as 1,4-BDO has a higher tendency to form internal hydrogen bonding than 1,3-BDO, thus the lifetime of internal hydrogen bonding in 1,4-butanediol (BDO) should be longer (Fishman & Chen, 1969). Based on these observations, and on the kinetic measurements, a good concordance was reported between the hydrogen bond life time and the reaction rate of different OH type in the urethane formation (Caraculacu & Coseri, 2001). The study on the effect of 1,4-BDO on PU products had been investigated further by Ojha et al. (Ojha et al., 2009). The use of BDO in synthesis of polyisobutylene based PU, the properties of PU was enhanced in the presence of PTMO as compatibilizer.

2.6.3.4 Catalyst

A number of catalysts can be used for the reaction of isocyanates and polyols and these include aliphatic and aromatic tertiary amines, and organometallic compounds. The catalytic activity depends on their structure, acidity and basicity. Organometallic catalysts are also used to accelerate the urethane formation. The most common organometallic catalysts are Sn(Oct)$_2$ and dibutyltin dilaurate (DBDTL) (Woods, 1990). As comparison between both catalysts, DBTDL is a more effective catalyst for the *one-step* bulk polymerization of PU. The synthesis of PU based on poly(hexamethylene oxide) (PHMO) and poly(dimethylsiloxane) (PDMS) using DBTDL as catalyst imparts improvement on mechanical properties compared when using the Sn(Oct)$_2$ as catalyst (Gunatillake et al., 2000). Meanwhile, the significant of using Sn(Oct)$_2$ as catalyst showed in the *two-step* polymerization reaction. The TPU based polyisobutylene in the presence of solvent had been shown to have better physical and mechanical properties by using Sn(Oct)$_2$ (Ojha et al., 2009). As for the catalyst, Sn(Oct)$_2$ known as stannous salts with organic complexing agents. It has the advantage of having some delayed action effect, thus avoiding premature action without prejudice to their final effectiveness. It may also be used in association with known tertiary amine catalysts, or with uncomplexed tin catalysts (Roy et al., 1972).

2.6.3.5 Crosslinking agent

Crosslinking agents were sometimes added in the formulation of PU. The agents have functionality of three or more and one also known as curing agents in certain PU formulation. They have an ability to increase the level of covalent bonding in rigid PU such as rigid foam and also act as additives in many semi-rigid foam systems. The commonly used crosslinking agents are diethanolamine (DEA), triethanolamine (TEA) and glycol (Dechant, 1991; Lamba et al., 1997). Both DEA and TEA are normally used in flex molded foams to build firmness and add the catalytic activity. According to the latest study of PU especially on TPU or elastomeric PU, most of the works are done by post-curing method of the samples without the addition of crosslinker. It has been found that the network structure of PU can be developed successfully (Gunatillake et al., 2000; Ojha et al., 2009; Prisacariu & Agherghinei, 2000).

2.6.4 Uses of polydiene polyol based polyurethane

The development of reactive oligomers or polyols from rubber or polydienes based PU has found a growing interest in research. This type of PU can be categorized as flexible, semi-rigid and rigid types and can be widely applied in shipbuilding, car, footwear, building industries and biomaterials (Dombrow, 1965; Woods, 1990). The most well-known polydienes based PU are hydroxy-telechelic polybutadiene (HTPB)-based PU and are mainly used in propellant binders (Celina et al., 2000; Iwama et al., Hasue, 1996). In addition, the modification of polydienes to hydrogenated hydrocarbon diol oligomers promote in the enhancement on solvent resistance, as well as hydrolytic, oxidative, thermal and mechanical properties of the resulting segmented PU due to the soft segment inertness (Brunette et al., 1982; Burel et al., 2005b; Flandrin et al., 1997; Iwama et al., 1996).

PUs have been widely used in various industrial applications due to their versatile properties and some of them are biodegradable and have been used as biomaterial applications (Lee et al., 2000; Lee et al., 2001; Moon et al., 2003) and biomedical fields. Generally, in the biomedical fields, PU materials play a major role in development of many medical devices. The interaction between PU chemistry and body chemistry for improved PU implant products has been studied (Phillips et al., 1988) and continuously augmented by new results (Dunn et al., 1992; Marion & Pollock, 1984; Smith et al., 1996; Ward et al., 2002), whereby biostability of the PU is of major concern. The application covers cardiovascular devices, artificial organs, tissue replacement and augmentation, enhancing coatings and many others. The associated properties for these applications are durability, elasticity, elastomer-like character, fatigue resistance, compliance and acceptance or tolerance in the body during the healing (Lamba et al., 1997; Zdrahala & Zdrahala, 1999).

Essentially, the nature of PU consists of hard and soft segment in the polymer structure. The hard segment isocyanate portion of the polymer contributes to the physical properties such as hardness and abrasion resistance while the polyol contributes to the soft segment and provides much of the chemical resistance. The biodegradable PU could be used as an alternative to replace the conventional non-degradable polymers such as polyethylene (PE) and polypropylene (PP) in the manufacture of packaging films in the near future and contributes to the abatement of the environmental problems (Moon et al., 2003). However, PUs have shown their vulnerability to degradation under the conditions of their performance. The significant changes leading to failure on the polymer mechanical properties, surface chemistry and structure of PU might be the cause of the degradation effect. The more controlling ways of degradation are hydrolysis and oxidation induced by various chemical environments, dissolution by solvents and environmental resistance (Gopalakrishnan & Fernado, 2011). Biodegradation of polymeric material is chemical degradation brought by the action of naturally occurring microorganisms such as bacteria or fungi via enzymatic action into metabolic products of microorganisms such as water, CO_2, methane or biomass. From previous research (Mohan & Srivastava, 2011), it was mentioned that polymers are more or less biodegradable to some extent due to the organic nature of their principle elements like resin and hardener. The complexity, structures and compositions of polymer materials is one of the important aspects which govern polymer biodegradation. Biodegradability is also primarily dependent on hydrolyzable and oxidizable chemical structures, balance of hydrophobicity and molecular weights. Besides that, the physical properties such as crystallinity, orientation, T_g, T_m and thickness affect the rate of degradation.

Previous study on NR based PU, using hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of PUs reported the modification of HTPI as a soft segment by various methods (Burel et al., 2005a; Kébir et al., 2005a; Kébir et al., 2005b; Morandi et al., 2007). These new materials for PU precursors showed the good development on PU industries. Many ideas on development of PU have been proposed from previous researches and findings from a variety of raw materials.

In the biomedical approaches, PUs have extensive structure/property diversity especially on the most bio- and blood compatible materials. These materials play a major role in the development of many medical devices ranging from catheters to total artificial heart (Zdrahala & Zdrahala, 1999). The work has been done on the biocompatible polyisoprene-PU IPN compositions and medical devices made therefrom (Sperling et al., 1998). The study reported that the properties required for use in the manufacture of medical devices had improved in mechanical properties. Besides that, polyisoprene derivatives such as telechelic cis-1,4-polyisoprene (oligoisoprene) can be used in the synthesis of bacterial ionic TPU and coPUs bearing ammonium groups (Kébir et al., 2007). This work demonstrated the potential of making biomaterials from natural rubber, as renewable sources. Meanwhile, the swelling behavior of NR/PU block copolymers and the effect of [NCO]/[OH] ratio on swelling behavior have also been investigated (Gopakumar & Gopinathan, 2005). The block copolymers based NR showed that the equilibrium sorption value decreased with increasing NCO/OH ratio. It was also observed that polarity factor predominated in the solvent transport through the presence of the block copolymer system. The sorption behavior was also found to vary with the [NCO]/[OH] ratio employed in the preparation of TPU oligomers.

CHAPTER 3: METHODOLOGY

3.1 Materials

The NR sample (M_n=1.207 x 10^6 g/mol) was supplied from the Felda Lurah Rubber Factory, Bilut, Pahang, Malaysia. All other reagents were supplied from Merck and are of analytical grade. The following materials were prepared and used in this work: 30% hydrogen peroxide (H_2O_2), 30% aqueous absolute ethanol, sodium nitrite ($NaNO_2$) solution (10% w/v in aqueous absolute ethanol), hydroquinone, toluene for depolymerization and hydroxylation reaction; tetrahydrofuran (THF) GPC grade for gel permeation chromatography (GPC) measurement; deuterated chloroform ($CDCl_3$) for NMR measurement; dry toluene, 1,4 butanediol, 4,4'-methylenebis-(phenylisocyanate) and stannous octoate ($Sn(Oct)_2$) for semi-rigid PU synthesis; chloroform, THF, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) for organic solvent stability test, hydrochloric acid (HCl) and sodium hydroxide (NaOH) for chemical resistance test and water, sodium chloride (NaCl) and methanol for hydrolytic stability test. All reagents used were analytical grade.

3.2 Preparation of functionalized liquid natural rubber

3.2.1 Depolymerization and hydroxylation of natural rubber by *in situ* method

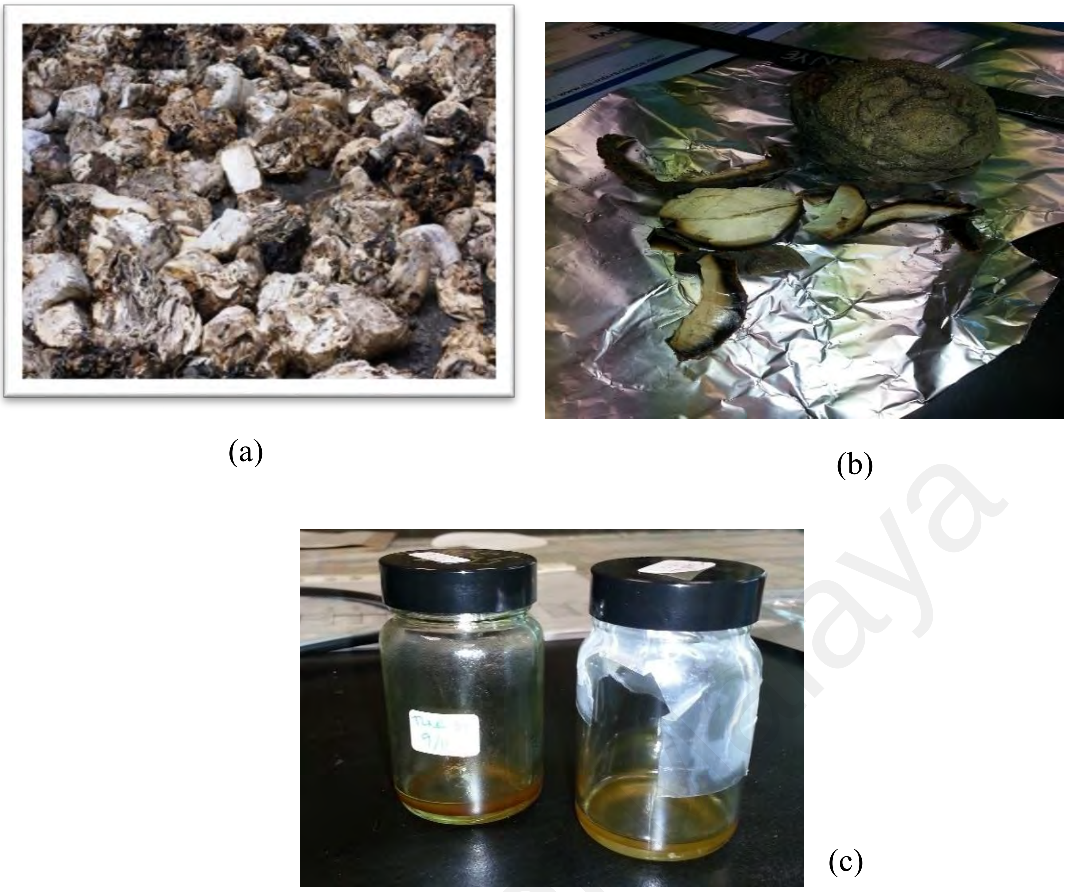
The formation of FLNR involved a redox system through thermal oxidation. The chemically modified structures of NR will be done by *in situ* technique of degradation and hydroxylation of NR to produce a low molecular weight (1.7 x 10^4 – 4.0 x 10^4 g/mol) FLNR as reactive intermediates polyol. The OH value was determined for further reaction to form PU. The reaction conditions employed include controlling the temperature, time, solvent nature, reactant ratio and stirring frequency.

Solid NR in cup lump form (Figure 3.1 (a) and (b)) (7.03 g) was cut into smaller pieces and dissolved toluene (1% w/v) was mechanically stirred at 215 rpm overnight at room temperature. The experimental set up for this reaction is shown in Appendix A1. The obtained homogenous NR solution was then heated to 60±1°C within 30 min to 1 h. H_2O_2 solution was then added dropwise to the NR solution and allowed to stir for 20 min. Alcoholic $NaNO_2$ solution was added dropwise and allowed to stir for another 30 min. The depolymerization temperature was maintained at approximately 90°C with different depolymerization times (30, 40, 50 and 70 hours) with continuously stirring.

After the heating period, the solution was allowed to cool to room temperature. Then about 0.01% (w/v) of hydroquinone was dispersed into the solution and left to stand for a while. This is needed for the removal of any radical species that may be present in the solution. The solution was then washed three times with distilled water and treated with anhydrous magnesium sulphate ($MgSO_4$) and kept overnight. The solution was then concentrated using a rotary evaporator (Appendix A1) to produce a viscous solution. The viscous solution coagulated in methanol to remove residual toluene. Finally, the sample was dried in a vacuum oven at 40°C to produce a brown light viscous FLNR (Figure 3.1(c)). For long term storage, FLNR samples were kept in a nitrogen environment to prevent the viscous solution from hardening. The formulation of FLNR preparation was shown in Table 3.1.

Table 3.1: Formulation of functionalized liquid natural rubber solution

Name	**Moles ratio**				
(H_2O_2/isoprene unit)	0.2	0.4	0.6	0.8	1.0
($NaNO_2$/H_2O_2)	0.2	0.4	0.6	0.8	1.0



(a)

(b)

(c)

Figure 3.1: Image of (a) waste of cup lump rubber at factory (b) waste of cup lump rubber and (c) functionalized liquid natural rubber solution

3.3 Characterization of functionalized liquid natural rubber

The measurements involved GPC for molecular weight determination, OH titration for OH value, FT-IR and NMR for structure confirmation.

3.3.1 Gel Permeation Chromatography

Molecular weight determinations were performed using a gel permeation chromatography (GPC) instrument (Waters 2414 refractive index detector coupled with a Waters 717 plus Autosampler and Waters 600 Controller) with polystyrene standards as reference and THF as the eluent. Samples for GPC measurement were prepared by complete dissolution in THF at 0.1% w/v. The sample solutions were transferred into

GPC sampling vials using a 0.22 μm Teflon filter. The GPC flow rate of sample measurement was 1.0 mL/min.

3.3.2 Fourier Transform Infrared spectroscopy

Attenuated total reflectance fourier transform infrared (ATR FT-IR) spectra of the samples were recorded with a Perkin Elmer 400 spectrometer. The acquisition parameters were done with a total of 16 accumulations at 4 cm^{-1} resolution with a spectral range from 4000-650 cm^{-1}.

3.3.3 Nuclear Magnetic Resonance spectroscopy

The nuclear magnetic resonance spectroscopy (NMR) spectra of PU film samples were obtained at 400 MHz using JEOL JNM-LA 400 FTNMR System spectrometer with 8 number of scan and acquisition time of 8.0 s. The samples were dissolved approximately 2% w/v solution in deuterated chloroform ($CDCl_3$).

3.3.4 Hydroxyl value determination

Hydroxyl value (OH) value is defined as a number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of a sample. The preparation of OH value determination in this work is according to **ASTM D4274-05**. 0.5 N solution of NaOH was prepared and standardized as follows: Potassium acid phthalate ($KHC_8H_4O_4$) was crushed to approximately 100 mesh and dried for 1 to 2 h at 100°C. 1.3-1.6 g of $KHC_8H_4O_4$ was accurately weighed into a 250 mL conical flask. 50 - 60 mL of distilled water was then added into the flask and gently swirled until the $KHC_8H_4O_4$ was fully dissolved. The sample was titrated with 0.5N NaOH solution to an end point using an autotitrator. The normality of the NaOH was calculated as follows:

$$\text{Normality} = W/(V \times 0.2042) \qquad \text{(equation 3.1)}$$

where, W = weight of $KHC_8H_4O_4$, g

V = volume of NaOH required for titration of $KHC_8H_4O_4$, mL

The OH value of FLNR was indicated as follows: 1-2 g of the FLNR sample was accurately weighed into a 250 mL conical flask and dissolved with 20 mL of 1.0 M phthalic anhydride-pyridine reagent. The flask was equipped with a reflux condenser and heated in an oil bath for 1 h at 130°C. After the heating period, the assembly was removed from the bath and cooled to room temperature. The condenser was washed down with 30 mL of pyridine, and then with 30 mL of distilled water into the flask. The sample was titrated with 0.5 N NaOH solution to an end-point using an autotitrator. The OH value, mg KOH/g, of the sample was calculated as follows:

$$\text{OH value} = [(B - A)\, N \times 56.1] / W \qquad \text{(equation 3.2)}$$

where:

A: NaOH required for titration of the sample, mL

B: NaOH required for titration of the blank, mL

N: normality of the NaOH

W: weight of sample, g

3.4 Optimization by response surface methodology

The optimization process was determined with response surface methodology (RSM) using the Design Expert® Version 6.0.6 software. The software was also used to analyze the data collected by performing analysis of variance (ANOVA).

3.5 Synthesis of semi-rigid polyurethane film

The synthesis of semi-rigid PU film was carried out using reactive intermediates polyol (FLNR) and MDI with chain extender (BDO). The *one-shot* method and *two-shot* method were used. All reactions will depend on parameters of OH value, percentage of catalyst, percentage of chain extender and [NCO]/[OH] ratio to compare the character of soft and hard segments of semi-rigid PU character. This final step to produce semi-rigid PU formed was cast as film. The formulation of the semi-rigid PU film is shown in Table 3.2.

Table 3.2: Formulations of semi-rigid PU films

Method	FLNR (polyol)[a]			[NCO/OH] ratio	Chain extender (pbw)	Catalyst (pbw)	Reaction time (h)
one-shot	T1	T2	T3	0.6-1.0	2-7	3-10	6
two-shot	T1	T2	T3	0.6-1.0	2-7	3-10	5

Note: a = refer to the optimization result for FLNR; pbw due to the overall rubber polyol

T1 (FLNR-17700; OH value: 190-200 mg KOH/g; equation weight: 280-295 (ratio of H_2O_2/isoprene unit= 0.2 and ratio of $NaNO_2/H_2O_2$=0.2); T2 (FLNR-20000; OH value: 200-230 mg KOH/g; equation weight: 244-280 (ratio of H_2O_2/isoprene unit=1.0 and ratio of $NaNO_2/H_2O_2$=0.24); T3 (FLNR-28700; OH value: 230-280 mg KOH/g; equation weight: 200-244 (ratio of H_2O_2/isoprene unit= 1.0 and ratio of $NaNO_2/H_2O_2$=0.39)

3.5.1 *One-shot* method

The *one-shot* method involves the adding of all reagents together. FLNR (polyol) and 1,4 BDO was added followed by dry toluene. The mixture was kept at 45°C overnight under vacuum. $Sn(Oct)_2$ was then added in the dry toluene. The mixture was heated at 80°C under dry nitrogen gas atmosphere. Then, 4,4'-methylenebis-(phenylisocyanate) (MDI) was added and the mixture was stirred vigorously for 6 h until the mixture become slightly viscous (Appendix A2). The mixture was cooled to room temperature, poured in a Teflon mold and the solvent was evaporated at room temperature in air for 48 hours. The polymer was dried under vacuum at 35°C for 24 h and then post-cured at 60°C for 24 h. The product of semi-rigid PU film presented in Figure 3.2.

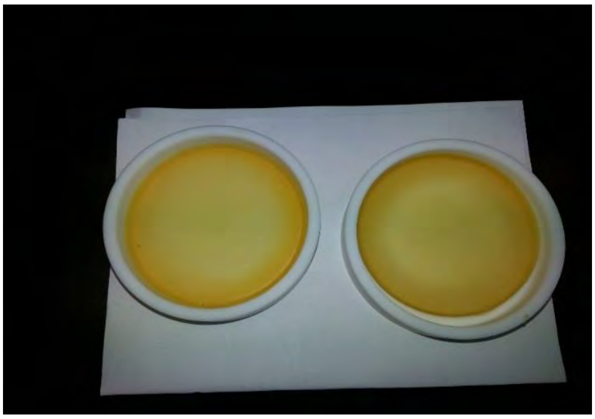


Figure 3.2: Image of semi-rigid polyurethane films

3.5.2 *Two-shot* method

The *two-shot* method involves the addition of BDO as last reagent. In this synthesis, FLNR in dry toluene was dried and kept at 45°C overnight under vacuum. Then, dried toluene was added followed by $Sn(Oct)_2$. The mixture was heated at 80°C under dry nitrogen gas atmosphere. MDI was then added, and the mixture was stirred vigorously for 1 h followed by addition of BDO and stirring continuously for 4 h. Thereafter, the mixture was cooled to room temperature, poured in a Teflon mold and the solvent was evaporated at room temperature, vacuum dried and post-cured similar to the *one-shot* method. However, in the modification of *two-shot* method samples, during addition BDO into the mixture, stirring was continued for 4 h at 100°C. The mixture was cooled to room temperature, poured in a Teflon mold and the solvent was completely evaporated at room temperature. Furthermore, the temperature of vacuum dried was increased to 60°C and kept for 48 h and then post-cured (60°C) about 48 to 50 h.

3.6 Characterization of the semi-rigid polyurethane film

GPC and FT-IR spectroscopy were employed for molecular weight determination and structure characterizations, respectively. The solubility test was also measured to study the transport behavior of organic solvent through the PU system. Differential scanning calorimetry (DSC) was used to study on thermal transition and thermal gravimetric analysis (TGA) was used to study on thermal stability of semi-rigid PU. Both the solubility and DSC examination could reveal the interactions of semi-rigid PU segmented product to see the relation between soft and hard segments. The stability of physical properties of semi-rigid PU samples were measured by organic solvent stability test, chemical resistance test (acid, base and oxidant) and hydrolytic stability (in different medium). The biodegradability study on environmental conditions was done by soil burial degradation. Two different modes were used: i) soil test by outdoor environment (open air and exposed naturally to weather, wind, sunrise and rain), ii) soil test by indoor environment (in the lab and the soil was treated in alkaline condition; pH=7.5 and low humidity).

3.6.1 Gel Permeation Chromatography

As described in Section 3.3.1.

3.6.2 Fourier Transform Infrared spectroscopy

As described in Section 3.3.2.

3.6.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurement were performed in a Netzsch DSC 200 F3 analyzer. Film samples ranging from 4 to 8 mg were heated from -50 to 300°C, under nitrogen (NO_2) atmosphere, at a heating rate of 10°C/min. The data were recorded in “exo up” mode.

3.6.4 Thermogravimetry Analyzer

Thermogravimetry analyzer (TGA) measurement for thermal stability of film samples were performed by Netzsch TG 200 F3 Tarsus analyzer. The semi-rigid PU film samples ranging from 2 to 4 mg were placed in a platinum sample pan and heated from 30 to 900°C, under N_2 atmosphere, at a heating rate of 10°C/min.

3.7 Solubility test

3.7.1 Test 1

The solubility of the semi-rigid PU for test 1 was performed by keeping the 0.01-0.03 g of polymer film in 20 mL solvent (chloroform, THF, toluene and DMSO). This solubility test was conducted at room temperature without stirring and heating. The mixture was kept for 24 h at room temperature (~30°C). The mixture was filtered through filter paper (porosity 2 μm) and dried under vacuum to a constant weight. From the weight of dissolved polymer, the weight loss was determined.

$$\text{weight loss} = ([W_0-W_t]/W_0) \times 100; \qquad \text{(equation 3.4)}$$

where W_0 is the weight of the original films and W_t is the weight of residual films after soluble test.

3.7.2 Test 2

The test 2 for solubility of the semi-rigid PU was conducted by stirring method. It was performed by keeping 0.01-0.03 g of polymer in 20 mL solvent (chloroform, THF, toluene, DMF and DMSO) and the mixture was stirred for 30 min and kept for 4 h at room temperature (~30°C). From the weight of dissolved polymer the solubility was determined (Umare & Chandure, 2008). The weight loss percentage calculation as described in equation 3.4.

3.7.3 Test 3

The test 3 for solubility of the semi-rigid PU was conducted to continue the test method as described in Section 3.10.2 if the polymer film insoluble in the appropriate solvent with additional of heating process. The mixture was stirred for 30 min with the additional of heating and the temperature referring to the boiling point temperature of each solvent. Then it was kept for 24 h at room temperature (~30°C). The mixture was filtered, and weight loss percentage was determined. For this solubility test, the percentage of swelling (increasing weight) was measured for the samples that were insoluble in any solvents.

3.8 Ageing test

The studies on the stability of semi-rigid PU under various conditions were carried out using the general guidelines of ASTM standards. The stability of the film sample was determined from the weight loss estimation. The loss of weight was determined after vacuum drying the exposed sample.

3.8.1 Stability in organic solvents

The chemical degradation of semi-rigid PU film was performed by using 0.01-0.03 g (size: 0.5 cm x 0.5 cm) sample and contacted it with variable organic solvents (chloroform, THF, toluene, DMF and DMSO) to see the behavior of film stability. The test of stability in organic solvents was carried out according to **ASTM C 267**. The conditioned samples were immersed in 6 mL of the organic solvent in an air-tight-container for a period of 60 days at room temperature (~30°C). The mixture was filtered through pre-weight sintered-glass crucible (porosity 2μm) and then the crucible was dried under vacuum to constant weight. The films were washed with deionized water, dried under vacuum at 50ºC and weighed to a constant weight. From the weight of dissolved polymer, the weight loss was determined. The calculation of weight loss of samples is as follows (Umare & Chandure, 2008) as mentioned in equation 3.4.

weight loss = $([W_0\text{-}W_t]/W_0)$ x 100;

where, W_0 is the weight of the original films and W_t is the weight of residual films after the degradation for different times.

3.8.2 Hydrolitic stability test

Hydrolytic stability test for the semi-rigid PU was carried out according to **ASTM D 3137**. The weight loss of the semi-rigid PU in media such as water, ethanol and salt solution (1 *N* sodium chloride) was estimated by immersing the samples for the total period of 60 days under ambient conditions. The medium was changed, and fresh medium was added at the interval of one week. The swelling rate of film samples was examined immediately after the samples were removed from the media before dried. Meanwhile, the rate of weight loss was calculated after samples were dried in vacuum oven at 40°C until constant weight. The weight loss was determined (equation 3.5).

3.8.3 Chemical resistance test

PUs are widely used in medical devices due to their broad property range, processing flexibility and biocompatibility. Increasingly, these devices are subjected to longer duration use, and exposed to a wide variety of chemically active agents. Chemical resistance test for the semi-rigid PU was carried out according to **ASTM C 267**. The film samples were cut into small pieces (0.5 cm x 0.5 cm) and diluted in 15 mL HCl (1*N*), NaOH (1*N*) and 30% H_2O_2) This test was kept for 60 days and the weight loss was determined (equation 3.5).

3.8.4 Soil burial degradation test

Two methods of environmental test in soil burial degradation were introduced. The first method, the indoor test of soil burial degradation was conducted for 60 days in an alkaline soil condition in the laboratory. The alkaline condition of soil was selected because habitually the microbial activity is active in alkaline medium. The second method, outdoor test or known as field test was conducted for 60 days under rainy, windy and hot atmosphere.

3.8.4.1 Indoor environment test

The soil burial degradation test of semi-rigid PU films (Appendix A3) was conducted as per **ISO: 846**. The semi-rigid PU films (15 mm×15 mm and thickness 0.2 mm) were buried in soil (garden composted soil) (pH7.5, water content capacity 45%) in which the relative humidity was maintained at 50–60% (maximum water-holding capacity) by adding water. The composted soil used in this study had been taken from the garden of nursery at Seksyen 18, Shah Alam, Selangor. The microbial activity of the soil was tested by using a cotton strip which loses its tensile strength within 10 days of exposure to soil. The buried semi-rigid PU films were removed after 60 days, then at regular interval of 10 days. Recovered film was washed with water, dried in vacuum at 30°C and weighed to a constant weight. The weight loss percentage calculation as described in equation 3.4.

3.8.4.2 Outdoor environment test

The soil burial degradation test of semi-rigid PU films samples (outdoor or field test) (Appendix A3) was similar to indoor method (Section 3.8.4.1) but it was modified by conducting outside (top roof building). The soil and buried samples was exposed to the natural open-air environment in the presence of rain, sunrise, air, wind and any outdoor microbial activity. The microbial activity of the soil also was tested by using a cotton strip which loses its tensile strength within 10 days of exposure to soil. The buried semi-rigid PU films were removed after 60 days. Recovered film was washed with water, dried in vacuum at 30°C and weighed to a constant weight. The weight loss was also calculated as described in equation 3.4.

CHAPTER 4: PRODUCTION OF FUNCTIONALIZED LIQUID NATURAL RUBBER

4.1 *In situ* depolymerization and hydroxylation of functionalized liquid natural rubber

FLNR was synthesized by depolymerization and hydroxylation of NR by the *in situ* redox method. The synthesis was done in the presence of hydrogen peroxide (H_2O_2) for hydroxyl bonding formation and sodium nitrite ($NaNO_2$) as a chain scissor. In the mechanism of depolymerization of NR by using both $NaNO_2$ and H_2O_2, oxidation cleavage on the NR chain will occur leading to the hydroxylation formation. The initial step in production of FLNR is specify the reaction time of depolymerization and hydroxylation to produce a lowest molecular weight of FLNR. Once the appropriate reaction time was optimized, mole ratios of H_2O_2 and $NaNO_2$ were varied. The mole ratio of H_2O_2/isoprene unit describes the effect of H_2O_2 on the isoprene structure, in particular the way OH bonds are formed in the FLNR. Meanwhile mole ratio of $NaNO_2/H_2O_2$ describes the efficiency of $NaNO_2$ as the chain scissor in the reduction of the chain length and molecular weight of NR.

In this study, the effectiveness of these two reagents (H_2O_2 and $NaNO_2$) in neutral medium on low quality grade NR as a raw material was investigated. Basically, this type of NR has a very high molecular weight (>1 million) with PDI of more than 4. The effectiveness of these two parameters (H_2O_2 and $NaNO_2$) in FLNR was optimized using response surface methodology (RSM). RSM is applied to study these variables for the depolymerization and hydroxylation process to predict the outcome of the molecular weight and OH value of FLNR. Finally, the analysis of variance (ANOVA) was carried out to confirm the predicted and observed parameter values of FLNR that can be used as semi-rigid PU precursor. Further detailed discussion is given in Section 4.3.

Based on the initial work of the *in situ* depolymerization and hydroxylation reaction time of FLNR, the reaction time determined was done with mole ratios of H_2O_2/isoprene unit and $NaNO_2/H_2O_2$ equal to 0.8 and 0.6, respectively. This mole ratio initially was chosen in a random manner to see how the trend in molecular weight reduce with reaction time. The reaction time of this *in situ* reaction between 0 and 70 h at 90°C was carried out in non-acidic medium. Under acidic medium, formic acid is commonly used. Formic acid reacts with H_2O_2 to form performic acid that can accelerate the reaction when added together with catalyst and is normally used in the large scale industrial production. However, the performic acid (boiling point at 50°C) has disadvantage because its reaction temperature must be kept below 80-85°C to avoid explosion. It readily decomposes upon heating and explodes upon rapid heating to 80-85°C. The major drawbacks of performic acid are handling dangers related to its high reactivity, as well as instability, especially upon heating, which means that the acid must be used within 12 h or less of it being synthesized (Bydzovska & Měrka, 1980; Huss et al., 2001; Preuss et al., 2001; Ripin et al., 2007). Thus, for that reason this work has purposely used non-acidic medium with the reaction temperature exceeding more than 80°C but less than 90°C. At certain condition of depolymerization and hydroxylation reactions, the existing of H_2O_2 at high temperature (more than 90°C) will form side reactions such as furanization and crosslinking (Zhang et al., 2010). This condition will be discussed further in FT-IR and NMR analyses sections. Moreover, H_2O_2 is unstable at high temperature and the reaction temperature above 90°C should be avoided (Zhang et al., 2010). Preliminary work was done at temperature exceeded 110°C. At the end of reaction, high viscous rubber solution was produced. In this situation, the crosslinking network might have taken part in the reaction and besides that, the toluene has achieved its boiling point and might have evaporated. From the previous study, the temperature dependent for *in situ* depolymerization and hydroxylation performed in the acidic medium was highly favorable at high depolymerization temperature (70ºC), compared to low temperature (60º C) (Isa et al., 2007).

From the preliminary works and results, the reaction time of this FLNR reaction was maintained at 50 h and the temperature must not be exceed more than 90ºC with the existing of rubber solution in toluene as a medium. After the reaction was completed, the molecular weight (M_n) of FLNR samples was determined by GPC. Figure 4.1 shows the molecular weight decreases with increasing reaction time from 0 to 50 h and becomes constant from 50 to 70 h. Hence, for this study, the 50 h reaction time was chosen as suitable time for the *in situ* depolymerization and hydroxylation reaction. The graph also shows that the coefficients of determination (R^2) value is close to 1.

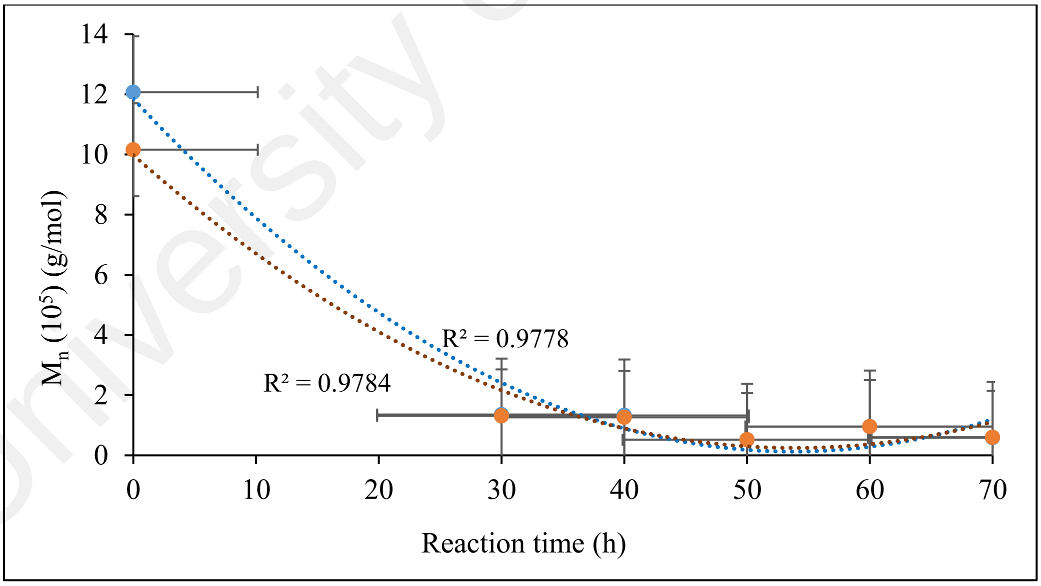


Figure 4.1: M_n versus reaction time of *in situ* synthesis of functionalized liquid natural rubber

In this work, ethanol was used as a part of the solvent mixture as it could stabilize the reaction system especially in terms of temperature control. It was reported that the addition of ethanol could efficiently prevent the crosslinking reaction of ozonolyzed butadiene rubber without interrupting the functional groups (Yang et al., 2010). The amount of ethanol used in this study was given in Appendix B1**.** A small amount of this solvent did not present significant effect on the rubber solution (1% rubber solution in 800 mL toluene). Ethanol is similar to methanol being a non-solvent to NR offers the advantage in that the viscosity of the reaction mixture will be slightly reduced by its addition (Ravindran et al., 1988). Ethanol also reacts with oxygen during oxidation to produce carbon dioxide (CO_2) that can control the stability of the *in situ* reaction:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad \text{(equation 4.1)}$$

The formation of water as in the equation 4.1 is not a main problem because at the end of reaction during purification step, all residual water will totally be removed by magnesium sulphate ($MgSO_4$) anhydrous. $MgSO_4$ acts as drying agent and it is believed also as an alcohol removal. Therefore, the residual ethanol present in the FLNR product could be removed by this drying agent.

The impurities of the low grade NR (the cup lump material) was used as received without purification. Prior to that several pilot runs were also made with cup lump materials that have been purified and results observed showed no significant differences in the final properties, indicating that the processing methods is robust and allows direct usage of the starting material without the necessity to be cleaned and purified.

4.2 Fourier Transform Infrared of functionalized liquid natural rubber

Chemical structures of the NR (M_n =1.207 x 10^6 g/mol) and FLNR were verified by FT-IR as shown in Figure 4.2. and the frequency changes of each peak are listed in Table 4.1.

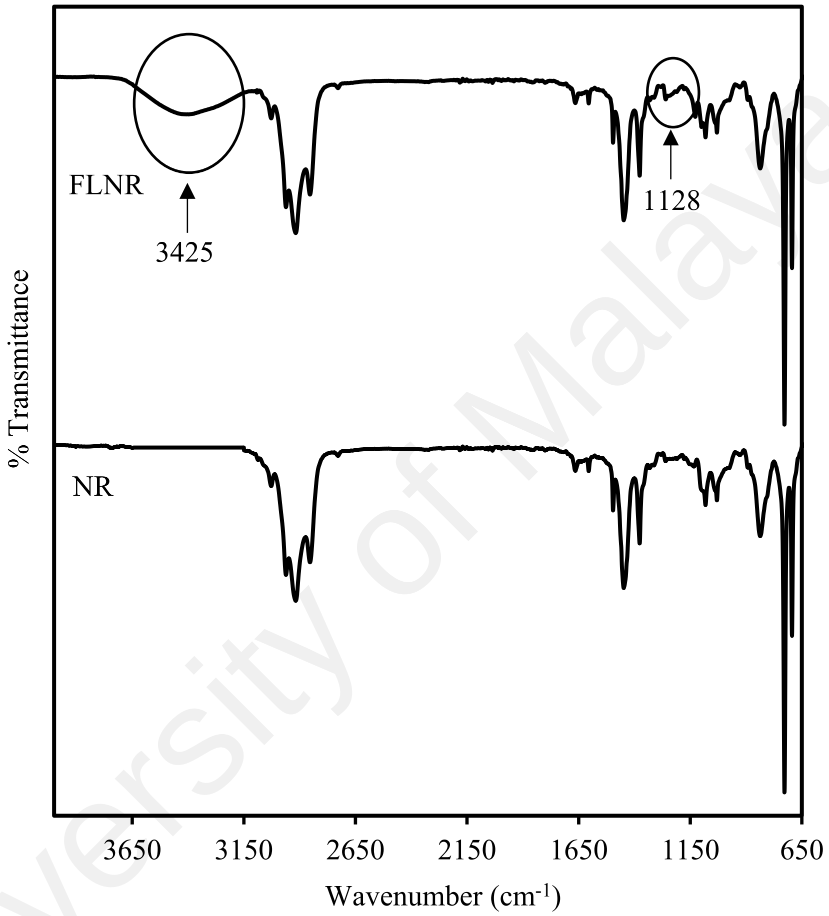


Figure 4.2: Fourier Transform Infrared spectra of natural rubber (NR) and functionalized liquid natural rubber (FLNR)

The FT-IR spectra of NR and FLNR contain characteristic peaks of the well-known structural features of NR. Identification of these peaks reveals that the hydroxylation process has not affected the backbone structure of the isoprene units (Brown et al., 1988; Dworjanyn et al., 1989; Nor & Ebdon, 1998). Stretching's of C=H and C=C from isoprene unit and its end group $–CH_2–C(CH_3)=CH–CH=CH_2$ give a peak at 3035 cm^{-1} and 1664 cm^{-1}, respectively. The peaks observed at 2961 and 2926 cm^{-1} are attributed to the –CH asymmetrical stretching of methyl and methylene groups, respectively and their symmetrical stretching occurs at 2855 cm^{-1}. The –CH symmetrical and asymmetrical bending vibrations of methylene and methyl groups are seen at 1449 and 1376 cm^{-1}, respectively. The peak at 1037 cm^{-1} is assigned to CH_3- dan -CH_2- deformations. Meanwhile, the peak at 837 cm^{-1} corresponds to out-of-plane deformation of $CH_2–C(CH_3)=CH–CH_2$.

Table 4.1: Fourier Transform Infrared assignment of natural rubber and functionalized liquid natural rubber

ν (cm^{-1})	**Assignment**	**Sample**
3425	-OH stretching intermolecular bonded	FLNR
3035	=CH stretching from NR and end group $–CH_2-C(CH_3)=CH-CH=CH_2$	NR, FLNR
2961	Assymmetric stretching of –CH from $–CH_3$	NR, FLNR
2926	Assymmetric stretching –CH from $–CH_2–$	NR,FLNR
2855	Asymmetric stretching –CH from $–CH_2–$ and $–CH_3$	NR, FLNR
1664	C=C stretching from isoprene unit and end group $–CH_2-C(CH_3)=CH-CH=CH_2$	NR, FLNR
1449	Symmetric bending of C-H from -CH_2-	NR, FLNR
1376	Asymmetric bending of C-H from CH_3-	NR, FLNR
1128	Stretching of C-OH from $–R_3C(OH)$-	FLNR
1037	Deformation of CH_3- and -CH_2-	NR, FLNR
837	Out of plane deformation, =CH from CH_2-$C(CH_3)=CH$- CH_2	NR, FLNR

The main difference of FLNR that sets it apart from NR is the appearance of a new peak at 3425 cm^{-1} belonging to the hydroxyl group. It has been shown previously that this spectral feature corresponds to the hydroxyl group of FLNR. This hydroxyl moiety makes FLNR useful for intermediary applications as it can react readily with other reactive groups (Brown et al., 1988; Cooper, 1980; Dworjanyn et al., 1989; Mohd et al., 1999). Besides that the observed peak at 1128 cm^{-1} is assigned as stretching from C-OH of –$R_3C(OH)$- structure that is similar to previous study investigated by Brown, *et al.* (Brown et al., 1988).

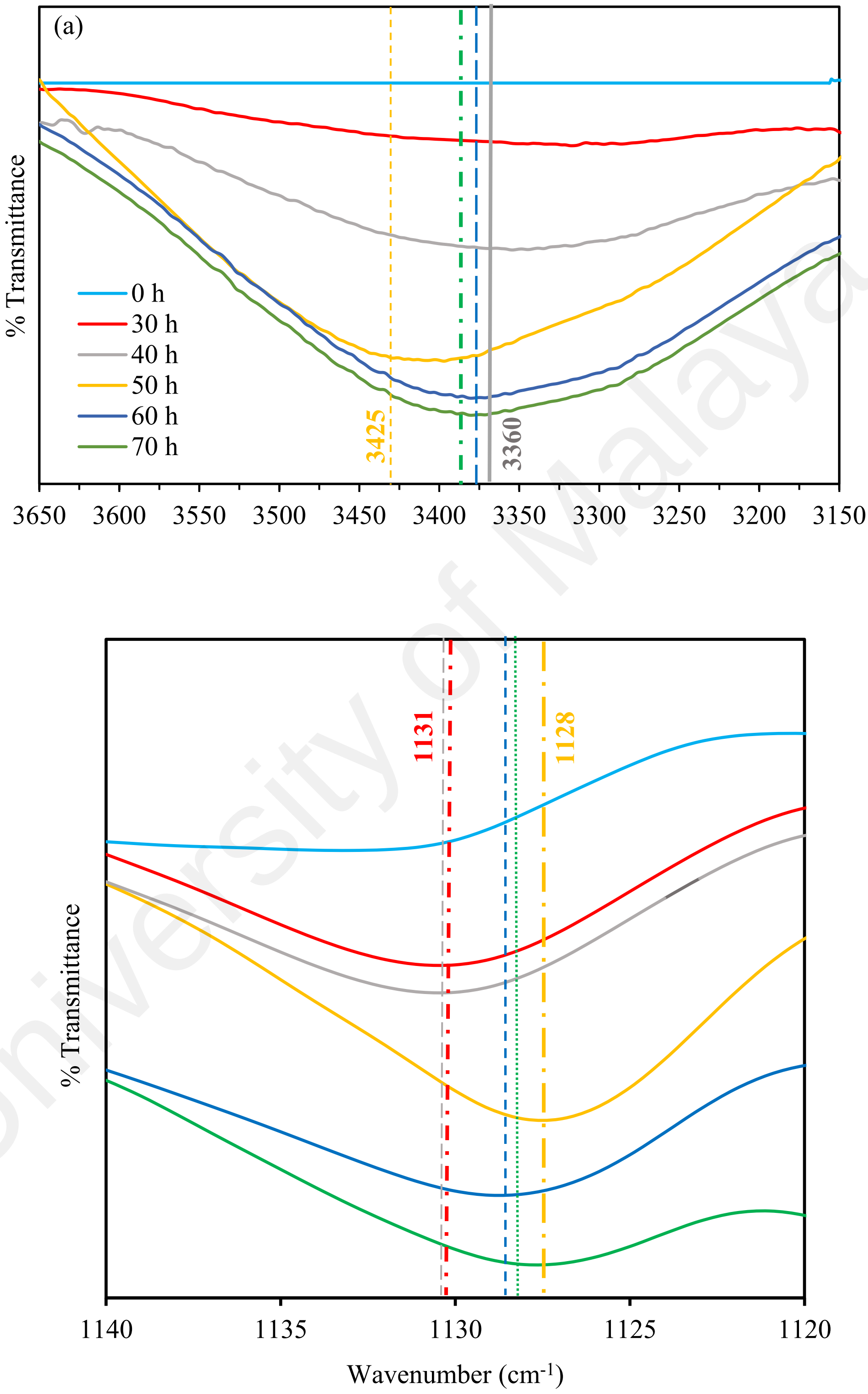


Figure 4.3: Fourier Transform Infrared bands of (a) OH ranging from 3150 to 3650 cm^{-1} and (b) –$R_3C(OH)$- ranging from 1120 to 1140 cm^{-1}

Based on preliminary study, the *in situ* reaction times between 30 h and 70 h were chosen. From Figure 4.3 (a), the OH band at 0 h is observed to have undergone significant changes particularly in the gradual appearance of the OH band at 3200-3700 cm^{-1}. The OH band increases starting at 30 h (3360 cm^{-1}) up to 50 h (3425 cm^{-1}) depolymerization and no significant changes are observed between 60 to 70 h. This shows that after 50 h of reaction, the formation of OH bond has attained the equilibrium state.

Figure 4.3 (b) shows peak at 1128 - 1131 cm^{-1} attributed to -C-OH of the hydroxylated group in FLNR. Different reaction times show different peak intensity, and this strongly support the formation of OH group in FLNR. Thus, the reaction time of 50 h of *in situ* degradation and hydroxylation was selected because of the clear observant peak at 1128 cm^{-1}. These reaction times was used as a fixed parameter in production of rubber polyol based semi-rigid PU.

4.3 Optimization by response surface methodology

For FLNR application as precursors of PU, the molecular weight of the FLNR must low and it must be highly functionalized with OH groups. Previous works (Cenens & Hernandez, 1999; Dirckx et al., 1999) had reported that the suitable molecular weight required of FLNR to produce semi-rigid PU should be about 25,000 g/mol and the best is less than 10,000 g/mol. In addition, the formulation of flexible PU requires OH value of less than 100 mg KOH/g, semi-rigid PU is between 100 and 300 mg KOH/g and rigid PU is between 200 and 1500 mg KOH/g (Cenens & Hernandez, 1999). Thus, knowledge of parameter control (variables) in the synthesis procedures is critical to achieve the desired molecular weight and OH value. In general, the step-wise experimental study approach for each of the parameters involved in the synthesis procedures is not only time consuming but also requires special attention in cases where there is a contribution of multiple parameters interacting simultaneously in the system. Therefore, an appropriate model can be of significant interest to simulate and predict the responses from the parameters involved in the synthesis process. Among the modeling approaches, the RSM is a powerful technique in optimizing the industrial process.

RSM also can be recognized as a simple and reliable tool for a multivariable system. It can effectively analyze the effects of several independent variables simultaneously without any knowledge on the relationship between the objective functions and variables (Aimi et al., 2014; Baş & Boyacı, 2007; Batista et al., 1998; Sangal et al., 2012; Sinha et al., 2013; Sun et al., 2011). RSM can be very helpful in designing the experiments and to elucidate the correlations among the many variables of any industrial process. It is then used to build the relationship between the input parameters and output response using fitness functions to measure fitness values by numerical approaches. The RSM uses the ANOVA to determine which parameters have the strongest interactions and/or which ones exhibit significant influence on the outputs of the process. The process responses are then represented as statistical developed models. The technique can model the response in terms of all parameters, their interactions and square terms. Finally, the RSM analysis can be used to predict the optimum conditions required for the parameter combination to yield responses from a set objective (Derringer & Suich, 1980; Martinez et al., 2009). The detail information of RSM is shown in Appendix B2.

4.3.1 Experimental design and analysis of functionalized liquid natural rubber

In this work, the mole ratio of (H_2O_2 /isoprene unit) and mole ratio of ($NaNO_2$/ H_2O_2) act as the key synthesis factors that affect the final properties of the FLNR. The control factors were coded as A and B, respectively. The value of each factor was varied over five levels between 0.2 and 1.0. The array with five levels and two factors are shown in Table 4.2. Each row in the array represents a trial condition of the factor levels, which are indicated by the numbers in the row. The columns correspond to the factor specified in this study, and each column contains two level 1, two level 2, two level 3, two level 4 and two level 5 conditions for the factors assigned to the column (a total of 25 conditions, for each condition the reaction experiment was run once, and for the product of each experiment, its properties were measured as the average of 3 replicate readings).

Table 4.2: Control factors and levels of different parameter

Control factors (variables)	**Levels**				
	1	2	3	4	5
A (H_2O_2/isoprene unit)	0.2	0.4	0.6	0.8	1.0
B ($NaNO_2$/H_2O_2)	0.2	0.4	0.6	0.8	1.0

Mathematical models describing the correlation between the responses and the two operational factors will be developed. Polynomial models for the response output was regressed with respect to the operational factors with hierarchy of increasing complexity listed as follows: linear, 2-factor interactions (2FI), quadratic, and cubic. The analysis, evaluation and estimation of the accuracy and applicability for the polynomial models were determined with Design Expert® Software Version 6.0.6. Statistical analyses and three-dimensional plots were obtained to determine both the interaction and optimal operational factors for the synthesis of FLNR. The aim of the present work is to study the effect of varying the amounts of H_2O_2 and $NaNO_2$ in the reaction feed towards the resulting properties of molecular weight and formation of OH functionality of the synthesized FLNR.

4.3.2 Effect of hydrogen peroxide and sodium nitrite on molecular weight and hydroxyl value

Few detailed studies have been made on the influence of the chain-scission reaction on the hydroxylation process and on the structure of the final product. H_2O_2 is an effective agent to break down the molecular chain and provides OH functionality on the polymer backbone of the NR (Ravindran et al., 1986; Wang et al., 2009). However, at high temperatures, H_2O_2 is unstable and will also form side reactions such as furanization and crosslinking (Zhang et al., 2010). Previous work had reported a method where NR was heated up to 150°C at a pressure of 200-300 psi to yield FLNR having M_n between 2500 and 3000 g/mol. Unfortunately, their data indicated that the efficiency of functionalization of NR by this method is low due to side reactions (Gupta et al., 1985).

To mitigate this effect, several other researchers have introduced $NaNO_2$ to the reaction mixture (Bac et al., 1993; Gazeley & Mente, 1987; Ibrahim et al., 2014; Ibrahim & Mustafa, 2014). This type of chain–scissor could be applied for hydroxylation of NR, leading to a more efficient reduction of molecular weight as well as avoiding crosslinking side products. From the results, it was indicated that the small amounts of $NaNO_2$ can exhibit as chain scission for the depolymerization process.

From Table 4.3 and Figure 4.4, the higher amount of $NaNO_2$ does not present the targeted low molecular weight. In addition, the amount of $NaNO_2$ must be control which is not lesser than 0.2 and not more than 0.6 mole ratio. Although $NaNO_2$ might serves to mitigate runaway or side reactions that could occur due to the nature of H_2O_2, the suggestion from the obtained results was determined that only lesser amounts of $NaNO_2$ is necessary to achieve the FLNR with expected low molecular weight (<30,000 g/mol).

The depolymerization reaction was done accordingly with the mole ratio between 0.2 and 1.0.

Table 4.3: Molecular weights results for functionalized liquid natural rubber

Control factors (variables)		**GPC results**	
A	**B**		
H_2O_2/Isoprene unit (mole ratio)	**$NaNO_2/H_2O_2$ (mole ratio)**	**M_n (g/mol)**	**MWD**
0	0	1,207,158	4.261
1.0	0	150,040	2.366
1.0	0.1	95,003	1.856
1.0	0.2	17,063	1.539
1.0	0.4	27,699	1.469
1.0	0.6	33,502	1.453
1.0	0.8	37,872	1.469
1.0	1.0	44,254	1.548
0.8	0.2	33,237	1.468
0.8	0.4	38,305	1.611
0.8	0.6	52,063	1.664
0.8	0.8	35,778	1.569
0.8	1.0	69,595	1.781
0.6	0.2	29,885	1.452
0.6	0.4	45,534	1.654
0.6	0.6	35,303	1.794
0.6	0.8	47,584	1.582
0.6	1.0	53,276	1.539
0.4	0.2	23,544	1.531
0.4	0.4	40,045	1.654
0.4	0.6	50,766	1.763
0.4	0.8	69,780	1.742
0.4	1.0	88,401	1.729
0.2	0.2	17,836	1.540
0.2	0.4	35,963	1.560
0.2	0.6	52,100	1.606
0.2	0.8	68,005	1.700
0.2	1.0	92,437	1.708

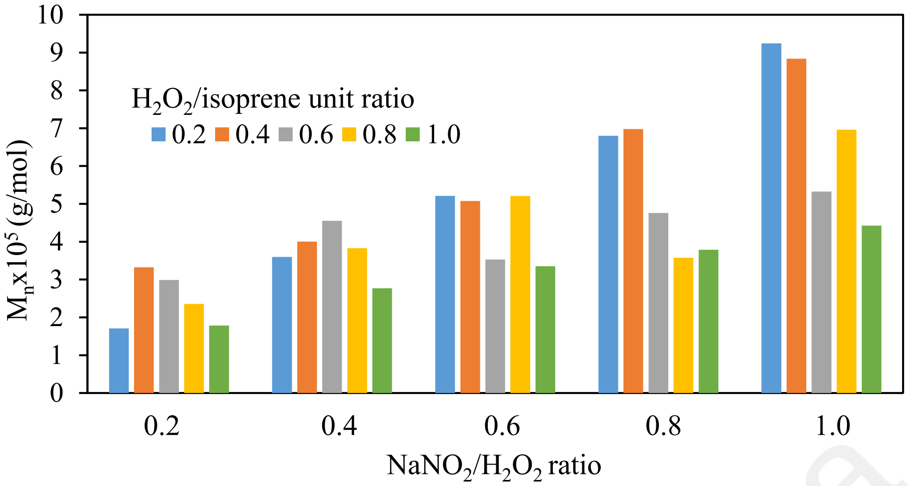


Figure 4.4: M_n of functionalized liquid natural rubber (effect of different ratio of $NaNO_2/H_2O_2$ and ratio of H_2O_2/isoprene unit)

As reported earlier, the suitable molecular weight of FLNR required to produce semi-rigid PU elastomer should be about 25,000 g/mol (Cenens & Hernandez, 1999; Dirckx et al., 1999). Thus, from the result, the appropriate molecular weight was obtained when the H_2O_2 was combined with the low amount of $NaNO_2$ (approximately at mole ratio 0.2). The mole ratio values of $NaNO_2$ to H_2O_2 proposed in this study were according to the previous research that described the depolymerization reaction of NR could be effective only with small amount (percentage) of $NaNO_2$ (Bac et al., 1993). But their report did not declare precisely the range of $NaNO_2$ needed. Therefore, for that reason, this study focuses on the effect of $NaNO_2$ together with the effect of H_2O_2 on the *in situ* depolymerization and hydroxylation process. This will indicate specifically the range of $NaNO_2$ (mole ratio of $NaNO_2/H_2O_2$) needed that could be effective for the formation of FLNR. From Figure 4.5 ratio of $NaNO_2/H_2O_2$ at 0.1 is not useful as the minimum value to effectively reduce the molecular weight of NR. Therefore, ratio at 0.2 which shows the best value was used for this study.

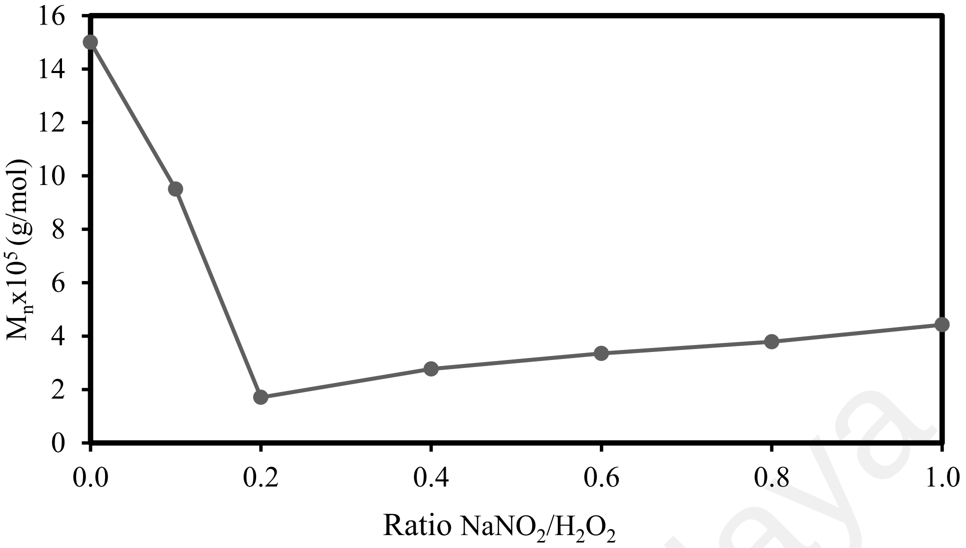


Figure 4.5: Molecular weight (M_n) of functionalized liquid natural rubber (effect of different ratio $NaNO_2/H_2O_2$ at ratio H_2O_2/isoprene unit=1.0)

For the application to form semi-rigid PU, the molecular weight of the FLNR must be low (less than 30,000 g/mol and more preferably less than 20,000 g/mol) (Cenens & Hernandez, 1999; Goldwasser & Onder, 1983) and it must be highly functionalized with OH groups (Cenens & Hernandez, 1999; Dirckx et al., 1999). Table 4.4 shows that the OH values of FLNR obtained increases accordingly with the increasing values of H_2O_2/isoprene unit mole ratio. If the OH value was not detected, a value of zero obtained shows that no OH is present in the structure. This phenomenon happens because of the mitigation effect from the $NaNO_2$ at high amount when it reacts together with H_2O_2, as has been mentioned earlier and these phenomena is explained further in the FT-IR and NMR discussion. The mole ratio of 1.0 for component A (H_2O_2/isoprene unit) and 0.1 for component B ($NaNO_2/H_2O_2$) proves that the OH value obtained is too high because the amount of $NaNO_2$ is not sufficient to break the NR chain and moreover the molecular weight is also high (Figure 4.6).

Table 4.4: Hydroxyl value results of functionalized liquid natural rubber

Control factors (variables)		**OH value**
A	**B**	
H_2O_2/Isoprene unit (mole ratio)	**$NaNO_2/H_2O_2$ (mole ratio)**	**(mg KOH/g)**
1.0	0	953.67
1.0	0.1	635.67
1.0	0.2	255.56
1.0	0.4	204.19
1.0	0.6	169.98
1.0	0.8	135.25
1.0	1.0	35.25
0.8	0.2	44.40
0.8	0.4	191.08
0.8	0.6	52.67
0.8	0.8	41.92
0.8	1.0	33.28
0.6	0.2	209.71
0.6	0.4	42.21
0.6	0.6	0
0.6	0.8	31.82
0.6	1.0	0
0.4	0.2	179.53
0.4	0.4	28.97
0.4	0.6	0
0.4	0.8	0
0.4	1.0	0
0.2	0.2	160.36
0.2	0.4	12.68
0.2	0.6	0
0.2	0.8	0
0.2	1.0	0

Figure 4.6 shows the effectiveness of $NaNO_2$ based on the different mole ratios of $NaNO_2/H_2O_2$ (from 0 to 1.0) at fixed mole ratio of H_2O_2/isoprene unit = 1.0. The reliable OH values are mostly in the targeted range with the mole ratio of $NaNO_2/H_2O_2$ at 0.2 and less than 0.8. For that reason, the optimization was proposed for prediction and observation on each parameter (ratio of H_2O_2 and $NaNO_2$) and the results obtained (M_n, MWD and OH value). The effects of both components (H_2O_2 and $NaNO_2$) were discussed and explained later by ANOVA analysis of RSM.

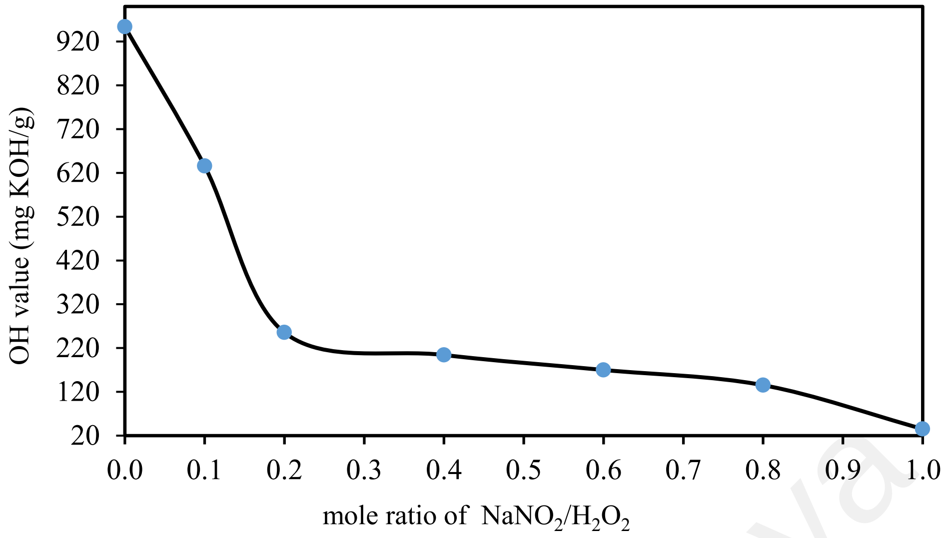


Figure 4.6: Hydroxyl value of functionalized liquid natural rubber (effect of different ratio of $NaNO_2/H_2O_2$ at fixed mole ratio H_2O_2/isoprene unit = 1.0)

4.4 Effect of reaction feed on functionalized liquid natural rubber formation

4.4.1 Hydrogen peroxide effect

The effect of H_2O_2 based on H_2O_2/isoprene unit that contribute to the OH formation was studied by FT-IR. Figure 4.7 to 4.10 show the comparison of intensities of the peaks involve in FLNR formation. The overall FT-IR spectra of FLNR synthesized with different ratios of H_2O_2/isoprene unit ratios are shown in Appendix B3. From Figure 4.7(a), it is clearly shown that the bands attributed to the OH group become stronger with increase in mole ratio of H_2O_2/isoprene unit from 0.2 to 1.0. The band is clearly observed at 3425 cm^{-1} for 0.2 of mole ratio of H_2O_2/isoprene unit but is slightly shifted to 3370 - 3405 cm^{-1}, probably due to the difference of OH content. The 0.4 and 0.6 of mole ratios show the similar intensity also by the different OH content. Previous research had reported that the hydroxyl group band decreased above 1.0 mole ratio of H_2O_2/isoprene unit (Isa, 2011). The decrease of the band intensity is probably due to the existence of legitimately fair side reaction such as crosslink network.

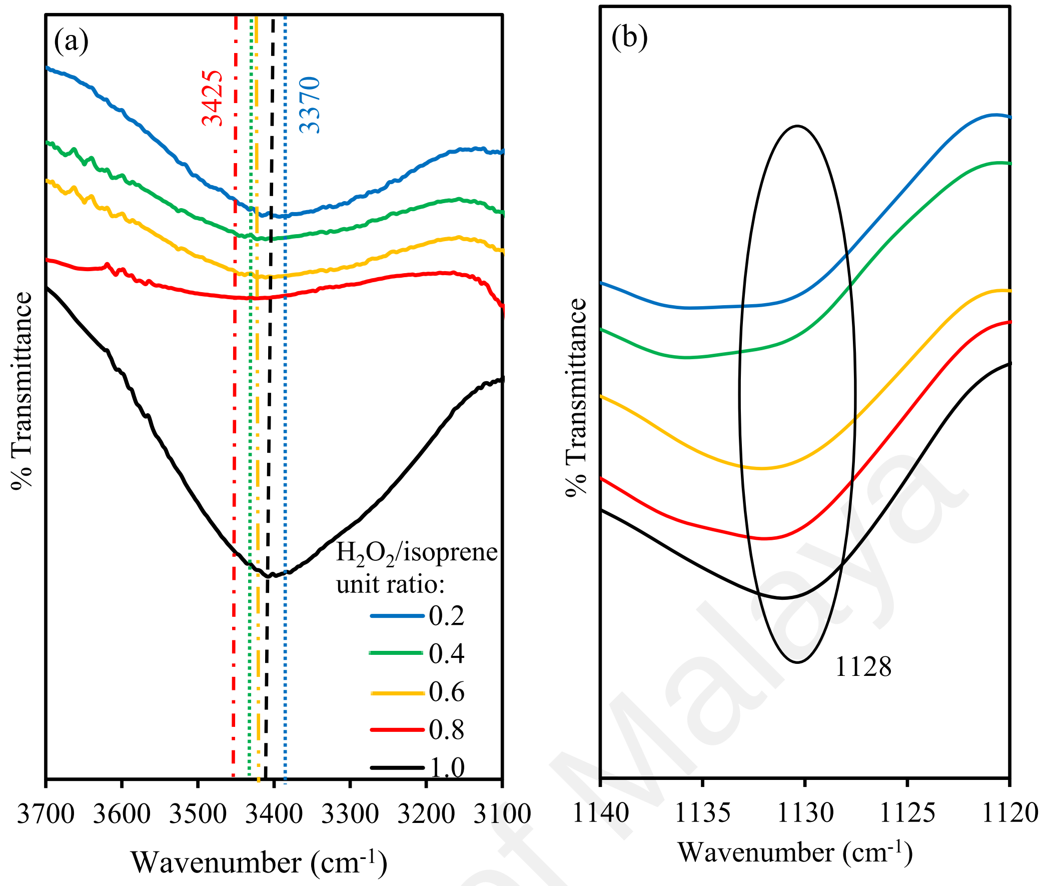


Figure 4.7: Fourier Transform Infrared bands of (a) OH ranging from 3100 to 3700 cm^{-1} and (b) $–R_3C(OH)$- ranging from 1120 to 1140 cm^{-1} at different H_2O_2/isoprene unit ratios; $NaNO_2/H_2O_2$ ratio = 0.2

As for the condition when the side reactions exist during *in situ* reaction, the assumption made is that this situation happens from the incomplete ring opening reaction during *in situ* reaction and producing epoxy or furan structure. The OH peak of mole ratio at 0.8 showed poor development to produce the hydroxylated NR as observed from the weak OH band and low OH value of less than 50 mg KOH/g and high M_n of more than 30,000 g/mol. It is believed that during the FLNR preparation, the presence of side reactions or incomplete reaction could not produce FLNR with the appropriate values of M_n and OH content. It is not worthy to mention that the reactions at this mole ratio (0.8) was prepared and repeated three times and consistent result were obtained.

Meanwhile, Figure 4.7(b) illustrates in detail the bands that contribute to the progress of OH bond in the FLNR structure arising from the stretching of C-OH from the $–R_3C(OH)-$ bonds at peak 1128 cm^{-1}.

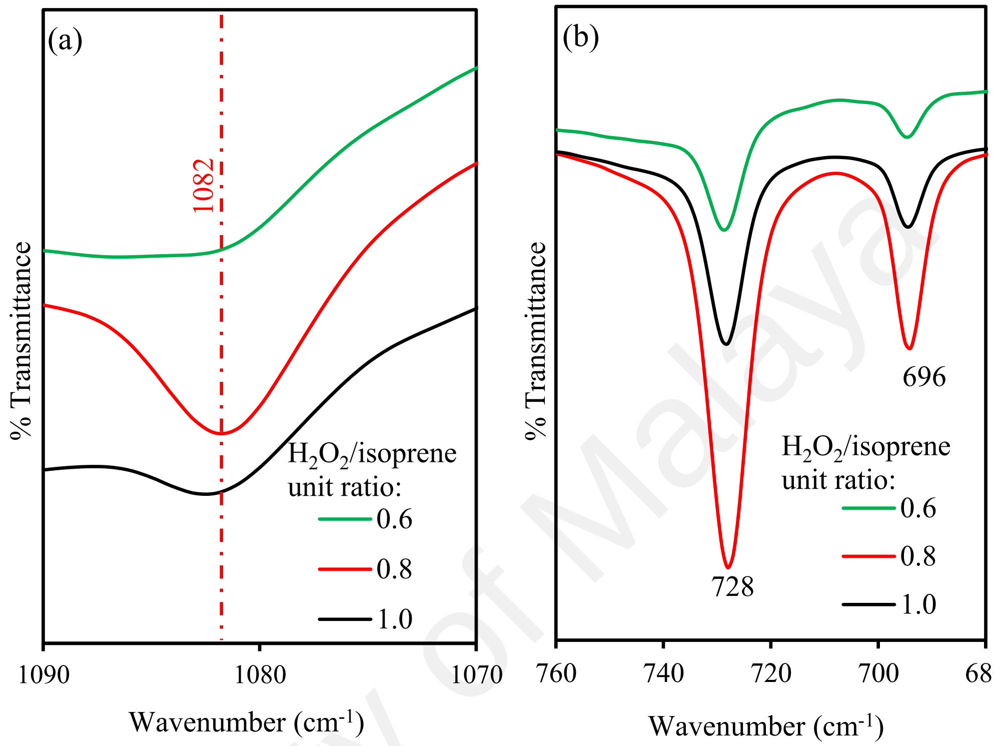


Figure 4.8: Fourier Transform Infrared of proposed furan bands at (a) 1082 cm^{-1} and (b) 728 cm^{-1} and 696 cm^{-1} at different H_2O_2/isoprene unit ratios; $NaNO_2/H_2O_2$ ratio= 0.2

The peak due to furan groups was proposed to exist at 1068 cm^{-1} (Isa et al., 2007) but as shown in Figure 4.8 (a) this was not clearly observed; instead a new peak at 1082 cm^{-1} appeared in samples with mole ratio of H_2O_2/isoprene unit of 0.8. This peak might possibly be furan group. The other furan group structures that had been proposed are at 728 and 696 cm^{-1} and this was clearly observed in Figure 4.8 (b).

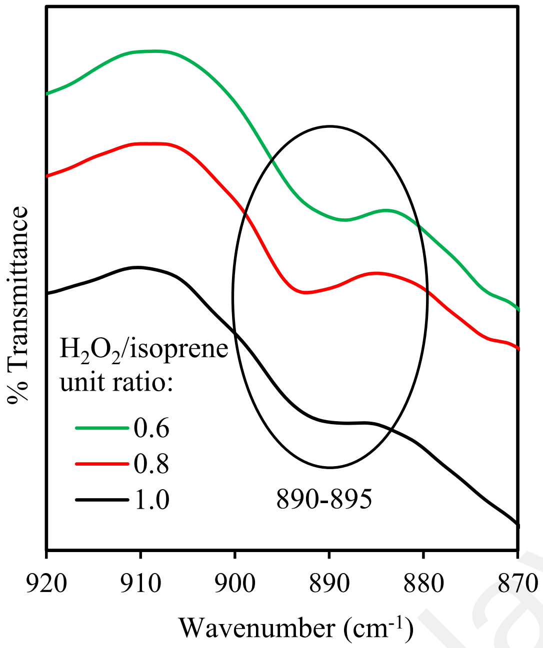


Figure 4.9: Fourier Transform Infrared of epoxy bands at 890-895 cm^{-1} in different H_2O_2/isoprene unit ratios; $NaNO_2/H_2O_2$ ratio= 0.2

Meanwhile, Figure 4.9 shows the appearance of epoxy peak in the range of 890-895 cm^{-1}. Previous study (Isa, 2011) reported the epoxy peak was observed at 874 cm^{-1}. Similarly Brown et al. and Cooper (Brown et al., 1988; Cooper, 1980) showed that the epoxy peak exists between 890-950 cm^{-1}.

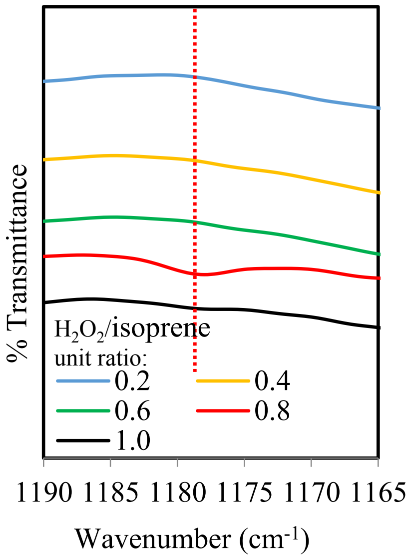


Figure 4.10: Fourier Transform Infrared of proposed aldehyde bands at 1178 cm^{-1} of different H_2O_2/isoprene unit ratios; $NaNO_2/H_2O_2$ ratio = 0.2

Besides that, the peak at 1178 cm^{-1} at mole ratio of 0.8 is also believed to be due to the appearance of aldehyde group (Ravindran et al., 1998). The discussion of the existence of any side reactions such as furan group, epoxy and aldehyde will be discussed further in Section 4.8 (NMR analysis).

4.4.2 Sodium nitrite effect

The presence of $NaNO_2$ in the *in situ* reaction was investigated to see how the effectiveness of this reagent acting as the chain scissor. This chain scissor is believed to be able to shorten the length of NR chain and will decreases the molecular weight of NR from more than 1 million to less than 30,000 g/mol. The study on $NaNO_2$ effect was investigated varying the mole ratio of $NaNO_2/H_2O_2$.

Figure 4.11 (a) shows the comparison of OH bands at 3370 - 3425 cm^{-1} for all the samples. Strong OH bands for FLNR is observed at 0.2 mole ratio of $NaNO_2/H_2O_2$. No significant difference of OH bands at mole ratios at 0.4, 0.6 and 0.8 while at 1.0, weakest OH bands is observed. This results support those obtained and discussed in Section 4.2 whereby higher amounts of both $NaNO_2$ and H_2O_2 will reduce the OH value and interfere the molecular weight reduction. Figure 4.11(b) shows the trend of bands in FLNR structure assigned for stretching of C-OH from $–R_3C(OH)-$ structure at 1128 cm^{-1}. The bands are clearly observed for mole ratios of $NaNO_2/H_2O_2$ at 0.6 and 0.8 and not obvious for the samples with mole ratios at 0.2, 0.4 and 1.0. This peak intensity is related to the OH values obtained in Section 4.3.2.

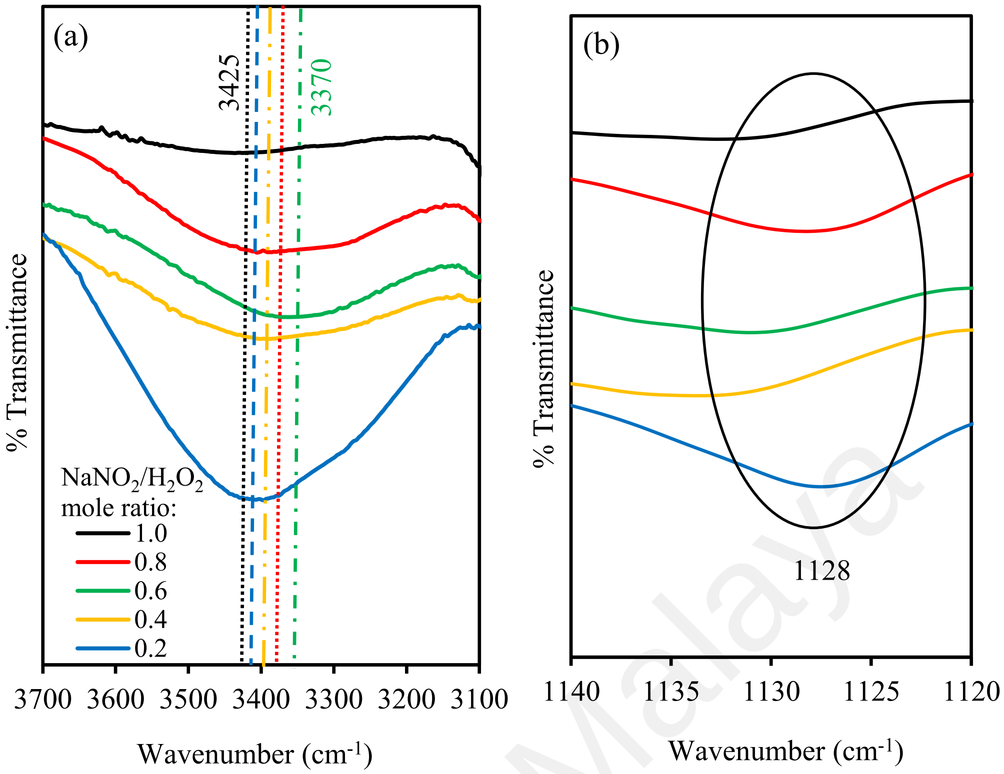


Figure 4.11: Fourier Transform Infrared bands at (a) OH ranging from 3100 to 3700 cm^{-1} and (b) –R$_3$C(OH)- ranging from 1120 to 1140 cm^{-1} in different NaNO$_2$/H$_2$O$_2$ ratios; H$_2$O$_2$/isoprene ratio = 1.0

Figure 4.12 shows the epoxy group at 890-895 cm^{-1} increases with the increase in NaNO$_2$/H$_2$O$_2$ ratio. The epoxy bands are observed at ratios of 0.6, 0.8 and 1.0. The addition of NaNO$_2$ in the in situ depolymerization and hydroxylation reaction in the presence of H$_2$O$_2$ has resulted in this unpredicted side structure in the FLNR. However, this epoxy band is not clearly seen at ratios of 0.4 probably because the FLNR structure was formed completely without interruption with this side reaction.

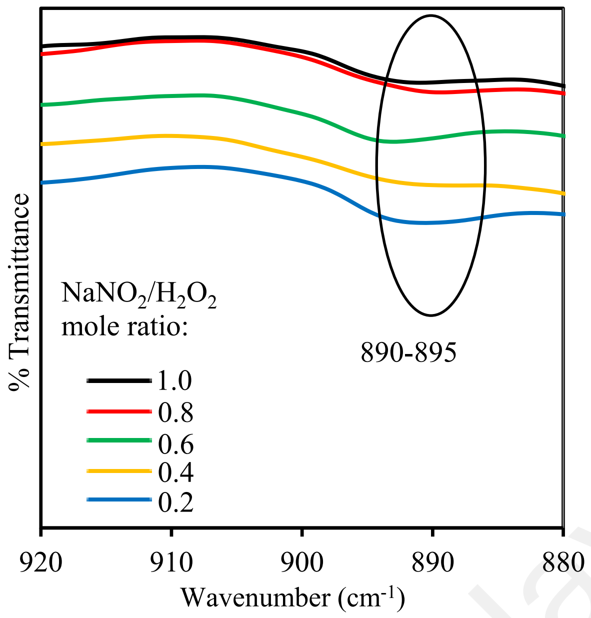


Figure 4.12: Fourier Transform Infrared of epoxy bands at 890-895 cm^{-1} at different NaNO$_2$/H$_2$O$_2$ ratios; H$_2$O$_2$/isoprene unit ratio= 1.0

High amount of NaNO$_2$ used in the degradation reaction has been shown to produce side effects. Radical initiated reaction in NR modification caused by radical species leading to chain rupture can be contributed by the unbalanced structure and weakened CH$_2$-CH$_2$ bond (Ravindran et al., 1988). This is induced by the steric hindrance occurring at the cis position of the NR chain. The C=C in the chain is the nucleophilic site which becomes favourable for cleavage by redox reaction. Thus, the reduction of C=C and C-C bonds indicates that the degradation of NR has occurred at both C=C and C-C bonds and suggests the possibility that more than one cleavage sites have occurred concurrently in the degradation reaction (Ibrahim & Mustafa, 2014; Ravindran et al., 1988).

Similar to the effect of H$_2$O$_2$ in the *in situ* reaction of FLNR, the furan groups are formed as shown in Figure 4.13 (a) and (b) for this part. The furan bands assigned at 1082 cm^{-1} (Figure 4.13 (a)) and 728 cm^{-1} and 696 cm^{-1}(Figure 4.13 (b)) are clearly observed at high value of NaNO$_2$ ratios of 1.0, 0.8 and 0.6 compared to 0.4 and 0.2. Thus, amounts of high H_2O_2 and $NaNO_2$ interfere the process to achieve the targeted low M_n and high OH value. The amount of $NaNO_2$ must be in the assured optimum value (between 0.2 and 0.4) to achieve target parameter of FLNR as precursor for semi-rigid PU. The mole ratios of 0.6, 0.8 and 1.0 gave high M_n and OH value. The discussion of $NaNO_2$ and H_2O_2 on the effect of OH values and molecular weight of FLNR formed are clearly verified in NMR analysis (Section 4.5).

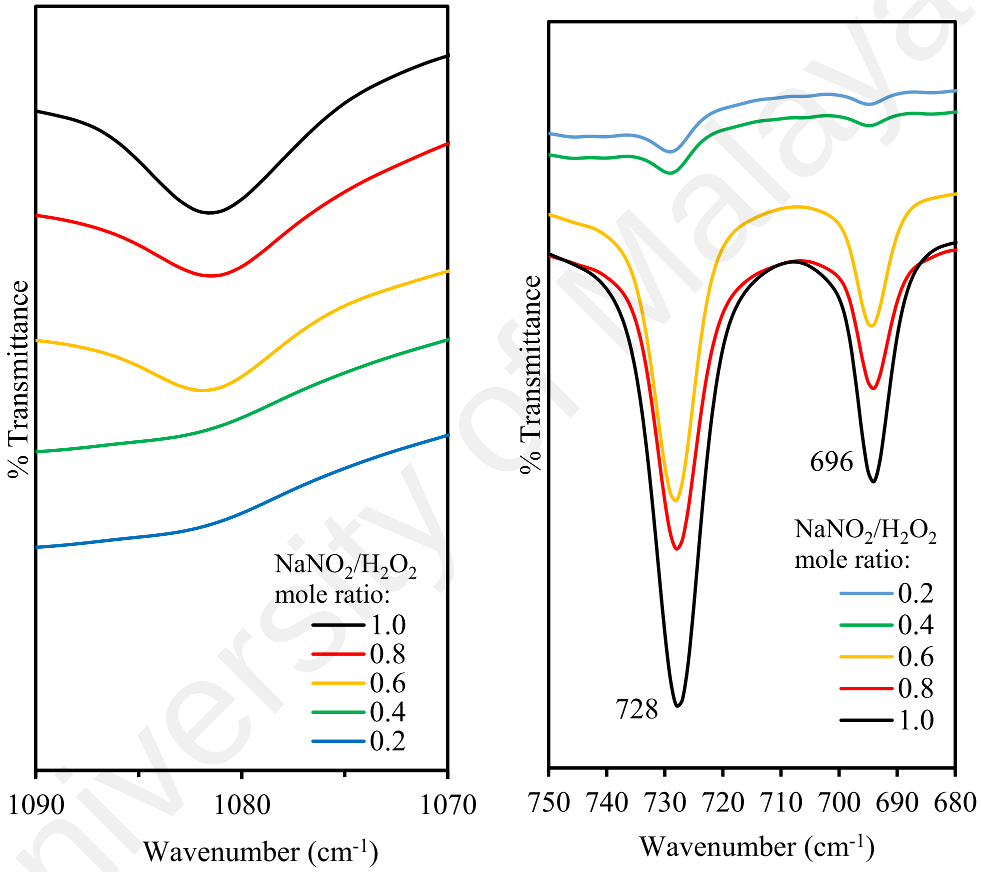


Figure 4.13: Fourier Transform Infrared of proposed furan bands at (a) 1082 cm^{-1} and (b) 728 cm^{-1} and 696 cm^{-1} at different $NaNO_2/H_2O_2$ ratios; H_2O_2/isoprene ratio = 1.0

4.5 Nuclear Magnetic Resonance of functionalized liquid natural rubber

The hydroxylation of FLNR was supported by NMR analysis. The discussion is focused more on the formation of FLNR with high OH value (>100 mg KOH/g) and low M_n (< 30,000 g/mol) in accordance with the objective of this work. For FLNR with low

M_n and high OH value, the samples were those with mole ratios of H_2O_2/isoprene unit: $NaNO_2/H_2O_2$ of 1.0:0.2, 1.0:0.4 and 0.2:0.2. For the FLNR with low OH value with high M_n, the selected FLNR samples were those with mole ratio of H_2O_2/isoprene unit: $NaNO_2/H_2O_2$ of 0.8:0.2, 0.8:0.6, 0.6:0.4 and 1.0:1.0.

4.5.1 Functionalized liquid natural rubber with high hydroxyl value and low M_n

The proton NMR spectrum and the assignment of chemical shifts are given in Figure 4.14 and Table 4.5. Three principal chemical shifts typical of the structure of NR, are observed at 1.69, 2.05 and 5.12 ppm, assigned to methyl protons (CH_3), methylene protons (—CH_2—) and methine proton (=CH—), respectively for the structure **—CH_2—$C(CH_3)$=CH—CH_2—** (Derouet et al., 2001; Isa et al., 2007; Kébir et al., 2005a; Nor & Ebdon, 1998; Zhang et al., 2010).

The FLNR with OH end group structure has five chemical shifts at 1.26 ppm for methyl proton (—CH_3), 5.11 and 3.66 ppm for methylene protons (=CH_2 and —CH_2—), 3.77 ppm for methine proton (—CH—) and 3.5 ppm which is assigned as hydroxyl (—OH) proton for the structure of **—CH_2—$C(CH_3)(OH)$ —CH=CH_2**. Another possible end groups in FLNR that could be formed is CH_2=C(CH_3) —**CH(OH)** —CH_2. The chemical shifts for this structure are at 1.26 ppm for methyl protons (—CH_3), 4.93 for methylene protons (=CH_2—) and 1.98 for the other methylene proton (—CH_2—), 3.74 for methine (—CH—) and 3.76 ppm for hydroxyl (—OH) proton (Derouet et al., 2001; Ibrahim & Mustafa, 2014; Isa et al., 2007; Sakdapipanich et al., 2005).

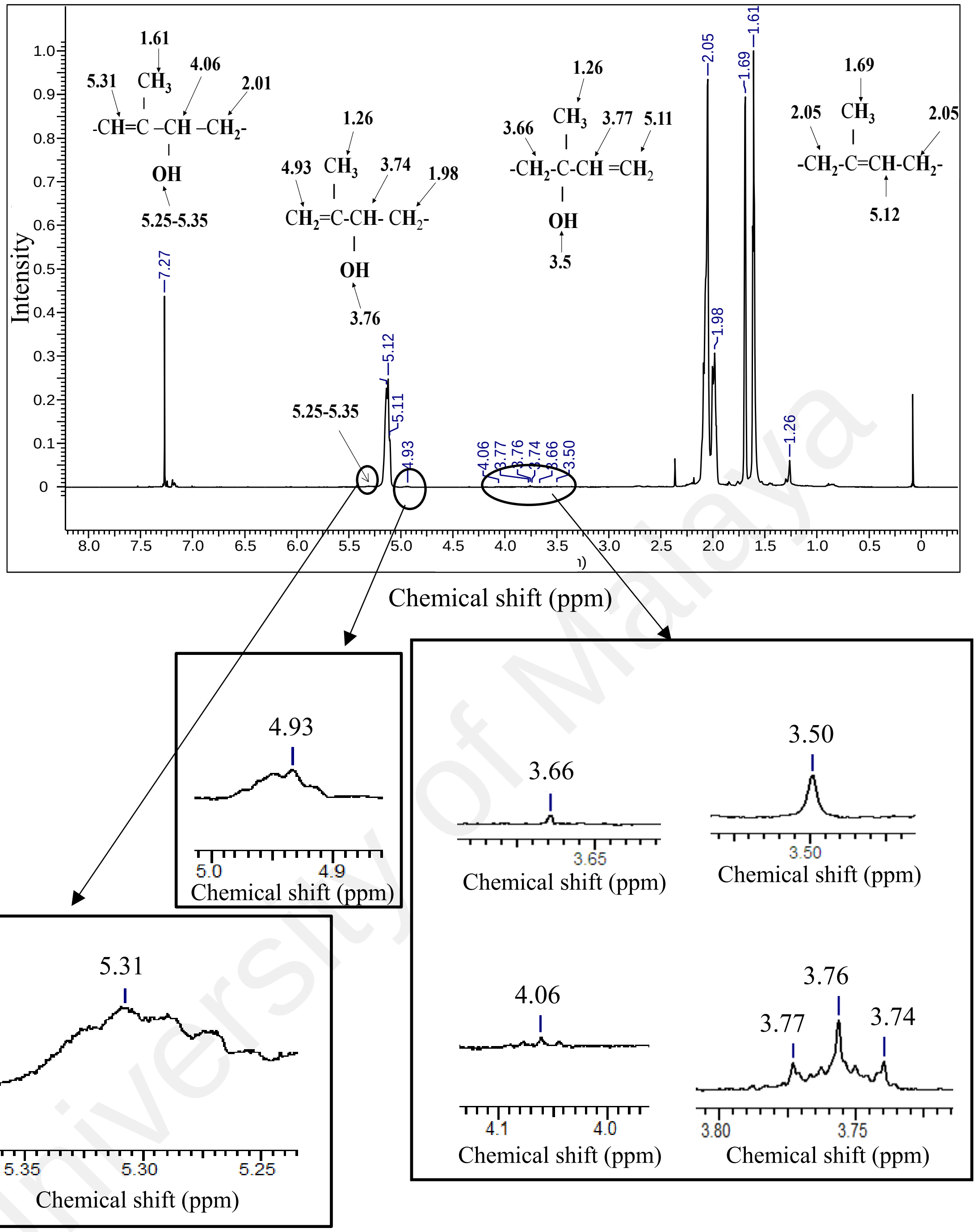
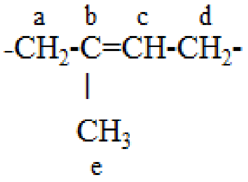
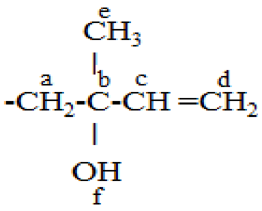
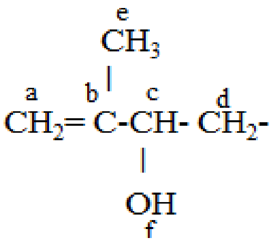
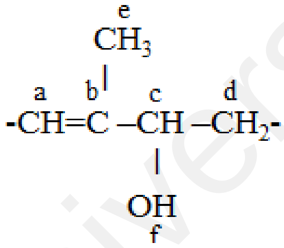


Figure 4.14: Proton Nuclear Magnetic resonance spectrum of functionalized liquid natural rubber with high hydroxyl value and low M_n

Table 4.5: The assignment of chemical shifts for proton and carbon-13 Nuclear Magnetic Resonance of functionalized liquid natural rubber with high hydroxyl value and low M_n

		Chemical shifts					
Structure		**a**	**b**	**c**	**d**	**e**	**f**
 $-\overset{a}{CH_2}-\overset{b}{C}(\underset{e}{CH_3})=\overset{c}{CH}-\overset{d}{CH_2}-$	^1H	2.05	-	5.12	2.05	1.69	-
	^{13}C	32.08	135.27	125.12	26.18	23.52	-
 $-\overset{a}{CH_2}-\overset{b}{C}(\overset{e}{CH_3})(\underset{f}{OH})-\overset{c}{CH}=\overset{d}{CH_2}$ OH end group (1)	^1H	3.66	-	3.77	5.11	1.26	3.50
	^{13}C	40.13	128.32		125.12- 125.39	15.59	-
 $\overset{a}{CH_2}=\overset{b}{C}(\overset{e}{CH_3})-\overset{c}{CH}(\underset{f}{OH})-\overset{d}{CH_2}-$ OH end group (2)	^1H	4.93	-	3.74	1.98	1.26	3.76
	^{13}C	125.12- 125.39	129.13			15.59	-
 $-\overset{a}{CH}=\overset{b}{C}(\overset{e}{CH_3})-\overset{c}{CH}(\underset{f}{OH})-\overset{d}{CH_2}-$ OH central group	^1H	5.31	-	4.06	1.98	1.61	5.25- 5.35
	^{13}C	125.12- 125.39	135.27- 135.48		124.02- 125.39	21.55	-

Besides that, FLNR also appears to have functionalization at the central group because of the high OH value obtained. The possible central group structure was believed as **—CH=C(CH$_3$) —CH(OH) —CH$_2$—**. The chemical shifts are assigned as methyl proton (—CH$_3$) at 1.61 ppm and methylene proton (—CH$_2$—) at 1.98 ppm(Cooper, 1980; Derouet et al., 2001; Ibrahim & Mustafa, 2014; Isa et al., 2007; Sakdapipanich et al., 2005). The chemical shift of OH proton for —CH**(OH)** structure is between 5.25-5.35

ppm (Derouet et al., 2001) appearing as weak signal (Figure 4.14), while the chemical shift of methine proton (CH) assigned as –**CH**(OH) is observed at 4.06 ppm and –**CH**=C at 5.31 ppm.

The clear appearance of OH structure at the indicated peaks (between 3.5 and 3.8 ppm) for the OH central groups structure: $-CH-C(CH_3)-CH(OH)=CH_2-$ and OH end groups structure; $CH_2=C(CH_3)-CH(OH)-CH_2$ of FLNR in Figure 4.14 are similar to the previous study (Ibrahim & Mustafa, 2014; Isa et al., 2007; Suksawad & Sakdapipanich, 2005). The chemical shift of proton for OH group can be shifted depending on the solvent used (Cooper, 1980). It can also be affected by the hydrogen bonding that might have formed. It can cause the OH proton, normally in singlet form, to shift rapidly and only shows the chemical shift from the other nuclei. In this study, the chemical shift of OH proton observed is small and wide between 3.5-3.77 ppm. It might be due to M_n of FLNR being slightly high (17,000 g/mol) and this can affect the NMR determination to detect the shifting of the OH proton.

The new peak of methyl protons adjacent to secondary alcohol at 1.26 ppm and two peaks corresponding to C-H (3.77 ppm) and $C-H_2$ (3.66 ppm) adjacent to alcohol groups at the chain-ends are observed, similar to those found by previous research (Zhang et al., 2010). The signal due to the allylic hydroxyl proton in the proton NMR is proposed by the multiplets at δ =5.1 (Ravindran et al., 1988). This shifting of OH could be affected by the solvent used. The small peak is also similar to previous study that had reported the effect of reagent ($NaNO_2$) concentration (Ibrahim & Mustafa, 2014). In addition, this FLNR also demonstrated a complete disappearance of both peaks of aldehyde proton at 9.80 ppm and methylic proton in ketone end group at 2.13 ppm. (Ravindran et al., 1988).

The indication of the formation of OH in carbon-13 NMR is assigned in Table 4.5 and also shown in Figure 4.15. The chemical shifts observed at δ = 21.55, 125.12-125.39, 135.27-135.48 and 124.02-125.39 ppm are assigned to methyl, methylene, methine and quaternary carbon in OH central group of -CH-C(CH_3)-CH(OH)=CH_2- structure, respectively. The tertiary carbon for OH end-chain group is suggested to appear at 128.32 and 129.13 ppm.

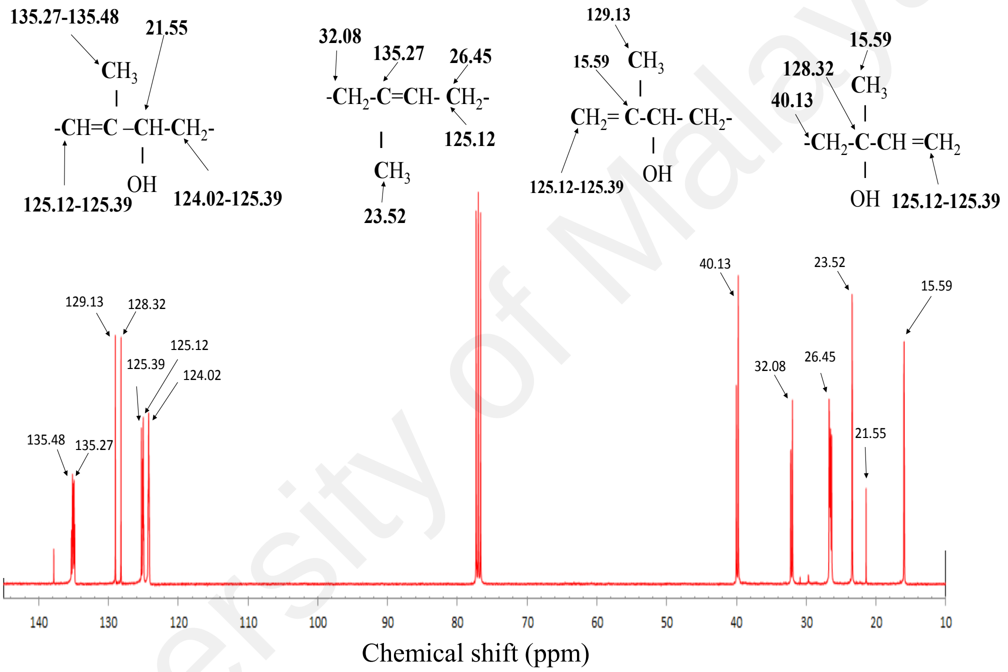
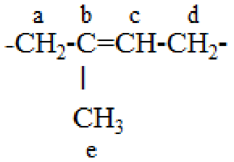
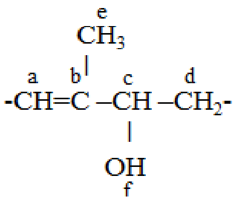
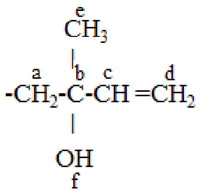
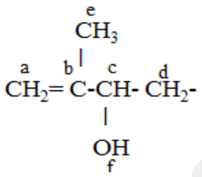
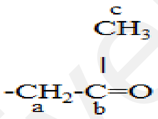
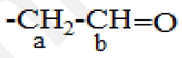
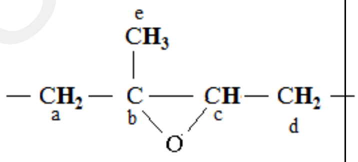
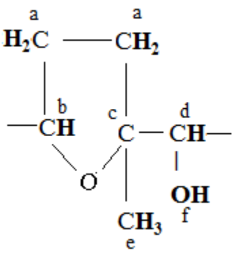


Figure 4.15: Carbon-13 Nuclear Magnetic Resonance spectrum of functionalized liquid natural rubber with high hydroxyl value and low M_n

4.5.2 Functionalized liquid natural rubber with low hydroxyl value and high M_n

The main structure for the FLNR with low OH value and high M_n is shown in Appendix B4. The assignment of chemical shifts of FLNR obtained are given in Table 4.6. Likewise, for overall chemical shifts of proton NMR assigned for the OH central group structure: -CH-C(CH_3)-CH(OH)=CH_2- and OH end group structure; CH_2=C(CH_3)-CH(OH)-CH_2 of FLNR at low OH value and high M_n also look similar for FLNR at high OH value and low M_n. Nevertheless, for low OH value FLNR, the chemical shift of central OH group observed was only slight compared to the high OH value FLNR at δ = 5.31 assigned to –CH=C (Appendix B4).

Table 4.6: The assignment of chemical shifts for proton and carbon-13 Nuclear Magnetic Resonance of functionalized liquid natural rubber with low hydroxyl value and high M_n

		Chemical shifts					
Structure		**a**	**b**	**c**	**d**	**e**	**f**
 $-CH_2-C(CH_3)=CH-CH_2-$	^{1}H	2.05	-	5.12	2.05	1.69	
	^{13}C	32.08	135.27	125.12	26.18	23.52	
 $-CH=C(CH_3)-CH(OH)-CH_2-$	^{1}H	5.31	-	4.06	1.98	1.61	5.2-5.23
	^{13}C	125.12 - 125.39	135.27 - 135.48	75.65	124.02 - 125.39	21.55	-
 $-CH_2-C(CH_3)(OH)-CH=CH_2$	^{1}H	3.66	-	3.77	5.11	1.26	3.50
	^{13}C	40.13	128.32	73.59	125.12 - 125.39	15.59	-
 $CH_2=C(CH_3)-CH(OH)-CH_2-$	^{1}H	4.95	-	3.74	1.98	1.26	3.76
	^{13}C	125.12 - 125.39	129.13	75.65	69.57	15.59	-
 $-CH_2-C(CH_3)=O$	^{1}H	2.22	-	2.14			
	^{13}C	43.9*	208.7*	43.9*			
 $-CH_2-CH=O$	^{1}H	2.22	9.82				
	^{13}C	**	**				
	^{1}H	1.76	-	2.77	1.76	1.26	
	^{13}C	36.5	60.68	62.69	21.14	60.68	
	^{1}H	2.01 and 4.69	3.97	-	4.43	1.99	4.05
	^{13}C	**	**	**	**	**	**

Note: * (Phinyocheep et al., 2005) , ** chemical shift difficult to detect

The evidence for the of side reaction occurring is given in Figure 4.16 (a) and (b) showing the aldehyde group. The peaks at 9.82 and 2.22 ppm are assigned as methine proton (—CH=) and methylene proton (—CH_2—) for the aldehyde structure, respectively. Besides that, the epoxy structure in the proton NMR spectra complements the analysis in the previous FT-IR analysis (Section 4.4) though the signal is slow. The chemical shift at 2.77 ppm is assigned as methine proton (—CH—) of epoxy structure as shown in Figure 4.17 (a).

In addition, the chemical shifts at 1.26 and 1.76 ppm are assigned for methyl protons (—CH_3) and methylene protons (—CH_2—) (Figure 4.17 (b) and (c)) (Derouet et al., 2001; Isa et al., 2007; Zhang et al., 2010). This epoxy peak might be produced from incomplete reaction of ring-opening during the *in situ* process of depolymerization and hydroxylation.

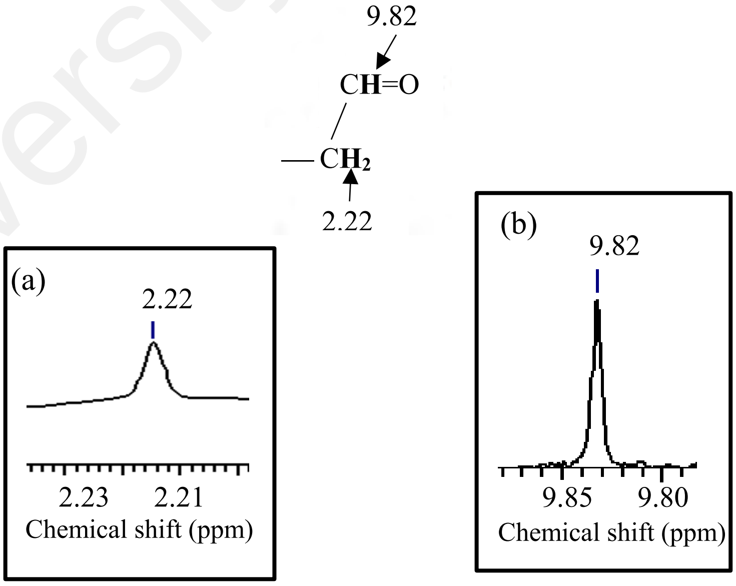


Figure 4.16: Chemical shifts in proton Nuclear Magnetic Resonance of aldehyde with low hydroxyl value and high M_n of (a) 2.22 ppm (—CH_2) and (b) 9.82 ppm (—CH=)

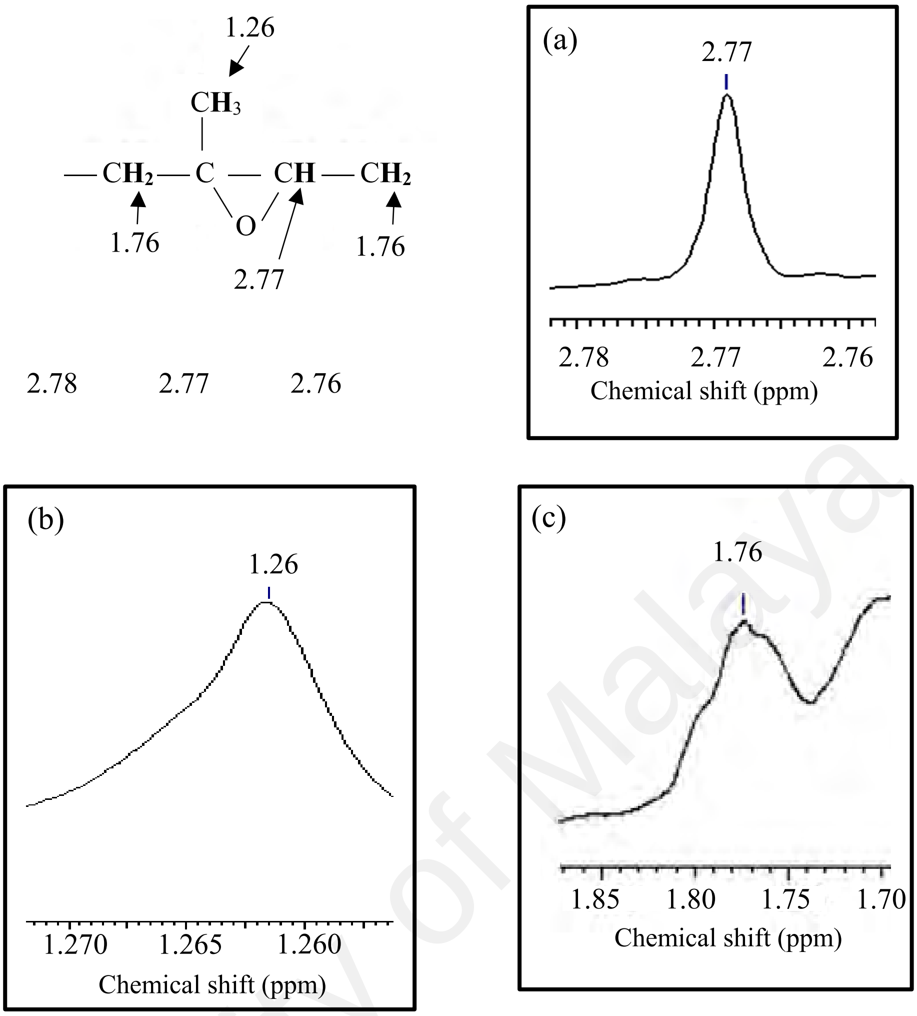


Figure 4.17: Chemical shifts in proton Nuclear Magnetic Resonance of epoxy with low hydroxyl value and high M_n of (a) 2.77 ppm (—CH—) (b) 1.26 ppm (—CH_3) and (c) 1.76 ppm (—CH_2—)

Besides that, Figure 4.18 (a) and (b) shows the new chemical shifts at 2.14 and 2.22 ppm, assigned for methyl protons (CH_3) and CH_2 in the terminal carbonyl function for ketone group (Phinyocheep et al., 2005; Tangpakdee et al., 1998)

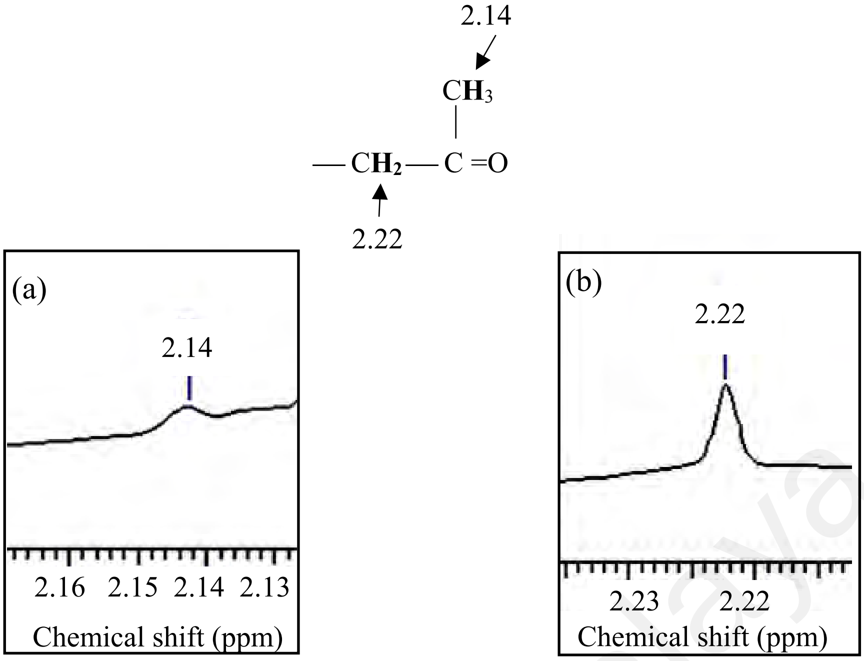


Figure 4.18: Chemical shifts in proton Nuclear Magnetic Resonance of ketone with low hydroxyl value and high M_n of (a) 2.14 ppm (CH_3-) and (b) 2.22 ppm (-CH_2-)

Meanwhile, the chemical shift for furanization was proposed to be between 3.8-4.8 ppm (Zhang et al., 2010) (Figure 4.19). For high M_n FLNR, the chemical shifts of methine protons (—CH—O—) and (—CH—OH—) are indicated at 3.97 (Figure 4.19 (b) and between 4.43-4.69 ppm (Figure 4.19 (c) while methyl protons (—CH_3) at chemical shift of 1.99 ppm (Figure 4.19 (a)). The clear chemical shift at 2.01 and 4.69 ppm are assigned as methylene protons (CH_2—CH) and CH_2—C in the furan group structure. Meanwhile, the chemical shift at 4.05 ppm is assigned as hydroxyl proton that overlaps with OH from central OH group —CH=C(CH_3) —CH(**OH**) —CH_2—.

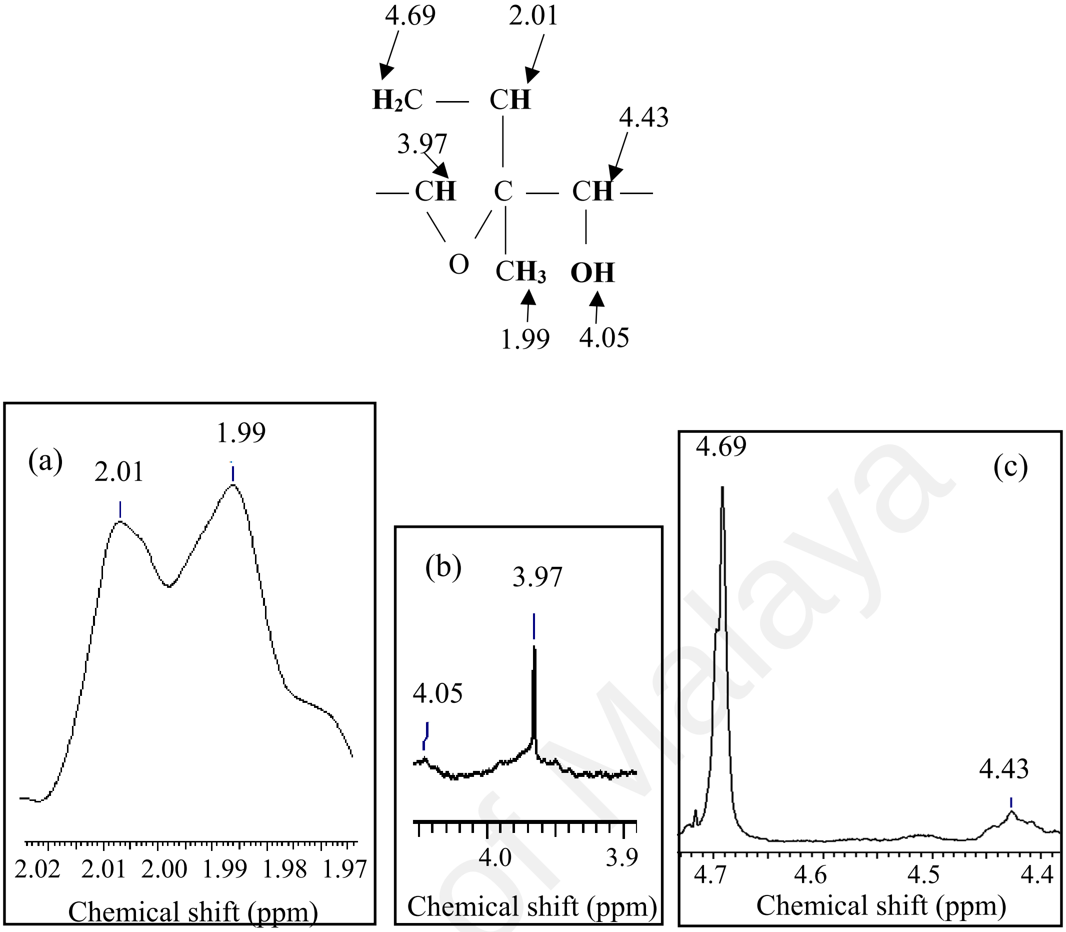


Figure 4.19: Chemical shifts in proton Nuclear Magnetic Resonance of furan group with low hydroxyl value and high M_n of (a) 1.99 ppm (—CH_3) and 2.01 ppm (—CH_2—C—) (b) 4.05 ppm (-OH) and 3.97 ppm (-CH-) and (c) 4.43 ppm (-CH (OH)- and 4.69 ppm (-CH_2)

Therefore, during the *in situ* reaction many possibilities could happen. The effect of unstable temperature control, number of reagents used, the incomplete ring opening reaction and chain breaking can encourage the increase in the rate of the formation of other side reactions such as epoxidation, furanization and/or crosslinking network.

The carbon-13 NMR for low OH value and high M_n FLNR is similar to the FLNR with high OH value and low M_n. Further evidence for the formation of epoxy group as side group is shown in Figure 4.20 (a) – (c). The chemical shifts at 60.68, 39.43 and 62.69 ppm are attributed to tertiary carbon, methylene and methine in the epoxy structure.

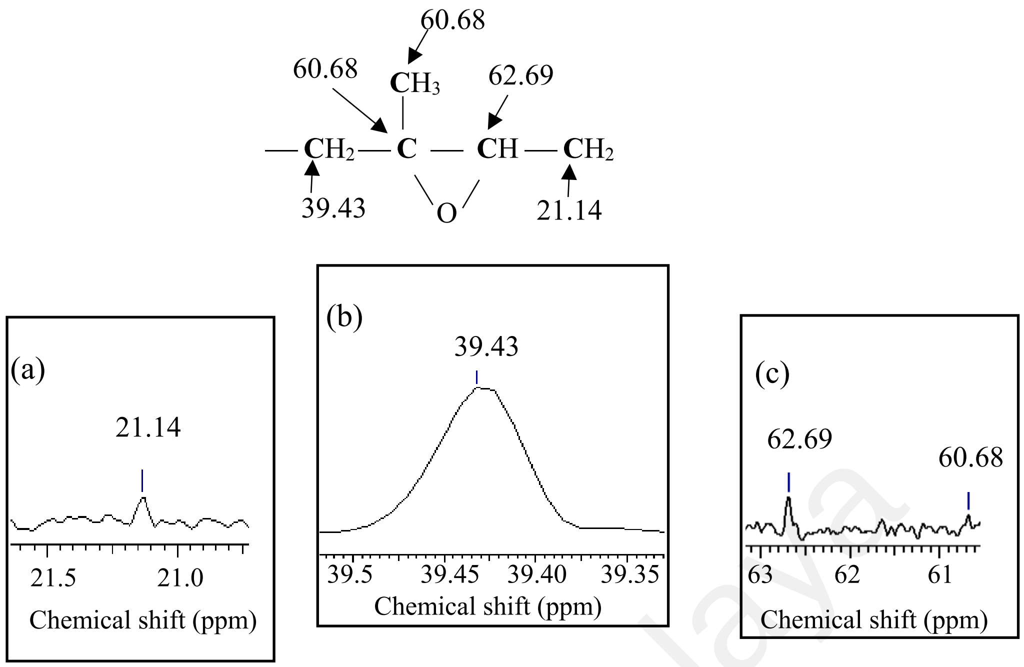


Figure 4.20: Chemical shifts in carbon-13 Nuclear Magnetic Resonance of epoxy group with low hydroxyl value and high M_n of (a) 21.14 ppm (-CH_2-) (b) 39.43 ppm (other -CH_2-) and (c) 60.68 ppm (both -C- and -CH_3) and 62.69 ppm (-CH)

The other chemical shift for methine in this epoxy structure is similar to previous study, i.e at peak of 21.14 ppm in Figure 4.20 (a) (Derouet et al., 2001). The carbon-13 NMR for furan, ketone and crosslinking formation are difficult to detect due to the weak resolution of the signals. Nevertheless, previous study had reported that the chemical shifts for ketone end group that appeared at 29.7, 43.9 and 208.7 ppm were assigned as methyl, methylene and tertiary carbon, respectively (Phinyocheep et al., 2005) .

4.6 Statistical analysis by analysis of variance

The results obtained in this study, were analyzed statistically by analysis of variance (ANOVA) method using Design Expert 6.0.6 software by RSM. The RSM use the ANOVA to determine which parameters have the strongest interactions and/or which ones exhibit significant influence on the outputs of the process. If the model looks good, then the three-dimensional graphs and contour plots will be plotted for interpretation. In brief, a good model must be significant, and the lack-of-fit must be insignificant. The various coefficient of determination (R^2) values should be close to 1. The diagnostic plots should exhibit trends associated with a good model and these will be elaborated subsequently (Idris et al., 2006).

It is noted ANOVA method provides the design model according to either significant or insignificant model terms. The selection model described by the "Sequential Model Sum of Sum Squares" which shows how terms of increasing complexity contribute to the total model. The model hierarchy is described as (i) Linear: the significance of adding the linear terms to the mean and blocks, (ii) Two-factor Interactions (2FI): the significance of adding the two factor interaction terms to the mean, block and linear terms already in the model, (iii) Quadratic: the significance of adding the quadratic (squared) terms to the mean, block, linear and two factorial interaction terms already in the model and (iv) Cubic: the significance of the cubic terms beyond all other terms.

The ANOVA reports list key data which provides brief explanations and guidelines to choose the significant model terms according to the suggested "Sequential Model Sum of Sum Squares". The best model was determined by stepwise elimination of insignificant coefficients that makes the model insignificant. Based on the data given, the "F-value", "prob>F, "R^2", "Predicted R^2", "Adjusted R^2" and "predicted residual sum of square (PRESS)" values are useful to know whether the model terms are significant or insignificant. Additionally, the computed value of 'adequate precision' gives the value which is equally to an index of the signal to noise ratio (S/N ratio). This value signifies whether the model can be used to navigate the design space. The result of adequate precision in RSM is the average value that shows if significant or insignificant (Montgomery, 1997).

The effects of two different factors (variables) on the responses of number average M_n, MWD, and OH value was studied. The first factor (A) is the mole ratio of H_2O_2/isoprene unit in the feed, and the second factor (B) is the mole ratio of $NaNO_2$/ H_2O_2. M_n and MWD response values were obtained directly from the GPC measurement. The response outputs of OH value for the FLNR samples were obtained and calculated according to ASTM D4274-05. For experimental runs where the OH value was not detected, a value of zero was given as the response output. Table 4.7 shows the experimental design of the factor combinations, together with the response outputs. These response outputs were then evaluated with the different types of response surface models (i.e. linear, 2FI, quadratic and cubic) to compare the appropriateness of each model.

Table 4.7: Design layout and experimental results

Run no.	**Factors**		**Responses**		
	A H_2O_2/Isoprene unit (mole ratio)	**B $NaNO_2$/H_2O_2 (mole ratio)**	**M_n (g/mol)**	**MWD**	**OH value (mg KOH/g)**
1	0.2	1.0	92437	1.708	0
2	0.2	0.8	68005	1.700	0
3	0.2	0.6	52100	1.606	0
4	0.2	0.4	35963	1.560	12.67
5	0.2	0.2	17836	1.540	160.36
6	0.4	1.0	88401	1.729	0
7	0.4	0.8	69780	1.742	0
8	0.4	0.6	50766	1.763	0
9	0.4	0.4	40045	1.654	28.97
10	0.4	0.2	23544	1.531	179.53
11	0.6	1.0	53276	1.539	0
12	0.6	0.8	47584	1.582	31.82
13	0.6	0.6	35303	1.794	0
14	0.6	0.4	45534	1.654	42.21
15	0.6	0.2	29885	1.452	209.70
16	0.8	1.0	69595	1.781	33.27
17	0.8	0.8	35778	1.569	41.92
18	0.8	0.6	52063	1.664	52.66
19	0.8	0.4	38305	1.611	191.07
20	0.8	0.2	33237	1.468	44.40
21	1.0	1.0	44254	1.548	35.25
22	1.0	0.8	37872	1.469	135.25
23	1.0	0.6	33502	1.453	169.97
24	1.0	0.4	27699	1.469	204.18
25	1.0	0.2	17063	1.539	255.56

4.6.1 Analysis of variance for M_n

Table 4.8 lists the outcomes for the suitability of each of the models. It was found that the 2FI is the best mathematical model for the M_n response output. The sequential model F-value tests the significance of adding new terms to the model. A small sequential model Prob>F (less than 0.05) indicates that the addition of new terms has a significant effect on improving the model. In this case, the 2FI model was selected as the highest order polynomial where the additional terms are significant (Prob>F value of 0.0007) and quadratic or cubic models were not chosen because the additional terms would lead to very high Prob>F values.

Table 4.8: Evaluation of different response surface models for M_n

Summary	**Linear**	**2FI**	**Quadratic**	**Cubic**
Sequential Model Sum of Squares	6.802×10^9	1.041×10^9	1.014×10^8	3.455×10^8
Sequential Model Model F-value	30.6850	15.6415	0.7433	1.3629
Sequential Model Prob>F	< 0.0001	0.0007	0.4889	0.2933
Standard Deviation	10528	8158	8259	7961
Mean	45593.08	45593.08	45593.08	45593.08
Coefficient of Variation %	23.09	17.89	18.12	17.46
PRESS	3.267×10^9	1.947×10^9	2.207×10^9	2.595×10^9
R^2	0.7361	0.8488	0.8597	0.8971
Adjusted R^2	0.7121	0.8272	0.8228	0.8354
Predicted R^2	0.6465	0.7893	0.7612	0.7192
(Adjusted R^2 – Predicted R^2)	0.0657	0.0378	0.0617	0.1162
S/N ratio	17.104	20.763	16.744	15.984
Residual	2.439×10^9	1.398×10^9	9.241×10^9	9.507×10^9

The R^2 indicates how well the data fits a statistical model. A good fit has R^2 values close to 1. The use of an adjusted R^2 is an attempt to take into account the phenomenon of the R^2 spuriously increasing when additional terms are added to the model. It is a modification of R^2 that adjusts for the number of terms in a model relative to the number of data points. The adjusted R^2 can be negative, and its value will always be less than or = that of R^2. Unlike R^2, the adjusted R^2 increases when a new term is added only if the new term improves the R^2 more than would be expected by chance. If a set of terms with a predetermined hierarchy of importance are introduced into a regression one at a time, with the adjusted R^2 computed each time, the level at which the adjusted R^2 reaches a maximum, and decreases afterward, would be the regression with the ideal combination of having the best fit without unnecessary terms. The predicted R^2 is a measure of the amount of variation in new data explained by the model. The predicted R^2 and the adjusted R^2 should be within 0.20 of each other. Otherwise there may be a problem with either the data (possibly outliers) or the model (a power transformation or a different order polynomial should be considered). In this regard, the 2FI would be the best model for the M_n response surface since it has the highest adjusted R^2 and the lowest (adjusted R^2 – predicted R^2) value. Although the quadratic and cubic model responses proposed the high value of R^2 but the values of (adjusted R^2 – predicted R^2) and Prob>F were higher, so these two model responses were neglected.

Table 4.9 shows the ANOVA analysis for the 2FI response surface model for M_n. The Prob>F value for the model which is less than 0.05 indicates that the model is significant, which is desirable as it indicates that the terms in the model have a significant effect on the response.

Table 4.9: Analysis of variance of two-factor interaction response surface model for M_n

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-Value**	**Prob>F**
Model	7.843×10^9	3	2.614×10^9	39.28	< 0.0001
A	1.305×10^9	1	1.305×10^9	19.61	0.0002
B	5.497×10^9	1	5.497×10^9	82.60	< 0.0001
AB	1.041×10^9	1	1.041×10^9	15.64	0.0007
Residual	1.398×10^9	21	6.655×10^7		
Cor Total	9.241×10^9	24			

In a similar manner, the main effect of the feed ratio factors of H_2O_2/isoprene unit (A), $NaNO_2/H_2O_2$ (B), and the interaction of both factors (AB) are significant model terms. The main effect of $NaNO_2/H_2O_2$ (B) is the most significant factor associated with the M_n response. The significant factors were ranked based on the value of F-ratio. The larger the magnitude of F-value and correspondingly the smaller the Prob>F value, the more significant is the contribution of the corresponding coefficient term (Myers, Montgomery, & Anderson-Cook, 2009). Thus, in this study, the ranking is as follows: B>A>AB. In terms of actual factors, the final empirical model for the response of M_n is as follows:

$$M_n = 427.12 + 22849.70A + 100822.60B - 80659.50AB \qquad \text{(equation 4.2)}$$

This model can be used to predict response values of M_n within the limits of the experiment. The signal to noise (S/N) ratio compares the range of the predicted values at the design points to the average prediction error and typically, ratios greater than 4 indicate adequate model discrimination (Montgomery, 1997). In this case, the S/N ratio value of 20.763 is well above 4; therefore, the design space can be navigated by the 2FI model. This model also has the lowest value of residuals. The residuals refer to the difference between actual and predicted values (Table 4.10). Also of note is the predicted residual error sum of squares (PRESS) which provides a measure of the fit of a model to a sample of observations that were not used to estimate the model. A fitted model having been produced, each observation in turn is removed and the model is refitted using the remaining observations. The squared residuals are then summed. Lower values of PRESS indicate better model structure among the candidate models; in the case of the M_n data set, this would be the 2FI model.

Table 4.10: Actual and predicted values of two-factor interaction response surface model for M_n

	Factors		Responses	
Run no.	A H_2O_2/Isoprene unit (mole ratio)	B $NaNO_2/H_2O_2$ (mole ratio)	M_n (g/mol) (actual)	M_n (g/mol) (predicted)
1	0.2	1.0	92437	89688
2	0.2	0.8	68005	72750
3	0.2	0.6	52100	55811
4	0.2	0.4	35963	38873
5	0.2	0.2	17836	21935
6	0.4	1.0	88401	78126
7	0.4	0.8	69780	64414
8	0.4	0.6	50766	50702
9	0.4	0.4	40045	36991
10	0.4	0.2	23544	23279
11	0.6	1.0	53276	66564
12	0.6	0.8	47584	56078
13	0.6	0.6	35303	45593
14	0.6	0.4	45534	35108
15	0.6	0.2	29885	24622
16	0.8	1.0	69595	55002
17	0.8	0.8	35778	47743
18	0.8	0.6	52063	40484
19	0.8	0.4	38305	33225
20	0.8	0.2	33237	25966
21	1.0	1.0	44254	43440
22	1.0	0.8	37872	39407
23	1.0	0.6	33502	35375
24	1.0	0.4	27699	31342
25	1.0	0.2	17063	27309

4.6.2 Analysis of variance of molecular weight distribution

Table 4.11 shows outcomes list for the suitability of each models for MWD response. As the result, it was recommended that the linear RSM is the only suitable mathematical model for the MWD response output. It is the only model with the lowest Prob>F value of 0.0053. The R^2 of 0.3787 is not as close to 1 as one might normally expect. This low value stems from the fact that the MWD response ranges from 1.452 to 1.794. The ratio of maximum to minimum response value that is 1.236 makes the data variance too low and difficult to distinguish a response trend (Table 4.12).

Table 4.11: Evaluation of different response surface models for molecular weight distribution

Summary	**Linear**	**2FI**	**Quadratic**	**Cubic**
Sequential Model Sum of Squares	0.1068	0.0066	0.0384	0.0138
Sequential Model F-value	6.7047	0.8280	2.8064	0.4451
Sequential Model Prob>F	0.0053	0.3732	0.0855	0.7743
Standard Deviation	0.0892	0.0896	0.0827	0.0880
Mean	1.6049	1.6049	1.6049	1.6049
Coefficient of Variation %	5.56	5.58	5.16	5.49
PRESS	0.2177	0.2193	0.2322	0.4024
R^2	0.3787	0.4023	0.5386	0.5875
Adjusted R^2	0.3222	0.3169	0.4171	0.3400
Predicted R^2	0.2279	0.2220	0.1761	-0.4274
(Adjusted R^2 – Predicted R^2)	0.0943	0.0949	0.2410	0.7674
S/N ratio	8.455	7.294	6.703	4.430
Residual	0.175	0.169	0.130	0.116

Table 4.12: Actual and predicted values of linear response surface model for molecular weight distribution

	Factors		**Responses**	
Run no.	**A** **H_2O_2/Isoprene unit (mole ratio)**	**B** **$NaNO_2/H_2O_2$ (mole ratio)**	**MWD (actual)**	**MWD (predicted)**
1	0.2	1.0	1.708	1.736
2	0.2	0.8	1.700	1.702
3	0.2	0.6	1.606	1.669
4	0.2	0.4	1.560	1.636
5	0.2	0.2	1.540	1.602
6	0.4	1.0	1.729	1.704
7	0.4	0.8	1.742	1.670
8	0.4	0.6	1.763	1.637
9	0.4	0.4	1.654	1.604
10	0.4	0.2	1.531	1.570
11	0.6	1.0	1.539	1.672
12	0.6	0.8	1.582	1.638
13	0.6	0.6	1.794	1.605
14	0.6	0.4	1.654	1.572
15	0.6	0.2	1.452	1.538
16	0.8	1.0	1.781	1.639
17	0.8	0.8	1.569	1.606
18	0.8	0.6	1.664	1.573
19	0.8	0.4	1.611	1.540
20	0.8	0.2	1.468	1.506
21	1.0	1.0	1.548	1.607
22	1.0	0.8	1.469	1.574
23	1.0	0.6	1.453	1.541
24	1.0	0.4	1.469	1.508
25	1.0	0.2	1.539	1.474

The results can also be attributed to the fact that fine control of the MWD property is known to be very difficult to obtain when radical species are involved in the reaction. Nevertheless, the S/N ratio of 8.455 is sufficiently high to allow navigation in the design space of the model. In terms of actual factors, the final empirical model for the response of MWD is as follows:

$$\text{MWD} = 1.6010 - 0.1601\text{A} + 0.1666\text{B} \qquad \text{(equation 4.3)}$$

Table 4.13 shows that both terms in the model are significant since the Prob>F values are less than 0.05 and the data also suggests that the nitrite species has a slightly larger edge of influence in the system. Thus, the factor contribution ranking is as follows: B>A.

Table 4.13: Analysis of variance of linear response surface model for molecular weight distribution

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-Value**	**Prob>F**
Model	0.1068	2	0.0534	6.7047	0.0053
A	0.0513	1	0.0513	6.4386	0.0188
B	0.0555	1	0.0555	6.9708	0.0149
Residual	0.1751	22	0.0080		
Cor Total	0.2819	24			

4.6.3 Analysis of variance analysis of hydroxyl value

Unlike M_n and MWD; the response from OH value has a very high maximum to minimum ratio which indicates that a power transform to the data set is required. This is a useful technique to stabilize variance and make the data more normal distribution-like. Most power transformation function can be described by a standard equation of:

$$\sigma = \text{fn}(\mu^{\alpha}) \qquad \text{(equation 4.4)}$$

where fn is the functionalized model used, σ is the standard deviation, μ is the mean, α is the power, and λ is (1−α) in all cases. The initial value of λ in the standard equation will be λ=1.

To yield the λ-value, the conventional Box–Cox plot was used. This plot enables a guideline for the selection of the correct power λ transformation (Box & Cox, 1964). Figure 4.21 shows the Box–Cox plot for the best λ-value when the starting λ = 1. From the Box–Cox plot, the best lambda value for each type of model was recommended in a range of -0.10 to 0.41 at a 95% confidence interval and substituted into the following equation:

$$y' = (y + k)^{\lambda} \quad \text{(equation 4.5)}$$

where y' is the transformed response, y is the original response, and k is a constant used to make the response values positive. For the response data set of OH value, k was determined to be 2.55561.

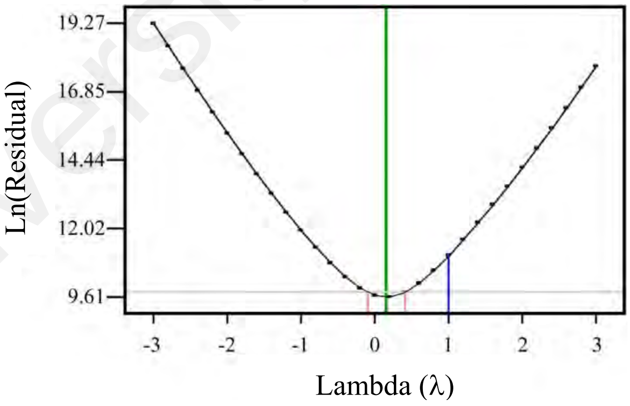


Figure 4.21: Box–Cox plot for determination of the best power-transformed response surface model

Table 4.14 lists the iteration outcomes for the suitability of each power order and mathematical transformed models. The transformed models were evaluated for its fittingness in representing the OH value response outputs. It was also lists the actual and predicted OH value for full cubic and reduced cubic responses. Initially, it was found that the cubic model was to be the best mathematical model for the OH value response output.

Table 4.14: Evaluation of different response surface models for hydroxyl value

Summary	**Linear**	**2FI**	**Quadratic**	**Reduced Cubic**	**Full Cubic**
λ	0.15	0.07	0.11	0.17	0.17
Sequential Model Sum of Squares	3.1727	0.0276	0.0870	N/A	0.4953
Sequential Model F-value	27.1959	4.1041	2.2496	N/A	2.2751
Sequential Model Prob>F	< 0.0001	0.0557	0.1328	N/A	0.1094
Standard Deviation	0.2415	0.0820	0.1558	0.2161	0.2333
Mean	1.6888	1.2666	1.4593	1.8197	1.8197
Coefficient of Variation %	14.30	6.47	9.53	11.88	12.82
PRESS *y'*	1.6515	0.2051	0.6857	1.468	2.171
R^2	0.7120	0.7563	0.8008	0.8714	0.8751
Adjusted R^2	0.6858	0.7215	0.7484	0.8285	0.8002
Predicted R^2	0.6294	0.6458	0.6333	0.7755	0.6678
(Adjusted R^2 – Predicted R^2)	0.0564	0.0757	0.1151	0.0530	0.1324
S/N ratio	17.030	15.629	13.446	13.284	9.594
Residual *y'*	1.283	0.141	0.368	0.841	0.816
Residual *y*	1.214×10^5	2.901×10^5	2.359×10^5	3.646×10^4	3.872×10^4

Closer inspection of the cubic model ANOVA in Table 4.15 shows that there are model terms with Prob>F values that are greater than 0.1 indicating that their contribution to the model is not significant. To improve the model fit, a backward regression procedure was performed from the full cubic model. The terms A^2B, A^3, B^3, which have high Prob>F values were removed stepwise.

Thus, ANOVA of the reduced cubic surface model in Table 4.16 shows better (lower) Prob>F values of the significant model terms. The contribution ranking of the terms to the system is as follows: $B>A>AB^2>AB>B^2>A^2$. Evaluation of the reduced cubic surface model shows improvement by having the highest adjusted R^2 and predicted R^2

and the smallest value for their difference. It also has a higher S/N ratio and lower coefficient of variation (C.V.) % over the full cubic model. (C.V.) % is the standard deviation expressed as a percentage of the mean. The power transformation for the OH value data set has caused their mean values to be widely different. C.V. % is independent of the power transformations and is therefore useful for model comparison because the standard deviation of data must always be understood in the context of the mean of the data.

Table 4.15: Analysis of variance of full cubic surface model for hydroxyl value

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-Value**	**Prob>F**
Model	5.7208	9	0.6356	11.6801	< 0.0001
A	0.6235	1	0.6235	11.4566	0.0041
B	0.1447	1	0.1447	2.6590	0.1238
A^2	0.1488	1	0.1488	2.7350	0.1189
B^2	0.1834	1	0.1834	3.3696	0.0863
AB	0.2365	1	0.2365	4.3464	0.0546
A^3	0.0068	1	0.0068	0.1245	0.7291
B^3	0.0165	1	0.0165	0.3024	0.5904
A^2B	0.0012	1	0.0012	0.0229	0.8818
AB^2	0.4708	1	0.4708	8.6506	0.0101
Residual	0.8163	15	0.0544		
Cor Total	6.5371	24			

Table 4.16: Analysis of variance of reduced cubic surface model for hydroxyl value

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-Value**	**Prob > F**
Model	5.6963	6	0.9494	20.3247	< 0.0001
A	2.2164	1	2.2164	47.4481	< 0.0001
B	2.4069	1	2.4069	51.5284	< 0.0001
A^2	0.1488	1	0.1488	3.1864	0.0911
B^2	0.1834	1	0.1834	3.9257	0.0630
AB	0.2365	1	0.2365	5.0638	0.0372
AB^2	0.4708	1	0.4708	10.0785	0.0052
Residual	0.841	18	0.0467		
Cor Total	6.5371	24			

In terms of actual factors the final empirical model for the response OH value is as follows:

$$(\text{OH value} + 2.55561)^{0.17} = 4.1781 - 3.0819A - 8.5810B + 1.1528A^2 + 5.6287B^2 + 9.9142AB - 7.2486AB^2 \qquad \text{(equation 4.6)}$$

4.7 Diagnostic graph

The normal probability plots in Figure 4.22 (a) - (c) show that the residuals generally fall on a straight-line implying that the errors are distributed normally for M_n, MWD and OH value.

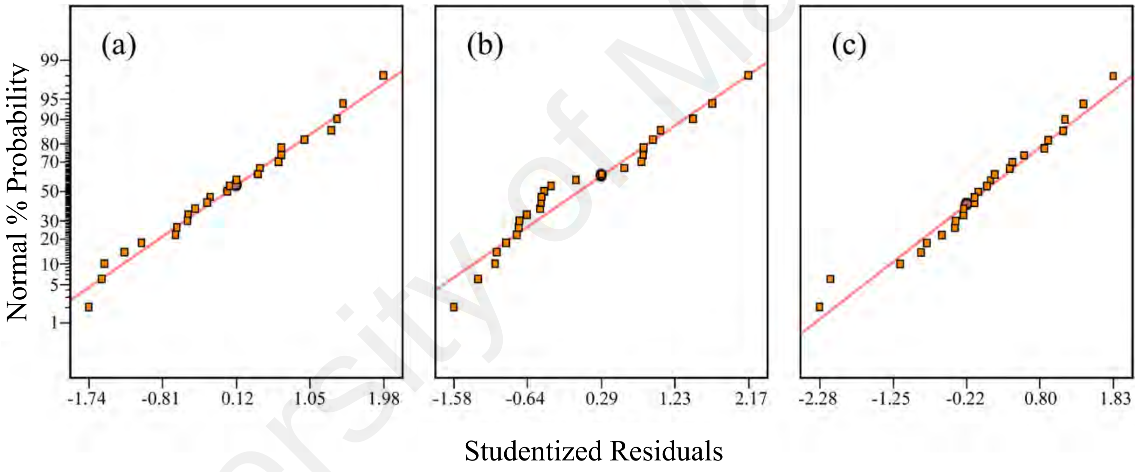


Figure 4.22: Normal probability plot of residual for (a) M_n (b) molecular weight distribution and (c) (hydroxyl value + 2.55561)$^{0.17}$

The plot of the residuals versus predicted response in Figure 4.23 (a) - (c) show approximately equal scatter across the graphs. These graphical diagnostic checks imply that the models proposed are adequate and there is no reason to suspect any violation of the independence or constant variance assumption.

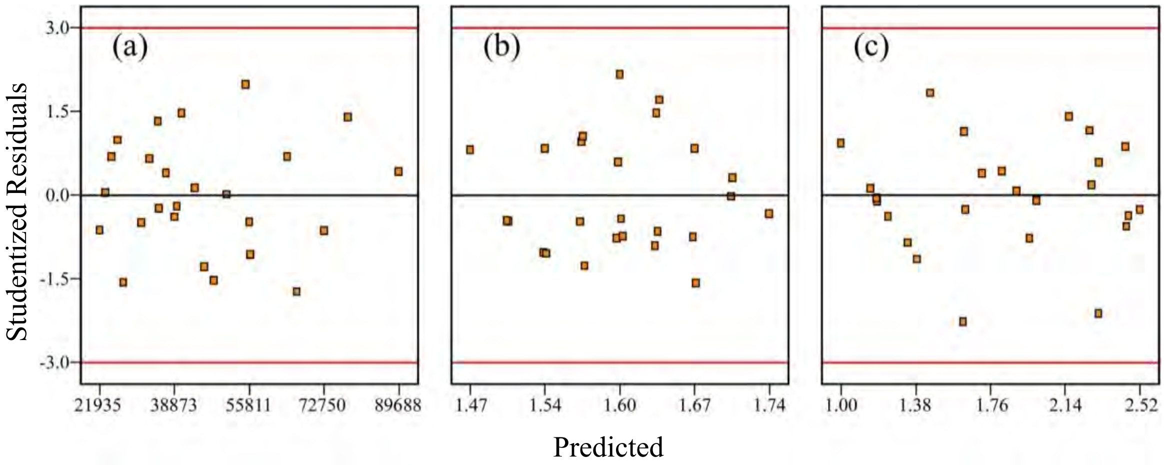


Figure 4.23: Plot of residual vs. predicted response for (a) M_n (b) molecular weight distribution and (c) (hydroxyl value + 2.55561)$^{0.17}$

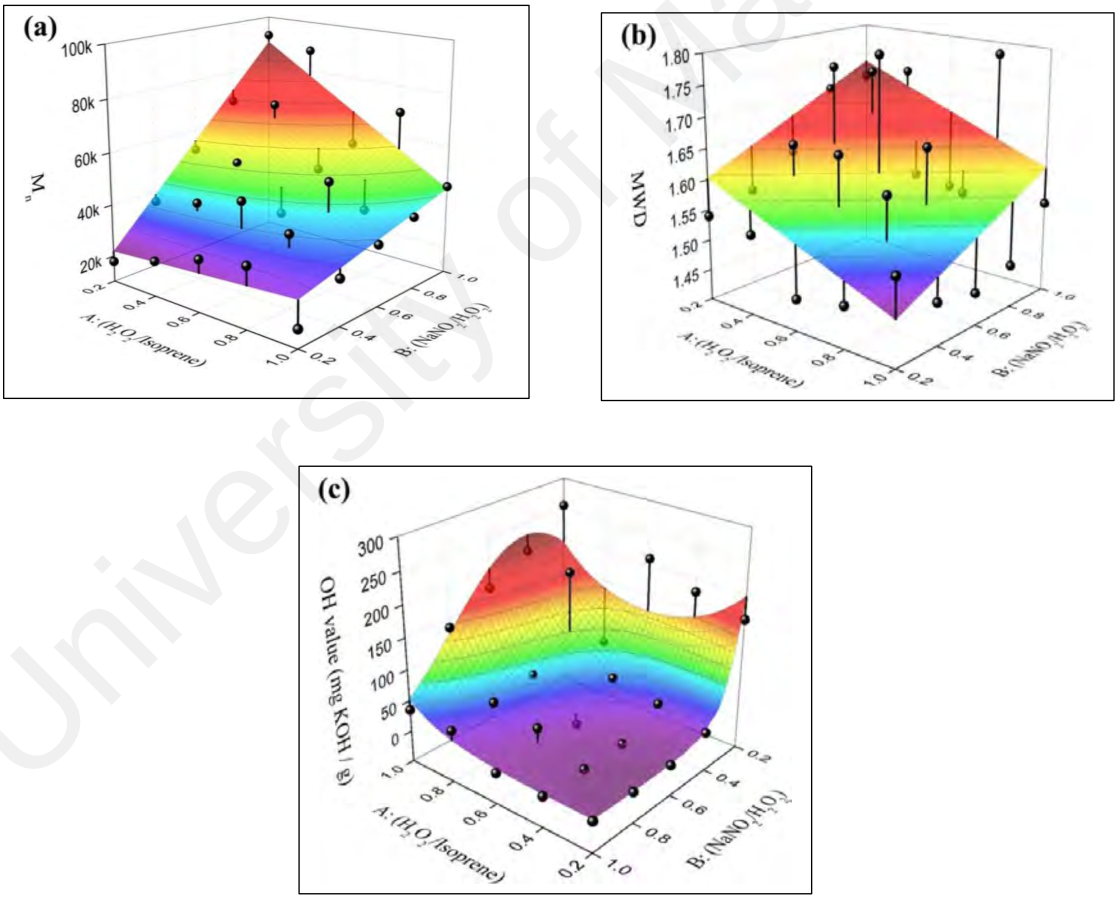


Figure 4.24: Plot of predicted surface and actual values for (a)M_n (b) molecular weight distribution and (c) (hydroxyl value + 2.55561)$^{0.17}$

Figure 4.24 (a) – (c) show the 3D surface graphs of the actual and predicted responses for M_n, MWD and OH value. It shows good agreement between the predicted and actual experimental values as evidenced by the distribution of approximately equal scatter points above and below the surface. The drop-lines drawn from the experimental data points to the 3D surface represent the deviation from the predicted RSM. Longer lines indicate larger deviations.

Since the ANOVA analysis for response of M_n and OH value revealed an AB interaction as part of the model term hierarchy, interaction graphs were plotted as shown in Figure 4.25.

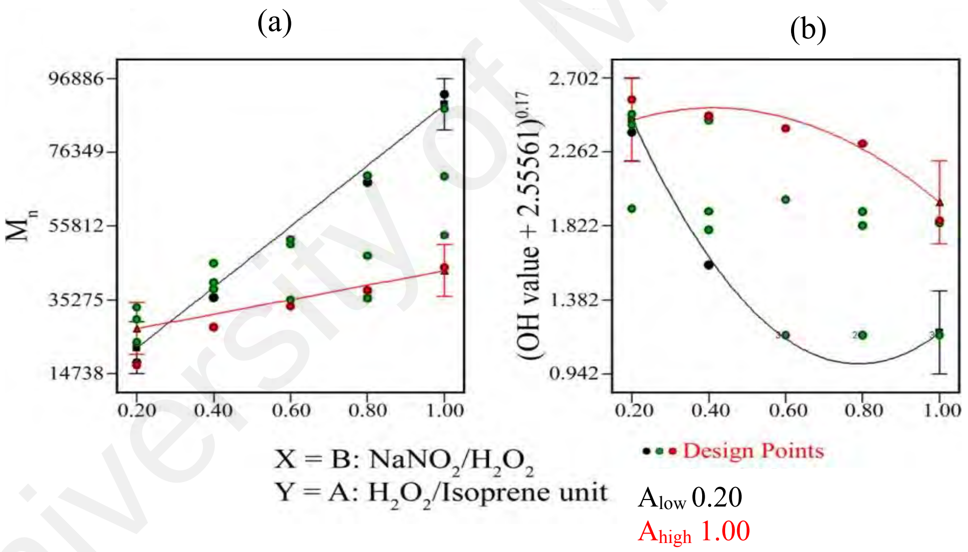


Figure 4.25: Interaction graphs for response of (a) M_n (b) (hydroxyl value + 2.55561)$^{0.17}$

They appear with two non-parallel lines, visually indicating that the effect of one factor depends on the level of the other. High H_2O_2 feed ratio leads to lower M_n and higher OH value. In general, the strongest contribution to the synthesized properties of FLNR can be attributed to the $NaNO_2$ feed ratio into the system. The significance of the AB term shows that the $NaNO_2$ species interacts synergistically with the H_2O_2 species at low levels of $NaNO_2$ but offensively at high levels of $NaNO_2$. A high amount of $NaNO_2$ does not promote formation of low M_n FLNR. It also suppresses OH formation. Nevertheless, a minimal amount of $NaNO_2$ feed ratio (B=0.20) is necessary to achieve the objectives of this work which is to produce FLNR of low M_n, low MWD and high OH value. In fact, even at the lowest H_2O_2 feed ratio (A=0.20), the predicted response is a M_n of 21,935 g/mole and an OH value of 194.42 which is acceptably near to the experimental objectives. Also of notable interest is the case when A=1.0, it appears that the optimum response for OH value is around B=0.4 instead of B=0.2. All of these observations corroborate with the ANOVA analysis of the models earlier where the ranking contribution of coefficient terms weighted heavily towards the B factor.

4.8 Multi response optimization

Design-Expert software's numerical optimization is expressed by the terms of maximize, minimize or target based on a single response, a single response with subject to upper and/or lower boundaries on other responses and combinations of two or more responses. The program uses five possibilities for a "Goal" to construct desirability indices (d_i): i) is maximum, ii) is minimum, iii) is at target, iv) is in range and v) is = (factors only). The desirability range is determined from zero to one for any given response. A value of one represents the ideal case and zero indicates that one or more responses fall outside desirable limits. This software uses an optimization method developed by previous researchers as described by Myers and Montgomery (Montgomery, 1997).

The primary objective of this work is to determine the optimum processing parameter conditions that will meet all the goals using the empirical models that have been developed thus far. The goals are to minimize the response of M_n and MWD while maximizing OH value. The simultaneous optimization of the three responses was solved using Design Expert® Software Version 6.0.6 which follows a modified version of the procedure developed by (Derringer & Suich, 1980). The method involves transformation of each predicted response, y_i (i = 1, 2, …, n), to a dimensionless partial desirability function, d_i ($0 \leq d_i \leq 1$), where $d_i = 0$ represents completely undesirable response and $d_i = 1$ represents completely desirable or ideal response. If a response variable is to be maximized, d_i is defined by:

$$d_i = \begin{cases} 0, & y_i < y_{min} \\ \left(\frac{y_i - y_{min}}{y_{max} - y_{min}}\right)^{w_i}, & y_{min} \leq y_i \leq y_{max} \\ 1, & y_i \geq y_{max} \end{cases}$$

(equation 4.7)

If the response of interest is to be minimized, d_i is defined by:

$$d_i = \begin{cases} 1, & y_i < y_{min} \\ \left(\frac{y_{max} - y_i}{y_{max} - y_{min}}\right)^{w_i}, & y_{min} \leq y_i \leq y_{max} \\ 0, & y_i \geq y_{max} \end{cases}$$

(equation 4.8)

where y_{min} and y_{max} are, respectively, the lowest and the highest values obtained for the response y_i, and w_i is the user-specified exponential parameter or the weight factor that determines the shape (convex for $w_i < 1$ or concave for $w_i > 1$) of desirability function. When the weight $w_i = 1$, the desirability function increases linearly. Choosing $w_i > 1$ places more emphasis on being close to the target value, and choosing $0 < w_i < 1$ makes this less important. The partial desirability functions of each response are then combined into a single composite response, the global desirability function (D), defined as the geometric mean of the different d_i values:

$$D = \left(d_1^{I_1} \times d_2^{I_2} \times \ldots \times d_n^{I_n}\right)^{\frac{1}{\sum I_i}}$$

(equation 4.9)

where n is the number of responses, I_i is the relative importance assigned to each of the response i. The relative importance I_i is a comparative scale for weighting each of the resulting d_i in the overall desirability product and it varies from the least important (I_i = 1) to the most important (I_i = 5). A value of D different from zero implies that all responses are in a desirable range simultaneously and, consequently, for a value of D close to 1, the combination of the different criteria is globally optimum. It is noteworthy that the outcome of the overall desirability D depends on the w_i and I_i values that offers flexibility specified by the user based on technical, economical and other considerations.

Input parameters for the optimization procedure and the calculated results are given in Table 4.17 and Table 4.18. The range of upper and lower limits of the process factors of A (H_2O_2/isoprene unit) and B ($NaNO_2$/H_2O_2) and response output (M_n, MWD and OH value) in the experimental design were considered as explicit constraints in order to avoid extrapolation. Since the analyses discussed earlier for the response of M_n and OH value showed very good fit, they were given the highest importance levels I_i compared to MWD which had a much poorer fit. Table 4.17 shows several cases with different combination levels of weight factors given for the responses of M_n and OH value. When the weight factors of M_n and OH value are equal, the predicted conditions for the optimum response values show good balance with high desirability. However, when OH value is given higher consideration, this leads to a compromise of M_n value (further value from the goal) and vice versa. There is a drop in global desirability D when one of the responses has to be sacrificed from the optimization.

Table 4.17: Range of input parameters for the optimization procedure

		Goal	Lower Limit	Upper Limit	Importance I_i
Factor	A	is in range	0.2	1	3
	B	is in range	0.2	1	3
Respons	M_n	minimize	17063	92437	5
	MWD	minimize	1.452	1.794	1
	OH value	maximize	0	255.5614	5

Table 4.18: Weight parameter adjustments and predicted optimum value solutions

Weight factor w_i			Optimum Factors		Optimum Response			Global Desirability *D*
M_n	**MWD**	**OH value**	**A**	**B**	**M_n**	**MWD**	**OH value**	
1	1	1	1.00	0.24	18166	1.481	205.04	0.894
1	1	10	1.00	0.39	31201	1.506	228.77	0.765
10	1	1	0.20	0.20	21935	1.602	194.42	0.673

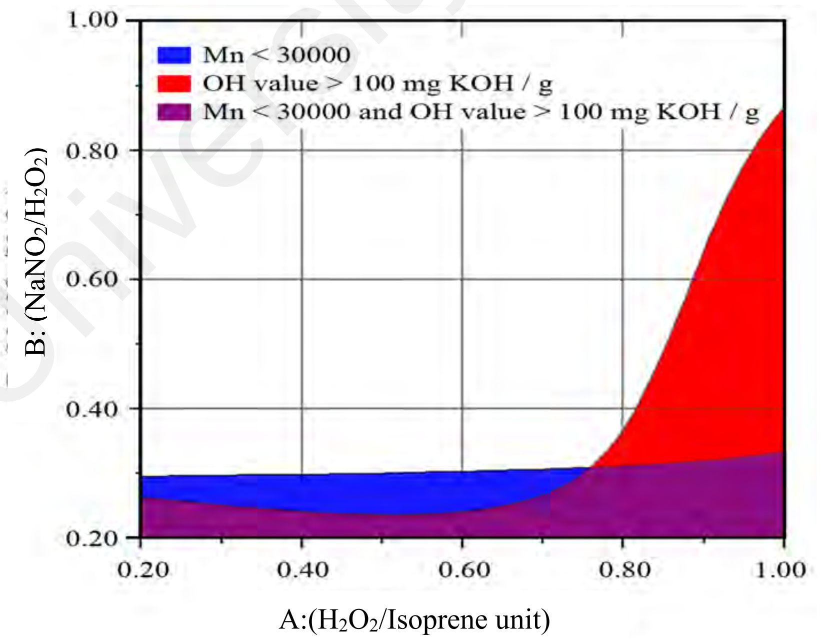


Figure 4.26: Process window for the preparation of semi-rigid polyurethane

Figure 4.26 shows the process windows for the preparation of semi-rigid PU. It was providing information about the limits of the chosen process parameters between which the acceptable responses.

4.9 Summary and proposed structure of functionalized liquid natural rubber

From FT-IR spectra and NMR results, comparison between high OH and low OH value analysis was done. Unlike sample preparation that produced FLNR with high OH values, those that possess low OH values (especially for mole ratio 0.8:0.2 ((H_2O_2/isoprene unit) : ($NaNO_2$/H_2O_2)) and 0.6:0.4 ((H_2O_2/isoprene unit):($NaNO_2$/H_2O_2)) also have other functional groups due to side reactions, as indicated in their spectra in Figure 4.27.

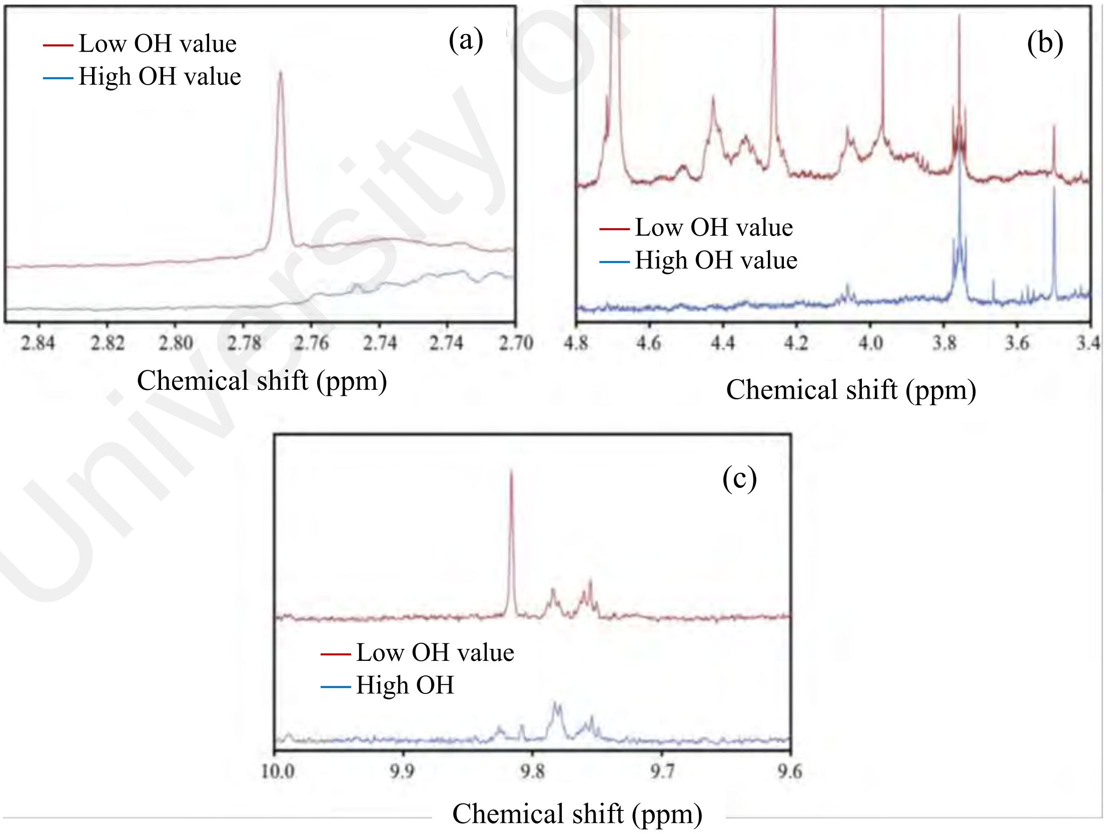


Figure 4.27: Comparison of proton Nuclear Magnetic Resonance spectrum at high and low hydroxyl value enlarged in the range of (a) 2.70–2.85 ppm (b) 3.4–4.8 ppm (c) 9.6–10.0 ppm

The incomplete ring-opening reaction during *in situ* process of depolymerization and hydroxylation may have caused the formation of epoxy groups, most notably with the appearance of a peak at 2.77 ppm attributed to (C-H) of the epoxy ring. Additional peaks in the range of 3.8–4.8 ppm is attributed to the formation of furan groups.

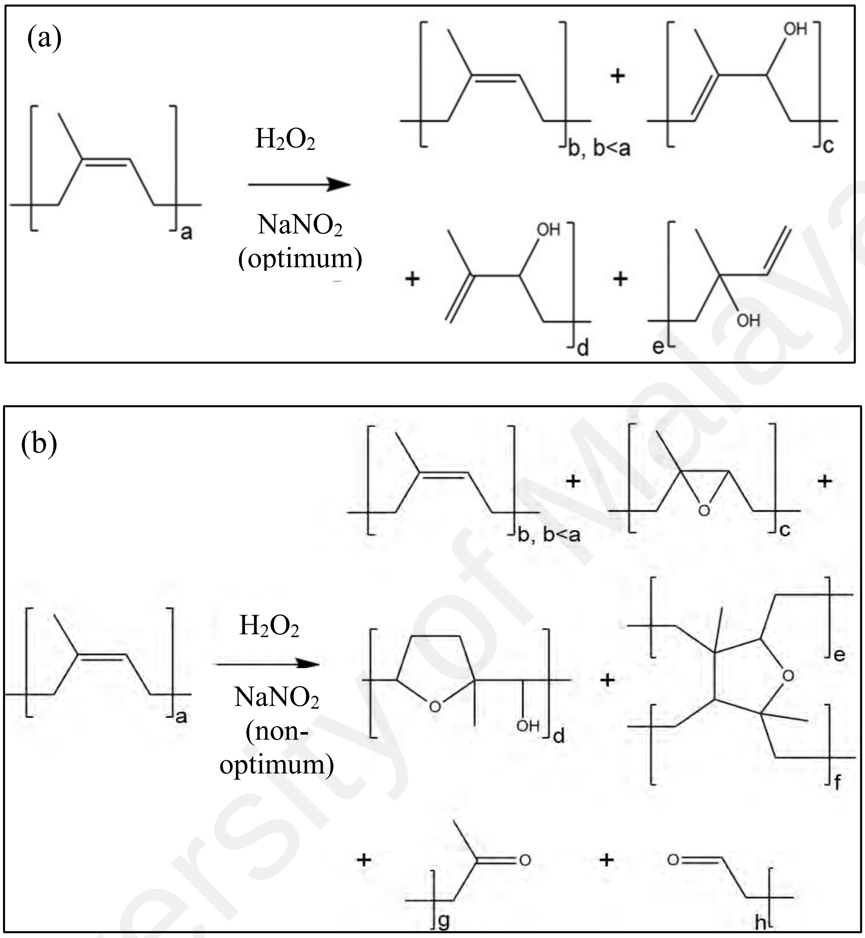


Figure 4.28: Microstructures formed at (a) optimum levels of sodium nitrite and (b) non-optimum levels of sodium nitrite

Furthermore, there was poor suppression of the end group aldehyde proton at 9.82 ppm which suggests that hydroxyl functionalization did not take place efficiently for the FLNR preparation methods which yielded low OH values. The reason for the behavior observed in the developed models thus far is described as follows: higher H_2O_2 leads to increase rate of epoxidation and chain scission, but when $NaNO_2$ is present in the optimum amounts, it will assist significantly in the simultaneous chain scission and/or hydroxylation of the epoxides (Figure 4.28(a)). However, in the presence of excessive levels of $NaNO_2$, the efficiency at which this process occurs begins to drop, which results in the yield of the OH incorporation onto the polymer chains to decrease. The abundance of the intermediary epoxide groups due to high H_2O_2 allows the excess $NaNO_2$ to produce other unfavorable side reactions instead of hydroxylation only (Figure 4.28(b)).

One such example is the cyclization reaction that forms furan groups. This intramolecular reaction leads to a drop-in hydroxylation but an increased presence of furan groups. Furthermore, during the cyclization process, crosslinking of the polymer can occur by interchain reactions involving both epoxidized units and polyisoprene units which lead to higher observed M_n values.

4.10 Optimization confirmation

FLNR with OH functionality was successfully synthesized. Relationship between processing factor for feed ratio of H_2O_2/isoprene unit and $NaNO_2/H_2O_2$ that influences the number average molecular weight M_n, molecular weight distribution MWD and OH value of FLNR have been developed using RSM. The polynomial models to predict M_n, MWD and OH value is 2FI, linear and reduced cubic, respectively. Table 4.19 shows the summary of evaluation and ANOVA response surface models for M_n, MWD and OH value.

Table 4.19: Evaluation and analysis of variance summary of response surface models

Summary	**Responses**		
	M_n	**MWD**	**OH value**
ANOVA model	2FI	Linear	Reduced cubic
Prob>F	< 0.0001	0.0053	< 0.0001
Contribution ranking of the terms to the system	B>A>AB	B>A	$B>A>AB^2>AB>B^2>A^2$
S/N ratio	20.763	8.455	13.284
R^2	0.8488	0.3787	0.8714

Although $NaNO_2$ serves to mitigate runaway or side reactions that could occur due to the nature of H_2O_2, these models suggest that only small amounts of $NaNO_2$ is necessary to achieve the optimum response properties for FLNR. The models also indicate that there is an interaction between $NaNO_2$ with H_2O_2 species in the reaction that influences the resulting M_n and OH value. Multi response optimization done using Derringer's desirability function predicted optimum responses for M_n was around 30,000 g/mol, MWD between 1.48 to 1.61 and OH value in the range of 194 to 229 mg KOH/g. These properties of FLNR will be useful for future application as a precursor for the preparation of semi-rigid PU.

Based on optimization confirmation, the selected parameters for semi-rigid PU synthesis purpose were itemized in Table 4.20 with the percentage error for experimental validation of the developed models for the responses with optimal parameter. The observed responses have been done due to the repeating experimental work based on optimal parameter of mole ratios.

Table 4.20: Predicted and observed values of optimal responses of functionalized liquid natural rubber

Factors		**Predicted Responses**			**Observed Responses**					
A^a	B^b	M_n	MWD	OH value	M_n	Error (%)	MWD	Error (%)	OH value	Error (%)
1.0	0.24	18166	1.481	205.04	20086	9.56	1.531	3.31	204.54	0.24
1.0	0.39	31201	1.506	228.77	28731	7.92	1.542	2.25	231.39	1.15
0.2	0.2	21935	1.602	194.42	17700	7.43	1.553	3.25	195.92	0.77

Note: a = mole ratio of H_2O_2/Isoprene unit; b= mole ratio of $NaNO_2/H_2O_2$

From the analysis in Table 4.20, it can be observed that the error calculated between predicted and observed responses is small. As the basic knowledge, the formulation of semi-rigid PU contains OH value is between 100-300 mg KOH/g with molecular weight is less than 30000 g/mol. The predicted and observed responses shows the parameters are in boundary limits. Observably these phenomena confirm an excellent reproducibility of the experiment conclusion of FLNR as precursor for semi-rigid PU formation. Therefore, from this RSM optimization process, any parameter of experimental work can be designed, analyzed and predicted according to the target or aim of the main objective study. The designated work can be done straight forward or reversible order, but the output responses must be valuable, available and predictable.

CHAPTER 5: SEMI-RIGID POLYURETHANE FILM

5.1 Formulation of semi-rigid polyurethane films

The formulation of semi-rigid PU composition was according to optimization parameters obtain by RSM (Section 4.10). From the result of the multi responses of optimization, the desirable optimum point for mole ratio was selected at 1.0 mole/mole for H_2O_2/isoprene unit and 0.24 mol/mol for $NaNO_2/H_2O_2$. According to the confirmation on prediction and observation, it was considered that all three parameters [(H_2O_2/isoprene unit):($NaNO_2/H_2O_2$)= 0.2:0.2, 1.0:0.24 and 1.0:0.39)] were acceptable and thus proposed in the formulation of semi-rigid PU film. The results express that the limit set of responses of M_n to be less than 30,000 g/mol and OH value to be between 100–300 mg KOH/g (equivalent weight between 180-570) (Cenens & Hernandez, 1999; Dirckx et al., 1999).

In semi-rigid PU synthesis, the effect of preparation method, rubber polyol length and [NCO]/[OH] ratio that relate to the interactions of soft and hard segment will be investigated. The criteria of each FLNR as precursor and semi-rigid PU samples prepared are listed in Table 5.1. According to the literature, the criteria of semi-rigid PU preparation is to use [NCO]/[OH] ratio between 0.6 and 1.1 (Heiss, 1978). Thus, the selected range of [NCO]/[OH] ratio in this study was between 0.6 and 1.0. Based on the preliminary works that showed the ratio below 0.6 gave very flexible or soft appearance, while the ratio exceeded 1.1 has a rigid appearance.

Table 5.1: Criteria of functionalized liquid natural rubber as polyol precursor in semi-rigid polyurethane films synthesis

Precursor code[a]	Ratio[b] (mol ratio/ mol ratio)	M_n (g/mol)	OH value (mg KOH/g)	PU code	[NCO]/[OH] ratio
FLNR-20000	1.0/0.24	20,000	204.5	PU1T2	0.72
FLNR-20000	1.0/0.24	20,000	204.5	PU2T2	0.78
FLNR-20000	1.0/0.24	20,000	204.5	PU3T2	0.92
FLNR-20000	1.0/0.24	20,000	204.5	PU4T2	0.84
FLNR-28700	1.0/0.39	28,700	231.4	PU5T3	0.90
FLNR-28700	1.0/0.39	28,700	231.4	PU6T3	0.89
FLNR-17700	0.2/0.2	17,700	195.9	PU7T1	0.6
FLNR-17700	0.2/0.2	17,700	195.9	PU8T1	0.8
FLNR-17700	0.2/0.2	17,700	195.9	PU9T1	1.0
FLNR-20000	1.0/0.24	20,000	204.5	PU10T2	0.6
FLNR-20000	1.0/0.24	20,000	204.5	PU11T2	0.8
FLNR-20000	1.0/0.24	20,000	204.5	PU12T2	1.0
FLNR-28700	1.0/0.39	28,700	231.4	PU13T3	0.6
FLNR-28700	1.0/0.39	28,700	231.4	PU14T3	0.8
FLNR-28700	1.0/0.39	28,700	231.4	PU15T3	1.0

Note: a = polyol (FLNR) as semi-rigid PU precursor, b = FLNR, ratio (H_2O_2/isoprene unit)/ratio ($NaNO_2$/H_2O_2)

The elastomeric properties of PU depend on the variation of soft segment (rubber polyol) and hard segment (isocyanate with/without chain extender) contents. Rubber polyol as soft segment typically has low molecular weight with a low glass transition temperature (T_g). The use of rubber based material is a good alternative because the T_g is low and the length of this type of polyol is variable according to the molecular weight itself. The hard segment usually has high T_g linked with a low molecular weight chain extender. PUs synthesized with chain extender, 1,4-butadiene (BDO) that consists of low molecular weight diols produces the additional urethane segments. The properties are supposed to be an assortment from very brittle and hard materials to partly soft, very soft or likely tacky appearance.

In this work, semi-rigid PUs were first prepared by two different methods; the *one-shot* method (simultaneous reaction method) and the *two-shot* method (pre-polymer method) to identify the differences between both methods in the semi-rigid PU synthesis. The identification is needed to determine which method is processable and produces better film products. The reaction time of synthesis also plays the main role in the production of a better film appearance while the chain length and OH values of the polyol (FLNR), chain extender (BDO) and catalyst ($Sn(Oct)_2$) complements further to achieve the good appearance of these film samples.

Fundamentally, the *one-shot* method will produce semi-rigid PU product when the diisocyanate and polyol are mixed and allowed to react together. In the *one-shot* method, all the monomers are fed into the reactor at the same time, and oligomeric diol (polyol) and short chain diol (chain extender) compete to react with the diisocyanates. The curing of material from *one-shot* method normally produces an elastomer. To achieve better mixing of soft segment and hard segments, *two-shot* method was performed. This synthetic procedure was modified by preparing the diisocyanate capped rubber polyol (FLNR) in the first step followed by *in situ* chain extension with BDO in the consecutive step to obtain the final polymer. The first step involves the reaction of polyol and diisocyanate to form an intermediate polymer called "prepolymer". It is then converted into final high molecular weight polymer by further reaction with diol and chain extender as a second step. This technique will produce the PU materials that is similar to multiblock copolymer.

Thereafter, the more preferable and processable method was selected in modifying the formulation that can be used for biomaterials purposes. The modification in the formulation of PU was based on the different length of rubber polyol (based on molecular weight) and [NCO]/[OH] ratio. The percentage of hard and soft segments in the semi-rigid PU film plays as a main role in the basic modification formulation. The same polyol, diisocyanates and chain extender contribute in this formula but some modifications on their amounts were made. The use of catalyst inside the semi-rigid PU reaction can also affect the interaction between isocyanate and OH bonding. From preliminary work that had been done, semi-rigid PU with the higher content of catalyst (more than 4.5%) and higher BDO (more than 7 pbw) could not form good films instead produce brittle film samples which consist a high excess of NCO content (Appendix C1).

5.2 Semi-rigid polyurethane by *one-shot* and *two-shot* methods

The formulation of the semi-rigid PU synthesis is shown in Table 5.2 with chain extender (BDO) percentage between 0 - 6.5 pbw and [NCO]/[OH] ratio between 0.7 and 0.95, approximately by *one-shot* and *two-shot*.

Table 5.2: Formulation of different method of semi-rigid polyurethane films

Sample code	**Method**	**[NCO]/ [OH] ratio**	**BDO (pbw)**[a]	**MDI:BDO**[b]	**Polyol/OH**[c]	**Catalyst**[d] **(%)**	**Hard segment**[e] **(%)**	**Soft segment**[f] **(%)**
PU1T2	*One-shot*	0.72	0	1:0	1.0	3.84	10.98	85.18
PU2T2	*Two-shot*	0.78	1.25	1:0.4	0.96	3.84	16.05	80.11
PU3T2	*One-shot*	0.92	6.54	1:0.7	0.83	3.18	35.45	61.37
PU4T2	*Two-shot*	0.84	2.33	1.:0.2	0.93	3.58	29.75	66.67
PU5T3	*One-shot*	0.91	6.22	1:0.3	0.85	3.65	34.52	61.83
PU6T3	*Two-shot*	0.89	4.96	1:0.2	0.87	2.94	33.77	63.29

Note: a = part by weight (pbw) based on pbw of polyol; M_n=1000 g/mol and OH value=660 mg KOH/g
b= based on mmole ratio (MDI:BDO)
c = based on equivalent ratio (polyol/(polyol+BDO)
d = % of catalyst= [wt. of (catalyst)/ wt. of (MDI+BDO + polyol + catalyst)] × 100
e= % of hard segment=[wt. of (MDI+BDO)/ wt. of (MDI+BDO + polyol + catalyst)] × 100
f = 100 - [(% of hard segment) + (% of catalyst)]

The length and distribution of hard segments can be affected by the polymerization methods. The lengths and chemical structures of hard and soft segments are important structural features which determine the properties of semi-rigid PU. Sample PU1T2 has no BDO and sample PU2T2 has lowest BDO as a chain extender acts as control samples for each method. The value of hard segment and soft segments of both samples are between 10.9 - 16.1% and 80 - 85.2 %. As seen in the Table 5.2, the hard segment of sample PU3T2 is higher than sample PU4T2 because of the BDO content in sample PU3T2 is higher by more than 4% compared to sample PU4T2 formulation. Thus, BDO as chain extender contributes more hard segments in elastomeric material.

Furthermore, samples PU5T3 and PU6T3 were compared with samples PU3T2 and PU4T2 to see the different character of PU formed based on different soft segment lengths, which was based on molecular weight and OH value of polyol. Samples PU5T3 and PU6T3 produced from FLNR with high molecular weight (28,700 g/mol) also fulfilled the criteria of semi-rigid film samples but exhibited hyperbranched PU with internal flexibility (Dirckx et al., 1999). Based on the Table 5.2, the hard segment of sample PU5T3 is also higher than sample PU6T3 because of the high BDO (more than 2%) involvement in the samples. The different values of hard segments obtained in this synthesis show that the BDO (chain extender) has effect on the elastomeric material based PU formed.

5.2.1 Molecular weights and physical appearance

The molecular weights (M_n and MWD) and physical appearances of semi-rigid PU obtained are listed at Table 5.3. The M_n of the *two-shot* method are higher compared to the *one-shot* method and the MWD are lower. Generally, all the obtained materials are yellowish, soft and transparent. When the [NCO]/[OH] ratio is nearly or equal to 1.0, the materials became less soft and opaque due to the increase in hard segments content and microphase segregation, respectively.

Table 5.3: Molecular weights of semi-rigid polyurethane films based on different synthesis method

Sample code	Method	[NCO]/[OH] ratio	M_n (g/mol)	MWD	Appearance
PU1T2	*One-shot*	0.72	60,808	1.43	yellowish; soft; transparent
PU2T2	*Two-shot*	0.78	61,840	1.66	yellowish; soft; transparent
PU3T2	*One- shot*	0.92	-	-	yellowish; partly soft; transparent
PU4T2	*Two-shot*	0.84	88,233	2.01	yellowish; partly soft; transparent
PU5T3	*One- shot*	0.91	-	-	yellowish; partly soft; opaque
PU6T3	*Two-shot*	0.89	-	-	yellowish; partly soft; opaque

Samples PU1T2 and PU2T2 give a low MWD compared to sample PU4T2 because of an absence and small amount of BDO in the formulation. The appearance of both samples (PU1T2 and PU2T2) is very soft and high flexible compared to sample PU4T2. The molecular weight of PU4T2 sample is higher because of the existence of chain extender in the formulation. The rest of samples, PU3T2, PU5T3 and PU6T3 do not give the proper result because of the percentage of BDO in formulation is higher and hindering the semi-rigid PU samples to dissolve in THF solvent.

5.2.2 Fourier Transform Infrared

Figure 5.1 (a) and (b) show FT-IR spectra of FLNR, semi-rigid PU and diisocyanate (MDI) containing the characteristic peaks of the well-known structural features of NR for FLNR and semi-rigid PU itself.

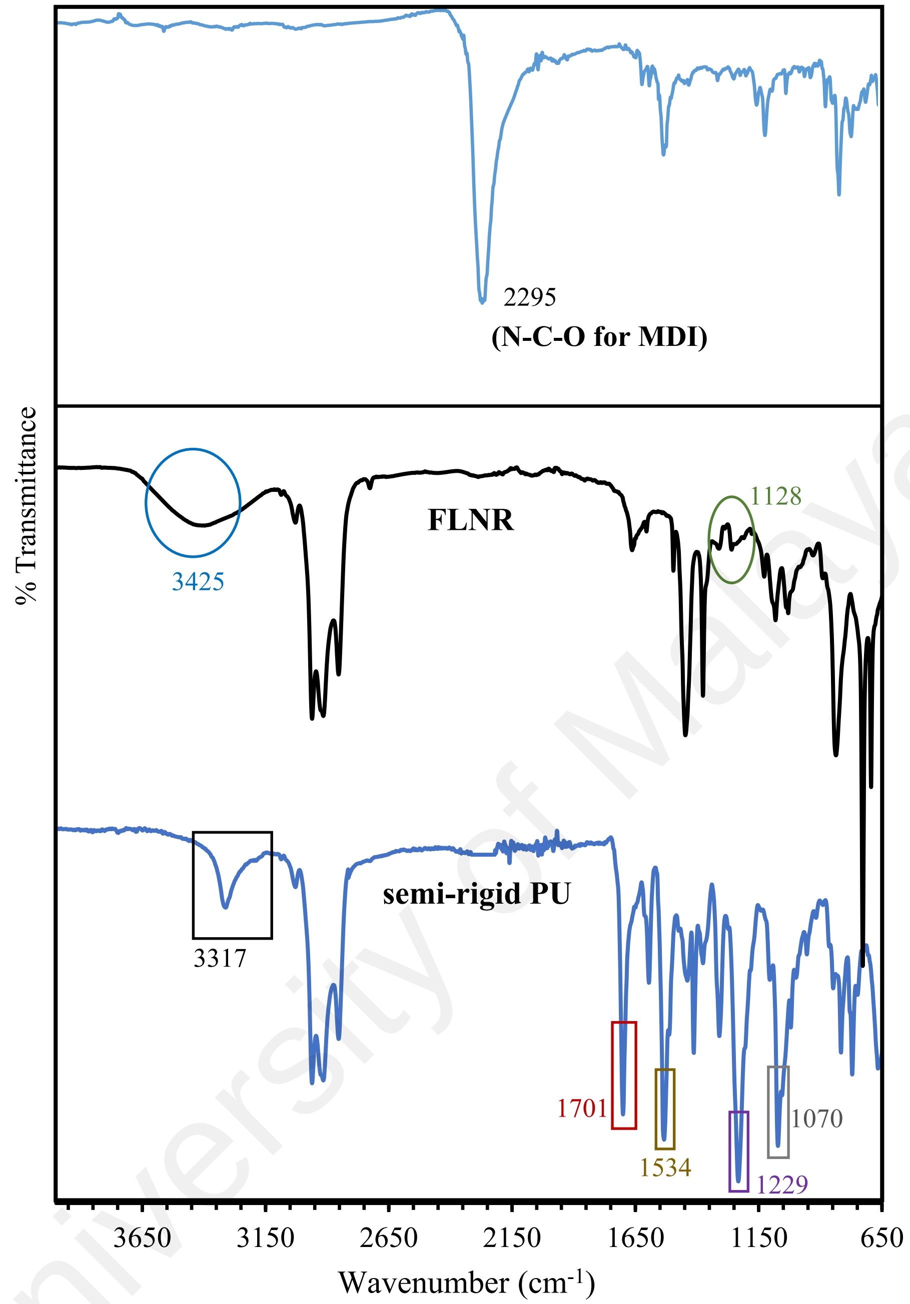


Figure 5.1: Fourier Transform Infrared spectra of (a) MDI and (b) functionalized liquid natural rubber and semi-rigid polyurethane films

The main difference that sets FLNR apart from NR is the appearance of a new peak at 3425 cm^{-1} belonging to the hydroxyl group (Figure 5.1 (b)). This hydroxyl moiety is what makes FLNR useful for intermediary applications as it can react readily with other reactive groups (Brown et al., 1988; Cooper, 1980; Dahlan et al., 1999). In this study, the FLNR was made to react with diisocyanate to produce semi-rigid PU. The FT-IR spectrum of semi-rigid PU shows the existence of absorption at 3317 cm^{-1} corresponding to N-H stretching vibration of urethane function. N-H group is a proton donor which can form hydrogen bonds and existence of hydrogen bonds is a very important feature and gives effects on the properties of the semi-rigid PU being formed.

From Figure 5.1(a), the strong absorption peak at 1701 cm^{-1} corresponding to C=O stretching (Kébir et al., 2005a) is assigned to the non-hydrogen bonded C=O . The peak at 1534 cm^{-1} is ascribed as combination of C-N stretching and N-H out of plane bending. Meanwhile, the peaks at 1229 cm^{-1} and 1070 cm^{-1} are assigned to C-O and C-O-C stretching vibrations from urethane carbonyl. The disappearance peak at 2295 cm^{-1} clearly shows complete reaction in forming the semi-rigid PU. This peak belongs to NCO (isocyanate group) which is the main structure of MDI (Figure 5.1 (a)). Previous study had reported that C-O stretching at 1062 and 1220 cm^{-1} and no NCO absorption at 2270 cm^{-1} were observed showing that the reaction was complete (Khaokong, 2008). All FT-IR assignments are listed in Table 5.4.

Comparison made between samples with and without BDO is shown in Figure 5.2. Band at 3317 cm^{-1} is attributed to N-H weak bond for sample without BDO compared to those with BDO system. Similarly, peaks at 1701 cm^{-1} and 1229 cm^{-1} assigned for C=O and C-O are observed. These results clearly show that the chain extender, BDO, is able to enhance the semi-rigid PU formation. The chain extender such as BDO will strengthen the hard phase domain in the semi-rigid PU.

Table 5.4: Fourier Transform Infrared assignment of functionalized liquid natural rubber, MDI and semi-rigid polyurethane films

ν (cm^{-1})	**Assignment**	**Sample**
3317	NH stretching	semi-rigid PU
3035	=CH stretching from NR and end group $–CH_2$-$C(CH_3)$=CH-CH=CH_2	FLNR
2961	Assymmetric stretching of –CH from $–CH_3$	FLNR, semi-rigid PU
2926	Assymmetric stretching –CH from $–CH_2–$	FLNR, semi-rigid PU
2855	Asymmetric stretching –CH from $–CH_2–$ and $–CH_3$	FLNR, semi-rigid PU
2295	NCO stretching (isocyanate asymmetric stretching)	MDI
1701	C=O stretching (non-H-bonded urethane carbonyl)	semi-rigid PU
1664	C=C stretching from isoprene unit and end group $–CH_2$-$C(CH_3)$ =CH-CH=CH_2	FLNR, semi-rigid PU
1534	Combination of C-N stretching and N-H out of plane bending	Semi-rigid PU
1449	Symmetric bending of C-H from -CH_2-	FLNR, semi-rigid PU
1376	Asymmetric bending of C-H from CH_3-	FLNR, semi-rigid PU
1229	Stretching of C-O from urethane carbonyl	semi-rigid PU
1128	Stretching of C-O from $–R_3C(OH)$-	FLNR
1070	Stretching of C-O-C from carbonyl urethane	semi-rigid PU
1037	Deformation of CH_3- and -CH_2-	FLNR, semi-rigid PU
837	Out of plane deformation, =CH from CH_2-$C(CH_3)$=CH-CH_2	FLNR, semi-rigid PU

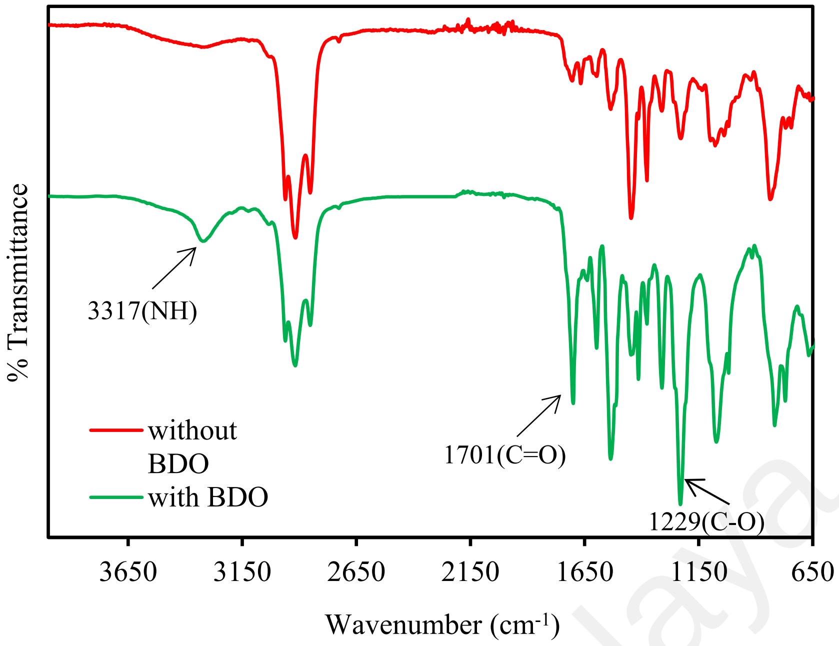


Figure 5.2: Fourier Transform Infrared spectra of semi-rigid polyurethane film with and without 1, 4 butanediol (BDO) as chain extender

The reaction times for *one-shot* and *two-shot* methods were conducted initially by trial and error based on previous studies (Burel et al., 2005b). Figure 5.3 shows the appearance of peak at 3317 cm^{-1} (NH) and disappearance of NCO peak at 2295 cm^{-1} indicating that the reaction of semi-rigid PU was completed. This reaction time for *one-shot* method was proposed at 6 h and 5 h for *two-shot* method. Comparison between *one-shot* method (6 h reaction) and *two-shot* method (5 h reaction) for semi-rigid PU synthesis were made by FT-IR. The FT-IR spectra for comparison of each band (3317 and 2295 cm^{-1}) were also shown in Appendix C2 and Appendix C3.

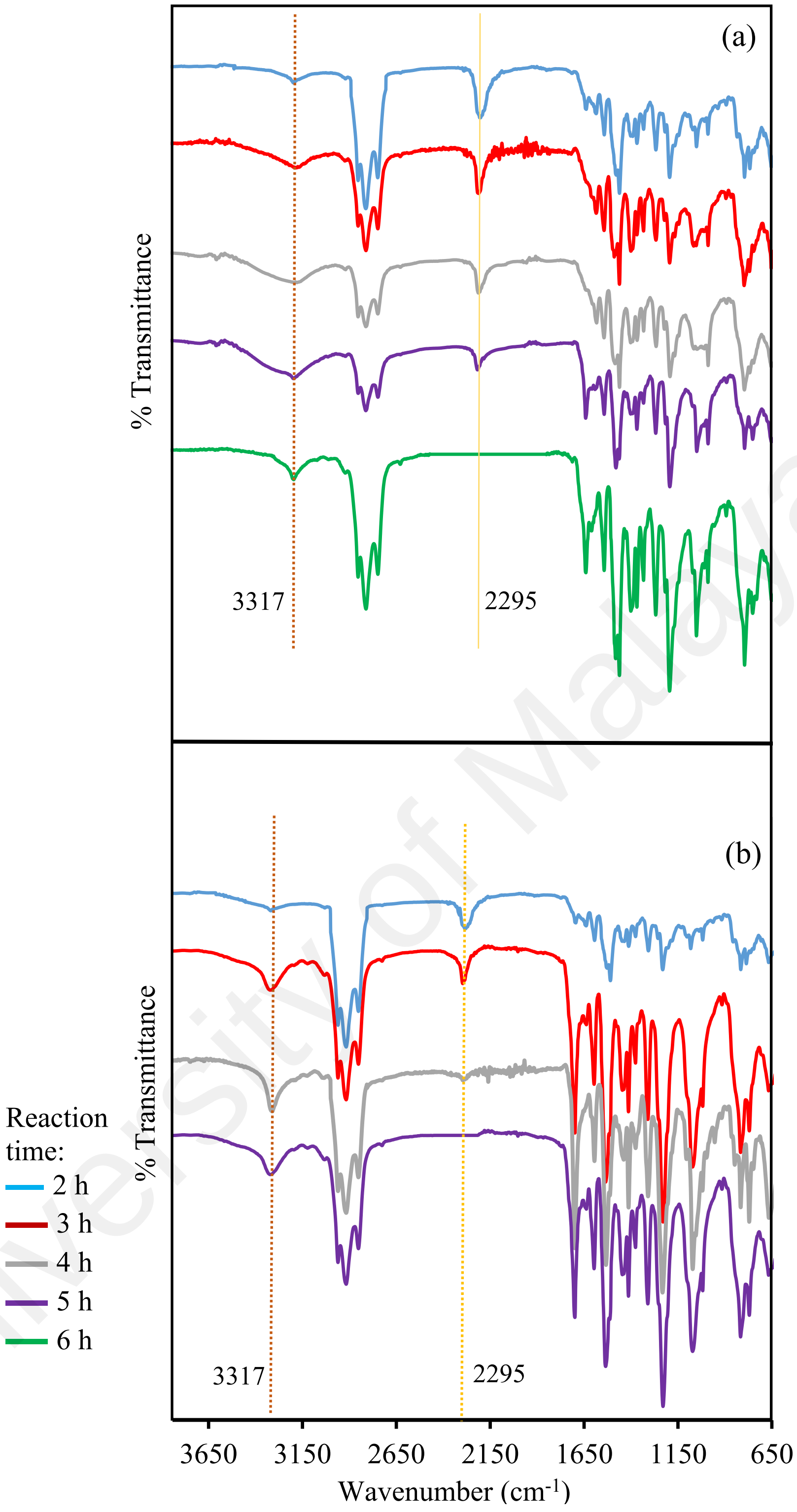


Figure 5.3: Fourier Transform Infrared spectra of (a) *one-shot* method and (b) two-shot method of semi-rigid polyurethane film at different reaction times

Since at any stage of the reaction time the concentration of CH_2 moieties in the reaction mixture remained generally the same, all spectra were normalized to this peak at 2920 cm^{-1}. The histograms in Figure 5.4 and 5.5 show the comparisons for relative percentage of peak intensities, I_r at 2295 and 3317 cm^{-1} corresponding to consumption of MDI and formation of –NH– urethane linkages, respectively for the *one-shot* and *two-shot* methods. It can be seen that as the reaction was carried forward, there was a noticeable decrease of the peak intensity at 2295 cm^{-1} which belonged to the –N-C=O of the isocyanate group in MDI.

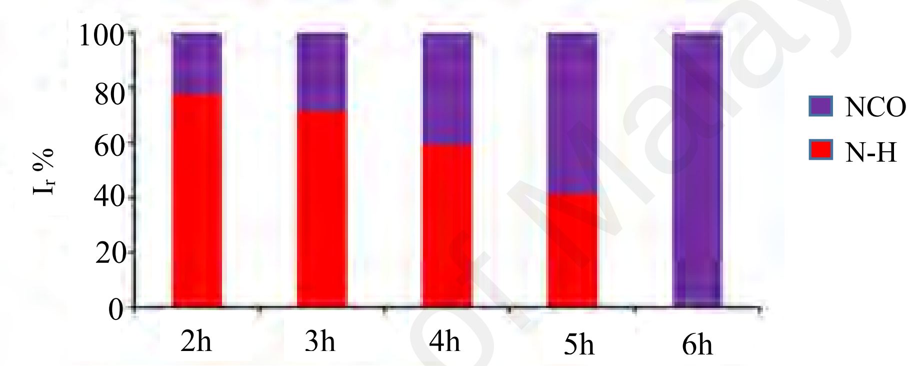


Figure 5.4: Relative percentage area of N-H band at 3317 cm^{-1} and NCO band at 2295 cm^{-1} in Fourier Transform Infrared spectra of *one-shot* method

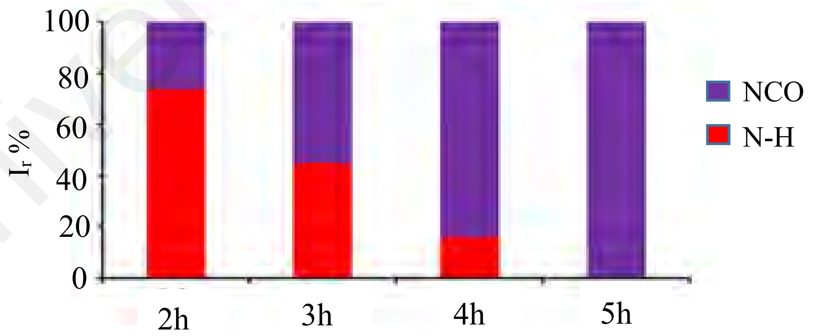


Figure 5.5: Relative percentage area of N-H band at 3317 cm^{-1} and NCO band at 2295 cm^{-1} in Fourier Transform Infrared spectra of *two-shot* method

It can be clearly seen that the *two-shot* method offers better formation of the semi-rigid PU by the fifth hour of reaction as opposed to the *one-shot* method. Another reason for the superiority of the *two-shot* method is that the reaction mixture in this procedure allows the FLNR and MDI to react first therefore imparting better solubility compatibility with the BDO that was added later on. In the case of the *one-shot* method, all reactants were present simultaneously, but the inhomogeneity caused by the mixture may have hindered efficient access to the reaction sites.

The curing reaction for the *one-shot* method worked very slowly at ambient temperature and the polymers were only partly cured upon prolonged storage and exposure to air. Thus, to overcome this problem, the vacuum dried curing at temperature exceeding 60°C, and about 72 h or 3 days were used in this work to ensure better film formation.

5.2.3 Solubility behaviour

The primary idea to evaluate the performance of semi-rigid PU film samples is by the solubility behaviour. The interaction and solvent transportation behavior of polymer could be determined through the solubility test. Appropriate solvents had been selected to observe the ability of semi-rigid PU films towards solvent resistant. Following this, the way to modify the formulation of PU especially in biomaterials can be approached. The evaluation of solubility behavior of these PU films was conducted in different organic solvents to observe the relation between solvent and semi-rigid PU films. The five different types of organic solvents were chloroform, THF, toluene, DMF and DMSO. These different solvents were selected to see the effect of polarity on the different types of PU films based on the different methods of preparation. The solubility test was conducted by immersing the semi-rigid PU samples at room temperature for 4 h and with agitation also for 4 h. If there were no changes in the weight loss, the test was continued by heating at 80ºC for 4 h with agitation.

Table 5.5: Solubility behavior of semi-rigid polyurethane films in organic solvents

Sample code	Solvents									
	toluene		chloroform		THF		DMF		DMSO	
	Solubility	Solubility fraction (%)	Solubility	Solubility fraction (%)	Solubility	Solubility fraction (%)	Solubility	Solubility fraction (%)	Solubility	Solubility fraction (%)
PU1T2*	++	100^{a}	±	99.4^{b}	++	100^{a}	±	88.30^{b}	–	16.9^{b}
PU2T2**	++	100^{a}	±	99.5^{b}	++	100^{a}	±	88.7^{b}	–	15.6^{b}
PU3T2*	–	67.2^{b}	–	73.21^{b}	–	97.7^{b}	–	42.3^{b}	–	5.41^{b}
PU4T2**	++	100^{b}	±	98.81^{b}	++	100^{b}	±	91.6^{b}	±	$40.^{b}$
PU5T3*	±	$74.7\ ^{b}$	–	67.95^{b}	±	$96.1\ ^{b}$	–	7.2^{b}	–	3.4^{b}
PU6T3**	–	16.5^{b}	–	12.71^{b}	–	48.7^{b}	–	11.5^{b}	–	2.1^{b}

Note: ^{a}: room temperature, ^{b}: heating
++: soluble; – insoluble; ± partly soluble
* *one-shot* method, ** *two-shot* method

From Table 5.5, the semi-rigid PU samples without BDO (PU1T2) and lowest BDO (PU2T2) show good solubility compared to other semi-rigid PU samples. But the solubility affects mostly on the sample with BDO even though in small amount. For the sample with the chain extender, BDO; i.e. PU4T2, it shows the ability to be soluble completely in THF and toluene. It is also partly soluble in chloroform and DMF, but has low solubility in DMSO. Meanwhile, samples PU3T2 and PU5T3 are partially dissolved in THF but insoluble in chloroform and toluene. Both samples are not soluble in DMF and DMSO. In the case of *one-shot* method for these two film samples (PU3T2 and PU5T3), since the diisocyanate and macrodiol components are usually incompatible at lower temperatures, the reaction will take place at the phase interface and the stoichiometric balance could be changed. Incompatibility results in structural heterogeneity, change of the average hard segment length, segregation during processing and lower solubility in solvents (Cella, 1973; Prisacariu, 2011; Xu et al.,1983). Incompatibility has the same effect on the *two-shot* process too, but with a greater regularity.

From observation of samples PU3T2, PU4T2, PU5T3 and PU6T3, the chain extender influences the properties of the PU as the hard segments-soft segments relation. Previous study (Prisacariu, 2011) stated that properties of PU formed are dependent on the chain extender content in the PU synthesis. Chain extender could drive phase separation, ability to promote inter hard segment hydrogen bonding and the ability to complement or interfere with a regular hard segment. In addition, chain extenders are low molecular weight OH compounds that play a significant role in the morphology of any PU materials. For samples PU4T2 and PU6T3 which were synthesized by the *two-shot* method, the elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as crosslinks between the amorphous polyol soft segment domains. This phase separation occurs because the mainly non-polar low melting soft segments are incompatible with the polar, high melting hard segments. The soft segments, which are formed from high molecular weight polyols, are mobile and normally present in coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency.

The choice of chain extender also determines the better properties such as chemical resistance properties. Among chain extenders, 1,4-BDO has been found to be a suitable chain extender in PU elastomer that can phase separate well and forms well defined hard segment domains and is melt processable. Besides that, the chain extender can also be used to modify hard segment structure in the PU. Without the chain extender, the PU formed by directly reacting with diisocyanate and polyol generally has very poor physical properties and often does not exhibit microphase separation through DSC characterization (Prisacariu, 2011).

Sample PU6T3 (Table 5.5) shows slight solubility in almost all organic solvents. The organic solvents do not affect this sample and has mild solubility performance. Therefore, the solubility behavior depends on the polarity of the solvent and the hard and soft segments of PU. The insolubility of semi-rigid PU samples might be due to the existence of urethane linkages, the molecular weight and OH values of intermediate polyol and final molecular weight of polymer (semi-rigid PU). The PU6T3 has moderate chain extender but high molecular weight and also high OH value of polyol that contribute to the high length and functionalities of polyol. PU6T3 has similar behaviour as rigid PU as it is stable towards organic solvents. In addition, the higher content of hard segment in the formulation compared to the other semi-rigid PU films contributes towards this insoluble character.

The solubility parameters of each solvent are listed at Table 5.6. The solvents are grouped into non-polar and polar aprotic solvents. The polarity is given as the dielectric constant. The solubility parameters of these polar aprotic solvents such as DMSO and DMF are higher compared to THF and non-polar solvents (toluene and chloroform). In previous study, most polyester and polyether based PUs had excellent solubility in polar aprotic solvents, i.e. DMSO and DMF solvents (Yeganeh & Shamekhi, 2004). However, in this work solubility is only in THF especially for PU samples without chain extender (PU1T2 and PU2T2) and with low chain extender content (PU4T2). DMSO has no significant effect on solubility in almost all PU samples based on the lower percentage of soluble fraction. DMF also has similar trend with DMSO but only for samples PU5T3 and PU6T3 (Table 5.5).

Table 5.6: Solubility parameters and dielectric constants of solvents

Solvents	Polarity group	Solubility Parameter, δ		Dialectric constant
		$(MPa)^{1/2}$	**$(cal\ cm^{-3})^{1/2}$**	
Toluene	Non-polar	18.2	9.09	2.4
Chloroform	Non-polar	19.0	9.29	4.8
Tetrahydrofuran (THF)	Polar aprotic	19.4	9.48	7.5
Dimethylformamide (DMF)	Polar aprotic	24.8	12.14	38
Dimethyl sulfoxide (DMSO)	Polar aprotic	26.4	12.93	47

The isoprene unit structure has solubility parameter between 19.5 and 23.0 $(MPa)^{1/2}$ and density of approximately 0.93 - 0.97 g/cm^3 (Fried, 2003). The NR is soluble in non-polar solvent such as toluene and chloroform and probable in polar aprotic solvents such as THF because the range of solubility parameter and dielectric constant is close. Therefore, rubber materials replacing polyester or polyether (polar polymer) in the formation of semi-rigid PU make it greatly influenced by non-polar solvent and low polar aprotic solvent. Besides that, because of the differences in molecular weight and OH value of polyol as precursor, i.e. PU4T2 and PU5T3 samples (Table 5.1), the amount of soft phase leads to the changes in partial solubility and in the composition of the phases. Due to the incompatibility (different polarity and chemical nature) between hard segment and soft segment, phase separation occurs in most semi-rigid PU samples. The degree of phase separation depends on nature and size between hard segment and soft segment, type of the diisocyanate and polyol employed to produce the pre-polymers, the type of chain extender, and the molecular weight soft segment. It is also influenced by the hydrogen bond formation between the urethane linkages, by the manufacturing process, and reaction conditions (Bonart, 1968; Clough et al., 1968; Oertel & Abele, 1985; Petrovi'c et al., 2007).

Figure 5.6 shows the effect of chloroform, toluene, THF and DMF (based on the solubility parameters) on the percentage of soluble fraction (based on weight loss) of the semi-rigid PU samples. The low solubility parameters of the non-polar solvent (chloroform and toluene) highly affect the solubility of each semi-rigid PU samples. The BDO content and catalyst also contribute some effects on semi-rigid PU properties. The high BDO content, resulted in the low weight loss of films for *one-shot* and *two-shot* method corresponding to samples PU3T2, PU5T3 and PU6T3 in chloroform. Meanwhile, samples PU3T2 and PU5T3 with high BDO and high catalyst resulted in the low weight loss in toluene.

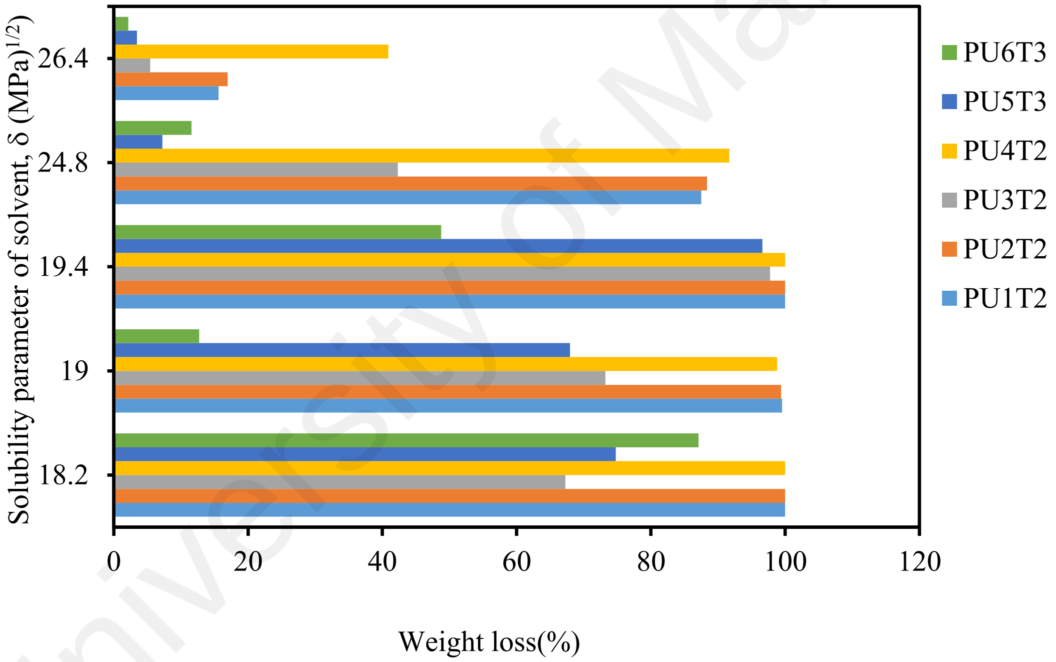


Figure 5.6: Percentage of soluble fraction of semi-rigid polyurethane films versus solubility parameter of the solvents (chloroform: 18.2, toluene: 19.0, THF: 19.4, DMF: 24.8, DMSO: 26.4 $(\text{MPa})^{1/2}$)

The effect of catalyst, as studied previously using the *one-shot* method, had reported that the use of $Sn(Oct)_2$ as catalyst to synthesize TPU based on polyisobutylene could not produce good appearance of film samples. The better film samples were synthesized by the *two-shot* method (Ojha et al., 2009). The catalyst is primarily used to promote crosslinking in the production of semi-rigid PU and also flexible and rigid PU. It is known that the *two-shot* method offers advantages over *one-shot* method in polymerizing incompatible monomers. The OH that attached at polyol to form the prepolymer in the first step of a *two-shot* polymerization changes the solubility character of the polyol. This enables one to prepare a more homogeneous polymer during chain extension in the second step because all the polyol OH are reacted with the diisocyanate in the first step.

Besides that, the catalyst has several advantages by providing high reaction rate, high conversion rate and high molecular weight even under rather mild polymerization conditions (Schwach et al., 1997). However, consideration must be taken on the environmental health as high content of tin catalyst will be toxic. Thus, to overcome this situation, modification on formulation of semi-rigid PU is required to develop better film performance taking into account the environmental friendly aspect.

5.2.4 Hydrolytic stability

Based on Table 5.7 and Figure 5.7, generally water has no significant contribution to the degradation thus the percentage of weight loss obtained for all semi-rigid PU samples are zero. The film samples without and less chain extender (PU1T1 and PU2T2) are found to swell in water. In the case of samples PU1T2 and PU2T2, water is found to penetrate into PU matrix causing the increase in weight. Water is also found to penetrate into PU matrix for sample PU4T2 which has the chain extender, but the rate is low. This situation might be due to the low chain extender (BDO) content followed by the low hard segment as compared to the other samples, thus allowing the water to penetrate inside. Besides that, water has not penetrated into PU matrix for samples PU3T2, PU5T3 and

PU6T3 that have high BDO content. The high hard segment compared to other samples probably causes this situation.

Table 5.7: Absorption rates of semi-rigid polyurethane films in hydrolytic condition

Sample code	**Hard segment** (%)	**BDO (pbw)**	**Soft segment** (%)	**Absorption rate**					
				Water		**Ethanol**		**NaCl solution (1N)**	
				Swell (%)	**Weight loss** (%)	**Swell** (%)	**Weight loss** (%)	**Swell** (%)	**Weight loss** (%)
PU1T2*	10.98	0	85.18	61.29	0	0	11.25	0	2.89
PU2T2**	16.05	1.25	80.11	70.78	0	6.32	9.09	0	1.04
PU3T2*	35.45	6.54	61.37	0	0	1.68	4.13	0	0.71
PU4T2**	29.16	2.33	66.67	6.49	0	3.17	10.86	0	8.33
PU5T3*	34.52	6.22	61.83	0	0	0	6.78	4.23	0
PU6T3**	33.77	4.96	63.29	0	0	1.68	6.07	0	3.41

Note: * *one-shot* method, ** *two-shot* method

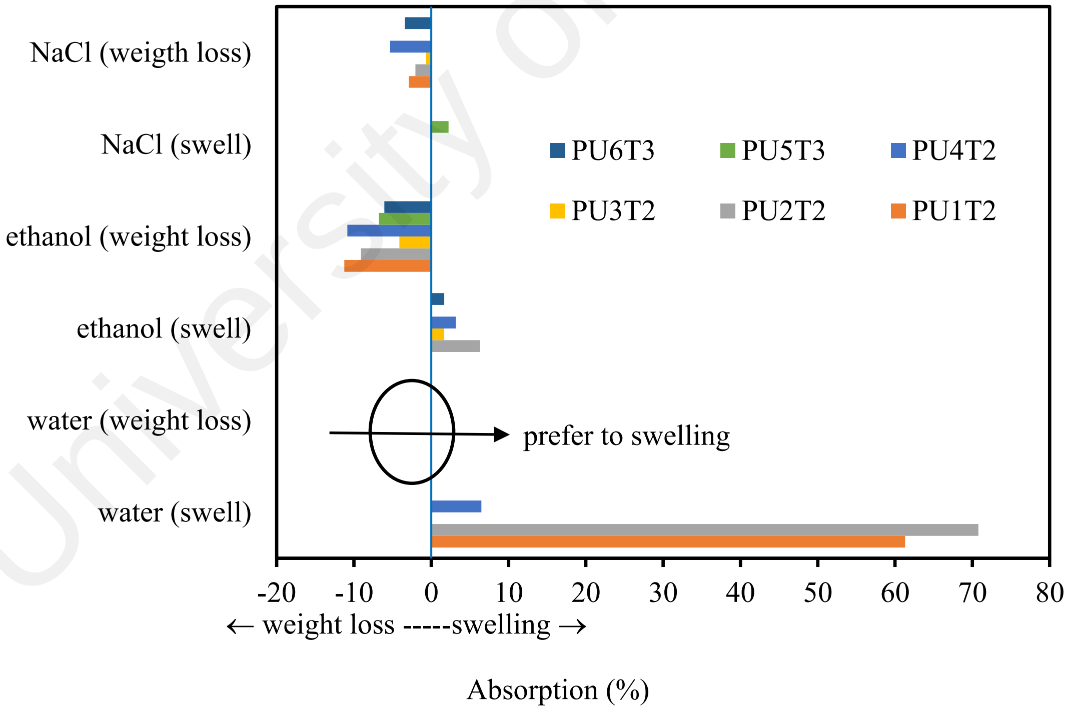
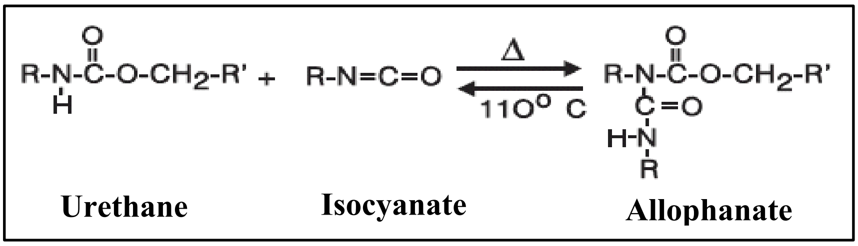


Figure 5.7: Absorption rates based on percentage of swelling and percentage weight loss of semi-rigid polyurethane film in hydrolytic condition

Ethanol has significant effect on the degradation and swelling in almost all of the film samples. Semi-rigid PUs prepared by the *one-shot* method is highly influenced by alcohol because hydrolytic attack is centered mainly on urethane group (Gopalakrishnan & Fernado, 2011). Ethanol degrades samples which do not contain chain extender i.e. sample PU1T2 based on the highest percentage of weight loss obtained. PU1T2 sample has no BDO which strengthens the hard phase domain in the semi-rigid PU. Meanwhile, for swelling effect, the increased weight in sample PU2T2 shows that ethanol has penetrated into PU matrix as it contains only a small amount of chain extender. For sample PU4T2 which has chain extender, the higher degradation effect by alcohol is because it has the lowest hard segment content compared to others (samples PU3T2, PU5T3 and PU6T3). The hydrolytic attack is much easier to destroy the weak linkages, i.e. N-H, C=O and C-O bonds of sample PU4T2.

As reported from the previous study (Gopalakrishnan & Fernado, 2011), the hydrolytic attack on polyester polyol based PU is mainly on ester and urethane groups. Meanwhile the hydrolytic attack on polyether polyol based PU is centered mainly on urethane group. The allophanate group (Scheme 5.1) in this PU endures the hydrolytic degradation (Gopalakrishnan & Fernado, 2011). Some investigators also observed the hydrolytic degradation of PU based on polyol (Gopalakrishnan & Fernado, 2011; Zhao et al., 1990). Therefore, the hydrolytic attack on rubber polyol based semi-rigid PU is observed on both the polyol and also the urethane groups.

Samples PU3T2 and PU6T3 are shown to be more stable compared to the other samples because of the higher hard segment content and being strengthened by the higher amount of chain extender. It is also affected by ethanol but only slightly as seen from small changes on percentage of swelling and loss of weight (Table 5.7).



Scheme 5.1: Formation of allophanate group in polyurethane

The influence of NaCl on the hydrolytic degradation is clearly observed for the *two-shot* method samples. This significant effect of Na^+ and Cl^- ions on the degradation is because the PU product prepared by the *two-shot* method is similar to block polymer structure and thus easier for sodium (Na) salt to attack the urethane groups. As for PU synthesized by the *one-shot* method, since the ionic permeation in the PU matrix is much less, the effect of Na^+ and Cl^- ions on the degradation is less (Wells et al., 1990). The random structure by the *one-step* method of this semi-rigid PU is believed to contribute to these phenomena. But for PU5T3 sample, the increasing of the weight shows that Na^+ and Cl^- ions penetrate easily into the PU matrix which contains high hard segment content.

5.2.5 Thermal behaviour

5.2.5.1 Thermal analysis by Differential Scanning Calorimetry

The main difference between the materials prepared by the *two-shot* method and the *one-step* method involves the chain build-up. The PUs obtained by the *two-shot* method (pre-polymer) are statistically more regular in the chain sequence of FLNR-MDI-BDO-MDI-FLNR, whereas PUs obtained by using the *one-shot* method, (assuming the FLNR and the BDO are of equal activity), have a more random sequence. A higher order of crystallinity is obtained in the *one-step* polymers. The *one-step* route begins with the slightly favored reaction between diol and diisocyanate which produces highly crystalline, mobile chain elements. Besides that, the introduction of chain extender in the synthesis of PU can increase the hard segment length that consists urethane groups to permit hard segment segregation thus resulting in better mechanical properties such as increase in modulus and increase in the hard-segment glass transition temperature (T_g) of the PU (Prisacariu, 2011).

Table 5.8: Glass transition temperatures and melting temperatures of *one-shot* and *two-shot* method of semi-rigid polyurethane films

Sample code	**Hard segment[a] (%)**	**Soft segment[b] (%)**	**MDI:BDO[c]**	**Glass transition temperature**		**Melting temperature**
				T_gs (°C)	T_gh(°C)	T_mh (°C)
NR	-	-	-	-40	-	-
PU1T2*	10.98	85.18	0.39:0	-	-	111.0
PU2T2**	16.05	80.11	0.41:0	-39.6	33.1	111.6
PU3T2*	35.45	61.37	1.86:0.12	-40.5	57.0	192.4
PU4T2**	29.16	66.67	0.92:0.14	-39.4	49.8	182.6
PU5T3*	34.52	61.83	1.84:0.64	-40.7	55.7	187.5
PU6T3**	33.77	63.29	3.33:0.95	-39.4	60.4	190

Note: a = % of hard segment=[wt. of (MDI+BDO)/ wt. of (MDI+BDO + polyol + catalyst)] × 100
b = % of catalyst= [wt. of (catalyst)/ wt. of (MDI+BDO + polyol + catalyst)] × 100
c = based on equivalent ratio (MDI:BDO)
T_gs = glass transition temperature of soft segment, T_gh = glass transition temperature of hard segment , T_mh = melting point of hard segment
* *one-shot* method, ** *two-shot* method

The DSC thermograms were used to recognize various thermal transitions associated with the semi-rigid PU films. The first transition involves the glass transition temperatures (T_g) for hard and soft segments, while the second evaluation is to collect data for melting temperatures (T_m) of semi-rigid PU samples. The composition dependence of the T_g of the phases as determined by DSC is presented in Table 5.8. From Figure 5.8, the heating traces show distinct T_g for the soft segment (T_gs) in the range of -39 to -41°C and for T_g for the hard segment (T_gh) in the range of 33 to 61°C. This indicates microphase separation of the immiscible segments in the polymer (Rogulska et al., 2008) and in this study it is referred to semi-rigid PU. The analysis of DSC traces shows very similar T_gs results for each sample. The identification of the T_gs is clear, while that of the T_gh is more difficult and the reliability of any quantity derived from the traces for the hard phase is much smaller (Bagdi et al., 2011).

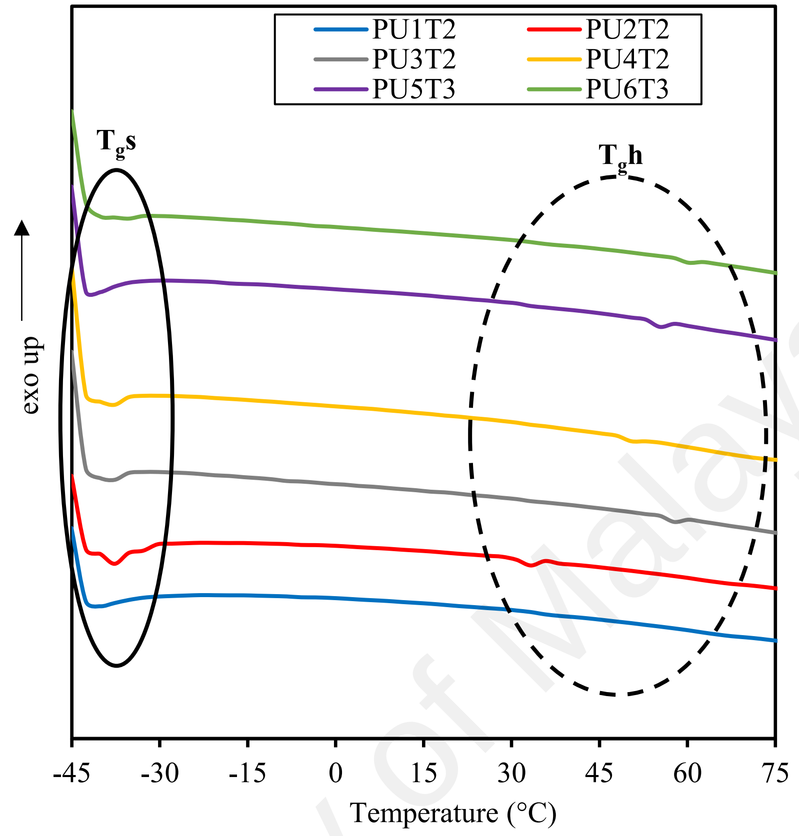


Figure 5.8: Glass transition temperature of semi-rigid polyurethane films samples PU1T2, PU2T2, PU3T2, PU4T2, PU5T3 and PU6T3

In addition, there is no significant difference from T_gs of semi-rigid PU with chain extender (sample PU4T2 and PU2T2) because the low chain extender content for both samples. The hard segment is probably too short compared to the soft segment, therefore, there is not much effect on the T_g value of polymer films. For this study, T_gh of sample PU1T2 (*one-shot* method) is not clearly observed, but the PU2T2 sample (*two-shot* method) is clearly detected and it is believed that even small amount of BDO could develop the phase separation between hard and soft segments.

The production of samples by the *one-shot* method, as in PU3T2 and PU5T3, begins with the slightly favored reaction of diol and diisocyanate which produces highly crystalline, mobile chain elements. Therefore, order can be established before extended polymer growth has occurred. These areas of crystallinity, acting as crosslinks, increase the strength of the *one-step* elastomers. Although materials are molded at high temperatures, the melting point of the *one-step* elastomer is still higher (Rausch Jr & Sayigh, 1965). Complete random disorder is not attained during short exposure to temperatures below the T_m and therefore the crystalline order persists in the *one-step* method (Prisacariu, 2011).

The high soft segment content in the segmented PU for almost all samples is believed to contribute to the low T_g and T_m values especially for sample PU1T2. Comparing the different methods of semi-rigid PU synthesis, the high soft segment content (between 61 and 85 %) for all samples could exhibit the interaction with hard segment content comprising of MDI without and with BDO as chain extender. The rubber based polyol as soft length only has a T_g and no T_m. As expected, the DSC analysis showed a decrease in T_m of the hard segment (T_mh) formed by the *two-shot* method and the thermal processing was easier as the PU formed uniform films. This is similar to previous study (Ojha et al., 2009) that has reported the significance of the *two-shot* method to form a cast TPU film based on polyisobutylene (PIB). From Figure 5.9, it shows that the sample PU4T2 (*two-shot* method) has low T_mh at 182.6 °C compared to sample PU3T2 (one-shot method) which has T_mh at 192.4°C. T_mh peak is also obviously observed for *two-shot* method samples (PU2T2, PU4T2 and PU6T3) compared to one-shot method samples (PU3T2 and PU5T3). Meanwhile, the T_mh of sample PU1T2 (without BDO) is lower (111°C) and not clearly observed compared to the others. This obviously proves that the chain extender has improved the hard segment segregation (Prisacariu, 2011).

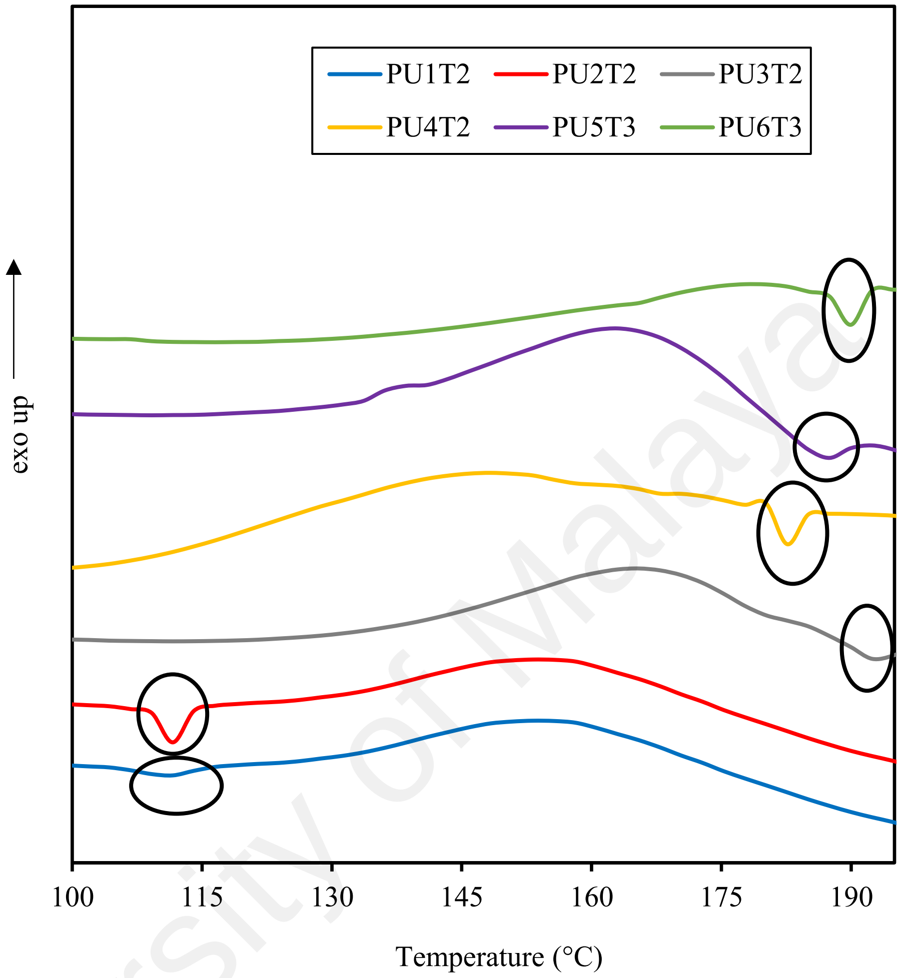


Figure 5.9: Melting temperature of semi-rigid polyurethane films of samples PU1T2, PU2T2, PU3T2, PU4T2, PU5T3 and PU6T3

The molecular weight and OH value of FLNR also affect the thermal transition behaviour especially for soft segment content. Generally, polymer with higher soft segment content will decrease the T_mh. This is indicated by samples PU4T2 and PU6T3 (*two-shot* method samples) whereby T_mh decrease due to increase in the soft segment content. Meanwhile, for samples PU3T2 and PU5T3 of the *one-shot* method, both T_mh values are high with no obvious trend difference on T_mh peaks because the soft segment content is almost same. Thus, the sample PU3T2 is more regular then sample PU5T3.

5.2.5.2 Thermogravimetric analysis

Thermogravimetric analyzer (TGA) thermograms and differential weight loss (DTG) curves of semi-rigid PU with M_n of polyol 20,000 g/mole and 28,700 g/mole were comparatively analyzed for verification of the degradation step of the polymers. The initial temperature of degradation (T_{onset}) and maximum rate degradation temperature (T_{max}) and weight loss in each step are shown in Table 5.9. Two decomposition steps corresponding to the two present phases are obtained. From the TGA thermogram in Figure 5.10, the first step (180-340°C) is attributed to the degradation of the hard segments basically as urethane (Kébir et al., 2006) and the second step (340-500°C) is related to the degradation of soft segments from polyisoprene backbone of oligomers. Overall TGA thermograms are shown in Appendix C5.

Table 5.9: Thermal degradation data and weight loss of *one-shot* and *two-shot* method of semi-rigid polyurethane films

Sample code	**Degradation temperature**				**Weight loss**		**Residue**
	1st step[a]		**2nd step**[b]		**(%)**		**(%)**
	T_{1onset} (°C)	**T_{1max} (°C)**	**T_{2onset} (°C)**	**T_{2max} (°C)**	**m_1**	**m_2**[c]	**m_3**
PU1T2*	270	315	353	498	12.8	84.2	4.9
PU2T2**	271	317	356	500	12.9	84.4	4.9
PU3T2*	285	334	362	552	27.8	64.6	7.8
PU4T2**	280	330	361	552	29.3	56.2	1.0
PU5T3*	287	329	361	565	28.2	63.9	1.3
PU6T3**	293	338	363	571	25.8	64.7	2.4

Note: a = temperature of first step of degradation
b = temperature of second step of degradation
c = rate of maximum degradation (weight % loss/min) at T_{2max}
* *one-shot* method, ** *two-shot* method

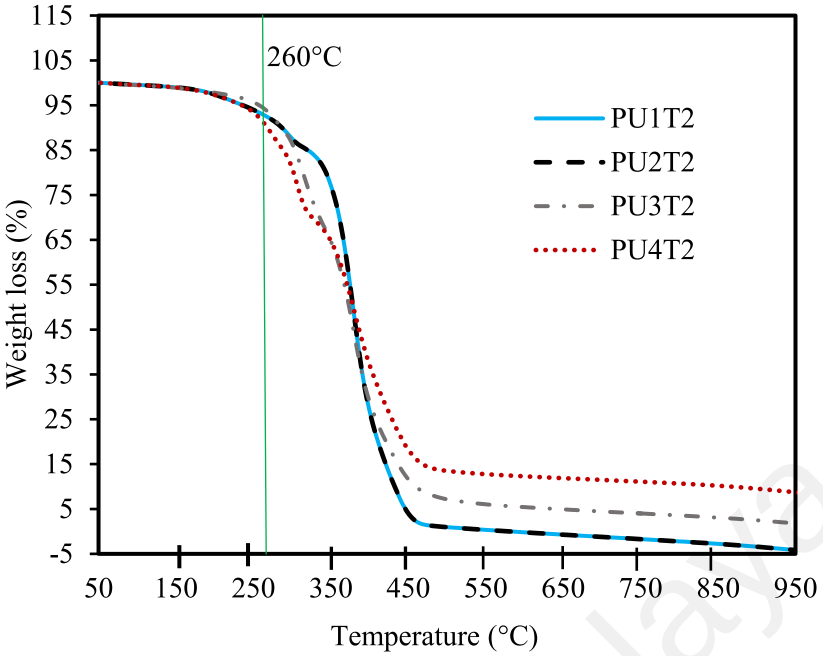


Figure 5.10. Thermogravimetric Analyzer thermogram variation of semi-rigid polyurethane films with same soft segment length of polyol of samples PU1T2, PU2T2, PU3T2 and PU4T2

The curves indicate that all semi-rigid PU films are stable up to 260°C, after which the first step of degradation occurs. This first step corresponds mainly to the urethane degradation. Whatever the nature and content of the hard segment, same apparent end urethane degradation temperature was observed (320°C), thus, only comparative apparent thermal stability in terms of weight loss was evaluated. The second and the third steps (if any) correspond mainly to the soft segments degradation. From Figure 5.10, there is no significant different of curves between samples PU1T2 and PU2T2 samples and it show similar of thermal stability for both samples that has no BDO and the lowest BDO. The urethane degradation is observed below 320ºC and the soft segment degradation is detected in between 350–500ºC. Meanwhile, the *one-shot* method sample (PU3T2) is more most thermally stable at the initial step compared to sample PU4T2 (the *two-shot* method) and similarly at second step. The percentage of residue of sample PU3T2 is higher than sample PU4T2. This shows the sample is more thermally stable for *one-shot* method preparation.

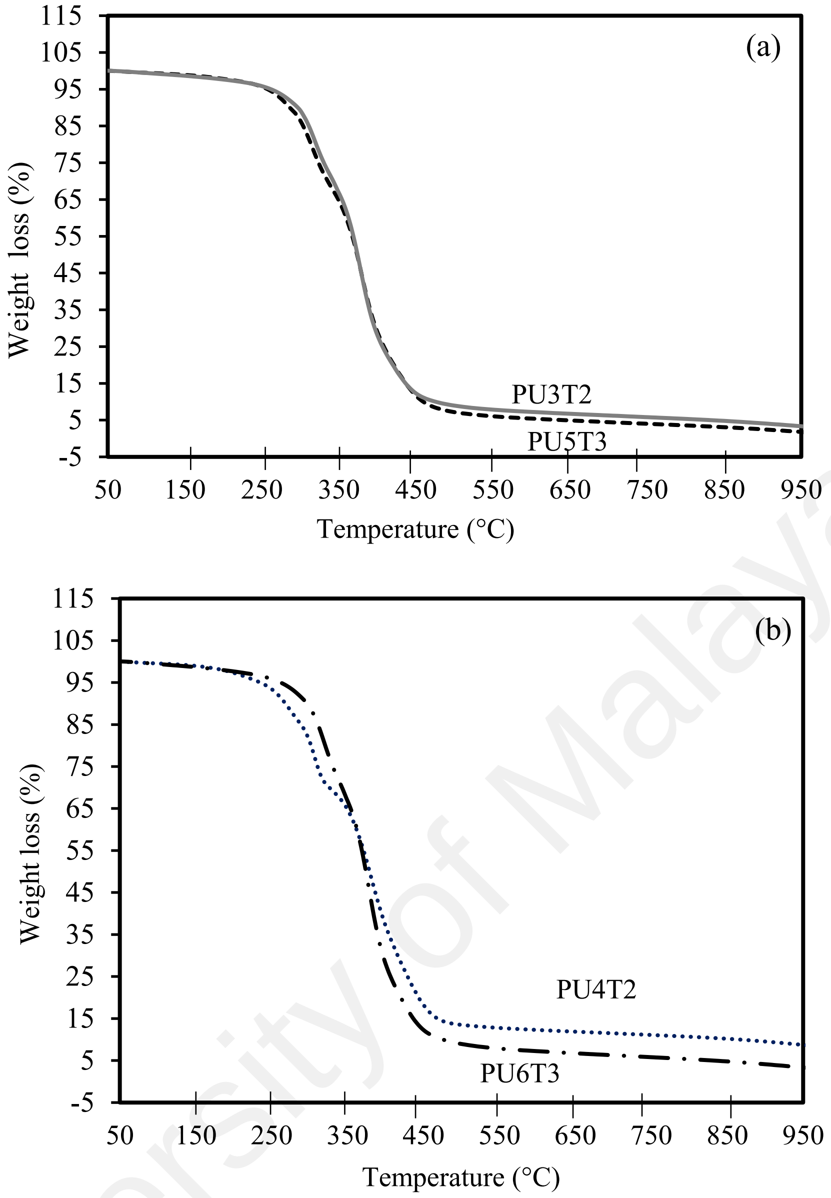


Figure 5.11. Thermogravimetric Analyzer thermograms of semi-rigid polyurethane film at different molecular weight of polyol (a) one-shot method; PU3T2 and PU5T3 and (b) *two-shot* method; PU4T2 and PU6T3

Figure 5.11 (a) and (b) shows the semi-rigid PUs with high molecular weight polyol as precursor have high thermal stability, i.e. samples PU5T3 and PU6T3. It can be seen in the Figure 5.11 (a) for the *one-shot* method preparation, sample PU5T3 has high thermal stability at second step of degradation even the residue percentage is low. The trend is same (Figure 5.11 (b)) for sample PU6T3 whereby high thermal stability is observed at 338ºC due to urethane degradation and soft segment degradation at 571ºC.

From the results obtained, urethane degradation behaviour is influenced by the preparation methods, chain extender content and the length of soft segment. These results prove that the high length of the soft segment and the presence of urethane linkage increase the PU stability.

Meanwhile, Figure 5.12 and 5.13 depict the behavior of DTG curves for the semi-rigid PU samples. The curves show that there are different stages of degradation which are not observable in TG curves, showing the close relation and mutual influence between degradation process of hard and soft segment by the *one-shot* and *two-sh*ot methods. The DTG curves show that the chain extender and soft segment length have a strong influence on the thermal profile of the samples as a whole. These factors are mostly affected by the films preparation (*one-shot* and *two-shot* method) and further on hard segment properties of semi-rigid PU films. This observation obviously shows that the thermal stability of soft segment degradation is similar compared to the urethane degradation. Even though the different method of films preparation for PU3T2 and PU4T2 samples (Figure 5.12) and the different length of soft segments for PU4T2 and PU6T3 samples (Figure 5.13), the degradation behaviour are different on urethane group. The urethane group is highly thermally stable for sample prepared by the *one-shot* method (PU3T2) and sample produced from high soft segment length (PU6T3). The curves also show the sample with a lower chain extender (PU2T2) do not have good thermal stability and likewise for the sample without chain extender (PU1T2).

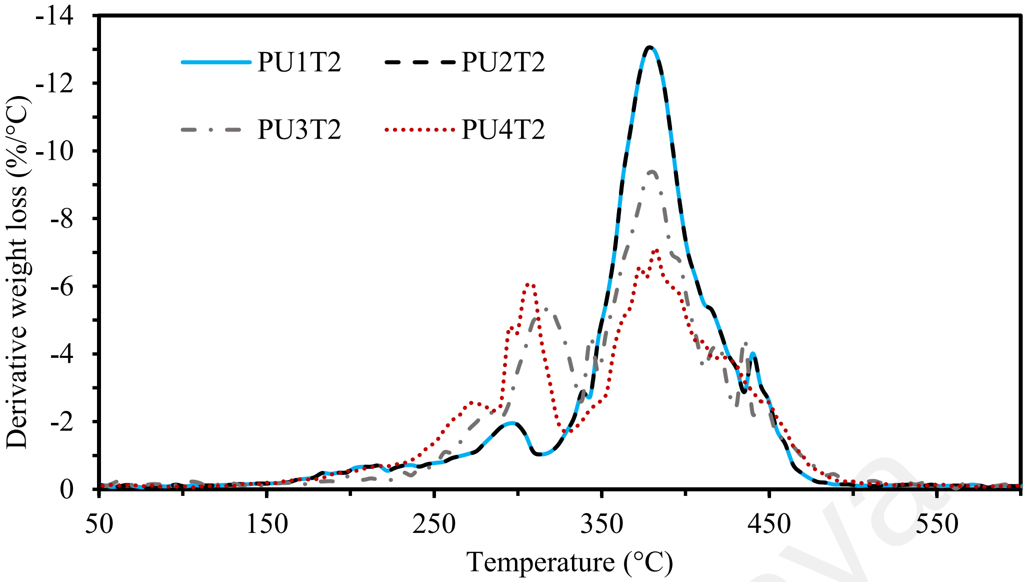


Figure 5.12: Differential weight loss curves of variation semi-rigid polyurethane films with same soft segment length of polyol of samples PU1T2, PU2T2, PU3T2 and PU4T2

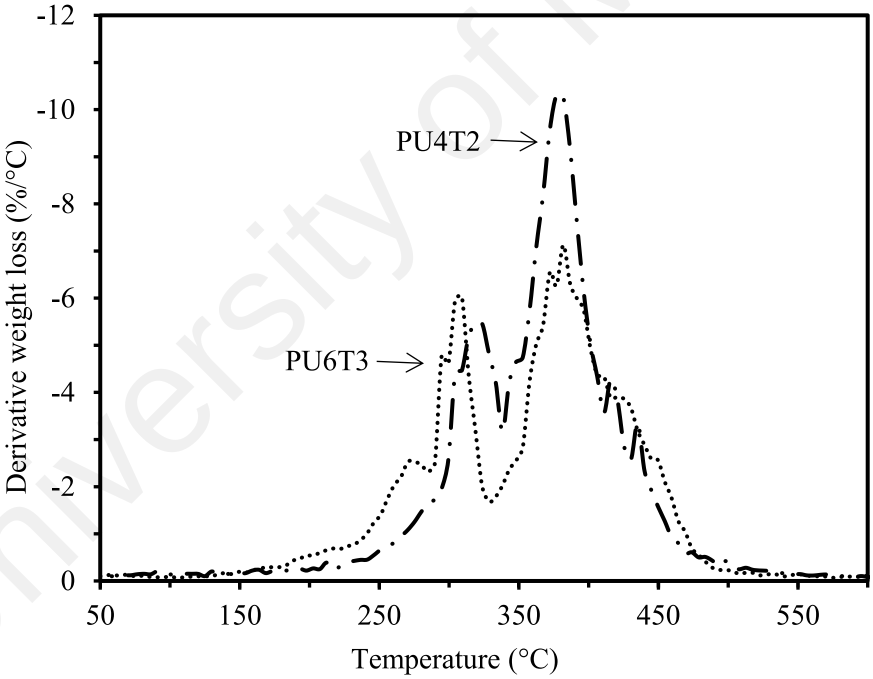


Figure 5.13: Differential weight loss curves of *two-shot* method of semi-rigid polyurethane films with different soft segment length of samples PU4T2 and PU6T3

5.3 Formulation of modified semi-rigid polyurethane films

It is useful to observe the thermal properties, i.e. T_g and T_m, of the soft and hard segment character that affect the thermal stability of film samples. The aging properties in different organic solvents, chemical environment, environmental resistances were conducted to determine the stability of polymer films in various media. Therefore, the synthetic procedure was modified in order to achieve better performance of semi-rigid PU. In this *two-shot* method modification, after the addition of BDO the temperature was increased to 100°C to evaporate the solvent. The mixture was then poured in the Teflon dish and allowed for a while to completely remove the solvent before vacum dried and post-cured at 60°C for 50 h.

Table 5.10: Formulation of modified semi-rigid polyurethane films

Sample code	[NCO]/[OH] ratio	BDO (pbw)[a]	MDI:BDO[b]	Polyol/OH[c]	Catalyst (%)[d]
PU7T1*	0.6	2.50	0.7:0.2	0.92	5.16
PU8T1*	0.8	2.48	1.2:0.2	0.92	3.93
PU9T1*	1.0	2.49	1.3:0.2	0.92	3.57
PU10T2**	0.6	2.50	0.9:0.2	1.0	4.92
PU11T2**	0.8	2.33	1.3:0.2	1.0	4.41
PU12T2**	1.0	2.50	1.7:0.2	1.0	4.69
PU13T3***	0.6	2.46	1.3:0.2	1.2	6.67
PU14T3***	0.8	2.02	1.8:0.2	1.2	4.47
PU15T3***	1.0	2.02	2:0.2	1.2	6.93

Note: a= part by weight (pbw) based on pbw of polyol; M_n=1000 g/mol and OH value =660 mg KOH/g
b = based on mmole ratio
c = based on equivalent ratio
d = % of catalyst = [wt. of (catalyst)/ wt. of (MDI+BDO + polyol+ catalyst)] × 100
* FLNR-17700, ** FLNR-20000 and *** FLNR-28700

The formulation of semi-rigid PU film samples in Table 5.10 and 5.11 was done according to selected amount of BDO (pbw based on rubber polyol) and catalyst that produce better film appearance. From previous study, the content of BDO will affect the hard and soft segment of PU products (Dirckx et al., 1999). Thus, the content of BDO for this semi-rigid PU product is limited between 2-2.5 (pbw based on polyol). Meanwhile the use of $Sn(Oct)_2$ as a catalyst should be low and was suggested between 2-4 (pbw based on polyol) or 2-6% (based on total weigh of hard and soft segment) to produce the PU film product. The choice of Sn(Oct)$_2$ as a catalyst was because it produces better appearance of film form as end product. But the selection of catalyst percentage was minimized to prevent the toxicology effect. As clarification, the *two-shot* method was selected in this modification because of the processable control and minor technically problem during film preparation. The advantage of this PU preparation method that was easily to synthesize and suitable with the structure by varying the type and the ratio of starting components during processing (Hepburn, 1992; Oertel & Abele, 1985; Prisacariu, 2011; Saunders & Frisch, 1964). The soft and hard segment contents of modified semi-rigid PU and also the percentage of MDI and BDO in the hard segment are shown in Appendix C6. In addition, the morphology of the semi-rigid PU samples is not clearly observed because of the rubber polyol contain is higher compared to isocyanates. No clear differences in morphology between high and low polyol length (Appendix C7).

5.3.1 Molecular weights and physical appearance

The molecular weights (M_n and MWD) and physical appearance of semi-rigid PU are listed in Table 5.11. The molecular weight corresponding to M_n of each sample varies accordingly depending on the [NCO]/[OH] ratio. Increasing this ratio will increase the soft segment length. The weight distribution (MWD) values show that the polydispersity of polymer obtained is nearly 2.0 similar to that reported in previous study. The study reported that the *two-step* method PU was more controlled and should produce linear PU chains, fewer side reactions and polydispersities of nearly 2 (Petrović et al., 2013; Prisacariu, 2011; Rausch Jr & Sayigh, 1965).

The PU structures from *two-shot* method obtained tend to be more regular than the corresponding polymers obtained by *one-step* route. The reason is because the pre-polymer route caps the polyol with the diisocyanate and then connects these oligomers with the chain extender. More regular segmented polymer (soft segment and hard segment) sequences will be formed and the hard segment size is narrower (Prisacariu, 2011). However, with increase in soft segment length (FLNR-28700 precursor) for samples PU13T3, PU14T3 and PU15T3, molar mass measurement could not be performed. This is probably due to very high molecular weights of semi-rigid PU and possible secondary isocyanate reactions, such as allophanate formation.

Table 5.11: Molecular weights and physical appearances of modified semi-rigid polyurethane films

Sample code	[NCO]/[OH] ratio	M_n (g/mol)	MWD	Appearance	Soft segment (%)	Hard segment (%)
PU7T1	0.6	77,100	1.9	yellowish; soft; transparent	71.33	23.51
PU8T1	0.8	79,500	1.9	yellowish; soft; transparent	67.17	28.90
PU9T1	1.0	81,500	2.2	yellowish; partly soft; transparent	62.95	33.48
PU10T2	0.6	82,300	2.1	yellowish; partly soft; transparent	67.25	27.83
PU11T2	0.8	88,200	2.1	yellowish; partly soft; transparent	66.49	29.10
PU12T2	1.0	88,700	2.3	yellowish; partly soft; transparent	56.95	38.36
PU13T3	0.6	-	-	yellowish; partly soft; opaque	59.25	35.08
PU14T3	0.8	-	-	yellowish; rigid; opaque	54.76	40.77
PU15T3	1.0	-	-	yellowish; rigid; opaque	48.32	44.75

The appearance of semi-rigid PU film samples was soft at [NCO]/[OH] ratio of 0.6 but at [NCO]/[OH] ratio of nearly or equal 1.0, materials became hard and opaque due to the increase in hard segment content and microphase segregation. This is similar to the preliminary study of semi-rigid PU carried out in this work whereby generally, all obtained materials were yellowish and light transparent except for the opaque samples produced from high molecular weight FLNR precursor, i.e. samples PU12T2, PU13T3, PU14T3 and PU15T3.

5.3.2 Solubility behaviour

Table 5.12 lists the solubility of modified semi-rigid PU in different solvents. Most of samples are soluble in THF and partly soluble in toluene and chloroform, while not soluble in DMF and DMSO. The soluble fraction expresses the similar properties as swelling behaviour that relates to the interaction between polymer matrix with the solvent.

Table 5.12: Solubility of modified semi-rigid polyurethane films in organic solvents

Sample code	Soft segment (%)	Hard segment (%)	[NCO]/ [OH] ratio	Solvents				
				toluene	chloroform	THF	DMF	DMSO
				Solubility				
PU7T1*	71.33	23.51	0.6	±	±	++	–	–
PU8T1*	67.17	28.90	0.8	±	±	++	–	–
PU9T1*	62.95	33.48	1.0	±	±	++	–	–
PU10T2**	67.25	27.83	0.6	±	±	++	–	–
PU11T2**	66.49	29.10	0.8	±	±	++	–	–
PU12T2**	56.95	38.36	1.0	±	±	++	–	–
PU13T3***	59.25	35.08	0.6	±	±	±	–	–
PU14T3***	54.76	40.77	0.8	±	±	±	–	–
PU15T3***	48.32	44.75	1.0	±	±	±	–	–

Note: ++: soluble; – insoluble; ± partly soluble
* FLNR-17700, ** FLNR-20000 and *** FLNR-28700

From Table 5.13, the solubility parameter of 19.4 $(MPa)^{1/2}$ for THF was found to have the highest percentage of soluble fraction of all semi-rigid PU samples except samples PU13T3, PU14T3 and PU15T3. These three samples have the highest molecular weight of FLNR as precursor. Meanwhile, all film samples are shown to be unaffected by DMF and DSMO because this high polar solvent do not strongly effect on solubility of rubber based PU.

Table 5.13: Percentage of soluble fraction of modified semi-rigid polyurethane films in organic solvents

Sample code	**[NCO]/[OH] ratio**	**Solvents**				
		toluene	**chloroform**	**THF**	**DMF**	**DMSO**
		Solubility parameter (MPa)$^{1/2}$				
		18. 2	19.0	19.4	24.8	26.4
		Soluble fraction (%)				
PU7T1*	0.6	99.0[b]	99.1[b]	100[a]	72.4[b]	46.9[b]
PU8T1*	0.8	97.2[b]	98.2[b]	100[a]	77.5[b]	45.6[b]
PU9T1*	1.0	97.1[b]	98.1[b]	100[a]	70.6[b]	44.9[b]
PU10T2**	0.6	96.8[b]	98.5[b]	100[a]	71.6[b]	45.9[b]
PU11T2**	0.8	96.5[b]	98.4[b]	100[a]	61.5[b]	40.9[b]
PU12T2**	1.0	96.4[b]	98.4[b]	100[a]	60.6[b]	36.8[b]
PU13T3***	0.6	95.3[b]	93.2[b]	95[b]	52.3[b]	35.4[b]
PU14T3***	0.8	95.5[b]	92.7[b]	92.5[b]	51.7[b]	32.2[b]
PU15T3***	1.0	86.1 [b]	87.9[b]	90.7[b]	37.2[b]	30.3[b]

Note: [a]room temperature, [b]: heating
* FLNR-17700, ** FLNR-20000 and *** FLNR-28700

From earlier study (Gopakumar & Gopinathan, 2005), similar findings were obtained on the solubility phenomena of NR/PU block copolymers. The high solubility parameter for THF is an indication of the better accommodation of the solvent molecules due to favourable interaction with the hard domains as well as the soft NR matrix and also due to the small size of the penetrant. Even though the THF acts as polar solvent but it is a low polar aprotic solvent with dielectric constant of 7.6. It is a moderately polar solvent and can dissolve a wide range of non-polar and polar chemical compounds. From observation in Table 5.13, THF is seen to penetrate into the polymer matrix that was produced from the combination of rubber based soft segment (non-polar) and urethane (polar) as hard segment. It shows that film samples with low molecular weight of FLNR as precursor (M_n = 17,700 g/mol for samples PU7T1, PU8T1 and PU9T1 and M_n = 20,000 g/mol for samples PU10T2, PU11T2 and PU12T2) exhibit a high percentage of soluble fraction. These samples have high soft segment content compared to samples PU13T3, PU14T3 and PU15T3 which produced from high molecular of FLNR (M_n = 28,700 g/mol).

In toluene and chloroform, the solubility behaviour of each sample looks similar. All samples are partly soluble in toluene and the percentage of soluble fraction for most semi-rigid PU samples fall in the ranges 95.3-99% respectively. Meanwhile in chloroform, the high percentage of soluble fraction are shown by all film samples except sample PU15T3. Only sample PU15T3 which has a higher hard segment content produces low percentage of soluble fraction and is more stable in toluene and chloroform. Besides that, based on the observation of percentage soluble fraction of semi-rigid PU, the penetration of DMF and DMSO into polymer matrix are less favoured. These high polar solvents are not appropriate solvents for semi-rigid PU based on rubber polyol, which is most likely attracted to low polarity solvents. Highly polar and non-polar solvents interact only with the appropriate phase in the film samples and the other phases, thus the soluble fraction is lower.

The sorption process also contributes to the solubility behaviour. The sorption process was reported to be more spontaneous in THF and chloroform and less so in toluene, DMF and DMSO whereby the process is controlled predominantly by thermodynamic factors rather than the penetrant size (Gopakumar & Gopinathan, 2005). The high activation energy of diffusion and activation energy of permeation correspond to the high values of enthalpy and entropy (free energy) of the sorption process in DMF and DMSO. The lowest percentage of soluble fraction of DMF and DMSO may be due to the unfavourable interaction with the NR phase. All values are in contrast with low polar aprotic solvent such as THF and non-polar solvents such as toluene and chloroform. Free energy of the process is positive suggesting that the sorption of different solvents gives an endothermic contribution to the process. The low enthalpy, free energy, energy of activation for diffusion and permeation promote better soluble character. In this study toluene is found to follow consistent behaviour where the solubility character is similar to chloroform and THF. This may be due to the non-polar toluene being able to interact with polar PU segments that are intact with the NR segment by physical crosslinks though in fact the non-polar substance is unable to interact with the polar component.

The [NCO]/[OH] ratio is found to play an important role in the solubility behaviour. The solubility character of each semi-rigid PU sample varies with [NCO]/[OH] ratio. As mentioned before, the degree of phase separation and domain formation depend on the hard segment and soft segment nature and size and also by molecular weight of the soft segment. It can also be observed from Table 5.13, that in all cases the percentage of soluble fraction of each sample decreases when the [NCO]/[OH] ratio is increased and irrespective of the nature of the solvents. It can be clarified that at high [NCO]/[OH] ratio, the excess of NCO favours more crosslinking in the polymer systems through allophanate linkage. Thus, the higher level of crosslinking causes lower penetration of solvent inside the film samples. In addition, previous study (Gopakumar & Gopinathan, 2005) also mentioned that the lowering of enthalphy, free energy, energy of activation for diffusion and permeation with decrease in [NCO]/[OH] ratio suggests that the polymer-solvent interaction is facilitated at lower values of the [NCO]/[OH] ratio.

5.3.3 Fourier Transform Infrared

FT-IR is a well-established analytical technique for functional group analysis and to study the hydrogen bonding and phase separation behavior of PUs. The frequency shifts in hydrogen bonded N-H and carbonyl peaks relative to free N-H and C=O peaks determine the extent of hydrogen bonding and microphase separation between hard and soft segments (Brunette et al., 1982; Lee & Hsu, 1989; Yilgor & Yilgor, 2007). If hydrogen bonding exists only within the hard segment domains (due to the hydrogen donor N-H group), phase separation occurs. On the other hand, if they can be formed between the hard and the soft segments via oxygen atom of oxirane rings, the interphase hydrogen bonding enhances the degree of phase mixing (Olabisi & Adewale, 2016).

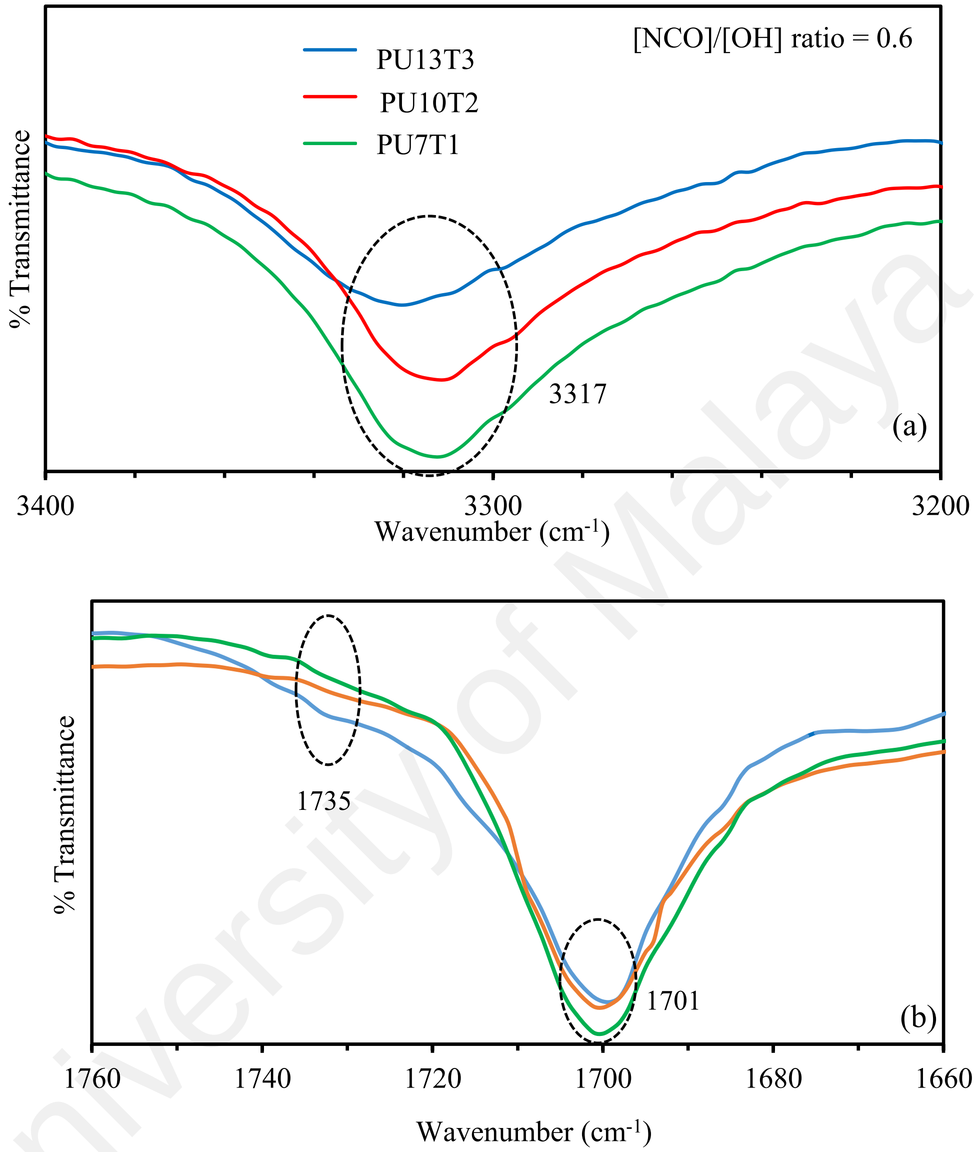


Figure 5.14: Comparison between Fourier Transform Infrared spectra at bands (a) 3200-3400 cm^{-1} and (b) 1660-1760 cm^{-1} of modified semi-rigid polyurethane films in different soft segment lengths of samples PU7T1, PU10T2 and PU13T3; [NCO]/[OH] = 0.6

The characteristic FT-IR spectrum of FLNR based semi-rigid PU has bands at 3317 cm $^{-1}$ (N-H stretching vibrations), at 1600-1800 cm^{-1} (C=O stretching vibrations), at 1534 cm^{-1} (N-H in plane bending) and at 1070 cm^{-1} (C-O-C stretching vibration). These bands are similar to those in earlier discussion in (Figure 5.1 and Section 5.2.2). As the major concern of this work focuses on hydrogen bonding and their relation to the segregation of hard and soft segments, two special regions are of main interest; the N-H stretching vibration at 3317 cm^{-1} (Figure 5.14 (a) and the C=O stretching vibration from 1700 to 1800 cm^{-1} (Figure 5.14 (b)).

Figure 5.14 (a) shows the FT-IR spectra of N-H stretching region for the semi-rigid PU with different soft segment length of samples with different M_n and OH values in FLNR soft segments. In all cases, the N-H stretching vibration exhibits a strong absorption peak centered at around 3317 cm^{-1}. The highest intensity of the characteristic band at 3317 cm^{-1} is observed for the lowest molecular weights of FLNR of sample PU7T1 at 17,700 g/mol compared to sample PU10T2 (M_n of FLNR is 20,000 g/mol) and PU13T3 (M_n of FLNR is 28,700 g/mol). This shows that the decrease of soft segment length will increase the intensity of urethane linkage. It is well explained by the higher proportion of urethane hard segment relative to NR soft segment. This band corresponds to hydrogen bonding between hard segments. The similar trend also observed in Figure 5.15 (a) for samples PU8T1 (M_n of FLNR is 17,700 g/mol), PU11T2 (M_n of FLNR is 20,000 g/mol) and PU14T3 (M_n of FLNR is 28,700 g/mol) with [NCO]/[OH] ratio of 0.8. The FT-IR bands around 1620-1780 cm^{-1} give more information on the ratio of C=O bonded to N-H and free C=O bonds. (Figure 5.14 (b)) represents the C=O stretching region around 1700-1740 cm^{-1}. Almost all spectra have a major band centered at approximately 1701 cm^{-1}, which is assigned to hydrogen-bonded urethane and slight shoulder at about 1735 cm^{-1} attributed to free C= O urethane groups. The band at 1701 cm^{-1} relates to hydrogen bonded -C=O, and the band at 1735 cm^{-1} relates to free -C=O. The higher proportion of hydrogen bonded -C=O versus free -C=O is observed as the molecular weight of the FLNR precursor is lower. Free -C=O bonds are in higher proportion in the obtained semi-rigid PU with high molecular weight rubber polyol precursors for samples PU10T2 and PU13T3 with molecular weights of 20,000 and 28,700 g/mol. In this case, steric hindrance of the high molecular weight soft segment may have decrease the probability of hydrogen bonding between the urethane hard segments.

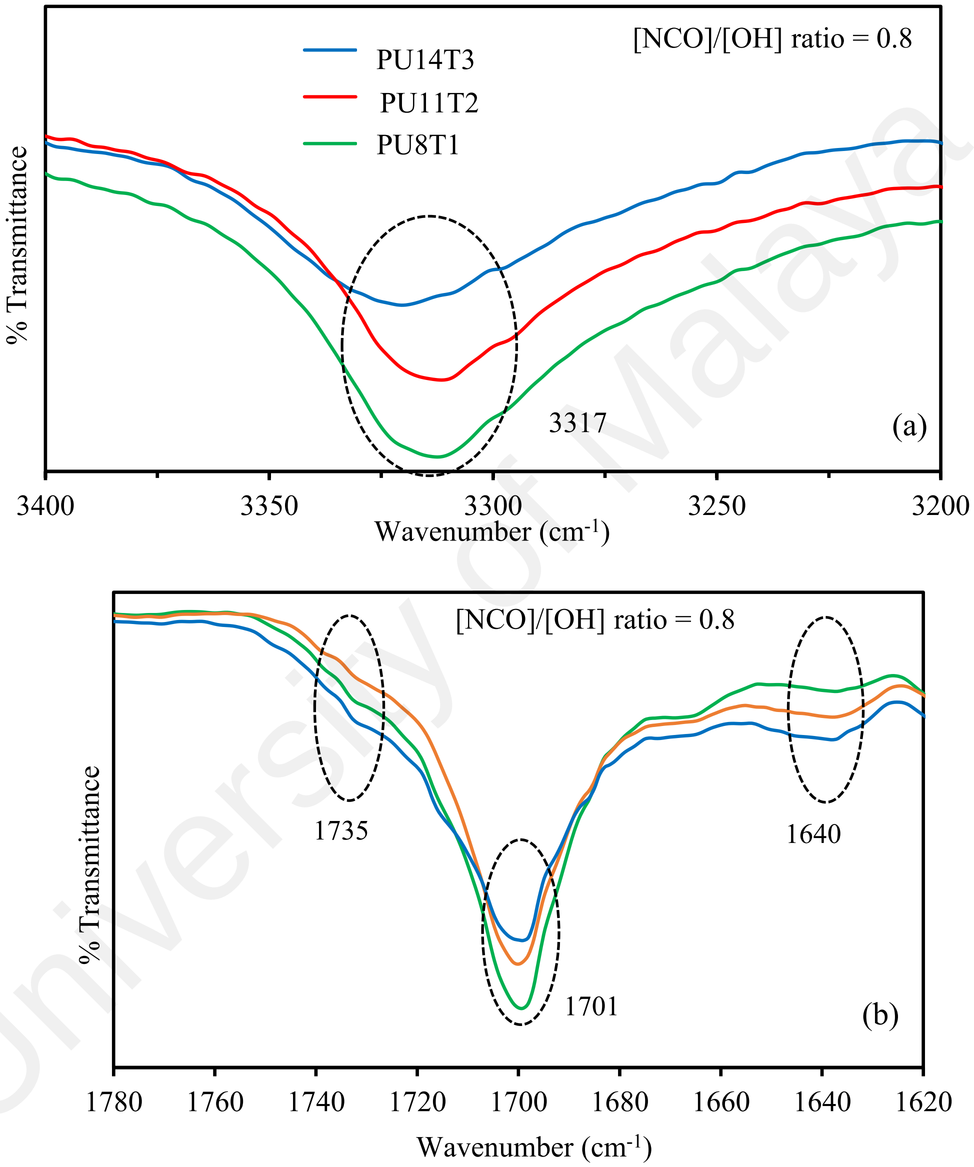


Figure 5.15: Comparison between Fourier Transform Infrared spectra at bands (a) 3200-3400 cm^{-1} and (b) 1620-1780 cm^{-1} of modified semi-rigid polyurethane films in different soft segment lengths of samples PU8T1, PU11T2 and PU14T3 at [NCO]/[OH] ratio = 0.8

For high M_n of polyol, the lower urethane content will also decrease the probability of interactions between hard and soft segment. At 1640 cm^{-1}, the characteristic band of vibration of C=C bond of the FLNR soft segments is observed. The intensity of this band is higher in the case of semi-rigid PU samples with high average molecular weight FLNR soft segments. This situation is obviously observed for average [NCO]/[OH] ratio of about 0.8 (Figure 5.15 (b)) but no significant changes for [NCO]/[OH] ratio of about 1.0 (Appendix C8).

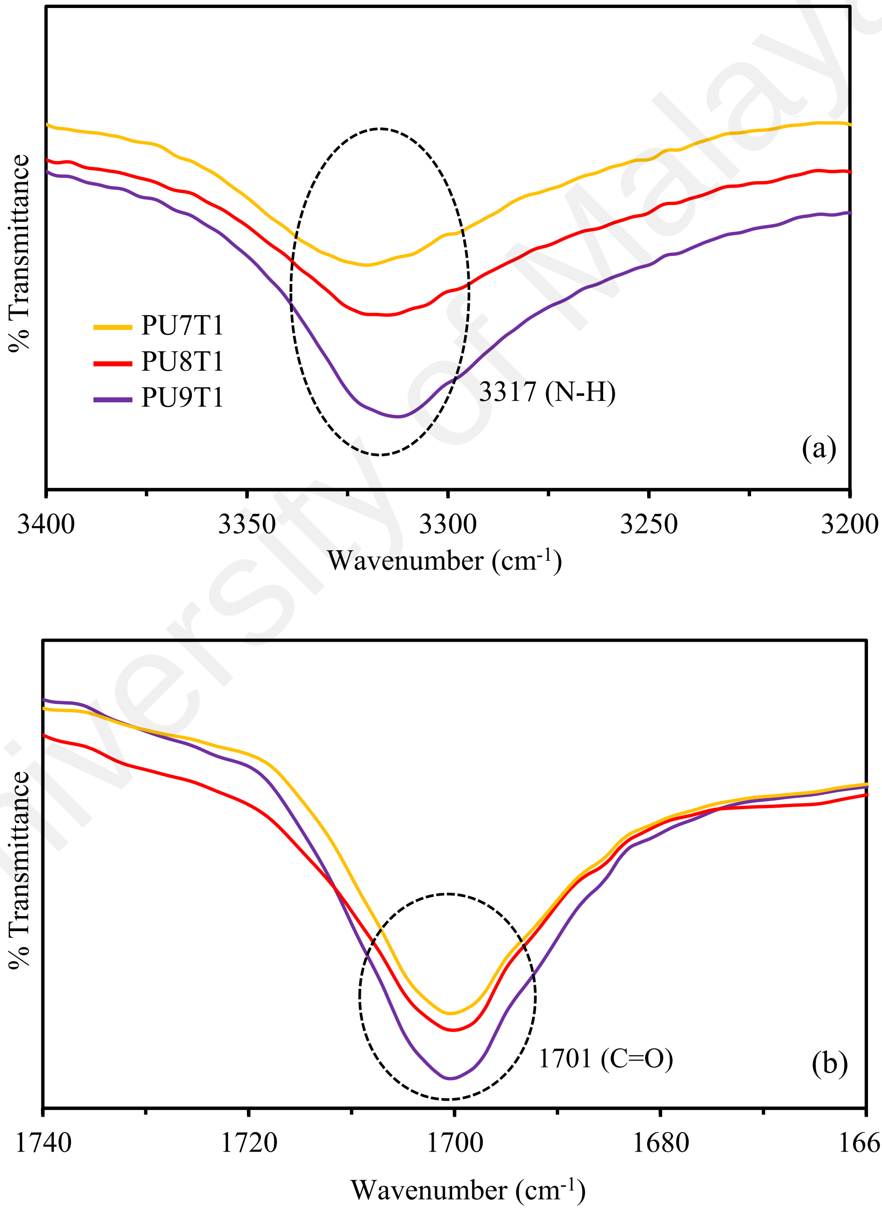
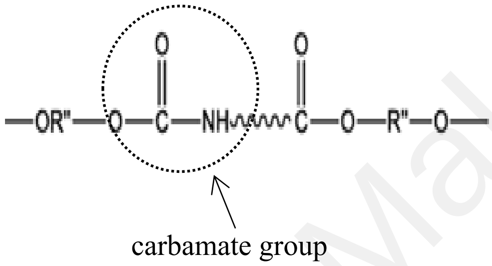


Figure 5.16: Comparison between Fourier Transform Infrared spectra at bands (a) 3200-3400 cm^{-1} and (b)1660-1740 cm^{-1} of modified semi-rigid polyurethane films at different [NCO]/[OH] ratios

From Figure 5.16 (a) and (b), in all cases the intensity of hydrogen bonded N-H at 3317 cm^{-1} and –C=O at 1701 cm^{-1} increase with increasing of [NCO]/[OH] ratios. The increase in [NCO]/[OH] ratios will increase the isocyanates content parallel to the increases of hard segments content of semi-rigid PU. The intensity band of PU9T1 sample with [NCO]/[OH] ratio of about 1.0 was allowed more effective network between soft and hard segments as more carbamate groups ($-NHCO_2$) or called as urethane linkage (Scheme 5.2) are being formed when [NCO]/[OH] ratio is high.



Scheme 5.2: Urethane linkage

5.3.4 Thermal behaviour

5.3.4.1 Thermal analysis by Differential Scanning Calorimetry

Table 5.14 lists the results obtained for T_g and T_m of the modified semi-rigid PU films. The values of thermal transitions are completely dependent on the segmented configuration of semi-rigid PU and also the rubber based material as polyol, i.e. soft phase and hard phase arising from polyols length (different molecular weight, M_n and polyol/OH ratio) and [NCO]/[OH] ratios. As shown in Table 5.14, all the modified semi-rigid PU films have two transition temperatures (T_g), i.e, T_gs corresponds to soft segment and T_gh corresponds to hard segment in the semi-rigid PU. These T_g values depend on the proportion of soft segment and hard segment in the mixture.

Table 5.14: Glass transition temperatures and melting temperatures of modified semi-rigid polyurethane films

Sample code	Polyol/ OH ratio	[NCO] /[OH] ratio	Soft segment (%)	Hard segment (%)	Glass transition temperature		Melting temperature	
					T_gs (°C)	T_gh (°C)	T_mh_1 (°C)	T_mh_2 (°C)
PU7T1*	0.92	0.6	71.33	23.51	-41.4	31.8	104.0	-
PU8T1*	0.92	0.8	67.17	28.90	-42.6	32.1	101.6	153.0
PU9T1*	0.92	1.0	62.95	33.48	-41.6	32.2	104.1	150.6
PU10T2**	1.0	0.6	67.25	27.83	-42.0	31.9	101.9	-
PU11T2**	1.0	0.8	66.49	29.10	-42.2	32.1	96.8	-
PU12T2**	1.0	1.0	56.95	38.36	-38.6	32.2	99.2	148.0
PU13T3***	1.2	0.6	59.25	35.08	-41.5	30.1	89.7	-
PU14T3***	1.2	0.8	54.76	40.77	-41.0	27.9	92.1	-
PU15T3***	1.2	1.0	48.32	44.75	-40.0	-	119.0	195.0

Note: a= part by weight (pbw) based on pbw of polyol; M_n=1000 g/mol and OH value =660 mg KOH/g
b = based on mmole ratio
c = based on equivalent ratio
d = % of catalyst = [wt. of (catalyst)/ wt. of (MDI+BDO + polyol+ catalyst)] × 100
* FLNR-17700, ** FLNR-20000 and *** FLNR-28700

The DSC traces showing T_gs and T_gh, and T_mh for modified semi-rigid PU containing FLNR-17700 (samples PU7T1, PU8T1 and PU9T1), FLNR-20000 (samples PU10T2, PU11T2 and PU12T2) and FLNR-28700 (samples PU13T3, PU14T3 and PU15T3) are attached in Appendix C9 – Appendix C10. The T_gs shows no significant changes in all samples probably because of the highest component of rubber polyol as soft segment in the sample formulation and only samples PU12T2 shows a small different from other T_gs. However, T_gs can still be observed and is influenced by the changes of polyol/OH ratios and molecular weight of the polyol. In fact, increase in the molecular weight consequently results in increase in the soft phase even though the polyol/OH ratios do not significantly change (only in between 0.92 - 1.2). Therefore, the stronger interactions among the soft and hard segments should lead to smaller mobility of the soft segment and its larger partial solubility in the hard phase, as well as to decreased number of relaxing species (Bagdi et al., 2011). The T_gs results, are most affected by the polyol/OH ratio (high molecular polyol) even though hard segment content is high. Sample PU15T3 with high polyol/OH ratio and high hard segment content, exhibits low

T_gs. Thus, high molecular weight polyol decreases the T_g; this may be caused by the obstruction of π ring to hydrogen bonding in the hard segment blocks, hence the interactions between chains are weaker and consequently leads to decrease in the T_g of the polymer.

Besides that, the transition temperature of hard phase (T_gh) is also affected by the polyol/OH ratio, and soft and hard segments. There are no significant changes on the T_gh values of each sample, while sample PU14T3 shows the lowest T_gh value. But the different values of T_gh can still be observed because of urethane structure as a hard phase affecting the T_gh of semi-rigid PU film samples. It is also shown that the high polyol/OH ratio affecting the T_gh of samples PU12T2 and PU13T3 based on the hydrogen bonding between the hard and soft segments results in softer domains dissolved in hard matrix. But the T_gh value of sample PU15T3 does not clearly exist because the softer domain is completely dissolved in the hard matrix and hinders detection of T_gh.

Meanwhile, for [NCO]/[OH] ratio effect, increase in T_gh values is due to the increase in the [NCO]/[OH] ratio for samples produced from FLNR-17700 (samples PU7T1, PU8T1 and PU9T1) and FLNR-20000 (samples PU10T2, PU11T2 and PU12 T2). This might be due to presence of more urethane groups which were formed at higher [NCO]/[OH] ratio and allowing more hydrogen bonding interaction and cohesion in both soft and hard segments. Besides that, the results obtained is in contrast with semi-rigid PU sample that was produced from FLNR-28700, i.e samples PU13T3, PU14T3 and PU15T3. The T_gh values are decreased with increases in [NCO]/[OH] ratio of 0.6 and 0.8 for samples PU13T3 and PU14T3. The absence of T_gh value for sample PU15T3 ([NCO]/[OH] ratio of 1.0) is due to the hard phase that might be influenced by the longer polyol length in the semi-rigid PU samples.

For T_mh_2 values, it can only be observed for samples PU8T1, PU9T1, PU12T2 and PU15T3 that have high [NCO]/[OH] ratio of 0.8 and 1.0. The T_mh values are shown to decrease with increases of soft segment content from 153ºC – 148ºC (from sample PU8T1 to sample PU12T2) but the value increases to 195ºC for sample PU15T3 that consists high hard segment content and high polyol/OH ratio. It is shown that the highest polyol/OH ratio affects the T_mh_2 in which the harder domains tends to soften in the soft matrix. Therefore, from all results of T_gs, T_gh and T_mh, slight increase in values even at low molecular weight polyol is because of the existence of chain extender that merges with MDI component which increases the proportion of hard segment. The increases of T_mh_2 values is due to the increase in [NCO]/[OH] ratio because of the stronger hydrogen bonding at higher [NCO]/[OH] ratio forming physical crosslinking and causing difficulty for segmental motion of the polymer chain. It is believed to result in more significant phase separation (Li-Hong et al., 2006).

5.3.4.2 Thermogravimetric analysis

TGA and DTG traces of semi-rigid PU with various polyol lengths are presented in Figures 5.17 (a) – (c) and 5.18 (a) – (c). The results obtained for TGA are listed in Tables 5.15 and 5.16. From the TGA curves, two step degradation of semi-rigid PU is observed; first step is urethane function in accordance to the results reported previously (Kébir, et al., 2005) and second step is polyisoprene backbone of oligomers. These trends are similar to the initial study on the formulated *one-sh*ot and *two-sh*ot methods (Section 5.2.5.2).

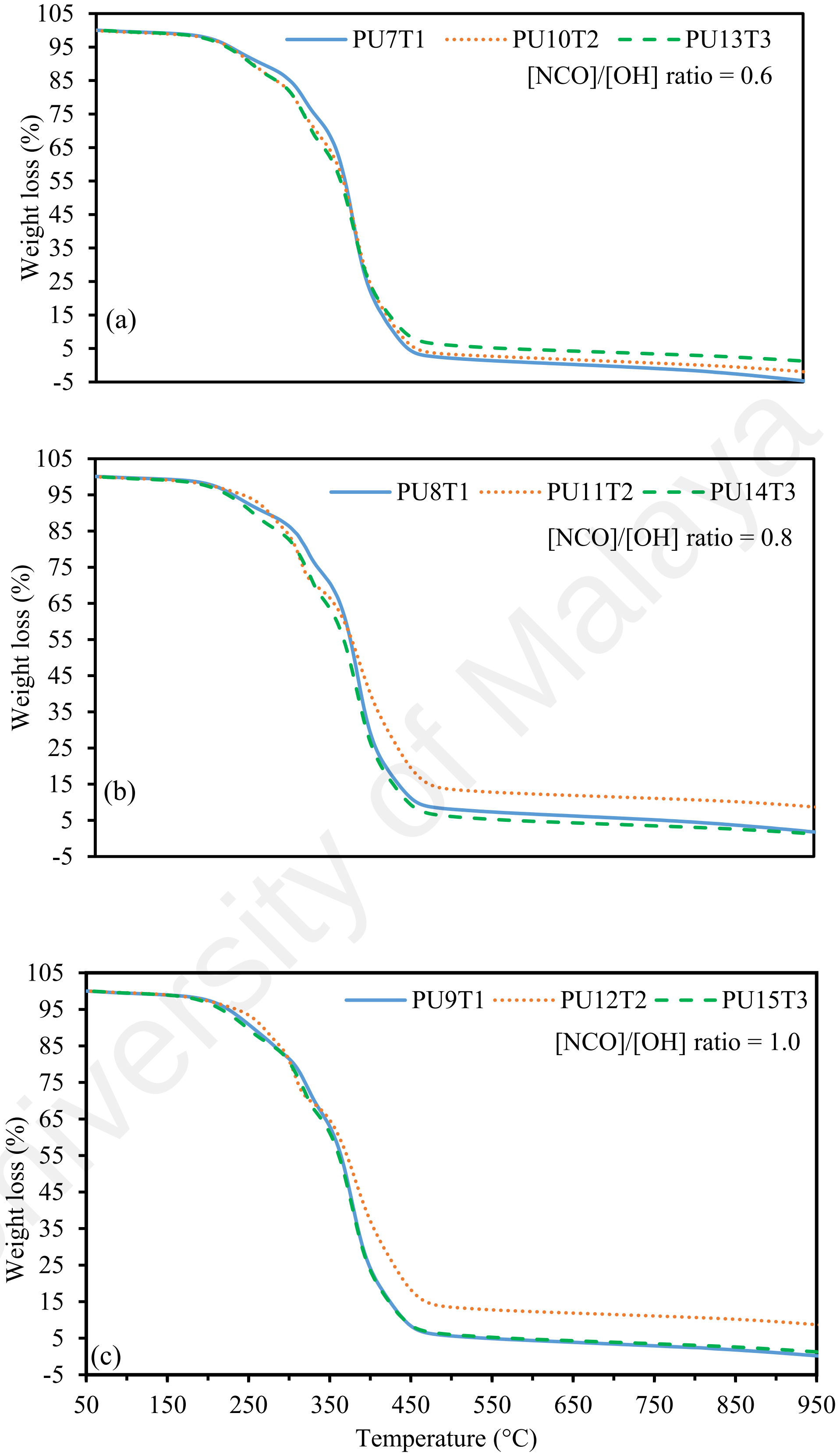


Figure 5.17: Thermogravimetry Analyzer thermograms of modified semi-rigid polyurethane based on different molecular weight of samples at [NCO]/[OH] (a) 0.6, (b) 0.8 and (c) 1.0

Table 5.15 shows that the degradation process has occurred in two stages; initial degradation occurs in hard segments and involves urethane linkage (involving two steps degradation), while second stage involves the degradation step of soft segments. It is known that the first stage degradation not only involves urethane bond decomposition but also the amount of residue (Table 5.16) which is correlated with the amount of unreacted isocyanate present in the polymers.

Table 5.15: Thermal degradation data and percentage of weight loss of modified semi-rigid polyurethane films

Sample code	**Degradation temperature**						**Weight loss**		
	1st step^a				**2nd step^b**		**(%)**		
	T_{1onset} (°C)	**T_{1max} (°C)**	**T_{2onset} (°C)**	**T_{2max} (°C)**	**T_{3onset} (°C)**	**T_{3max} (°C)**	**m_1**	**m_2**	**$m_3{}^c$**
PU7T1*	202	270	301	330	359	495	9.9	16.1	67.4
PU8T1*	201	275	306	330	361	497	9.7	15.6	63.8
PU9T1*	221	300	312	350	362	500	16.5	17.9	58.1
PU10T2**	210	275	300	327	359	500	13.1	15.7	65.9
PU11T2**	220	275	296	330	360	550	9.9	15.6	57.0
PU12T2**	173	275	298	335	361	560	17.0	13.7	52.9
PU13T3***	209	275	301	325	359	500	12.9	18.9	59.1
PU14T3***	265	280	306	340	362	575	15.5	20.7	56.3
PU15T3***	267	285	308	350	362	580	16.0	21.0	56.5

Note: a = temperature of first step of degradation, b = temperature of second step of degradation
c = rate of maximum degradation (weight % loss/min) at T_{3max}
* FLNR-17700, ** FLNR-20000 and *** FLNR-28700

Table 5.16: Percentage of weight loss of residue

Sample codes	**Soft segment (%)**	**Hard segment (%)**	**Residue**
			Weight loss (%)
			m_4
PU7T1	71.33	23.51	0.49
PU8T1	67.17	28.90	0.72
PU9T1	62.95	33.48	1.32
PU10T2	67.25	27.83	0.77
PU11T2	66.49	29.10	5.8
PU12T2	56.95	38.36	7.8
PU13T3	59.25	35.08	1.8
PU14T3	54.76	40.77	1.32
PU15T3	48.32	44.75	1.35

From Table 5.15, it indicates that in the first step a weight loss of 9 - 17 % has occurred at about 200 – 260°C, because of releasing trapped solvent and decomposing of some peroxide linkages produced from FLNR especially for the higher polyol length. In the second step, a rapid weight loss starting approximately at 270°C and continues up to 360-362°C. This decomposition step corresponds to the breaking of urethane bond and the decomposition temperature shifts to higher temperature as polyol length is increased. The third degradation step is related to the decomposition of soft segments. From Figure 5.17(a), a uniform trend is observed which is the increase of thermal stabily due to the increase of polyol length. Sample PU13T3 that is comprised of FLNR-28700 have the highest T_{3max} for [NCO]/[OH] ratio of 0.6 compared to samples PU7T1 and PU10T2. The residual mass also shows a higher value with a higher polyol length. Thus, at the low ratio of [NCO]/[OH], the soft and hard segments are well incorporated in each other.

On average, the decomposition temperature at different percentage of weight loss and residual mass are higher at higher polyol length. This also implies that the semi-rigid PU samples with longer polyol length will present higher thermostability and validates the enhancement of physical crosslinking. The high values of residual mass percentage of samples PU11T2 and PU12T2 are probably due to the soft segment not being incorporated well with the hard segment to allow crosslinking in soft segment.

Besides that, the T_{max} values for samples PU9T1, PUPU12T2 and PU15T3 for semi-rigid PU with [NCO]/[OH] ratio of 1.0 is more thermally stable than the low ratios. This is because, the temperature for the complete decomposition for [NCO]/[OH] ratio of 1.0 is higher especially for longer polyol length (FLNR-28700). The increase in [NCO]/[OH] ratio means increase in the isocyanate content, thus hard segment content of the semi-rigid PU increases. More hard segments allow more effective intermolecular hydrogen bonding between the segments. As the percentage of hard segments increases, the intermolecular attraction between hard and hard segments due to hydrogen bonding between N-H and C=O of hard segments leads to higher temperature that is needed for complete decomposition of the samples.

It is noted that an increase in polyol length with high [NCO]/[OH] ratio can lead to higher thermal stability. Semi-rigid PU samples containing low polyol lengths for samples PU7T1, PU8T1 and PU9T1 (FLNR-177000) and samples PU10T2, PU11T2 and PU12T2 (FLNR-20000) at low [NCO]/[OH] ratio of 0.6 and 0.8 remained stable up to 270°C. But, the semi-rigid PU with low polyol length and [NCO]/[OH] ratio of 1.0 showed low stability contrast with the higher polyol length for samples PU13T3, PU14T3 and PU15T3 (FLNR-28700). In addition, sample PU8T1 (FLNR-20000 with [NCO]/[OH] ratio of 0.8) and sample PU12T2 (FLNR-20000 with [NCO]/[OH] ratio of 1.0) displayed low decomposition temperatures for urethane degradation probably due to the soft phase being more dominant in the semi-rigid PU structure compared to the hard phase.

The behaviour of DTG curves are illustrated in Figure 5.18 (a) - (c). The curves corresponding to the semi-rigid PU with [NCO]/[OH] ratio of 0.8 for samples PU8T1, PU11T2 and PU14T3 have more complex behaviour than the semi-rigid PU with [NCO]/[OH] ratio of 0.6 for samples PU7T1, PU10T2 and PU13T3) and [NCO]/[OH] ratio 1.0 for samples PU9T1, PU12T2 and PU15T3). The curves show that the degradation of samples is not a random process specially to PU11T2 with [NCO]/[OH] ratio of 0.8 (Figure 5.18 (b)). The urethane linkages seem to have stabilizing effect on the degradation process of FLNR soft segments, forming more stable intermediate species which reduce the stages of degradation.

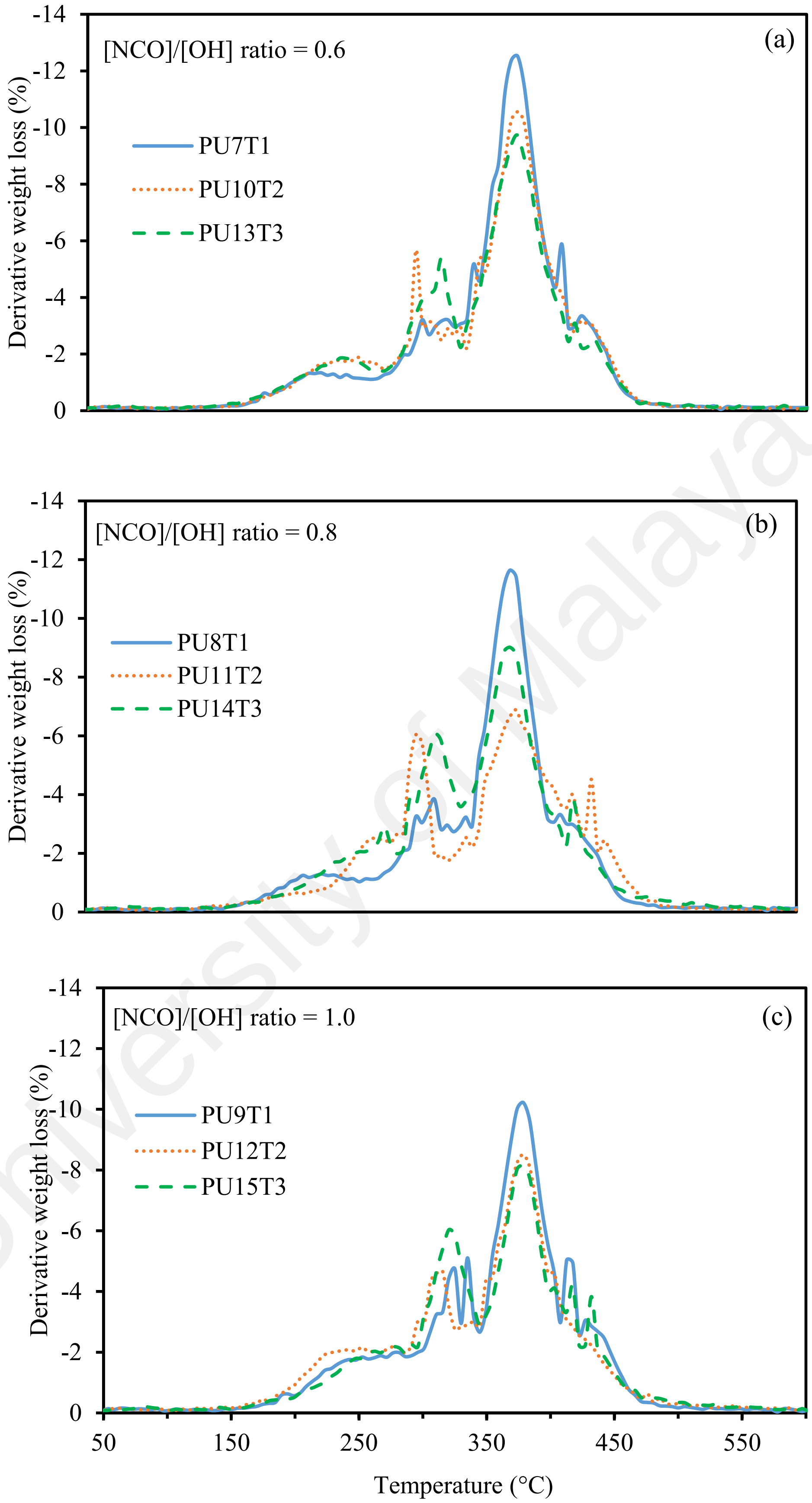


Figure 5.18: Differential weight loss curves of modified semi-rigid polyurethane based on different molecular weights at [NCO]/[OH] (a) 0.6, (b) 0.8 and (c) 1.0

Figure 5.18 (a) and (c) show more uniform process of degradation of semi-rigid PU samples. The increase of [NCO]/[OH] ratio (from 0.6 to 1.0) leads to higher thermal stability of the samples. This is due to more hydrogen bonds being formed between carbonyl in the soft segments and N-H in the hard segments because of the greater polarity of urethane groups. The DTG curves show that the hard segment content has a strong influence on the thermal profile of the samples.

5.4 Ageing performance and degradability of semi-rigid polyurethane

The ageing performance and degradability study were determined to perceive the significance of semi-rigid PU film especially in biomaterial purposes. The ageing under outdoor exposure and end-use continuous exposure lead to loss of properties due to degradation of polymer. In this study, the selected routes of degradation are dissolution by organic solvents, hydrolysis and oxidation induced by various chemical environments and microbial degradation were conducted.

5.4.1 Stability in organic solvents

The stability of semi-rigid PU samples was conducted for 60 days by immersing in different types of solvents. The non-reactive chemical environment influences the stability of semi-rigid PU by solvation and dissolution of polymers. Aromatic organic solvent like toluene which is compatible for dissolution of rubber based polyol and DMF and DMSO which are commonly compatible for dissolution of PU materials were selected for the present work. In addition to these organic solvents, the commonly used organic solvent such as chloroform and THF were also used in this work.

Table 5.17: Percentage weight loss of modified semi-rigid polyurethane in chemical solvents for 60 days degradation

Sample code	**[NCO]/[OH] ratio**	**Weight loss (%)**				
		toluene	**chloroform**	**THF**	**DMF**	**DMSO**
PU7T1*	0.6	100	100	100	44.7	31.33
PU8T1*	0.8	100	100	100	44.1	36.75
PU9T1*	1.0	100	100	100	42.0	44.66
PU10T2**	0.6	100	100	100	34.4	40.98
PU11T2**	0.8	100	100	100	38.1	40.92
PU12T2**	1.0	100	100	100	48.3	43.12
PU13T3***	0.6	75	80	100	36.1	35.42
PU14T3***	0.8	50	50	50	40.3	37.23
PU15T3***	1.0	40	40	40	42.1	38.13

Note: * FLNR-17700, ** FLNR-20000 and *** FLNR-28700

Table 5.17 shows that the non-polar solvent (toluene and chloroform) and polar aprotic solvent (THF) affect almost all the semi-rigid PU samples, i.e. PU7T1, PU8T1, PU9T1, PU10T2, PU11T2 and PU12T2. These samples have high soft segment present in the PU with [NCO]/[OH] ratio of 0.6 and 0.8, giving the 100% degradatation. In comparison, samples PU13T3, PU14T3 and PU15T3 that comprise of low soft segments with NCO]/[OH ratio of 1.0 are not fully degraded. The increase of urethane groups inside the film samples hindered the THF, chloroform and toluene to penetrate into polymer matrix. The non-polar solvents (chloroform and toluene) exhibit the degradability by these solvents and dissolution of these semi-rigid PU samples. As discussed in Section 5.2.3 and Section 5.3.2, the presence of rubber material gave the main effect. The rubber based materials are normally miscible and easily attacked by non-polar solvent. Only THF solvent having low dielectric constant is shown to be a suitable polar solvent allow these PU types samples to be soluble. THF is classified as borderline polar aprotic solvent that has low dielectric constant and intermediate polarity than the non-polar solvents.

Meanwhile, DMF and DMSO solvents did not affect these semi-rigid PU samples and only partly degraded with low percentage weight loss. DMF and DMSO solvents are categorized as a polar aprotic solvents that have large dielectric constants (>20) and large dipole moments, but do not participate in hydrogen bonding (no O-H or N-H bonds). Based on Table 5.17, the trend of percentage weight loss for film samples that were attacked by DMF and DMSO increases with increasing the [NCO]/[OH] ratio. The samples PU9T1, PU12T2 and PU 15T3 with [NCO]/[OH] ratio of 1.0 have a high percentage weight loss. It is believed that the DMF and DMSO solvents attack more of the urethane (hard phase) compared to the polyol (soft phase). It is contrasts to samples PU7T1, PU10T2 and PU13T3 with short polyol length that not highly affected by DMF and DMSO. The weight loss increases with increasing the [NCO]/[OH] ratios indicates that these types of solvents attack mainly at the soft phase domain.

5.4.2 Stability in hostile chemical environment

PUs are widely used in medical devices due to their broad property range, processing flexibility and biocompatibility. Increasingly, these devices are subjected to longer duration use, and exposed to a wide variety of chemically active agents. The hostile reactive chemical environment such as acid, base and oxidizing agent also induces degradation of PU. Dilute acids and bases induce hydrolytic attack on PU materials, while oxidizing agent induces oxidation of PU. Acid and base induced hydrolysis is similar with water induced hydrolysis, though the magnitude of hydrolytic degradation is larger in the case of the former. Table 5.18 shows the weight loss changes of film samples in various chemical environments.

Table 5.18: Percentage weight loss of modified semi-rigid polyurethane films in hostile chemical environment

Sample codes	**[NCO]/[OH] ratio**	**Weight loss (%)**		
		1.0 N NaOH	**1.0 N HCl**	**30% H_2O_2**
		Alkaline	**Acidic**	**Oxidant**
PU7T1*	0.6	6.60	0.00	65.33
PU8T1*	0.8	0.00	6.59	18.28
PU9T1*	1.0	3.49	8.54	22.83
PU10T2**	0.6	2.73	2.31	39.58
PU11T2**	0.8	6.67	2.78	6.06
PU12T2**	1.0	8.86	6.33	23.08
PU13T3***	0.6	2.98	17.07	10.48
PU14T3***	0.8	1.92	5.75	0.00
PU15T3***	1.0	2.16	4.87	0.00

Note: * FLNR-17700, ** FLNR-20000 and *** FLNR-28700

The semi-rigid PUs are found to be more stable in alkaline condition but less stable in oxidant environment. The decreased stability of samples PU11T2 and PU12T2 may be attributed to the fact that as the polyol length of semi-rigid PU increases, the distance between networks of soft and hard phases increases leading to weaker network structure even though at high urethane content. On the other hand, for the highest polyol length samples, i.e. PU14T3 and PU15T3 with high [NCO)]/[OH] ratios of 0.8 and 1.0, the stability becomes much controllable probably due to the network of long chain polyol which consists of high functionality and will form the crosslink network, thus will hinder the alkaline solution from attacking further. From Table 5.18, the stability of the semi-rigid PU films towards alkaline solution at lowest polyol length (PU8T1 sample) with [NCO]/[OH] ratio of 0.8 is maintained as there was no change in weight loss.

The oxidant environment gives low stability for all samples, except sample PU11T2 with small changes and no change in weight loss is observed for samples PU14T3 and PU15T3. So, the high stability is found for the semi-rigid PU samples with longer soft segment length and high urethane content. In this case, the oxidation of semi-rigid PU largely occurs at low [NCO]/[OH] ratio, i.e. sample PU7T1 and it shows that the degradation is more prominent at soft phase compared to hard phase.

The results for acidic stability differ from both alkaline and oxidant stability. No weight loss changes are found for sample PU7T1 containing the lowest [NCO]/[OH] ratio of 0.6 and shorter polyol length (FLNR-17700). In this situation, the acid solution has decomposed the hard phase more compared to soft phase. However, from the overall results obtained, the mild degradation observed in higher [NCO]/[OH] ratio of film samples is probably due to the advantageous aspect of crosslinked structure of these PU materials.

5.4.3 Environmental resistance

PU materials can be used under many environmental conditions, but not all conditions can be accepted. In the present work, the soil burial degradation has been carried out for evaluation of environmental resistance for semi-rigid PU films. The use of soil burial degradation is one of the methods to see either microbial degradation takes place on the polymer materials. The polyether-based PUs have been shown to be significantly superior in humid conditions and in acidic or basic environments (Mohan & Srivastava, 2011). They exhibit high hysteresis and some of them can heat up easily. In addition to their physical properties, the resistant to microbial attack and hydrolysis depend on the soft segment and hard segment contents. These criteria are similar to the current study that propose the rubber polyol based PU can have effect on degradation behaviour. Furthermore, it is believed that the humid conditions and alkaline environment play the important role in this degradation behavior.

The percentage weight loss for outdoor and indoor in soil burial degradation tests are listed in Table 5.19. Generally, the percentage weight loss in relation to [NCO]/[OH] ratio depends on hard and soft segments. The semi rigid PU samples with low hard segment content, i.e PU7T1 and PU8T1, show high degradation compared to PU samples with high hard segment content phase, i.e. PU14T3 and PU15T3. From the previous research, the most fruitful biodegradation test is laboratory test (indoor test) because of the optimized condition for the activity of the particular microorganisms is controlled by temperature, humidity and pH conditions (Mohan & Srivastava, 2011). Polymers often exhibit a much higher degradation rate in laboratory test than observed under natural conditions (outdoor test). In this work, the opposite result was obtained where the biodegradation for the outdoor test is more compared to indoor test.

Table 5.19: Weight loss of modified semi-rigid polyurethane under soil burial test

Sample code	**[NCO] /[OH] ratio**	**Soft segment (%)**	**Outdoor (field test)**			**Indoor (laboratory test)**		
			Weight		**Weight loss (%)**	**Weight**		**Weight loss (%)**
			Initial	**Final**		**Initial**	**Final**	
PU7T1*	0.6	71.33	0.0119	0.0098	15.96	0.0147	0.0137	6.80
PU8T1*	0.8	67.17	0.0140	0.0126	10.23	0.0148	0.0139	6.71
PU9T1*	1.0	62.95	0.0206	0.0190	7.49	0.0209	0.0195	6.66
PU10T2**	0.6	67.25	0.0167	0.0151	9.99	0.0261	0.0242	7.19
PU11T2**	0.8	66.49	0.0135	0.0124	8.46	0.0140	0.0130	7.01
PU12T2**	1.0	56.95	0.0174	0.0162	6.57	0.0178	0.0171	4.07
PU13T3***	0.6	59.25	0.0283	0.0261	8.40	0.0210	0.0206	2.11
PU14T3***	0.8	54.76	0.0177	0.0163	6.51	0.0153	0.0152	1.09
PU15T3***	1.0	48.32	0.0069	0.0064	5.97	0.0039	0.0039	1.02

Note: * FLNR-17700, ** FLNR-20000 and *** FLNR-28700

From Table 5.19, the percentage weight loss of indoor test is lower than outdoor test especially for the high hard segment samples, i.e. PU13, PU14T3 and PU15T3, indicating that the outdoor test has higher degradation compared to indoor test. This is probably due to the humidity effect from the heavy rain causing microbial degradation of polymers. From the meteorology report (60 days from 28th April to 28th June 2015)

(Appendix C11), the soil burial test was conducted during the heavy rain with high water level on the test area (top roof of Block C, Fakulti Sains, Universiti Malaya). The humid and watery condition could probably have caused the increase in the microbial activity compared to the hot weather.

The increase in percentage weight loss has been attributed to the increase of soft phase presence in rubber polyol. The amorphous soft phase degrades faster compared to the crystalline hard phase. The urethane structure consisting of isocyanates and chain extender as a hard phase can delay or hinder the microorganism's activity to attack further on the samples. This condition is shown by samples PU14T3 and PU15T3 which have high urethane linkage giving lower changes on weight loss compared to samples PU7T1 and PU8T1. Synthetic condensation polymers are generally biodegradable based on the factors of chain coupling (ester>ether>amide>urethane), molecular weight (lower is faster than higher), morphology (amorphous is faster than crystalline), hardness (softer is faster that harder) and hydrophilicity versus hydrophobicity (hydrophilic is faster than hydrophobic) (Mohan & Srivastava, 2011). In this work, samples PU7T1, PU8T1 and PU10T2 consist with higher soft segment contents and gave the high changes in weight loss. These results show that the soft phase based on rubber material as amorphous phase gave the significant effect on percentage weight lost.

CHAPTER 6: CONCLUSION

In this study, FLNR with OH functionality was successfully synthesized and developed based on the existence peak of OH bond at 3425 and 1128 cm^{-1}. FLNR with OH functionality as a renewable polyol source was selected to be used as a precursor for semi-rigid PU preparation. Depolymerization and hydroxylation occurred simultaneously, i.e. *in situ* by redox method using low quality NR to obtain the FLNR. Both the scission and oxidant reagents, H_2O_2 and $NaNO_2$, were found to have influence on the properties of the FLNR formed. Relationship between processing factors for feed ratio of H_2O_2/isoprene unit and $NaNO_2/H_2O_2$ that influences the number average molecular M_n, MWD and OH value of FLNR as developed using RSM, showed that the polynomial models to predict M_n, MWD and OH value was two-factor interaction, linear and reduced cubic, respectively. The optimization confirmation was done, and the minor error of percentage calculated from the predicted and observed responses was obtained.

The preparation of semi-rigid PU was formulated by one step (*one-shot*) and two step (*two-shot*) methods. Comparison of semi-rigid PU prepared by *one-shot* and *two-shot* methods of the same and also different molecular weights of polyol precursors proved that the segmented interaction determined the solubility behavior and thermal stability of these materials. It was identified that the *two-shot* method was better than the *one-shot* method in terms of thermal processing of polymers according to the reaction time of preparation. From solubility test, the *two-shot* method offered advantages over *one-shot* method in polymerizing incompatible monomers. The rubber based polyol that formed the pre-polymer from the *two-shot* method changed the solubility character of the film products, thus enabling preparation of a more homogeneous polymer during chain extension in the second step as all the polyol hydroxyls are reacted with diisocyanate in the first step. The differences in glass transition temperatures obtained indicated stronger interaction between hard and soft segments in semi-rigid PU produced by *two-shot* method. The interaction increased when the high molecular weight of polyol was used. For *one-shot* method, a non-uniform trend of transition behavior was observed. Thermal stability as presented by TGA thermograms and DTG curves showed that the chain extender and soft segment length had a strong influence on thermal stability of the whole film samples.

Besides thermal stability, the *two-shot* method films of semi-rigid PUs preparation also showed better physical and chemical on degradable stability. The stability on degradability is heavily dependent on percentage of soft and hard segments in terms of various polyol lengths and [NCO]/[OH] ratios. The chemical and solvent resistivities and the soil degradation showed that the lowest polyol length and lowest [NCO]/[OH] ratio samples gave higher degradability. This indicates that amorphous phase (rubber polyol) plays an important role in the degradable performance.

In addition, the optimization method in the production of FLNR as precursor for semi-rigid PU using RSM was developed. Overall, the results showed that FLNR with targeted properties from low grade NR modification, could be used as good precursor for the semi-rigid PU by *two-shot* method.

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List of Publications and Papers Presented

Published articles / Publications:

1. **Radin, S. F. N. H.**, Ahmad, D. A., Rosiyah, Y., Aziz, H. and Hairani, T. (2018). The behaviour of semi-rigid polyurethane film based on functionalized rubber by *one-shot* and *two-shot* method preparation. *Journal of Materials Science*, *53*, 13280-13290.

2. **Radin, S. F. N. H.**, Rosiyah, Y. & Aziz, H. (2018). Preparation of one-shot and two-shot method of semi-rigid polyurethane film based on functionalized liquid natural rubber. *AIP Conference Proceedings 1985*, 1-8.

3. **Radin, S. F. N. H.**, Ahmad, D. A., Rosiyah, Y. & Aziz, H. (2015). Optimizing the usability of unwanted latex yield by *in-situ* depolymerization and functionalization. *Industrial Crops & Products*, *74*, 773-783.

Presentations:

1. 4th Federation of Asian Polymer Societies International Polymer Congress 2015 (4FAPS-IPC 2015). 5-8 October 2015. PWTC Kuala Lumpur. Semi-Rigid Thermoplastic Polyurethane Film Based on Hydroxylated Liquid Natural Rubber.

2. 5th International Conference on Functional Material and Devices 2015 (ICFMD 2015. 4-6 August 2015. New York Hotel, Johor Bahru. Functionalized Liquid Natural Rubber Based Thermoplastic Polyurethane Membrane from Unwanted Latex Yield.

3. The 6th International Conference on Postgraduate Education (ICPE-6 2014). 17-18 December 2014. UTeM Melaka, Malaysia. Optimization of Processing Parameter by Response Surface Methodology for Functionalized Liquid Natural Rubber as Polyurethane Precursor.