SYNTHESIS AND CHARACTERIZATION OF FLEXIBLE POLYURETHANE FOAM FROM LIQUID NATURAL RUBBER-BASED POLYOL

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ABSTRACT

Flexible polyurethane (PU) foams were prepared using a liquid natural rubber (LNR) -based polyol. At the first stage, the polyol was synthesized by *in –situ* reaction of latex and hydrogen peroxide using sodium nitrite as a degradation agent. At second stage, polyurethane foams were prepared from reaction of the LNR-based polyol with methylene diphenyl 4,4-diisocyanate (MDI) in the presence of catalysts, silicone surfactant, chain extender, and water as the blowing agent.

In this work, thermal degradation of NR was carried out at different temperature to obtain LNR-based polyol by varying the reaction times and concentration of H_2O_2/isoprene ratio. The effect of H_2O_2/isoprene ratio, the molecular weight and polydispersity of the LNR-based polyol decrease with increasing of H_2O_2/isoprene ratio, whereby the average molecular weight of the LNR-based polyol decrease almost half from 31000 to 16000 when H_2O_2/isoprene ratio increase twice from 0.6 to 1.2 mol. These phenomena were due to the chain-scission that may have taken place simultaneously with epoxidation and hydrolysis, resulting in reduced molecular weight of LNR, having the epoxide and hydroxyl groups. Meanwhile, the increase of the H_2O_2/isoprene from 0.6 to 1.0 mol had led to an increase of the hydroxyl value. However, when the ratio H_2O_2/isoprene was increased to 1.2 mol, the hydroxyl value decreased. This phenomenon may be due to the formation of hydrofuran. Besides, the LNR-based polyol synthesized using temperature at 90°C has high the hydroxyl value. The average molecular weights ($\overline{M}_w$) of the LNR-based polyols decreased with increasing reaction time while polydispersity (PDI) indices increased. The average molecular weight, $\overline{M}_w$ in the final product is 15368. The PDI increases with increasing of

the reaction time from 6 to 24 h. However, when the reaction time was increased to 36 h, the PDI decreased rapidly. It can be concluded that the longer reaction time, the lower will be the molecular weight of the products formed.

The LNR-based polyol was used in the production of flexible PU foam. Generally, flexible PU foam is formed by simultaneous reaction between an isocyanate with polyether polyol and water. The increasing water content in the polyurethane formulation produces foams with lower density. Meanwhile, the compression stress of the foams is increases with the increasing of water content in the formulation. These phenomena were due to the formation of urea hard segment when the amount of water content increases. The tensile strength and tear strength of the foams increased with increasing water content. The tensile strength (10.9 kg cm^{-2} for H and 10.7 kg cm^{-2} for K) and tear strength property (0.28 N mm^{-1} for H and 0.27 N mm^{-1} for K) of the foams were at a maximum with 5 g of water content. Meanwhile, the water content of 4 g was chosen as the optimal water content as it produced foam with highest elongation at break (75 % for H and 88 % for K). However, at low water content (2 g), cell structures are smaller and also more uniform. The foams produced using higher water content is thermally more stable.

Irrespective of the starting polyol, increasing of isocyanate index from 90 to 100 causes an increase of foam density but when the isocyanate index increases from 100 to 110, a reduction of the foam density occurred. Foams made using isocyanate index of 100 possessed the highest density (46 $\pm$ 1 kg m^{-3}), in comparison to foams having isocyanate index of 90 and 110, which gave lower densities of 45 $\pm$ 1 kg m^{-3} and 44 $\pm$ 1 kg m^{-3} respectively. Meanwhile, the compression stresses for both MI and NI samples of the PU foams increased with increasing isocyanate index from 90 to 110. The tensile strength and tear strength of the foams increased with increasing of isocyanate index from 90 - 100 but decreased for 110. The isocyanate index of 100 gave the maximum tensile strength for both

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MI and NI (9.9 kg cm^{-2}) and tear strength (0.27 N mm^{-1} for MI and 0.16 N mm^{-1} for NI) respectively. Meanwhile, the elongation at break for foams of MI and NI are decreased when isocyanate index increased. The foams produced from higher isocyanate index are more stable thermally.

ABSTRAK

Busa poliuretan (PU) fleksibel dihasilkan dengan menggunakan poliol getah yang diturunkan dalam bentuk cecair (LNR). Pada tahap pertama, poliol ini disintesiskan melalui tindak balas *in-situ* antara latek dengan peroksida hidrogen menggunakan natrium nitrit sebagai agen degradasi. Pada tahap kedua, busa poliuretan dihasilkan melalui tindak balas antara getah dalam bentuk cecair dengan diphenyl metilena 4,4 diisosianat (MDI) di dalam kehadiran katalis, surfakton silikon, extender rantai dan air sebagai agen bertiup.

Dalam kajian ini, degradasi suhu bagi NR dilakukan pada suhu yang berbeza menghasilkan getah dalam bentuk cecair melalui masa tindak balas dan nisbah keperkatan H_2O_2/isoprene. Kesan daripada nisbah H_2O_2/isoprene, berat molekul dan polidispersiti bagi getah cecair menurun dengan peningkatan nisbah H_2O_2/isoprene, di mana berat molekul bagi getah cecair menurun hampir separuh daripada 31000 kepada 16000 bila nisbah H_2O_2/isoprene meningkat 2X dari 0.6 kepada 1.2 mol. Kejadian ini terjadi apabila pemutusan rantai berlaku serentak antara epoksidasi dan hidrolisis menghasilkan berat molekul yang rendah dan mempunyai kumpulan epoksida dan hidroksil. Manakala, kenaikkan nisbah H_2O_2/isoprene dari 0.6 kepada 1.0 mol menyebabkan kenaikkan nilai hidroksil. Walau bagaimanapun, bila nisbah H_2O_2/isoprene meningkat kepada 1.2 mol, nilai hidroksil menurun. Ini berlaku disebabkan oleh pembentukan hidrofuran. Selain itu, getah cecair yang dihasilkan pada suhu 90^oC mempunyai nilai hidroksil yang lebih tinggi. Purata berat molekul bagi getah cecair menurun dengan peningkatan masa tindak balas sementara indek polidispersiti meningkat. Purata berat molekul terakhir bagi getah cecair adalah 15368. PDI meningkat dengan peningkatan masa tindak balas dari 6 ke 24 jam. Walau

bagaimanapun, bila masa tindak balas meningkat 36 jam, PDI menurun. Kesimpulannya, lagi panjang masa tindak balas, berat molekul bagi produk menjadi semakin rendah.

Getah cecair digunakan di dalam penghasilan busa poliuretan fleksibel. Secara umum, busa poliuretan fleksibel terbentuk melalui tindak balas serentak antara poliisosianat dengan poliol polieter dan air. Kenaikkan kandungan air di dalam formula poliuretan menghasilkan busa dengan ketumpatan yang rendah. Manakala, mampatan stress meningkat dengan peningkatan kandungan air di dalam formula. Fenomena ini terjadi kesan daripada pembentukan segmen urea keras bila kandungan air meningkat. Kekuatan regangan dan koyakan bagi busa meningkat dengan peningkatan kandungan air. Maksimum kekuatan regangan (10.9 kg cm^{-2} untuk H dan 10.7 kg cm^{-2} untuk K) dan sifat kekuatan koyakan (0.28 N mm^{-1} untuk H dan 0.27 N mm^{-1} untuk K) adalah pada 5 g kandungan air. Kandungan air pada 4 g dipilih sebagai kandungan air optimum di dalam menghasilkan busa dengan pemanjangan paling tinggi (95% untuk H dan 88% untuk K). Namun begitu, pada kandungan air yang rendah, struktur sel adalah kecil dan serupa. Busa yang dihasilkan daripada kandungan air yang tinggi lebih stabil.

Peningkatan indek isosianat daripada 90 kepada 100 menyebabkan ketumpatan busa meningkat tetapi bila indek isosianat meningkat daripada 100 kepada 110, penurunan ketumpatan busa berlaku. Busa yang dihasilkan daripada indek isosianat 100 mempunyai ketumpatan paling tinggi (46 ± 1 kg m^{-3}) berbanding indek isosianat 90 dan 110 yang mempunyai ketumpatan rendah 45 ± 1 kg m^{-3} dan 44 ± 1 kg m^{-3}. Manakala, mampatan stress bagi kedua-dua busa MI and NI meningkat dengan peningkatan indek isosianat daripada 90 kepada 110. Kekuatan regangan dan koyakan busa meningkat dengan peningkatan indek isosianat daripada 90 kepada 100 tetapi menurun pada 110. Indek isosianat 100 memberi kekuatan regangan bagi MI and NI (9.9 kg cm^{-2}) dan kekuatan koyakan (0.27 N mm^{-1} untuk MI dan 0.16 N mm^{-1} untuk NI) maksimum. Manakala,

pemanjangan busa bagi MI dan NI menurun bila indek isosianat meningkat. Busa yang

dihasilkan daripada indek isosianat tinggi adalah lebih stabil.

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LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CHDI	Cyclohexyl diisocyanate
CFC	Chlorofluorocarbon
DSC	Differential scanning calorimetry
DRC	Dry rubber content
DMF	Dimethylformamide
DBTDL	Dibutyltin dilaurate
DMA	Dynamic Mechanical Analysis
EO	Ethylene oxide
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
H_2O_2	Hydrogen peroxide
HDI	Hexamethylene diisocyanate
HMDI	Hydrogenated diphenylmethane diisocyanate
$K_2S_2O_8$	Potassium persulfate
LNR	Liquid natural rubber
MDI	Methylene diphenyl 4,4-diisocyanate
MST	Mechanical stability time
MOE	Modulus of elasticity
$\overline{M}_w$	Average molecular weight
$\overline{M}_n$	Number average molecular weight

NaNO$_2$	Sodium nitrite
NH$_3$	Ammonia
NDI	1,5-Naphthalene diisocyanate
NMR	Nuclear Magnetic Resonance
NR	Natural rubber
PO	Propylene oxide
PU	Polyurethane
phr	part hundred resin
ppm	part per meter
RIM	Reactive injected moulded
SAXS	Small Angle X-ray Scattering
T$_g$	Glass transition
Tan δ	Tan delta
TSC	Total solid content
T9	Stannous octoate
TGA	Thermogravimetric Analysis
TDI	Tolylene diisocyanate
wt%	Percentage of weight loss
LNR	Liquid natural rubber
H$_2$O$_2$	Hydrogen peroxide
DEA	Diethylolamine
A1	70% bis(dimethylaminoethyl)ether and 30% diproylene glycol

CHAPTER 1

INTRODUCTION

1.1 Polyurethane

Polyurethanes are among the most important class of specialty polymers. The term polyurethane includes materials that are not derived from polymerizing a urethane monomer, nor polymers containing primarily urethane groups. Polyurethanes include those polymers containing a plurality of urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain. Thus, a typical polyurethane may contain, in addition to the urethane linkage, aliphatic and aromatic hydrocarbons, esters, ethers, amide, urea and isocyanate groups.

The chemistry of urethanes makes use of the reactions of organic isocyanates with compounds containing active hydrogens. When polyfunctional isocyanates and intermediates containing at least two active hydrogens per mole are reacted at proper ratios, a polymer results that can produce rigid or flexible foams, elastomers, coatings, adhesives and sealants. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkage, as shown in **Equation 1.1**

$$HO{-}R{-}OH \ + \ O{=}C{=}N{-}R'{-}N{=}C{=}O \longrightarrow HO{-}R{-}O{-}\underset{\underset{O}{\|}}{C}{-}N{-}R'{-}N{=}C{=}O$$

POLYOL   ISOCYANATE   URETHANE
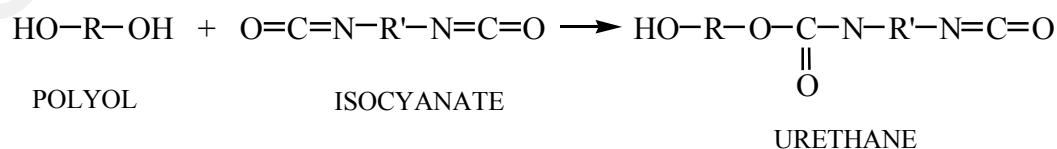
Equation 1.1: Formation of urethane

Polyurethanes are a heterogeneous family of polymers unlike PVC, polyethylene, or polystyrene. The mechanical properties and morphological structure of polyurethane depend mainly on polyol structure, molar mass, its functionality and isocyanate used. The stoichiometric ratios of isocyanate to hydroxyl group, the amount of chain extender used and the processing method also have significant effects on the polyurethane properties. Polyurethanes are used in a surprising array of commercial applications. **Figure 1.1** presents the universe of polyurethanes applications. For convenience, the applications can be divided into seven major groups: flexible slab, flexible molded foams, rigid foams, solid elastomers, RIM, carpet backing, and two component formulations.
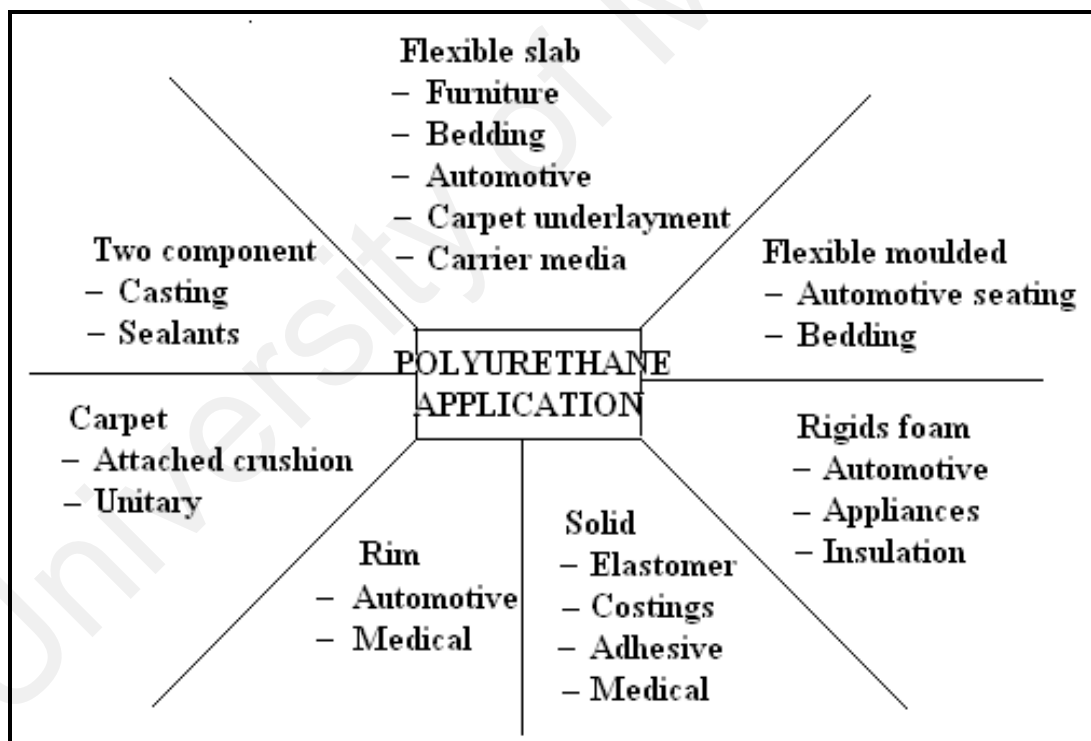
Figure 1.1: The application of polyurethane [1].

1.2 Types of polyurethane foam

Foams are microcellular structure, produced by gas bubbles formed during the polyurethane polymerization mixture. The process of bubble formation in polyurethane foams is called blowing. The blowing reaction is one of several reactions occurring in the final polyurethane mixture while it is forming. The chemical ingredient in the formulation that provides the gas is called the blowing agent. Polyurethane foam can be divided to three categories: flexible foam, rigid foam and semi-flexible foam. Flexible polyurethane foam is most often used in bedding and upholstery, while the more rigid variety is used for thermal insulation and in automobile dashboards.

1.2.1   Flexible polyurethane foam

Flexible polyurethane foams are used in many applications because they are easy to handle and provide excellent cushioning and physical properties [1]. They are used in variety of commercially established applications like mattresses, automotive and furniture cushions, carpet backing and packaging. Flexible polyurethane foams are produced by slab stock or molded process. Some materials can substitute for this application of polyurethane foam, such as polyester fiber or steel springs. However, polyester fiber does not recover nearly as well as foam does after compression. Steel springs recover well, but can become noisy as they get worn out. They also require some form of cushioning between them and the user.

1.2.2 Rigid polyurethane foam

Rigid polyurethane foam has many relevant applications in construction. Many odd and detailed shapes such as sculptures and domed ceilings are far easier to make with foam than with wood. Some manufacturers sell specialty rigid foam that is used to replace wood in carved signs and three-dimensional topography models. It is also used as home insulation, rigid boat hulls, tennis racket grips, and even surfboards.

1.2.3 Semi-rigid polyurethane foam

In addition to the flexible and rigid types, semi-rigid polyurethane foam also exists, and is used extensively in automobile interiors. Seats, armrests, and headrests are frequently made from the semi-rigid variety of this material. In the case of seats, the polyurethane foam is formed in a mold, and then removed and upholstered. Like flexible foams, semi-rigid foams have more than 90% open cell structure. A fundamental difference, however, between semi-rigid and flexible foams is the considerably higher compression hardness of the semi-rigid foams. If other properties, such as tensile strength, elongation, tear strength and resilience are measured, semi-rigid foams will displays properties intermediate between flexible and rigid plastics. Semi-rigid molded foams are produced by the prepolymer production method.

1.3   Base raw material for the production of polyurethane foam

1.3.1   Isocyanates

Isocyanates with two or more functional groups are required for formation of polyurethane (PU) polymer. The diisocyanates utilized in polyurethane chemistry can be either aliphatic or aromatic. Many commercial grades of diisocyanates used for making polyurethanes are aromatic in nature. Firstly, the aromatic linked isocyanate group is more reactive than the aliphatic one. Second, aromatic isocyanates are more economical to use.

Polyurethanes from aliphatic polyisocyanates are often more sensitive to light induced degradation than the yellowing aromatic polyurethanes, especially when combined with polyethers. Each isocyanate will give different properties to the end product, requiring different curing systems and, in most cases, different processing systems.

An important property of an isocyanate is its functionality, i.e. the number of isocyanate groups (-NCO) per molecule. The higher functionality isocyanates are used for special applications. When a di-functional isocyanate is used with a di-functional polyol a long linear polyurethane molecule for elastomeric applications is formed.

Aromatic diisocyanates. More than 90% of polyurethanes are still produced from aromatic diisocyanates. The most important aromatic diisocyanates are shown in **Figure 1.2**.
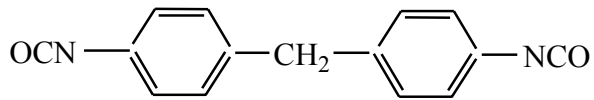
a) Methylene diphenyl 4,4-diisocyanate (MDI)

2,4-TDI

2,6-TDI
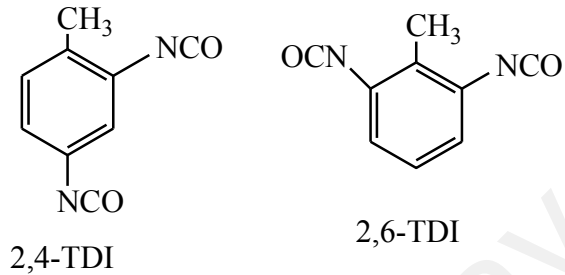
b) Tolylene diisocyanate (TDI)
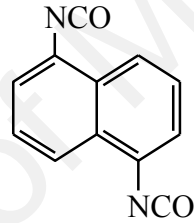
c) 1, 5-Naphthalene diisocyanate (NDI)

Figure 1.2: Structures of aromatic diisocyanates: a) MDI b) TDI and c) NDI

Aliphatic diisocyanates. Linear aliphatic, such as hexamethylene diisocyanate (HDI), hydrogenated diphenylmethane diisocyanate (HMDI), etc. or cycloaliphatic diisocyanates, such as cyclohexyl diisocyanate (CHDI) are more stable under UV compared to their aromatic counterparts. The structure aliphatic diisocyanates are shown in **Figure 1.3**.

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OCN-$(CH_2)_5$NCO

a) HDI

NCO—⬡—CH_2—⬡—NCO

b) HMDI

OCN—⬡—NCO
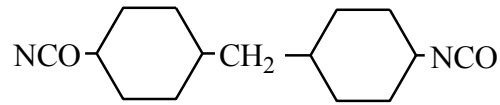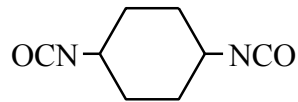
c) CHDI

Figure 1.3: Structures of aliphatic diisocyanates: a) HDI b) HMDI and c) CHDI

1.3.2 Polyols

There are two main types of polyols used in the polyurethane industry namely, polyethers and polyesters. Typical polyols used are shown in **Figure 1. 4**.

$$HO(CH_2)_2 + OCO(CH_2)_4CO + O(CH_2)_2 — OH$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad_n$$
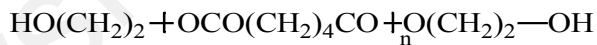
Polyethylene adipate (polyester)

$$HO-((CH_2)_4O)_n \quad H$$
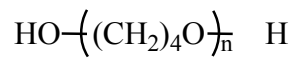
Poly(tetramethylene ether)glycol (polyether)

Figure 1.4: Typical polyols

1.3.2.1 Polyethers

The more widely used polyethers have a relatively low molecular weight in the range of 500 to 3000 and are manufactured from propylene oxide (PO) and ethylene oxide (EO).

PO is the major constituent of the polyol, whereas EO is only included in small amounts to modify the properties of the polyol.

The functionality of the polyether polyol (number of active hydroxyl groups per molecule) can be varied and is normally 2 for elastomers, approximately 3 for flexible foams and up to 6 or more for rigid foams.

1.3.2.2 Polyesters

The polyester polyols are typically produced by the condensation reaction of a diol such as ethylene glycol with a dicarboxylic acid.

Polyester polyols tend to be more expensive and are usually more viscous and difficult to handle but develop polyurethanes with superior tensile, abrasion, flexing and oil resistance properties. Consequently they are used to make PUs for more demanding applications.

1.3.3   Common additives

1.3.3.1   Catalyst

Catalysts have a key role in polyurethane production being required to maintain a balance between the reaction of the isocyanate and polyol. The combination of very complex polyurethane chemistry and diverse processing and moulding conditions make great demands of the catalyst. Its main function is to exploit the diverse reactions to create a product with the desired properties. There are two main classes of catalyst used in polyurethane production.

1) Organometallics are used to accelerate the reaction and formation of urethane linkages and hence promote rapid curing. The most popular organometallic catalysts are dibutyltin dilaurate (DBTDL) and stannous octoate. Tin catalysts are used to catalyse micro cellular elastomers and reactive injected moulded (RIM) systems.

2) Amines are the other major class of catalysts widely used in the making of PU foams. Some amine catalysts promote crosslinking whilst others assist in controlling the cell structure of the foam. A list of typical amine catalyst used in polyurethane foams is given in **Table 1.1**.

Table 1.1: Polyurethane foam catalysts

Catalyst	Application
Triethylenediamine	General purpose gel catalyst
Bis(N,N-dimetylaminoethyl)ether	Blowing catalyst for flexible foam
N,N,N-trimethyl-N-hydroethyl bis(aminoethyl)ether	Blowing catalyst and low odour in foam

1.3.3.2 Chain extenders

Chain extenders are low molecular weight reactant that produces the familiar elastomeric properties of the polyurethanes. Chain extenders typically have molecular weights in the range 40 to 300 Daltons and can be classified as either hydroxyl-terminated or amine terminated. The chain extenders provide the hard/ soft segment to segmented polyurethane elastomers. Introduction of high hard segment content in the polyurethane backbone is important in determining the final properties and performance of the polymer. Hard segment content of the polymer urea usually controls the mechanical properties such as modulus and ultimate strength, in addition to the thermal and hydrolytic stability of the finished product. Examples of common chain extenders are shown in **Table 1.2**.

Table 1.2: Examples of common chain extender

Chain extender	Structure
Linear diol: 1,4-butane diol	$HO-CH_2CH_2CH_2CH_2-OH$
Linear amine: ethylene diamine	$H_2N-CH_2CH_2-N_2H$
Branched diol: trimethylol propane	$CH_2-O-CH_2CH_2-OH$ $\mid$ $H_2C-CH_2-C-CH_2-CH_2-OH$ $\mid$ $CH_2-O-CH_2CH_2-OH$

1.3.3.3 Blowing agents

A blowing agent is a substance that is incorporated into a mixture for the purpose of producing foam. Blowing agents are classified as either organic or inorganic. Inorganic agents such as sodium bicarbonate, ammonium carbonate and sodium boron hydride generate gas slowly and the gas produced by these agents is generally difficult to control. Organic agents generate gas much more rapidly. If heated at an appropriate rate, the gas production by an organic agent can be easily controlled.

The reaction between isocyanate with water producing carbon dioxide is the main blowing agent to form polyurethane foam. The stoichiometric amount of water and isocyanate used will determine foam density, provided most of the gas formed is used to expand the urethane polymer. The use of water as chemical blowing agent will generate urea linkages that will increase foam hardness and change other properties [1]. If water content is increased without increasing the isocyanate, foam with coarse cells and harsh textures may be obtained. Lower tensile and tear strengths and compression modulus will result. In addition to water, auxiliary blowing agents may be included in the foam formulation to further reduce the foam density. An example is the use of methylene chloride or fluorocarbon-11 in either polyether- or polyester-based systems for softenings in the resulting foam.

1.3.3.4 Surfactant

A surfactant, or a "surface acting agent," changes the properties of a liquid at its surface or interface. The structure of a surfactant includes hydrophilic and hydrophobic portions. The hydrophilic portion is polar and the hydrophobic portion is water-insoluble, containing long fatty or hydrocarbon chains. Surfactants are commonly used in cleansers and detergents. Their roles in cleansers and detergents include modifying or controlling foam, modifying viscosity and emulsification.

Silicone surfactants were introduced into the foam industry in 1992, to replace some of the more hazardous materials found in foam. They eliminated the need for auxiliary blowing agents, which produce gases other than carbon dioxide.

Surfactants are used to reduce interfacial tension between monomers and the aqueous phase, prior to the onset of polymerization. Generally, quantity of surfactant in the polyurethane formulation is in a range of 0.5-2.5 parts per hundred polyol (pphp) and the actual quantity of surfactant added is dependent on the type of surfactant used as well as on the other constituents of the foam formulation. Below a certain minimum concentration of surfactant, the foam can result in serious imperfections such as splitting, densification or collapse. Addition of more than required quantities of surfactant has its own drawbacks. This usually results in over–stabilization of the foam, resulting in close cells, which results in a decreased airflow through the foam (**Figure 1.5**). Also, a high number of close cells in the foam leads to foam shrinkage on cooling, which is undesirable.
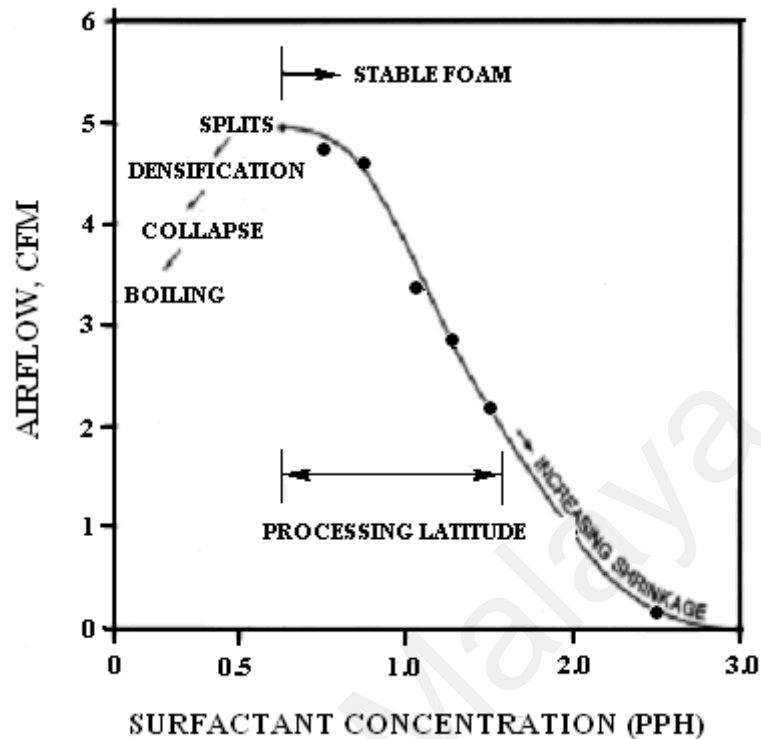
Figure 1.5: Effect of surfactant concentration on foam stability [2].

1.4. Natural rubber (NR)

NR is obtained from the latex of the *Hevea Brasiliensis* tree. It consists entirely of Cis-1, 4-polyisoprene (**Figure 1.6**) with a very broad molecular weight distribution and an average mol weight of above 10^6. It adopts an irregular conformation in the solid state, is unable to crystallize under normal conditions, and therefore exists as an amorphous, rubbery material [3]. Due to its excellent elastic property, NR latex has been classified as one of the most important natural resources used industrially.

Owing to its plant origin, natural rubber latex contains not only Cis-1,4-polyisoprene but also non rubber components which vary from source to source. A typical composition of NR latex consists of TSC (total solid content), 60% DRC (dry rubber content), ammonia, fatty acid and potassium hydroxide.
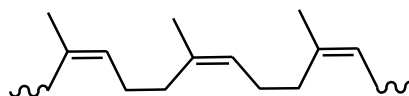
Figure 1.6: Structure of Cis-1, 4-polyisoprene

Professor Tanaka in 1997 developed a process of deproteinization of NR latex [4]. The low protein NR latex could be used to prepare rubber goods for medical purposes and opens the possibility to study the chemical modifications of NR. The modification reaction of NR latex phase could be conducted easier because most protein and phospholipids coating the rubber particle surface and bond chemically to rubber molecule have been removed. The formation of rubber with these compounds will change the chemical and physical properties of NR hence the type of rubber goods could be varied.

NR can be degraded into shorter chain segments called liquid natural rubber (LNR). LNR should be considered as a new material instead of a new type of rubber though they have same configuration as the rubber used as it is easy to chemically modify because of its lower molecular weight. The processes that produce degraded rubbers include mechanical, thermal, chemical and photo-chemical method.

Chemically, by varying reaction conditions and addition of certain chemicals, different degraded NR products can be obtained. Tangpakdee and Tanaka et al. [4] reported a new method of preparing LNR from deproteinised natural rubber latex by oxidative depolymerisation in the presence of $K_2S_2O_8$ and propanal. Klinklai and coworker [5] reported that the NR, purified by deproteinization with proteolytic enzyme and surfactant, was epoxidized in the latex stage with freshly prepared peracetic acid and propanal. The modification of NR latex with peracetic acid was reported by I.R. Gelling [6]. By varying the amount of phenylhydrazine in the system of phenylhydrazine-oxygen developed by Phinyocheep and coworker [7], the desired molecular weight of LNR can by achieved.

Photo-chemical degradation of NR in the presence of H_2O_2 resulted in hydroxyl-terminated LNR and was reported by Ravindran and coworker [8]. Factors which influence scissoring of NR chains and reaction at C=C bonds need to be considered in this degradation reaction. Example, the chain cleavage mechanisms during hydrogen peroxide catalysed photo-oxidative degradation of high molecular weight NR was reported by S.S. Solasky and coworkers [9]. Meanwhile, the use of UV radiations for the preparation of LNR has been reported by Dos Santos and coworkers [10].

1.5   The aims and scope study

The objective of this project is to produce liquid natural rubber-based polyols for making and developing new flexible polyurethane foams and evaluate their properties. The production of liquid natural rubber-based polyols could have a number of advantages such as low capital cost and lower raw material cost. Malaysia is the world"s biggest user of natural rubber latex, which consists of latex from Malaysia rubber plantations and neighboring countries such as Thailand and Indonesia. Besides, low processing cost, it also has lower impacts on our environment. The work is divided into 2 main sections;

1. Synthesis of liquid natural rubber-based polyols from natural rubber.
2. Making flexible polyurethane foams from natural rubber-based polyols and measuring the foam properties by standard test methods.

CHAPTER 2

LITERATURE REVIEW

2.1. Flexible polyurethane foam

The polyurethanes are among the most recent additions to many commercial important classes of polymers. Ever since their discovery by Otto Bayer and co-workers [1], polyurethanes have developed as a unique class of materials and have found use in a wide variety of applications. The name polyurethane was derived from ethyl carbamate, also known as urethane. Besides incorporating the urethane linkage, these materials also sometimes contain several other types of linkages such as amide, urea, ether, and ester [2]. The urethane linkage is formed by the reaction of an isocyanate group of one reactant with the hydroxyl group of another component.

By controlling variables such as the functionality, chemical composition, and the molecular weight of the polyols and isocyanates, different polyurethanes with significantly varying properties can be obtained. This flexibility has led polyurethanes to find use as synthetic polymers in foams, elastomers, coatings, sealants, and adhesive based products.

In Malaysia, domestic polyurethane consumption reached about 80 000 tons in 2004 with polyols constituting 40 000 tons (data by Ooi of Akashi). The bulk of this is in flexible foams as shown in **Figure 2.1**.
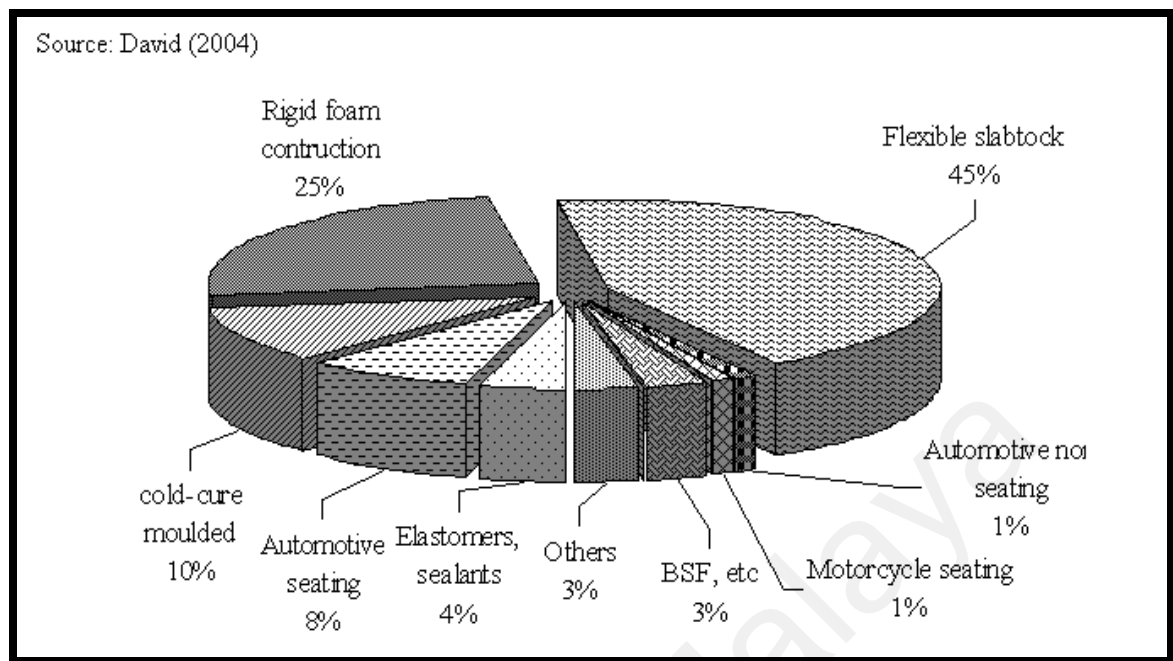
Figure 2.1: Polyol consumption in Malaysia [12].

In polyurethane synthesis, tuning the ratio and composition of the isocyanate and alcohol components results in a segmented block copolymer consisting of alternating hard and soft blocks. The reaction of an isocyanate group with a chain extender and subsequent phase separation of the hard segments formed from this reaction results in the formation of hard blocks; which are referred to as „hard", since they are below their softening temperature at ambient conditions. These hard blocks are covalently bound through urethane linkages to „soft" polyether or polyester segments which are above their softening temperature, T_g, at ambient conditions. The phase separation generally leads to good elastomeric properties wherein the hard blocks serve as filler particles and also act as physical cross-linking points.

One of the major sectors of the polyurethane industry are flexible foams, which are manufactured by the controlled expansion of a gas during the polymerization process [2]. Flexible polyurethane foams are designed to be open-celled, i.e., at the completion of foam

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expansion, the cells open and form a structure composed of polymer struts, which allow the free movement of a gas within the foam cells.

The properties of flexible polyurethane foams depend on both, the elastomeric character of the polymer comprising the foams, as well as the geometry of the cells. As shown in **Figure 2.2**, flexible polyurethane foams are used in applications such as seating, cushioning, fabric backing, insulation, and packaging.
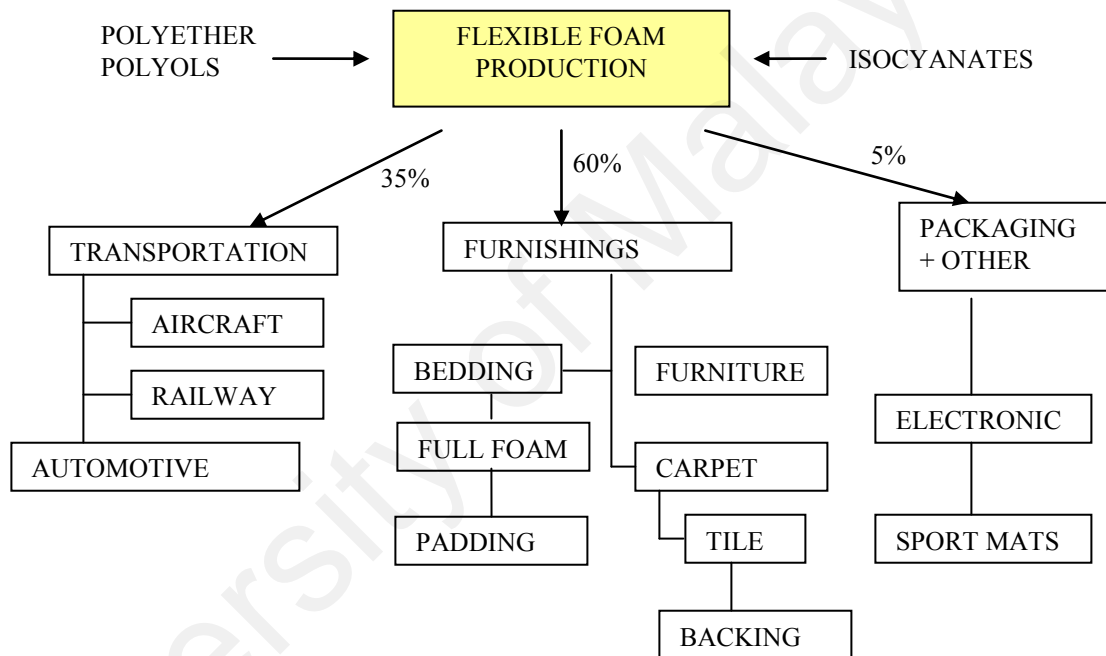
Figure 2.2: Applications of flexible polyurethane foam [2].

The first commercial production of flexible polyurethane foams, based on the reaction between an aromatic isocyanate and a polyester polyol, was carried out in 1954 [2]. However, these foams were unable to withstand the severe humidity and temperature conditions in which they were used, and thus foams based on polyether polyols were developed. These second generation foams provided better durability as well as comfort. A major advancement in polyurethane technology was the introduction of the „one-shot"

system using new catalysts and silicone-based surfactants. In the one-shot process; the isocyanate, polyol, water, and other ingredients are rapidly and intensively mixed and immediately poured to carry out the foaming. Since then, advances in flexible polyurethane foam technology have been numerous, all targeted to provide the customer with enhanced performance properties, while trying to improve processability, increase production rates, and lower costs. The more than five-decade-old technology of polyurethane foams might have been expected to reach a mature growth by now. However, formulations based on newer and more sophisticated applications continue to develop, thus demanding a better understanding of the structure-property correlations. Also, the evaluation of foam morphology using techniques such as atomic force microscopy [13] and small-angle X-ray scattering [14] has opened avenues to improve the understanding of these materials.

These days flexible polyurethane foams are produced either by a semi-continuous slabstock process or a batchwise molded process [2]. Currently, both these schemes employ the one-shot method. In the former process, the various foaming ingredients are mixed in a transverse mixing head and sprayed on a conveyor belt. Subsequent foaming reactions lead to the polymerization of the reacting mixture which gives the foam its integrity; and also release carbon-dioxide, which helps the entrained air bubbles to develop into foam cells. When the entrapped air bubbles in the reacting mixture grow large enough to scatter visible light, a visible coloration change, known as „creaming" is observed (**Figures 2.3** and **2.4**). The point where the majority of the cells open is accompanied by a „sigh back" of the foam, since at this time, gas can move freely through the foam cells, and this lets the foam to assume its final height. The large buns of foam produced from this process are then placed in a storage area for a period of at least forty-eight hours to complete the curing.
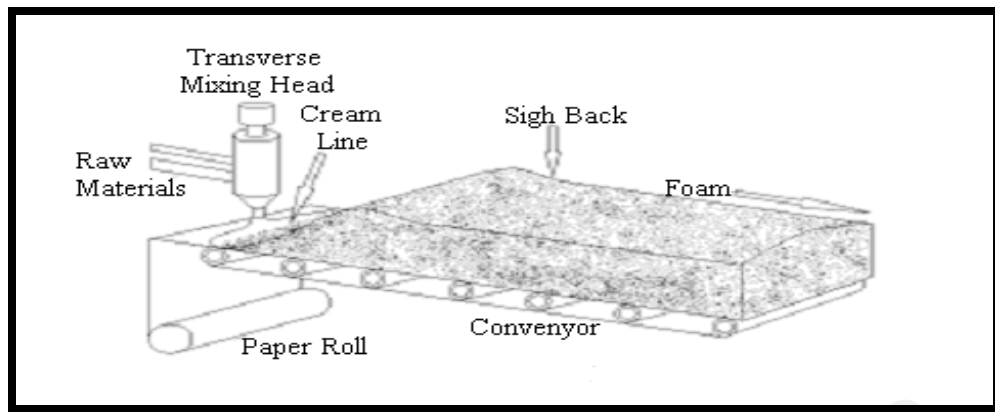
Figure 2.3: Slabstock process [2].

Since flexible polyurethane foams expand and flow, at least prior to the onset of gellation, manufacturers have often found it useful to produce foams using a batchwise molded process [2]. This method is especially useful where the final foam product has a complex shape, for example in car seats and headrests. The foams produced by this method, therefore, help to save trimming costs and minimize wastage. Currently, flexible foams produced by this method account for approximately 20% of the total flexible polyurethane foam market. A typical carousel molding line is shown in **Figure 2.4**.
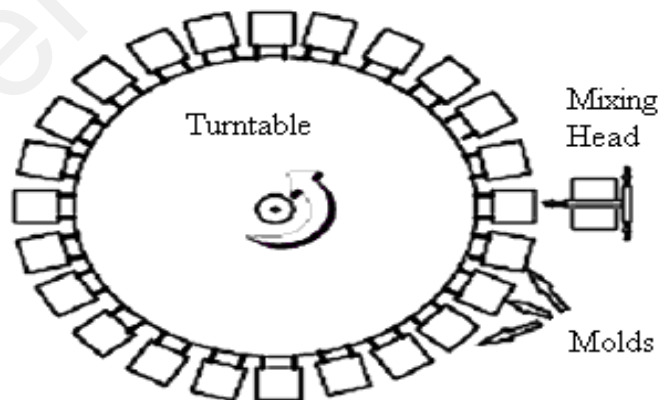
Figure 2.4: Carousel molding process [2].

As will be discussed in the following Section 2.1.1, the formation of flexible polyurethane foams relies on a complex interaction between physical and chemical phenomena. Perhaps the most important aspect of flexible foam manufacture is that there are no „independent" chemical or process variables in producing flexible foams. Therefore, the effect of altering a single variable (such as a foam component or a process condition) cannot be studied, since changing a particular parameter will affect the strong interplay which exists between the different variables.

2.1.1 General chemical reactions

Flexible polyurethane foam chemistry particularly features two reactions – the „blow" reaction and the „gellation" reaction. A delicate balance between the two reactions is required in order to achieve foam with a stable open-celled structure and good physical properties. The commercial success of polyurethane foams can be partially attributed to catalysts which help to precisely control these two reactions (**Equations 2.1** and **2.4**). An imbalance between the two reactions can lead to foam collapse, serious imperfections, and cells that open prematurely or not at all.

2.1.1.1 Blow reaction

The first step of the model blow reaction (**Equation 2.1**) involves the reaction of an isocyanate group with water to yield a thermally unstable carbamic acid which decomposes to give an amine functionality, carbon dioxide, and heat [15]. In the second step (**Equation 2.2**), the newly formed amine group reacts with another isocyanate group to give disubstituted urea and additional heat is generated. The total heat generated from the blow reaction is approximately 47 kcal per mole of water reacted [2], along with the carbon

dioxide released in the first step and serves as the principal source for „blowing" the foam

mixture, though some auxiliary blowing agents are also usually utilized. Also, since the

typical isocyanates utilized in foam production are difunctional, the second part of the blow

reaction serves as a means to chain extend the aromatic groups of the typically used

isocyanate molecules to form linear hard segments.

$$R-N=C=O \quad + \quad H-O-H \longrightarrow \left[R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-OH \right]$$

Isocyanate   Water

Carbamic acid

$$\left[R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-OH \right] \longrightarrow R-NH_2 \quad + \quad CO_2\uparrow \quad + \quad HEAT$$

Carbamic acid   Amine   Carbon dioxide
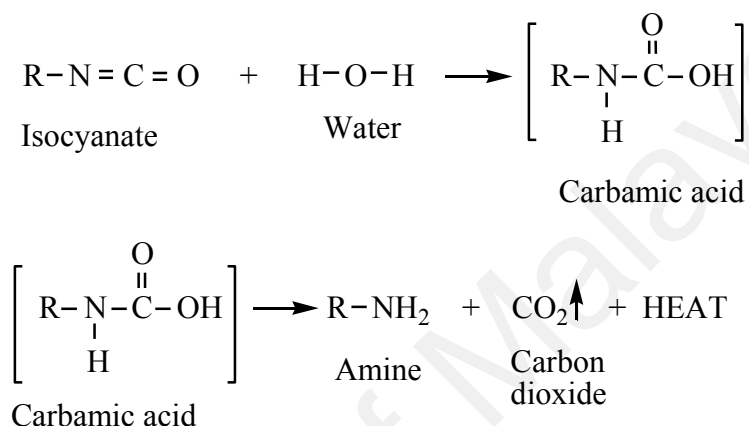
Equation 2.1: First step of the blown reaction

However, it should be noted that this reaction scheme can also produce covalent

cross-linking points when molecule with functionality greater than two, such as ethanol

amine, are added to the formulation [2].

$$R-N=C=O \quad + \quad R'-NH_2 \quad \xrightarrow{-\Delta} \quad R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R'$$

Isocyanate   Amine

Disubstituted Urea
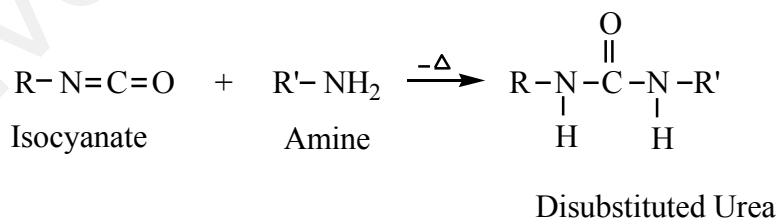
Equation 2.2: Second step of the blow reaction

There are other secondary reactions, involving the formation of biuret and

allophanate linkages which could lead to formation of covalent cross-linking points. In the

formation of biuret, a hydrogen atom from the disubtituted urea reacts with an isocyanate

group to form a biuret linkage, as shown in **Equation 2.3** [1]. The allophanate forming reaction is discussed in the next section.

$$R-N=C=O \;+\; \underset{\substack{| \\ H}}{R-N}-\overset{\overset{\textstyle O}{\|}}{C}-\underset{\substack{| \\ H}}{N-R'} \;\rightleftharpoons\; \begin{array}{c} \overset{\overset{\textstyle O}{\|}}{R-N-C-N-R'} \\ | \quad\;\; H \\ C=O \\ | \\ H-N \\ | \\ R \end{array}$$

Isocyanate   Disubstituted Urea   Biuret
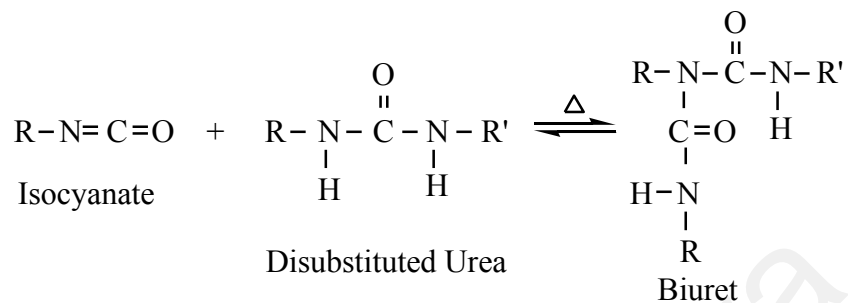
Equation 2.3: Formation of a biuret linkage

2.1.1.2 Gellatin reaction

The gellatin reaction also sometimes called the polymerization reaction, involves the reaction of an isocyanate group with an alcohol group to give a urethane linkage as shown in **Equation 2.4**. The heat of this reaction is reported to be approximately 24 kcal per mole of urethane formed [1]. Since polyurethane foams usually utilize polyfunctional reactants (typically difunctional isocyanates and trifunctional polyol), this reaction leads to the formation of a cross-linked polymer.

$$R-N=C=O \;+\; R'-CH_2-OH \;\xrightarrow{-\Delta}\; \underset{\substack{| \\ H}}{R-N}-\overset{\overset{\textstyle O}{\|}}{C}-O-CH_2-R'$$

Isocyanate   Alcohol   Urethane
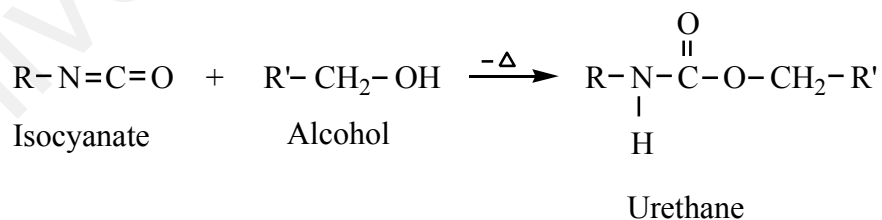
Equation 2.4: The gellatin or cross-linking reaction

The reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer as shown in **Equation 2.5**. In uncatalyzed systems this reaction is known to be insignificant [2]. Also, this reaction is generally not favorable under the catalytic conditions for flexible foam production.

It is important to note that both reaction (blown and gellatin) equations described in **Equations 2.1-2.4** occur simultaneously, and therefore it is critical to control the relative rates of these reactions in order to obtain foam with a stable cellular structure and good physical properties. If the blow reaction takes place too fast in comparison to the gelatin reaction, it would result in the cells opening before there is sufficient viscosity build-up to provide the foam with enough strength to uphold the foam, leading to the collapse of the foam, which is not desirable. The relative rates of reaction of the isocyanate component with other foam reactants at $25^{\circ}C$ under uncatalyzed condition are provided in **Table 2.1**. These can serve as a guideline to make appropriate catalyst adjustments to achieve a suitable balance of the two reaction schemes.

$$R-N=C=O \quad + \quad \underset{\underset{H}{|}}{R-\overset{\overset{O}{\|}}{N-C}-O-CH_2-R'} \quad \xrightleftharpoons{\Delta} \quad \underset{\underset{\underset{R}{|}}{H-N}}{\overset{\overset{O}{\|}}{\underset{|}{\overset{R-N-C-O-CH_2-R'}{C=O}}}}$$

Isocyanate   Urethane   Allophanate
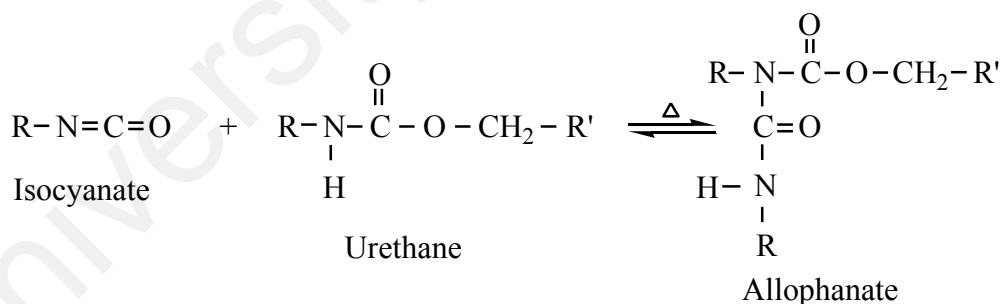
Equation 2.5: Formation of an allophanate linkage

Familiarity with the above two reaction equations is important to develop a fundamental understanding of the solid-state morphology which results in flexible polyurethane foams. As discussed in Section 2.1.1.1, the blow reaction not only helps in foam expansion, but also leads to the generation of urea hard segments. The gelation reaction covalently bonds these urea hard segments to soft polyol segments.

Table 2.1: Reactivity of isocyanate with active hydrogen compound [2].

Active Hydrogen Compound	Typical Structure	Relative Reaction Rate (uncatalyzed at 25°C)
Primary aliphatic Amine	RNH$_2$	100,000
Secondry Aliphatic Amine	R$_2$NH	20,000-50,000
Primary Aromatic amine	ArNH$_2$	200-300
Primary Hydroxyl	RCH$_2$OH	100
Water	H$_2$O	100
Carboxylic Acid	RCOOH	40
Secondry Hydroxyl	R$_2$CHOH	30
Urea	RNHCONHR	15
Tertiary Hydroxyl	R$_3$COH	0.5
Urethane	RNHCOOR	0.3
Amine	RCONH$_2$	0.1

When the concentration of hard segments exceeds a system dependent solubility limit, the hard segments phase separate out and form what are commonly referred to as „urea microdomains". Due to asymmetric nature of the isocyanates utilized in foam manufacture (discussed in Section 1.3.1), the microdomains are not crystalline but have been suggested to possess ordering of a paracrystalline nature [2]. In addition, at higher water contents (and thus at higher hard segment contents), the urea microdomains are known to aggregate and form larger urea rich structures commonly termed „urea microdomains and these are known to aggregate and form larger urea rich structures commonly termed „urea balls" or „urea aggregates". These urea balls are regions which are richer in urea as compared to the general surrounding polyol matrix which also contains dispersed urea microdomain. A schematic representation of this phase-separated

morphology is provided in **Figure 2.5**. Further aspects of this phase-separation behavior and its influence on physical properties of foams will be discussed in section 2.3.
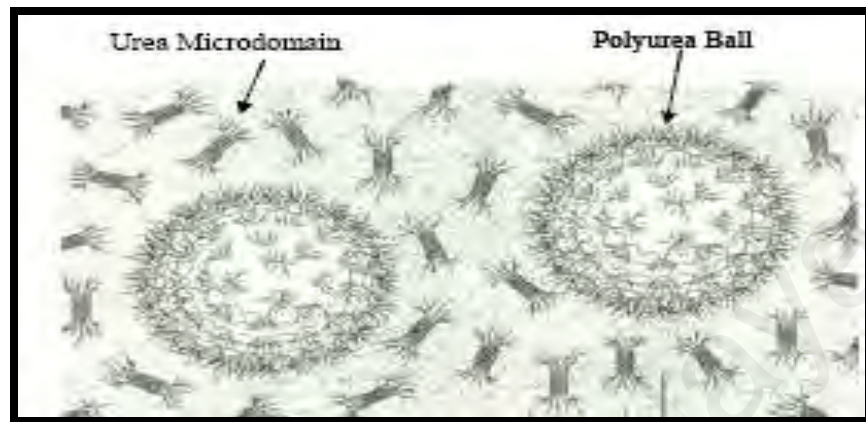
Figure 2.5: Schematic representation of the phase separation behavior in polyurethane foam [2].

2.1.2 Basic foam components

These are many different components needed to synthesize flexible foam. The seven major ones are isocyanate, polyol, water, physical blowing agents, catalyst, surfactant and cross-linking agent. The desired end properties of the foam dictate the choice of specific component along with their required quantities. For example, one way to adjust foam modulus would be controlling the percentage of hard segments formed from water-isocyanate reaction [2]. In other cases, it might be required to have foam with more cells openness. This would be possible by controlling the type and quantity of surfactant used.

Table 2.2 lists the components which are commonly involved in a formulation and gives a typical range of quantities for each component utilized. As can be seen from the Table, the quantities of all components listed are based on the amount of polyol utilized in the formulation. For example, water is typically used in the range of 1.5-7.5 pphp. However, the isocyanate added to formulation is usually reported by an index number. An isocyanate

index of 100 indicates that the stoichiometric amount of isocyanate added to react with the functional groups from the polyol, water and cross-linkers added in the formulation [1].

Table 2.2: Formulation basics for flexible polyurethane foam [2].

Component	Parts by weight
Polyol	100
Inorganic Fillers	0-150
Water	1.5-7.5
Silicone surfactant	0.5-2.5
Amine catalyst	0.1-1.0
Tin catalyst	0.01-0.5
Chain-extender	0-10
Cross-linker	0-5
Additive	Variable
Auxiliary Blowing Agent	0-35
Isocyanate	25-85

2.2 The forming process

The sequence of the forming reactions has been extensively studied by FTIR [2]. In general, there is an agreement amongst different workers that the water-isocyanate reaction takes place sooner and faster as compared to the polyol-isocyanate reaction [2]. This is supported by the growing urea carbonyl absorption at 1715 cm^{-1} early in the reaction which is observed to shift to 1660 cm^{-1} once half the foam rise height is reached. Model studies carried out on diphenyl urea have indicated that the urea carbonyl absorption in a good solvent (DMF) and a poor solvent (THF) appears at 1715 and 1660 cm^{-1} respectively [16]. This suggests that a stage is reached when the polyurea being formed is no longer soluble in the forming mixture and phase separation takes place. Bailey and Critchfield [17] observed

that the urea formation took place quickly with most of it taking place within the first 5 min of the foaming process. The urethane formation, however was not significant in the first 5-10 min, but was found to increase at a steady rate for the next 30 min. These results were also confirmed by Rossmy and co-workers [18] who observed that the ratio of isocyanate to water consumption was 2:1 in early part of the foam reaction, indirectly indicating that urethane formation was not significant in earlier stages [19]. The same workers also confirmed, using reactive and non-reactive polyols, that the heat generated by the urethane reaction in the earlier stage was negligible, indicating the significant urethane formation.

McClusky and coworkers [20] used a vibrating rod viscometer as a probe to examine the rheology of the reacting foam mixture during the forming process. Based on their investigation, the reaction scheme was divided into three regimes. During the first regime, which began from mixing of the reagents and continued up to the point of cell opening, it was observed that there was a continuous reduction in the system viscosity due to the increase in temperature resulting from exothermic nature of the reactions. In the second regime, a rapid increase in the viscosity was observed, due to the precipitation of the urea which led to the formation of hydrogen bonded physically cross-linked network. The third regime displayed a gradual increase in the system viscosity, due to the formation of the covalent network in the polymer.

The rigidity of rising foams was measured by Bailey and Critchfield [17] based on the ball bearing (BB)-drop test developed by Rowton. This test consists of dropping BB"s from constant height on the foam sample at different times during the foaming process. The distance traveled by the BB after hitting the foam can be related to the integrity of the foam. It was observed that the BB"s sank through the foam until precipitation of the urea occurred. The phase separation of the urea, therefore, was responsible to give the foam its structure integrity. It has also been observed by Rossmy and coworkers [18] that cell rupture took

place just after the urea precipitation. In light of this observation, it has been suggested that the precipitation of the urea destabilizes the foam mix and aids in cell opening.

2.3 Morphology

The physical properties of flexible polyurethane foams are function of both, the cellular structure and the phase separated morphology of the polymer comprising the struts of the foam [2]. These two factors are intimately related because both are influenced by the forces exerted during the expansion and stabilization of the foam. There has been considerable effort to try and understand how these two factors influence the physical properties of the foam such as load bearing, compressive stress-relaxation and also how these properties are a function of varied temperature and humidity condition.

2.4. Development of flexible polyurethane foam morphology

Several length scales characterize the polyurethane (PU) foam morphology and underscore its complexity. Very few commercial polymer based products possess a morphology that consists of coexisting covalent and physical cross-linked networks. The evidence of the presence of a microphase separated morphology in slabstock PU foams was first presented by Dounis and Wilkes [21] in a brief study. A more in-depth morphological investigation of TDI and PPO based water blown flexible PU foams from the same research group [13] followed thereafter. These studies confirmed the fact that conventional flexible PU foams possessed a microphase separated morphology. Moreover, based on the results of techniques such as DSC, DMA, SAXS, etc. the degree of microphase separation in conventional slabstock foams was found to be independent of the water content. At low water content, small hard domains were randomly distributed in the soft matrix. At higher

water content, the development of interconnected hard domain morphology was suggested. The formation of larger hard urea „aggregates" or urea „balls" (300 nm in size) were also seen. These were a result of the precipitation of the urea hard segment (HS) during the foaming reactions. Their formation was noted when the growing urea carbonyl IR absorbance peak shifted from 1715 cm^{-1} to 1640 and 1660 cm^{-1} due to the formation of bidentate and monodentate hydrogen bonding with the urea hard segment (HS) [13].

2.5. Liquid natural rubber (LNR)

As mentioned earlier, natural rubber degraded into shorter chain segments with low molecular weight of about 10^3-10^4 obtained is called liquid rubber [6, 47]. It has been used as raw material for polyurethane foam, adhesives and reactive plasticizer for improving processing properties of compounded rubber for types. It was first produced commercially under the trade name of DPR on a small scale basis by Hardman [23]. He succeeded in depolymerizing NR to yield a product which then found use in setting bristles in paint brushes. Several reports appeared later on the depolymerization by thermal, mechanical, chemical and photochemical degradations.

Basically, LNR is prepared via oxidative chain scission of the polyisoprene backbone. By varying the amount of phenylhydrazine in the system of phenylhydrazine-oxygen developed by Phinyocheep and coworkers [7], the desired molecular weight of LNR can by achieved. Tangpakdee and Tanaka [4] reported a new method of preparing LNR from deproteinised natural rubber latex by oxidative depolymerisation in the presence of $K_2S_2O_8$ and propanal. In the old methods, LNR was prepared by milling NR at 60-80°C in the presence of oil-soluble salts of heavy metals, such as cobalt linoleate or naphthenate, until degraded sufficiently. The degraded rubber was then dissolved in petroleum ether to

give a 20% solution having a viscosity of about 3000 Poise at 25°C. LNR, which was known as „rubbones" when obtained by this method, is a viscous gum, yellow to orange red in colour, and contains about 10% oxygen.

The method for the preparation of LNR was developed further by degrading NR at 110-140°C for several hours or at 250-300°C for a shorter period in the presence of plasticizers (peptizers) such as mercaptobenzthiazole (MBT). LNR obtained by this method has a molecular weight of -2000, a viscosity of 5000-25000 Poise at 20°C and contains about 1% oxygen [26].

LNR obtained from the previous methods still contains in-chain carbon-carbon double bonds and hence can be transformed into useful products by compounding with vulcanizing ingredients followed by vulcanization at 140°C [25, 26]. Because LNR is a liquid, the ingredients can be mixed easily without consuming a lot of energy, as in the case of NR, and hence the cost of making products from it is reduced. Further advancement in LNR technology came from the use of new compounding ingredients, for example, p-quinone dioxime as a curing agent, lead peroxide as a filler and amines as accelerators. These ingredients permit great latitude in work life, reduce surface tackiness, aid stability in storage and more importantly give products that can be cured (vulcanized) at room temperature [27].

In general, the methods developed for the production of LNR discussed before do not give molecules bearing consistent types of reactive terminal groups. Therefore, vulcanizates obtained from such LNR did not offer good mechanical properties owing to the presence of a high proportion of elastically inactive chain ends [28]. Hence, the applications of such LNR are limited only to products which are not necessarily required to have good mechanical properties such as heat-resisting finishes, insulators for electrical components, brush-bristle, cements, binders for abrasives in grinding wheels, battery boxes,

printing rollers, corrosion resistant coatings, processing aids such as a rubber softener in conventional rubber compounding, and additives in greases and lubricants [24]. However, further advances in LNR compounding ingredients, giving rise to vulcanizates having good mechanical properties useful for film, adhesive or coating components, have been reported by Hiroshima [29] in which organic diamines, such as diethylenetriamine or triethylenetetramine, were used as vulcanizing agents, and diglycidyl esters or ethers were used as reinforcing agents.

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. Therefore, upon curing, this class of LNR not only can be crosslinked through its carbon-carbon double bonds but also can be chain extended through its terminal groups which eliminate, or at least reduce, the presence of elastically inactive chain terminal groups, depending on the ingredients used in the curing system. This, additional element of curing contributes to the mechanical properties of the vulcanizates.

CHAPTER 3

EXPERIMENTAL

3.1 Liquid natural rubber (LNR)-based polyol

3.1.1 Materials

Natural rubber (La-TZ) latex concentrate [60.2 % dry rubber content] and Vulcastab LW were supplied by Lembaga Getah Malaysia (LGM) Sungai Buloh, Malaysia. Sodium nitrite and hydrogen peroxide (30%) were purchased from R&M Chemical. Formic acid (99%) was purchased from Ajax Chemical. All chemicals were used as-received.

3.1.2 Procedure

Liquid natural rubber (LNR)-based polyol was prepared from LA-TZ latex, hydrogen peroxide (H_2O_2) and sodium nitrite ($NaNO_2$) by direct *in-situ* method [23]. The parameter of chemicals in LA-TZ latex is shown in **Table 3.1.**

Table 3.1: Parameter of chemicals in LA-TZ latex

Chemical	%
Dry rubber content	60.2
Total solids content	61.6
NH_3	0.257
Volatile fatty acid number	0.024
Potassium hydroxide	0.432
pH	9.84

Natural rubber (LA-TZ) latex was stabilized by Vulcastab LW in a 1 liter round bottom flask submerged in a silicone bath, equiped with a stirrer, a thermometer and a condenser, under continuous stirring. The NR latex was acidified by formic acid to the required pH followed by successive treatment with 30% aqueous H_2O_2, formic acid, water and 10% solution of $NaNO_2$ and heat. The product obtained was washed with methanol and dried in a vacuum oven. The setup for LNR-based polyol reaction was shown in **Appendix A**.

3.2.   Hydroxyl value determination

The hydroxyl value is defined as a number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of the sample. The hydroxyl values of liquid natural rubber (LNR)-based polyol very important to determine NCO/OH ratio in the foam formulation and it was determined by a procedure adapted from ASTM D4274. Firstly, 1 g of sample was weighed into a 250 ml conical flask. 25 ml of prepared pyridine-phthalic anhydride (pyridine reagent) solvent (pyridine: pthalic anhydride = 111 g: 700 ml) was then pipetted into the flask for sample and blank. The flask was equipped with a air condenser and placed onto an oil bath for 1 h at 115°C. When the flask was cooled to room temperature, 50 ml of redistilled pyridine was added through the condenser into the flask and titrated with 0.5 N NaOH solutions to a pink colour end point using autotitrator. The hydroxyl value of the sample was calculated using the following formula:

Hydroxyl value   = $\dfrac{[(B-A)] N \times 56.1]}{W}$ [3.1]

Where:

$\quad\quad$ B = volume titration of blank, ml

$\quad\quad$ A = volume titration of sample, ml

$\quad\quad$ W = weight of sample, g

$\quad\quad$ N = Normality of the KOH

Example:

	First determination	Second determination
Weight of sample used, g	0.0152	0.0122
KOH required for titration of sample, ml	100.55	100.56
KOH required for titration of the blank, ml	100.60	100.60
Normality NaOH	0.5	0.5
Hydroxyl number	92.3	92.0
Average hydroxyl number	92.1 ± 0.05	

3.2.1. Standardization of sodium hydroxide

Firstly, 4-5 g of dried potassium acid phthalate that dried it for 1-2 h at 100°C was weighed into a 250 ml conical flask. 200 ml of distilled water was then added into the flask and swirled until the potassium acid dissolved. When the potassium acid was dissolved, titrate this solution with 0.5 N NaOH solutions to a pink colour end point using autotitrator. The normality of sodium hydroxide was calculated using the following formula:

$$\text{Normality} \quad = \quad \frac{W}{V \times 0.204} \qquad\qquad [3.2]$$

Where:

W = weight of potassium acid phthalate (KHC$_8$H$_4$O$_4$), g

V = volume of NaOH, ml

3.3. Characterization methods for LNR-based polyol

3.3.1. Nuclear magnetic resonance (NMR) spectroscopy

The NMR spectra of polyol samples were obtained at 400 MHz using JEOL JNM-LA 400 FTNMR System spectrometer with 8 scan rate and acquisition time of 8.0 s. The samples were dissolved as approximately 4% w/v solution in deuterated chloroform (CDCl$_3$), and ^{1}H-NMR spectra were obtained at room temperature.

3.3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were performed on Perkin-Elmer model RX-1. The blank spectrum of sodium chloride cell was used as background for subtraction during the analysis. A drop of liquid sample was coated on the sodium chloride cell to obtain a thin film, and then was positioned by using cell holder. The sample was scanned for wave number from 650 cm^{-1} to 4000 cm^{-1} in order to obtain the spectrum with resolution at 1 cm^{-1}.

3.3.3. Gel permeation chromatography (GPC)

Gel permeation chromatography, also known as size exlusion chromatography or gel filtration and provide a rapid method for separation for the polymeric species. The separation is based on the molecular size differences in solution. In this study, the average

molecular weight, number average molecular weight and polydispersity index of the LNR-based polyols was determined by GPC technique using the Water 600 GPC. THF was used as the eluent and temperature and flow rate were set as 40°C and 1 ml min^{-1} with 16 bar pressure. Polystyrene was used for the running of calibration curves.

3.4 . Preparation of flexible polyurethane foam

3.4.1 Materials

In this study the following chemicals were used for preparation of the flexible polyurethane foams:

- Polyol: two types of polyols from liquid natural rubber, S3 and S1 with hydroxyl value (OHV) = 92 and 64 mg KOH/ g sample respectively. These polyols were synthesized from first part (Section 3.1).

- Isocyanate: Modified MDI supplied by Maskimi Polyols Sdn Bhd.

- Blowing agent: Distilled water.

- Tin Catalysts: Stannous octoate ($C_{16}H_{32}O_4Sn$) supplied by Merck Sdn. Bhd.

- Amine catalyst: Niax A1 (70 % bis(dimethylaminoethyl)ether and 30% dipropylene glycol) supplied by Maskimi Polyols Sdn. Bhd.

- Surfactant S3002: Silicone is a cell stabilizer supplied by Maskimi Polyols Sdn Bhd.

- Chain extender: DEA (diethylolamine, $C_4H_{11}NO_2$) supplied by Maskimi Polyols Sdn. Bhd.

3.4.2 Foam preparation

In the preparation of flexible polyurethane (PU) foam, the LNR-based polyol, amine catalyst, tin catalyst, DEA, water as blowing agent and surfactant (*Component A*) were placed in a polyethylene plastic cup and stirred for 15 s at 2500 rpm with a laboratory stirrer. Then, the previously weighed of modified MDI (*component B*) was added and mixture was stirred for 4 s.

The mixture was then poured into a rectangular mould for free rising of the foam and curing at room temperature for 24 h. Following that the foam was removed from the mould and was compressed and allowed to stand at room temperature for one week before further tests.

The formulation for the preparation of flexible PU foam used in this study is summarized in the **Table 3.2**

Table 3.2: Formulation component in the preparation of flexible PU foam

Component A	Part (g)
Polyol	100.0
DEA	1.5
Stannous octoate	0.4
Silicone S3002	2.5
Water	4.0
Niax A1	0.2
Component B	
Modified MDI	86.8
Isocyanate Index	100

3.5. Characterization methods for the flexible PU foams

3.5.1. Fourier transform infrared (FTIR) spectroscopy

As described in Section 3.3.2

3.5.2 Thermal gravimetric analysis (TGA)

Foam sample weighing 4-5 mg was used in thermal gravimetric analysis. Measurements were made using thermal gravimetric analyzer (Perkin-Elmer) at a temperature range from 50 to 900°C with heating rate of 10°C min^{-1} under nitrogen atmosphere flow rate of 20 ml min^{-1}.

3.5.3 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is a combination of thermal analysis and rheology. It looks at material properties, specifically mechanical properties like modulus and their dependence on temperature and or time and also used to evaluate other materials like T_g and other transitions, crystallinity and cross-linking effects, fatique and other time-dependent effects. In this work, it was carried out using a TA Q800 DMA. The samples were clamped by compression mode and heated from -100°C to 20°C at rate of 20°C min^{-1}, from which storage modulus, loss modulus and tan δ data were collected at a frequency of 1 Hz.

3.5.4   Optical microscope

The characterization of the cell structure of foam is performed using the optical microscope (PRIMO STAR-ZEISS) that was connected to programmable computer. The image of cell structure of the foam can be captured on the screen for observation.

3.6   Physical properties test for flexible PU foam

3.6.1   Density

For density measurement, the foams were cut into cubes with dimensions of about 25 X 25 X 25 mm (width X length X thickness) using electrical saw and carefully weighed using an analytical balance. All dimensions were measured using a vernier caliper. Three specimens were tested for each sample. Foam density was calculated according to the following formulation.

$$Density = M/V \qquad\qquad [3.3]$$

Where:

M = mass of specimen in kg

V = volume of specimen in m^3

3.6.2   Tear strength

The tear strength of the foam was determined according to **ASTM D3574** (Foam Tear Resistance Test F). This test was carried out using shear testing machine (Instron model 4469) by continuously trying to tear a foam block sample after split or break has started. The load capacity used was 50 kN and testing speed was 450 mm min^{-1}. The

samples used were 25 mm X 25 mm in cross-section and 152.4 mm long (**Figure 3.1**). Each sample was split in the middle along its length to depth of 38.1 m. The maximum force (tear strength) registered on the testing machine was recorded. Five specimens per sample were tested and the mean derived.
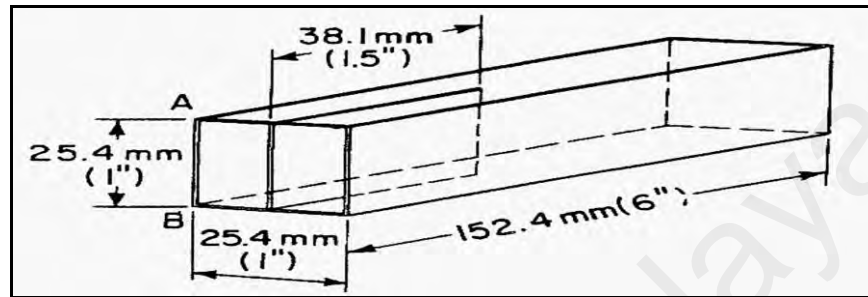
Figure 3.1: Tear resistance test specimens

3.6.3   Compressive stress

The compression stress of the foams was determined using an Instron universal Testing Machine (Instron model 4469) of 50 kN load capacity and testing speed was 50 mm min^{-1}. The test was performed according to **ASTM D3574.** The foam sample was between two flat metal plates and was subsequently compressed to 50% of original thickness. A piece of foam of 25 mm X 25 mm X 25 mm was compressed between two flat plates until 50% of its original thickness (**Appendix X**). Based on the stress against strain curve graph, compressive stress was recorded. A minimum of five specimens were tested for each sample.

3.6.4 Tensile strength

This was done according to procedure recommended in **ASTM D638-94b**. The tensile strength of foams was measured with an Instron Universal Testing Machine (Instron model 4469). The load capacity use was 50 kN. The foams were cut into strips with 165 X 19 X 25 in mm by using electrical band saw (**Figure 3.2**). The samples were gripped by two screw-type plate grips and pulled at a crosshead of 450 mm min^{-1}. The ultimate tensile strength and modulus of elasticity (MOE) were recorded. The tensile strength can be calculated by dividing the maximum load in newtons by the original cross-sectional area of the specimen in square meters. A minimum five specimens were tested for each sample.

$$\text{Tensile strength} = \frac{\text{Max load (N)}}{\text{Cross-sectional area of specimen}} \qquad [3.4]$$

Where:

Maximum load = force in Newton (N)

Cross-sectional area of specimen = (length X width) in m^2
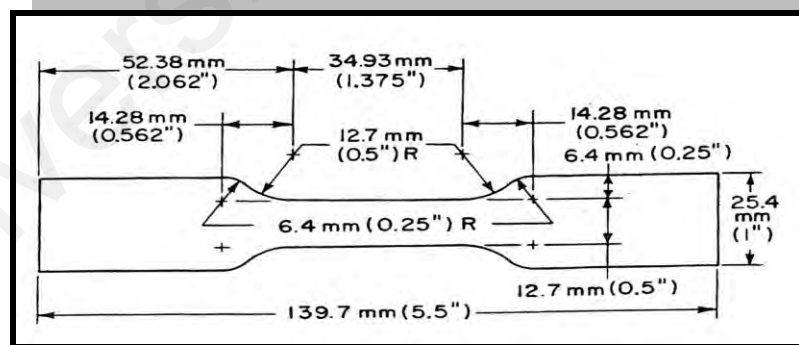
Figure 3.2: Tensile specimen

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of liquid natural rubber (LNR) -based polyol from NR latex

In this work, thermal degradation of natural rubber latex was carried out at different temperatures to obtain LNR-based polyol. Variation in the reaction times and concentrations of hydrogen peroxide/isoprene were also investigated. The synthesis is to target LNR having hydroxyl groups in backbone chain that is suitable for the synthesis flexible polyurethane foam.

In the synthesis of LNR-based polyol from NR latex using hydrogen peroxide (H_2O_2) and sodium nitrite ($NaNO_2$) as reagents, two parallel reactions occur, i.e. epoxidation and ring-opening as shown in **Equation 4.1** [11, 22].

a) Formation of epoxidized natural rubber (ENR) latex
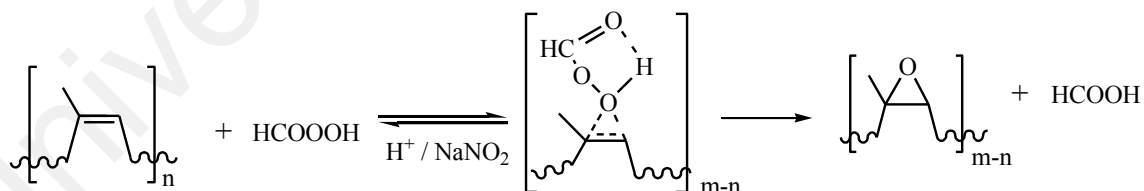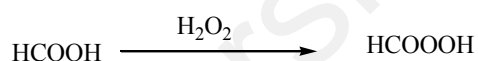
b) Ring-opening ENR latex
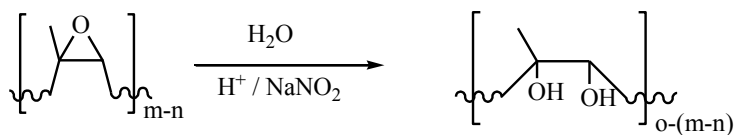
Equation 4.1: Mechanism reaction of LNR-based polyol

The addition of NaNO$_2$ simultaneously with H$_2$O$_2$, results in chain scissoring reaction together with epoxidation. The C=C bond in the latex reacts to form epoxy groups which is followed by hydrolysis reaction. Consequently, the product is ring-opened and has low molecular weight with both epoxy and hydroxyl groups present. Evidence of the presence of these two functional groups will be discussed in Section 4.2.1. The physical appearances of LNR-based polyol synthesized are generally are sticky, brownish like liquids (**Figure 4.1**).

Figure 4.1: LNR-based polyol

4.1.1   Reaction temperature

Figure 4.2 shows the effect of temperature on yield and hydroxyl (OH) value of LNR synthesized for 24 h with 1.0 mol of H$_2$O$_2$/isoprene ratio. The percentage yield and OH value of LNR-based polyol increases with increasing of temperatures. By increasing the reaction temperature from 60°C to 90°C for 24 h, it is possible to prepare LNR-based polyol with hydroxyl values ranging from 46-92 mg KOH/g sample and yield ranging from 54-90%. Higher reaction temperatures manage to provide a more complete conversion of epoxy groups to hydroxyl functional group as reflected from the higher OH value.
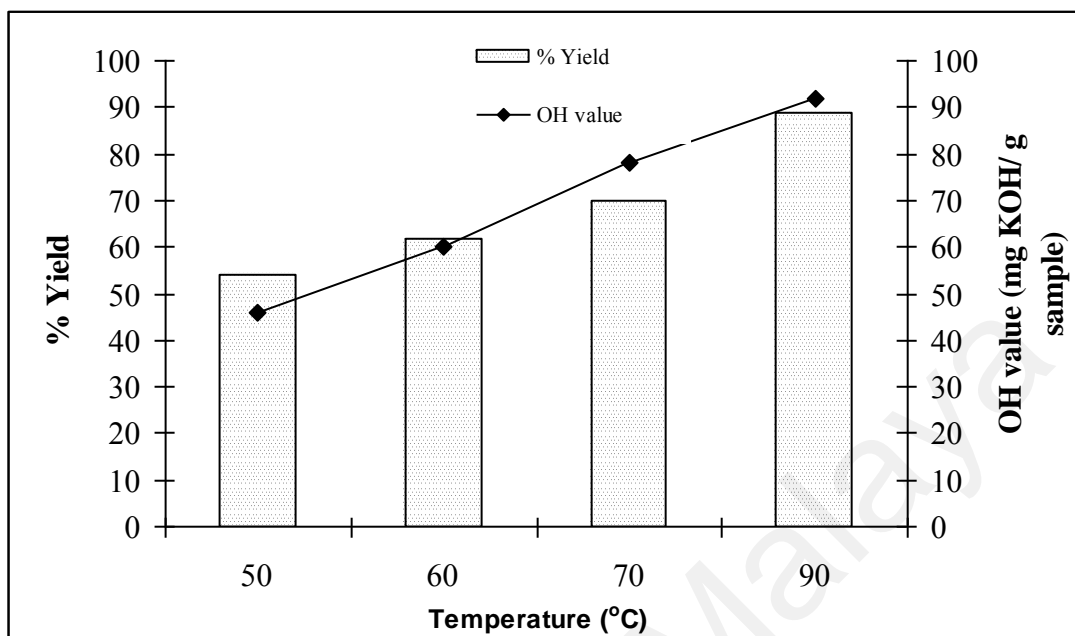
Figure 4.2: Effect of different temperature on percentage of yield and OH value of the LNR synthesized for 24 h.

4.1.2 Ratio [H$_2$O$_2$/isoprene]

Meanwhile, **Figure 4.3** illustrates the effect of the variation in the mol ratios of H$_2$O$_2$/isoprene at 90°C for 24 h on molecular weight, polydispersity and OH value of the LNR-based polyol (S1 - S4). The data show that molecular weights and polydispersity index of the samples decrease with increasing H$_2$O$_2$/isoprene ratio whereby the average molecular weight decreases ($\overline{M}_w$) almost half from $\approx$ 31000 to 16000 when H$_2$O$_2$/isoprene ratio increases twice from 0.6 to 1.2 mol. The chain-scission may have taken place simultaneously with epoxidation and hydrolysis, resulting in reduced molecular weight of LNR-based polyol, having the epoxide and hydroxyl groups as is evidently shown earlier from FTIR and NMR results. The polydispersity index (PDI) is calculated by dividing $\overline{M}_w$ over $\overline{M}_n$ [39]. The polydispersity indices of LNR-based polyols are shown to be in the

range of 5 - 7. The data also shows that the increase in H_2O_2/isoprene ratio from 0.6 to 1.0 mol has led to an increase in the hydroxyl value for the LNR-based polyol, i.e. from 64 mg KOH/ g sample to 92 mg KOH/ g sample. However, when the H_2O_2/isoprene increases to 1.2 mol, a decrease in the hydroxyl value (82 mg KOH/ g sample) is obtained. By increasing H_2O_2/isoprene ratio, the C=C bonds have undergone epoxidation and hydrolysis, resulting in high hydroxyl groups being formed. When H_2O_2/isoprene ratio is 1.2 mol, probably hydrofuran is formed, thus lower hydroxyl groups (evidence from FTIR and NMR results in Section 4.2). Similar trend has also been observed when temperature was at $70^{\circ}C$ (See **Appendix B**). Thus, higher [H_2O_2/isoprene] ratio results in higher molecular weight and higher OH value. The hydroxyl values of LNR-based polyols are determined for the purpose of formulating the amount of isocyanate needed in polyurethane foam making [24].
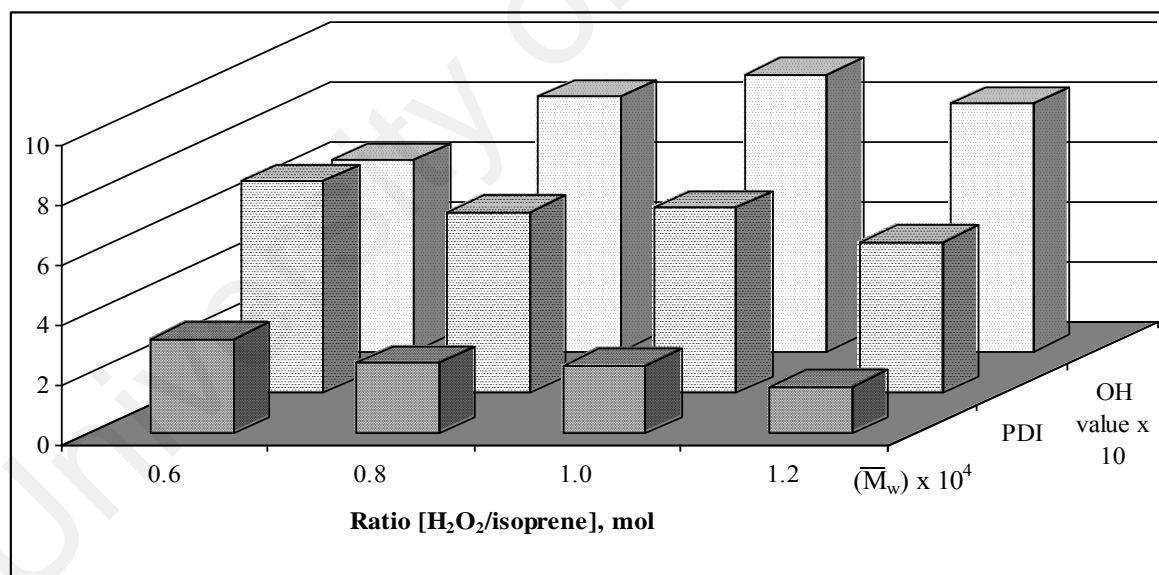
Figure 4.3: Effect of H_2O_2/isoprene ratio on the hydroxyl value, average molecular weight and polydispersity (PDI) of the LNR-based polyol.

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4.1.3 Reaction time

The effect of variation in the reaction times on the molecular weight of LNR based polyol is represented in **Figure 4.4**. Polydispersity indices ($\overline{M}_w$/ $\overline{M}_n$) of the LNR are also given in this Table. The results are consistent to those obtained by N. Radhakrishnan Nair and coworkers [33] whereby, the reduction in molecular weight of LNR depends on reaction time. The average molecular weights ($\overline{M}_w$) of the LNR based polyols decrease with increasing reaction time. Meanwhile, PDI increases with increasing reaction time from 6 to 24 h. However, when the reaction time increases to 36 h, the PDI decreases. The OH values, however increases with reaction time. It can be concluded that the longer reaction time, the lower will be the molecular weight and higher OH value of the products formed.
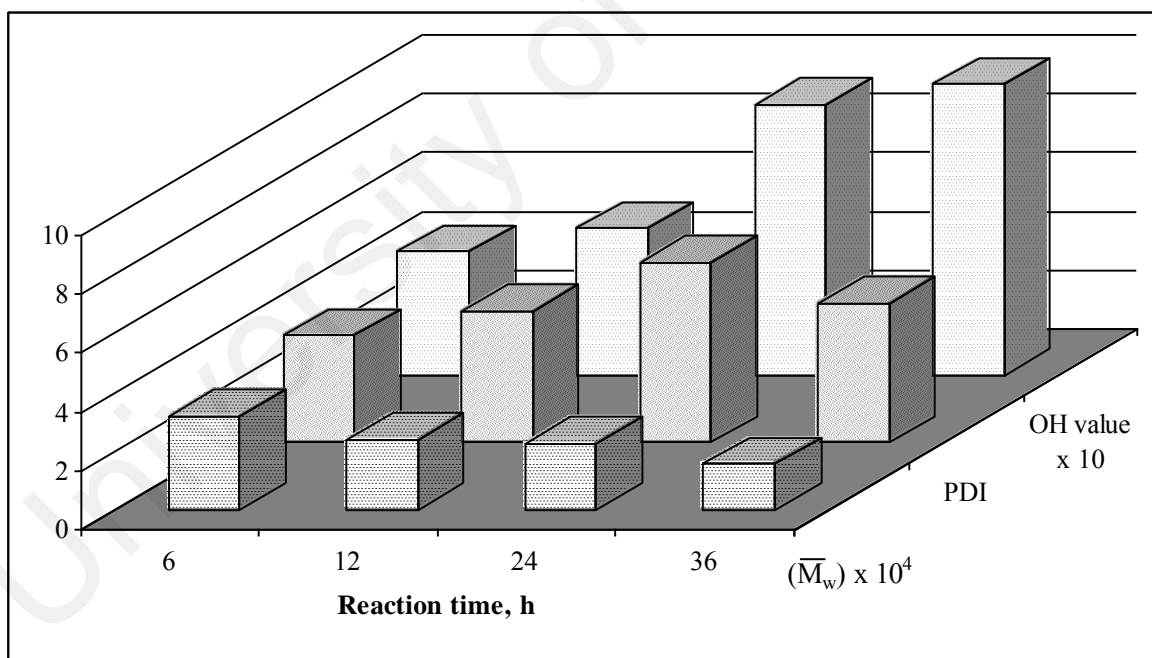
Figure 4.4: Effect of reaction time on the hydroxyl value, the average molecular weight and polydispersity (PDI) of the LNR-based polyol at 90°C.

4.2   Analysis of liquid natural rubber (LNR)-based polyol

4.2.1   FTIR

The FT-IR technique was employed to analyze the functional groups in both latex and the degraded NR product. FTIR bands which are characteristic of LA-TZ latex (before degradation and after degradation at 90°C) are shown in **Tables 4.1**, **4.2** and **Figure 4.5**. From **Figure 4.5b**, the spectrum indicates the appearance of characteristic signals of hydroxyl group in the LNR-based polyol as indicated by the broad band in the region between 3400 - 3500 cm^{-1}. There are also the absorption band of epoxide ring at 875 cm^{-1} (asymmetric stretching of epoxide ring) and 1249 cm^{-1} (symmetric stretching of epoxide ring). Such bands are absent in NR (**Figure 4.5a**). This is consistent with work done by P. Phinyocheep and coworkers [7] who prepared chemical degradation of epoxidized natural rubber using periodic acid.
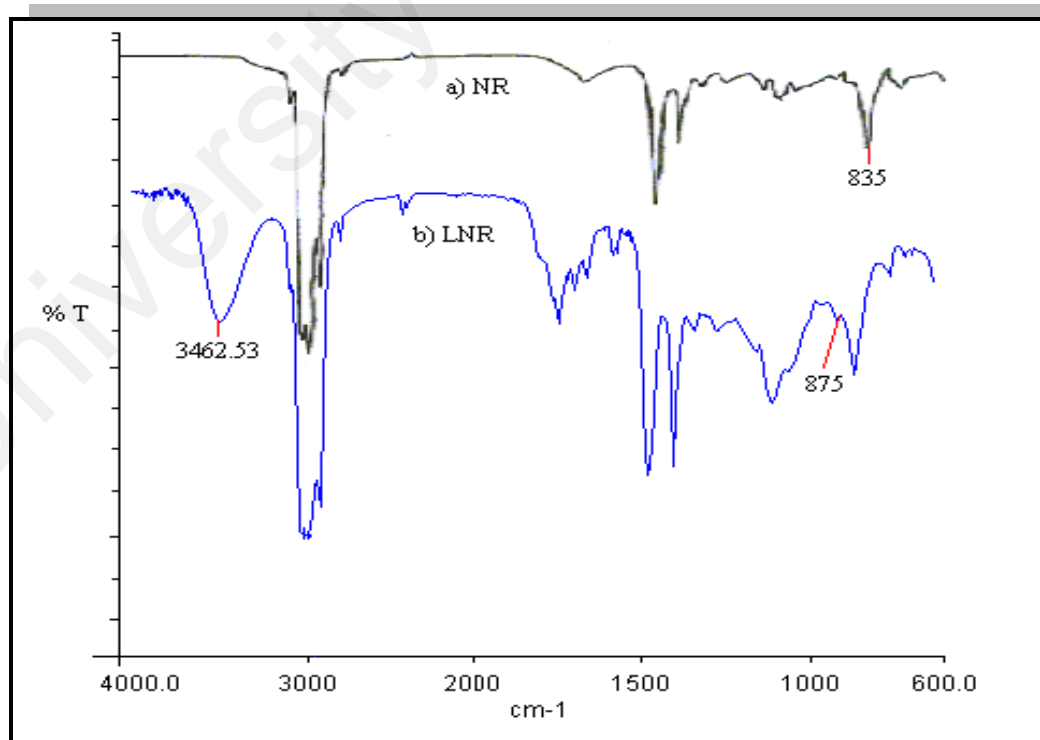
Figure 4.5: FTIR spectra of LA-TZ latex: a) before degradation (NR) b) after degradation (LNR) at 90°C.

Table 4.1: Characteristics of FTIR bands of LA-TZ latex (before degradation)

Wavenumber (cm^{-1})	Type of vibration
2956	CH$_3$ stretching
2615	CH$_2$
1614,1574,1525, 835	C=C stretch

Table 4.2: Characteristics of FTIR bands of LNR (after degradation)

Wavenumber (cm^{-1})	Type of vibration
3462	OH
2954	CH$_3$ stretch
2618	CH$_2$
1249, 875	Epoxide stretch
1614,1574,1525, 837	C=C stretch

The presence of both epoxy and hydroxyl groups indicates that the C=C bonds in the NR have undergone epoxidation and hydrolysis [30]. **Figures 4.6** and **4.7** show the FTIR spectra of LNR prepared using different reaction times at two different temperatures, which are 70°C and 90°C. The NR is observed to have undergone significant changes, particularly in the gradual appearance of the epoxy group band at around 875 cm^{-1} and hydroxyl group band at around 3400 cm^{-1} when reaction time changes from 6 h to 36 h. The absorption band at 3462 cm^{-1} region at high temperature (90°C) is broader than that at low temperature (70°C), suggesting that the epoxide group has further hydrolyzed to form the ring-opened product.
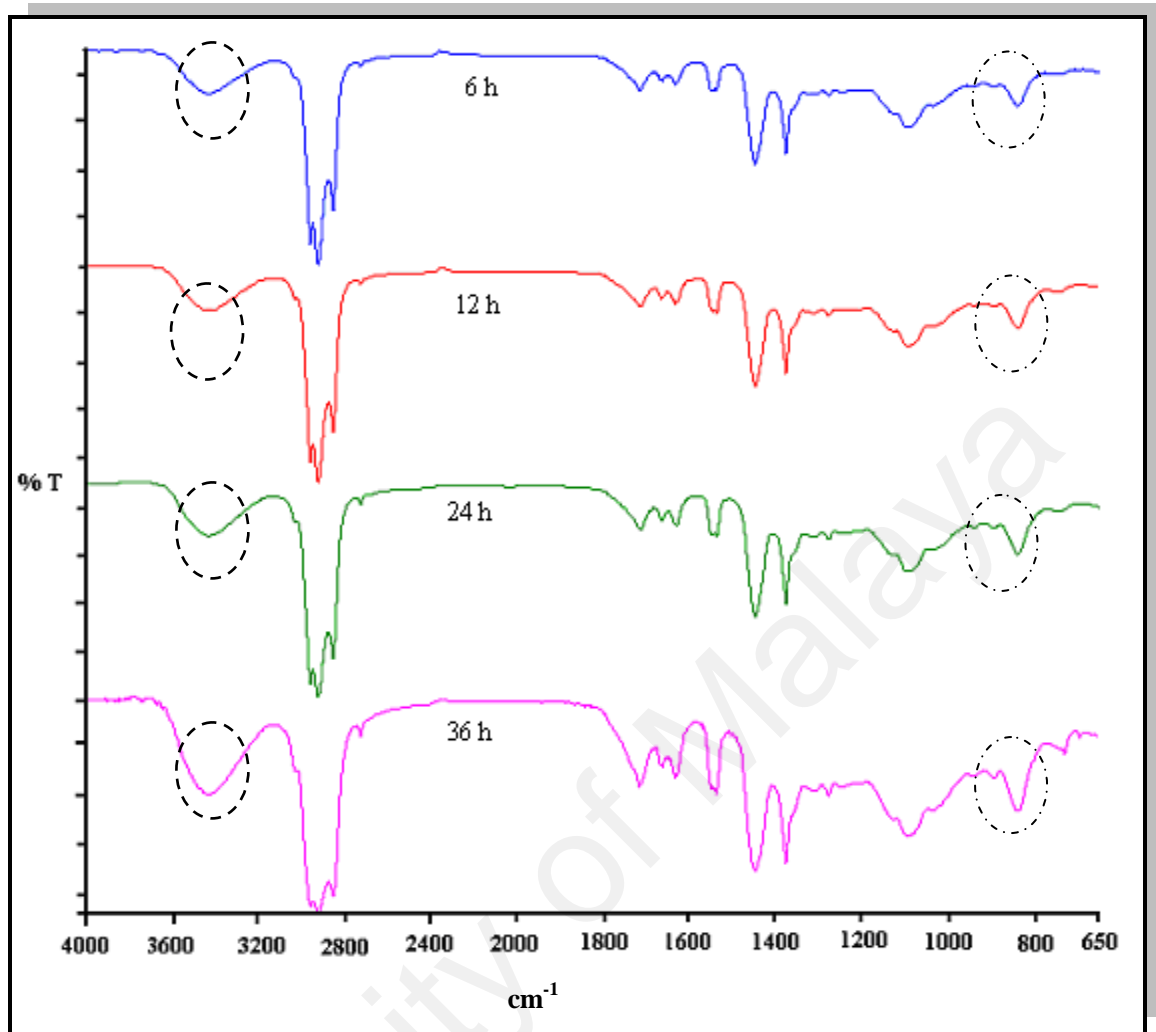
Figure 4.6: IR bands showing the hydroxyl groups (----) and the epoxy groups (-.-.-) present in the LNR product synthesized at $70^{\circ}C$ under different reaction times.
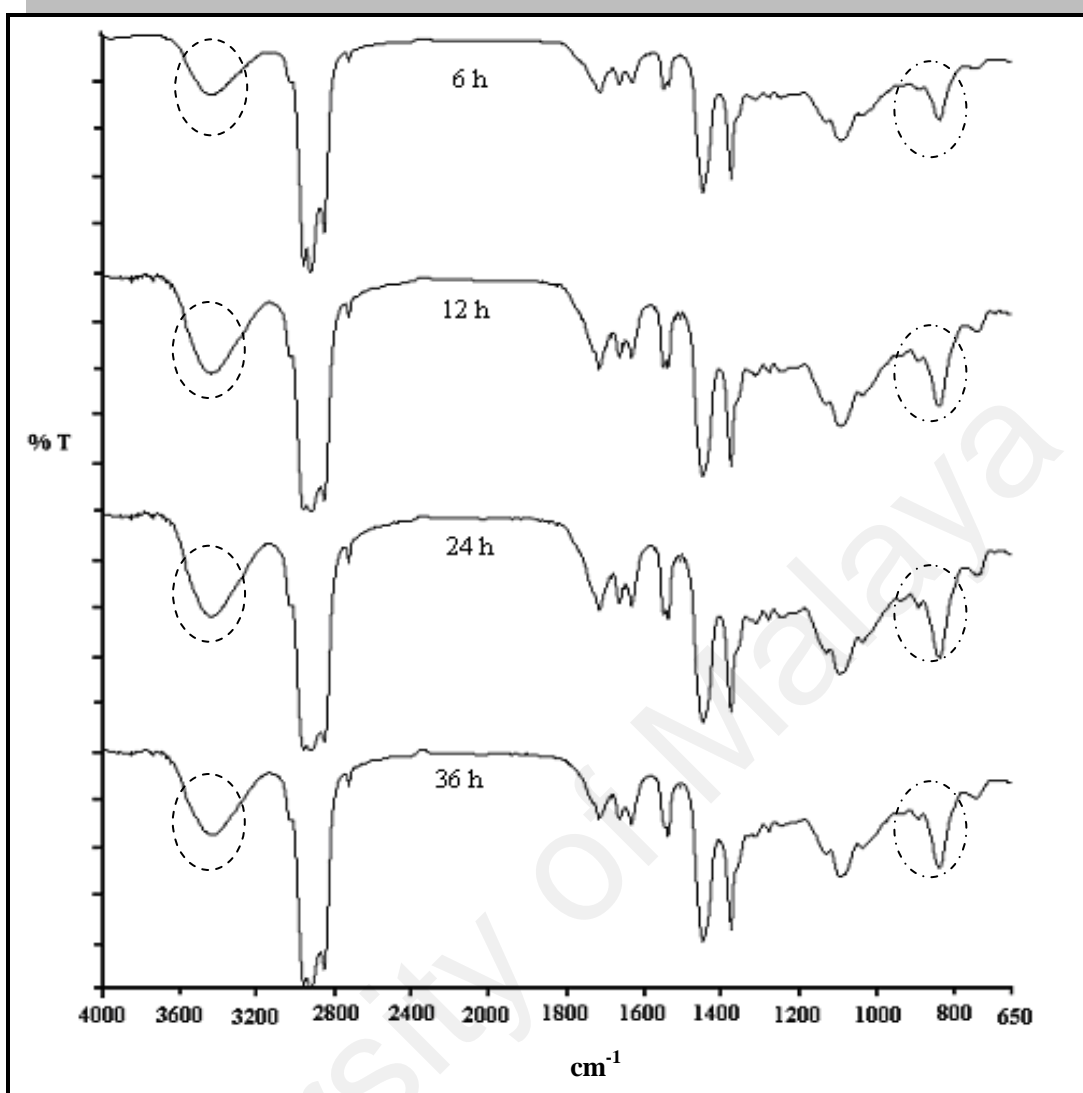
Figure 4.7: IR bands showing the hydroxyl groups (----) and the epoxy groups (-.-.-) present in the LNR product synthesized at 90°C under different reaction times.

Meanwhile, **Figure 4.8** shows the IR spectra of LNR synthesized at 90°C after 24 h with different of H_2O_2/isoprene ratios. The bands at 3400 cm^{-1} attributed to the hydroxyl group increase with increasing of the H_2O_2/isoprene ratio from 0.6 to 1.0. After 1.0, the hydroxyl group band decreases. As expected, this may be due to the formation of cyclic ether (furan) group as band at 1068.21 cm^{-1} assigned to this group is observed.
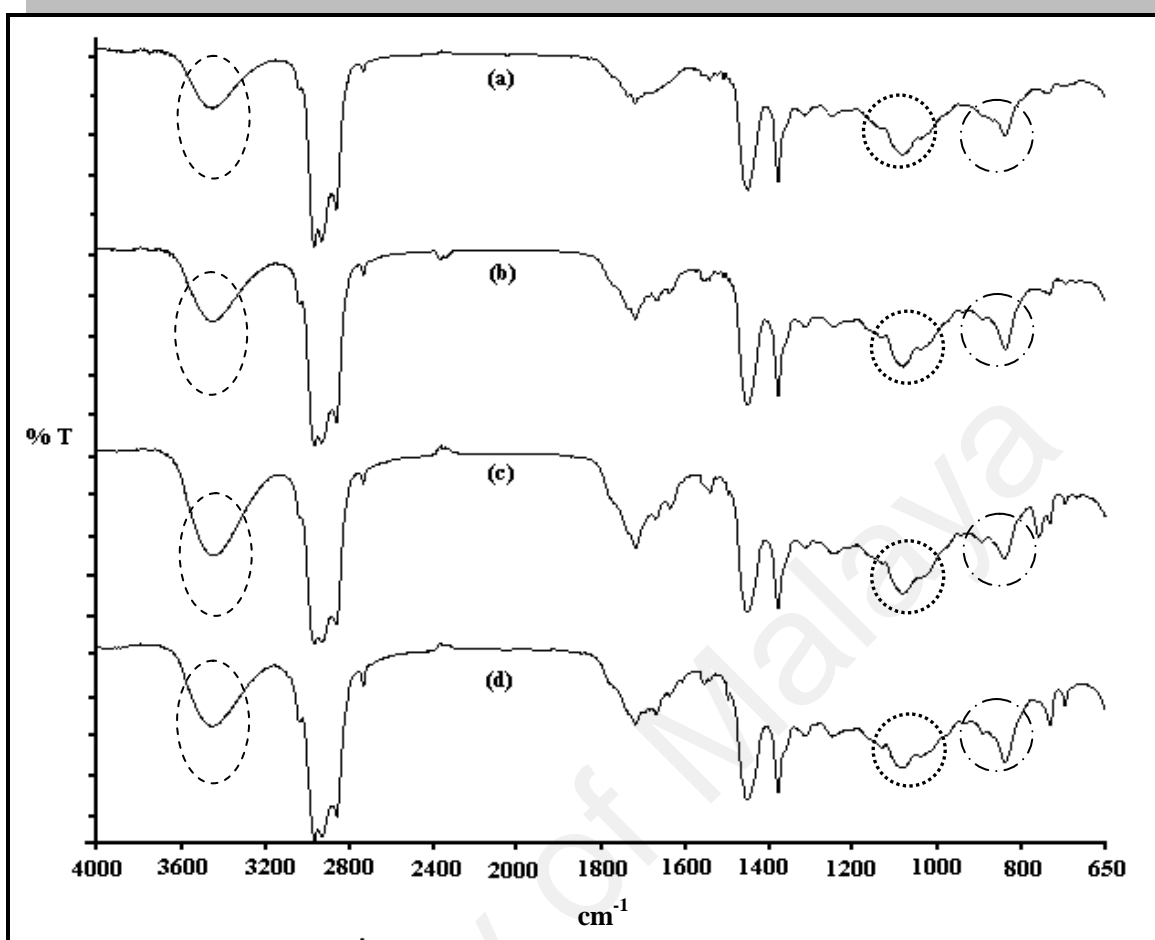
Figure 4.8: IR spectra of LNR synthesized at 90°C after 24 h with different of H$_2$O$_2$/ isoprene ratio. a) 0.6 mol b) 0.8 mol c) 1.0 mol and d) 1.2 mol.

Note: The hydroxyl groups (---), epoxy group (-.-.) and hydrofuran (…)

4.2.2 ^{1}H-NMR

The presence of hydroxyl and epoxide groups in the degraded products at temperature 90°C is further confirmed from the ^{1}H-NMR spectrum .The ^{1}H-NMR spectra for NR latex before and after degradation are shown in **Figure 4.9** while **Tables 4.3** and **4.4** show the chemical shift values of the sample. According to D.L. Pavia [31], the protons attached to epoxidized carbon give signals at around 2.70 - 3.20 ppm and the chemical shift value for hydroxyl carbon is at around 3.5 - 4.0 ppm [32]. As shown in **Figure 4.9**, methyl,

methine and methylene protons of isoprene unit in ^{1}H-NMR spectrum give rise to signals at 1.6, 2.1 and 5.1 ppm, respectively. After epoxidation and hydrolysis of NR (**Figure 4.9(b)**), two other signals appear at 2.7 and 1.2 ppm, which correspond to methylene and methyl protons of the resulting epoxy group and another signal corresponding to hydroxyl group at 3.6 ppm.
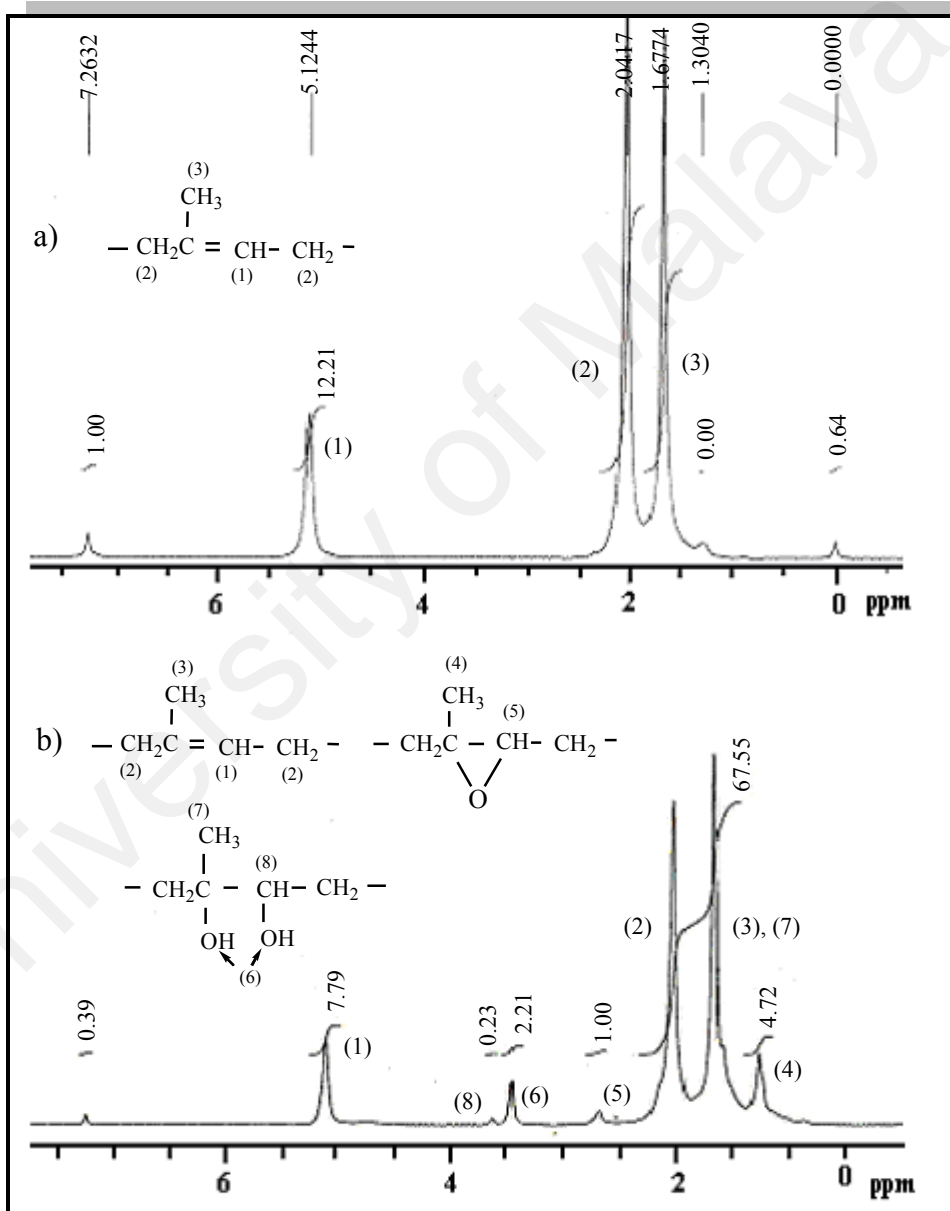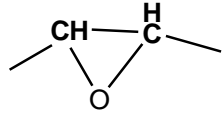
Figure 4.9: ^{1}H-NMR spectrum of LA-TZ latex (a) before degradation and (b) after degradation at 90°C.

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Table 4.3: ^{1}H-NMR of LA-TZ latex (before degradation)

Chemical shift (ppm)	Reference (ppm)	Assignment
0.8256, 1.2179	0.7 - 1.3	**CH₃**-C=C
1.6091, 1.9703, 2.0966	1.6 - 2.6	**CH₂**-C=C
5.0542	4.5 - 6.5	**H**-C=C

Table 4.4: ^{1}H-NMR of LA-TZ latex (after degradation)

Chemical shift (ppm)	Reference (ppm)	Assignment
0.8256, 1.2179	0.7 - 1.3	**CH₃**-C=C
1.6091, 1.9703, 2.0966	1.6 - 2.6	**-CH₂**-C=C
5.0542	4.5 - 6.5	**H**-C=C
3.5757	3.2 - 3.8	**CH-OH**
2.7354	2.70 - 3.20	

The degree of epoxidation and thereafter hydrolysis was determined by comparing the integration of the methine proton adjacent to the oxirane ring at 2.7 ppm and that of the proton adjacent to the carbon-carbon double bond of polyisoprene structure at 5.1 ppm. The epoxy and hydroxyl groups can be estimated from intensity ratio of signals, as follows:

$$\chi_{epoxy} = \left(\frac{I2.7}{I2.7 + I5.1}\right) \times 100 \quad \text{and} \quad \chi_{OH} = \left(\frac{I3.6}{I3.6 + I5.1}\right) \times 100$$

Where I is intensity of signals and the subscript represents chemical shift (^{1}H-NMR).

Table 4.5 illustrates the effect of reaction times on the intensities of epoxide and hydroxyl groups of the LNR-based polyols. By increasing reaction time from 6 to 36 h, it is possible to prepare polyol with intensity of epoxide and intensity of hydroxyl ranging from 8 - 19 and 2 - 7. However, the intensity epoxide of LNR-based polyol starts to be constant after 24 h of reaction whereby the reaction is considered to be complete (See **Appendix D**). Meanwhile, **Table 4.6** illustrates the effect of H_2O_2/ isoprene on intensity of epoxide and intensity of hydroxyl at temperatures $70^\circ C$ and $90^\circ C$ after 24 h. From this Table, intensities of both epoxides and hydroxyl groups for both temperature increases with increasing H_2O_2/isoprene ratio from 0.6 to 1.0. However, when the H_2O_2/ isoprene ratio increase to 1.2, the intensities of epoxide and the hydroxyl groups decrease. The LNR-based polyol synthesized at $90^\circ C$ give the higher of intensity of epoxide and hydroxyl group compared to the LNR-based polyol at temperature $70^\circ C$. The H_2O_2/isoprene ratio of 1.0 mol was chosen as the optimum concentrations of H_2O_2 and isoprene to produce the LNR-based polyols that have high hydroxyl groups. At H_2O_2/isoprene ratio of 1.2, the hydroxyl group for both temperatures decreases. This probably due to the formation of hydrofuran as confirmed from FTIR results (**Figure 4.8**).

Table 4.5: Intensities of epoxide and hydroxyl groups of the synthesized LNR at various reaction times at $90^\circ C$.

Reaction time (h)	Intensity epoxide [a]	Intensity hydroxyl[a]
6	11	2.9
12	12.3	3.4
24	17.0	6.4
36	17.4	6.9

Note: [a] refer to ^{1}H-NMR, H_2O_2 / isoprene =1.0

Table 4.6: Intensities of epoxide and hydroxyl groups at different ratios of H_2O_2/isoprene at temperatures of $70^\circ C$ and $90^\circ C$

Temperature / H_2O_2/isoprene (mol)	($70^\circ C$)		($90^\circ C$)	
	Intensity epoxide [a]	Intensity hydroxyl[a]	Intensity epoxide [a]	Intensity hydroxyl[a]
0.6	9.8	3.1	11.5	4.4
0.8	15.5	4.5	16.8	6.2
1.0	16.6	5.3	17.0	6.4
1.2	15.2	4.2	16.5	5.6

Note: [a] refer to ^{1}H-NMR
Reaction time = 24 h

4.3 Preparation of flexible polyurethane foam from LNR-based polyol

The LNR-based polyol was used in the production of flexible polyurethane foam. Generally, flexible polyurethane foam is formed by simultaneous reaction between an isocyanate with polyether polyol and water [34]. **Figure 4.10** shows the basic reaction chemistry that takes place during foam formation. Combination of these two exothermic reactions leads to the formation of a segmented block copoly (urethane-urea).
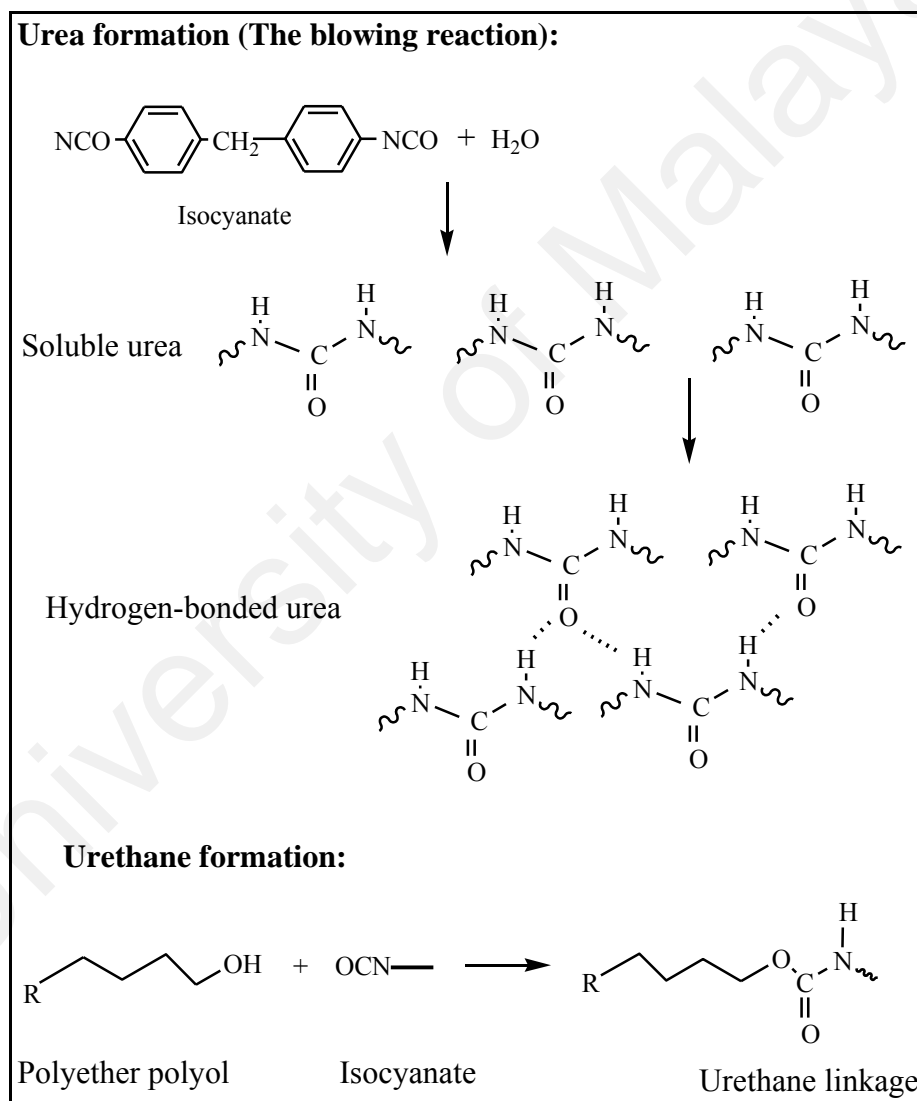
Figure 4.10: Schematic representation of the reaction chemistry taking place during polyurethane foam formation.

Conventionally, the physical blowing action can be achieved by using a volatile liquid such as chlorofluorocarbons (CFC) or pentane in polyurethane production. However, water has emerged as an alternative blowing agent after CFC was phased out due to ozone layer depletion effect [35].

Motte [36] also reported the study of flexible polyurethane molded foam using water as blowing agent in comparison to foam prepared by CFC-11. Foams blown with carbon dioxide gases (CO_2) show improved properties in low density foam [37]. When water is used as a blowing agent, a reaction occurs between the water and the isocyanate group to form an amine and carbon dioxide gas in the form of bubbles. After several seconds, the carbon dioxide produced *in-situ* will diffuse into small air bubbles and enlarge giving the mixture a creaming appearance. The time taken for appearance to change, as measured from the initial mixing, is known as the cream time. As more carbon dioxide is generated, the bubbles expand and the foam begins to rise. While the bubbles are expanding, a polymerization reaction takes place in the liquid phase and viscosity starts to increase.

In this work, the effect of water content and isocyanate index (MDI) in the formulation on the physical properties, morphology and thermal character of the flexible polyurethane foams were studied.

4.4 Effect of water content on properties of flexible PU foams

The introduction of water in polyurethane foam formulation allows expansion into the cellular structure. Besides being able to contribute to a more vigorous blowing reaction, water will also lead to more gelling reaction [38]. This is attributed to the formation of unstable carbamic acid when isocyanate reacts with water. The unstable carbamic acid will then dissociate into carbon dioxide and amine. The amine will continuously react with isocyanate to form urea as shown in **Equation 4.2**. Different water contents will give different of physical properties [37]. In this work, the flexible polyurethane foams were prepared using isocyanate (MDI) and two types of the LNR based polyols i.e. S3 and S1 having OH values of 92 mg KOH/g and 64 mg KOH/g respectively. The details of the formulation are given in **Table 4.7a and 4.7b** based on formula in The International Polyurethane Conference and Exhibition for Asia Pacific [50]. The isocyanate index of every production of the PU foam was fixed at 100 (See **Appendix E**) and water content was altered by 2 g, 3 g, 4 g and 5 g of water.

$$RNCO \; + \; H_2O \; \longrightarrow \; R-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-OH \; \longrightarrow \; RNH_2 \; + \; CO_2$$

Carbamic acid

$$RNH_2 \; + \; RNCO \; \longrightarrow \; \left[R-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R \right]$$
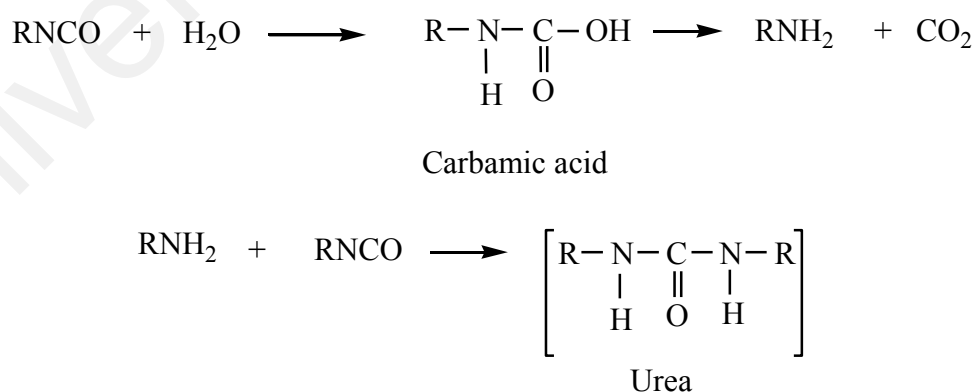
Urea

Equation 4.2: The formation of urea by reaction of isocyanate with water

Table 4.7a: Preparation of flexible polyurethane foam by varying water content for S3

Chemical (phr/ g)	Product code			
	HI	H2	H3	H4
Polyol, S3	100.0013	100.0021	100.0015	100.0017
DEA	1.5053	1.5084	1.5091	1.5178
Niax-A1	0.2034	0.2051	0.2038	0.2086
Stannous octoate	0.4068	0.4102	0.4075	0.4036
Silicone A3002	2.5422	2.50768	2.5381	2.5296
H_2O (blowing agent)	2.0018	3.0068	4.0021	5.0593
Modified MDI	57.2524	73.2351	86.8983	102.5877
Isocyanate index	100	100	100	100
Reactivity Characteristics				
Cream Time (s)	35	33	33	30
Track Free Time (s)	1422	1410	1398	1363

Note: Polyol, S3 with hydroxyl value = 92.065 mg KOH/ g sample

Table 4.7b: Preparation of flexible polyurethane foam by varying water content for S1

Chemical (phr/ g)	Product code			
	KI	K2	K3	K4
Polyol, S1	100.0032	100.0019	100.0026	100.0018
DEA	1.5084	1.5184	1.5283	1.5111
Niax-A1	0.2011	0.2051	0.2038	0.2108
Stannous octoate	0.4022	0.4102	0.4075	0.4170
Silicone A3002	2.5084	2.5076	2.5265	2.5122
H_2O (blowing agent)	2.0218	3.0768	4.0754	5.0162
Modified MDI	50.8140	66.4900	81.3132	95.1895
Isocyanate index	100	100	100	100
Reactivity Characteristics				
Cream Time (s)	35	33	34	30
Track Free Time (s)	1423	1410	1397	1363

Note: Polyol, S1 with hydroxyl value = 63.646 mg KOH/ g sample

4.4.1 Characterization of the polyurethane (PU) foam

In continuation with the synthesis work, characterization is indeed very important for purpose of process development and also quality control on the polyurethane foam. Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Optical Microscopy and Dynamic Mechanical Analysis (DMA) were used for this purpose as described in **Section 3.5**. Meanwhile, the physical properties of foams are measured by using Instron equipment.

4.4.1.1 FTIR

A typical FTIR spectrum of the starting material, isocyanate (MDI) and LNR-based polyol are shown in **Figure 4.11** [**(a)** and **(b)**]. The assignments of these bands are recorded in **Tables 4.8**. The NCO isocyanate band at 2245 cm^{-1} is characteristic of isocyanate (MDI) and hydroxyl band at 3434 cm^{-1} is characteristic of LNR-based polyol. After isocyanate reacts with polyol, the disappearance of hydroxyl band at 3434 cm^{-1} and isocyanate band at 2245 cm^{-1} are observed. On the other hand, the appearance of urethane broad band at 3385 cm^{-1} appeared (**Figure 4.11 (c)** which is the formation of urethane linkage in the foam.
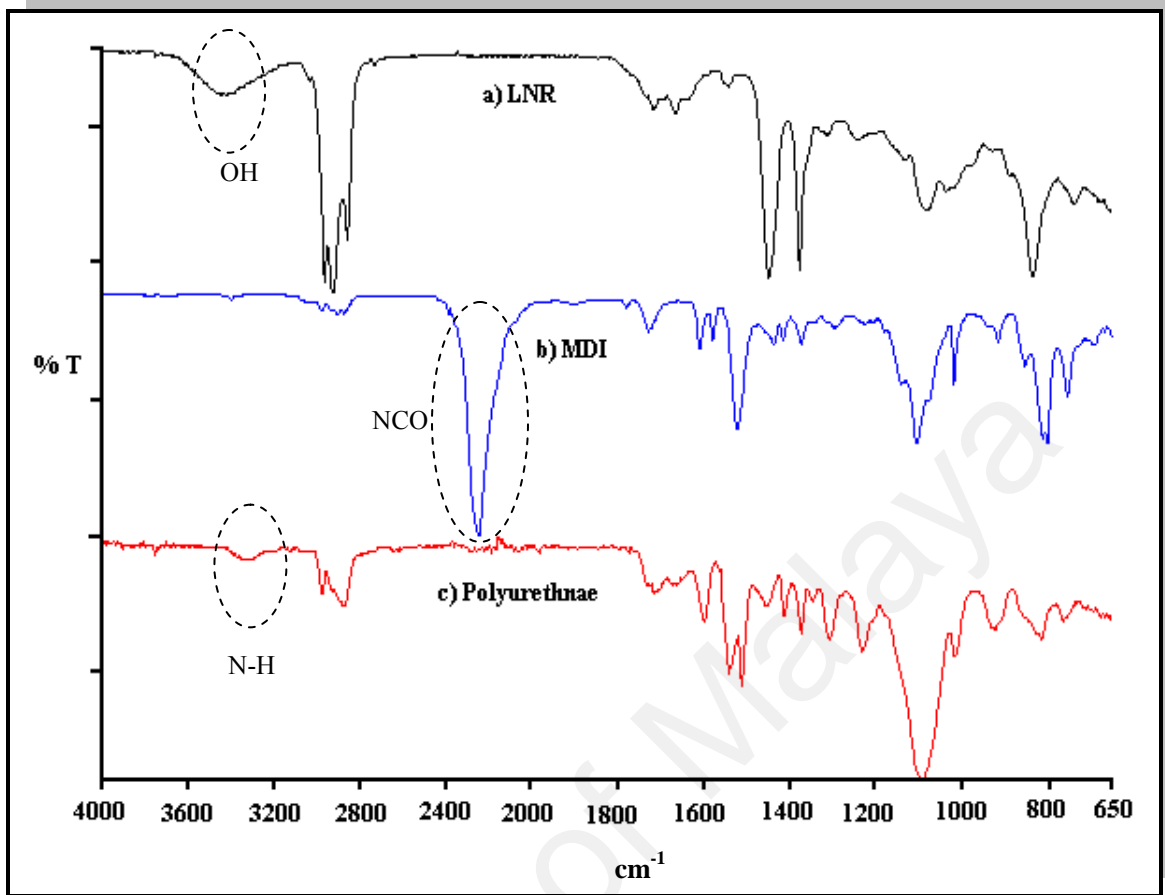
Figure 4.11: IR spectra for LNR (a), MDI (b) and polyurethane (c)

Table 4.8: FTIR band assignments for MDI, LNR and PU

Material	Wavenumber (cm^{-1})	Type of vibration
MDI	3394	NH
	2914	CH$_3$ stretch
	2245,1434	NCO stretch
	1614,1574,1525	Aromatic C=C stretch
	1534	CN stretch
LNR	3434	OH
	2914	CH$_3$ stretch
	2618	CH$_2$
	875	epoxide
	1614,1574,1525	Aromatic C=C stretch
PU	3385	NH (urethane)
	2915	CH$_3$ stretch
	2619	CH$_2$
	1450	NCO
	1614,1574,1525	Aromatic C=C stretch
	1536, 1230	CN stretch

FTIR spectra for the variation of water content on formation of urethane linkage are shown in **Figure 4.12.** It is observed that the presence of water as blowing agent to give highest intensity of N-H group for urethane occurs at maximum water content of 3 g. When the water content is below 3 g, the reaction between polyol and isocyanate form urethane out-wins the reaction between isocyanate with water. However, when the amount of water added in the formulation is higher than 3 g of water, intensity of N-H group for urethane decreases as the reaction of water with isocyanate is more than reaction of isocyanate with polyol. This reaction produced more of the carbamic acid compared to urethane. The equation for this reaction is as shown in **Equations 2.1** and **2.4**. Bailey and Critcfield [17]

reported that the urea formation takes place quickly compared to urethane formation and it

only takes place within the first 5 min of the foaming process.
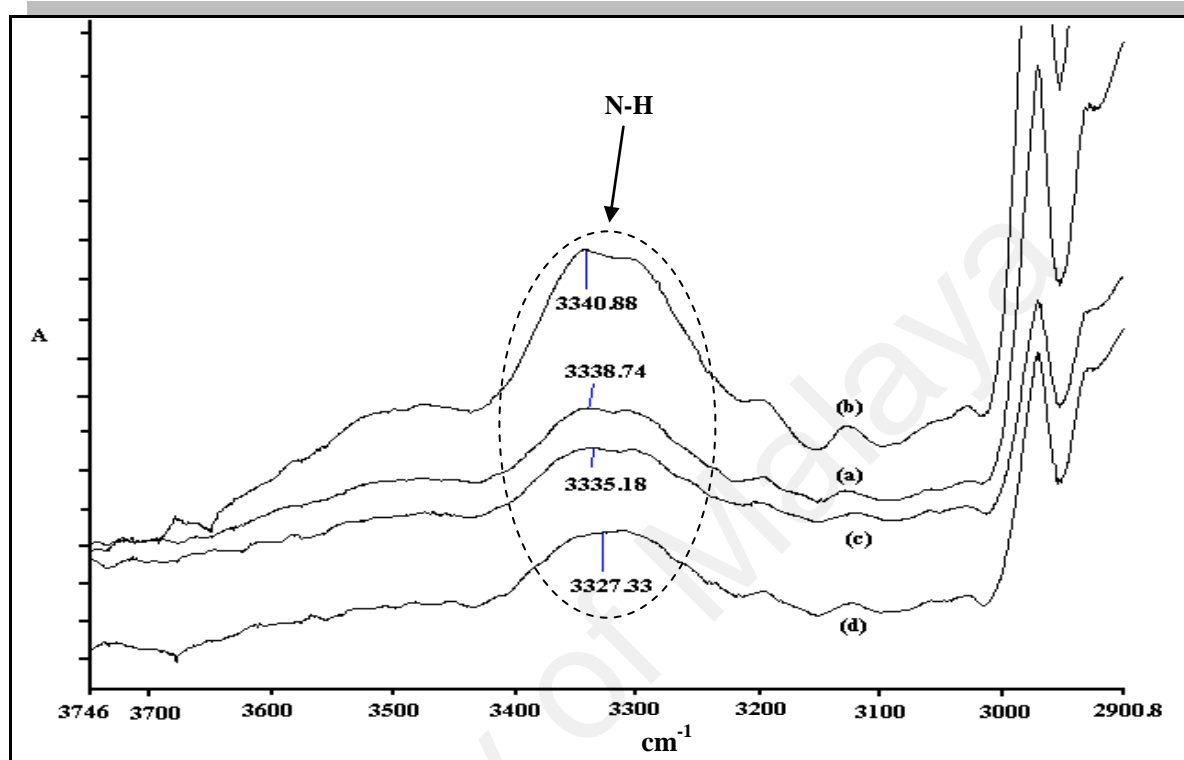
Figure 4.12: Effect of varying water content on the N-H absorbance in FTIR spectra of
foams: a) 2 g   b) 3 g   c) 4 g   and d) 5 g
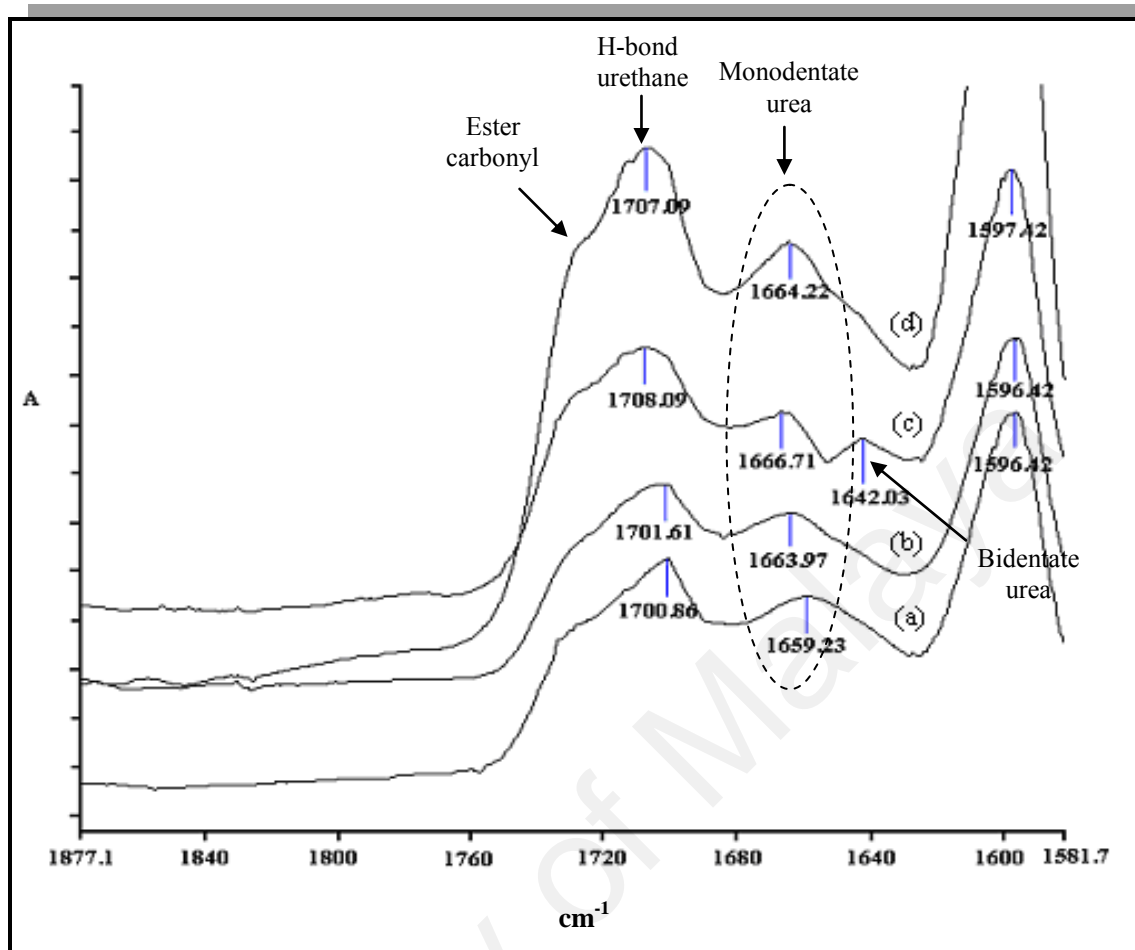
Figure 4.13: Effect of varying water content on the monodentate urea absorbance in FTIR spectra of foams: a) 2 g b) 3 g c) 4 g and d) 5 g

FTIR spectrum can be used to study the hydrogen bonding within the hard segments of the polyurethane foams when water content is increased. The hydrogen-bonded ureas, including both monodentate and bidentate, are indications of hard domain ordering. **Figure 4.13** shows the bands for monodentate and bidentate H bonded urea at around 1659 -1666 cm^{-1} and 1642 cm^{-1} respectively. The monodentate urea increases with increasing of water content. This may be due to the formation of hard domain urea linkage when the reaction between isocyanate and water takes place and forms carbamic acid that further reacts to give urea and carbon dioxide.

4.4.2 Physical properties

In this work, the effects of different water contents on the physical properties of the foams, such as density, compression stress, tensile strength, elongation at break and tear strength were studied. The formulation of PU foams were fixed at 100 g of polyols and water content was varied from 2 g to 5 g.

4.4.2.1 Density and compression stress

In general, foam with high density will typically retain its original properties to provide support and comfort of original design [39]. Reaction between isocyanate with addition of water content in formulation, results in more carbamic acid which consequently reacts to give urea and carbon dioxide. The surplus carbon dioxide will blow up the polyurethane foam and consequently produce lower density foam.

As such, water, when used as blowing agent, plays an important role in polyurethane foam formulation. **Figure 4.14** shows the changes in density and compression stress of the foams (H1 - K4) using different amount of water in the formulation. Data calculation for the density and compression stress of the polyurethane foams (H1 - H4) are given in **Appendix F** and **Appendix G**. The effect of water as blown agent on the density and compression stress of flexible polyurethane foams shows a correlation between the density and the compression stress of the foam. High density foams were prepared using 2 g of water content while low density foams were prepared using 4 g - 5 g of water. Increase in of water content in the polyurethane formulation produces foams with lower density. This is consistent with work done by Lin and coworkers [40] who prepared water-blown flexible polyurethane foam extended with biomass materials.
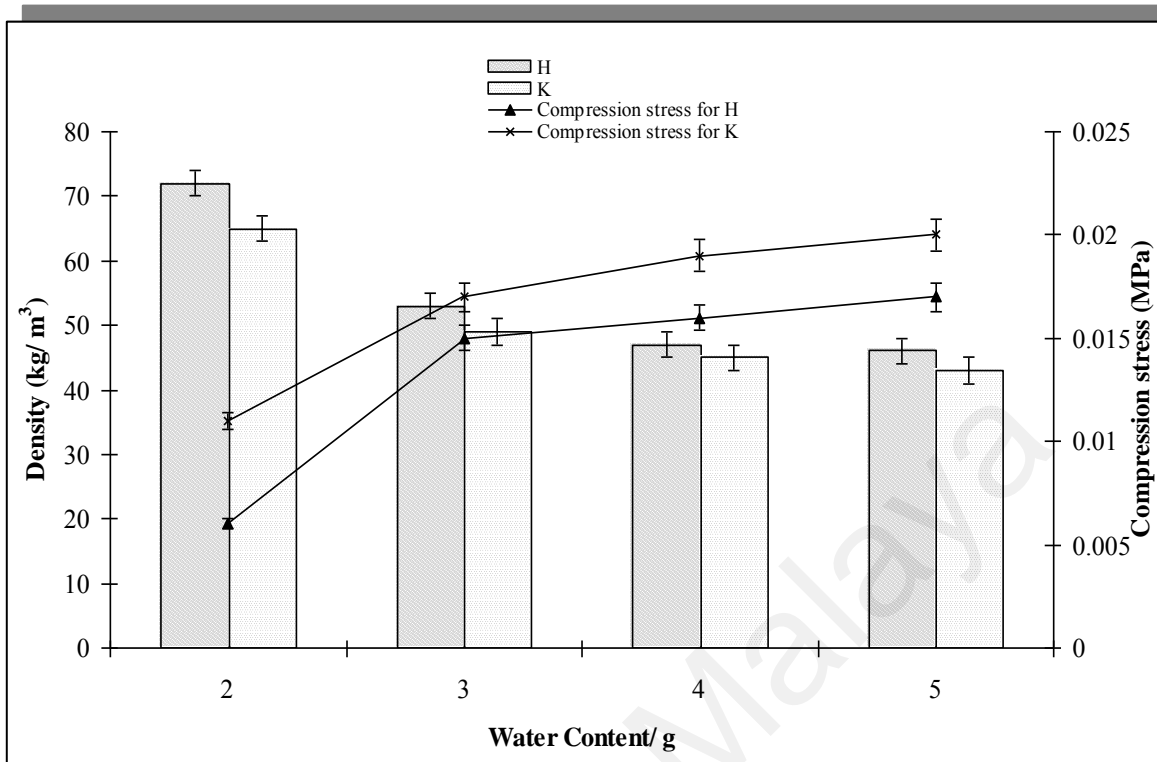
Figure 4.14: Effect of amount of water on density (kg m^{-3}) and compression stress (MPa) of the PU foams.

Meanwhile, the compression stress of the foams increases with the increasing of water content in the formulation. There is a correlation between the compressions stress of the foam corresponding with the increment of water content used in the foam formulation. The reaction with isocyanate leads not only to the formation of carbon dioxide, but also to the formation of urea hard segment when the amount of water content increases [34]. These urea compounds can continue to react with isocyanate to form biurets linkages, another hard compound in polyurethane (**Equation 2.3**).

4.4.2.2 Tensile strength, elongation at break and tear strength

The effect of amount of water on the tensile strength, elongation at break and tear strength of the foams are shown in **Figures 4.15** and **4.16**. The tensile strength and tear strength of the foams increase with increasing water content. Foams with higher tensile strength exhibit higher tear strength property. The tensile strength (10.9 kg cm^{-2} for H and 10.7 kg cm^{-2} for K) and tear strength property (0.28 N/ mm for H and 0.27 N/ mm for K) of the foams are at a maximum with 5 g of water content. This is probably due to the increase in the formation of biuret linkage when water content is increased. More detail will be given in **Appendices I** and **J**.

Meanwhile, reduction in the elongation at break of the foam indicates that the foam has become less flexible as the water is increased. Increase in water content from 2 g to 3 g has led to a decrease in the elongation at break in the foam. However, an increase in the elongation at break is recorded when the water content is increased to 4 g, but when the water content is further decreased to 5 g, lower elongation at break is recorded. The water content of 4 g was chosen as the optimal water content as it produced foam with highest elongation at break (75 % for H and 88 % for K).
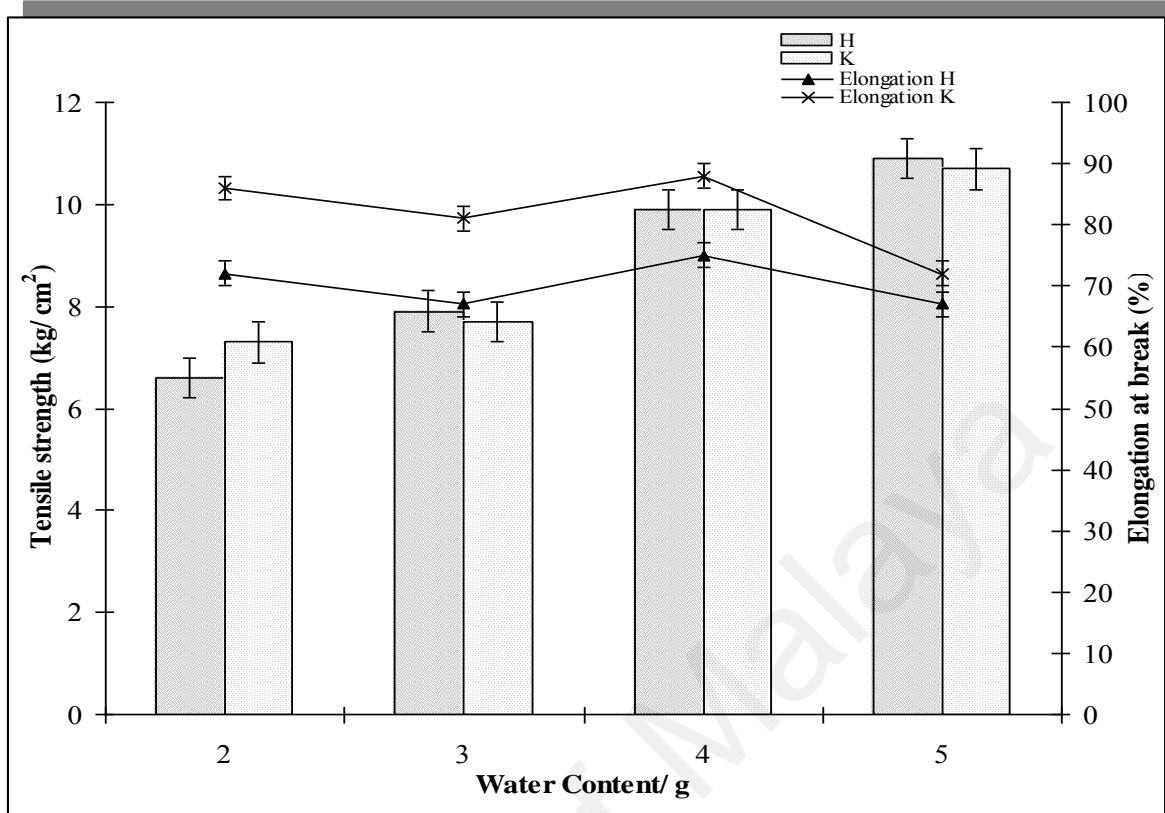
Figure 4.15: Effect of amount of water on tensile strength (kg cm^{-2}) and elongation at break (%) of the PU foams.
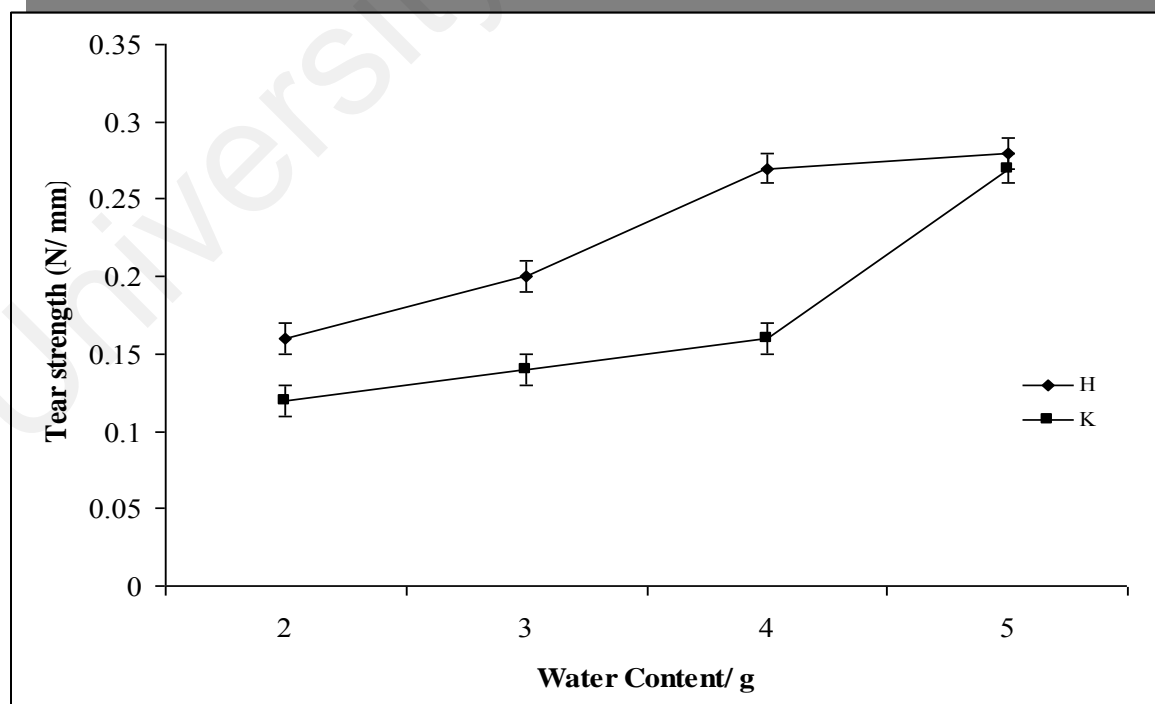
Figure 4.16: Effect of amount of water on tear strength of the PU foams.

4.4.2.3   Morphology of PU foam

Morphology from optical microscope of the polyurethane foams prepared using water content ranging from 2 g, 3 g, 4 g and 5 g are shown in **Figure 4.17**. Foams prepared using high water content (5 g) have bigger sizes of pentagon and hexagon shaped open cells in the structure. These phenomena are due to the increment of carbon dioxide generation causing the blowing reaction to take place faster, thus producing more open cell foams. However, at low water content (2 g), cell structures are smaller and also more uniform.
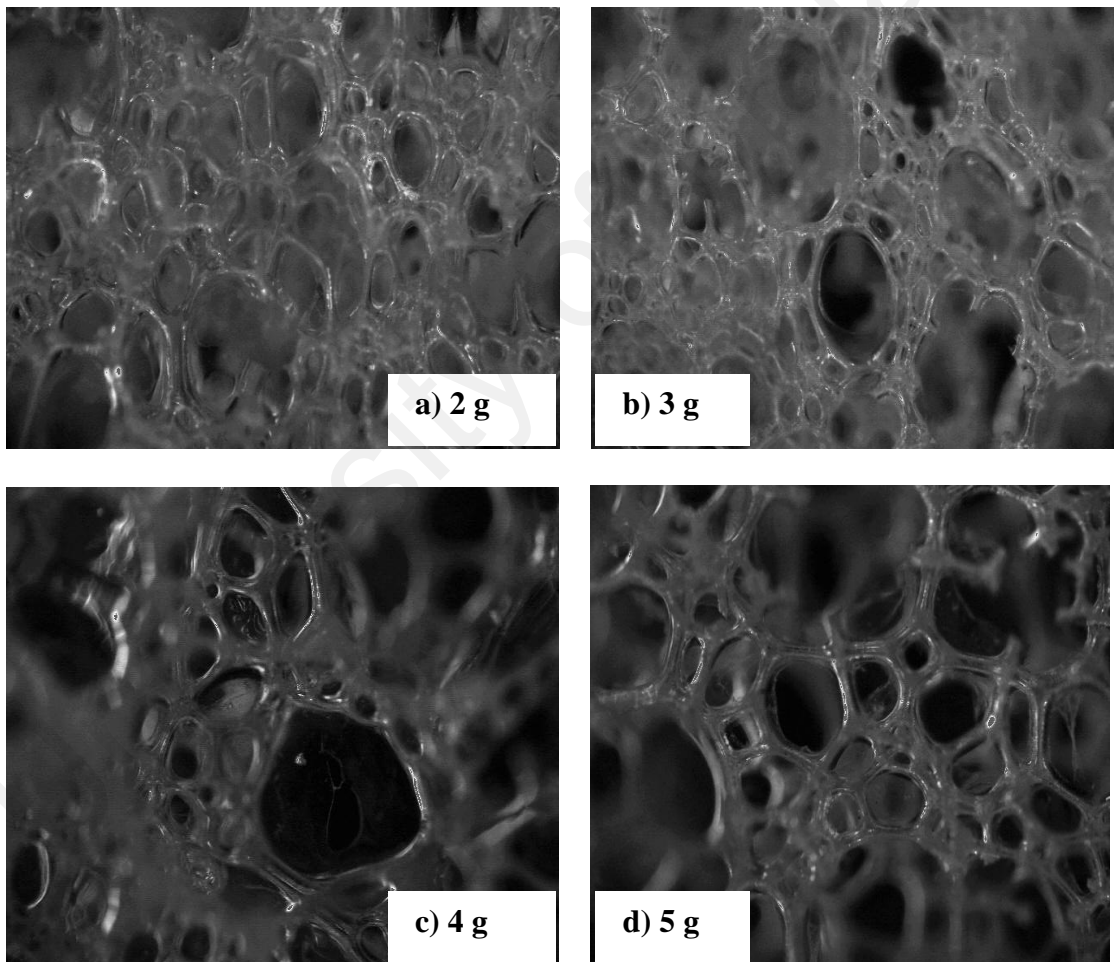
Figure 4.17: Structure of open cell for foams produced using different amount of water at 4X magnification

4.4.2.4 Thermal properties

4.4.2.4.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) method has been used to evaluate the morphology and thermal characters of polyurethane. **Table 4.9** shows the thermal characteristic of the foams produced from polyols, S3 and S1, with different water content. This Table also shows the decomposition temperatures of foams 10%, 50% and 90% of weight losses increase with increasing water content. The TGA profiles of these foams are shown in **Appendices M** and **N**. The decomposition temperature at 264 - 285°C that gives 10% weight loss of the foam is attributed to the additional formation of urea hard segments in the foam structure caused by the water content. Meanwhile, the decomposition temperature in the range of 331 to 348°C resulted in 50% of foam weight loss. This may be due to polyol decomposition [41]. The weight loss of 90% recorded at 516 - 794°C could be due to the decomposition of hard segment of the isocyanurate ring. Generally, the results from TGA show that the foams produced using higher water content are thermally more stable.

Table 4.9: The effect of water contents on thermal character of the PU foams.

Polyol	Water content/ g	Decomposition temperature (^{o}C)		
		$T_{10\%}$	$T_{50\%}$	$T_{90\%}$
H1	2	272.13	345.24	520.46
H2	3	273.11	345.41	560.90
H3	4	278.59	347.87	629.35
H4	5	285.57	348.07	794.62
K1	2	264.48	331.89	516.97
K2	3	269.58	337.63	622.97
K3	4	271.74	340.02	656.05
K4	5	273.01	342.89	725.34

4.4.2.4.2. Dynamic mechanical analysis

One important application of DMA is measurement of the glass transition temperature of the polymers. The glass transition temperature is an important indicator for applications of polymeric material. The criterion for selection of glass transition temperature (T_g) from DMA data is usually either the peak loss modulus or peak tan δ. The peak tan δ is the most prevalent criterion appearing in the literature because it corresponds more closely to the transition midpoint, while the peak loss modulus more closely denotes the initial drop from the glassy state into the transition [46]. In this works, the effects of various water contents on the dynamic mechanical storage modulus (E''), loss modulus (E''') and tan δ (E''/ E''') for the polyurethane foams (H1 - H4) were studied. The results from DMA analyses are recorded in **Table 4.10**. The tan δ (T_g) of the foams observed no significant changes at water content below 4 g. These phenomena were due to low degree of cross-linking between PU molecules, where long segments of the backbone molecule are still free to move. But when water content increasing to 4 g, increasing cross-linking polymer, reduces molecular mobility and raises tan δ to -28.95^{o}C. However, at 5 g of water content, tan δ decrease. This may be 4 g of water content was chosen as the optimum to produced foam with higher T_g. After 4 g, higher degree cross-linking had led the PU molecules are thoroughly immobilized and become rigid thermo-plastic [1]. This Table also shows that the storage modulus of the foams decrease with increase of water content. This may be increasing of cross-linking had led to increase in modulus of elasticity for flexible PU foams. Nevertheless, the maximum value of loss modulus near the glass transition region decreases as shown in **Appendix K**. This phenomenon was due to the decrease viscosity of the foams as water content increase thus the polymer chains begin to move.

Table 4.10: The effect of water content on tan δ, storage modulus and loss modulus of the PU foams.

Sample name	Water content/ g	Tan δ	Storage modulus (MPa)	Loss modulus (MPa)
H1	2	-34.70	4.781	2.0930 (-43.63 ^{o}C)
H2	3	-33.94	2.981	0.8447 (-42.47 ^{o}C)
H3	4	-28.95	2.515	0.3552 (-42.31 ^{o}C)
H4	5	-33.70	2.364	0.3111 (-42.58 ^{o}C)
K1	2	-34.26	2.526	0.3114 (-43.19 ^{o}C)
K2	3	-30.63	1.062	0.1685 (-43.12 ^{o}C)
K3	4	-29.97	0.686	0.1026 (-40.67 ^{o}C)
K4	5	-32.65	0.517	0.0769 (-45.72 ^{o}C)

4.5   Effect of isocyanate index on the properties of PU foam

In this study water content of 4 g was fixed, while the isocyanate index was varied. It is expected that varying the isocyanate index will bring about changes in physical properties and morphology with the general trend being that as the isocyanate index is increased, the level of cross-linking is also increased. It is also believed that as the level of covalent cross-linking is increased, the morphology is also influenced, thereby decreasing the level of phase separation between urea hard segment and soft segment.

The formulation components used for the preparation foams are given in **Table 4.11** [**(a)** and **(b)].** This formula is used to determine the effect of different isocyanate contents on the foam properties, such as tensile strength, density, compression stress, tear strength and elongation at break. The isocyanate index is varied from 90 to 110. The effect of varying the isocyanate index on certain physical properties of TDI and MDI based on automotive seating foam had been studied by Cavender and Howker [42]. In general, they found that the tensile strength, tear strength and compression set increased with increasing isocyanate index. The percent elongation, however, decreased with increasing isocyanate index.

Petrovic et al. [43] had introduced cross-links into a segmented polyurethane elastomer based on 4,4-diphenylmethane diisocyanate (MDI), by varying the ratio of poly(oxypropylene) diol to poly(oxypropylene/oxyethylene) triol. They found that the tensile strength and tear strength enhanced with increasing the level of crosslinking while the modulus was raised at very high triol ratios. Based on these results, they concluded that the hard domains significantly contribute to this particular mechanical property of these elastomers. Besides, the thermal stability was decreased with increasing cross-linking where the domains structure was easily disrupted at a given temperature as the level of cross-linking was increased.

In our work, this trend can be explained from FTIR results (Section 4.5.1), where the concentration of hard segment domains is lower at lower isocyanate index and their ordering was disrupted at high index due to more extensive covalent crosslinking prior to completion of phase separation.

Table 4.11a: Preparation of flexible polyurethane foams (MI 90 – MI 110) by varying isocyanate index .

Chemical (phr/ g)	Product code		
	MI 90	**MI 100**	**MI 110**
Polyol, S3	100.0019	100.0015	100.0021
DEA	1.5042	1.5091	1.5043
Niax-A1	0.2021	0.2038	0.2016
Stannous octoate	0.4034	0.4075	0.4015
Silicone A3002	2.5019	2.5381	2.5023
H_2O (blowing agent)	4.0023	4.0021	4.0026
MDI	78.1964	86.8983	95.5734
Isocyanate index	90	100	110
Reactivity Characteristics			
Cream time (s)	30	33	30
Track Free Time (s)	1432	1397	1362

Note: Polyol, S3 with hydroxyl value = 92.065 mg KOH/ g sample.

Table 4.11b: Preparation of flexible polyurethane foams (NI 90 – NI 110) by varying isocyanate index.

Chemical (phr/ g)	Product code		
	NI 90	**NI 100**	**NI 110**
Polyol, S1	100.0021	100.0026	100.0018
DEA	1.5018	1.5283	1.5012
Niax-A1	0.2021	0.2038	0.2107
Stannous octoate	0.4032	0.4075	0.4214
Silicone A3002	2.5019	2.5265	2.5044
H_2O (blowing agent)	4.0321	4.0754	4.0065
MDI	72.5099	81.3132	88.2126
Isocyanate index	90	100	110
Reactivity Characteristics			
Cream time (s)	30	34	30
Track Free Time (s)	1431	1398	1362

Note: Polyol, S1 with hydroxyl value = 63.646 mg KOH/ g sample

4.5.1 FTIR analysis

Figure 4.18 shows that MI 100 has relatively stronger monodentate urea peak (1662 -1663 cm^{-1}) than MI 90, which believed to be due to a higher concentration of hard segment domains. However, monodentate urea peak decreases at higher isocyanate as seen with MI 110. This may be due to disruption of the hard segment ordering by the increasing covalent cross-linking. That is, the increased covalent cross-linking that occurs in this high index foam makes it more difficult for the urea segments to associate (through diffusion) and to pack well with other hard segments, thereby limiting perfection of the hard segments domains with monodentate urea hydrogen bonding that must principally occur prior to the covalent gel point.
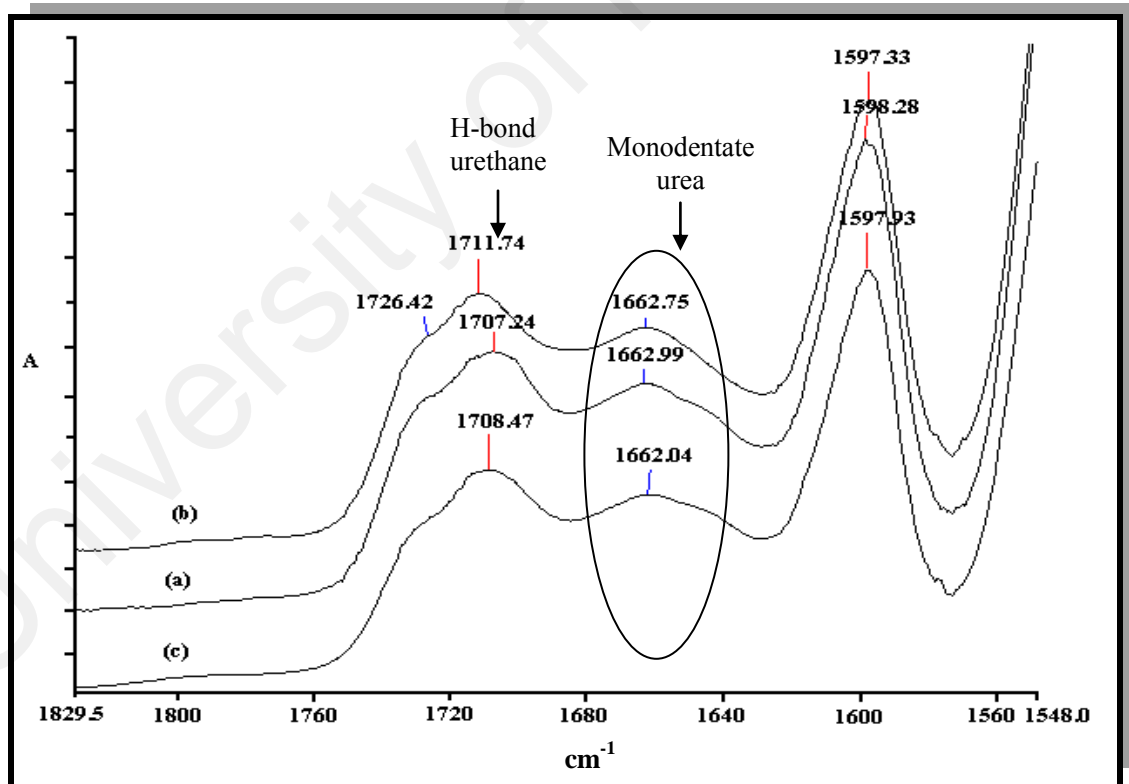
Figure 4.18: Effect of isocyanate index on the monodentate urea absorbance in the FTIR spectra of the PU foams a) MI 90, b) MI 100 and c) MI 110

The N-H absorbance peaks of the polyurethane foams as shown in **Figure 4.19** illustrate that the hydrogen bonded N-H absorbance centers, at about 3385 cm^{-1}. The peak is relatively highest for MI 100 and lowest for MI 110 with the absorbance for MI 90 lying in between. This may be due to MI 100 having the highest hard segment domains while with MI 110 the hard segment ordering or perfection of the domains have somehow being disrupted.
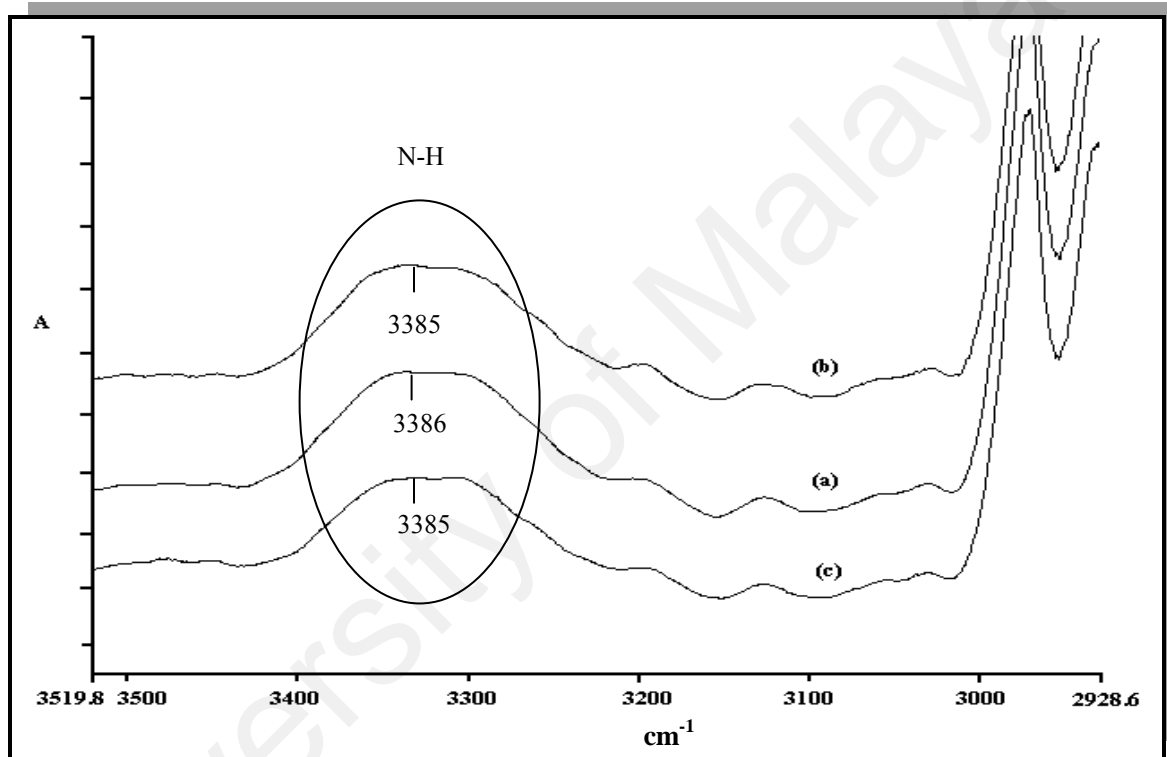
Figure 4.19: Effect of varying isocyanate index on the N-H absorbance in FTIR spectra of the PU foams: a) MI 90 b) MI 100 c) MI 110

4.5.2 Physical properties

4.5.2.1 Density and compression stress

In this section, flexible PU foams were produced by using fixed amount of water as blowing agent and the amount of isocyanate was varied to investigate the influences of isocyanate index on the physical properties of the foams. The isocyanate index was varied from 90 to 110, to increase the level of cross-lingking.

Figure 4.20 shows the changes in density and compression stress of flexible polyurethane foams by varying the isocyanate index in the formulation. Irrespective of the starting polyol, increasing of isocyanate index from 90 to 100 causes an increase of foam density but when the isocyanate index increases from 100 to 110, a reduction of the foam density occurs. These phenomena maybe due the formation of carbon dioxide that will blow up when the isocyanate reacts with water and consequently producing lower foam density [46]. Foams made using isocyanate index of 100 possess the highest density (46 ± 1 kg/ m$^{3)}$, in comparison to foams having isocyanate index of 90 and 110, which give lower densities of 45 ± 1 kg/ m^3 and 44 ± 1 kg/ m^3 respectively.
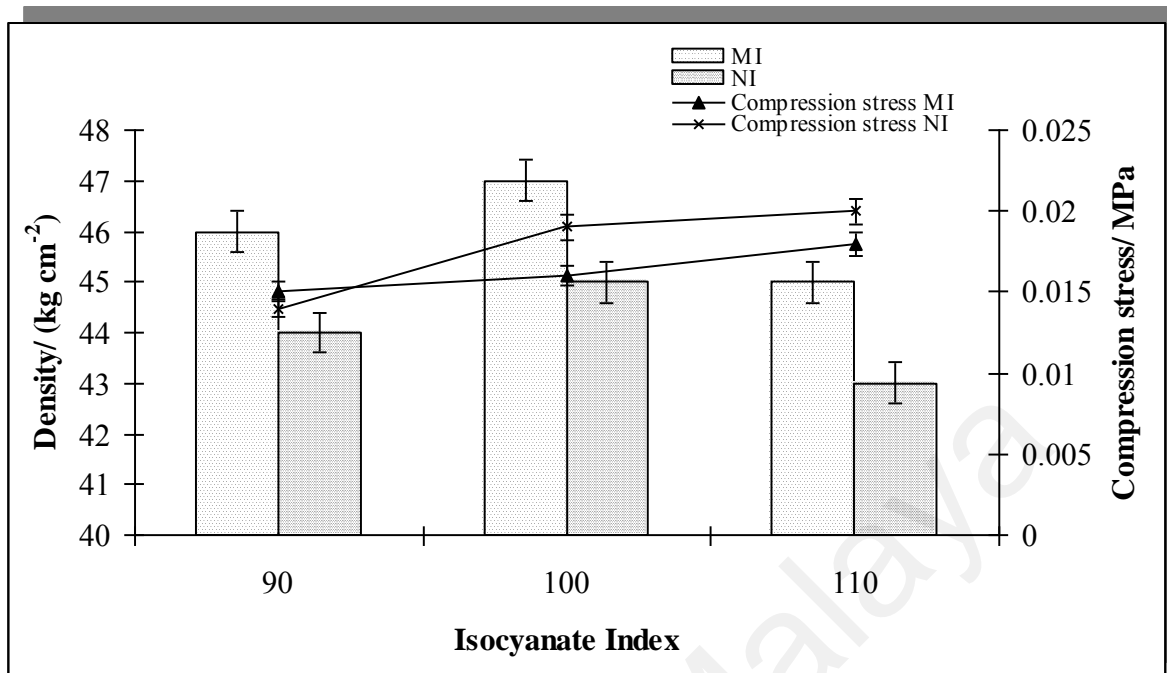
Figure 4.20: Effect of isocyanate index on density and compression at break of the PU foams.

Meanwhile, the compression stresses for both MI and NI samples of the PU foams increase with increasing isocyanate index from 90 to 110. These phenomena were due to increase of the amount isocyanate that may have resulted in the hard segment formation of isocyanurate, biuret and allophanate. These hard segment groups would in turn produce harder foam with higher compression stress.

4.5.2.2 Tensile strength, elongation at break and tear strength

The effect of isocyanate index on the tensile strength, elongation at break and tear strength of the PU foams are shown in **Appendix Q**. From **Figures 4.21 - 4.22**, the tensile strength and tear strength of the foams for both MI and NI increase with increasing of isocyanate index from 90 - 100 but decrease for 110. This phenomenon was due to isocyanate index of 100 having the highest hard segment domain while with isocyanate

index of 110, disruption of the hard segment ordering by the increasing covalent cross-linking. The tensile strength and tear strength of the foams were found to increase with higher isocyanate index, but it only limited from 90 to 100 indexes [48]. When the isocyanate index is further increased from 100 to 110, it can be seen that the tear strength of the foam decreased from 0.27 to 0.16 N mm^{-1} for MI and 0.16 to 0.15 N mm^{-1} for NI (**Figure 4.22**) while the tensile strength of the foam decreased from 9.9 to 6.5 kg cm^{-2} for MI and 9.9 to 7.3 kg cm^{-2} for NI respectively (**Figure 4.21**). It can be concluded that isocyanate index of 100 give the maximum tensile strength for both MI and NI (9.9 kg cm^{-2}) and tear strength (0.27 N mm^{-1} for MI and 0.16 N mm^{-1} for NI) respectively .

Meanwhile, the elongation at break for foams of MI and NI are decreases when isocyanate index increases to 110. This is probably due to the increase of hard segment formation of biuret linkage when isocyanate index is increased. However, 90 of isocyanate index were chosen as the optimal isocyanate amount as it produced foam with highest elongation at break.
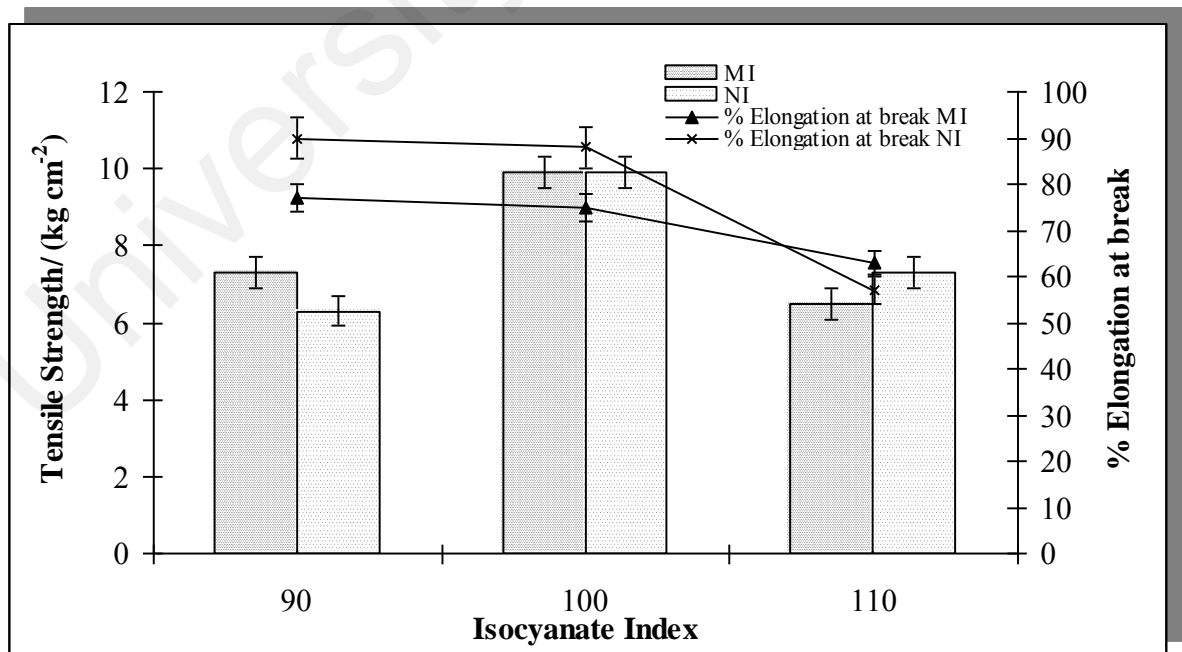
Figure 4.21: Effect of isocyanate index on tensile strength and elongation at break of the PU foams.
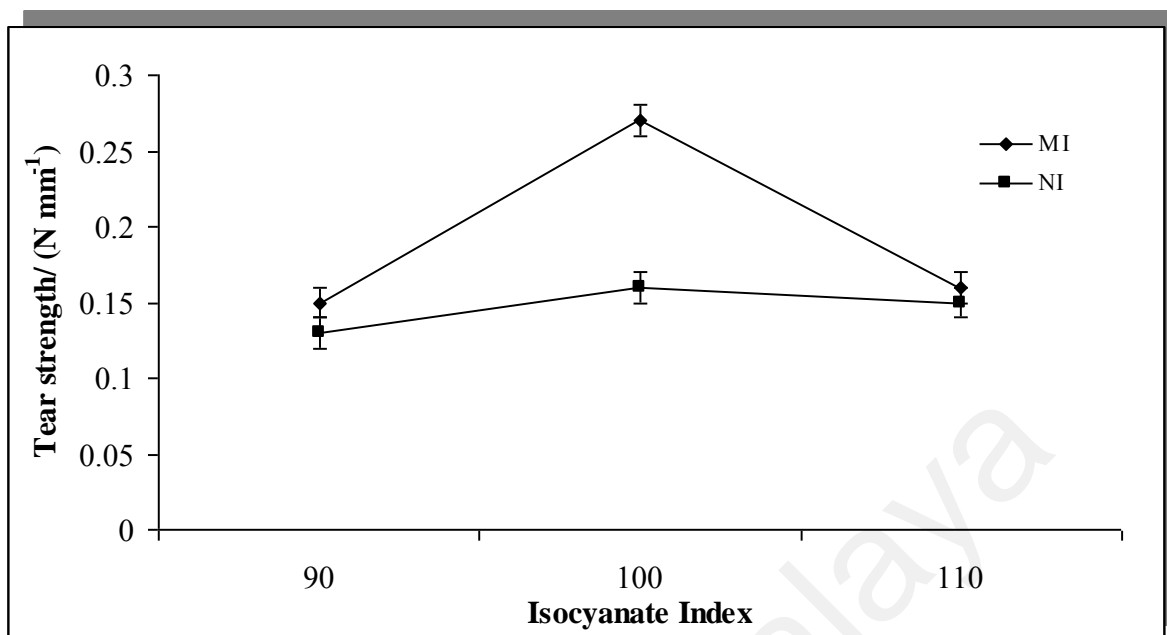
Figure 4.22: Effect of isocyanate index on tear strength of the PU foams.

4.5.2.3 Thermal properties

4.5.2.3.1   Thermalgravimetric analysis

The decomposition temperatures at which 10%, 50% and 90% of weight losses were achieved are shown in **Table 4.12** while the decomposition trace profiles of the foams, MI 90 - MI 110 and NI 90 - NI 110 are shown in **Appendices U** and **V** respectively. Generally, the decomposition temperatures increase with increasing isocyanate index for 10%, 50% and 90% of weight loss of the foams for both MI and NI. At 10% of foam weight loss, the decomposition temperature in the range of $278^{o}C$ to $286^{o}C$. This is attributed to the decomposition of urea and urethane groups in the foam [47]. The decomposition temperatures in the range of $301 - 358^{o}C$, 50% of foam weight loss may be due to polyol decomposition. Meanwhile at 90% foam weight loss, the decomposition temperatures are from $461^{o}C$ to $561^{o}C$, probably due to the depolymerization of hard

segment of the isocyanurate rings. From TGA results, it can be concluded that foams produced from higher isocyanate index are more stable thermally.

Meanwhile, the foams (MI 90 - MI 110) produced from polyol, S3 have the thermal stability higher compared to foams (NI 90 - NI 110) from polyol, S1. This is probably due to cross-linking between urethane and urea linkages as S3 possess more OH groups. The thermal stability has been shown to relate directly to the cross-linking [1].

Table 4.12: The effect of isocyanate index on thermal character of the polyurethane foams.

Sample name	Isocyanate index	Decomposition temperature (^{o}C)		
		$T_{10\%}$ (^{o}C)	$T_{50\%}$ (^{o}C)	$T_{90\%}$ (^{o}C)
MI 90	90	285.23	357.47	544.02
MI 100	100	278.11	345.41	546.12
MI 110	110	286.51	358.12	560.90
NI 90	90	278.28	301.85	461.69
NI 100	100	269.58	340.02	467.93
NI 110	110	284.51	329.72	482.97

4.5.2.3.2 Dynamic mechanical analysis

Table 4.13 illustrates the storage modulus (E"), loss modulus (E"") and tan δ (E"/ E"") of the foams, MI 90 - MI 110 having different isocyanate index (NCO/ OH) in the formulation. The T_g obtained from tan δ for foams MI 90- MI 110 shows insignificant changes with increase in isocyanate index (Appendix T and Table 4.13). However, the glass transition temperatures (T_g) from loss modulus show an observable increase from -45°C to -40°C with increase in isocyanate index from 90 to 110 (Appendix S). This can be

attributed to the increase in crosslink density that restricts the molecular motion of the polymer chains and lead to the increase in T_g. At temperatures below its glass transition, the storage modulus remains relatively constant and when the glass transition temperature (T_g) is reached, the storage modulus decreases rapidly as the polymer chains begin to move. The storage modulus (**Appendix T**) continues to decrease until it reaches a plateau at around 20^oC.

Table 4.13: The effect of isocyanate index on tan δ, storage modulus and loss modulus of flexible foams.

Sample name	Isocyanate index	Tan δ (^oC)	Storage modulus (MPa)	Loss modulus (MPa)
MI 90	90	-33.12	4.331	0.5724 (-44.80 ^oC)
MI 100	100	-32.94	5.981	0.8448 (-42.47 ^oC)
MI 110	110	-31.45	2.451	0.3155 (-40.40 ^oC)

Note: Samples (MI 90- MI 110) synthesized from polyol (S3) with OH value = 92 mg KOH/ g sample.

4.5.2.4 Morphology of PU foam

Morphology from optical microscope showed that foams prepared from higher isocyanate index produced open cell in the structure (**Fig. 4.23**). The cell structure was not altered when isocyanate index was changed from 90 to 110. Similar results were also observed by Dounis and Wilkes [21] whereby the evaluation of cellular structures by scanning electron micrograph showed no relative effect when TDI index was varied.
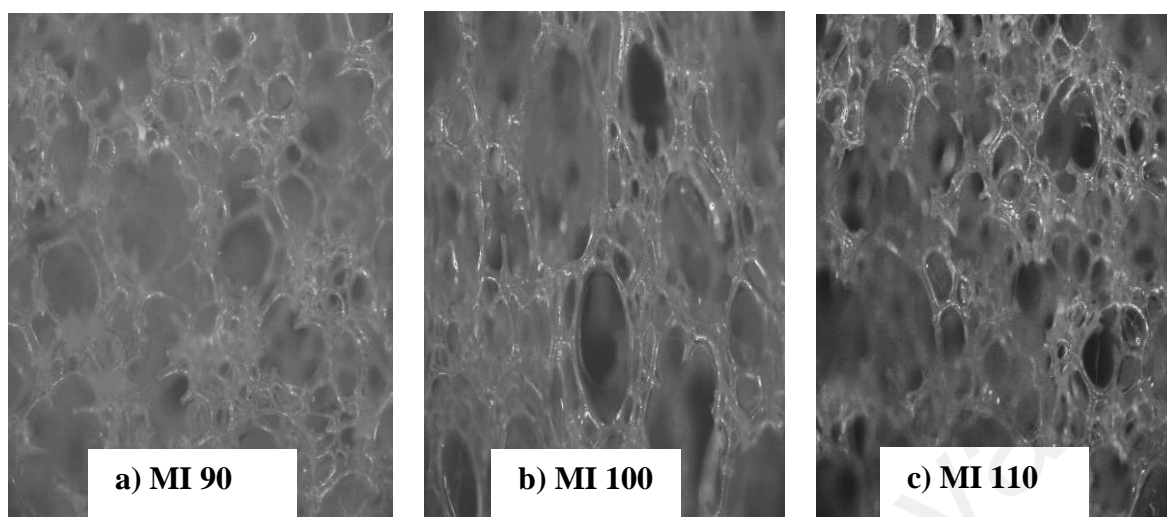
Figure 4.23: Structure of open cell for foams, MDI 90, MDI 100 and MDI 110 at 4X magnification.

4.5.2.5 Comparison of flexible PU foam from LNR-based polyol with commercial foams.

Table 4.14: Mechanical properties of the two flexible PU commercial foams and foam made from LNR-based polyol.

Mechanical properties	Commercial I	Commercial II	Foam from LNR based polyol/ K4
Density, kg m^{-3}	43	41	43
Tear strength, N/ mm	0.19	0.32	0.27
Elongation %	98	117	72
Compression stress, MPa	0.05	0.06	0.02
Tensile strength, kg cm^{-2}	1.5	1.6	10.7

The physical properties of flexible PU commercial foams and foam from LNR-based polyol (K4) are presented in **Table 4.14**. Commercial I are foams made by Air Product and Chemical Inc. [49] while commercial II (Hyperlite II) made by Lyondell Chemical World Inc. [50]. All mechanical properties data in the commercial foams were

tested under the same procedures as applied to the foam made from LNR-based polyol. The density of K4 is found similar to that of commercial foam I, which is 43 kg m^{-3} compared to commercial foam II which is lower (41 kg m^{-3}). The compression stress of commercial foams in a range 0.05 – 0.06 MPa compared to K4 (0.02 MPa). The commercial II has the highest elongation at break and tear strength compared to other commercial I. The foam from LNR-based polyol has the lowest elongation at break among the commercial foams, which is 72%.

Overall, foam from LNR-based polyol is comparable to other commercial foams for density and tear strength but inferior towards compression stress, tensile strength and elongation. This could possible be due to insignificant isocyanate used in the PU foam formulation. As urea is known to influence these properties, increasing isocyanate, will results in more urea formation hence can improve these properties

CHAPTER 5

CONCLUSION

5.1 Summary

Liquid natural rubber-based polyol was successfully synthesized from natural rubber latex with addition of sodium nitrite and hydrogen peroxide as a degradative and an oxidative agent. The hydroxyl value for the polyol increases when hydrogen peroxide/isoprene ratio increases and is with in the range of 64 - 92 mg KOH/g sample. The molecular weights and polydispersities of the polyols decrease with increasing hydrogen peroxide/isoprene ratio, higher temperature and longer reaction time.

The liquid natural rubber-based polyols obtained were then reacted with isocyanate (MDI), with added water as the blowing agent, in the presence of catalyst and surfactant to produce flexible polyurethane foams. The effects of amount of the water content and isocyanate index on foam properties such as density, compression strength, tensile strength, elongation at break and tear strength were studied. It is found that the density of foams decreases whereas the compression strength is increased with increasing amount of the water content. The densities and compression stresses are in the range 43 - 72 kg m^{-3} and 6.0×10^{-3} – 19×10^{-3} MPa respectively.

Flexible foam with highest tensile stress for both MI and NI (7.9 kg cm^{-2}) and tear strength (0.27 N mm^{-1} for MI and 0.16 N mm^{-1} for NI) were achieved in formulation at isocyanate index of 100. However, variation in isocyanate index by ±10 did not give any significant impact to cell structure of the foams. In terms of thermal stability, the foams

produced from higher isocyanate index (110) and water contents (5 g) are found to be more stable thermally. This is mainly because of hard segments of isocyanurate, biuret and allophanate being incorporated into the polyurethane linkages.

The properties obtained for the flexible foams made from LNR-based polyols are comparable to commercial flexible foams besides being more environmental friendly since it is using sustainable raw materials as compared to the conventional petroleum-based polyurethane foams. These foams have potential to be used in the production of mattresses, pillow, cushion, footwears, car seats and bags.

5.2   Suggesting for future work

1. In the preparation of flexible polyurethane foam from LNR-based polyol, only the water as blowing agent was used. It would be interesting to investigate the performance of the polyurethane foam using other blowing agents.

2. In this study, only MDI was used in the foam formulation. Future works can investigate the effect of other isocyanates such as TDI or polymeric isocyanates on the properties polyurethane foam.

3.   The LNR-based polyol can be used to prepare semi rigid and rigid foams by increasing the hydroxyl value of polyol.

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