



**Preparation of Polyurethane Foams from Hydroxytelechelic Oligoisoprenes  
Obtained by Controlled Degradation of Natural Rubber: Study of  
Their Physico-mechanical, Thermal, and Acoustic Properties**

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### ABSTRACT

Polyurethane foam (PUF) is the largest of polyurethane materials widely studied and used in many applications such as furniture, automobile, insulation, acoustic absorber. Hydroxyl compounds currently used in the production of PUF are petrochemical products (polyester and polyether polyols). However, they have some disadvantages as they are non-renewable resources, they may cause environmental pollution, and they tend to be exhausted in the near future. Natural rubber (NR) is an interesting choice to use as a starting material in PUF synthesis, due to the fact that they are renewable source, abundant polymer and they have good mechanical properties and are easy to chemically modify.

In this work, a new hydroxytelechelic natural rubber (HTNR) having a hydroxyl functionality of 2 was successfully performed *via* controlled epoxidation and cleavage of natural rubber, following by a selective reduction reaction of the obtained carbonyltelechelic oligoisoprenes. These HTNR with different molecular weights (1000-3400 g mol<sup>-1</sup>) were reproducibly obtained with high yields. Chemical modifications on HTNR were performed by epoxidation (10-35%, EHTNR), hydrogenation and oxirane opening reactions. The different microstructures of these oligomers were evidenced by the characterization techniques FT-IR, NMR, SEC and MALDI-TOF MS. Their thermal properties were also investigated by TGA and DSC.

Polyurethane foams were successfully prepared from a renewable source, HTNR with different molecular weights and EHTNR having a variation of epoxide content, by one shot technique. The chemical structure and cell structure as well as physico-mechanical, thermal and acoustic properties were characterized to compare with commercial polyol analogues. It was investigated that the obtained HTNR based foams are open cell structures and have cell

dimensions between 0.38 and 0.47 mm. Concerning, physico-mechanical properties, HTNR1000 based foam exhibits higher tensile and compressive strengths than commercial polyol analogue, but the elongation at break is lower. However, HTNR3400 based foam shows the best for elastic properties. In series of EHTNR based foams, the tensile and compressive strengths give a trendy increasing with increasing the epoxide content. Same results were observed with increasing amount of 1,4-butanediol. For thermal properties, HTNR based foams show better low temperature flexibility than that based on commercial polyol. Moreover, HTNR based polyurethane foams give an excellent acoustic absorber.

**Keyword:** Natural rubber, Polyurethane foam, Telechelic oligomer, Degradation, Mechanical properties, Thermal properties, Acoustic absorption properties.

<b>Titre de thèse</b>	Préparation de Mousses de Polyuréthane à Partir d'Oligoisoprènes Hydroxytéléchéliques Obtenus par Dégradation Contrôlée du Caoutchouc Naturel:Étude de Leurs Propriétés Physico-mécaniques, Thermiques et Acoustiques
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### RÉSUMÉ

Les mousses de polyuréthane constituent les matériaux polyuréthane les plus largement étudiés et utilisés pour de nombreuses applications telles que l'ameublement, l'automobile, l'isolation thermique et phonique. Les composés hydroxylés couramment utilisés pour la production des mousses de polyuréthane sont des produits issus de la pétrochimie (polyols à base de polyesters ou de polyéthers). Ces produits ont le désavantage d'être issus de sources non renouvelables pouvant provoquer des pollutions de l'environnement et risquant de se tarir à court terme. Le caoutchouc naturel constitue un matériau de base pour la synthèse des polyuréthanes particulièrement intéressant en tant que matériau issu d'une source renouvelable abondante, avec des propriétés mécaniques intéressantes et une structure chimique facilement modifiable.

Dans ce travail, un nouveau caoutchouc naturel hydroxytéléchélique (HTNR) de fonctionnalité 2 a été obtenu par l'intermédiaire de réactions contrôlées d'époxydation et de clivage du caoutchouc naturel, suivies d'une réduction sélective des oligoisoprènes carbonyltéléchéliques obtenus. Ces HTNR de différentes masses molaires ( $1000-3400 \text{ g mol}^{-1}$ ), ont été obtenus de façon reproductible et avec des rendements élevés. Des modifications chimiques de ces HTNR ont été effectuées par époxydation (10-35% EHTNR), hydrogénation et réactions d'ouverture des oxiranes. Les différentes microstructures de ces oligomères ont été caractérisées par FT-IR, RMN, SEC et MALDI-TOF MS. Leurs propriétés thermiques ont été déterminées par TGA et DSC.

Des mousses de polyuréthane ont été préparées à partir d'HTNR et d'EHTNR de différentes masses molaires et de différents taux d'époxydation en une étape. Les structures chimiques, les caractéristiques physiques des mousses, leurs propriétés mécaniques, thermiques et

acoustiques ont été déterminées et comparées à celles des mousses de polyuréthane analogues synthétisées à partir de polyols commerciaux. Les mousses de polyuréthane à base d'HTNR ont une structure de cellules ouvertes de dimensions 0,38 à 0,47 mm. Les propriétés mécaniques varient selon les masses molaires des oligomères hydroxytéléchéliques : les mousses de polyuréthane issues d'HTNR1000 présentent des forces d'élongation et de compression supérieures à celles de leurs homologues commerciaux, mais l'élongation à la rupture est plus faible. Les mousses à base d'HTNR3400 présentent les meilleures propriétés élastiques. Pour la série des mousses à base d'EHTNR, les forces d'élongation et de compression augmentent avec l'augmentation des taux d'époxydation. Les mêmes résultats sont observés avec des quantités croissantes de butane-1,4-diol. Pour ce qui concerne les propriétés thermiques, les mousses de polyuréthane à base d'HTNR présentent une meilleure flexibilité à basse température que leurs homologues à base de polyols commerciaux. De plus, elles présentent d'excellentes propriétés d'absorption acoustique.

**Mots clés :** Caoutchouc naturel, mousse de polyuréthane, oligomères téléchéliques, dégradation contrôlée, propriétés mécaniques, propriétés thermiques, propriétés d'absorption acoustique

**ชื่อวิทยานิพนธ์** การเตรียมโพลีพอลิยูรีเทนจากไฮดรอกซีเทเลคลิกโอลิโกไอโซพรินที่ได้จากการควบคุมสลายของยางธรรมชาติ: การศึกษาคุณสมบัติกายภาพเชิงกล ความร้อน และคุณสมบัติทางเสียงของโพลีพอลิยูรีเทน

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### บทคัดย่อ

โพลีพอลิยูรีเทนเป็นวัสดุพอลิยูรีเทนที่มีการศึกษา และใช้งานในด้านต่าง ๆ มากที่สุดเช่น เฟอร์นิเจอร์ ยานยนต์ ฉนวน วัสดุดูดซับเสียง ในปัจจุบันไฮดรอกซีเทเลคลิกโอลิโกไอโซพรินที่ใช้ในการผลิตโพลีพอลิยูรีเทนเป็นผลิตภัณฑ์ปิโตรเลียม (พอลิเอสเตอร์ และพอลิอีเทอร์) อย่างไรก็ตามสารเหล่านี้มีข้อเสียคือเป็นวัสดุที่ได้จากแหล่งที่ไม่สามารถทดแทนได้ อาจจะเป็นสาเหตุปัญหาด้านสิ่งแวดล้อม และมีแนวโน้มที่จะหมดไปในอนาคตอันใกล้ ยางธรรมชาติเป็นตัวเลือกที่น่าสนใจเพื่อที่จะนำมาใช้เป็นสารตั้งต้นในการสังเคราะห์โพลีพอลิยูรีเทน เนื่องจากเป็นแหล่งที่สามารถเกิดใหม่ทดแทน มีอยู่อย่างอุดมสมบูรณ์ สมบัติเชิงกลดี และง่ายต่อการดัดแปลงโดยวิธีทางเคมี

ในงานนี้ประสบความสำเร็จในการเตรียมยางธรรมชาติที่มีน้ำหนักโมเลกุลต่ำแบบใหม่ ที่มีหมู่ปลายไฮดรอกซิล (HTNR) และมีค่าฟังก์ชันนาลิตี้เท่ากับ 2 ที่ผ่านการควบคุมตัดโมเลกุลของยางธรรมชาติ โดยผ่านปฏิกิริยาออกซิเดชันที่มีการควบคุม และปฏิกิริยาการตัดสายโซ่ของยางธรรมชาติ ตามด้วยปฏิกิริยารีดักชันที่เลือกเฉพาะตำแหน่งของคาร์บอนิเลเทคลิกโอลิโกไอโซพรินที่ได้ HTNR ที่ได้เหล่านี้ที่มีน้ำหนักโมเลกุลแตกต่างกัน ( $1000-3400 \text{ g mol}^{-1}$ ) สามารถเตรียมซ้ำได้ด้วยเปอร์เซ็นต์ผลผลิตที่สูง การดัดแปลงทางเคมีของ HTNR โดยปฏิกิริยาออกซิเดชัน (10-35%, EHTNR) ปฏิกิริยาไฮโดรจิเนชัน และปฏิกิริยาเปิดวงแหวนออกซิเรน โอลิโกเมอร์ที่มีโครงสร้างต่างกันเหล่านี้สามารถวิเคราะห์ด้วยเทคนิค FT-IR, NMR, SEC และ MALDI-TOF MS รวมถึงคุณสมบัติทางความร้อนสามารถตรวจสอบโดย TGA และ DSC อีกด้วย

โพลีพอลิยูรีเทนเตรียมได้สำเร็จจากแหล่งวัตถุดิบที่สามารถเกิดใหม่ทดแทนอย่าง HTNR ที่มีน้ำหนักโมเลกุลต่างๆ และ EHTNR ที่มีการแปรปริมาณหมู่พอกไซค์โดยเทคนิคผสมสารแบบขั้นตอนเดียว (one shot technique) ศึกษาโครงสร้างทางเคมี และโครงสร้างของเซลล์ รวมถึงสมบัติทางกายภาพเชิงกล สมบัติทางความร้อน และสมบัติการผ่านเสียงของโพลีเหล่านี้เปรียบเทียบกับโพลีที่เตรียมขึ้นจากโพลีออลทางการค้า จากการทดลองพบว่าโพลีที่เตรียมขึ้นจาก HTNR มีลักษณะเป็นเซลล์เปิด และมีขนาดระหว่าง 0.38 ถึง 0.47 มิลลิเมตร ด้านสมบัติทางกายภาพเชิงกล

พบว่าโพลีที่เตรียมขึ้นจาก HTNR1000 แสดงค่าความต้านทานต่อแรงดึง และแรงกดสูงกว่าโพลีที่เตรียมขึ้นจากโพลีเอทิลีนการค้า แต่ระยะยืดขาดมีค่าต่ำกว่า อย่างไรก็ตามโพลีที่เตรียมขึ้นจาก HTNR3400 แสดงสมบัติความยืดหยุ่นสูงสุด ส่วนโพลีที่เตรียมขึ้นจาก EHTNR ที่มีปริมาณอีพอกไซด์ต่างกัน พบว่าความต้านทานต่อแรงดึงและแรงกดมีแนวโน้มเพิ่มขึ้น ตามปริมาณอีพอกไซด์ที่เพิ่มขึ้น ผลที่ได้ในทำนองเดียวกันเมื่อเพิ่มปริมาณของ 1,4-butanediol สำหรับสมบัติทางความร้อน พบว่าโพลีที่เตรียมขึ้นจาก HTNR แสดงให้เห็นถึงการใช้งานที่อุณหภูมิต่ำได้ดีกว่าโพลีที่เตรียมขึ้นจากโพลีเอทิลีนการค้า นอกจากนี้โพลีที่เตรียมจาก HTNR ให้สมบัติในการเป็นวัสดุดูดซับเสียงที่ดีเยี่ยม

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## LIST OF ABBREVIATIONS

NR	Natural rubber
NRL	Natural rubber latex
TLNR	Telechelic liquid natural rubber
ENR	Epoxidized natural rubber
ENRL	Epoxidized natural rubber latex
CTNR	Carbonyltelechelic natural rubber
HTNR	Hydroxytelechelic natural rubber
EHTNR	Epoxidized hydroxytelechelic natural rubber
HHTNR	Hydrogenated hydroxytelechelic natural rubber
(HTNR $\overline{fn} > 2$ )	Multifunctional hydroxytelechelic natural rubber
P-MDI	Polymethylene polyphenylpolyisocyanate
BD	1,4-Butanediol
Gly	Glycerol
PU	Polyurethane
PUF	Polyurethane foam
T <sub>g</sub>	Glass transition temperature
IR	Infrared spectroscopy
ATR	Attenuated total reflection
SEC	Steric exclusion chromatography
PDI	Polydispersity index
NMR	Nuclear magnetic resonance spectrometer
MALDI-TOF MS	Matrix assisted laser desorption time of flight mass spectroscopy
DRC	Dry rubber content
TGA	Thermogravimetric analyzer
DSC	Differential scanning calorimeter
rpm	Round per minutes
phr	Part per hundred
$\alpha$	Acoustic absorption coefficient

## CHAPTER 1

### INTRODUCTION

Polyurethanes are all around us, playing a vital role in many industries because of their widely ranging mechanical properties and their ability to be relatively easily machined and formed as plastics, foams and elastomers. In particular, urethane materials, such as foams and elastomers, have been found to be well suited for many applications. Automobiles, for instance, contain a number of components, such as cabin interior parts, that comprise urethane foams and elastomers. Urethane foams are also used as carpet backing. Such urethane foams are typically categorized as flexible, semi-rigid, or rigid foams with flexible foams generally being softer, less dense, more pliable, and more subject to structural rebound subsequent to loading than rigid foams.

The production of polyurethane foams is well known in the art. It includes two important reactions. The first one is the reaction between isocyanate groups and hydroxyl groups leading to urethane groups. The most common method of urethane production is *via* the reaction of a polyol and a diisocyanate, which forms the backbone urethane group. The second reaction is the gas production by the isocyanate groups reaction with water to form amine and carbon dioxide gas (chemical blowing agent) in the form of bubbles. Moreover, a low boiling solvent (physical blowing agent) evaporates as heat is produced during the exothermic reaction and produces bubbles. Both blowing agents assist in creating the size of the void cells in the final foam.

Polyols currently used in the production of urethanes are petrochemical, being generally derived from propylene or ethylene oxides. Polyester polyols and polyether polyols are the most common polyols used in urethane production. For flexible foams, polyester or polyether polyols with molecular weights greater than  $2500 \text{ g mol}^{-1}$  are generally used. For semi-rigid foams, polyester or polyether polyols with molecular weights of  $2000\text{-}6000 \text{ g mol}^{-1}$  are generally used, while for rigid foams, shorter chain polyols with molecular weights of  $200 \text{ to } 4000 \text{ g mol}^{-1}$  are generally used. There is a very wide variety of polyester and polyether polyols available for use, with particular polyols being used to engineer and produce a particular urethane elastomer or

foam having desired particular final toughness, durability, density, flexibility, compression set ratios and modulus, and hardness qualities (Kurth *et al.*, 2006).

Use of petrochemicals such as polyester or polyether polyols is disadvantageous for a variety of reasons. As petrochemicals are ultimately derived from petroleum, they are non-renewable resources. The production of a polyol requires a great deal of energy, as oil must be drilled extracted from the ground, transported to refineries, refined, and otherwise processed to yield the polyol. These required efforts add to the cost of polyols and to the disadvantageous environmental effects of its production. Also, the price of polyols tends to be somewhat unpredictable and tends to be exhausted in the near future.

Also, as the consuming public becomes more aware of environmental issue and exhaustive issue, there are distinct marketing disadvantages to petrochemical based products. Consumer demand for “bio-based” or “green chemistry” products continues to grow. The term “bio-based” or green chemistry” polyols for the purpose of this application is meant to be broadly interpreted to signify all polyols not derived exclusively from non-renewable resources. As a result, it would be most advantageous to replace polyester or polyether polyols, as used in the production of urethane foams and elastomers, with more versatile, renewable, less costly, and more environmentally friendly components (Kurth *et al.*, 2006)

Researchers have successfully synthesized PU elastomers using vegetable oil-derived polyols and observed improvements in both thermal stability and oxidation resistance (Javni *et al.*, 2000; Javni *et al.*, 2003; Suresh and Kishanprasad, 2005). The success in incorporating vegetable oil-based polyols in PU elastomer synthesis has generated interest in using the same polyols in PU foams. Foams constitute more than 60% of all PU products (Smith, 2005). The use of vegetable oil derived polyols in foam synthesis is not only desirable but also reducible petroleum components in PU.

Thus far, processed vegetable oils, such as palm, rapeseed, and soybean oil, have been used to synthesize rigid foams. The resulting products not only exhibit improved thermal stability but also share comparable mechanical properties with their petroleum-based analogues (Chuayjuljit *et al.*, 2007; Guo *et al.*, 2000; Hu *et al.*, 2002)

The largest PU production goes into flexible foam, thus use of bio-renewable polyols for flexible foams is much more desirable. A direct approach is to use the natural polyol from castor

oil. Foams made solely from this natural polyol are low in resiliency and semi-rigid properties (Ogunniyi and Fakayejo, 1996). Further, John and coworkers (2002 ) synthesized flexible foam using entirely soybean oil-derived polyol (SBOP) but the data indicated that improvements in both surfactant efficiency and SBOP reactivity were needed. Partial incorporation of vegetable oil-derived polyols has been much more successful (Ron and Jeffrey, 2005). Not only good quality foams have been made, but also higher resiliency has been achieved with these foams. Palm oil is also used as starting material in both flexible polyurethane foams preparation (Tanaka *et al.*, 2008; Tuan Noor Maznee *et al.*, 2001). Other renewable sources are possible opportunities to be polyols for replacing or blending with petrochemicals polyols for foams applications such as starch (Kwon *et al.*, 2007), saccharide (Hyo Hatakeyama, 2005), biopitch (Araujo *et al.*, 2005), cellulose (Marova *et al.*, 2007; Rivera-Armenta *et al.*, 2004), and soyflour (Chang *et al.*, 2001).

Natural rubber (NR) is an abundant renewable source polymer. It is an important industrial material, particularly in the tire industry or in the manufacture of various products including household, engineering, medical and commercial goods. Thailand can produce approximately 3,000,000 tons in 2007 located mostly in southern and eastern and partial in north-east and north parts of the country and is the world's largest rubber producer followed by Indonesia and Malaysia. These three countries produce around 90% of the world's natural rubber (The Thai Natural Rubber Association, 2008).

The chemical modification of NR is one of alternative methods to increase its value and to develop versatile applications. Actually, the NR double bonds in the chains are prone to varieties of chemical reactions. An alternative way to transform NR into useful products is by starting with a low molecular weight NR which is widely known as liquid natural rubber.

In the couple of decade an Indian scientist group has been interested the possibility of developing new polymeric materials from hydroxyl terminated liquid natural rubber (Ravindran *et al.*, 1988; Ravindran *et al.*, 1986). HTNR is the interesting choice of the starting materials in use in the development of block copolymers polyurethanes as soft segment (Gopakumar and Nair, 2005a; Gopakumar and Nair, 2005b; Paul *et al.*, 1999; Ravindran *et al.*, 1991). A wide range of physical and morphological properties can be obtained, depending upon the composition and chemical structure of the hard segments in the block copolymer structure to prepare solid

polyurethane such as membrane, coating or film applications. However, the article of preparation or properties of polyurethane foam based natural rubber has never reported.

In this present thesis, telechelic natural rubbers were investigated by controlled selective degradation technique using periodic acid both in latex and solvent medium. FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , MALDI-TOF MS techniques were employed to investigate the chemical structure. In addition, the modification of oligomer structure also was studied (i.e., hydrogenation, epoxidation). The mass molar of telechelic natural rubber is defined by SEC,  $^1\text{H-NMR}$ , and MALDI-TOF MS. Polyurethane foams were also prepared by various molar mass and microstructure of hydroxytelechelic natural rubber, the amount and type of chain extenders compared to commercial polyols analogues. Their properties such as physico-mechanical, thermal, acoustic and morphological properties were also investigated.

## CHAPTER 2

### OBJECTIVES

The present thesis aims to find and added value for natural rubber (NR) by modification of natural rubber to be precursor which has potential use in starting material for preparing polyurethane foams, particularly for making flexible polyurethane foams. For this reason, it is necessary to transform NR into suitable molecular weights. The modified natural rubber should also contain exactly hydroxyl functional groups functionality ( $\overline{fn} = 2$ ). These oligomers with molecular weight in order of 1000 to 3000 g mol<sup>-1</sup> and with two functionalities are suitable for further application in synthesis of flexible polyurethane foams. The hydroxytelechelic natural rubber can be done by two steps. The first step is selective degradation of partially epoxidized natural rubber and the later step is the reduction of the obtained product to obtain hydroxyl in the end chain. Moreover, the other modifications of this precursor *via* epoxidation or hydrogenation or ring opening reaction are studied. The effect of molecular weight and microstructure of precursors and of the type and amount of chain extenders on the physico-mechanical, thermal, morphological, and acoustic properties as well as chemical structure of polyurethane foams were studied and compared to commercial polyols analogues.

The objectives of this work are the followings:

1. Preparation and analysis of telechelic natural rubber as precursor materials used in the synthesis of polyurethane foams
2. Preparation and testing of polyurethane foams based on telechelic natural rubber

The scope of work is divided into 3 parts.

**Part I:** Degradation reaction in latex phase

This part concerns the study of degradation of natural rubber and epoxidized natural rubber in latex medium. At various reagents and conditions to degrade molecule chains of natural rubber and epoxidized natural rubber were carried out. FT-IR and  $^1\text{H-NMR}$  were used for analysis a structure of products.

**Part II:** Degradation and modification reaction in solvent phase

In this part, the study of the degradation of partially epoxidized natural rubber in THF medium was performed with specific amounts of periodic acid. Then, hydroxytelechelic oligoisoprenes were also modified by various conditions and reagents to prepare epoxidized, hydrogenated, and polyhydroxylated hydroxytelechelic oligoisoprenes. The structure (by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR, and MALDI-TOF MS) and thermal properties (by TGA, DSC) of precursors were investigated.

**Part III:** Preparation and physico-mechanical, thermal, acoustic and morphological properties of polyurethane foams

In the final part, polyurethane foams were prepared from previous precursors by one shot technique. The effect of the molecular weight and microstructure of precursors, of the chain extender types and also of the amount of chain extenders on the properties of polyurethane foams such as physico-mechanical (tensile property, compressive strength, and compression set), thermal ( $T_g$  and thermal stability), morphological and acoustic properties were investigated.

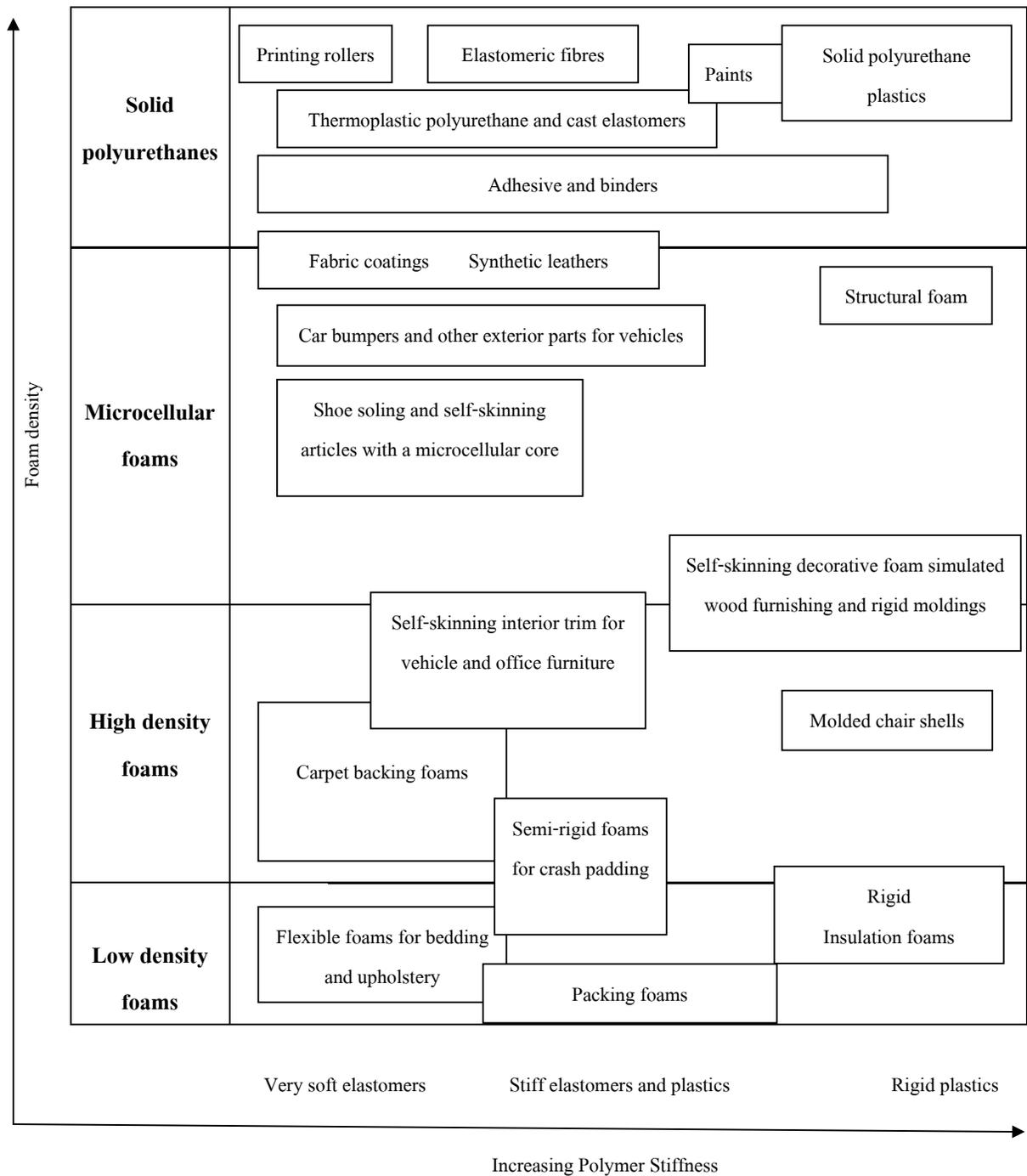
## CHAPTER 3

### LITERATURE REVIEW

#### 3.1 Introduction

Commonly abbreviated PU, Polyurethanes are the polymers containing a significant number of urethane groups ( $-\text{NH}-\text{CO}-\text{O}-$ ) in the molecular chain. The foundations of the polyurethanes industry were laid in the late 1930s with the discovery, by Otto Bayer, of the chemistry of the poly-addition reaction between diisocyanates and diols to form polyurethanes. The first commercial applications of polyurethane polymers, for millable elastomers, coatings and adhesives, were developed between 1945 and 1947, followed by flexible foams in 1953 and rigid foams in 1957 (Woods, 1990c). Relatively few basic isocyanates and a far broader range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials. Additionally, several other chemical reactions of isocyanates are used to modify or extend the range of isocyanate based polymeric materials. The chemically efficient polymer reaction may be catalyzed, allowing extremely fast cycle times and making high volume production variables.

Since that time they have been finding use in an ever-increasing number of applications and polyurethanes are now all around us, playing a vital role in many industries for furniture, footwear, construction and cars. Polyurethanes appear in an astonishing variety of forms, making them the most versatile of any family of plastic materials. Comfortable, durable mattresses and automotive and domestic seating are manufactured from flexible foams. Rigid polyurethane foam is one of the most effective practical thermal insulation materials, used in applications ranging from domestic refrigerators to large industrial buildings. Polyurethanes can be manufactured in an extremely wide range of grades, in densities from 6 to  $1,220 \text{ kg m}^{-3}$  and polymer stiffness from flexible elastomers to rigid, and hard plastics. **Figure 3.1** illustrates the broad range of polyurethanes, with reference to density and stiffness.

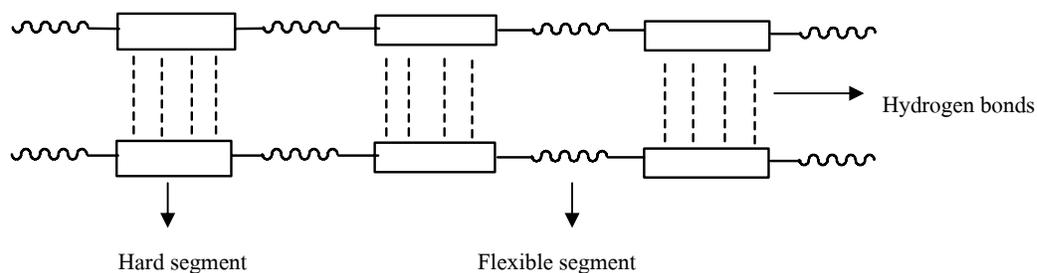


**Figure 3.1** Property matrixes of polyurethanes (Randall and Lee, 2002)

## 3.2 Properties of polyurethanes

### 3.2.1 General

Polyurethanes are segmented polymers which are built from alternating hard and soft segments. Polyurethane properties are the resultant of the overlap, often in a fairly complex manner, of a number of parameters related to molecular structure. The parameters involved are segmental flexibility, size of flexible and rigid segments, together with the ratio of both kinds of segment in the polymer, hydrogen bonds, van der waals, size and symmetry of the aromatic rings, intertwining of chains, segment orientation, crosslink bonds, microphase separation and crystallization. Polyurethane structure chain is showed in **Figure 3.2**.



**Figure 3.2** Structure of linear segmented polyurethane chain (Wirpsza, 1993d)

### 3.2.2 Physical Properties

The generalities of structure-property relationships in polyurethane are interpreted in 3.2.2.1-3.2.2.6

#### 3.2.2.1 Molecular interactions

Values of the cohesion forces for individual bonds that typically occur in polyurethane are given in **Table 3.1**

**Table 3.1** Cohesion energy of constituent groups of polyurethanes (Wirpsza, 1993c)

Group	Cohesion energy (kJ mol <sup>-1</sup> )	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )
-CH <sub>2</sub> -	2.85	21.8
-O-	4.2	7.3
-CO-	11.1	21.6
-COO-	12.1	28.9
-C <sub>6</sub> H <sub>4</sub> -	16.9	83.9
-CONH-	35.6	36.2
-OCONH-	36.5	43.5
-NHCONH-	50-100	-

The barrier to rotation of a single C-C bond is 12.6 kJ mol<sup>-1</sup>. The bonds mentioned in **Table 3.1** may be divided into two groups: those for which the value is below 12.6 kJ mol<sup>-1</sup> are free to rotate, thus forming flexible chains (segments) which render the polyurethane flexibility. In the other hand those for which the value lies above 12.6 kJ mol<sup>-1</sup> with hindered or no free rotation, which form rigid segments. However, the ether bond exhibit a stronger cohesion than methylene bond, imparts greater flexibility to polymer on account of the ball-joint effect of the ether oxygen atom. The aromatic ring makes the polymer chain stiff by being incorporated into the rigid segments. These stiffening remain even at elevated temperature. The ester bond also participates in a considerable degree in hydrogen bonding with the urethane groups which is significant especially at room temperature.

The urethane group, although its cohesion barely exceeds that of the amide group due to its extra oxygen atom, imparts rather minor stiffness to the polymers. The greatest cohesion is found in the urea group, as it contains two NH moieties capable of hydrogen bonding. The urethane groups in polyurethane form hydrogen bonds mainly owing to interaction of the NH groups with the urethane and urea carbonyl functions, and to a lesser extent with ester and ether groups (Wirpsza, 1993c).

### 3.2.2.2 Segment and domain structure

Properties of polyurethane depend on several factors such as the composition of soft or flexible segment, hard or rigid segment. Hard segments of polyurethane are composed of isocyanate residues, extenders, urethane groups, and possibly also of urea and ionic groups, if present in the polymer. The flexible segments consist of methylene and ether or ester groups. Their glass transition temperature ( $T_g$ ) are commonly below  $-30\text{ }^\circ\text{C}$ . They account for 60-80% of flexible polyurethanes composition (Wirpsza, 1993b).

**Table 3.2** illustrates the effect of the length of the glycol derived hydrocarbon segment on the  $T_g$  and melting point (m.p.) of the linear polyurethanes synthesis from isocyanate and glycol. The highest  $T_g$  values are observed for polyurethanes containing the largest number of aromatic rings: in such polyurethanes the relation between  $T_g$  and aliphatic chain length is also the strongest.

**Table 3.2** Glass transition temperature and melting point of glycol  $\text{HO}(\text{CH}_2)_x\text{OH}$  based polyurethane made from different isocyanates (Noshay and McGrath, 1977)

Glycol x	T <sub>g</sub> (°C)			Melting point (°C)	
	HDI	MDI	TDI	HDI	MDI
2	56	139	52	166	> decomp.
3	55	119	72	163	241
4	59	109	42	182	248
5	58	95	52	157	192
6	59	91	32	171	200

TDI = Toluene diisocyanates, HDI = Hexamethylene diisocyanates, MDI = Methylene diphenyl diisocyanates

The highest m.p. of rigid segments is observed in the 1,4-butylene glycol extended polyurethanes. The rigid segment m.p. increases with their size (the number of repeating units) and with their ordering (crystallinity) as shown in **Table 3.3**

**Table 3.3** Characteristics of MDI and 1,4-butanediol derived rigid segment (Qin *et al.*, 1985)

Repeating units	Molecular weight of oligomer	Melting point (°C)	
		Before annealing	After annealing
1	430	118-125	133
2	770	183-187	190
3	1110	208-213	213
5	1790	233	237

The more the hard segment content in polyurethane, the greater are its elastic modulus, rigidity, abrasion resistance and maximum permissible service temperature. The more the flexible segments in a polymer, the greater are its flexibility, elongation at break, and resistance to low temperatures and the lower its hardness, elastic modulus (Zdrahala *et al.*, 1979).

### 3.2.2.3 Crystallization

Crystallization in polymers is promoted by linearity, close and regular fit of polymer chains, strong intermolecular forces, and stiff units in the chain which restrict rotation. In many ways the effect of crystallization are similar to those of crosslinking: reduction of solubility, flexibility, elasticity, and elongation, and increase of hardness, tensile strength and melting point. The bonding of one chain to another by crystalline forces is different from that by true crosslinking in that the crystalline portion of the polymer may be disruption reversibly by heat (Saunders and Frisch, 1962).

### 3.2.2.4 Stiffness of chain units

Chain units having very limited rotational or configurational possibilities tend to stiffen polymer chains. Such units are best typified by aromatic rings, where the ring itself is a rigid unit. Such a stiffening effect favors high melting point, glass transition temperature, hardness, strength, and reduced elasticity and solubility. On the other hand, group which import a high order of flexibility because of unusual ease of rotation favor softness, flexibility, elasticity, low melting point, and low glass transition temperature. For samples of a very flexibility group is

the ether (Saunders and Frisch, 1962) and polydienes diol (Sartomer, 2005) such as polybutadiene diol.

### 3.2.2.5 Chemical structure and composition

#### a) Isocyanates

Isocyanates are mainly constituents of hard segments of polyurethanes. With increasing symmetry of the isocyanate, the following properties increase: the ability of the polyurethane to crystallize, microphase separation, modulus of elasticity, tensile strength, hardness. From isocyanates of a more regular structure and with an aromatic backbone structure, improvement of the strength of polyurethane is obtained. Many publications studied the effect of the isocyanate structure on the polyurethane properties.

Lee and Tasi (2000) studied the effect of types of diisocyanates on properties of polyurethane material with hard segment content of 40% by bulk polymerization of a poly(tetramethylene ether) glycol with  $\overline{Mn}$  of 2000 g mol<sup>-1</sup>, 1,4-butanediol and various diisocyanates (MDI, TDI, IPDI, HMDI and HDI). The data from DSC and DMA showed that the thermal transitions are influenced significantly by the diisocyanates structure. In the segmented polyurethane materials with aliphatic hard segment, the polyether soft segment is immiscible with the hard segment. However, in the segmented polyurethane materials with aromatic hard segment, the soft segment is partially miscible with the hard segment. The isocyanate structures also influence the mechanical properties significantly. MDI showed the best tensile strength and tear strength and IPDI showed the poorest tensile strength in these segmented polyurethane materials. They were described as the effect of symmetry and chemical structure of the hard segment.

Javni and coworkers (2003) studied the influence of different isocyanates on the properties of soy based polyurethanes. They indicated that the properties of the soy based polyurethanes strongly depend on crosslinking density and structure of isocyanates. Aromatic triisocyanates impart the highest density, modulus and tensile strength but the lowest elongation at break, swell in toluene and impact resistance. Aliphatic triisocyanates and diisocyanates give rubbery materials with the highest elongation at break, the highest swelling and the lowest tensile strength. Polyurethanes with aromatic and cyclodiisocyanates showed values between those of the two previous groups.

Kébir *et al.* (2006) studied the influence of the structure and an amount of different isocyanates in polyurethanes based on hydroxyl telechelic *cis*-1,4-polyisoprene (HTPI) on mechanical behavior and thermal properties. They reported that the diisocyanate structure (TDI, MDI, H<sub>12</sub>-MDI) had no notable effect on the behavior of the polyurethanes properties. On the contrary, I-IPDI showed higher crosslink and higher the amounts of hard segment. Moreover, the increase of the isocyanate equivalent ratio ( $[\text{NCO}]/[\text{OH}] = 1.75$ ) (I-IPDI), enhanced an increase of  $E'$  at the rubbery plateau and a decrease of  $\tan\delta_{\text{max}}$ . The following order of thermal stability depending on the isocyanate structure is observed:  $\text{PU}(\text{TDI}) < \text{PU}(\text{H}_{12}\text{-MDI}) < \text{PU}(\text{I-IPDI})$ .

### **b) Polyols**

The next materials that have important role in polyurethane structure are polyols. The polyol flexible segments impart flexibility to polyurethane and are responsible to their high elongation at break, low temperature resistance and low  $T_g$ . The best strength properties of polyurethane are achieved by using polyols of symmetrical structure. Some examples of polyols structure and the polyurethane properties are desired.

Ako and Kennedy (1989) studied the properties of flexible polyurethane foams (PIB-PUF) on the basis of three armed star hydroxyl-terminated polyisobutylenes and toluene diisocyanates. It was found that PIB-PUF excellently exhibited high tensile strength, low resilience, water permeability but high hydrolytic and hot air stability due to the structure of soft segment.

Kébir *et al.* (2005a) presented the use of hydroxyl telechelic *cis*-1,4-polyisoprene (HTPI) in synthesis of polyurethanes. The influence of molecular weight, as well as the chemical structure of the polyisoprene backbones including hydrogenated, and epoxidized moieties on the thermo-mechanical and thermal behavior of the synthesized polyurethanes was investigated. The study of the thermo-mechanical properties showed that material flexibility is reduced with the decrease of HTPI molecular weight or with increase in epoxide content and enhanced increase in temperature transitions ( $T_a$ ) and storage modulus ( $E'$ ) at the rubbery plateau but decrease of  $\tan\delta_{\text{max}}$ . The same variations of  $\tan\delta_{\text{max}}$  and  $E'$  were observed for hydrogenated polyurethane but without evolution of  $T_a$ .

### c) Chain extenders

A chain extender also affects polyurethane properties to an extent far greater than suggested by its mass fraction. Each extender molecule incorporates more than double of the length of the hard segment. Furthermore, amine (or water) chain extenders introduce urea groups which are more polar than the urethane group and facilitate phase separation. Diol extender polyurethane exhibit lower hardness and strength than diamine extender polyurethanes (Chun *et al.*, 2006). The ethylene glycol extender polyurethanes exhibit a minor compression set and the least hysteresis. By using bulky aromatic diols hard, high modulus elastomers are obtained (Iobst and Cox, 1979).

Shaari and coworkers (2004) studied the properties of flexible polyurethane foams prepared from palm oil with modified methylene diphenyl diisocyanates by various amount of triethanolamine. It was observed that the adding TEA used as chain extender to the formulations decreased the tack free time and compressive stress and increased the open cell content. However, TEA also had the disadvantages of increasing the density and decreasing the energy absorption but had no effect on the tear strength.

Kébir and coworkers (2006) studied the influence of chain extenders on properties of polyurethanes based HTPI with toluene diisocyanates. It was found that the increase of the chain extender equivalent ratio leads to an increase of  $E'$  at the rubbery plateau, an increase of length of the rubbery plateau and a decrease of  $\tan\delta_{\max}$  due to the increase of the hard segments ratio in the polyurethane. 1,6-Hexanediol leads to polyurethane with higher value of  $E'$  at the rubbery plateau, and failure temperatures were observed for tetraethylene glycol and 1,4-phenylene dimethanol. The following order of thermal stability depending on the nature of the chain extender is observed: PU (tetraethylene glycol) < PU (n-alcanediol) < PU (glycol) < PU (1,4-diphenyl dimethanol).

#### 3.2.2.6 Covalent crosslink

Polyurethane foams, and most castable elastomers and reactive systems, are crosslinked systems. The chemical crosslinking in polyurethane is one of the following three types (Wirpsza, 1993j):

(i) Crosslinking using mainly trifunctional compounds (polyols with more than two hydroxyl groups, low molecular weight triols) with di- or tri-isocyanate compounds. The isocyanate index is then closed to unity. The branching points are present in the carbon chain of the flexible segments, if this is a polyol chain or of the rigid segments, if this is a low molecular weight triol. The branching point may also occur at the nitrogen atom.

(ii) Crosslinking due to reaction of excess isocyanate groups (isocyanate index > 100) with the urethane and urea groups of the polyurethane to form some branching allophanate and biuret groups in the rigid segments.

(iii) Crosslinking resulting from trimerization of excess isocyanate groups to give branching isocyanurate rings.

Examples of effect of covalent crosslink on physico-mechanical properties by the following below:

Dounis and Wilkes (1997) studied the effect of TDI index on the physical properties of polyurethane foams based on a 2,700 ( $\text{g mol}^{-1}$ ) molecular weight triol, 6 pph water and varying amounts of an 80/20 mixture of 2,4- and 2,6-TDI. The index was varied from 85 to 110. It was found that as the index was increased, the hardness at 65% compression also increased. The amount of extract with DMF for 48 h decreased systematically with increasing index. However, there was essentially no significant difference in extractability between the 100 index foam and the 110 index foam. The stress and elongation at break increased as a function of index with the exception of the highest index where the strain to break was much lower.

Petrovic' and coworkers (2002) studied the effect of NCO/OH molar ratio on properties of polyurethane based from soy polyol that was derivative of the soy triglyceride of molecular weight 874  $\text{g mol}^{-1}$  and functionality 3.6. It was found that the casting polyurethane with a high NCO/OH ratio displayed a rigid and brittle nature, but the cast resin with a low ratio became more and more flexible. For thermal analysis,  $T_g$  of the cast polyurethane decreased when the NCO/OH molar ratio was decreased from 64 °C for the NCO/OH ratio of 1.05 to below 0 °C for the NCO/OH ratio of 0.4. Tensile strength decreased but elongation increased with decreasing molar ratio of NCO/OH. The highest flexural modulus and lowest impact resistance are obtained from the cast resin with an NCO/OH ratio of 1.05.

### 3.2.3 Thermal properties

Thermal properties of polyurethane and thermal analysis techniques are explained in 3.2.3.1 and 3.2.3.2.

#### 3.2.3.1 General

Thermal properties of polyurethane depend on the structure of block copolymer, and on the glass transition and melt temperature of crystalline structure of soft and hard segments (Król, 2007).

There are several transition points in polyurethane (Wirpsza, 1993i):

1. In the temperature range of  $-90$  to  $-80$  °C there is the glass transition temperature,  $T_g$ , related to the flexible segment i.e., polyether chains in polyether urethane.
2. In the temperature range of  $-45$  to  $-12$  °C there is the  $T_g$  that refers to the polyester chains in polyesterurethanes.
3. In the  $20-60$  °C temperature range, the physical properties of linear polyurethanes remain virtually unaffected, while up to  $100$  °C they halve.

The modulus of elasticity varies with temperature: below the  $T_g$  of the flexible segments, the polymer behaves as a rigid plastic, whereas above  $T_g$ , it behaves as an elastomer. The elastic plateau remains at the same level but at a modulus which increases with the content of rigid segment in the polymer.

Over the range  $80-150$  °C (depending on the degree of ordering of the polymer) cleavage of the hydrogen bonds between the NH groups of the urethane bond and the oxygen atoms of the flexible segments occurs. In the range  $130-170$  °C cleavage of the majority of urethane hydrogen bonds take place and the remainder break only above  $197$  °C. In the temperature  $100-130$  °C the allophanate and biuret bonds dissociate. At  $183-247$  °C the rigid segments domains vanish.

Polyurethanes decomposition is initiated in the rigid segments. These decomposition products in the rigid segments undergo further conversion to stable solid products. The next stage of decomposition refers to the flexible segments and urethane group linked to an aliphatic group. In the third stage, ester groups in flexible segments undergo decomposition. The presence of

aromatic rings in the polymer chain has a stabilizing effect and reduces the tendency to form volatile decomposition products. The rigid segments stabilize the decomposition of the flexible segments

The decomposition temperatures of the urethane bonds were also considered to depend on the urethane bond structure:

Ar-NHCOOAr bonds decomposed at 120 °C, R-NHCOOAr at 180 °C, Ar-NHCOOR at 200 °C, and R-NHCOOR bonds decomposed at 250 °C, where Ar is an aromatic substituents and R is aliphatic (Dombrow, 1965).

The thermal stability of an urethane bond formed by reaction of RNCO with R'OH to give RNHOOR' increases in the order (R = *tert*-butyl > cyclohexyl > *n*-alkyl > benzyl > phenyl > *p*-nitrophenyl) (R' = aryl > aralkyl > cycloalkyl > *n*-alkyl > *sec*-alkyl > *tert*-alkyl). Cyclic systems of greater thermal stability are formed in untypical reaction of isocyanate groups with esters, anhydrides, and epoxy compounds. The thermal stabilities of particular groups in polyurethanes are in the following order: -COO- > -COC- > -NHCONH- > -NHCOO- > -NHCONCNH- ≥ -NHCONCOO- (Wirpsza, 1993h).

The limiting thermal resistance of the flexible segments of polyurethanes corresponds to about 250 °C, whereas the polyester urethanes start decomposing about 300 °C. The higher temperature decomposition was caused by higher ester groups content. However, the flexible segments of unsaturated oligoester exhibited lower thermal stability.

Chemical crosslinking effects on thermal stability of polyurethanes are also considered. The thermal stabilities of these types of chemical crosslinking are in the order: crosslinking from trimerization of excess isocyanates > crosslinking from trifunctional of polyols > crosslinking from excess of isocyanates with urethane or urea groups of polyurethane. A general indication of presence of covalent crosslinking is the infusibility and insolubility of the polyurethane in powerful solvents such as DMF (Wirpsza, 1993j). Thermal stability data of individual bonds present in polyurethane are collated in **Table 3.4**

**Table 3.4** Thermal stability of groups formed by the isocyanate reaction (Wirpsza, 1993g)

Name of group	Decomposition temperature (°C)
Isocyanurate ring	> 270
Carbodiimide group	>270
Urea group	180-250
Urethane group	150-250
Biuret group	120-180
Allophanate group	120-180
Uretidione ring	120-170

In flexible polyurethane foams, biuret and allophanate are the thermally weakest links. Dissociation of both types generally takes place above 110 °C and completes by about 170 °C. Next in thermal stability are the urethanes (Lefebvre *et al.*, 2005), closely followed by ureas, with the isocyanurate group being the most stable of these nitrogen-containing derivatives (Ravey and Pearce, 1997).

### 3.2.3.2 Thermal analysis techniques

Thermal methods of analysis of polymers are important in that these techniques can provide information about the thermal stability of polymers, their lifetime or shelf-life under particular conditions, phases and phase changes occurring in polymers, and information on the effect of incorporating additives in polymers.

#### a) Differential scanning calorimeter (DSC)

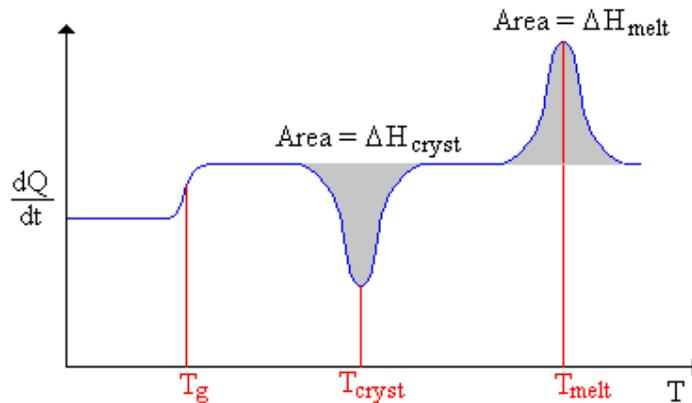
A number of important physical changes in a polymer can be measured by DSC. These include the glass transition temperature,  $T_g$ , and the crystallization temperature,  $T_c$ .

Calorimetry involves the measurement of relative change in temperature and heat or energy. The operation mode can be isothermal and adiabatic conditions. An adiabatic measurement is carried out on a closed system where determination of the heat,  $Q$ , associated with a change in temperature,  $dT$ , yields the heat capacity of the material.

Considering only the assumption of no difference in the heating rates for the sample and the reference and that the DSC curve turns to the original baseline after the transition, hence, the enthalpy can be described in the following:

$$\Delta H = \int_{T_i}^{T_f} C_p dT \quad (3.1)$$

where the  $T_i$  and  $T_f$  refer to the initial and final temperatures of the transition. DSC is a thermal analysis technique which is used to measure the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide qualitative information about physical and chemical changes that involve endothermic processes, or changes in heat capacity. The typical DSC thermograms is schematically illustrated in **Figure 3.3**



**Figure 3.3** The typical DSC thermograms (Sepe, 1997)

From a thermodynamic point of view, the glass transition,  $T_g$ , is one of the most important parameters for characterizing a polymer system. A polymer may be amorphous, or may have crystalline and amorphous regions, i.e., may be a semi-crystalline polymer. The DSC measures the transition so called glass transition temperature,  $T_g$ . The  $T_g$  is a transition related to the motion in the amorphous regions of the polymers. Below the  $T_g$  an amorphous polymer can be said to have the characteristics of a glass, while it becomes more rubbery above  $T_g$ . On the

molecular level, the  $T_g$  is the temperature of the onset of motion of short chain segments. The DSC is an important technique to measure the glass transition temperature which depends on the heating rate of the experiment and on the thermal history of the samples. Also, any molecular parameter affecting chain mobility affects the  $T_g$ .

#### **b) Thermogravimetric analyzer (TGA)**

Thermogravimetric analyzer (TGA) is an analytical technique which uses heat to drive reactions and physical changes in materials. TGA provides a quantitative measurement of mass change in the polymer or material associated with a transition or thermal degradation under a controlled air or inert atmosphere such as nitrogen, argon. TGA can directly record the change in mass due to decomposition, or oxidation of a polymer with time and temperature while the material is subjected to a controlled temperature program. Because mass is a fundamental attribute of a material, any mass change is more likely to be associated with a chemical change, which may, in turn, reflect a composition.

The sample is placed in a furnace while being suspended from one arm of a precise balance. The change in sample weight is recorded while the sample is either maintained isothermally at a temperature of interest or subjected to a programmed heating. The TGA curve may be plotted in either the weight loss of the sample or in differential form, the change of sample weight with time, as a function of temperature and compositional analysis.

### **3.2.4 Acoustic property**

#### **3.2.4.1 Definition**

Acoustic property is term as sound absorption, which is an important property of automotive interior components because it measures how effectively sound is dissipated once it enters the interior, which affects the overall sound level. When a sound wave strikes a surface, a fraction of the acoustic energy is absorbed and the remainder is reflected (**Figure 3.4**). The ratio of absorbed energy to incident energy average over all possible angles of incidence is the absorption coefficient of surface. The absorption coefficient ( $\alpha$ ), for material, is defined as the

ratio of energy entering a material (absorbed or transmitted energy), to the incident energy in relation below (Maekawa and Lord, 1994 quoted in Dimon *et al.*, 2006):

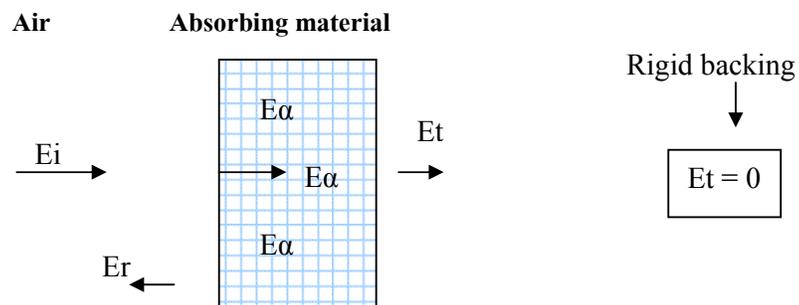
$$\alpha = \frac{E_i - E_r}{E_i} = \frac{E_\alpha + E_t}{E_i} \quad (3.2)$$

where:  $E_i$  is the incident acoustic energy

$E_r$  is the reflected acoustic energy

$E_t$  is the transmitted acoustic energy

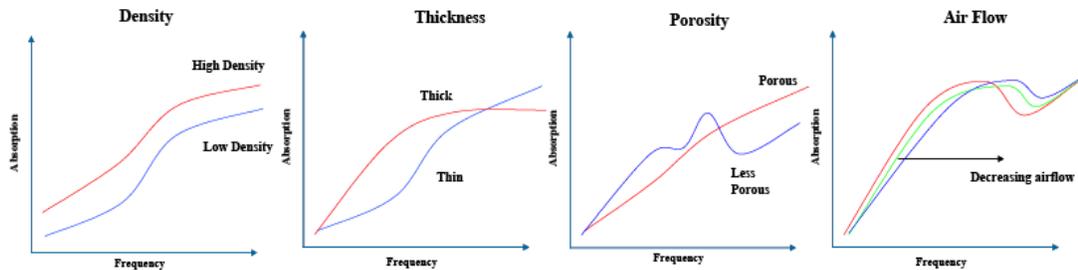
$E_\alpha$  is the absorbed acoustic energy



**Figure 3.4** The breakdown of incident sound energy striking on acoustic layer

### 3.2.4.2 Effect of parameter on acoustic property

Normally, the sound absorption ability of polymer foams depends on two major factors. The first is the macroscopic physical state of the foam, such as cell morphology, porosity, thickness and density (**Figure 3.5**), and the second is the molecular structure of the polymer, such as flexibility and crosslinking density. In principle, the noise contacts the open-celled foam structure in the form of a sound pressure wave within the porous structure. It is partially converted to heat energy due to the effect of air friction, and part of the sound energy is dissipated in the form of heat energy due to the molecular chain damping effect of the polymer. Examples of mainly polyols based polyurethane foams that were claimed such as polyether, polyester, polycaprolactone, and polybutadienes with phenolic resin were used for acoustic absorber hybrid foams (Chen *et al.*, 1990).



**Figure 3.5** The key features driving absorption performance (Skinner *et al.*, 2006)

The physical effects highlighted in the graphs (increasing density, thickness, porosity and airflow) will result in increased level of absorption performance and then potential to improve the acoustic comfort of these materials.

#### 3.2.4.3 Measuring of acoustic performance (Skinner *et al.*, 2006)

From these previously defined relationships, it is possible to determine acoustic absorption by a combination of direct methods and indirect methods. Over the past two decades significant research effort has been devoted to the development of experimental techniques dedicated to the measurement of local absorbing characteristics. Many of these involve the combination of direct and indirect methods to solve Biot's equations which govern the propagation of acoustic and elastic waves in porous media.

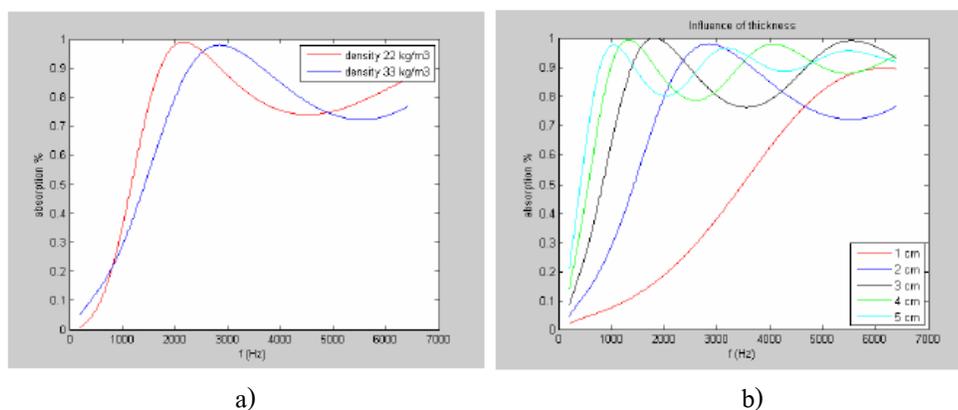
(i) Direct methods to determine acoustic impedance include:

- Kundt's tube
- Alpha-cabin
- Reverberation room

(ii) Indirect method

- Airflow measurement as function of pressure drop
- Direct tortuosity measurements

Examples of the measurement of the commercial polyurethane foams samples (Acoustiflex<sup>®</sup> R foam) produced under standard processing conditions with Kundt's tube and associated software allows the determination of the Biot parameters for a given system. The example output that was studied on the effect of density and thickness on acoustic property is given in **Figure 3.6**. It was found that their acoustic coefficients are shifted to a high range of frequency with increasing of density or decreasing of thickness of samples.



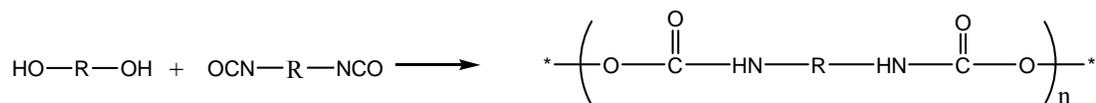
**Figure 3.6** Acoustiflex<sup>®</sup> R foam: (a) impact of foam density, (b) impact of foam thickness on absorption behavior (Skinner *et al.*, 2006)

### 3.3 Types of polyurethane

A consideration of particular properties of certain grade of polyurethanes and the way in which these are served to demonstrate their versatility.

#### 3.3.1 Polyurethane foam (Woods, 1990m)

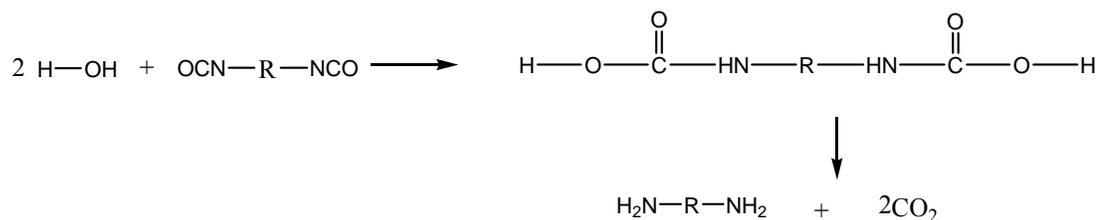
Polyurethane foams account for an estimated 90% of all polyurethane applications. The first polyurethane foams obtained were due to Bayer in 1947. In flexible polyurethane foam the active hydrogen containing groups are usually hydroxyl end groups of long chains, such as polyether, polyester, or telechelic polydienes which are reacted with di-or poly-isocyanates (**Figure 3.7**) to provide the basic step-growth polymerization.



**Figure 3.7** Reaction of hydroxyl end groups of compound with diisocyanates

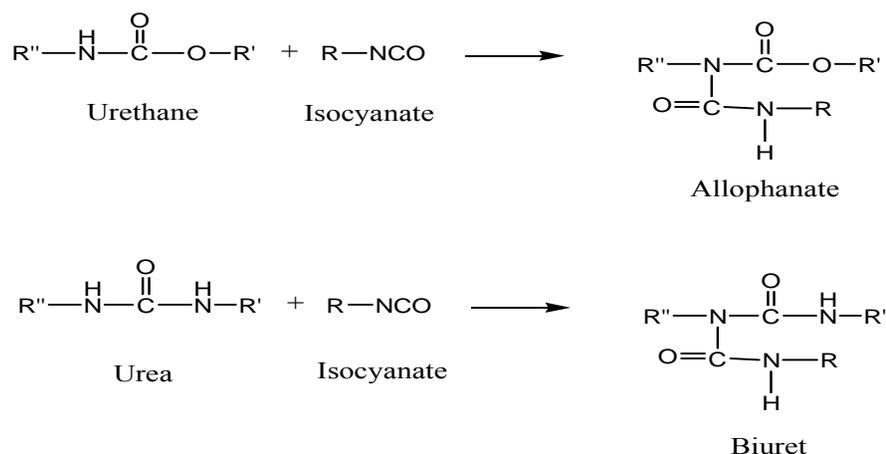
The reaction is exothermic, but with polyols of high equivalent weight it proceeds only slowly at room temperature in the absence of a catalyst. The most important primary reactions in flexible polyurethane foam are the reaction of isocyanate with hydroxyl groups and with amine groups (**Figure 3.8**). The reaction of isocyanate and water is particularly important in low density flexible foam manufacture as it provides the principle source of gas for blowing the foam, as well as the major source of heat for the expansion and cure of the polymer. The amine then can react with further isocyanate to yield a substituted urea as shown in **Figure 3.9**.

The reaction of isocyanate with water is very important, not only in releasing heat and gas but also in chain extending the polymer and providing both covalent and hydrogen bonding sites on the polymer chains.



**Figure 3.8** Reaction of water with diisocyanates

The most important secondary reactions of isocyanate in flexible foam are those which occur, under suitable conditions with the products of primary reactions. Isocyanate may react with the active hydrogen atoms in ureas and urethane to form biuret and allophanate linkage respectively.



**Figure 3.9** The secondary reactions of isocyanate

Both reactions are potential crosslinking reactions, but the biuret linkage is of greater practical importance because urethanes are less reactive to isocyanates than are ureas.

There are three types that, in quantity terms, are particularly significant: low density flexible foams, low density rigid foams and high density flexible foams.

#### 3.3.1.1 Low density flexible foams

They are materials of densities 10-80 kg m<sup>-3</sup>, composed of lightly crosslinked, open cells. Flexible foams are produced as slabstock or individually moulded and pads. Semi-rigid variants also have an open cell structure but different chemical formulations.

#### 3.3.1.2 Low density rigid foams

They are highly crosslinked polymers with a closed cell structure-each bubble within material has unbroken walls so that gas movement is impossible. These materials offer good structure strength in relation to their weight, combined with outstanding thermal insulation properties. These foams must have at least 90 percent of closed cells and the density is above about 30 kg m<sup>-3</sup>.

#### 3.3.1.3 High density flexible foams

They are defined as those having densities above 100 kg m<sup>-3</sup>. The range includes molded self-skinning foams and microcellular elastomers. Self-skinning foam systems are used to

make mould parts having a cellular core and a relatively dense, decorative skin. There are two types, those with an open cell core and an overall density in the range up to about  $450 \text{ kg m}^{-3}$  and those with a largely closed cell or microcellular core and an overall density above about  $500 \text{ kg m}^{-3}$ . Microcellular elastomers have a substantially uniform density in the range from about  $400\text{--}800 \text{ kg m}^{-3}$  and those mostly closed cells. The biggest applications of self-skinning foams and microcellular elastomers are in mould parts for upholstery and vehicle trim and for shoe-soles.

### **3.3.2 Solid polyurethanes**

Although foamed polyurethane forms some 90% by weight of the total market for polyurethanes, there is a wide range of solid polyurethanes used in many applications.

#### **3.3.2.1 Polyurethane elastomers**

Most polyurethane elastomers have excellent abrasion resistance with good resistance to attack by oil, petrol and many common non-polar solvents. Types of polyurethane elastomers commercially available include thermoplastic elastomers (TPU), cast elastomers, elastomeric coating on textiles and other flexible substrates.

Almost all of these polyurethane elastomers are based upon segmented block copolymers of the general molecular structure having alternating soft and hard segments. The soft segments are flexible molecules at room temperature such as saturated aliphatic polyester or polyether chains. The hard segments are rigid or stiff, are the reaction products of a polyfunctional (usually difunctional) isocyanate and a chain extender (diol, diamine) of low molecular weight.

Thermoplastic polyurethane elastomers are relatively expensive materials that find very wide use in applications requiring their toughness and high resistance to abrasion, lubricating and fuel oils, combined with a wide range of operating temperatures such as in automotive, engineering, biomedical, hose and cable sheathing etc.

#### **3.3.2.2 Adhesive, binder, coating, paints, lacquers**

Polyurethanes are also used in flexible coating and adhesives for film fabric laminates, plastics, aluminum foil, paper, rubber, leather, plasticized PVC, polyurethane, bonding metal to metal and metal to rubber. Polyurethane paints and lacquers coatings give the highest

wear resistance to surfaces such as floors and the outer skins of aircraft in protective and decorative surface coating.

### **3.4 The formation of polyurethane foam (Woods, 1990d)**

Although it is simple in concept, the formation of flexible polyurethane foam in one stage from liquid materials is a complex interaction of both chemical and physical factors. There are no independent chemical or process variable in flexible foam manufacture.

The mixing together the liquid chemicals is used to make the foam. The mixer must also nucleate the reaction mixture to provide growth-points for the bubbles. Controlled nucleation is essential in order to control the cell size and the cell structure of the final product. If there are too few nucleation sites, the carbon dioxide, formed by the reaction of water and isocyanate, forms a supersaturated solution. Suddenly, self-nucleation occurs. The first bubbles to be formed then grow very rapidly, the concentration of the carbon dioxide in solution falls and no further bubble nucleation occurs.

The result is a foam with large cells or even the escape of the gas bubbles that may lead to the collapse of the foam. The nucleation of foam mixture is possible by using finely divided solids or liquids that are insoluble in the foam mixture, however almost all low density foam manufactures employ nucleation obtained by fine dispersion of a gas, usually air or nitrogen, in the reaction mixture. The formation of bubble nuclei is achieved by metering the nucleating gas into the polyol or the isocyanate stream flowing to the mixer, or by direct injection into the mixer barrel.

Nucleation of the foam reaction mixture by effervescence of the dissolved gas is controlled by the pressure in the mixer and by the agitator speed. The nucleation of the foam mixture increases with increasing agitator speed or increasing pressure drop across the mixer pins. The mixed, nucleated, foam reaction mixture is usually deposited in the mold or continuous trough than one second after the start of mixing.

There is then an induction period before the mixture becomes opaque with visible bubbles. This induction period is known as the cream time. During this induction period the nucleation bubbles formed in the mixer become fewer in number and larger in size. The large bubbles grow

by diffusion of gas through the liquid at expense of the smaller bubbles which have a higher internal pressure. The initial number of bubble nuclei created in the mixer is thus not the only factor influencing the cell size of the foam; other factors are:

- An increase in the cream time which increases the cell size
- An increase in the foam reaction rate, by increasing the catalyst level or temperature of the components for example, which increases the cell count (the number of cells per centimeter), and reduces the average cell size. A secondary effect of high stirrer speeds is to increase the temperature of the reaction mixture. This reduces the cream time and therefore, the cell size.
- An addition of surfactants, especially the usual polysiloxane-polyether block copolymers, which reduces the rate of nucleation bubble loss during the induction period giving a foam with a higher cell count.

During the initial period, the reactions of diisocyanate with water and with polyol proceed together. All low density foams tend to be anisotropic. The small nucleation bubbles are spherical but as they expand under the increasing pressure resulting from the generation of carbon dioxide, they tend to elongate in the direction of foam rise. The fewer and larger the bubbles, the greater will be their elongation.

In low density foam formation, the volume of the expanding gas bubbles quickly becomes much larger than the volume of the polymerizing liquid reaction mixture and the area of contact between adjacent bubbles becomes a membrane. The membrane is planar if the bubbles are of equal size and the line of contact between three adjacent membranes forms a rib that is roughly triangular in section.

The gas pressure within the expanding foam remains low until the reaction temperature rises above about 90 °C. The pressure within the foam increases as gelation proceeds until the thinning wall-membranes of the cells rupture and the blowing gas is released. The production of low density flexible foams with a high permeability to air depends to a large extent on the rate at which the cell wall membranes thin and on the amount of polymer from the membrane that becomes incorporated into the fibril struts or ribs at the joint between adjacent membranes.

This depends largely on the rate of polymerization compared with the rate of blowing. That, in turn, varies with the temperature inside the reacting foam as well as with the level and type of

catalysis used. The foam structure is also affected by the pressure of surface-active agents that dissipate local expansion stresses and help to prevent premature cell wall rupture. The cell membranes are broken by the increasing internal gas pressure, in combination with a rapid loss in the extensibility of the polymerizing material. The release of water loosely bonded to the polyether chains is also thought to play some part in cell opening by providing water for reaction to give carbon dioxide at a late stage in the foam expansion.

Most water-blown TDI-based low density flexible foam systems remain homogenous until the reaction temperature reaches about 80 °C when molecules of substituted and polymeric ureas begin to form a separate phase within the polymer network. This separation, which also plays a part in cell opening by creating areas of stress concentration, represents the beginning of hard block separation in the polymer. At the time of the cell opening, the polymer strength is low, with a significant proportion of the isocyanate groups remaining unreacted. The temperature at the moment of cell opening is thought to be a measure of cell stability and is related to the chemical composition of the foam system. The temperature continues to rise after the foam has fully expanded because of the continuing reaction of isocyanate groups with water with amine end-groups (resulting from the reaction of bound isocyanate groups with water vapor) and also depending on the temperature, with the reactive hydrogen atoms in the urea linkages.

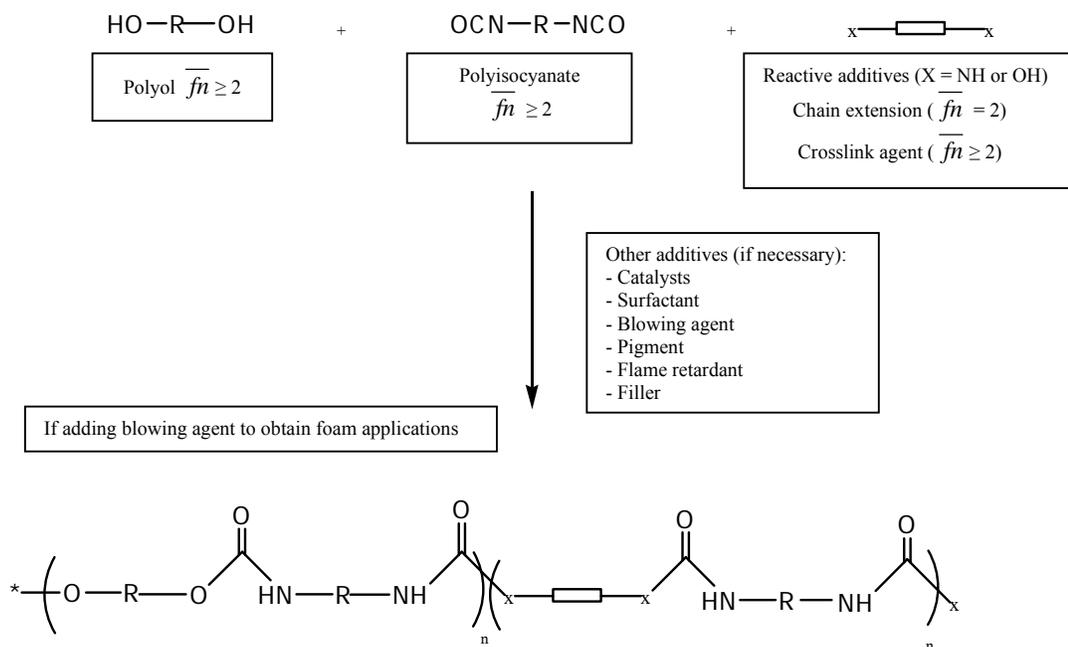
Some bound but reactive isocyanate groups remain, even when the foam has reached its maximum reaction temperature. This maximum occurs, in large foam blocks, between about 30 min and 1 h after manufacture start. It may remain near to this level for 1 to 8 h, depending on the block size, the amount of excess isocyanate present, and the ambient conditions and the orientation of the foam block, because orientation affects the rate and direction of flow of convected air through the permeable foam.

### **3.5 Method of polyurethane synthesis**

#### **3.5.1 One shot process**

In the one shot process the diisocyanates and the polyols are mixed simultaneously, along with suitable catalysts, stabilizers, and addition blowing agents (physical and chemical

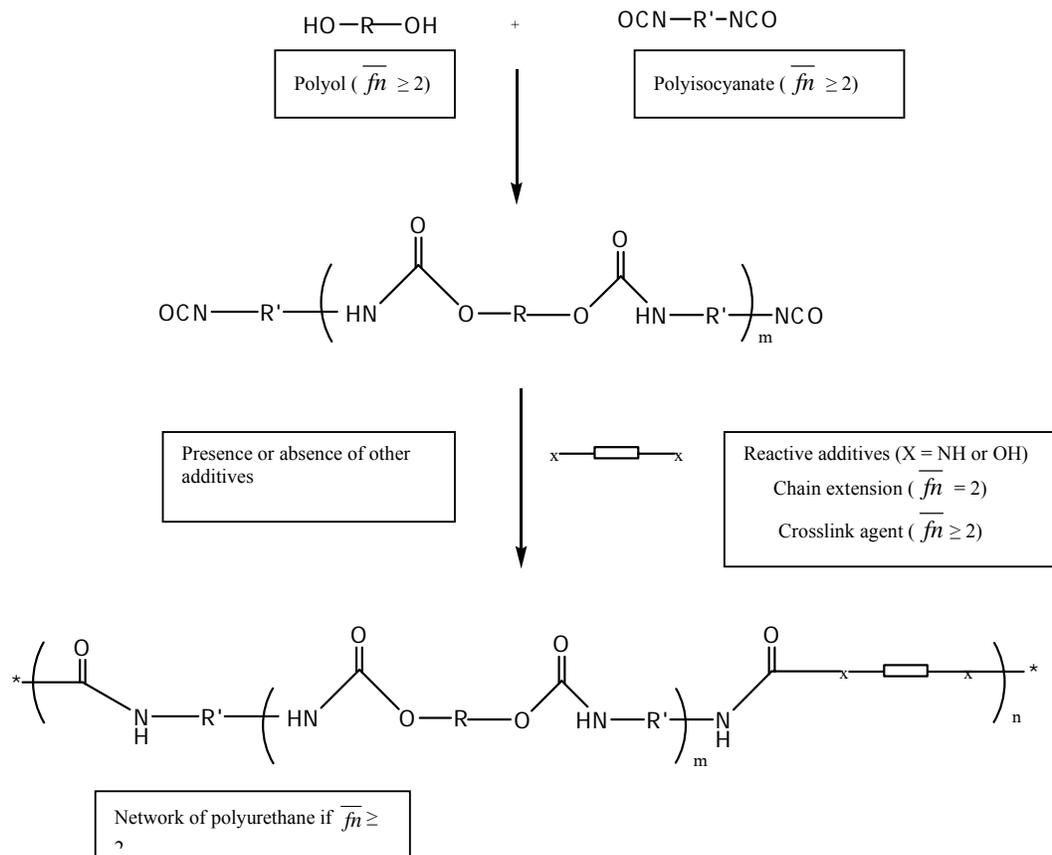
agents) if desired (**Figure 3.10**). The reactions begin immediately and continue to cure for several hours to a day (Chen *et al.*, 1992; Lee *et al.*, 2007; Wang *et al.*, 2008).



**Figure 3.10** Synthesis of polyurethane by one shot technique

### 3.5.2 Prepolymer

A substance formed by pre-reacting an isocyanate with some or all of a polyol. A final amount of polyol and / or extender (referred to as the "curative") is added to the prepolymer to complete the reaction (Chen *et al.*, 2003; Furukawa *et al.*, 2005; Heintz *et al.*, 2003) as shown in **Figure 3.11**.



**Figure 3.11** Synthesis of polyurethane by prepolymer technique

### 3.6 Chemical reagents for polyurethane foams synthesis

The varieties of chemical reagents for polyurethane foams synthesis are showed in 3.6.1-3.6.7.

#### 3.6.1 Polyols

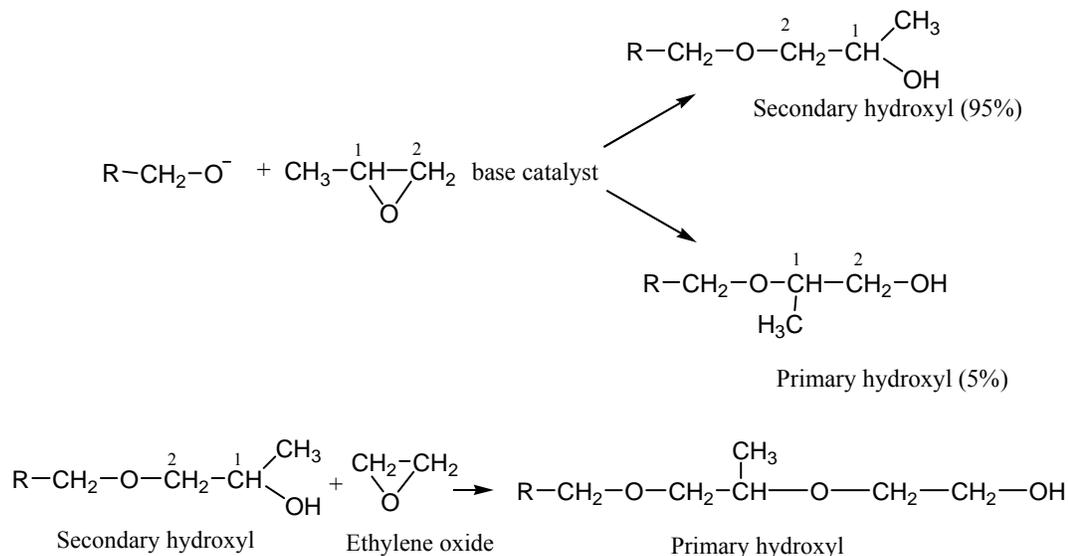
The mostly polyols used in marking polyurethanes are polyethers and polyesters with terminal hydroxyl groups. The polyols that are used to make polyurethanes have been developed to have the required reactivity with commercially available isocyanates and to produce polyurethanes with specific properties. The choice of polyols, especially the size and flexibility of

their molecular structure and their functionality, controls, to a large extent, the degree of cross-linking achieved in the polymer that is formed in the reaction with the polyisocyanate.

### 3.6.1.1 Polyether polyols (Woods, 1990a)

About 90% of the polyols used in polyurethane manufacture are hydroxyl-terminated polyethers. There are made by the addition of alkylene oxides, usually propylene oxide, onto alcohols or amines which are usually called starters or initiators. The addition polymerization of propylene oxide occurs with either anionic (basic) and cationic (acidic) catalysis although commercial polyols production is usually by base catalysis.

Polyethers based on propylene oxide thus contain predominantly secondary hydroxyl end groups. Secondary hydroxyl end groups may have inconveniently low reactivity. The primary hydroxyl content may be increased by the separate reaction of the polyoxypropylene polyols with ethylene oxide to form a block copolymer with an oxyethylene "tip". By this means the primary hydroxyl end group content may be varied from about 5% to over 80% of the total hydroxyl end groups as shown in **Figure 3.12**.



**Figure 3.12** The manufacture of polyether polyols

The use of polymers of ethylene oxide alone for polyurethane manufacture is rather limited, as these are water soluble and readily hydrolyzed. Of much higher hydrolytic resistance are polymers of propylene oxide (Wirpsza, 1993a).

### **3.6.1.2 Polyester polyols** (Woods, 1990j)

Saturated polyesters with terminal hydroxyl-groups are used to make both flexible and rigid polyurethane polymers. Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and therefore more difficult to handle. They also yield polyurethane polymers which are more easily hydrolyzed. Consequently they are only used to make polyurethanes for demanding applications where the particular physical properties obtainable from polyester are important. Polyesters are also less easily oxidized and resist to higher temperatures than polyethers do.

Polyesters are typically made by the condensation reaction between glycols and dicarboxylic acids. Branching cap is introduced by the addition of a small amount of a triol to the reaction mixture. As the esterification proceeds the water produced is removed from the reaction. Relatively low cost polyester polyols, based on recovered materials, are also available. For example, mixed adipic, glutaric and succinic acid polyesters are made using purified nylon waste acids or a depolymerising waste poly(ethylene terephthalate, PET) recovered from scrap bottles and films.

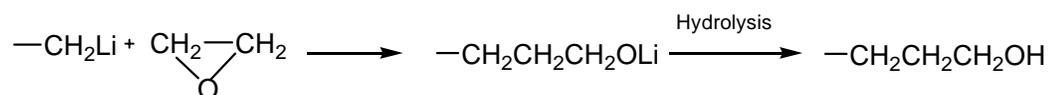
There are four main classes of polyester polyols: (Sparrow, 2002)

- Linear or lightly branched aliphatic polyester polyols (mainly adipate) with terminal hydroxyl groups.
- Low molecular weight aromatic polyesters for rigid foam
- Polycaprolactone
- Polycarbonate

### **3.6.1.3 Hydroxyl terminated hydrocarbons** (Wirpsza, 1993f)

The hydroxyl-terminated oligohydrocarbons, referred to as liquid rubbers, are made either by the free radical polymerization of dienes or diene mixtures with vinyl monomers (styrene, acrylonitrile, isobutylene) with the addition of 2,2-azobis (5-hydroxy-2-

methylvaleronitrile) as initiator or by the anionic organometallic catalyst,  $+Me-R-Me+$  ( $M =$  metal) and the reaction of the “living polymer” with alkylene oxides, aldehydes, or ketones, for example as shown in **Figure 3.13**.



**Figure 3.13** The reaction of the living polymer with ethylene oxide

Thus, anionic polymerization gives low-viscosity oligomers which contain 80-95% of diols. The most difunctional macromolecules (up to 100%) are formed by a free radical polymerization in the presence of azodinitrile initiators.

The example of the low molar mass polybutadiene (such as PolyBd R45 HT®) is the one choice of a commercial polyol that is hydroxyl telechelic polymer (HTPB) synthesized by radical polymerisation route. Its main characteristics are an average molar mass,  $\overline{Mn} = 2800 \text{ g mol}^{-1}$  and an average hydroxy functionality ( $\overline{fn} \text{ OH}$ ) = 2.4. Microstructure studies, (using  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, spectra) indicate 22% of 1,2 units (vinyl units) and 78% of 1,4-units (23.7% *cis* and 54.3% *trans*). Industrially, HTPB was used as polyol on starting material for the synthesis of polyurethane network in many applications (Coutinho *et al.*, 2001; Haska *et al.*, 1997; Jain *et al.*, 1993; Patri *et al.*, 2006) and foams application (Sartomer, 2005): also, hydroxyl telechelic polyisobutylene was applied in polyurethane foams (Ako and Kennedy, 1989).

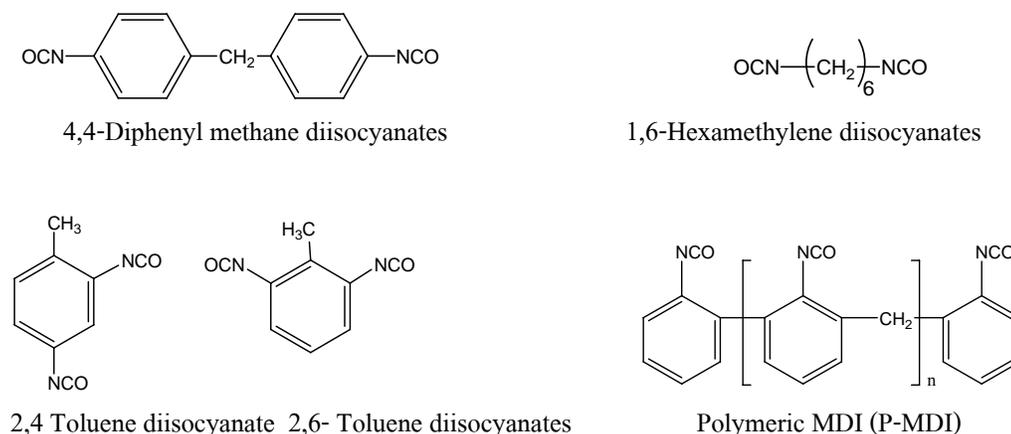
#### 3.6.1.4 Renewable source polyols

In the present, the driving force for such research is the availability of vegetable oils or hydroxyl compounds, replacement of petrochemicals polyols with environmentally friendly renewable resource, and adding values to existing agricultural products to benefit farming and industry, as well as developing the properties of new polyols. A number of researchers have investigated the possibilities of converting vegetable oils and hydroxyl compounds into polyols or blending with petrochemicals polyols for foams, elastomers, films, thermoplastics applications. For example, these vegetable oils may be soy bean oil (Guo *et al.*, 2006; Javni *et al.*, 2003; John *et al.*, 2002; Petrovic' *et al.*, 2002; Zlatani *et al.*, 2004), castor oil (Ogunniyi, 2006; Ogunniyi and

Fakayejo, 1996; Saxena *et al.*, 1992) palm oil (Badri *et al.*, 2001; Badri *et al.*, 2005; Chian and Gan, 1998; Chuayjuljit *et al.*, 2007; Tanaka *et al.*, 2008), rape seed oil (Hu *et al.*, 2002; Stirna *et al.*, 2006) cashew nut shell liquid (Bhunia *et al.*, 1998), starch (Barikani and Mohammadi, 2007; Kwon *et al.*, 2007), saccharide (Hyo Hatakeyama, 2005), biopitch (Araujo *et al.*, 2005), cellulose (Marova *et al.*, 2007; Rivera-Armenta *et al.*, 2004), glucose (Donnelly *et al.*, 1993) and soy flour (Chang *et al.*, 2001) as well as modified of natural rubber (Gopakumar and Nair, 2005; Gupta *et al.*, 1985; Nair and Nair, 2008; Paul *et al.*, 1998b).

### 3.6.2 Isocyanates

Isocyanates are commercially prepared by phosgenation of primary amines. Several aromatic and aliphatic diisocyanates are available but some 95% of all polyurethanes are based on the two aromatic diisocyanates, toluene diisocyanates (TDI), diphenyl methane diisocyanates (MDI), and its derivatives such as P-MDI. Aromatic isocyanates are more reactive than aliphatic one (Woods, 1990f). Example isocyanates are showed in **Figure 3.14**.



**Figure 3.14** Commercial isocyanates

### 3.6.3 Catalysts

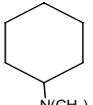
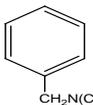
All commercially manufactured flexible polyurethane foams are made with the aid of at least one catalyst. Many classes of compounds have been investigated and the amines and the organometallics have been found most useful. Various combinations of catalysts are used in order to establish a balance between the chain propagation (isocyanate with polyol) reaction and the

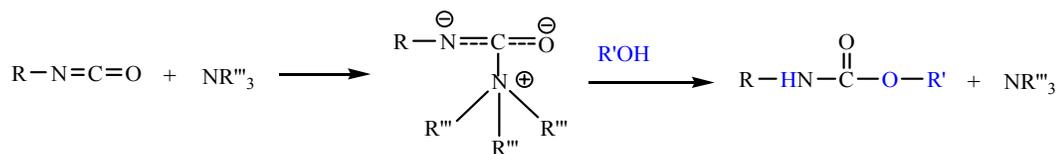
blowing reaction (isocyanate with water). The polymer formation rate and the gas evolution rate must be balanced so that the gas is entrapped efficiently in the gelling polymer while the foam cells develop sufficient strength to maintain their structure without collapse or shrinkage. Catalysts are also important for assuring completeness of reaction or cure in the finished foam.

Tertiary amines are the most commonly used as flexible foam catalysts. Generally regarded as blowing catalysts, most amines also offer some contribution to the gelling reaction. The catalytic activity of amines is due to the presence of a free electron pair on the nitrogen atom. Some commonly used tertiary amine catalysts (Woods, 1990e) are shown in **Table 3.5**.

Tertiary amines are the most widely used polyurethane catalysts. Two mechanisms have been proposed for amine catalysis (Zimmerman, 2002b). Barker proposed one mechanism in **Figure 3.15**. The activation starts by the amine using its lone pair of electrons to coordinate with the carbon of the isocyanate group. This intermediate then reacts with active hydrogen from an alcohol to produce an urethane group.

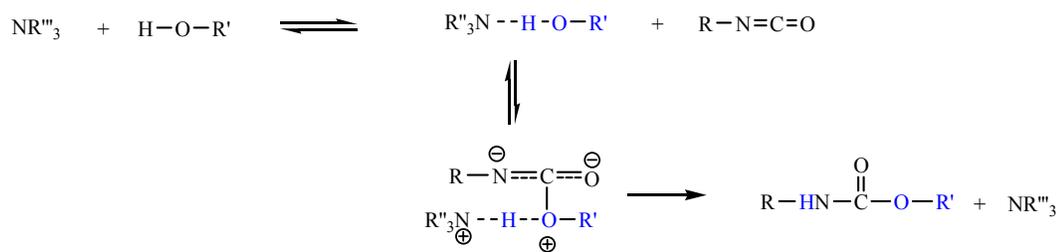
**Table 3.5** Commercial amine catalysts and applications

Amine catalyst	Application
 Diaminobicyclooctane (DABCO)	Solid, soluble in water, glycols and polyethers. May be used in most types of polyurethanes.
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  N,N,N',N',N''-Pentamethyldiethylene-triamine	Flexible foams and semi-rigid foams.
 N,N-Dimethylcyclohexylamine	Liquid with an intense odour. Rigid foams, polyester-based flexible foams and some semi-rigid foams.
 N,N-Dimethylcetylamine	Liquid with characteristic smell used in polyester-based flexible foams, semi-rigid foams and for prepolymer making.



**Figure 3.15** Barker mechanism amine catalyst

In the second mechanism which supports in the more recent literature is proposed by Farka in **Figure 3.16**. The activation starts by the amine interacting with the proton source (polyol, water, amine) to form a complex, which then reacts with the isocyanate.



**Figure 3.16** Farka mechanism amine catalyst

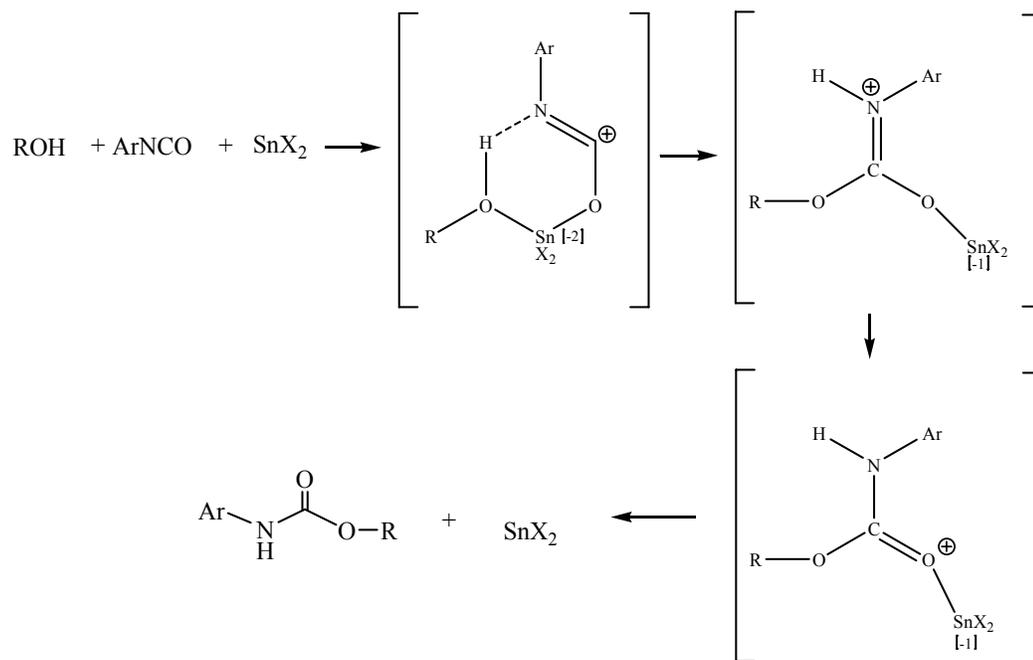
Organometallic catalysts strongly promoted the polyurethane formation or gelation between the isocyanate and a polyol. Of the many metals available, tin compounds are the most widely used. These compounds act as Lewis acids and are generally thought to function by interacting with basic sites in the isocyanate and polyol compounds. Some commercially available organometallic catalysts (Woods, 1990b) are showed in **Table 3.6**.

**Table 3.6** Commercial tin catalysts and applications

<b>Organometallic catalysts</b>	<b>Applications</b>
Stannous octoate	Slabstock polyether-based flexible foams, moulded flexible foams.
Dibutyltin dilaurate	Microcellular foams, RIM, two-pot moulding systems, elastomers.
Dibutyltin mercaptide	Hydrolysis resistant catalyst for storage stables two-pot systems.
Dibutyltin thiocarboxylates	Delayed action (hindered) catalysts for RIM and high resilience foams.

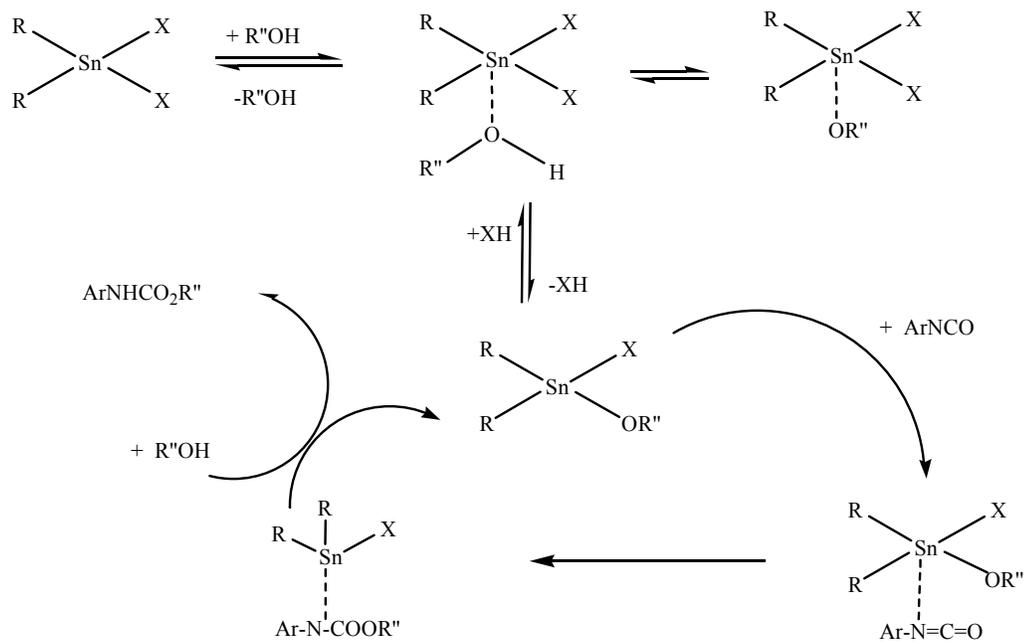
For the tin II and IV salts the following mechanism has been proposed in **Figures 3.17-3.18** as well as a synergy between tin and amine catalyst is also observed in **Figure 3.19** (Zimmerman, 2002a).

The isocyanate, polyol and tin catalyst form a ternary complex, which then gives the urethane product. Two routes have been proposed. In the first one the tin first adds to the polyol then the isocyanate. In the second one the tin adds to the oxygen of the isocyanate then reacts with the polyol.



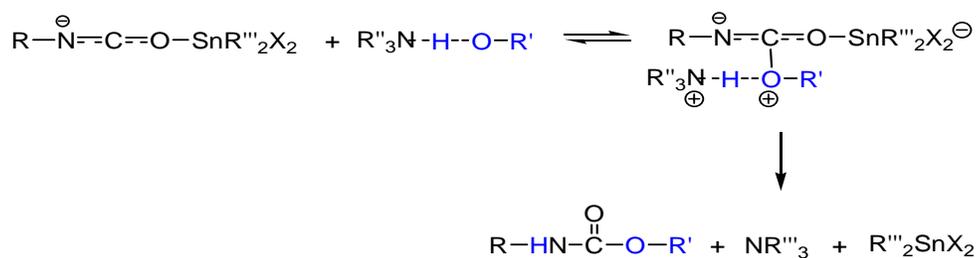
**Figure 3.17** Mechanism for tin II salts

The proposed mechanism for tin IV catalyst, dialkyltin dicarbonates and dialkyltin dialkylthiolates, is the reaction of the tin with a polyol forming a tin alkoxide, which can then react with the isocyanate to form a complex in **Figure 3.18**. Transfer of the alkoxide anion onto the co-ordinated isocyanate affords an N-stannylurethane, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide.



**Figure 3.18** Mechanism for tin IV compounds

For convenience the tin alkoxide has shown as being monomeric, but in solution dialkyltin alkoxides are usually mixtures of oligomers with the alkoxide group acting as a bridging ligand. Different oligomers most likely exhibit different levels of catalytic activity.



**Figure 3.19** Mechanism of tin-amine synergism

### 3.6.4 Chain extenders

There are low molecular weight polyols or polyamines which are also sometimes known as curing agents. Chain-extenders are difunctional substances, glycols, diamines or hydroxyl amine (ethylene glycol, 1,4-butanediol, *m*-phenylene diamine); cross linking agents have a functionality of three or more (triethanolamine, glycerol). The chain extender reacts with

diisocyanates to form a polyurethane or polyurea segment in the urethane polymer (Woods, 1990b).

### 3.6.5 Blowing agents

Cellular polyurethanes are manufactured by using blowing agents to form gas bubbles in the polymerizing reaction mixture. Flexible polyurethane foams are usually made using the carbon dioxide formed by the reaction of water with diisocyanates as shown in **Figure 3.8**, chemical blowing agents or physical blowing agents (methylene chloride, hydrochlorofluorocarbon) as well as adding directly carbon dioxide gas to mixture (Woods, 1990l). CFCs have been banned and HCFC (hydrochlorofluorocarbon) production has been scheduled to be phased out by the 21<sup>st</sup> century by the Montreal Protocol and the revised Protocol in Copenhagen because of their negative impact on the environment (Modesti *et al.*, 1998).

### 3.6.6 Surfactants

Surface-active materials are essential ingredients in the manufacture of most polyurethane foams. Selected surfactants or mixtures of surfactants help mixing incompatible components of the reaction mixture. They are particularly useful in foam making where they help to control size of the cells by stabilizing the gas bubbles formed during nucleation and may stabilize the rising foam by reducing stress-concentration in the thinning cell-wells. In flexible foams manufacture, surfactants also help control the degree of cell opening and increase the operating margin between the extremes of foam collapse, when cell opening occurs before the reaction mixture has sufficiently polymerized, and a high content of closed cells which results from cell opening being too long delayed (Woods, 1990k).

Early polyurethane foams used one or more organic, usually non-ionic surfactants such as substituted nonyl phenols, fatty acid ethylene oxide condensates or alkylene oxide block copolymers. These surfactants are still used for some specific semi-rigid foams and low density polyester based foams. Most polyurethane foams are now made using silicon based surfactants either simple silicone oils, poly(dimethylsiloxanes, PDMS) with no pendent side chains, or more complex polyoxyalkylene polysiloxane copolymers with varying levels of pendent side chains (Hamilton, 2002a).

### **3.6.7 Others additives**

In addition to the basic materials need to synthesized polyurethanes a wide range of other chemicals can be modify and control both the polyurethane chemicals reaction as well as the properties of the final polymer. the others additives are pigments, filler, flame retardants, and antioxidants.

#### **3.6.7.1 Pigments**

Most low density flexible foam is color-coded during manufacture to identify the grade and the density of the foam. Organic and inorganic pigments are both used. The pigments employed must not react with isocyanates and must be stable at the high curing temperatures reached in the manufacture of low density foams. Dispersions must also be free from trace. The most widely used coloring material is carbon black which gives some protection against surface discoloration of the foam caused by UV light (Woods, 1990h).

#### **3.6.7.2 Fillers**

Particulate and fibrous fillers may each be used in most kinds of polyurethanes. There are many reasons for adding fillers. Fibrous fillers (glass fibre, aramid fibre, etc) are reinforcing to give increase stiffness and increase the range of operating temperature of products. Mineral filler (calcium carbonate, clay, barium sulphate, etc) are sometime used to reduce cost and to increase the compressive strength of rigid foams used in composite building panels (Woods, 1990i).

#### **3.6.7.3 Flame retardants**

Flame retardants are added to polyurethanes to reduce the flammability. The most widely used flame retardants in both flexible and rigid foam systems are chlorinated phosphate ester. The presence of both chlorine and phosphorus is necessary for the optimum effect upon flammability. The addition of aluminum trihydrate gives a further reduction in flammability and minimizes the increase in smoke formation on burning, resulting from the addition of halogenated organic phosphates (Woods, 1990g).

### 3.6.7.4 Antioxidants

Polyether polyols are prone to degrade by thermal oxidative attack and require the addition of antioxidants, which also protect slabstock foam from discoloration or scorch. There are many products that can be used, most of which are mixture of sterically hindered phenol, diphenylamines or benzofuranone derivatives. The most widely used stabilizer has been butylated hydroxytoluene (BHT) (Hamilton, 2002b).

A typical formulation of flexible polyurethane foam is as follows in **Table 3.7**

**Table 3.7** A typical formulation of flexible polyurethane foams (Wirpsza, 1993e)

<b>Ingredients</b>	<b>Part by weight (g)</b>
Polyol	100
Isocyanate	(isocyanate index 80-115)
Water	1.8-5.0
Physical blowing agent	0-30
Surfactant	0.3-2.5
Amine Catalyst	0.1-2.5
Organotin Catalyst	0.2-0.4
Pigments, dyes	0-10
Filler, flame retardant, etc	1-200

### 3.7 Natural rubber based polyurethane

Natural rubber is an important natural polymer that is used in many applications both in latex form and solid form such as automotive parts, gloves, condoms etc. NR which has been known as highly *cis*-1,4-polyisoprenic structure, is easily oxidized due to having reactive double bond along the molecular chain. But this disadvantage become a good opportunity for a new product in novel applications of NR such as adhesive, coating, additives in rubber compound, or synthesis a new polymer based natural rubber etc. Many reagents and conditions can be done to degrade main chain as subscribe in the next topic.

In the couple of decade the Indian scientist group has been interested the possibility of developing new polymeric material form natural rubber. They investigated a novel for the preparation of hydroxyl terminated liquid natural rubber (HTNR) by photodegradation of natural rubber in solution in presence of hydrogen peroxide. Their functionality remained slightly less than 2 (vide infra). The by product in 10% yield is a lightly crosslinked liquid rubber with carbonyl, carboxyl and hydroxyl functional groups (Ravindran *et al.*, 1988; Ravindran *et al.*, 1986). HTNR is the interesting choice of the starting materials in use in the development of block copolymers polyurethanes. Many publications presented by using HTNR as a soft segment and toluene diisocyanates with other chain extenders as a hard segment such as poly(ethylene oxide) (Ravindran *et al.*, 1991), propylene glycol (Paul *et al.*, 1998a), 1,3-butanediol (Paul *et al.*, 1998b) and bisphenol A (Paul *et al.*, 1999). Their structure, thermal, mechanical and morphology properties were evaluated. The authors observed that the final product had NH- and carbonyl bands at 3440-3150  $\text{cm}^{-1}$  and 1690-1720  $\text{cm}^{-1}$ , respectively and the strong absorption band of NCO group at 2,260 disappeared. These bands are corresponding to urethane structure.

Ravindran *et al.* (1991) synthesized block copolymers of hydroxy-terminated liquid natural rubber (HTNR,  $\overline{Mn} = 3,000$ ,  $\overline{fn} = 1.94$ ), poly (ethylene oxide) (PEO) and the mixture (80/20) of 2,4- and 2,6- toluene diisocyanates and varied molecular weight of poly (ethylene oxide) in the range 1,000 to 6,000  $\text{g mol}^{-1}$ . It was found that tensile properties of block copolymers of HTNR-TDI-PEO depended on the molecular weight of PEO that act as hard segments. The block copolymer at the ratio of NR/TDI/PEO 6000 (1/2.01/1) showed the highest initial modulus and tensile strength, but the lowest elongation at break was obtained.

Paul *et al.* (1999) also prepared block copolymers of HTNR with bisphenol A (BPA) and TDI by varying the ratio of HTNR/BPA: (70/30), (60/40), (50/50) and (60/40). They found that modulus, tensile strength, tear strength and hardness were lower and behaved like as soft elastomers when decreasing the amount of BPA or decreasing of hard segments. Two relaxation temperatures from DMA and also two-stage thermal decomposition of the samples were observed. These results confirmed complete phase segregation.

Nair and Nair (2008) studied the effect of different chain extender diols on the thermal properties of soluble block copolymers from HTNR and TDI based polyurethanes by maintaining low hard segment content (30%) and keeping optimum NCO/OH ratio (1.08). The results from DSC and TGA indicate that these block copolymers are completely phased segregated systems.

Gopakumar and Nair (2005) studied the effect of NCO/OH ratio on swell behavior of block copolymers from HTNR and TDI 1,3-butanediol based polyurethane in many solvents such as THF, DMF, chloroform, toluene etc. Block copolymers with different NCO/OH ratio from 1.96 to 1.26 were studied. The authors found that the equilibrium sorption decreases with the increase of the NCO/OH ratio. Because the excess of NCO can form allophanate crosslink in the polymer systems, the increase of the NCO/OH ratio causes lower solvent uptake.

Many publications about polyurethane based natural rubber deal only with the study in solid applications such as membrane, coating or film applications. However, preparation and properties of polyurethane foams based on natural rubber have never been reported.

### **3.8 Introduction of natural rubber**

Natural rubber, NR, a renewable polymeric material, can be synthesized by numerous plants, over 2,000 species, but *Hevea brasiliensis* tree is the only one that can produce NR, which is highly used in industry. NR contains about 94% polyisoprene in almostly 100% *cis*-1,4-configuration. The remainder consists of mainly protein and lipids (phospholipids, esters of higher fatty acids and sterols) (Hourston and Tabe, 1996). The natural rubber possesses excellent physical properties, especially high tensile and tear strength, remarkable elastic behavior, which have not yet been competed by synthetic elastomers. Six decades of industrial research have not

produced synthetic rubber materials (such as styrene butadiene rubber, butyl rubber, chloroprene rubber, or polyisoprene) with price-performance ratios that match those of natural rubbers. Consequently, it is used in over 40,000 products, including more than 400 medical devices, surgical gloves, aircraft tires and countless engineering and consumer products. The market share of natural rubber has increased from close to 30% in the 1970s and 1980s to the present 40%. Over 90% of natural rubber is produced in Asia, particularly in Malaysia, Indonesia and Thailand (Beilen and Poirier, 2007).

### 3.8.1 Field natural rubber latex

On tapping the *Hevea brasiliensis* tree, natural rubber latex, which has rubber content between 25 and 40 % by weight exudes. The variation is due to factors such as the type of tree, the tapping method, the soil conditions, and the season. The latex is normally called “field latex” and its average rubber content is 30% by weight. A typical composition is as follows:

**Table 3.8** Typical field natural rubber latex composition

Compositions	%
Total solid content	41.5
Dry rubber content	36
Amino acids and N-bases	0.30
Neutral lipids	1
Proteins	1.6
Phospholipids	0.6
Inositols-carbohydrates	1.5
Salts (mainly K,P and Mg)	0.5
Water	58.5

As soon as possible the latex is temporarily preserved with ammonia in order to prevent bacterial contamination or at least to limit its effects (Resing, 2000).

### 3.8.2 Concentrated natural rubber latex

The original form of NR latex contains quite high water content which makes high cost for transportation and susceptibility to bacterial attack. It is necessary both to preserve and concentrate it, so that the end product is stable and contains 60 % or more of rubber. Latex concentrate is differentiated by the method of concentration and type of preservative used (**Table 3.9**). Three methods of concentration are employed, i.e. centrifugation, evaporation and creaming. The centrifugation is the preferred method and accounts for 95% of total production (Gazeley *et al.*, 1988). Therefore centrifugation technique has been mainly prepared in the latex manufacture to reduce the amount of water practically to make the latex having around 60% or more of dry rubber and obtain skim rubber as by-product contained about 7% total solid content (TSC) and 5% dry rubber content (DRC). The commercial product has nowadays two types made on a large scale: High Ammonia, HA and Low Ammonia, LA-TZ latex. HA latex is preserved with 0.7% ammonia whereas LA-TZ latex is preserved with 0.2% ammonia, 0.025% of TMTD/ZnO and 0.04-0.05% of lauric acid as ammonium laurate.

**Table 3.9** The ISO 2004 requirements for centrifuged and creamed latex concentrates (ISO 2004)

Properties	Centrifuged latex		Creamed latex	
	HA latex	LA-TZ latex	HA latex	LA-TZ latex
Total solid content (%)	61.5 min	61.5 min	66.0 min	66.0 min
Dry rubber content (%)	60.0 min	60.0 min	64.0 min	64.0 min
Non-rubber content (%)	2 max	2 max	2 max	2 max
Ammonia content (%)	0.60 min	0.29 max	0.55 min	0.35 max
KOH number	1 max	1 max	1 max	1 max
Volatile fatty acid number (VFA) (%)	0.2 max	0.2 max	0.2 max	0.2 max
Mechanical stability @ 55% TSC (sec)	650 min	650 min	650 min	650 min
Coagulum content (%) max.	0.05	0.05	0.05	0.05
Sludge content (%) max.	0.10	0.10	0.10	0.10

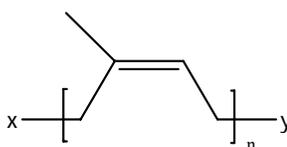
### 3.9 Telechelic liquid natural rubber

Natural rubber can be chemical modified by possessing double bonds on the polymeric backbone in latex phase, solvent phase, biphasic systems and solid phase. Chemically modified natural rubber would increase the areas of application and well expanding opportunities for novel polymers such as epoxidized natural rubber, chlorinated natural rubber, and hydrogenated natural rubber as well as liquid telechelic natural rubber (Brosse *et al.*, 2000).

#### 3.9.1 Definitions

Uraneck *et al.* (1960) proposed originally the term “telechelic polymers” that is low molecular weight polymers bearing two functional end groups. Nowadays, this term is also applied to oligomers having two or more terminal groups. TLNR can be defined as a low molecular weight NR having molecular weight in order between 100 and 10000 g mol<sup>-1</sup> approximately, and bearing reactive terminal groups capable of being used in further chain extension and crosslinking (Nor and Ebdon, 1998).

TLNR still possesses the basic structure of NR consisting of isoprene units as shown in **Figure 3.20**. The main difference is that TLNR has reactive functional groups at the end-chain, as denoted by X and Y. (X or Y are hydroxyl, carbonyl, amine, phenylhydrazone).



**Figure 3.20** Chemical structure of telechelic natural rubber that X and Y are reactive functional groups

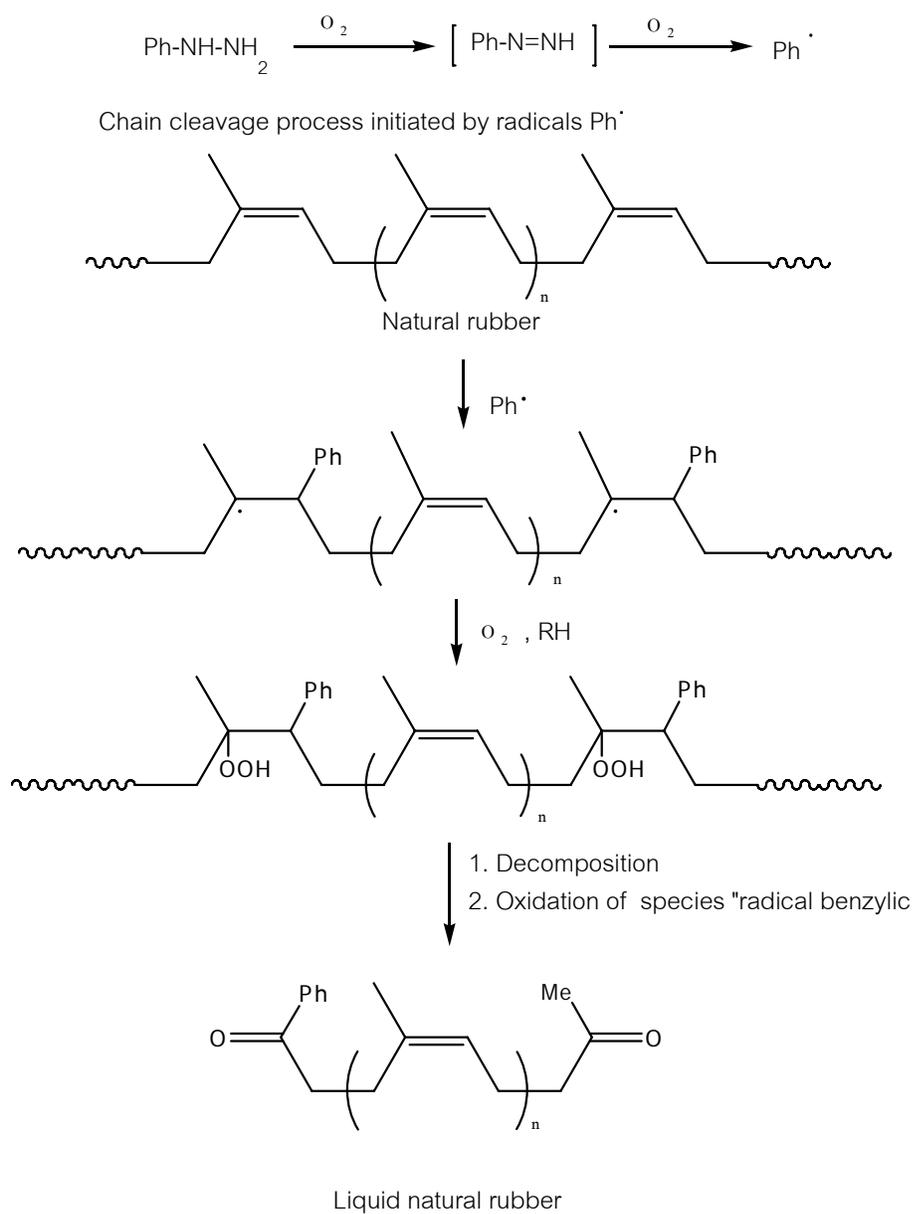
#### 3.9.2 Methods of telechelic liquid natural rubber synthesis

The development of methods for the preparation of TLNRs was begun in the 1970's ago. Generally, the methods involve controlled degradation or depolymerization of the NR backbone via oxidative chain scissions by either chemical or photochemical routes. The methods

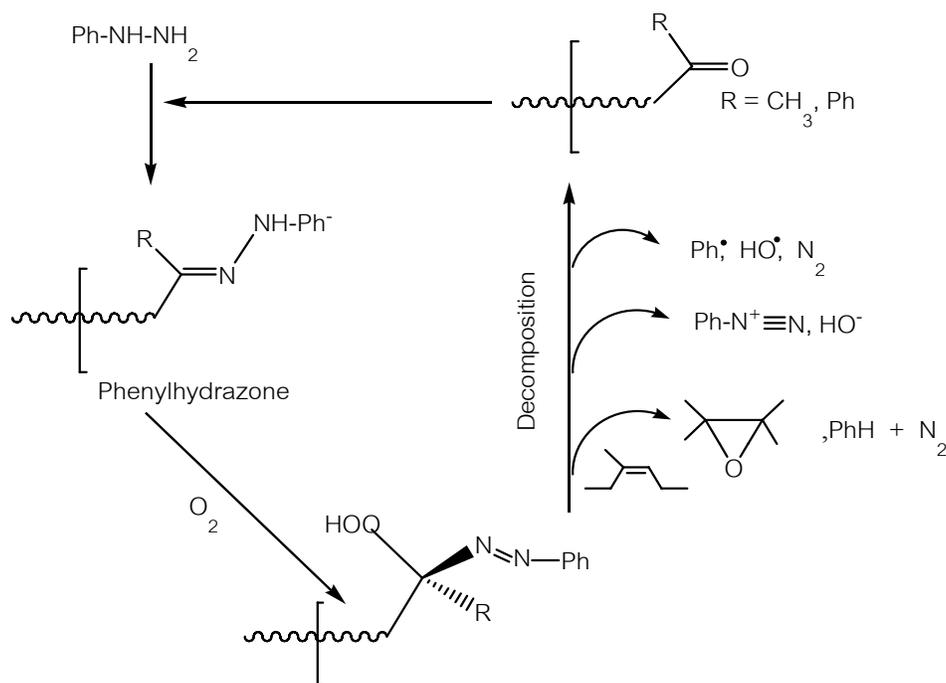
can be classified into five main categories, i.e., redox, photochemical, oxidation at high temperature and pressure, specific oxidative cleavage of double bonds and metathesis degradation.

### **3.9.2.1 Oxidation in presence of redox system**

The redox couple can cleave polymer chains with the concomitant introduction of reactive terminal groups on the resulting oligomers. Thus, an oxidizing agent such as an organic peroxide, hydrogen peroxide, atmospheric oxygen or ferric chloride-oxygen, coupled with a reducing agent such as an aromatic hydrazine or sulphanic acid were employed to depolymerize NR to yield TLNR bearing phenylhydrazone, carbonyl or hydroxyl terminal groups. The depolymerization reaction can be carried out either in an organic solvent or directly in the latex phase. The later method led to the commercial production of TLNR, was carried out as part of a UNIDO project at Ivory Coast by Pautra and Marteau (1976; 1974). A reaction mechanism of controlled degradation of NR in the latex form by combination of phenylhydrazine and atmospheric oxygen yielding carbonyl telechelic natural rubber (CTNR) is proposed and shown in **Figure 3.21** (Process A) and **Figure 3.22** (Process B).



**Figure 3.21** Cleavage mechanism of the carbon-carbon double bonds of natural rubber in latex phase by the redox couple between oxygen and phenylhydrazine (Process A)

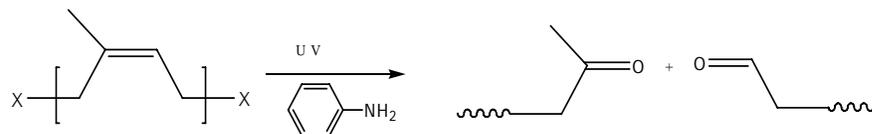


**Figure 3.22** Cleavage mechanism of the carbon-carbon double bonds of natural rubber in latex phase by the redox couple between oxygen and phenylhydrazine (Process B)

The obtained TLNR possessed reactive functional end-groups such as phenylhydrazone, carbonyl or hydroxyl depending on the type of redox system. Their molecular weights ( $\overline{Mn}$ ) are between 3000 and 35000  $\text{g mol}^{-1}$  and the polydispersities are between 1.70 and 1.97 (Brosse *et al.*, 1981). However, phenylhydrazine is toxic and may cause cancers.

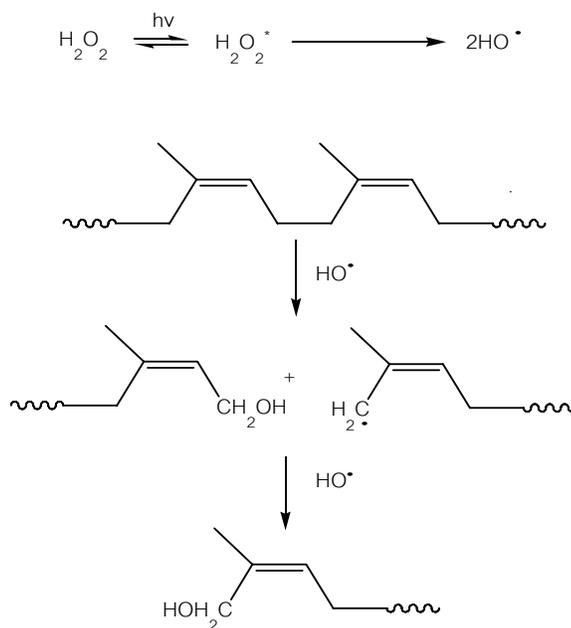
### 3.9.2.2 Photochemical oxidation

Controlled degradation of NR by photochemical chain scission for the preparation of TLNR was first explored by Cunneen (1973). NR was irradiated with ultraviolet light in the presence of nitrobenzene as a photosensitizer to give CTNR having  $\overline{Mn}$  of about 3000  $\text{g mol}^{-1}$ . However, no detail about number average functionality was given. The reaction involved was suggested to be that shown in **Figure 3.23**, but no detailed mechanism was proposed and the oligomer obtained was not well characterized.



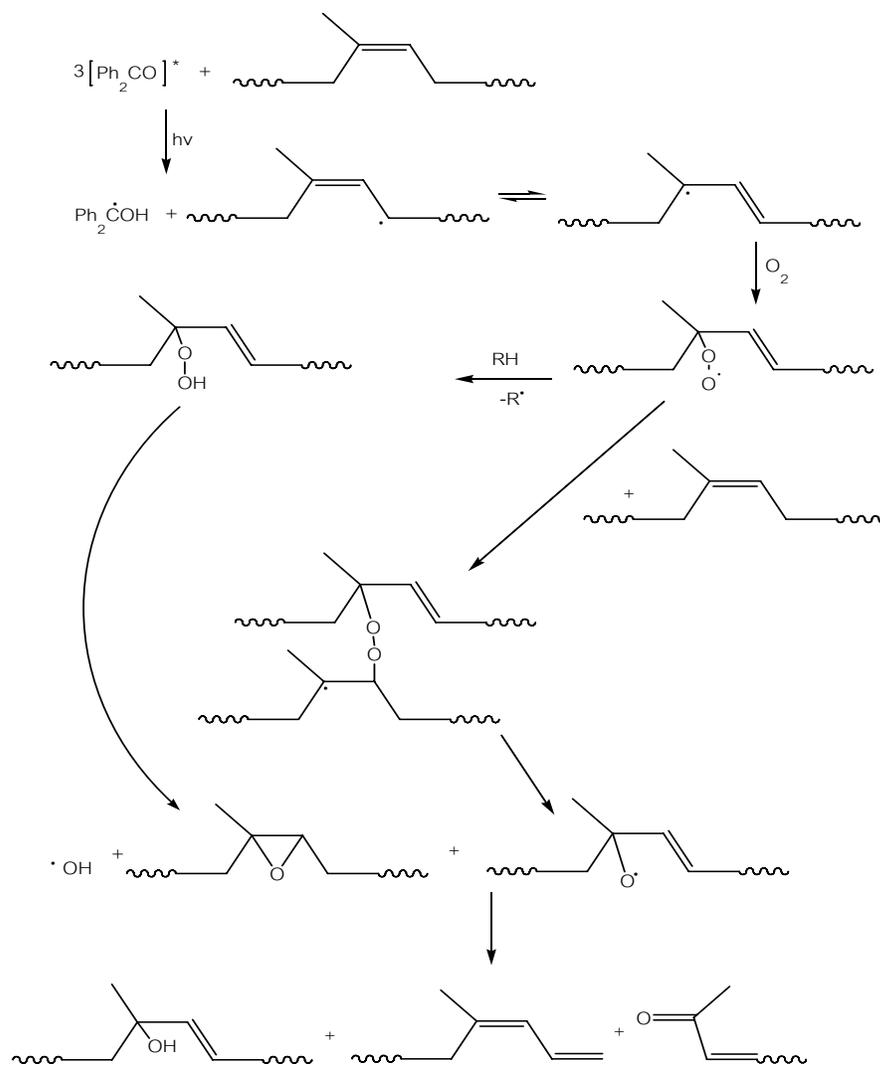
**Figure 3.23** Cleavage reaction of natural rubber in the presence of nitrobenzene under irradiation with ultraviolet light

Ravindran and coworkers (1986,1988) studied the preparation of hydroxyl telechelic natural rubber (HTNR) *via* photo-chemical degradation from natural rubber using hydrogen peroxide and light energy both medium pressure mercury vapor lamp and sunlight. They reported that the both resources have efficient in degradation and lead to oligomers bearing hydroxyl end-groups, but their functionality was less than 2. Methyl alcohol was more suitable than THF solvent in large production of HTNR. However, the side products were observed around 10% such as carbonyl and carboxylic compounds. The mechanism of this reaction is shown in **Figure 3.24**.



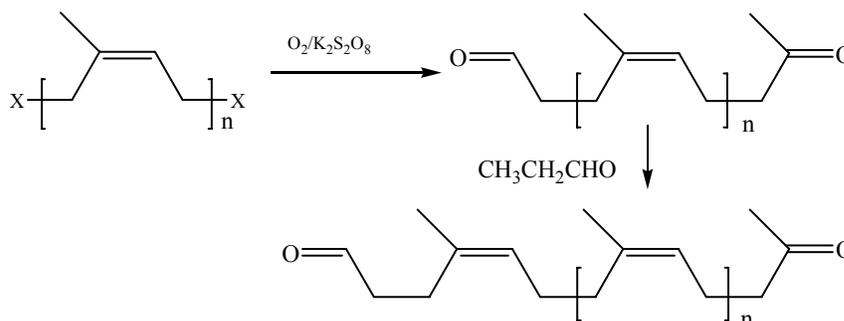
**Figure 3.24** Mechanism of cleavage reaction of natural rubber by hydrogen peroxide under UV radiation

One of the initiators of photochemical degradation is benzophenone presented by Gupta *et al.* (1985) as shown in **Figure 3.25**. Under suitably controlled conditions, the free radicals produced can be used to cleave natural rubber chains to give telechelic oligomers.



**Figure 3.25** Proposed mechanism for the degradation of natural rubber by benzophenone under irradiation UV

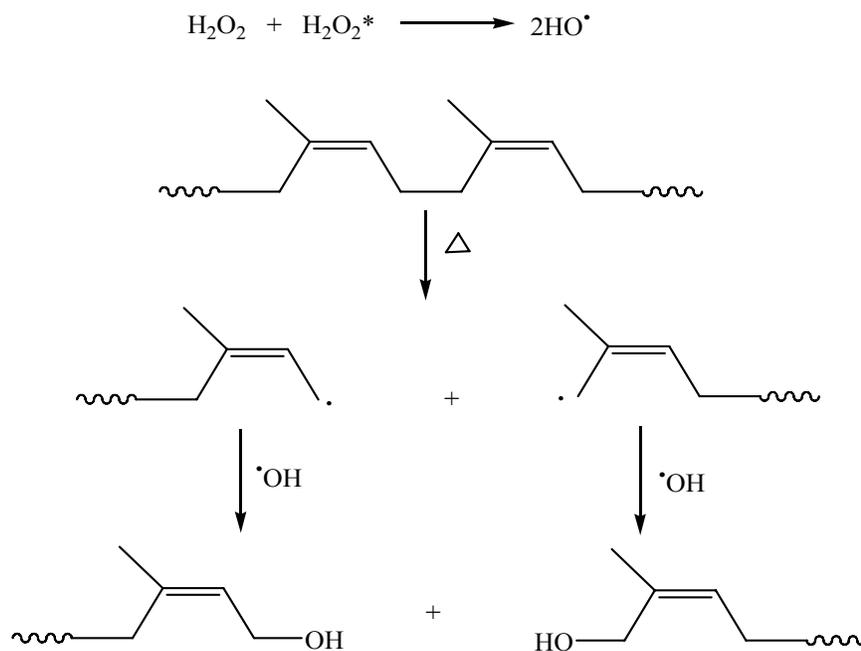
Tangpakdee and coworkers (1998) studied the preparation of low molecular weight oligomers from deproteinised natural rubber, DPNR, by oxidative degradation of 1 phr of  $K_2S_2O_8$  and 15 phr of propanal, by shaking at 60 °C. It was found that the intrinsic viscosity  $[\eta]$  of DPNR with only  $K_2S_2O_8$  decreased from 7.2 to 5.5 after 2 h and then increased to 6.5 after 3 h. The LNR latex is stable as the latex form and the dried rubber coagulated from latex is transparent and colorless. The LNR was a telechelic polymer containing aldehyde and ketone groups at both terminals as determined by NMR. However, the competition of epoxidation was also occurred. The reaction of degradation of natural rubber in presence of  $K_2S_2O_8$ /propanal is showed in **Figure 3.26**.



**Figure 3.26** Reaction of degradation of natural rubber in presence of  $K_2S_2O_8$  and propanal

### 3.9.2.3 High pressure and high temperature oxidation

The preparation of hydroxytelechelic natural rubber (HTNR) via degradation reaction of hydrogen peroxide at high temperature (150 °C) and high pressure (200-300 psi) was reported (Gupta *et al.*, 1985). The obtained HTNR have  $\overline{Mn}$  between 2500 and 3000  $g\ mol^{-1}$ . The average hydroxyl functionality was found to be 1.4. This was explained by side reactions. A mechanism for reaction is proposed as shown in **Figure 3.27**.

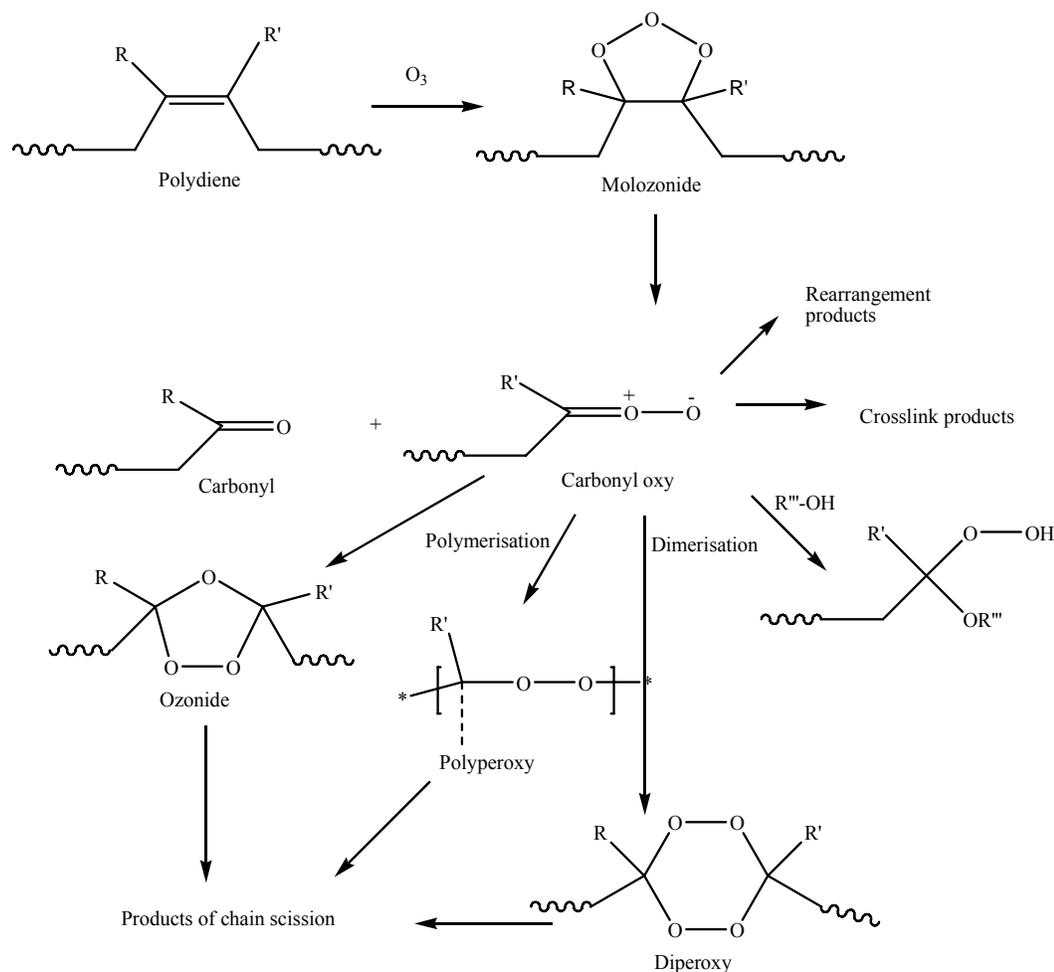


**Figure 3.27** Mechanism of degradation of natural rubber by hydrogen peroxide at high temperature and pressure

### 3.9.3 Oxidative reaction in presence of reactive specific of carbon-carbon double bonds

#### 3.9.3.1 Ozone cleavage

In general, the mechanism of ozone attack on carbon-carbon double bonds of polydiene rubber backbones, causing chain scissions and yielding various peroxides products, is based on the mechanistic route proposed by Criegee (1975) as shown in **Figure 3.28**.

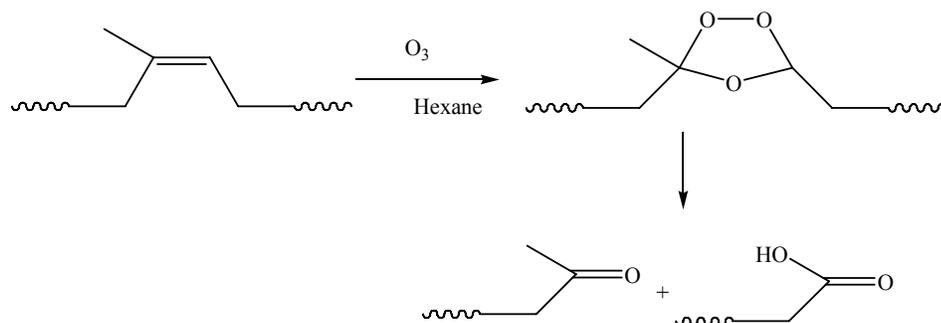


**Figure 3.28** Mechanism of attack of ozone on carbon-carbon double bonds of polydienes.

The reaction between the carbon-carbon double bonds and ozone leads to the formation of an unstable molozonide. This unstable species can easily cleave to a stable carbonyl compound (aldehyde or ketone) and an unstable carbonyl oxide (a zwitterion). The carbonyl oxide then undergoes reactions leading to final, stable products. This reaction results in a decrease in the molecular weight and an increase in species containing oxygenated functional groups (aldehyde, ketone, acid, peroxide, etc.).

Montaudo *et al.* (1992) reported that ozonolysis reaction of *cis*-1,4-polyisoprene in hexane at ice-bath temperature without further treatment with either oxidizing or reducing agents can lead to the formation of telechelic oligomers bearing only ketone and carboxylic acid end

groups (**Figure 3.29**). However, the ozone is highly toxic and can react with protein and other bio-molecules of plant and animals



**Figure 3.29** Ozonolysis of *cis*-1,4-polyisoprene in hexane

### 3.9.3.2 Cleavage by Ruthenium oxide ( $RuO_4$ )

Guizard and Cheradame (1981) developed the method of the selective oxidative cleavage of unsaturated copolymers of isobutene with conjugated dienes using ruthenium tetroxide in presence of peracid. Various bifunctional oligomers were obtained.

### 3.9.3.3 Cleavage by periodic acid or lead acetate

Lead tetraacetate,  $Pb(OAc)_4$  and periodic acid ( $H_5IO_6$ ) are other interesting reagents used for degradation of polyisoprene chains. Generally, both reagents are known to cleave vic-glycols to carbonyl compounds. Burfield and Gan (1977) studied the chain cleavage of natural rubber and epoxidized synthetic rubber by using these compounds. They found that  $Pb(OAc)_4$  degraded hydrolyzed EIR faster than EIR. It can also slowly degrade the synthetic polyisoprene (IR), which presumably does not contain 1,2-diols. They proposed that the chain scission by  $Pb(OAc)_4$  occurred through radical oxidative degradation process. In addition, the authors found that  $H_5IO_6$  did not cleave the chain of the controlled IR, but it can be used as a chemical to degrade NR and acid hydrolyzed NR. In the case of NR, it is believed that the degradation occurs as NR contained a few 1,2-diol groups in the molecular chain.

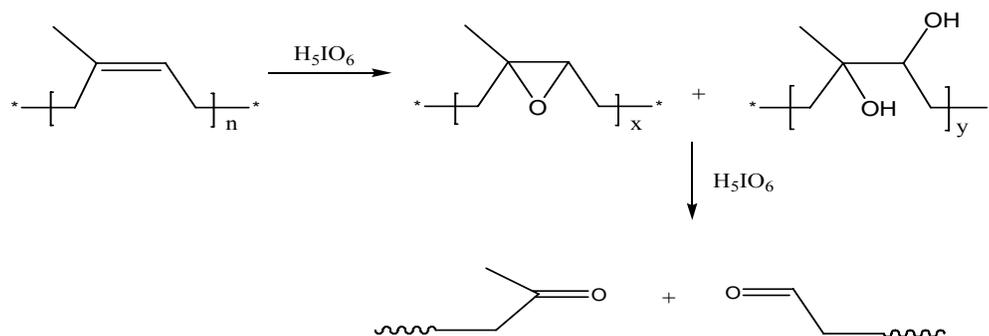
Mauler *et al.* (1995) investigated the chain cleavage of styrene-butadiene rubber (SBR) by using  $H_5IO_6$  and/or ultrasonic radiation. They showed that the degradation of SBR

chains is much better in the presence of  $\text{H}_5\text{IO}_6$  than using only ultrasonic radiation of 40 kHz.  $\text{H}_5\text{IO}_6$  can induce degradation of SBR from  $\overline{M}_w$  of 325000 to 80000  $\text{g mol}^{-1}$ . In the condition of  $\text{H}_5\text{IO}_6$  in conjunction with 40 kHz of ultrasonic radiation, the  $\overline{M}_w$  of SBR was reduced to 40000  $\text{g mol}^{-1}$ .

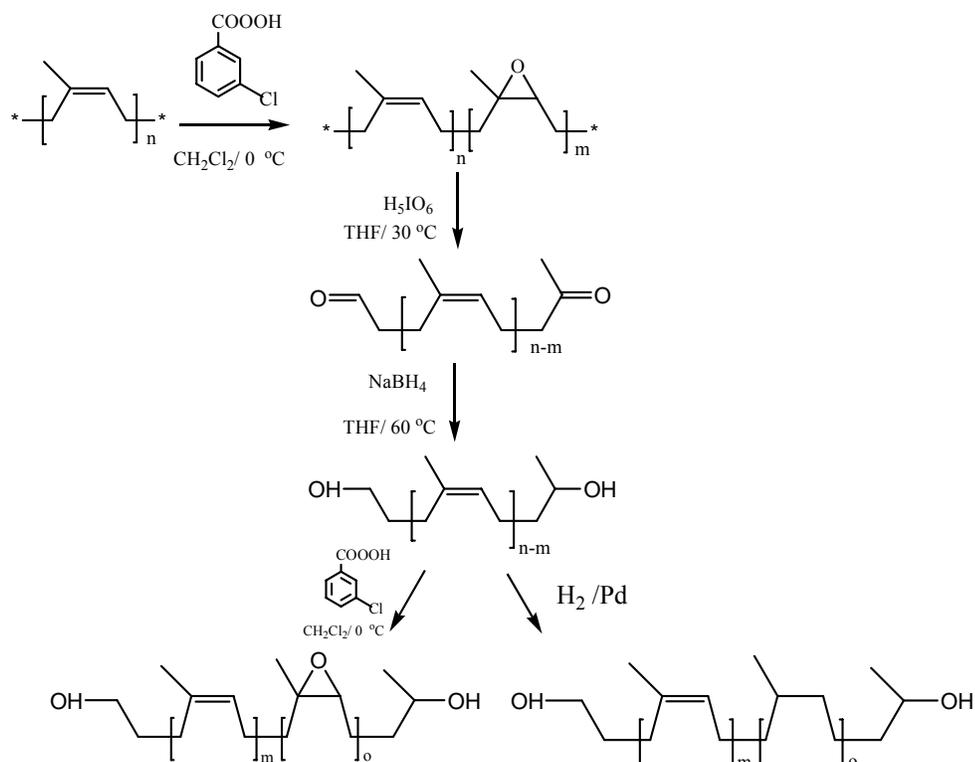
Later on, Mauler and coworkers (1997) studied the chain cleavage of natural rubber (*Hevea brasiliensis*), using  $\text{H}_5\text{IO}_6$  (2/10 v/v) in various solvents and reaction temperatures. It should be noted that at low temperature, the chain degradation using  $\text{H}_5\text{IO}_6$  is better in chloroform than in toluene and *n*-hexane. They explained that from the solvent dielectric constant ( $\epsilon/D$ ) values. The increase of  $\epsilon/D$  might bring about the increase of ionic activity coefficient, then the dissociation constant of electrolyte in solution increases. The  $\epsilon/D$  values of chloroform, toluene and *n*-hexane are found to be 4.806, 2.379, and 1.89, respectively. Therefore, the dissociation of periodic acid ( $\text{H}_5\text{IO}_6$  reactivity) is expected to be highest in chloroform solution. Moreover, periodic acid dissociation increases with increased reaction temperature, resulting in increasing the reaction rate constant of chain degradation.

Reyx and Campistron (1997) used  $\text{H}_5\text{IO}_6$  to prepare telechelic liquid natural rubber from epoxidized rubber. They found the decrease of epoxidized unit content from 25% in the starting rubber to 8% in the resulting degraded rubber. The molecular weight of the degraded rubber was found to be  $\overline{M}_n = 3100 \text{ g mol}^{-1}$ .  $^1\text{H-NMR}$  spectrum revealed the presence of aldehyde and methylketone at the chain ends, residual oxiranes and secondary furanic and cyclic structures.

Gillier-Ritoit S. and coworkers (2003) studied the chain degradation of polyisoprene (IR) and epoxidized polyisoprene (EIR) using  $\text{H}_5\text{IO}_6$  in organic solution (THF). The degraded IR showed similar  $^1\text{H-NMR}$  spectrum as the degraded EIR. Both final products contained aldehyde and ketone terminal ends. They found that the cleavage reaction of IR with  $\text{H}_5\text{IO}_6$  was slower than in the case of EIR. They proposed that the  $\text{H}_5\text{IO}_6$  reacted with carbon-carbon double bond resulting in epoxide or  $\alpha,\beta$ -glycol structure before the breakage by second equivalent of  $\text{H}_5\text{IO}_6$  (**Figure 3.30**).



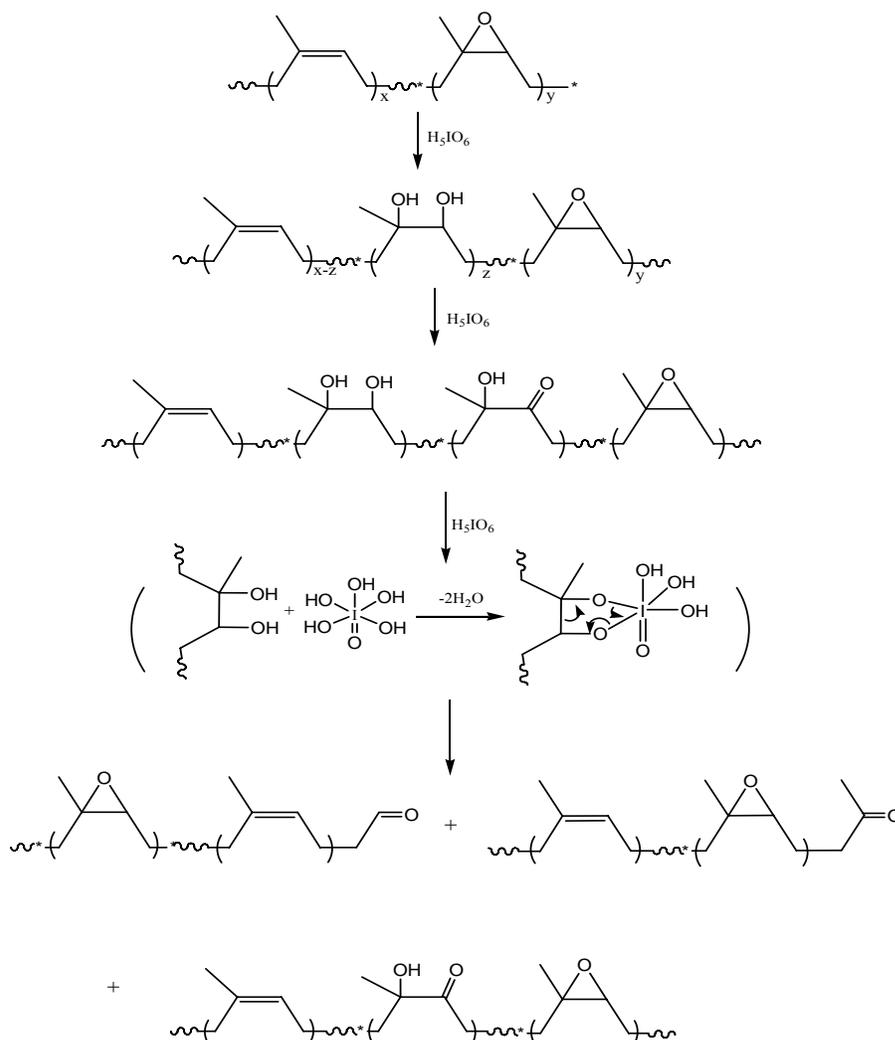
**Figure 3.30** Proposed degradation pathway of polyisoprene by periodic acid



**Figure 3.31** Reaction of preparation and following modifications of hydroxytelechelic *cis*-1,4-polyisoprene

Kébir *et al.* (2005a) reported that new telechelic *cis*-1,4-polyisoprene oligomers bearing an hydroxyl groups at the end of the polyisoprene backbone and possessing controlled molecular weights were used as soft segments in the elaboration of polyurethane elastomers. Besides, the well defined hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) structure obtained through a controlled methodology as shown in **Figure 3.31**. These oligomers were chemically modified leading to hydrogenated and epoxidized oligoisoprenes based polyurethanes.

Phinyocheep and coworkers (2005) reported that the low molecular weight rubber containing epoxide groups can be effectively prepared by the oxidative cleavage reaction of epoxidized natural rubber (ENR) in latex phase using periodic acid at 30 °C. The authors investigated that the molecular weight of ENR was significantly decreased after 10 min of reaction time by using  $(\text{H}_5\text{IO}_6)/(\text{epoxidized unit})$  equal to 1.13 mol.mol<sup>-1</sup>.  $\overline{Mn}$  of ENR and ELNR (epoxidized liquid natural rubber) after 10 min of degradation was 14.58 and  $3.74 \times 10^4$  g mol<sup>-1</sup>, respectively. The epoxide content of liquid rubber was approximately the same as that of the ENR starting materials. The degraded rubbers are considered to be telechelic liquid rubber containing aldehyde at one end and ketone at the other end of the rubber chain characterized with IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The mechanism of degradation epoxidized natural rubber latex by periodic acid is shown as in **Figure 3.32**.



**Figure 3.32** The mechanism of epoxidized natural rubber latex degradation by periodic acid

### 3.9.3.4 Degradation *via* metathesis

The few reports had been in degradation by metathesis catalyst of polyisoprene degradation (Lapinte *et al.*, 2002; Solanky *et al.*, 2005). Solanky and coworkers (2005) studied *cis*-1,4-polyisoprene degradation using first and second generation Grubbs catalysts to achieve end-functionalized acetoxy oligomers in both an organic solvent and a latex phase at room temperature. Well-defined acetoxy telechelic polyisoprene structures were obtained in a selective manner with a range of  $\overline{Mn}$  from 10000 to 30000  $g\ mol^{-1}$  with a polydispersity index of around 2.5.

### 3.9.4 Reactivity and reactions of telechelic liquid natural rubber

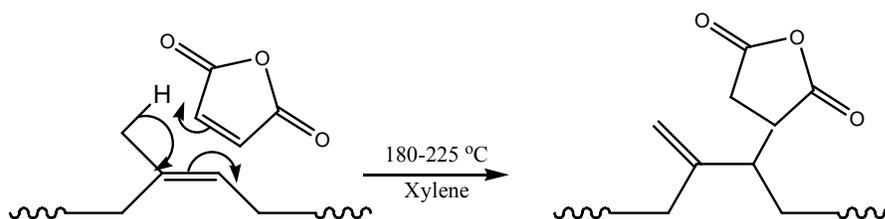
TLNRs possess not only isoprene units in the main chains, but also reactive end groups at the chain terminals. Therefore, they can undergo various reactions at the double bonds of isoprene units and various chain extension reactions.

#### 3.9.4.1 Modification of backbone

Generally, the structure of TLNR is very close to that of an alkene. Therefore its chemical reactivity is influenced by the presence of carbon-carbon double bonds. Moreover, the presence of the methyl group at the carbon-carbon double bonds, electrophilic group, increases the reactivity further compared to those of the carbon-carbon double bonds in polybutadienes.

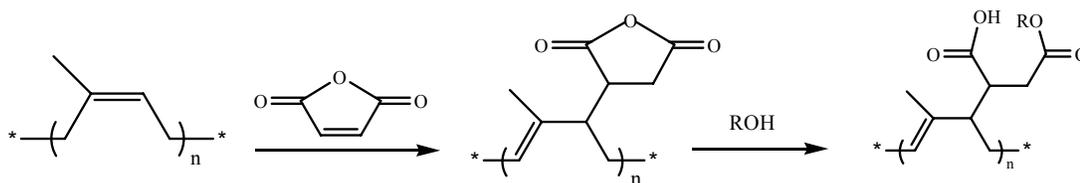
##### a) Maleinization

The reaction of TLNR with maleic anhydride was reported to yield a product having adhesive properties. It is well-known that the double bonds of NR can undergo ‘ene’ reactions as shown in **Figure 3.33**.



**Figure 3.33** Mechanism of maleinization reaction

In a further study, modifications of TLNR with maleic anhydride followed by subsequent reaction with photo-reactive alcohols (Derouet *et al.*, 1990) such as 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl cinnamate (HEC) were found to give TLNR, respectively, having pendent succinic anhydride functionality, which was ultraviolet curable. These reactions are shown in **Figure 3.34**.



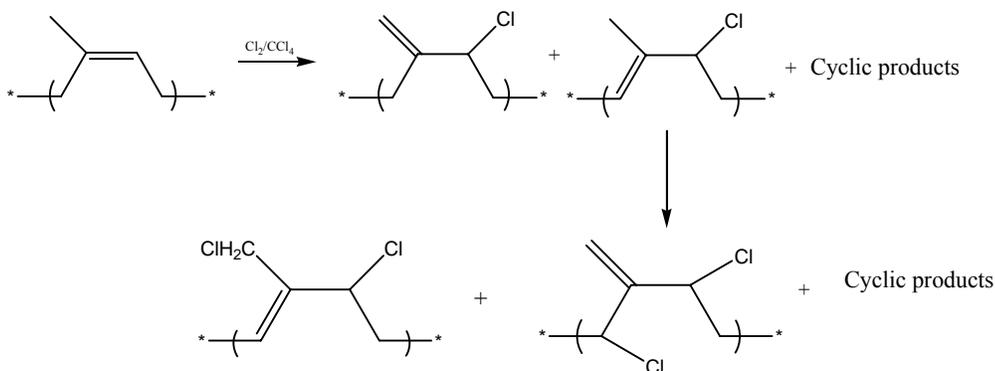
Where R =  $-\text{CH}_2\text{CH}_2\text{OCOCH}=\text{C}_6\text{H}_5$  (cinnamate group)

$-\text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$  (acrylate group)

**Figure 3.34** Modification of Telechelic natural rubber for ultraviolet application

### b) Chlorination

TLNR can be chlorinated to give chlorinated TLNR containing 65%-68% chlorine (Pande *et al.*, 1956). The reaction proceeds as shown in **Figure 3.35**. The product obtained can be used as an anti-corrosion adhesive and its characteristics are comparable to those of the adhesives which are available commercially.



**Figure 3.35** Reaction of chlorination on TLNR

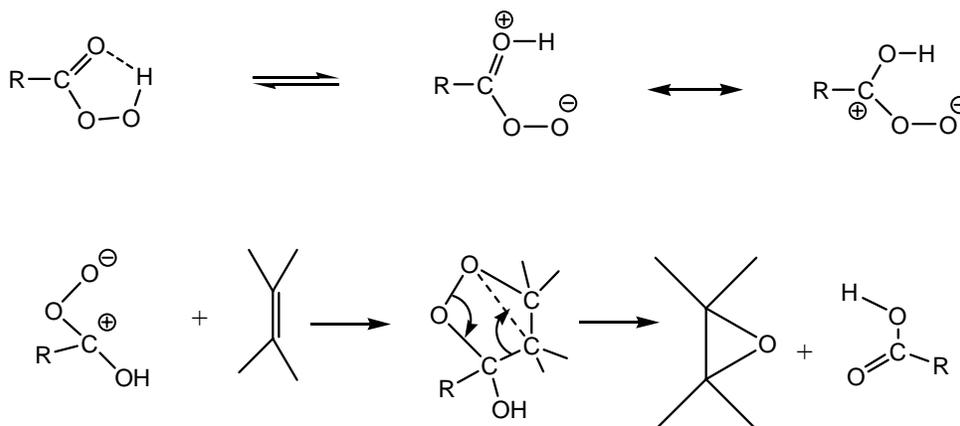
### c) Grafting

The modification of TLNR could be the grafting of monomers onto the TLNR backbone to give a graft copolymer. It was reported that chemical grafting of styrene and methyl methacrylate onto TLNR of  $\overline{Mn}$  10000-20000  $\text{g mol}^{-1}$  by radical polymerization (using peroxy or diazo compounds as initiator) gives 43% graft polystyrene and 49% graft poly(methyl methacrylate), respectively (Brosse *et al.*, 1981). Unfortunately, the mechanical properties of the vulcanizates obtained from these grafted TLNRs are inferior compared with those of NR

vulcanizates. Polystyrene (30%-50%) graft copolymer was found to give a thermoplastic rubber suitable for use as heat-resistant adhesive (Pautra and Marteau, 1976).

#### d) Epoxidation

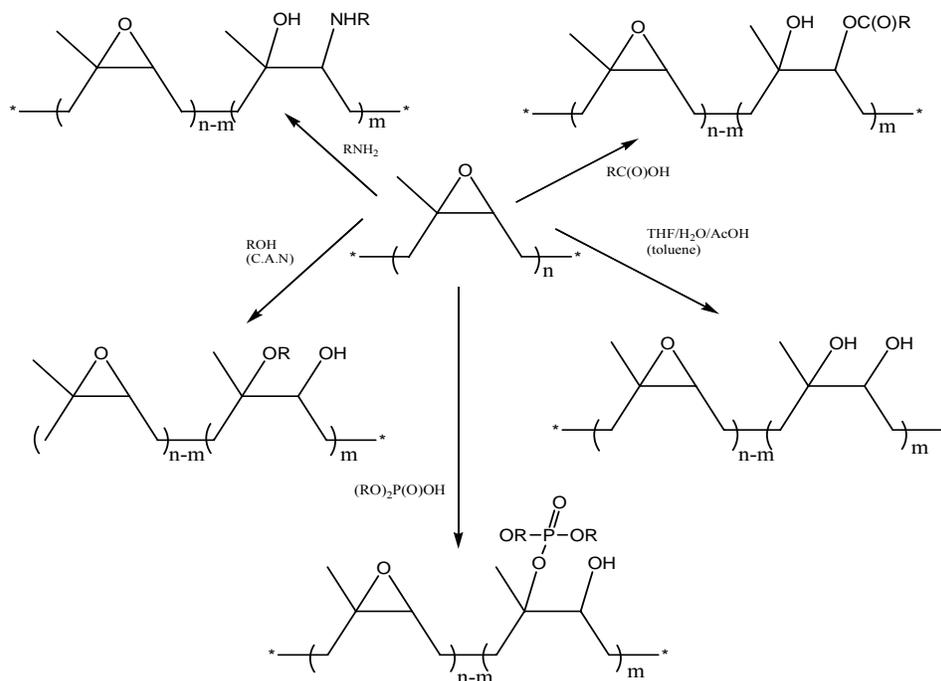
In this process, backbone double bonds are converted into oxiranes (epoxides) using an organic peracid. It has been reported that TLNR can be epoxidized *in situ* in the latex form, using organic peracids derived from formic or acetic acids, in two-step reactions. In the first step, peracid is formed by reaction between the acid and hydrogen peroxide. Then, in the second step, the peracid is reacted with TLNR to give telechelic epoxidized liquid natural rubber (TELNR). The reaction was proposed by Kwart and Hoffman (1966) as shown in **Figure 3.36**. Our laboratory was also successful in preparation of epoxidation of hydroxyl telechelic *cis*-1,4-polyisoprene with *m*-chloroperbenzoic acid in solvent phase (Kébir *et al.*, 2005a).



**Figure 3.36** Mechanism of epoxidation reaction on isoprene unit from peracid

ELNRs are the starting products and their chemical modification may allow new properties and technological interests. Indeed, the presence of carbon-carbon double bonds, or oxirane rings on the rubber backbone is of great interest because of the number of chemical reactions that can be used to add reagents. The reactivity of the epoxide groups toward carboxylic acids (Brosse *et al.*, 1979; Soutif and Brosse, 1984), amines (Jayawardena *et al.*, 1984), phosphoric acid derivatives (Derouet *et al.*, 2001b) and alcohols (Derouet *et al.*, 2001a) is well

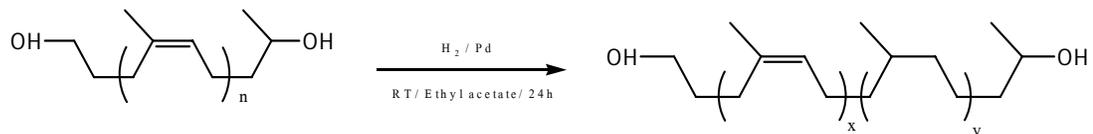
known (**Figure 3.36**). Some recent studies have shown the importance of these compounds in the synthesis of higher value added materials.



**Figure 3.37** Possibilities of chemical transformations *via* epoxide groups

### e) Hydrogenation

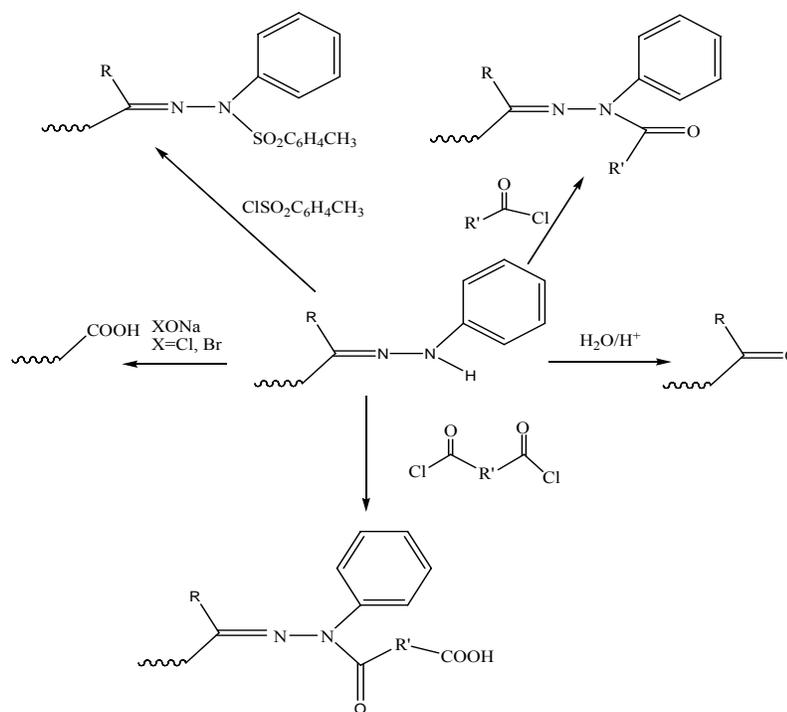
Almost hydrogenation is a useful method for the reduction of unsaturated in diene polymers. It can be performed with elemental hydrogen in the presence of a transition metal catalyst (Hinchiranan *et al.*, 2006; Tangthongkul *et al.*, 2005) or by a noncatalytic method (Samran *et al.*, 2005). Our laboratory was successful in preparation of hydrogenation of hydroxyl telechelic *cis*-1,4-polyisoprene (HTPI) under hydrogen pressure with catalyst in acetate medium (Kébir *et al.*, 2005a) as shown in **Figure 3.38**.



**Figure 3.38** Hydrogenation of HTPI

### 3.9.4.2 Modification of functional end –groups of telechelic natural rubber

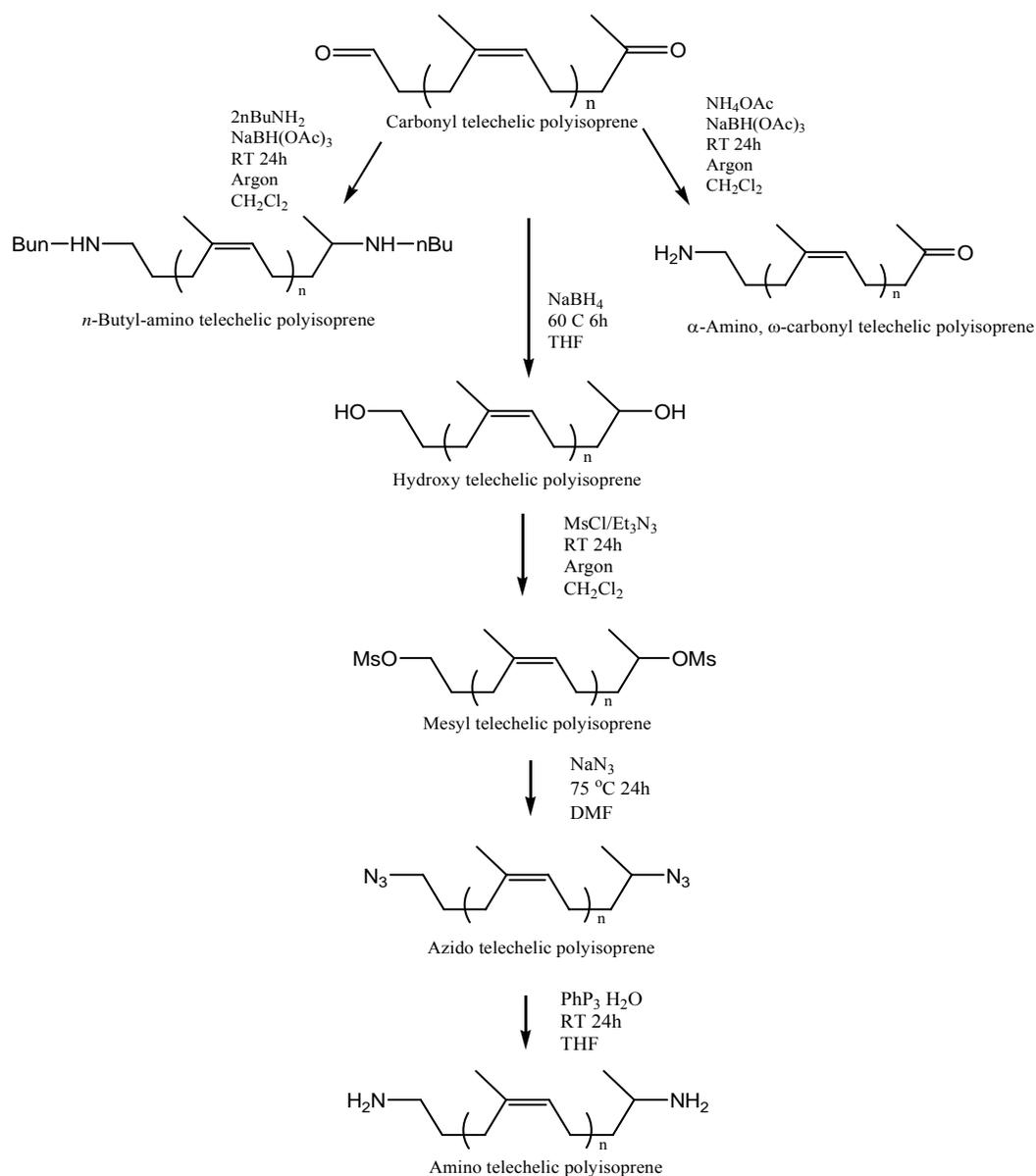
The possibility of chemical modification of TLNR bearing phenylhydrazone end-chains were proposed (Brosse *et al.*, 2000) as shown in **Figure 3.39**.



**Figure 3.39** Possible reactions of chemical modification of phenylhydrazone end-groups

Recently, our laboratory reported that chemical modifications of carbonyl oligoisoprenes can lead to hydroxyl or amino end-groups (Kébir *et al.*, 2005a; Kébir *et al.*, 2005b; Morandi *et al.*, 2007). It was found that new well defined hydroxyl or amino telechelic *cis*-1,4-oligoisoprenes have been obtained in a mass range of 1600–2300 g mol<sup>-1</sup>. For successful synthesis of these amino telechelic oligoisoprenes, two approaches were described. The first approach

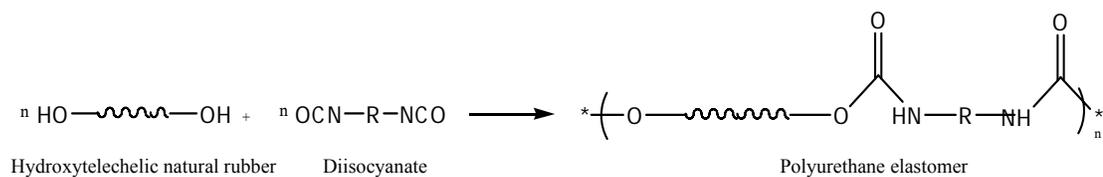
involved a standard mesylate displacement by sodium azide followed by smooth reduction using triphenylphosphine. The second pathway implied a reductive amination sequence. Primary and secondary amine functions have thus been selectively obtained at both oligomer chain-ends depending on reaction conditions. These reactions are shown in **Figure 3.40**.



**Figure 3.40** Reaction pathways for aminations of carbonyl-telechelic oligoisoprene

### 3.9.4.3 Chain extension reaction of telechelic natural rubber

The chain extension reactions of TLNR can lead to polyurethane block copolymers (Gopakumar and Nair, 2006; Ravindran *et al.*, 1991) in **Figure 3.40** both thermoplastic and elastomers applications. Their mechanical properties of polyurethane elastomers were obtained by varying isocyanate functions natural, molecular weight of oligomers and the ratio of (NCO)/(OH).



**Figure 3.40** Synthesis of polyurethane

## CHAPTER 4

### MATERIALS AND METHODS

#### 4.1 Materials

##### 4.1.1 Field natural rubber latex

Field natural rubber latex preserved ammonia solution 0.4% used as a raw material for a preparation of the epoxidized natural rubber was supplied by Pattani Industry Co., LTD. Pattani, Thailand.

##### 4.1.2 Hydrogen peroxide

Hydrogen peroxide (35%, H<sub>2</sub>O<sub>2</sub>) used as a reactant for the preparation of the epoxidized natural rubber was manufactured by Acros organics, Belgium.

##### 4.1.3 Formic acid

Formic acid (99%, HCOOH) used as a reactant for the preparation of the epoxidized natural rubber was manufactured by Acros organics, Belgium.

##### 4.1.4 Non-ionic surfactants

Sinnopal NP 307 ( $\alpha$ -(nonylphenoxy) poly(ethylene oxide)) used as a stabilizer the latex during epoxidation reaction was manufactured by Cognis, Meaux, France.

##### 4.1.5 Periodic acid

Periodic acid (99%, H<sub>5</sub>IO<sub>6</sub>) used as a reactant for the degradation of epoxidized natural rubber was manufactured by Aldrich, Germany.

##### 4.1.6 Sodium borohydride

Sodium borohydride (99%, NaBH<sub>4</sub>) used as a reactant for reduction of carbonyl telechelic natural rubber was manufactured by Acros organics, Belgium.

##### 4.1.7 *m*-Chloroperbenzoic acid

*m*-Chloroperbenzoic acid (70%-75%, *m*-CPBA) used as a reactant for the epoxidation reaction of hydroxyl telechelic natural rubber was manufactured by Acros organics, Belgium.

#### **4.1.8 Lithium aluminum hydride**

Lithium aluminum hydride (95%,  $\text{LiAlH}_4$ ) used as a reactant for oxiranes ring opening of epoxidized hydroxyl telechelic natural rubber was manufactured by Aldrich, Germany.

#### **4.1.9 Palladium on activated carbon**

Palladium on activated carbon (18%) used as a catalyst for the preparation of hydrogenated hydroxyl telechelic natural rubber was manufactured by Acros organics, Belgium.

#### **4.1.10 N-iodosuccinimide**

N-iodosuccinimide (98%,  $\text{C}_4\text{H}_4\text{INO}_2$ ) used as co-reagent with periodic acid for degradation of natural rubber was manufactured by Avocado research chemical LTD, England.

#### **4.1.11 Polymeric MDI (Lupranate M 20S)**

Lupranate M20S is a polymeric MDI (Polymethylene polyphenylpolyisocyanate) with a functionality of approximately 2.7. Its appearance is dark brown liquid, having % NCO = 31.5, viscosity 200 cPs at 25 °C, density 1.23 g cm<sup>-3</sup>. Polymeric MDI used as a reactant for the preparation of flexible polyurethane foam was manufactured by BASF, Germany.

#### **4.1.12 Silicone surfactant**

Silicone surfactant (B 8110) is polyether-modified polysiloxane used as a reactant for the preparation of flexible polyurethane foam was manufactured by Goldschmidt, Germany.

#### **4.1.13 Dabco 33-LV**

Dabco 33-LV is the mixture of 33% triethylenediamine and 67% dipropylene glycol used as an amine catalyst for the preparation of flexible polyurethane foam was manufactured by Air products, USA.

#### **4.1.14 Dibutyltin dilaurate (Dabco-T12)**

Dibutyltin dilaurate (95%, DBTL) used as a tin catalyst for the preparation of flexible polyurethane foam was manufactured by Aldrich chemical, Germany.

#### **4.1.15 Glycerol**

Glycerol (99%,  $\text{C}_3\text{H}_8\text{O}_3$ ) used as a chain extender for the preparation of flexible polyurethane foam was manufactured by Riedel de Haen, Germany.

#### **4.1.16 1,4-Butanediol**

1,4-Butanediol (99%,  $\text{C}_4\text{H}_{10}\text{O}_2$ ) used as a chain extender for the preparation of flexible polyurethane foam was manufactured by Acros organics, Belgium.

#### 4.1.17 Commercial polyols

Three different molecular weights polyoxypropylene glycols (polyether polyol) have been used in the preparation of flexible polyurethane foams. They were supplied by TPI Co. LTD., Thailand as properties shown in **Table 4.1**.

**Table 4.1** Typical properties of three grade polyether commercial polyols

Typical properties	Raypol1010	Raypol1020	Raypol3003
Appearance	Clear liquid	Clear liquid	Clear liquid
$\overline{Mn}$ (g mol <sup>-1</sup> )	1000	2000	3000
Hydroxyl value (mg KOH g <sup>-1</sup> )	117	56.4	56.0
Viscosity @ 25 °C (cPs)	120-180	290-340	500-600
Water content (%)	0.10	0.10	0.10
Acid number (mg KOH g <sup>-1</sup> )	0.10	0.05	0.02
Density (g cm <sup>-3</sup> )	1.00	1.00	-

#### 4.1.18 Sodium hydrogencarbonate

Sodium hydrogencarbonate (99%, NaHCO<sub>3</sub>) used as a purified agent was manufactured by Acros organics, Belgium.

#### 4.1.19 Sodium thiosulfate

Sodium thiosulfate (99%, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) used as a purified agent was manufactured by Acros organics, Belgium.

#### 4.1.20 Magnesium sulfate

Magnesium sulfate (99%, MgSO<sub>4</sub>) used as a purified was manufactured by Acros organics, Belgium.

#### 4.1.21 Tetrahydrofuran

Tetrahydrofuran (THF, C<sub>4</sub>H<sub>8</sub>O) was manufactured by Acros organics, Belgium.

#### 4.1.22 Deuterated chloroform

Deuterated chloroform (99.8%, 0.03% TMS) with tetramethylsilane (TMS) as internal standard used as a solvent in NMR analysis was manufactured by Merck, Germany.

#### 4.1.23 Sodium Chloride

Sodium chloride (NaCl) used as a purified agent was purchased in local market.

#### 4.1.25 Blowing agents

a) Chemical blowing agent is water that reacted with diisocyanates to produce carbon dioxide gas.

b) Physical blowing agent is dichloromethane that was evaporated by exothermic reaction of polyurethane and gas reaction.

#### 4.1.25 Solvents

Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), methanol ( $\text{CH}_3\text{OH}$ ), ethyl acetate ( $\text{CH}_3\text{COOC}_2\text{H}_5$ ), acetone ( $\text{CH}_3\text{COCH}_3$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ) and water ( $\text{H}_2\text{O}$ ) were distilled before use.

## 4.2 Instruments

All instruments used in this research are listed in **Table 4.2**

**Table 4.2** Instruments used in the experiment for characterizations

Instruments	Model	Manufacturer
Nuclear magnetic resonance spectrometer (NMR)	DPX 400	Bruker
Fourier transforms infrared spectrometer (FT-IR)	1750	Perkin-Elmer
Steric exclusion chromatography (SEC)	Spectra system	ThermoFinnigan
Mass spectrometer (MALDI-TOF MS)	Biflex III	Bruker
Differential scanning calorimeter (DSC)	DSC Q 100	TA Instruments
Thermogravimetric analyzer (TGA)	TGA Q 100	TA Instruments
Tensile testing machine	H 10KS	Hounsfield
Homogenizer	Ultra-Turrax	KIKA-WERKE GMBH
Viscometer	RVF 100	Brookfield Synchroelectric
Kundt's tube	-	CTTM

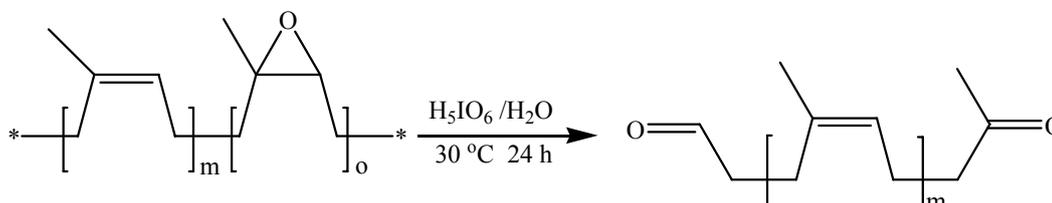
## 4.3 Experimental

### 4.3.1 Degradation of natural rubber in latex phase

The degradation of natural rubber latex and epoxidized natural rubber latex was studied as in described in 4.3.1.1-4.3.1.2

#### 4.3.1.1 Degradation of epoxidized natural rubber latex using periodic acid

The cleavage reaction was carried out in the jacketed reactor at 30 °C. The epoxidized natural rubber (ENR) (16.7%) in latex phase (20% DRC) was treated with periodic acid solution. After 24 h the sample latex was precipitated in methanol and then was dissolved in dichloromethane for overnight. After that the polymer solution was washed with saturated  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , and  $\text{NaCl}$ , respectively and dried with  $\text{MgSO}_4$ . The solvent was evaporated and dried by vacuum oven until constant weight was obtained. The sample was analyzed by  $^1\text{H-NMR}$ , FT-IR, and SEC. The reaction is occurred as described in **Figure 4.1**.

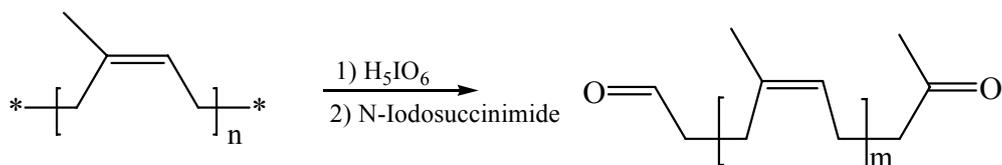


**Figure 4.1** The degradation reaction of natural rubber latex by using periodic acid

#### 4.3.1.2 Degradation of natural rubber latex by using periodic acid and

##### N-iodosuccinimide

The cleavage reaction was carried out in the three necked round bottom flask at 30 °C. The natural rubber latex (20% DRC, non ionic surfactant 3 phr and agitated for 12 h) was treated with periodic acid solution (8% mole of rubber) and then N-iodosuccinimide solution (NIS, 0.5 M in acetonitrile) was added slowly in the reaction at various volumes (added every-hours started at 3 to 6 h after added periodic acid ). The latex samples were coagulated with methanol and washed with  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , water and methanol, respectively. The samples were dried by vacuum oven and then analyzed with  $^1\text{H-NMR}$ . The reaction is described in **Figure 4.2**.



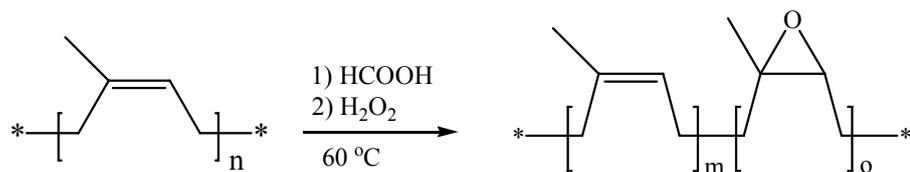
**Figure 4.2** The degradation reaction of natural rubber latex by using periodic acid and NIS

### 4.3.2 Controlled degradation of natural rubber in solvent phase

Controlled degradation of natural rubber in solvent phase has two steps. Each step is described in 4.3.2.1 and 4.3.2.2.

#### 4.3.2.1 Preparation of epoxidized natural rubber (ENR 2)

Field latex was diluted to 20%DRC, stabilized with Sinnopal NP 307 3 phr and stirred through a night at room temperature to eliminate ammonia and to homogenize for 12 h. The epoxidation reaction was carried out in a three necked reactor with controlled speed stirrer at 300 rpm and 60 °C. The determined amount of formic acid (0.3 mol) was slowly dropped over about 15 min and then was stirred for 15 min after slowly added the desired amount of hydrogen peroxide (0.3 mol) under continuous stirring. The reaction time was varied to 1, 3, 3 and 8 h. The epoxidized latex was coagulated in methanol and washed with water several times then washed with methanol, cut it into small pieces and finally dried in vacuum oven. The sample was analyzed with  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ . The reaction is presented in **Figure 4.3**.



**Figure 4.3** The epoxidation reaction of natural rubber

#### Characterization:

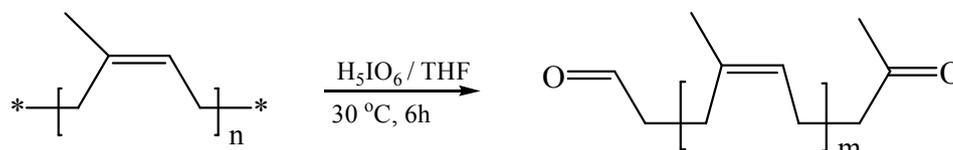
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.29 (s,  $\text{CH}_3\text{COCH-}$ ), 1.67 (s,  $-\text{CH}_3$  isoprenic), 2.04 (m,  $-\text{CH}_2$  isoprenic), 2.70 (t,  $\text{H}$  (epoxide group)), 5.10 (t,  $=\text{CH}$  isoprenic)

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 22.21 ( $\text{CH}_3\text{COCH-}$ ), 25.90 ( $\text{CH}_2\text{CH}=\text{C}_{\text{isoprenic}}$ ), 31.70 ( $\text{CH}_2-\text{C}=\text{CH}_{\text{isoprenic}}$ ), 60.81 ( $\text{CH}_3\text{COCH-}$ ), 64.50 ( $\text{CH}_3\text{COCH-}$ ), 124.50 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ ), 134.70 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ )

**FT-IR:**  $\nu_{(\text{H}-\text{C}=\text{C})} = 3035 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} = 2900\text{--}2730 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{O})} = 1721 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C})} = 1664 \text{ cm}^{-1}$ ;  
 $\nu_{(\text{CH}_2, \text{CH}_3) \text{ cis-1,4-isoprene}} = 1448, 1376 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C}-\text{H})} = 834 \text{ cm}^{-1}$

#### 4.3.2.2 Preparation of carbonyltelechelic natural rubber (CTNR 3)

The cleavage reaction was carried out in a jacketed reactor with a controlled speed of 300 rpm and 30 °C. The epoxidized natural rubber solution in THF (0.4 mol L<sup>-1</sup>) was mixed with periodic acid (1.1 mol equivalent) solution (0.4 mol L<sup>-1</sup>). After 6 h iodic acid was filtered, THF was evaporated and then the polymer is dissolved again in dichloromethane. The solution was washed with saturated NaHCO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and NaCl, respectively and dried with MgSO<sub>4</sub>. After that the solvent was evaporated and the product was dried in vacuum oven. The sample was analyzed with <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR, MALDI-TOF MS and SEC. The reaction is occurred following in **Figure 4.4**.



**Figure 4.4** The cleavage reaction of epoxidized natural rubber in THF

#### Characterization:

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.67 (s,  $-\text{CH}_3_{\text{isoprenic}}$ ), 2.04 (m,  $-\text{CH}_2_{\text{isoprenic}}$ ), 2.13 (s,  $\text{CH}_3\text{COCH}_2$ ), 2.25 (m,  $\text{CH}_3\text{COCH}_2\text{CH}_2$ ), 2.34 (m,  $\text{CH}_2\text{CH}_2\text{CHO}$ ), 2.43 (t,  $\text{CH}_3\text{COCH}_2\text{CH}_2$ ), 2.49 (m,  $\text{CH}_2\text{CHO}$ ), 5.10 (t,  $=\text{CH}_{\text{isoprenic}}$ ), 9.77 (s,  $\text{CH}_2\text{CHO}$ ) and disappearance  $\delta$  (ppm): 1.29 (s,  $\text{CH}_3\text{COCH-}$ ), 2.7 (t,  $\text{CH}_3\text{COCH-}$ )

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 21.81 ( $\text{CH}_3\text{COCH}_2$ ), 25.9 ( $\text{CH}_2\text{CH}=\text{C}_{\text{isoprenic}}$ ), 30.5 ( $\text{CH}_2\text{CH}_2\text{OH}$ ), 31.7 ( $\text{CH}_2-\text{C}=\text{CH}_{\text{isoprenic}}$ ), 41.88 ( $\text{CH}_2\text{CHO}$ ), 43.53 ( $\text{CH}_3\text{COCH}_2$ ), 124.5 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ ), 134.7 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ ), 201.61 ( $\text{CH}_2\text{CHO}$ ), 208.21 ( $\text{CH}_3\text{COCH}_2$ )

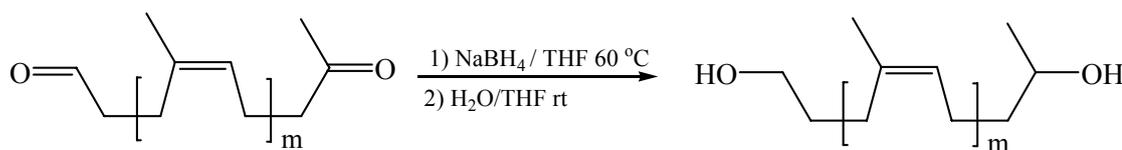
**FT-IR:**  $\nu_{(\text{H}-\text{C}=\text{O})} = 3035 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} = 2900\text{--}2730 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{O})} = 1721 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C})} = 1664 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} \text{ cis-1,4-isoprene} = 1448, 1376 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C}-\text{H})} = 834 \text{ cm}^{-1}$

### 4.3.3 Modification of telechelic natural rubber

Oligomers were modified to obtain oligomers having different structures i.e., epoxide, hydrogenated structure as described in 4.3.3.1-4.3.3.4

#### 4.3.3.1 Preparation of hydroxytelechelic natural rubber (HTNR 4)

The reduce reaction was carried out in three neck round bottle at  $60^\circ\text{C}$ . The CTNR 3 solution in THF ( $0.1 \text{ mol L}^{-1}$ ) was performed with  $\text{NaBH}_4$  (5 mol equivalent) solution ( $1 \text{ mol L}^{-1}$ ) for 6 h and then hydrolyzed by adding the mixture of THF with ice (30 ml and 20g) in drop by drop at room temperature. After that, the mixture was washed with saturated NaCl and dried with  $\text{MgSO}_4$ . The solvent was evaporated and the polymer was dried in vacuum oven. The sample was analyzed with  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR, MALDI-TOF MS and SEC. The reaction is described in Figure 4.5.



**Figure 4.5** The reduction of carbonyltelechelic natural rubber

#### Characterization:

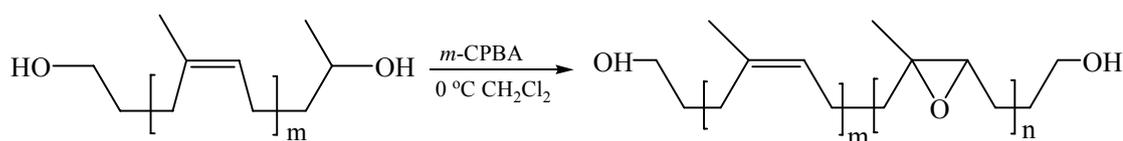
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.20 (d,  $\text{CH}_3\text{CHOH}$ ), 1.67 (s,  $-\text{CH}_3_{\text{isoprenic}}$ ), 2.04 (m,  $-\text{CH}_2_{\text{isoprenic}}$ ), 3.65 (t,  $\text{CH}_2\text{OH}$ ), 3.80 (m,  $\text{CHOH}$ ), 5.10 (t,  $=\text{CH}_{\text{isoprenic}}$ ) and disappearance: 2.04 (m,  $-\text{CH}_2_{\text{isoprenic}}$ ), 2.13 (s,  $\text{CH}_3\text{COCH}_2$ ), 2.25 (m,  $\text{CH}_3\text{COCH}_2\text{CH}_2$ ), 2.34 (m,  $\text{CH}_2\text{CH}_2\text{CHO}$ ), 2.43 (t,  $\text{CH}_3\text{COCH}_2\text{CH}_2$ ), 2.49 (m,  $\text{CH}_2\text{CHO}$ ), 9.77 (s,  $\text{CH}_2\text{CHO}$ )

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 25.9 ( $\text{CH}_2\text{CH}=\text{C}_{\text{isoprenic}}$ ), 30.5 ( $\text{CH}_2\text{CH}_2\text{OH}$ ), 31.7 ( $\text{CH}_2-\text{C}=\text{CH}_{\text{isoprenic}}$ ), 39.0 ( $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ), 62.5 ( $\text{CH}_2\text{OH}$ ), 67.5 ( $\text{CH}_3\text{CHOH}$ ), 124.5 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ ), 134.7 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ )

**FT-IR:**  $\nu_{(\text{OH})} = 3350 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C}-\text{H})} = 3035 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} = 2900\text{--}2730 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C})} = 1664 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)}$  *cis*-1,4-isoprene = 1448, 1376  $\text{cm}^{-1}$ ;  $\delta_{(\text{C}=\text{C}-\text{H})} = 834 \text{ cm}^{-1}$  and disappearance of  $\nu_{\text{C}=\text{O}}$  at 1721  $\text{cm}^{-1}$

#### 4.3.3.2 Preparation of epoxidized hydroxytelechelic natural rubber (EHTNR 5)

The epoxidation reaction of HTNR 4 (1 mol) was carried out in three neck round bottle at 0 °C. The determined concentration of *m*-chloroperbenzoic acid (0.1 mol, 0.2 mol and 0.3 mol for 10%, 20% and 30% epoxidation) in dichloromethane (0.2 mol L<sup>-1</sup>) was added dropwise in a solution of HTNR (0.1 mol L<sup>-1</sup>). After stirring 4 h, the reaction mixture was washed with NaHCO<sub>3</sub> aqueous, saturated NaCl aqueous and was dried with MgSO<sub>4</sub>, respectively. The solvent was evaporated and the polymer was dried in vacuum oven. The sample was analyzed with <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MALDI-TOF MS and FT-IR. The reaction is described in **Figure 4.6**.



**Figure 4.6** The preparation of epoxidized hydroxytelechelic natural rubber

#### Characterization:

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.20 (d,  $\text{CH}_3\text{CHOH}$ ), 1.29 (s,  $\text{CH}_3\text{COCH-}$ ), 1.67 (s,  $-\text{CH}_3_{\text{isoprenic}}$ ), 2.04 (m,  $-\text{CH}_2_{\text{isoprenic}}$ ), 2.7 (t,  $\text{CH}_3\text{COCH-}$ ), 3.65 (t,  $\text{CH}_2\text{OH}$ ), 3.80 (m,  $\text{CHOH}$ ), 5.10 (t,  $=\text{CH}_{\text{isoprenic}}$ )

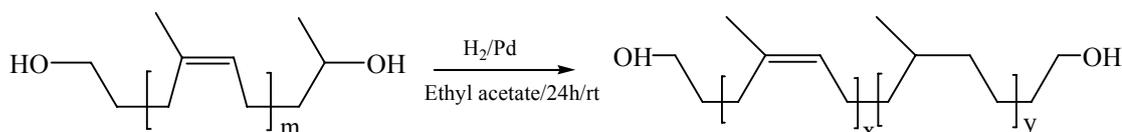
$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 21.81 ( $\text{CH}_3\text{COCH-}$ ), 25.9 ( $\text{CH}_2\text{CH}=\text{C}_{\text{isoprenic}}$ ), 30.5 ( $\text{CH}_2\text{CH}_2\text{OH}$ ), 31.7 ( $\text{CH}_2-\text{C}=\text{CH}_{\text{isoprenic}}$ ), 39.0 ( $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ), 60.81 ( $\text{CH}_3\text{COCH-}$ ), 64.50 ( $\text{CH}_3\text{COCH-}$ ), 62.5 ( $\text{CH}_2\text{OH}$ ), 67.5 ( $\text{CH}_3\text{CHOH}$ ), 124.5 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ ), 134.7 ( $\text{C}=\text{CH}_{\text{isoprenic}}$ )

**FT-IR:**  $\nu_{(\text{OH})} = 3350 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C}-\text{H})} = 3035 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} = 2900\text{--}2730 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C})} = 1664 \text{ cm}^{-1}$ ;  
 $\nu_{(\text{CH}_2, \text{CH}_3)}$  *cis*-1,4-isoprene = 1448, 1376  $\text{cm}^{-1}$ ;  $\delta_{(\text{C}=\text{C}-\text{H})} = 834 \text{ cm}^{-1}$ ,  $\nu_{(\text{C}-\text{O}-\text{C})}$  (epoxide) = 870  $\text{cm}^{-1}$

#### 4.3.3.3 Preparation of hydrogenated hydroxytelechelic natural rubber

(HHTNR 6)

HTNR 4 ( $\overline{Mn} = 1050 \text{ g mol}^{-1}$ , 0.83g, 0.43 mmol) was dissolved in ethyl acetate (50 ml) in the presence of palladium on activated carbon (500 mg) and was then introduced into catalytically hydrogenation device under 3.2 bar of hydrogen pressure at room temperature. After 24 h the pressure dropped to 2.4 bar, the reaction mixture was filtered to remove the catalyst. The solvent was eliminated under vacuum. HHTNR was kept in vacuum oven for 48 h at 40 °C and was then analyzed with  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR and SEC. The reaction is described in **Figure 4.7**.



**Figure 4.7** Hydrogenation reaction of hydroxytelechelic natural rubber

#### Characterization:

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.84 (s,  $\text{CH}_3\text{CHCH}_2$ ) saturated unit), 1.37 (s,  $\text{CH}_3\text{CHCH}_2$ ), 1.20 (d,  $\text{CH}_3\text{CHOH}$ ), 1.67 (s,  $-\text{CH}_3$  isoprenic), 2.04 (m,  $-\text{CH}_2$  isoprenic), 3.65 (t,  $\text{CH}_2\text{OH}$ ), 3.80 (m,  $\text{CHOH}$ ), 5.10 (t,  $=\text{CH}$  isoprenic)

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 19.75 ( $\text{CH}_3\text{CHCH}_2$ ) saturated unit), 25.9 ( $\text{CH}_2\text{CH}=\text{C}$  isoprenic), 30.5 ( $\text{CH}_2\text{CH}_2\text{OH}$ ), 31.7 ( $\text{CH}_2-\text{C}=\text{CH}$  isoprenic), 32.80 ( $\text{CH}_3\text{CHCH}_2$ ), 37.10 ( $\text{CH}_3\text{CHCH}_2$ ), 39.0 ( $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ), 62.5 ( $\text{CH}_2\text{OH}$ ), 67.5 ( $\text{CH}_3\text{CHOH}$ ), 124.5 ( $\text{C}=\text{CH}$  isoprenic), 134.7 ( $\text{C}=\text{CH}$  isoprenic)

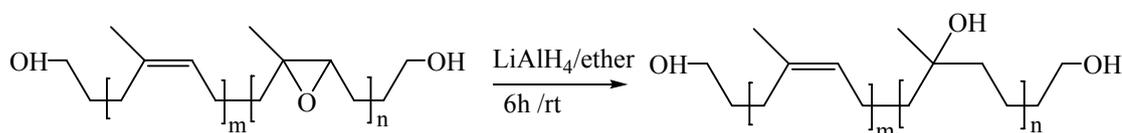
**FT-IR:**  $\nu_{(\text{OH})} = 3350 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C}-\text{H})} = 3035 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} = 2900\text{--}2730 \text{ cm}^{-1}$

Intensity decreased of the isoprene double bond  $\text{C}=\text{C}$  bonds after hydrogenation

#### 4.3.3.4 Preparation of multifunctional hydroxytelechelic natural rubber

(HTNR ( $\overline{fn} > 2$ ) 7)

EHTNR **5** in ether solution was added dropwise into the three necks round bottle which the  $\text{LiAlH}_4$  (5 mol equivalent) was dissolved. The reaction was carried out with stirring at 300 rpm for 24 h under nitrogen atmosphere. After that the reaction mixture was hydrolyzed and then extracted with dichloromethane several times and dried with  $\text{MgSO}_4$ . Finally, the solvent was eliminated under vacuum and the product was kept in vacuum oven for 24 h at 40 °C. The sample was analyzed with  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR and SEC. The reaction is described in **Figure 4.8**.



**Figure 4.8** Reduction of epoxidized hydroxytelechelic natural rubber

##### Characterization:

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.15 (s,  $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ ), 1.20 (d,  $\text{CH}_3\text{CHOH}$ ), 1.42 ( $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ ), 1.67 (s,  $-\text{CH}_3$  isoprenic), 2.04 (m,  $-\text{CH}_2$  isoprenic), 3.65 (t,  $\text{CH}_2\text{OH}$ ), 3.80 (m,  $\text{CHOH}$ ), 5.10 (t,  $=\text{CH}$  isoprenic) and disappearance  $\delta$  (ppm): 1.29 (s,  $\text{CH}_3\text{COCH}$ ), 2.7 (t,  $\text{CH}_3\text{COCH}$ )

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 25.9 ( $\text{CH}_2\text{CH}=\text{C}$  isoprenic), 28.69 ( $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ ), 30.5 ( $\text{CH}_2\text{CH}_2\text{OH}$ ), 31.7 ( $\text{CH}_2-\text{C}=\text{CH}$  isoprenic), 39.0 ( $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ), 40.92 ( $\text{CH}_2\text{C}(\text{OH})\text{CH}_3\text{CH}_2$ ), 62.5 ( $\text{CH}_2\text{OH}$ ), 67.5 ( $\text{CH}_3\text{CHOH}$ ), 71.63 ( $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ ), 124.5 ( $\text{C}=\text{CH}$  isoprenic), 134.7 ( $\text{C}=\text{CH}$  isoprenic)

FT-IR:  $\nu_{(\text{OH})} = 3350 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{H})} = 3035 \text{ cm}^{-1}$ ;  $\nu_{(\text{CH}_2, \text{CH}_3)} = 2900\text{--}2730 \text{ cm}^{-1}$ ;  $\nu_{(\text{C}=\text{C})} = 1664 \text{ cm}^{-1}$ ;  
 $\nu_{(\text{CH}_2, \text{CH}_3)}$  *cis*-1,4-isoprene = 1448, 1376  $\text{cm}^{-1}$ ;  $\delta_{(\text{C}=\text{H})} = 834 \text{ cm}^{-1}$

#### 4.3.4 Analysis of telechelic natural rubber

All samples of oligomers were characterized their chemical structure, molecular weight and thermal property as well as viscosity as described in 4.3.4.1-4.3.4.7.

##### 4.3.4.1 Chemical structure characterization

The chemical structure of natural rubber, ENR, telechelic natural rubber and polyurethane foam were investigated using FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and MALDI-TOF MS.

###### a) Nuclear magnetic resonance spectroscopy (NMR)

$^1\text{H-NMR}$  spectrum of a molecule consists of series of peaks corresponding to the resonance frequencies of chemically different protons in molecule. These peaks may show fine structure (splitting) due to mutual interaction with non-equivalent nuclei. The peak areas are proportional to the number of protons that resonate at the particular frequencies; the number of protons is dependent on the number of molecule. Peak areas are usually integrated electronically and recorded with the spectra. The dependence of peak position on chemical environment and of peak area on the number of protons is the basis of kinetic measurements using NMR. If some of the nuclei responsible for a resonance present a change in environments during the course of a reaction, a peak corresponding to the reactant will diminish in size and new peaks corresponding to the products will increase.

The larger  $^{13}\text{C}$  chemical shift range enables very subtle structural and conformational changes to be discerned. In addition, the  $^{13}\text{C}$  spectrum may be simplified by proton decoupling which makes all the carbon resonances appear as singlet. This is in contrast to proton NMR where spectra of large molecules are complex because of homonuclear spin-spin splitting and congested because of the small proton chemical shift range.

The major limitation of the NMR technique is the requirement of high sample concentrations, as previously mentioned. Furthermore, the high expense of NMR spectrometers limits their availability for length kinetic measurements. The use of NMR measurements for study of concentration changes is practical for reactions with half-times of about one minute or longer. Typically, a reaction will be followed by recording and integrating the entire spectra at various

time intervals when slow reactions are involved. NMR may also be used for kinetic measurements of some fast reactions at equilibrium, by studying line broadening effects.

In this work,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of samples in solution state were recorded on a Bruker, Fourier Transform spectrometer at 400.13 and 100.62 MHz respectively. Tetramethylsiloxane (TMS) was used as an internal reference.  $^1\text{H}$ -NMR analysis sample was dissolved in deuterated chloroform ( $\text{CDCl}_3$ ) around 10 mg whereas  $^{13}\text{C}$ -NMR analysis sample was employed around 30 mg.

### **b) Fourier transforms infrared spectroscopy (FT-IR)**

Infrared spectroscopy (IR) provides more useful information for identifying polymers and modified polymers. IR spectroscopy yields both qualitative and quantitative information about chemical nature of polymer such as structural repeating units, end groups, and branch units, additives and impurities. IR spectroscopy is also sensitive to change in the dipole moments of vibration groups in molecules and, accordingly, yields useful information for the identification of the polymers after modification. In practice, it is very difficult to observe the absorption intensity changes of an important characteristic of polyisoprene after modification. Then this method can be used only on qualitative mode. Generally, there are two kind of fundamental vibrations for molecules: stretching, in which the distance between two atom increases or decreases, but the atoms remain in the same bond axis, and bending (or deformation), in which the position of the atom changes relative to original bond axis.

IR spectra were recorded on a Fourier transform Perkin-Elmer 1750 spectrometer in the  $4000\text{-}500\text{ cm}^{-1}$  range. A diamond ATR device (attenuated total reflection) MKII Golden Gate was used for all samples. The plate ATR has a characteristic in the following:

- a heating plate allowing to a temperature reached until  $200\text{ }^\circ\text{C}$
- accessories allowing to fix optic fiber connected to a UV lamp above an analysis crystal
- diamond crystal index  $(n_1) = 2,4$  at  $1000\text{ cm}^{-1}$
- incidence angle  $\theta = 45^\circ$
- monoreflexion system

### c) MALDI-TOF mass spectroscopy

Matrix Assisted Laser Desorption-Time of Flight mass spectroscopy (MALDI-TOF MS) was initially developed for use with large biomolecules in 1988 by Karas and Hillenkamp (1987). MALDI-TOF has advanced very rapidly into a powerful technique for synthetic polymer analysis (Esser *et al.*, 2000; Jackson and Simonsick, 1997; Montaudo *et al.*, 2006; Nagahata *et al.*, 2007; Willemse *et al.*, 2004). It can be used to determine average molecular weights and molecular weight distributions of narrow polydispersity polymers. It can also provide structural information on end-groups, repeat units, and chemical modifications of a polymeric system. The ability to ionize a broad range of materials, its high sensitivity, large mass range, fast sample preparation, and the absence of fragmentation are the characteristics of this powerful technique (Rashidzadeh and Guo, 1998; Yalcin *et al.*, 1998).

#### 1) Principle

The matrix assisted laser desorption (MALDI) process is the key feature of the method, because it is responsible for the accessibility of a very high mass range up to several hundred thousand dalton. It works similarly to the laser desorption (LD) method developed earlier, which is capable of producing intact molecular ions only in the low mass range up to a few thousand dalton. Contrary to laser desorption, where the analyte is irradiated directly by UV-laser light, in matrix assisted laser desorption the analyte is assumed to be homogeneously embedded in a matrix material, which absorbs the laser energy and is responsible for the transfer of the analyte into the gas phase without thermal stress (Rader and Schrepp, 1998). The laser energy that are used with the nitrogen laser ( $\lambda=337$  nm) causes a portion of the sample/matrix mixture to be desorbed from the surface and ionized. The analysis case of synthetic polymers ionization is usually achieved by cation attachment, which is a matrix-independent process. Some commonly used matrices for synthetic polymers are dithranol (1,8,9-trihydroxyanthracene), DHB (2,5-dihydroxybenzoic acid) sinspinic acid, IAA (3- $\beta$ -indoleacrylic acid). The selection of a good matrix is still a trial and error process

In general, MALDI MS has been more successful for the analysis of polar synthetic polymers than for non-polar synthetic polymers. It has been established that analysis of hydrocarbon polymers such as polystyrene, polybutadiene or polyisoprene requires a different

approach; standard MALDI protocols do not work for these types of polymers. Hydrocarbon polymers do not undergo protonation or metal cationization by monovalent Group I metal salts ions. To date, only silver ( $\text{Ag}^+$ ) and copper salts ( $\text{Cu}^+$  and  $\text{Cu}^{2+}$ ) have been found to work relatively well for non-polar polymer cationization in MALDI. The performance of these two metal salts is matrix dependent (Macha and Limbach, 2002).

The time of flight mass analyzer is most commonly coupled with MALDI-TOF due to the pulsed nature of the desorption laser. The laser beam is focus on sample surface in the ion source. Once the ions are formed after a laser pulse, they are accelerated simultaneously by a static electric field of up to 35 kV. Depending on their mass-to-charge ratio, they have different velocities when they leave the acceleration zone and pass the following field-free drift tube with different flight times. The time of flight for each ion is then measured by the time difference between the start signal, given by the laser pulse and the stop signals, caused by the ions impinging on the detector. According to the simple relationship of equation (4.1), the square of the flight time is proportional to the mass-to-charge ratio.

$$\frac{m}{z} = \frac{2Ut^2}{s^2} \quad (4.1)$$

when:  $m$  = mass of the ion,  $z$  = number of charge,  $U$  = accelerating voltage,  $t$  = ion flight time,  $s$  = flight distance.

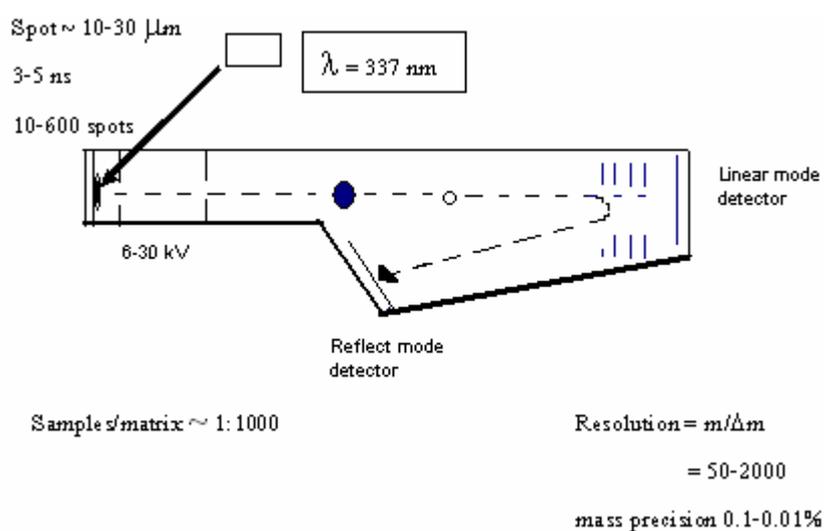
The accelerated ions can be detected in two different ways, the linear and the reflection mode. The main differences between the two detections are higher resolution in the reflection mode and higher sensitivity for larger molecular in the linear mode (Rader and Schrepp, 1998).

## 2) Limitations of MALDI

The main challenges that limit widespread application of MALDI MS to hydrocarbon analytes include availability of proper matrices for specific analytes, proper cationization reagents, common solvents for both analyte and matrix, as well as challenges in sample preparation technique. These limitations and various others inherent in MALDI instrumentation such as problems in ion formation (desorption/ionization), ion transmission and

detection, and difficulties in reproducing spectra, have rendered this technique applicable for qualitative purposes only. MALDI is generally employed as a tool for obtaining the analyte mass but not the analyte concentration or even its relative amount from the measured ion abundance values (Macha and Limbach, 2002).

In this work, MALDI experiments were performed using a Bruker Biflex III MALDI-TOF mass spectrometer. The instrument is equipped with a nitrogen laser emitting at 337 nm, a 2-GHz sampling rate digitizer, a pulsed ion extraction source and a reflectron. The laser pulse width is 3 ns and its maximum power is 200 mJ. Mass spectra were recorded in the linear mode. The acceleration voltage was 19 kV. The delay time was 200 ns. Typically, 100 single-shot acquisitions were summed to give a composite mass spectrum. All data were reprocessed using the Bruker XTOF software. The mass scale was calibrated externally using PEG 1500. The matrix, dithranol (DIT), was dissolved in methanol ( $10 \text{ mg mL}^{-1}$ ) and the solution was mixed with the polymer solution.



**Figure 4.9** MALDI-TOF mass spectroscopy (Kébir N., 2005)

#### 4.3.4.2 Determination of epoxide content

The epoxide content of the epoxidized natural rubber can be calculated from the  $^1\text{H-NMR}$  spectra. The integrated area of signal at 2.70 ppm ( $I_{2.70}$ ) represents the proton adjacent to oxirane ring and at 5.12 ppm ( $I_{5.12}$ ) represents the proton adjacent to carbon-carbon double bonds. The epoxide content of the epoxidized natural rubber can be calculated from the equation 4.2.

$$\text{Epoxide content (\%)} = \frac{I_{2.70}}{I_{2.70} + I_{5.12}} \times 100 \quad (4.2)$$

#### 4.3.4.3 Determination of percent of hydrogenation

The characteristic peak assignment of  $^1\text{H-NMR}$  spectra of the hydrogenated natural rubber was used to analyze the percentage of hydrogenation as shown in equation 4.2. The ( $I_{0.84}$ ) and ( $I_{5.12}$ ) are the integrated areas of signals of methyl protons of the hydrogenated sample and proton signal adjacent to carbon-carbon double bond units, respectively.

$$\% \text{ Hydrogenation} = \left( \frac{(I_{0.84})/3}{(I_{0.84})/3 + I_{5.12}} \right) \times 100 \quad (4.3)$$

#### 4.3.4.4 Determination of functionality of hydroxytelechelic natural rubber

In our work, the divert formulations for calculation of average functionality is shown in equation 4.4.

$$\overline{fn} = [(I_{\text{CH}_2\text{OH}}/2) + (I_{\text{CHOH}})] [(1/I_{\text{C=CH}})] [\overline{Mn}/68] \quad (4.4)$$

Where:

$I_{\text{CH}_2\text{OH}}$  is integration of signal of proton ( $\text{CH}_2$ ) at  $\alpha$  position of primary alcohol group of HTNR

$I_{\text{CHOH}}$  is integration of signal of proton ( $\text{CH}_2$ ) at  $\alpha$  position of secondary alcohol group of HTNR

$I_{\text{C=CH}}$  is integration of signal of ethylenic proton at 5.12 ppm.

$\overline{Mn}$  is number average molecular weight of HTNR obtained by SEC after correction with Benoît factor

#### 4.3.4.5 Determination of molecular weight

All average molar mass of telechelic natural rubbers were determined by NMR technique and steric exclusion chromatography (SEC) as well as MALDI-TOF technique.

### a) Nuclear magnetic resonance spectroscopy (NMR)

<sup>1</sup>H-NMR spectra of telechelic natural rubbers in solution state were recorded on a Bruker, Fourier Transform spectrometer at 400.13 MHz. Tetramethylsiloxane (TMS) was used as an internal reference. <sup>1</sup>H-NMR analysis sample was dissolved in deuterated chloroform (CDCl<sub>3</sub>) around 10 mg. In their spectra were used for calculation of molecular weight as shown in equation 4.5-4.9.

#### 1) Determination of molecular weight of CTNR 3

Molecular weight of CTNR was calculated as shown in equation 4.5.

$$\overline{Mn} \text{ (CTNR)} = \frac{I_{5.12} \times 68}{I_{9.70}} + 100 \quad (4.5)$$

Where ( $I_{9.70}$ ) and ( $I_{5.12}$ ) represent the integrated areas of proton signal of aldehyde and signal of proton adjacent to carbon-carbon double bond, respectively.

#### 2) Determination of molecular weight of HTNR 4

Molecular weight of HTNR was calculated as shown in equation 4.6.

$$\overline{Mn} \text{ (HTNR)} = \frac{I_{5.12} \times 68}{I_{3.80}} + 104 \quad (4.6)$$

Where  $I_{3.80}$  and  $I_{5.12}$  represent the integrated areas of proton signal attached to secondary alcohol and signal of proton adjacent to carbon-carbon double bond, respectively.

#### 3) Determination of molecular weight of EHTNR 5

Molecular weight of EHTNR was calculated as shown in equation 4.7.

$$\overline{Mn} \text{ (EHTNR)} = \frac{I_{5.12} \times 68}{I_{3.80}} + \frac{I_{2.70} \times 84}{I_{3.80}} + 104 \quad (4.7)$$

Where  $I_{2.70}$ ,  $I_{3.80}$  and  $I_{5.12}$  represent the integrated areas of proton signal attached to oxirane ring, secondary alcohol and signal of proton adjacent to carbon-carbon double bond, respectively.

#### 4) Determination of molecular weight of HHTNR 6

Molecular weight of HHTNR was calculated as shown in equation 4.8.

$$\overline{Mn} \text{ (HHTNR)} = \frac{I_{5.12} \times 68}{I_{3.80}} + \frac{((I_{0.84})/3) \times 70}{I_{3.80}} + 104 \quad (4.8)$$

Where  $I_{0.84}$ ,  $I_{3.80}$  and  $I_{5.12}$  represent the integrated areas of signal of methyl protons of the hydrogenated sample, signal of proton attached to secondary alcohol and signal of proton adjacent to carbon-carbon double bond, respectively.

#### b) MALDI-TOF technique

With MALDI-TOF technique, The average molecular weight and polydispersity ( $\overline{Mn}$ ,  $\overline{Mw}$  and PDI, respectively) were calculated by these below equations (4.9-4.11) (Nagahata *et al.*, 2007).

$$\overline{Mn} = \frac{\sum (I_i M_i)}{\sum I_i} \quad (4.9)$$

$$\overline{Mw} = \frac{\sum (I_i M_i^2)}{\sum (I_i M_i)} \quad (4.10)$$

$$\text{PDI} = \frac{\overline{Mw}}{\overline{Mn}} \quad (4.11)$$

when  $I_i$  signal intensity at point  $i$  and  $M_i$ : mass at point  $i$

### **c) Steric exclusion chromatography (SEC)**

The number-averaged molecular weight ( $\overline{Mn}$ ) and molecular weight distribution (PDI) were measured at 35 °C on a Thermo Finnigan SEC instrument (equipped with Spectra System RI150 detectors), using a polymer laboratories (PL) gel 5  $\mu\text{m}$  MIXED-D columns, calibrated with a series of standard polystyrene ( $580\text{-}483 \times 10^3 \text{ g mol}^{-1}$ ). THF ( $1.0 \text{ mL min}^{-1}$ ) was used as eluent. All samples are 10 mg in THF 2 ml. They were filtered before test.

#### **4.3.4.6 Thermal analysis**

Thermal behaviors of all telechelic natural rubber and polyurethane foams were investigated with differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA).

##### **a) Differential scanning calorimeter (DSC)**

In this work, differential scanning calorimeter (DSC) was performed on a TA Instruments (DSC Q 100) with a heating rate of  $10^\circ\text{C min}^{-1}$ . The temperature testing was between  $-80$  and  $200^\circ\text{C}$  under nitrogen atmosphere with flow rate  $50 \text{ cm}^3 \text{ min}^{-1}$ . The sample weight was about 5 mg. Calibration was achieved with indium as reference material. The result was reported in glass transition temperature,  $T_g$  ( $^\circ\text{C}$ ).

##### **b) Thermogravimetric analyzer (TGA)**

In this work, thermogravimetric analyzer was performed on a TA Instruments (TGA Q 100) with a heating rate of  $10^\circ\text{C min}^{-1}$ . The temperature testing was between room temperature and  $600^\circ\text{C}$  under nitrogen atmosphere. The sample weighed around 10 mg. The thermal stability of all samples was investigated.

#### **4.3.4.7 Viscosity of hydroxytelechelic natural rubber**

The viscosity of polyols was measured by Brookfield Synchroelectric Viscosity, model RVF 100, USA. The torque on a suitable spindle at a constant speed of 100 rpm in the viscous liquid sample at room temperature  $30^\circ\text{C}$  is recorded, according to ASTM D 4878-03. The viscosity results are obtained in mPa.s (cPs, centipoises) unit.

### 4.3.5 Preparation of polyurethane foams

Flexible polyurethane foams were prepared by the one-shot method. All ingredients (polyol, water, surfactant, chain extender, catalyst, P-MDI and dichloromethane) were mixed together in a 250 ml beaker under atmosphere until the whitening of liquid occurred (20-50 sec) by homogenizer at speed 11,000 rpm (model Ultra-Turrax, type T 25B (KIKA-WERKE GMBH & CO.KG, Germany) and magnetic stirrer at a speed of 1000 rpm. The mixture was then poured into plastic mould ( $12 \times 21 \times 5 \text{ cm}^3$ ) and put in an oven at  $40^\circ\text{C}$ . The samples were continued to stand for curing for 48 h at  $40^\circ\text{C}$  before test.

In this work, the influence of speed of mixing process, the effect of molecular weight and microstructure of precursors and the effect of type and amount of chain extenders on their physico-mechanical, thermal and acoustic properties comparison with commercial precursor analogues were performed. The various parameters were studied in polyurethane foam formulations as shown in **Tables 4.3-4.6**.

#### 4.3.5.1 Effect of mixing speed on polyurethane foam process

The speed of mixing of polyurethane foam ingredients (HTNR based on polyurethane foam (PUF1) and commercial polyether polyol (PUF9 and PUF 5)) was studied in two levels such as 1,000 and 11,000 round per minute (rpm). The appearance, cell count, cell size and density of foams were observed to consider that which speed suitable to study later the mechanical properties of polyurethane foams.

#### 4.3.5.2 Effect of molecular weight of precursors

Polyurethane foams prepared with different molecular weight HTNR precursors (1000, 2000, and  $3400 \text{ g mol}^{-1}$ ) were compared to those prepared with commercial polyols (Raypol1010). These formulations present in **Table 4.3**. (Isocyanate index = 100)

**Table 4.3** The different of molecular weight of precursors in polyurethane foam formulations

Ingredients	Weight (g)			
	PUF1	PUF2	PUF3	PUF4
HTNR1000	40	-	-	-
HTNR2000	-	40	-	-
HTNR3400	-	-	40	-
Raypol1010	-	-	-	40
B 8110	0.34	0.70	0.70	0.34
Water	1.60	1.60	1.60	1.60
1,4-Butanediol	0.19	0.19	0.19	0.19
Dabco 33-LV	0.06	0.30	0.30	0.06
Dabco T-12	0.04	0.20	0.20	0.04
CH <sub>2</sub> Cl <sub>2</sub>	10	10	10	10
P-MDI	36.8	29.3	27.9	35.5

#### 4.3.5.3 Effect of epoxide content

Polyurethane foams prepared with HTNR having molecular weight  $2000 \text{ g mol}^{-1}$  (HTNR2000) precursors containing different epoxide content (approximately 10%, 20%, 30% mole epoxide) were compared to those prepared with commercial polyols (Raypol1020). These formulations present in **Table 4.4**. (Isocyanate index = 100)

**Table 4.4** Epoxide content on HTNR in polyurethane foam formulations

Ingredients	Weight (g)				
	PUF2	PUF6	PUF7	PUF8	PUF9
HTNR2000	40	-	-	-	-
9%EHTNR2000	-	40	-	-	-
23%EHTNR2000	-	-	40	-	-
35%EHTNR2000	-	-	-	40	-
Raypol1020	-	-	-	-	40
B 8110	0.70	0.70	0.70	0.70	0.34
Water	1.60	1.60	1.60	1.60	1.60
1,4-Butanediol	0.19	0.19	0.19	0.19	0.19
Dabco 33-LV	0.30	0.30	0.30	0.30	0.06
Dabco T-12	0.20	0.20	0.20	0.20	0.04
CH <sub>2</sub> Cl <sub>2</sub>	10	10	10	10	10
P-MDI	29.3	29.3	30.1	30.4	29.6

#### 4.3.5.4 Effect of type and amount of chain extenders

Polyurethane foams prepared with different types of chain extenders (di or tri-functional hydroxyl chain extenders) in HTNR2000 and Raypol3003 and with different amounts of chain extenders (1, 2 and 4 times) in HTNR1000, were studied. These formulations present in **Table 4.5.** (Isocyanate index = 100)

**Table 4.5** The amount and type of chain extenders in polyurethane foam formulations

Ingredients	PUF5	PUF14	PUF2	PUF13	PUF1	PUF11	PUF12
HTNR1000	-	-	-	-	40	40	40
HTNR2000	-	-	40	40	-	-	-
Raypol3003	40	40	-	-	-	-	-
B 8110	0.34	0.34	0.70	0.70	0.34	0.34	0.34
Water	1.60	1.60	1.60	1.60	1.60	1.60	1.60
Glycerol	-	0.19	-	0.19	-	-	-
1,4-Butanediol	0.19	-	0.19	-	0.19	0.38	0.78
Dabco 33-LV	0.06	0.06	0.30	0.30	0.06	0.06	0.06
Dabco T-12	0.04	0.04	0.20	0.20	0.04	0.04	0.04
CH <sub>2</sub> Cl <sub>2</sub>	10	10	10	10	10	10	10
P-MDI	29.6	29.6	29.3	29.5	36.0	36.6	37.7

### 4.3.6 Properties of polyurethane foams

The physico-mechanical, morphology and acoustic properties of the polyurethane foams are described in 4.3.6.1-4.3.6.6.

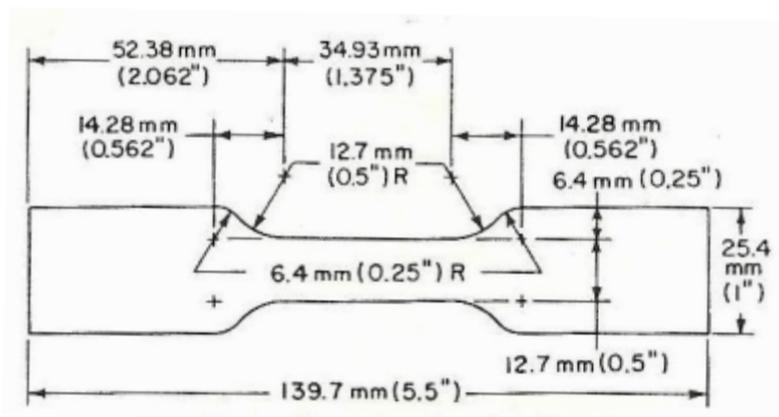
#### 4.3.6.1 Density

The density of polyurethane foams was measured according to ASTM D 3574 Test A. Three specimens were cut into the specimens with dimension of 10 mm × 10 mm × 10 mm. After that these specimens were precisely weighed. The result of dividing between weight (M) and volume (V) of the specimens was the density in the unit of kg m<sup>-3</sup> as shown in equation 4.12.

$$\text{Density} = \frac{M}{V} \quad (4.12)$$

#### 4.3.6.2 Tensile strength and elongation at break

Tensile strength and elongation at break of polyurethane foams were measured with a crosshead speed of 500 mm min<sup>-1</sup> according to ASTM D 3574 Test E by universal tensile testing machine on tensile testing mode. Drum-bell specimens were stamped by die A of Test Methods D 412. The dimension of die A is shown in **Figure 4.11** and **Table 4.6**.



**Figure 4.10** Shape of die A for stamping tension specimens

**Table 4.6** Dimension of die A according to ASTM D 412

<b>DieA</b>	<b>Dimension (inch/mm)</b>
A. Overall length	5.5/139.7
B. Width of ends	1/25.4
C. Length of narrow portion	1.375/34.9
D. Width of narrow portion	0.5/12.7
E. Transition radius outside	0.25/6.4
F. Transition radius inside	0.5/12.7

The tensile strength is calculated by dividing the maximum breaking force ( $F$ ) by the original cross-sectional area of the specimen ( $A$ ) in unit of kilopascal (kPa) as shown in equation 4.13.

$$\text{Tensile strength} = \frac{F}{A} \quad (4.13)$$

The ultimate elongation was calculated by subtracting the original distance between the bench marks from the total distance between the bench marks at the time of rupture and expressing the difference as a percentage of the original distance as shown in equation 4.14.

$$\text{Elongation at break (\%)} = \frac{(d_f - d_o) \times 100}{d_o} \quad (4.14)$$

$d_o$  = original distance between bench marks, 20 mm

$d_f$  = distance between bench marks at the break point (mm)

The obtained results are the average values of five specimens.

#### **4.3.6.3 Compressive strength**

The compressive strength of polyurethane foams was investigated according to ASTM D 3574 Test C by universal tensile testing machine (model H 10KS) in compression mode

testing. The dimension of specimens was 50 mm × 50 mm × 25 mm. The specimens were compressed 50% of their thickness at speed 50 mm min<sup>-1</sup> and determined the final force after 60 s. Three specimens per sample were tested. The compressive strength was obtained from the average value of three specimens and was reported in unit of kilopascal (kPa) as written in equation 4.15.

$$\text{Compressive strength} = \frac{F}{A} \quad (4.15)$$

$F$  = Final force at 50% compression of thickness of the specimen (N)

$A$  = Cross section area of specimen (mm<sup>2</sup>)

#### 4.3.6.4 Compression set

The compression set was a percentage change of the original thickness after the specimens were consistently deflected under specific condition of temperature and time according to ASTM D 3574 Test D. The dimension of specimens was 50 mm × 50 mm × 25 mm. These specimens were deflected at 50% of their measured original thickness by compression device which is showed in **Figure 4.11**, consisting of two or more flat plates arranged so the plates are held parallel to each other by bolts and the space between the plates is adjustable by spacers to obtain the 50% deflection thickness of samples through testing. All specimens were kept under 70 °C in period of 22 h, and then removed from the apparatus. The thickness of specimens was measured after waiting 45 min. The constant deflection compression set value was calculated as follow in equation 4.16.

$$C (\%) = \frac{(T_o - T_f) \times 100}{T_o} \quad (4.16)$$

$C$  = compression set (%)

$T_o$  = original thickness of test specimens (mm)

$T_f$  = final thickness of test specimens (mm)



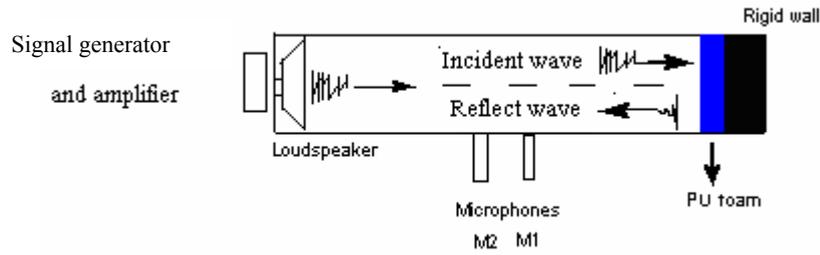
**Figure 4.11** Compression set device

#### **4.3.6.5 Cell size and cell structure**

Cell dimension of polyurethane foams was determined according to BS 4443-Part I: 1988. Cell count is the number of cell per 1 centimeter of length of sample. Cell size is the average of dimension cell. The samples were multiply ( $\times 22$ ) and photographed by Optical microscopy, Olympus model SZ-PT, Japan.

#### **4.3.6.6 Acoustic properties**

Acoustic property was studied in term of performance acoustic absorption coefficient in varied on frequency (Hz). The principle is based on the measurement of the transfer function  $H$  of pressure between 2 signals of microphones mounted flush with inside of the tube. A loudspeaker is placed at the end of the tube and fed by a broad band noise (see **Figure 4.12**). A system of stationary plane waves is created and measured by two microphones systems can be decomposed into its incident and reflected energies.



**Figure 4.12** Schematic diagram of the impedance tube for the two-microphone transfer function method.

The complex reflection coefficient ( $R$ ) is calculated from the following equation (4.17):

$$R = \left( \frac{H - e^{-jkd}}{e^{-jkd} - H} \right) e^{2k(l+d)} \quad (4.17)$$

with:

$k$  = wave number ( $k = (2\pi f / c)$ ;  $f$  = frequency,  $c$  = speed of sound)

$d$  = spacing between microphones (20 mm for small tube, 50 mm for the large tube)

$l$  = distance between the first microphone at the front of the sample (35 mm for the small tube and 100 mm for the large tube)

$H$  = the calibrated transfer function between microphone 1 and 2

$j = \sqrt{-1}$  (complex number)

From this parameter, the normalized impedance ( $Z$ ) and the sound absorption coefficient ( $\alpha$ ) can be calculated from the following equations (4.18):

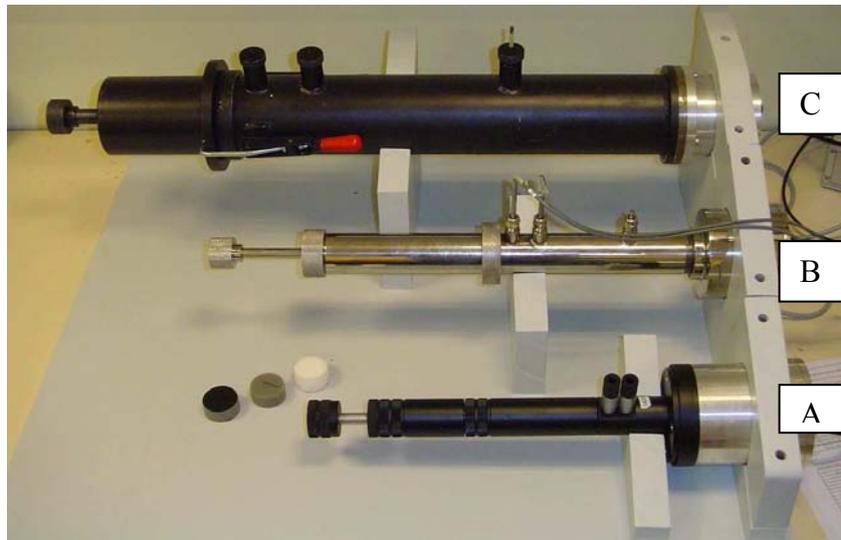
$$\alpha = 1 - |R|^2 \quad \frac{Z}{\rho c} = \frac{1 + R}{1 - R} \quad (4.18)$$

with:

$\rho$  = density

$c$  = speed of sound

Phase and amplitude responses of the 2 microphones are not perfectly identical: a calibration procedure is necessary, which consists in measuring the frequency response function with the two microphones interchanged, and then again in their initial position. The correction factor corresponds to the geometric mean of these two results. The frequency response function is so corrected by the correction factor, in order to eliminate errors due to any mismatches in the microphones channels. Measurements are done with two different tubes in order to cover a wide frequency range: a 100 mm diameter tube (50Hz - 1600Hz) and a 29 mm diameter tube (500Hz - 6400Hz). The absorption coefficient is physically limited to a value that lies between 0 and 1.



**Figure 4.13** Kundt's tube in the different diameter A) 29 mm, B) 45 mm and C) 100 mm at Centre de Transfert de Technologie du Mans (CTTM) Le Mans, France

In this experiment, all cylindrical samples were cut off each formulation foams with thickness 13 mm and their acoustic absorption were measured using 29 mm diameter Kundt's tube varied the frequency in the range 400 Hz to 6400 Hz according to ASTM E 1050.

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1. Degradation of natural rubber

Degradation of natural rubber for preparation of precursors used for preparation of polyurethane foams was performed in two-way possibilities. The first way is the degradation of natural rubber in latex medium and the second way is the degradation of natural rubber in solvent medium. The selectivity of the used reactions allows obtaining telechelic natural rubber with controlled molecular weights and microstructures as well as functionality for use them as starting materials in polyurethane foams applications.

##### 5.1.1 Degradation of natural rubber in latex

In this part, the degraded natural rubber was obtained from epoxidized natural rubber (ENRL) and natural rubber latex (NRL) by periodic acid ( $H_5IO_6$ ) (entry 1) and periodic acid with N-iodosuccinimide (NIS) (entry 2-4), respectively, at 30 °C for 24 h as shown in **Table 5.1**.

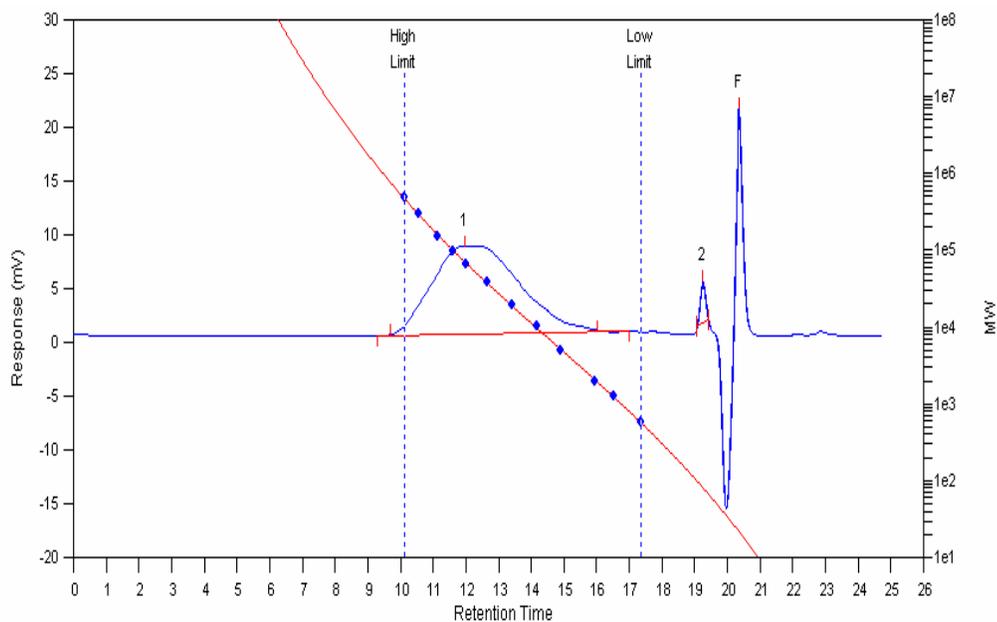
**Table 5.1** The results and degradation conditions of NRL and ELNR latex medium at 20% DRC

Entry	Types of NR	NR (g)	Reagent (mole)		$\overline{Mn}$ (g mol <sup>-1</sup> ) (SEC)	PDI	E <sup>a</sup> (%)	Status latex
			H <sub>5</sub> IO <sub>6</sub>	NIS				
1	16.7%ENRL	20	1.1	-	>50000	-	14	G <sup>b</sup>
2	NRL	20	0.08	1.7×10 <sup>-3</sup>	-	-	0	G
3	NRL	20	0.08	7.0×10 <sup>-3</sup>	-	-	0	G
4	NRL	20	0.08	1.7×10 <sup>-2</sup>	8290	5.20	3.5	D <sup>c</sup>

G<sup>b</sup> (good stabled)      D<sup>c</sup> (partially destabilized)

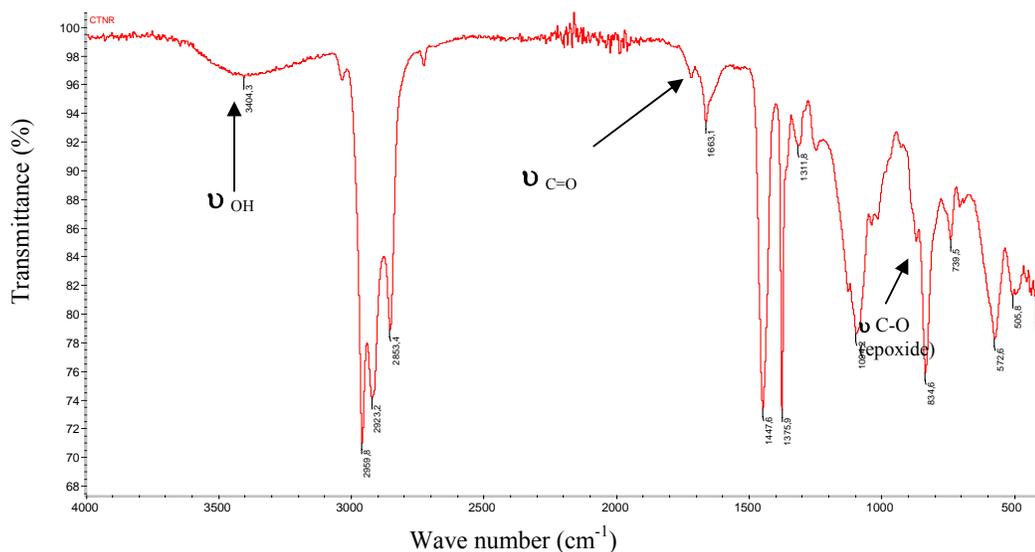
E<sup>a</sup> = Epoxide contents

- = not measured



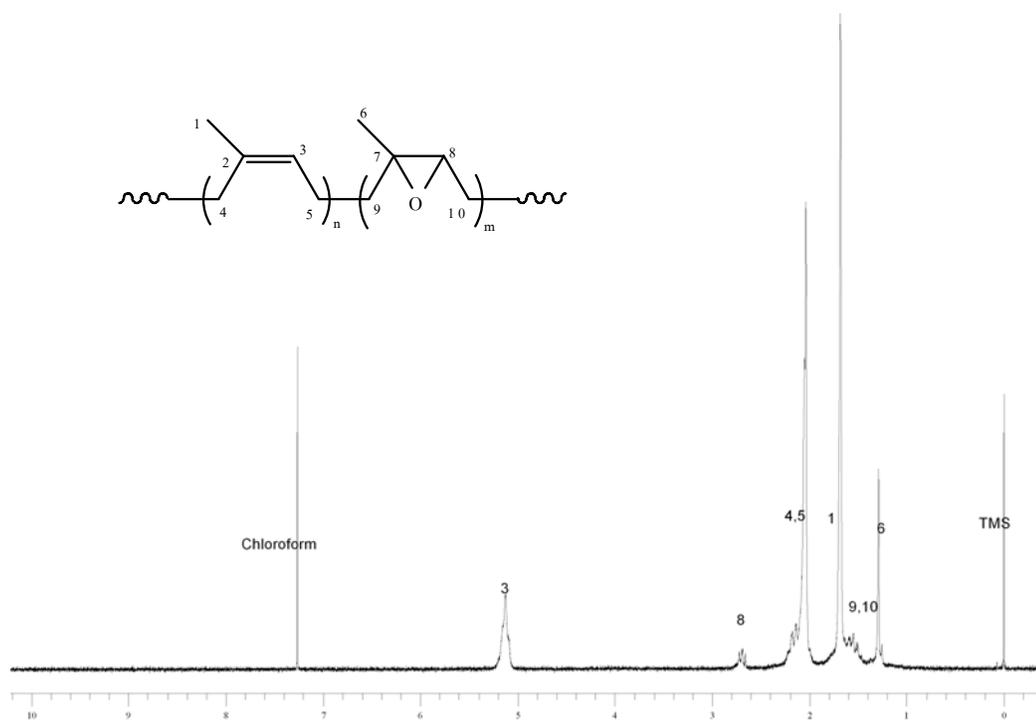
**Figure 5.1** SEC chromatogram of the degraded epoxidized natural rubber latex (Entry 1)

The obtained product was high viscous yellowish material, with an average molecular weight ( $\overline{Mn}$ ) higher than  $50000 \text{ g mol}^{-1}$  (Table 5.1). Because this chromatogram is an out of range of limited of polystyrene standard at  $50000 \text{ g mol}^{-1}$  as shown in Figure 5.1. FT-IR analysis in Figure 5.2 shows the small peak of carbonyl absorption in the regions of  $1700 \text{ cm}^{-1}$ , peak of epoxide absorption at  $870 \text{ cm}^{-1}$  and band of hydroxyl absorption at  $3400 \text{ cm}^{-1}$ .

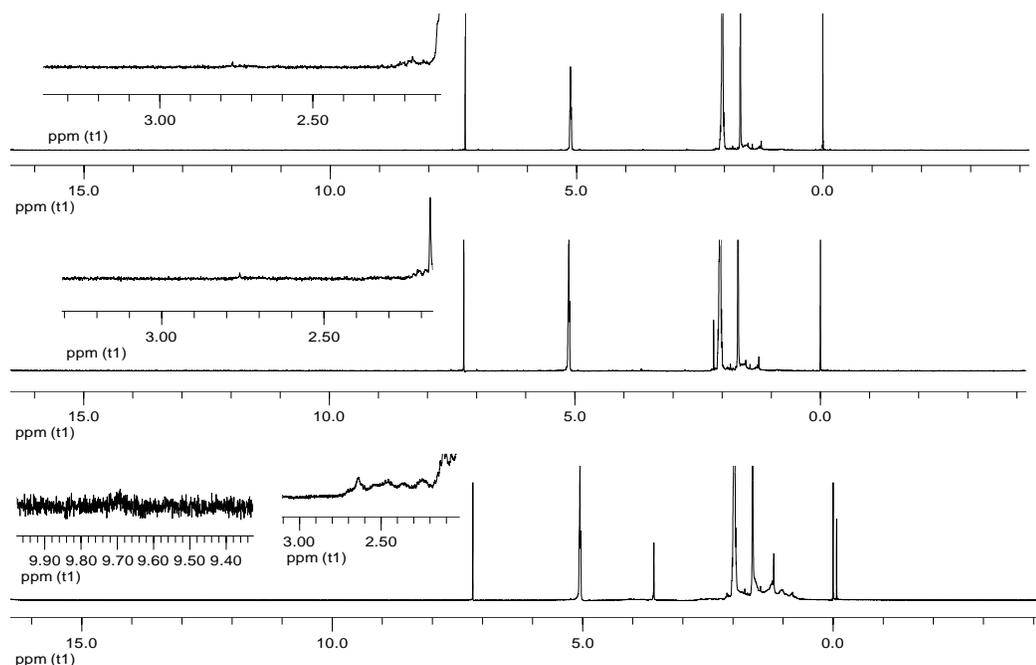


**Figure 5.2** IR spectrum of the degraded epoxidized natural rubber latex (Entry 1)

$^1\text{H-NMR}$  analysis in **Figure 5.3** did not allow the observation of the new signal corresponding to the functional groups at chain-ends due to high molecular weight of the degraded ENRL (16.7). Whereas the signal of proton adjacent to oxirane ring at 2.7 ppm did not show significant change in the amount of the epoxide content after 24 h compared to the starting material. Phinyocheep and co-workers (2005) showed the degradation of ENRL from purified deproteinised natural rubber latex performed by periodic acid during 30 h at room temperature. They reported that the degraded ENRL (18.6) had an  $\overline{Mn}$  of about  $5000 \text{ g mol}^{-1}$ . The liquid rubber obtained is colorless and transparent. It was found that the ENRL from purified natural rubber latex was effectively more degraded than that from field latex. The presence of the non-rubber products (proteins, sugars, phospholipids) around the latex particles in the field latex used, may explain the less degraded polymer obtained. These non-rubber products may disturb the penetration of the periodic acid out the latex particles.

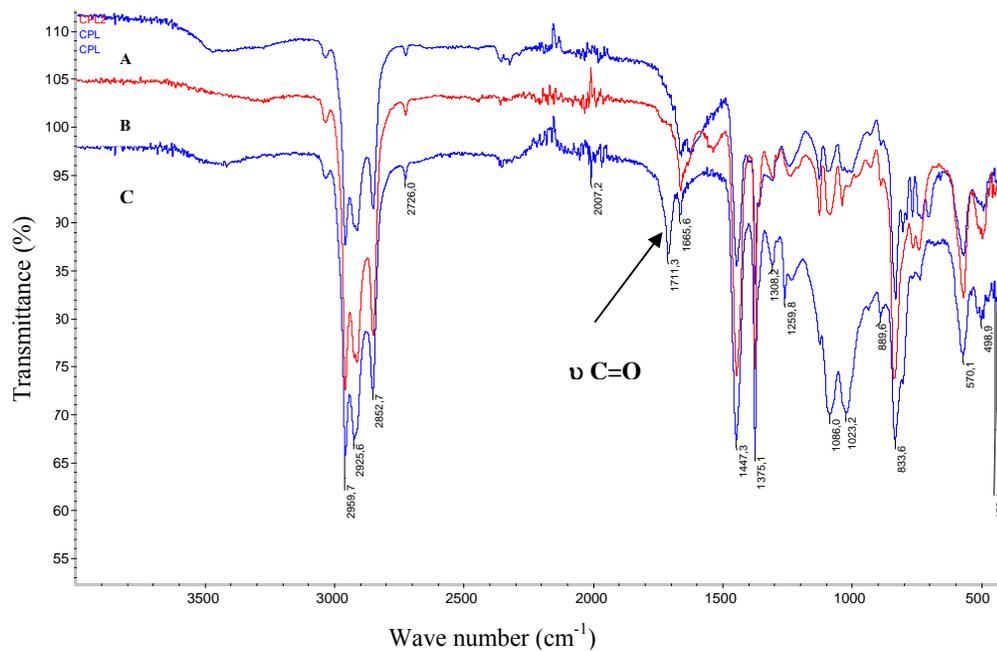


**Figure 5.3**  $^1\text{H-NMR}$  spectrum of the degraded epoxidized natural rubber latex (Entry 1)

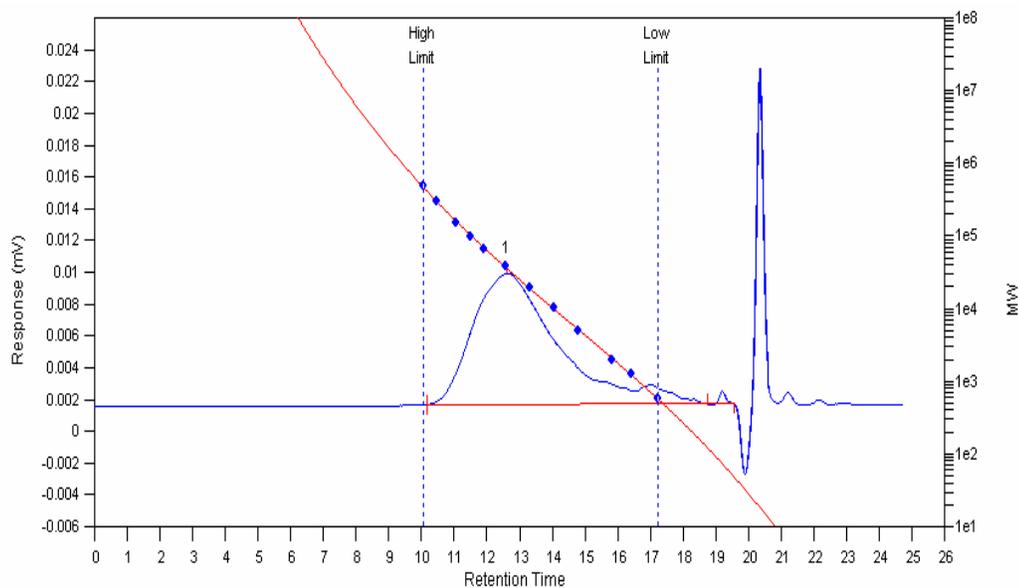


**Figure 5.4**  $^1\text{H}$ -NMR spectra of degradation of natural rubber by using periodic acid and NIS (A:entry 2, B:entry 3, and C:entry 4)

The degradation of natural rubber with periodic acid and NIS were performed using various amount of NIS in entry 2-4. It was found that the reaction in entry 4 gives more efficient cleavage than the first experiment on ENRL with periodic acid alone (**Table 5.1**). In **Figure 5.4** shows that  $^1\text{H}$ -NMR spectra of the obtained degraded natural rubber in entry 4 exhibits a weak signal corresponding to epoxide proton at 2.7 ppm. Few weak signals at 2.1, 2.15-2.6, and 9.8 ppm could be assigned to the three types of protons adjacent to carbonyl group ( $\text{CH}_3\text{-C=O}$ ,  $\text{CH}_2\text{-C=O}$ , and  $\text{H-C=O}$ , respectively) at the chain-ends. These signals confirm the degradation which is conformed by the presence of peak of carbonyl group found in FT-IR spectrum (**Figure 5.5**). The degraded NRL obtained has  $\overline{Mn} = 8290 \text{ g mol}^{-1}$  and PDI = 5.20. However, the latex is not stable through reaction due to the solvent effect. It seems that the increasing amount of N-iodosuccinimide (entry 4) acted as catalyst allows a better degradation reaction, but we found that the appearance of a small signal of epoxide group was observed and a PDI = 5.2 shows a obtained broad molecular weight after cleavage reaction.



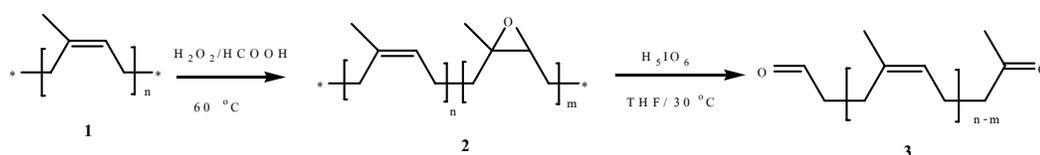
**Figure 5.5** IR spectra of the degraded natural rubber latex by using periodic acid and NIS (A:entry 2, B:entry 3, and C:entry 4)



**Figure 5.6** SEC chromatogram of degraded of natural rubber by using periodic acid and NIS (entry4)

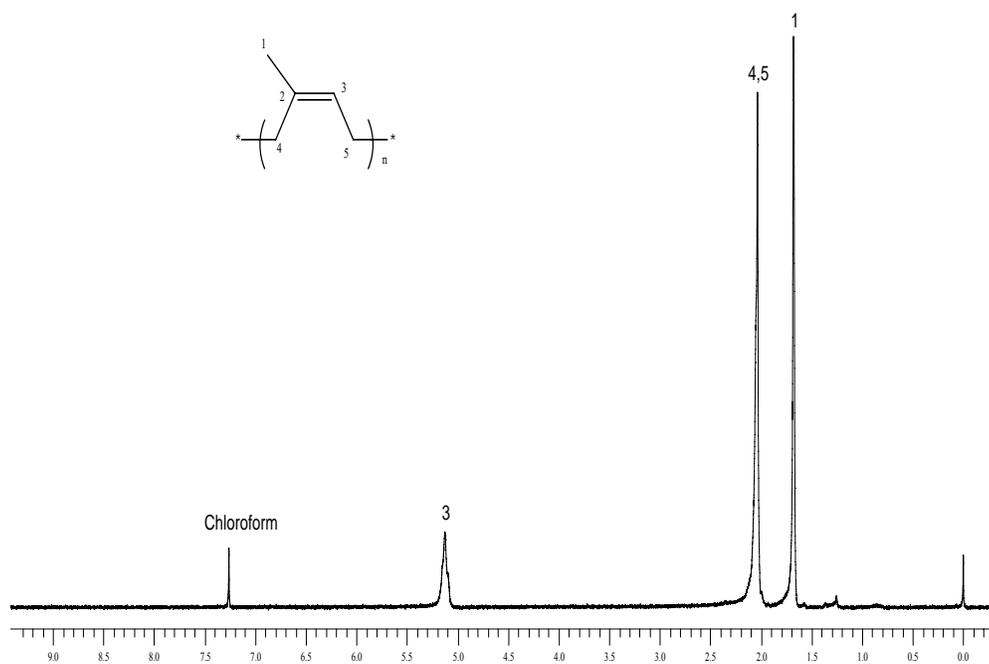
### 5.1.2 Degradation of natural rubber in organic solvent

In order to obtain a better control of the degradation reaction, we have performed the reaction in two steps. The first step is the epoxidation reaction of natural rubber in latex which was performed by using *in situ* peracid generated from a specific amount of formic acid and hydrogen peroxide with non-ionic surfactant at 60 °C. The second step is the selective cleavage of the epoxide groups of the epoxidized natural rubber obtained by the first step and dissolved in THF, with periodic acid ( $H_5IO_6$ ) at 30 °C as shown in **Figure 5.7**.



**Figure 5.7** Controlled degradation reaction of natural rubber

$^1H$ -NMR analysis of natural rubber (NR **1**) shows the evidence on the structure of *cis*-1,4-polyisoprene in **Figure 5.8**



**Figure 5.8**  $^1H$ -NMR spectrum of NR **1**

### 5.1.2.1 Preparation of epoxidized natural rubber

In this experiment we prepared the epoxidized natural rubber at 30% mole was desired, and mole ratio of formic acid and hydrogen peroxide was equal to 1. The preparation of epoxidized natural rubber was carried out with *in-situ* generated peracid from formic acid and hydrogen peroxide in diluted field natural rubber latex which was stabilized with Sinnopal NP 307 (3 phr) by varying reaction time (1.30, 4 and 8 h) as shown in **Table 5.2**.

The  $^1\text{H-NMR}$  spectrum of ENR in **Figure 5.9** shows the presence of signals at 5.12 and 2.70 ppm assigned to the olefinic proton of *cis*-1,4-polyisoprenic structure and the methine proton adjacent to the epoxide ring, respectively. The signals of methyl and methylene groups adjacent to the epoxide unit were observed at 1.26 and 2.16 ppm respectively. The positions at 1.67 and 2.09 ppm show the signals of methyl and methylene protons next to the carbon-carbon double bonds. The analysis by  $^{13}\text{C-NMR}$  (**Figure 5.10**) also reveals the presence of peaks corresponding to carbons of oxirane ring (secondary carbon at 59.6 ppm and tertiary carbon at 63.7 ppm).

These were no other signals indicating the formation of secondary units resulting from secondary reaction such as epoxide ring opening at 3.4 ppm (signal proton adjacent to hydroxyl group) and 3.90 ppm (proton at furan unit). It can be confirmed that the obtained epoxidized natural rubber have no side reaction.

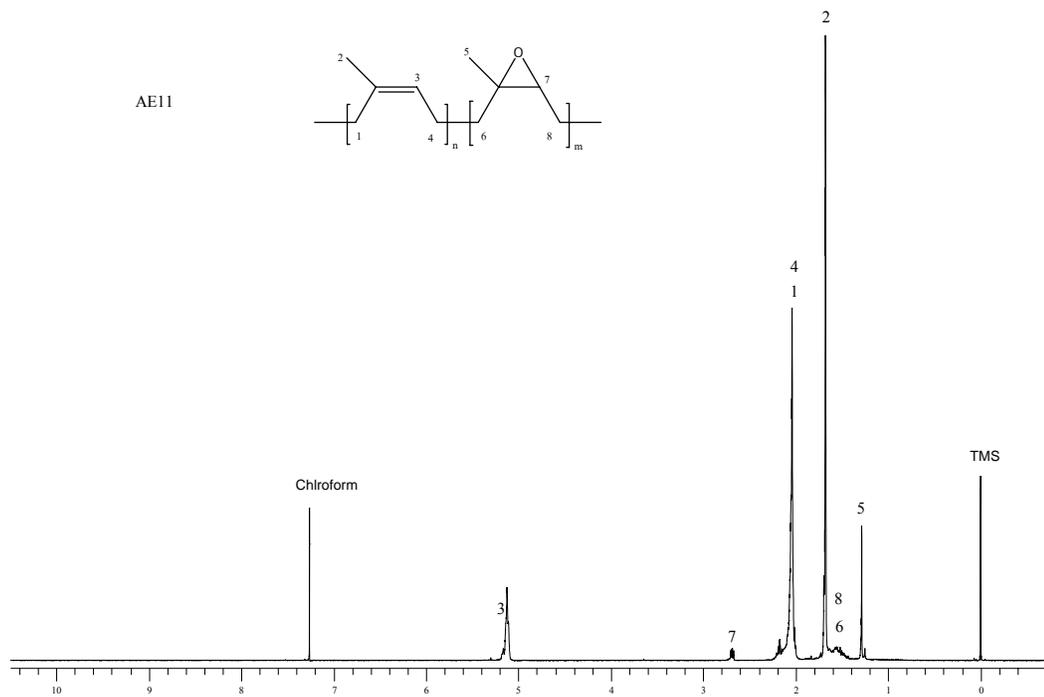


Figure 5.9  $^1\text{H-NMR}$  spectrum of ENR 2

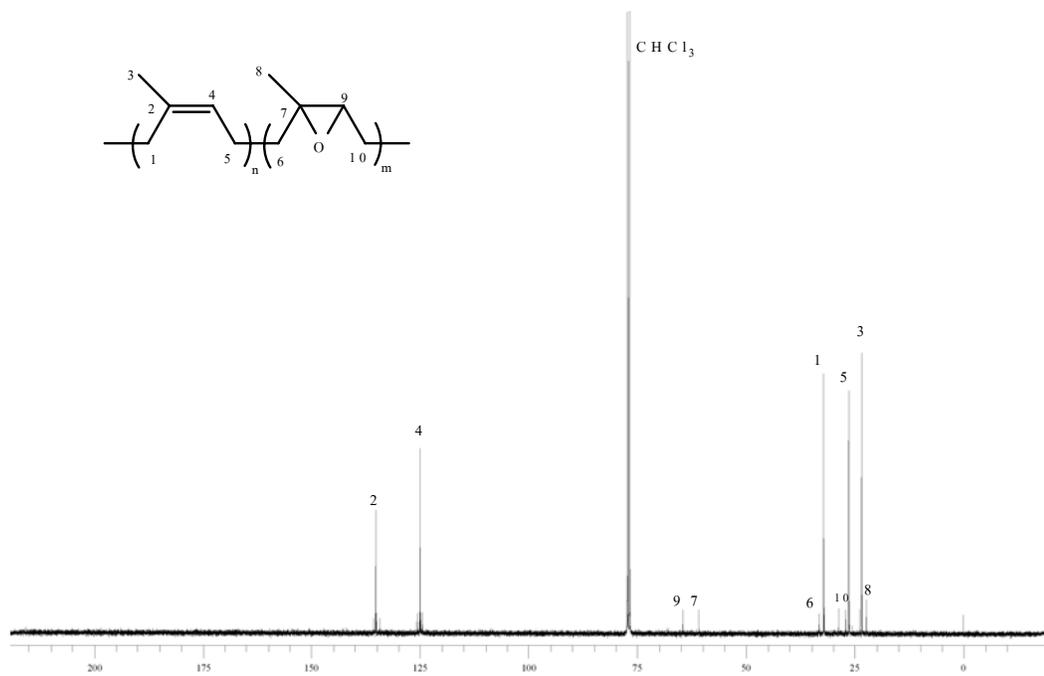


Figure 5.10  $^{13}\text{C-NMR}$  spectrum of ENR 2

The degree of epoxidation was determined by comparing the integration area of the methine proton adjacent to the oxirane ring at 2.70 ppm and that of the proton adjacent to the carbon-carbon double bond of polyisoprenic structure at 5.12 ppm. The epoxide content of the epoxidized natural rubber can be calculated according to equation 4.2.

It was found that the obtained epoxidized natural rubbers have 2.5, 4.1 and 10.0% mole epoxide of ENR corresponding to the reaction time 1.30, 3 and 8 h, respectively.

#### 5.1.2.2 Cleavage reaction of partially epoxidized natural rubber

These oxirane rings are greatly reactive toward nucleophilic reagents, for examples, cleavage reaction by periodic acid (Gillier-Ritoit *et al.*, 2003; Kébir *et al.*, 2005; Morandi *et al.*, 2007), reaction with phosphoric acid derivatives (Derouet *et al.*, 2001), alcohol (Challioui *et al.*, 2004). Therefore, the chemical modifications are possible to start from this site. In particular, periodic acid causes the cleavage of carbon-carbon bond of oxirane groups on polymer chain to obtain a low molecular weight oligomer with aldehyde and ketone groups at the chain-ends.

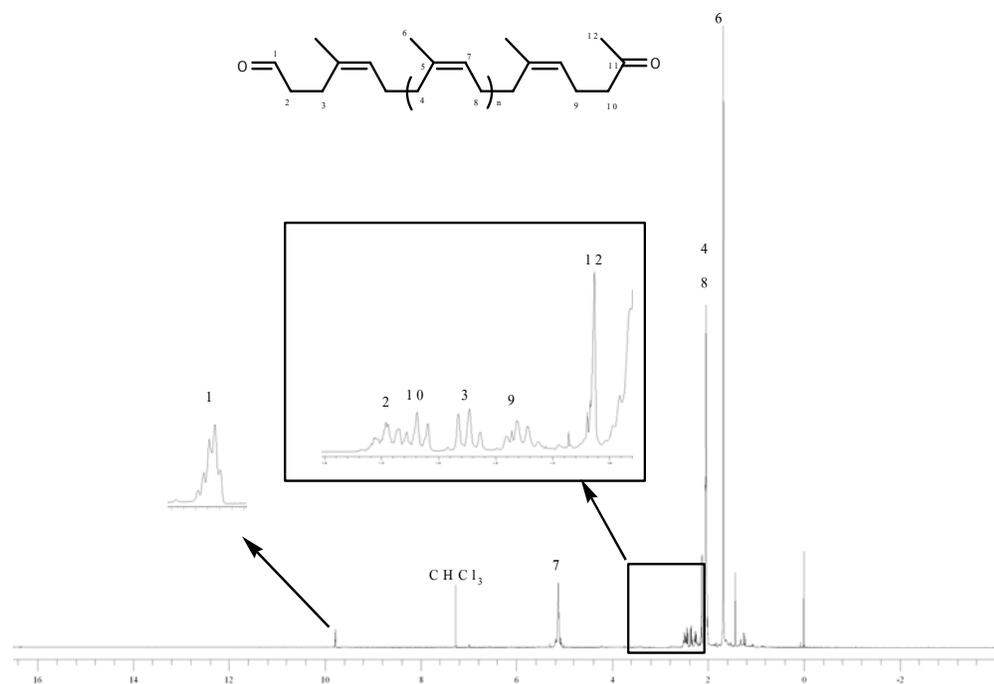
The degradation of epoxidized natural rubber was performed by an accurate amount of periodic acid according to epoxide amount in THF at 30 °C for 6 h (**Figure 5.7**). These isolated degradation products were yellowish viscous liquids. The apparent viscosity of the degradation products after cleavage reaction of 2.5% ENR was higher than that of the products from 4% and 10% ENR, respectively. The yields (%) of degradation reactions of natural rubber chains were more than 80% and the degradation reactions were reproducible as shown in **Table 5.2**.

<sup>1</sup>H-NMR spectrum in **Figure 5.11** shows the complete disappearance of oxirane structure and the appearance of the novel peaks corresponding to an aldehyde proton at 9.80 ppm, other peaks corresponding to a CH<sub>2</sub> in α and β of carbonyl terminal functional between 2.20 and 2.60 ppm and the peak of methylic protons in ketone end group at 2.13 ppm. The integrations of the signal of aldehyde proton (I<sub>CHO</sub>) and the signal of ethylenic proton (I<sub>C=CH</sub>) was allowed to calculate the average molecular weight of telechelic oligomers according to equation 4.5.

The obtained  $\overline{Mn}$  were 1000, 2000 and 3400 g mol<sup>-1</sup> for degradation of 10%, 4% and 2.5% epoxidized natural rubbers, respectively.

The analysis by  $^{13}\text{C}$ -NMR spectrum in **Figure 5.12** shows the presence of signals characteristic of aldehyde carbon and ketone carbon at 208.7 and 202 ppm, respectively. In addition, the presence of a strong peak of stretching vibration of carbonyl group at  $1720\text{ cm}^{-1}$  is found in FT-IR spectrum of the obtained carbonyltelechelic natural rubber in **Figure 5.13**. The average molecular weight ( $\overline{M}_n$  and  $\overline{M}_w$ ) and polydispersity index (PDI) were determined by steric exclusion chromatography using calibration with standard polystyrenes as shown in **Table 5.2**.

The conversion of the molecular weight values obtained from equivalent polystyrene to real values by using Benoit's factor,  $B = 0.67$  (Busnel, 1982; Kébir *et al.*, 2005) using the relation  $M_{\text{PI}} = B \times M_{\text{PS}}$  ( $M_{\text{PI}}$  = corresponding to real molecular weight of *cis*-1,4-polyisoprene,  $M_{\text{PS}}$  = molecular weight from standard polystyrenes) gives values relatively close to the results obtained by  $^1\text{H}$ -NMR in **Table 5.2**



**Figure 5.11**  $^1\text{H}$ -NMR spectrum of CTNR 3

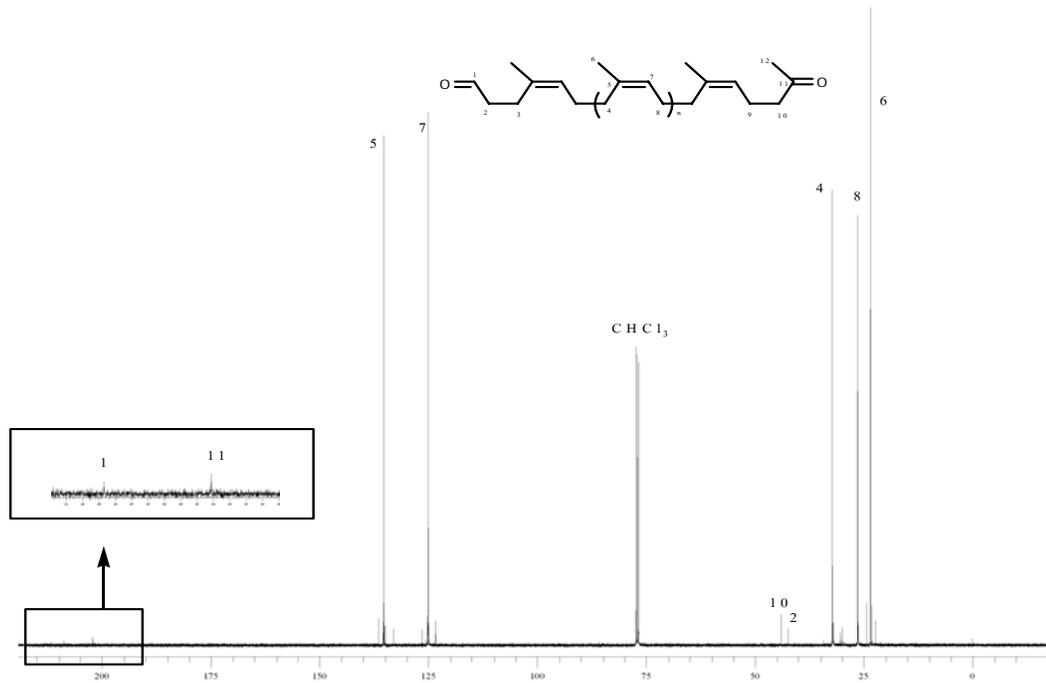


Figure 5.12  $^{13}\text{C}$ -NMR spectrum of CTNR 3

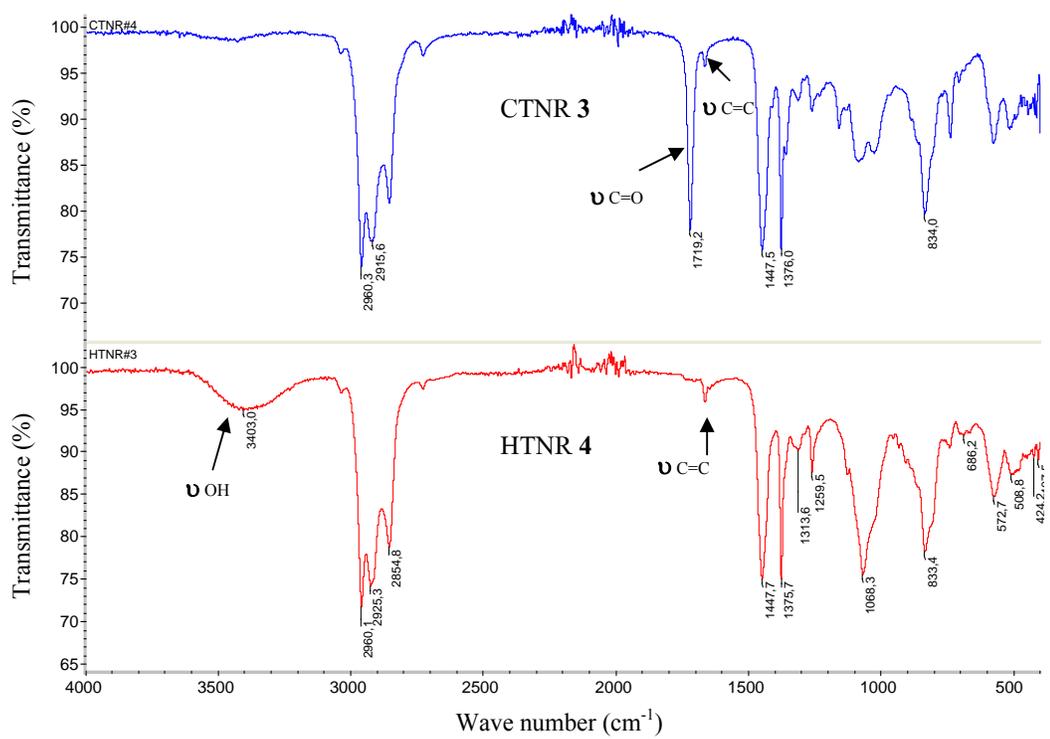


Figure 5.13 Comparison of IR spectrum of CTNR 3 and HTNR 4

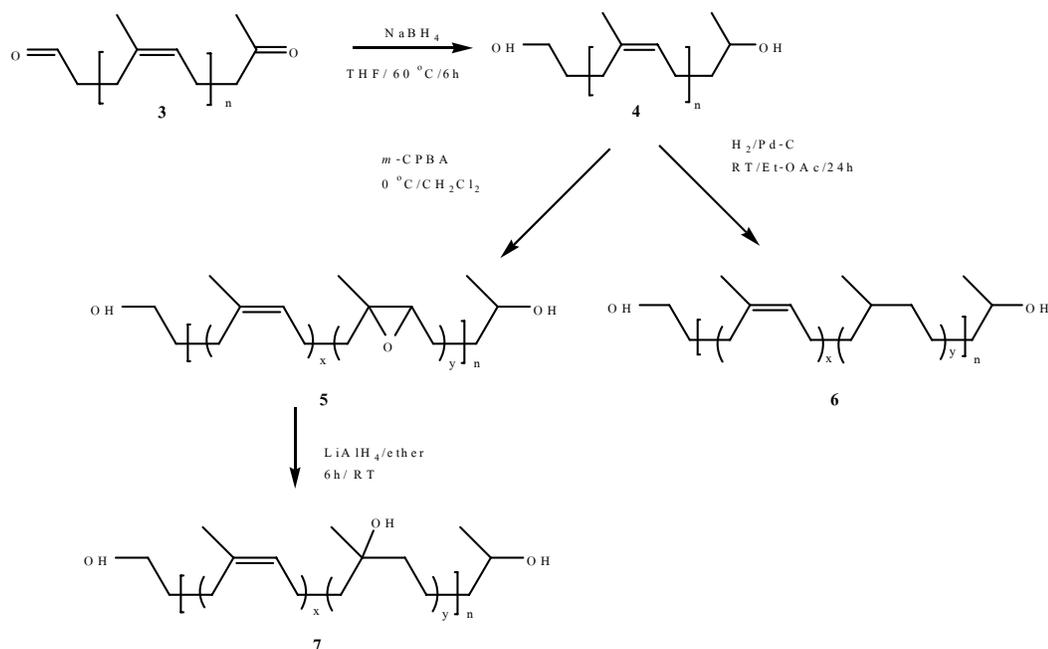
**Table 5.2** Conditions and the results of preparation of oligomers

Epoxidation			Degradation					Reduction				
T= 60 °C (DRC =20%)			T= 30 °C					T= 60 °C				
[H <sub>2</sub> O <sub>2</sub> ]/[NR] = 0.30			0.4 mol L <sup>-1</sup> in THF					0.1 mol L <sup>-1</sup> in THF				
[H <sub>2</sub> O <sub>2</sub> ]/[HCOOH] = 1			time = 6 h					time = 4 h				
Synthesis of ENR 2			Synthesis of CTNR 3					Synthesis of HTNR 4				
Entry	time	E (%)	m <sub>ENR</sub>	yield	$\overline{Mn}$ (NMR)	$\overline{Mn}$ (SEC)	PDI	m <sub>CTNR</sub>	yield	$\overline{Mn}$ (NMR)	$\overline{Mn}$ (SEC)	PDI
	(h)		(g)	(%)	(g mol <sup>-1</sup> )	(g mol <sup>-1</sup> )		(g)	(%)	(g mol <sup>-1</sup> )	(g mol <sup>-1</sup> )	
1	8	10.5	13.33	83	1000	1330	1.92	9.87	94	850	800	2.03
2		10.5	13.24	82	1050	1310	1.89	9.82	93	860	770	1.94
3		8.3	12.67	80	1300	1330	1.92	10.17	91	1070	1200	1.71
4		8.3	12.78	77	1320	1310	1.89	9.82	92	1100	1220	1.72
5		10.1	12.03	90	950	1130	2.11	11.08	75	830	1150	1.95
6	3	4.1	10.08	85	2100	1790	2.04	10.08	93	1810	1830	2.02
7		4.1	14.84	80	2090	1880	1.98	10.53	85	1860	1880	1.98
8		4.1	13.56	77	2160	2030	2.12	9.31	82	1920	1880	2.01
9		3.6	17.10	81	2410	2470	2.00	10.50	88	2047	2630	2.06
10	1.3	2.5	67.79	77	3600	*	*	50.89	82	3400	5000	1.95

E(%) = percent of epoxidation, m<sub>ENR</sub> = mass of ENR, m<sub>CTNR</sub> = mass of CTNR, Yield (%) = polymer recovery yields,  $\overline{Mn}_{(NMR)}$  = determined with NMR,  $\overline{Mn}$  (SEC) = determined with SEC using polystyrene standards and correcting with Benoit factor (0.67 for polyisoprene), PDI = polydispersity index

## 5.2 Modification of telechelic natural rubber

The carbonyltelechelic natural rubber (CTNR **3**) was modified to hydroxytelechelic natural rubber (HTNR **4**). With different methods and reagents, hydroxytelechelic oligoisoprene was modified into partially epoxidized hydroxytelechelic oligoisoprene (EHTNR **5**) and into hydrogenated hydroxytelechelic oligoisoprene (HHTNR **6**) as well as into hydroxyl multifunctional oligoisoprene (HTNR( $\overline{fn} > 2$ ) **7**) as shown in **Figure 5.14**. These hydroxyl functionalized oligoisoprenes were later used as starting materials for the preparation of polyurethane foams especially, HTNR **4** and EHTNR **5**.

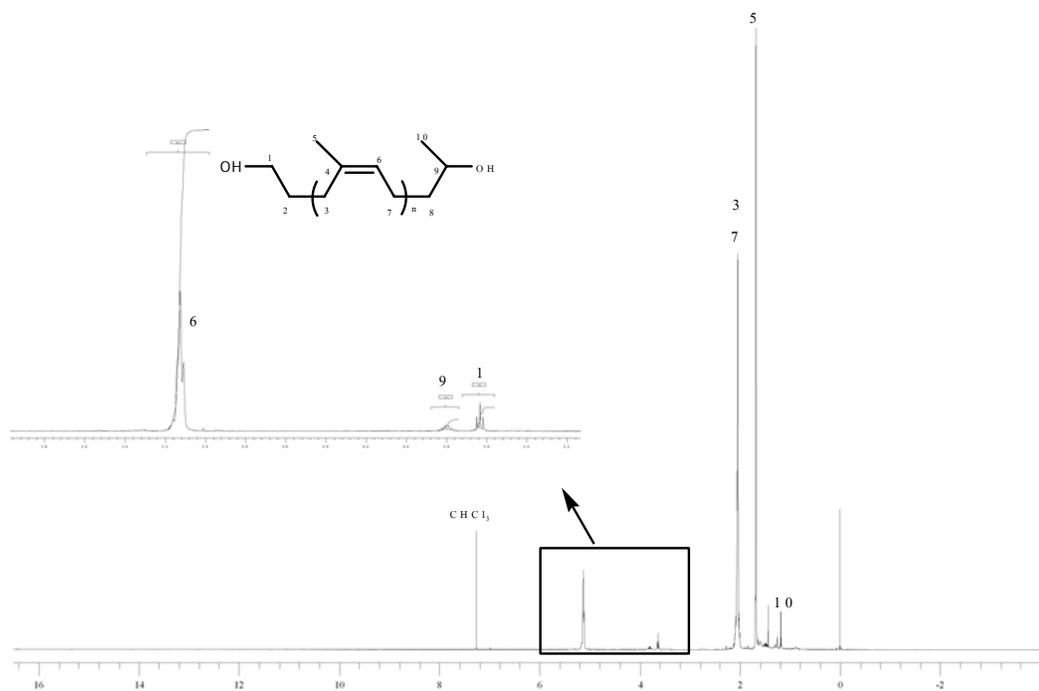


**Figure 5.14** Modification of carbonyltelechelic natural rubber

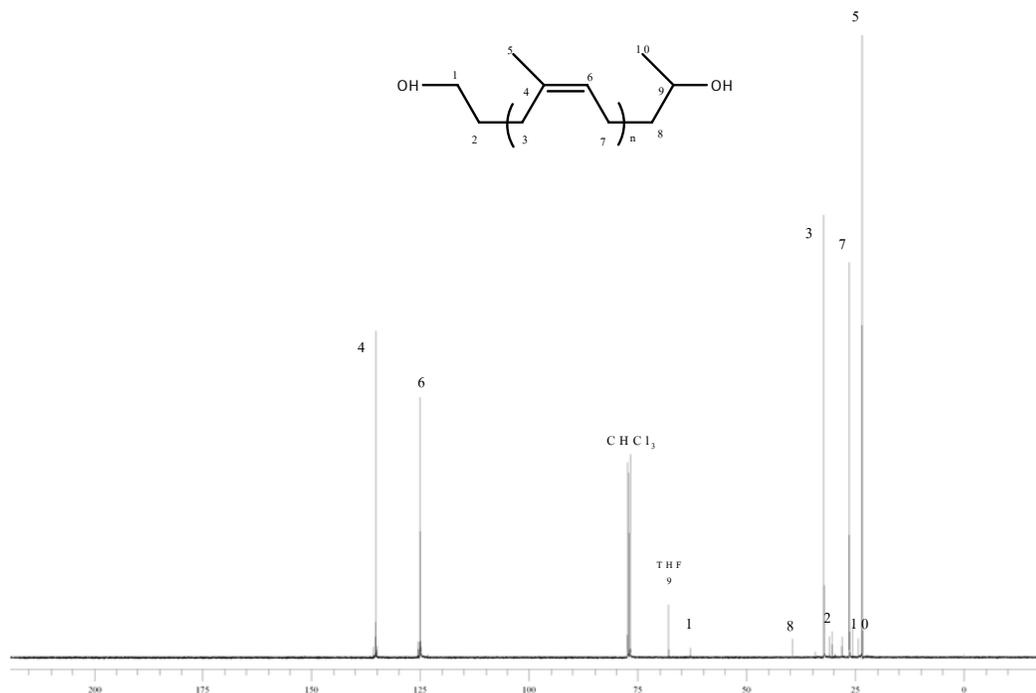
### 5.2.1 Reduction of CTNR 3

CTNR **3** was treated by  $\text{NaBH}_4$  that is a specific reducing reagent of the carbonyl groups (aldehyde and ketone) and has no effect on carbon-carbon double bonds. This reaction was performed in THF at  $60^\circ\text{C}$  for 6 h as shown in **Figure 5.14**. The separated product was yellowish-viscous liquid. The  $\overline{Mn}$  and PDI are presented in **Table 5.2**.

$^1\text{H-NMR}$  spectrum in **Figure 5.15** shows that the ethylenic proton (5.12 ppm) is unchanged and the complete disappearance of both peaks of aldehyde proton at 9.80 ppm and methylic proton in ketone end group at 2.13 ppm as well as the peak of  $\text{CH}_2$  in  $\alpha$  and  $\beta$  of terminal carbonyl functions between 2.20 and 2.60 ppm. We observed the novel peak of methylic protons adjacent to secondary alcohol at 1.20 ppm and two peaks corresponding to  $\text{CH}$  (3.80 ppm) and  $\text{CH}_2$  (3.68 ppm) adjacent to alcohol groups at the chain-ends. The analysis by  $^{13}\text{C-NMR}$  in **Figure 5.16**, we observed the presence of peaks at 62.4 and 67.4 ppm corresponding to carbons ( $\text{CH}_2$ ) and ( $\text{CH}$ ) adjacent to alcohol functions at chain-ends. The presence of the methyl peak at chain-end at 23.8 ppm and two peaks of  $\text{CH}_2$  at chain-ends at 30.5 and 39.0 ppm confirms also the total reduction of the carbonyl groups. FT-IR spectrum in **Figure 5.13** confirmed the structure of the obtained oligoisoprene by the presence of a strong peak of hydroxyl group at  $3500\text{ cm}^{-1}$  and by the absence of the peak of carbonyl group at  $1720\text{ cm}^{-1}$ .



**Figure 5.15**  $^1\text{H-NMR}$  spectrum of HTNR 4



**Figure 5.16**  $^{13}\text{C}$ -NMR spectrum of HTNR 4

### 5.2.2 Epoxidation of carbon-carbon double bonds of HTNR 4

Hydroxytelechelic natural rubber,  $\overline{M}_n = 1000$  and  $2000 \text{ g mol}^{-1}$  were approximately 10%, 20% and 30% epoxidized using *m*-chloroperbenzoic acid as reagent. This reaction was controlled at  $0^\circ\text{C}$  for 4 h as shown in **Figure 5.14**. The results of analysis by  $^1\text{H}$ -NMR in **Figure 5.17** shows the evidence of the presence of the proton adjacent to oxirane ring at 2.70 ppm and the signal at 1.29 ppm corresponding to the methylic protons adjacent to oxirane ring. The analysis by  $^{13}\text{C}$ -NMR in **Figure 5.18** revealed also the presence of the peaks at 60 ppm and 65 ppm corresponding to carbons of oxirane ring. The appearance of signal of epoxide group at 1252 and  $870 \text{ cm}^{-1}$  were also observed in FT-IR spectrum in **Figure 5.23**. The obtained molecular weights of EHTNR1000 were order:

$$11\% \text{EHTNR } \overline{M}_n = 1,480 \text{ g mol}^{-1} (\text{Eq. PS}), \text{PDI} = 1.70$$

$$23\% \text{EHTNR } \overline{M}_n = 1,200 \text{ g mol}^{-1} (\text{Eq. PS}), \text{PDI} = 1.90$$

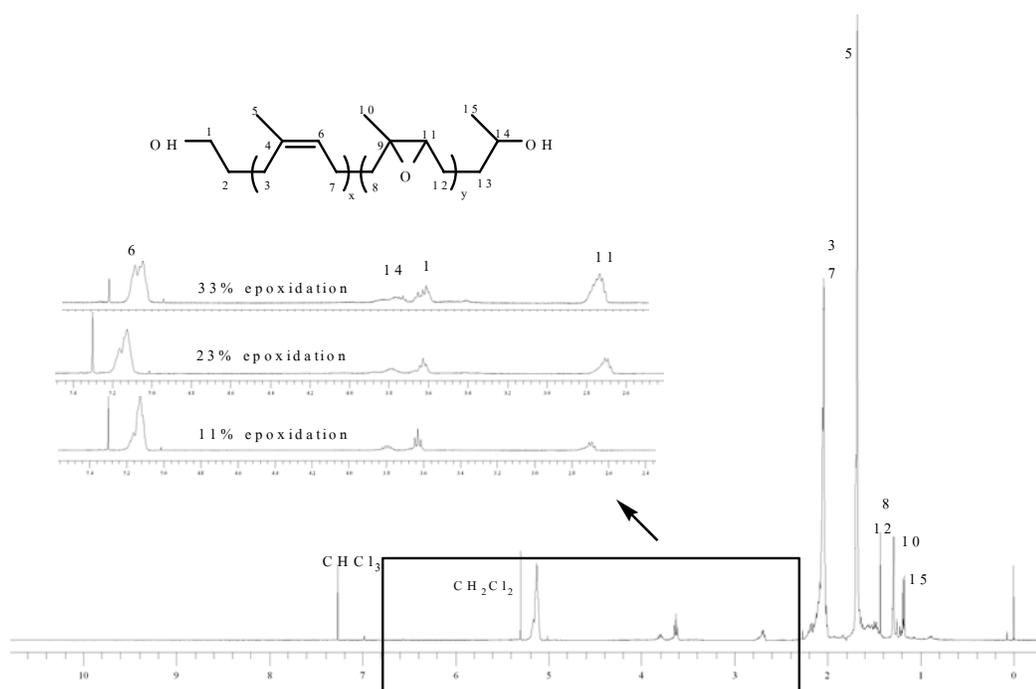
$$33\% \text{EHTNR } \overline{M}_n = 1,290 \text{ g mol}^{-1} (\text{Eq. PS}), \text{PDI} = 1.97$$

The obtained molecular weights of EHTNR2000 were order:

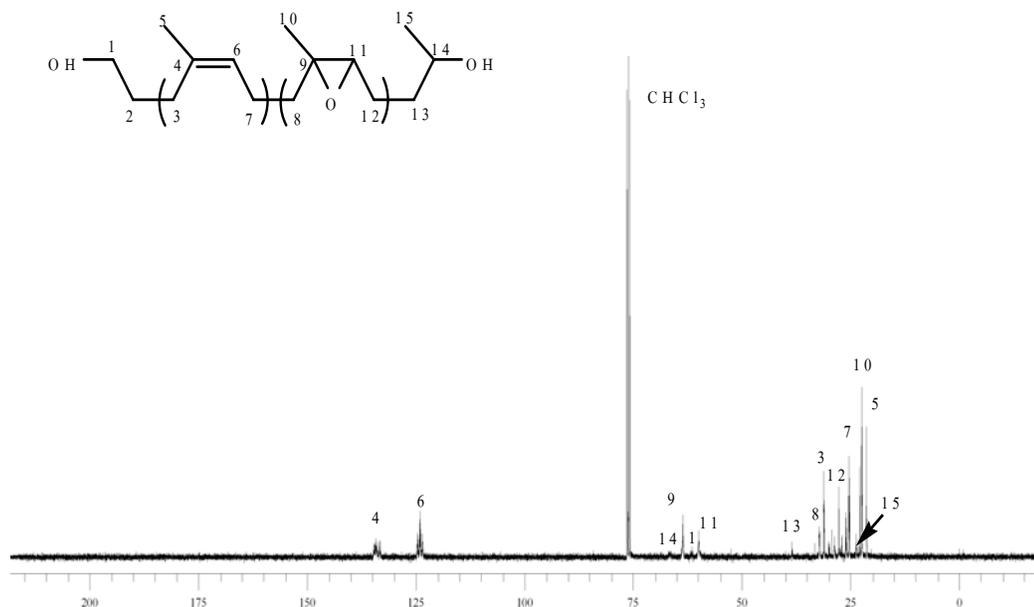
9%EHTNR  $\overline{Mn} = 3180 \text{ g mol}^{-1}$  (Eq. PS), PDI = 2.51

23%EHTNR  $\overline{Mn} = 3670 \text{ g mol}^{-1}$  (Eq.PS), PDI = 2.19

35%EHTNR  $\overline{Mn} = 3230 \text{ g mol}^{-1}$  (Eq.PS), PDI = 2.13



**Figure 5.17**  $^1\text{H-NMR}$  spectrum of EHTNR 5



**Figure 5.18**  $^{13}\text{C}$ -NMR spectrum of EHTNR 5

### 5.2.3 Catalytic hydrogenation of carbon-carbon double bonds of HTNR 4

Hydroxytelechelic natural rubber (HTNR),  $\overline{M}_n = 1000$  (HTNR1000) was hydrogenated under hydrogen pressure at 3.2 bar for 24 h at room temperature with catalyst (palladium supported on carbon (18%)) as shown in **Figure 5.14**.

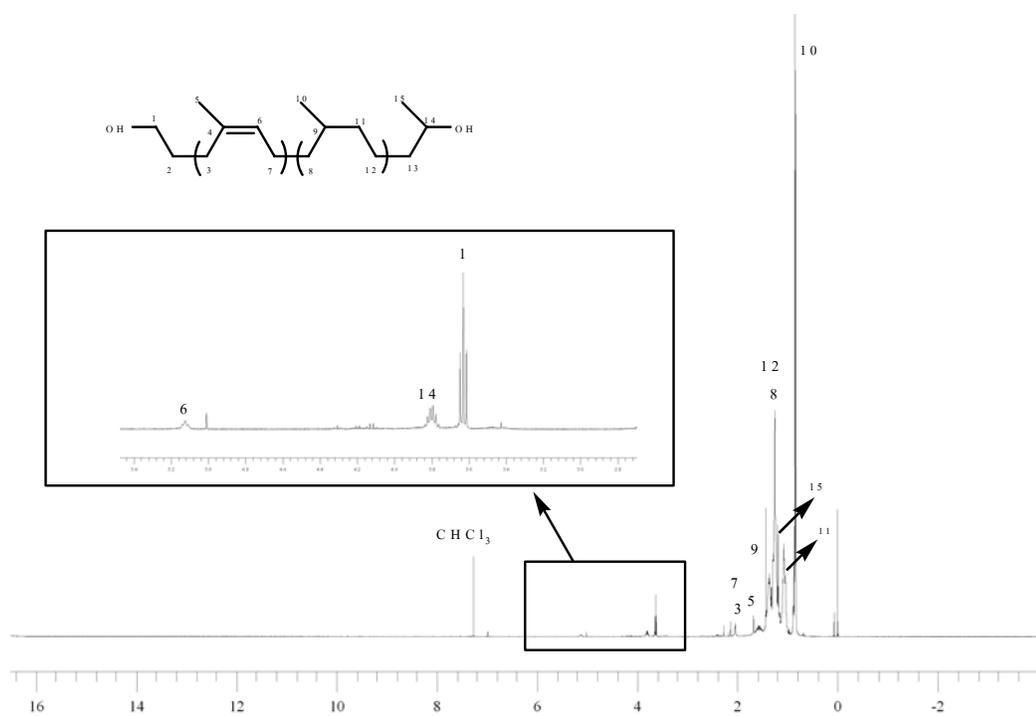
The  $^1\text{H}$ -NMR spectrum in **Figure 5.19** shows that the intensities of the characteristic signals of isoprene ( $\text{C}=\text{CH}$ ) are notable decreased and shows the novel signals at 0.84 and 1.37 ppm corresponding to the methyl and methylene protons of saturated units. The integration of signals of methyl group in isoprene unit and saturated (1.67, 0.84 ppm, respectively) allowed calculating the hydrogenation ratio (equation 4.3). This confirms the hydrogenation reaction process on hydroxytelechelic natural rubber's structure. The  $^{13}\text{C}$ -NMR spectrum of hydrogenated hydroxytelechelic natural rubber is shown in **Figure 5.21**. The peaks at 19.75 and 37.28 ppm were assigned to the carbon of methyl and methine of saturated unit, respectively. Thus, this oligomer possesses percentage of hydrogenation of 98%.

The FT-IR analysis of hydrogenated hydroxytelechelic natural rubber in **Figure 5.23** shows the disappearance of two important characteristic peaks at  $1665$  and  $836\text{ cm}^{-1}$ , assigned to

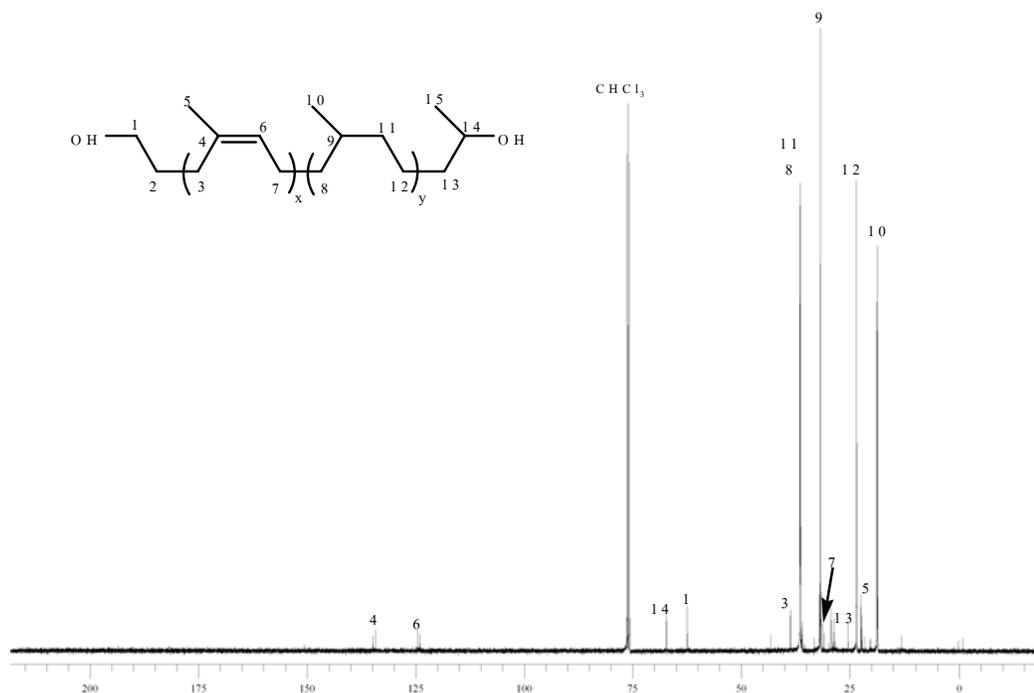
the C=C stretching and the C-H out of plane deformation of trisubstituted olefin of polyisoprene, respectively.

The obtained molecular weight of 98%HHTNR **6** was order:

$$\overline{Mn} = 1,440 \text{ g mol}^{-1} \text{ (Eq. PS), PDI} = 2.2$$



**Figure 5.19**  $^1\text{H-NMR}$  spectrum of 98%HHTNR **6**



**Figure 5.20**  $^{13}\text{C}$ -NMR spectrum of 98% HHTNR 6

#### 5.2.4 Determination of functionality of HTNR 4

Fortunately, the direct measurement by integration of peaks on  $^1\text{H}$ -NMR of HTNR allowed quantifying of hydroxyl functionality since that peaks of protons adjacent to hydroxyl are separated from other peaks in spectra. Fages and Pham (1978) propose the evaluated average functionality formulation of hydroxyl polybutadiene synthesized by anionic polymerization as shown below:

$$fn = [(I_{\text{CH}_2\text{OH}}/2)(3x + 2y)/(I_{\text{olefin}})] [\overline{Mn}/54] \quad (5.1)$$

Where:  $I_{\text{CH}_2\text{OH}}$  and  $I_{\text{olefin}}$  are the relative intensities of characteristic peaks of methylenic proton at  $\alpha$  position of hydroxyl and ethylenic proton; X and Y are the fractions of repeating units of (1,2) and (1,4) structures, respectively; 3 and 2 are the number of olefin protons in repeating units of (1,2) and (1,4), respectively,  $X+Y = 1$ .  $(3x+2y)$  represents the average composition of protons contribution in every unit. 54 is the molar mass of repeating unit.

In our work, the divert formulation for calculation of average functionality of hydroxy telechelic oligoisoprene is shown in equation 4.4. The average functionality was  $2.1 \pm 0.1$  from  $^1\text{H-NMR}$  spectrum of HTNR.

### 5.2.5 Reduction of EHTNR 5

The reduction of epoxide ring on epoxidized hydroxytelechelic natural rubber (EHTNR 5) 1000 at 11 % and 23 % epoxide (5) with lithium aluminum hydride ( $\text{LiAlH}_4$ ) introduced the new structure of *cis*-1,4-oligoisoprene possessing tertiary alcohol functions through the polymer chain (7) and included the primary and secondary alcohol functions at chain-ends. These reactions were carried out for 6 h at room temperature as shown in **Figure 5.14**.

The analysis of hydroxytelechelic natural rubber ( $\bar{fn} > 2$ ) 7 by  $^1\text{H-NMR}$  in **Figure 5.21** and  $^{13}\text{C-NMR}$  in **Figure 5.22** show the complete disappearance of signals corresponding to  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  groups of oxirane ring and reveal the presence of signals of  $\text{CH}_2$ ,  $\text{CH}_3$  groups adjacent to tertiary alcohol (1.42 and 42.92 ppm, 1.15 and 28.69 ppm, respectively). The signal of tertiary carbon appeared at 71.63 ppm.

FT-IR spectrum in **Figure 5.23** shows the increasing of absorption at  $3340\text{ cm}^{-1}$  ( $\nu_{\text{OH}}$ ) and disappearance of the characteristic band of epoxide function ( $870\text{ cm}^{-1}$ ). The functionalities of modified hydroxytelechelic oligomers 7 approximately 10% and 20% epoxidation were calculated below:

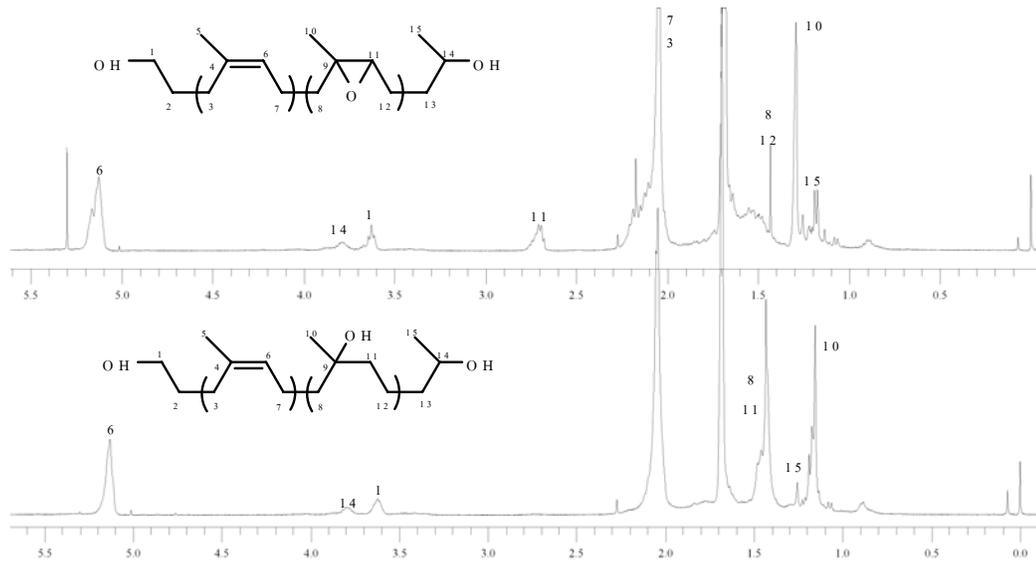
$$\bar{fn} = [(I_{(\text{CH}_3 \text{ tertiary alcohol})} + I_{(\text{CH}_3 \text{ secondary alcohol})} - 3 I_{(\text{CHOH})}) / (3 \times I_{(\text{CHOH})})] + 2 \quad (5.2)$$

$I_{(\text{CHOH})}$  = intensity of signal of proton in  $\alpha$  of the secondary alcohol at 3.8 ppm

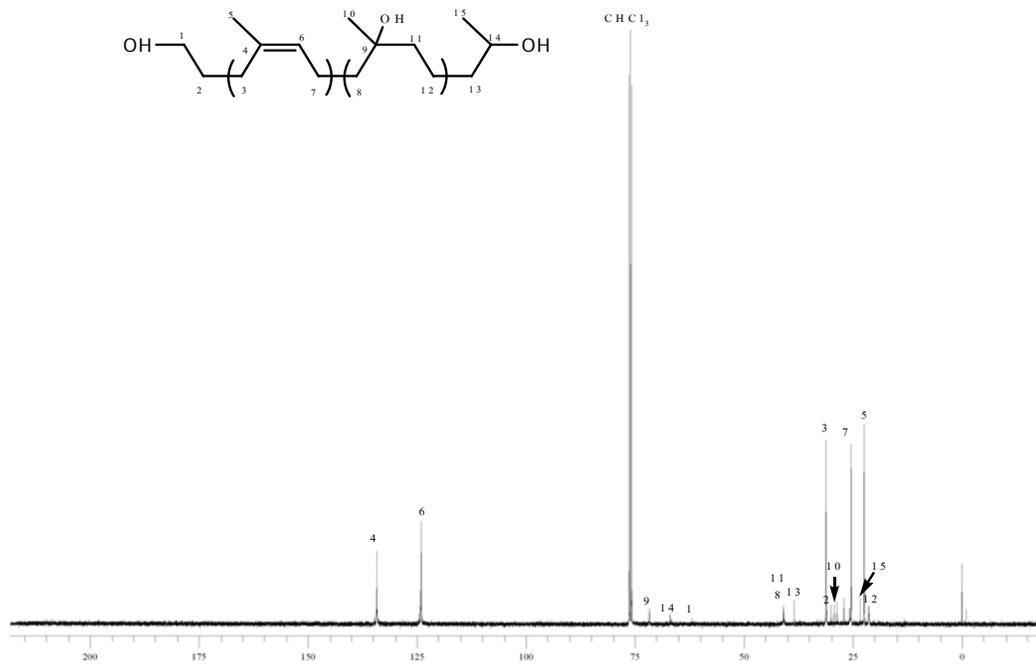
$I_{(\text{CH}_3 \text{ tertiary alcohol})}$  = intensity of signal of protons of methyl in  $\alpha$  of the tertiary alcohol at 1.15 ppm.

$I_{(\text{CH}_3 \text{ secondary alcohol})}$  = intensity of signal of protons of methyl in  $\alpha$  of the secondary alcohol at 1.18 ppm.

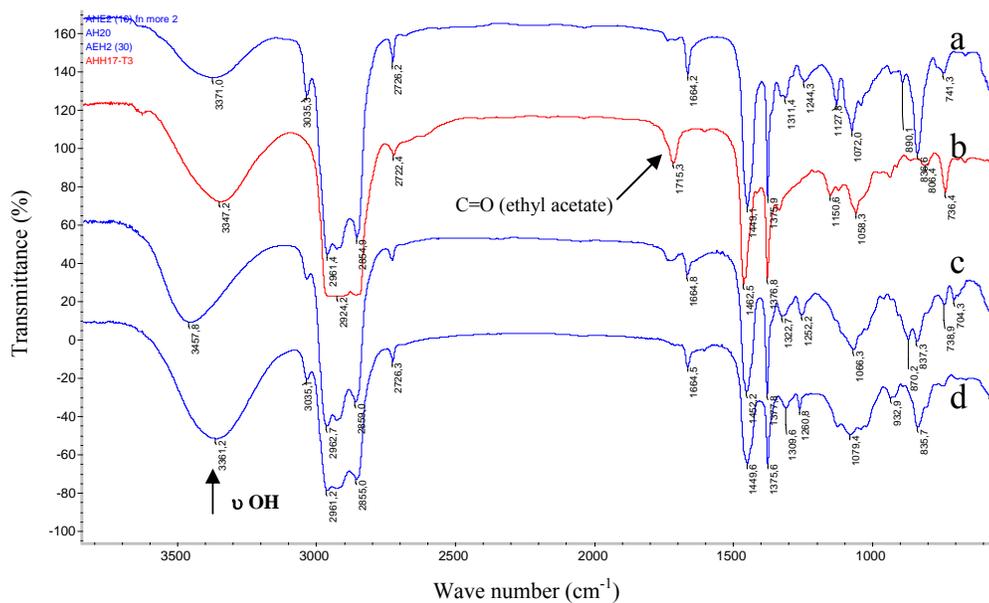
These functionalities of modified hydroxytelechelic oligomers 7 approximately 10% and 20% epoxidation were 2.7 and 4.3 respectively.



**Figure 5.21** Comparison of  $^1\text{H-NMR}$  spectrum of EHTNR **5** and HTNR( $\overline{fn} > 2$ ) **7**



**Figure 5.22**  $^{13}\text{C-NMR}$  spectrum of HTNR( $\overline{fn} > 2$ ) **7**



**Figure 5.24** IR spectra of a) HTNR 4, b) HHTNR 6, c) EHTNR 5, d) HTNR( $\overline{fn} > 2$ ) 7

### 5.2.6 MALDI-TOF MS analysis

Carbonyltelechelic natural rubber (CTNR 3) and hydroxytelechelic natural rubber (HTNR 4) were analyzed by MALDI-TOF MS technique. Ditrinol was used as matrix and AgTFA was used as doping agent. Some examples of mass spectra were shown in **Figure 5.24** and **5.25**. We clearly observed that the sample peaks identified the mass corresponding to the ionized of CTNR 3 and HTNR 4 molecules with silver (Ag) as shown in **Appendix A**. The theoretical masses were calculated with the equation below:

$$M = M(\text{end group}) + M(\text{Ag}) + nM(\text{repeating units}) \quad (5.3)$$

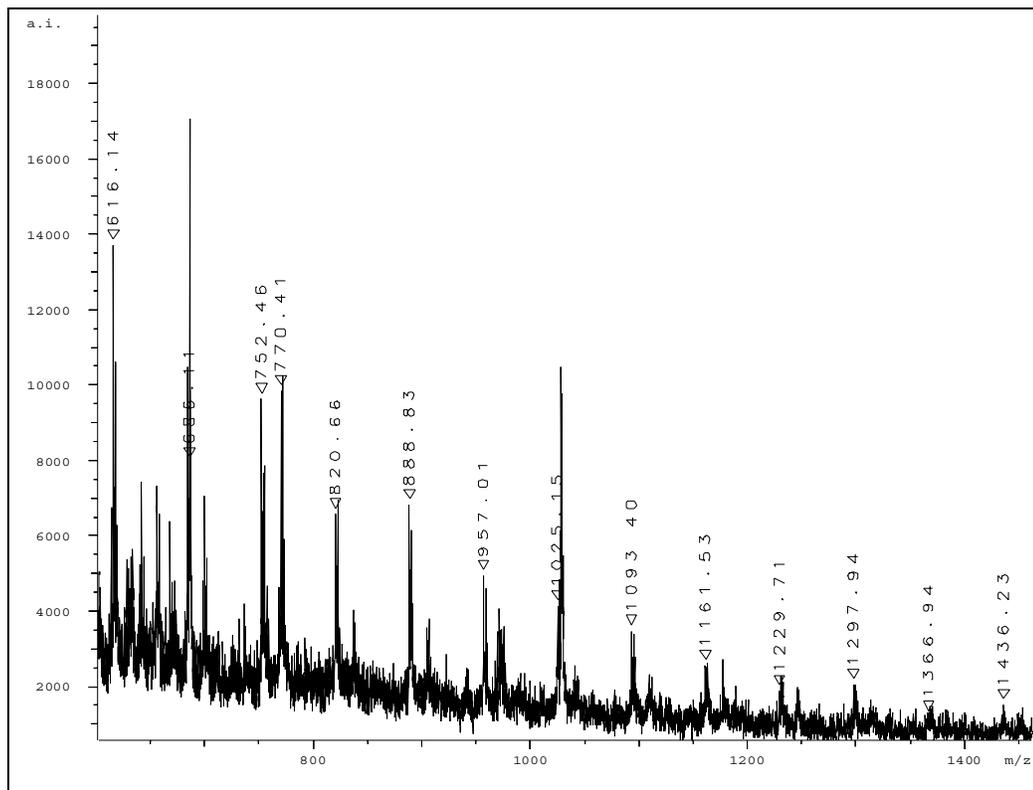


Figure 5.24 MALDI-TOF mass spectrum of CTNR 3

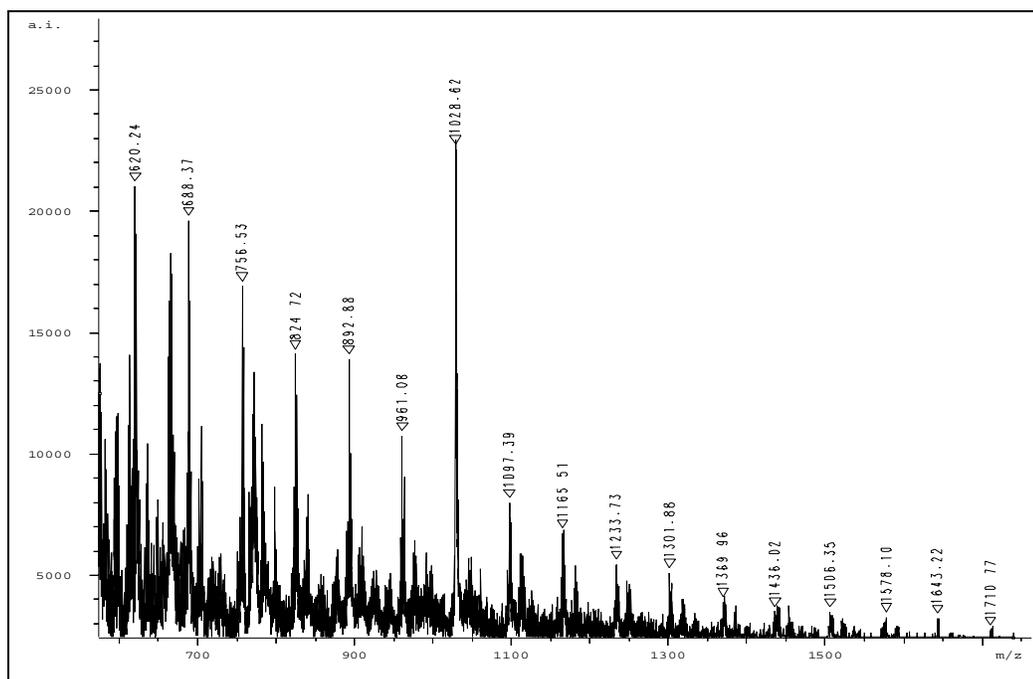
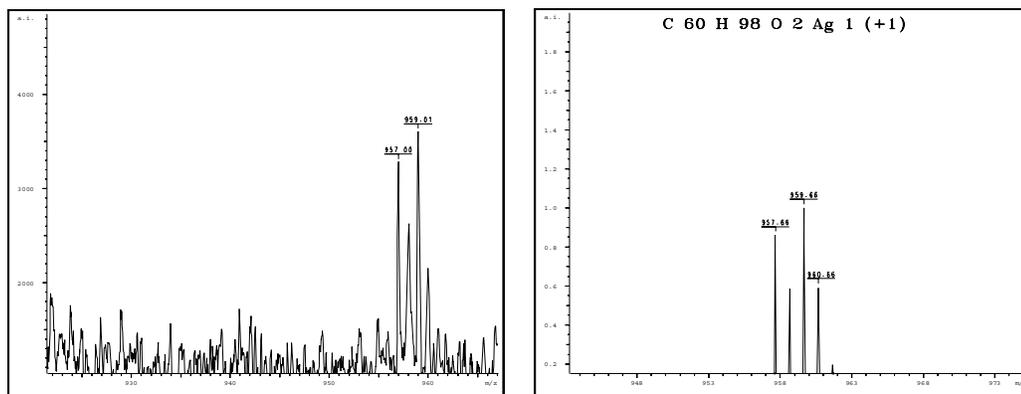
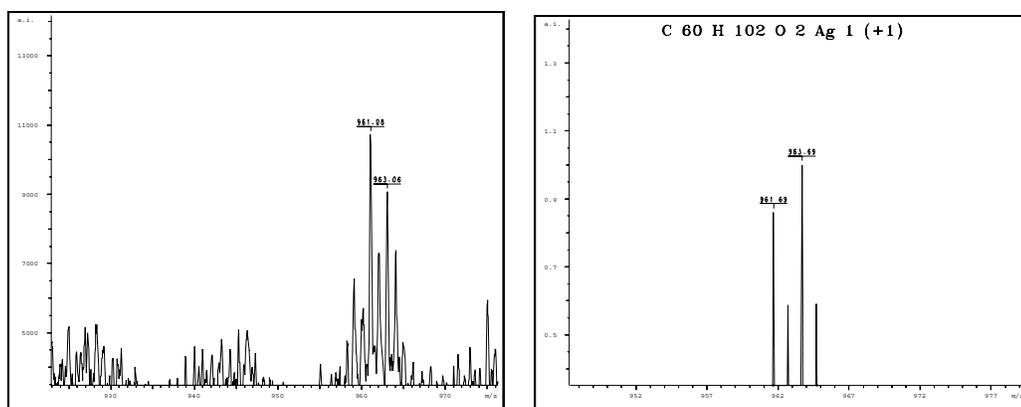


Figure 5.25 MALDI-TOF mass spectrum of HTNR 4



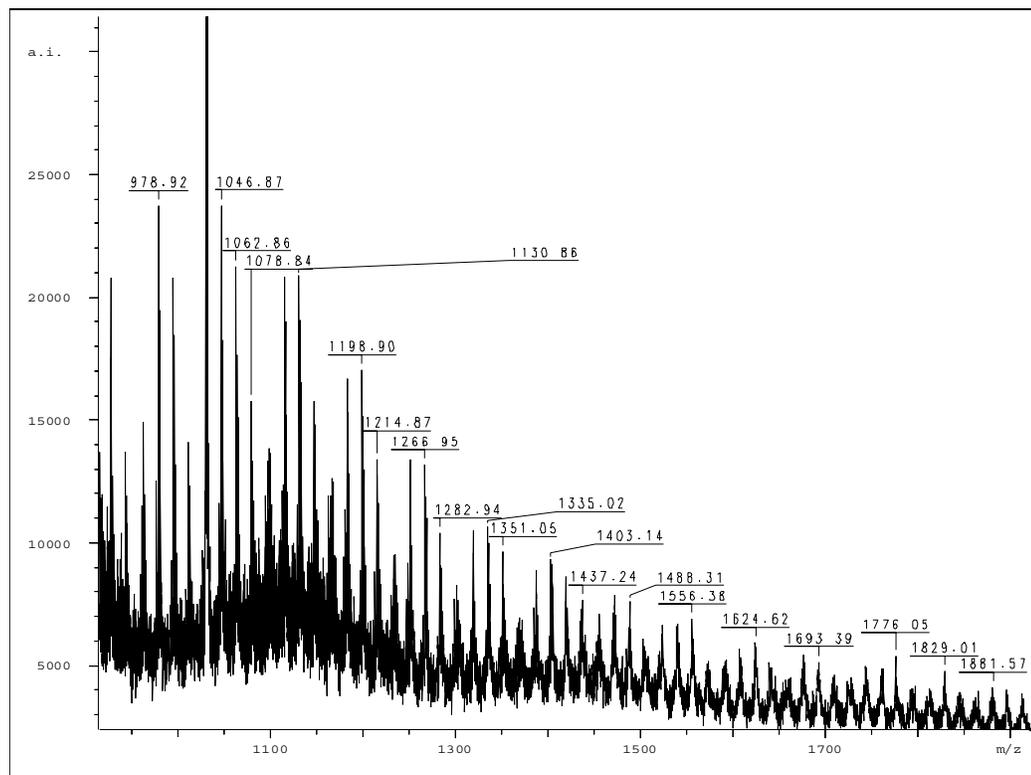
**Figure 5.26** Isotopic distribution observed (a) and simulation (b) of CTNR 3 at  $n=11$  ionized by silver (Ag)



**Figure 5.27** Isotopic distribution observed (a) and simulation (b) of HTNR 4 at  $n=11$  ionized by silver (Ag)

The isotopic distribution of observed peaks was identical to that of the simulation in **Figure 5.27** and **5.28**. The difference between the main peaks in spectrogram are equal to the repeating units mass of isoprene ( $M = 68$ ). In comparison, the difference between the CTNR 3 peaks and HTNR 4 peaks correspond to the equivalent weight (in the same repeating unit number,  $n$ ) of four hydrogen atoms added into CTNR molecule *via* the reduction step by reducing agent ( $\text{NaBH}_4$ ). Therefore, the structure and the end functional groups of both oligomers were confirmed with this analysis method. In the addition, the MALDI-TOF mass spectra present an

epoxidized repeating chain with one epoxide and rarely two epoxides (peak at M+16 and M+32, respectively). However, these impurity products were not detected at all in both  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analysis.



**Figure 5.28** MALDI-TOF mass spectrum of 11%EHTNR1000

The results obtained from the MALDI-TOF mass spectra for  $\overline{Mn}$ ,  $\overline{Mw}$  and PDI are 960, 1050 and 1.09 for HTNR1000 and 1610, 1740 and 1.08 for HTNR2000, respectively. The observed difference by comparison with the value obtained by  $^1\text{H-NMR}$  spectroscopy and SEC may be due to the non quantitative desorption of all the oligomers, especially the higher molecular weight oligomers, which explains the lower values of PDI.

Moreover, MALDI-TOF mass spectrum of EHTNR at level 11% epoxide (**Figure 5.28**) (using Ditrinol and NaTFA as matrix and doping agent, respectively) presents an increasing number of important peaks corresponding to epoxidized chains with one, two, or three epoxides (M+16, M+32 and M+48), and the peaks at M+68 (isoprene repeating units) (**Appendix A**).

### 5.2.7 Viscosity and thermal properties of precursors

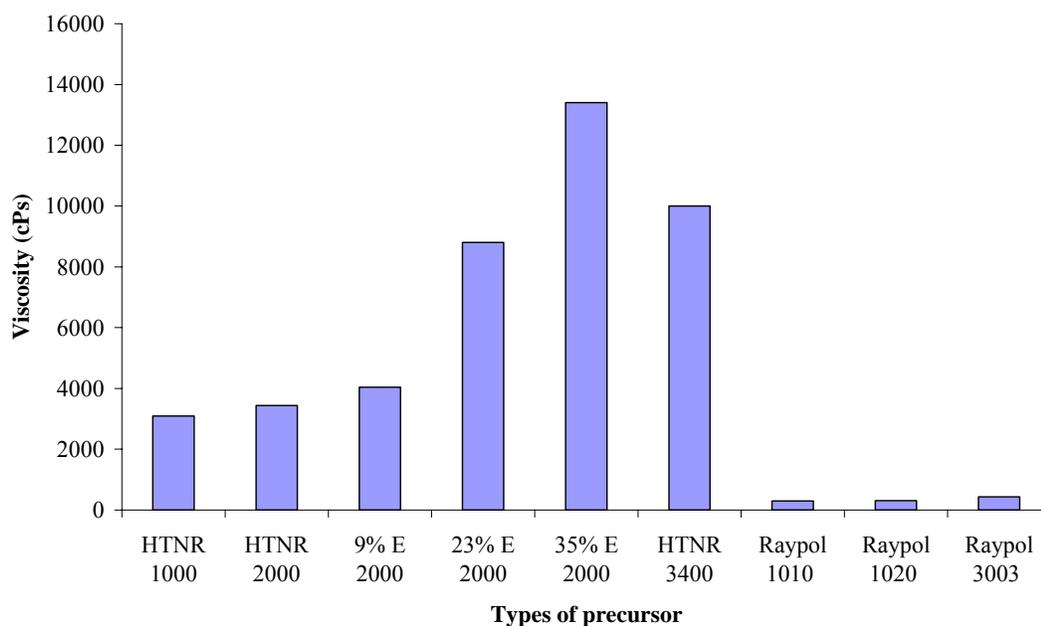
The samples of precursors with different in molecular weight or in microstructure were carried out to analyze viscosity, thermal behavior by DSC and TGA for determining glass transition temperature ( $T_g$ ), thermal degradation and weight loss, respectively. These results are shown in **Table 5.3**.

**Table 5.3** Viscosity and thermal characteristics of precursors form natural rubber and of commercial polyols

Samples	Viscosity (cPs)	$T_g$ ( $^{\circ}$ C)	Thermal degradation steps			
			1 <sup>st</sup> step		2 <sup>nd</sup> step	
			T max ( $^{\circ}$ C)	weight loss (%)	T max ( $^{\circ}$ C)	weight loss (%)
NR	*	-68	381	99	-	-
HTNR1000	3100	-59	378	99	-	-
HTNR2000	3650	-63	377	99	-	-
HTNR3400	9600	-66	382	99	-	-
11% EHTNR1000	*	-49	283	15	378	83
23% EHTNR1000	*	-41	248	18	398	78
36% EHTNR1000	*	-36	278	13	400	83
9% EHTNR2000	4050	-52	297	9	376	93
23% EHTNR2000	8900	-49	271	6	378	99
35% EHTNR2000	13440	-34	270	5	386	99
98% HHTNR	*	-59	462	99	-	-
HTNR $\overline{fn} > 2$ (11)	*	-43	385	99	-	-
HTNR $\overline{fn} > 2$ (23)	*	-27	382	99	-	-
Raypol1010	300	*	*	*	*	*
Raypol1020	310	-70	373	99	-	-
Raypol3003	450	-67	350	99	-	-

\* No measurement

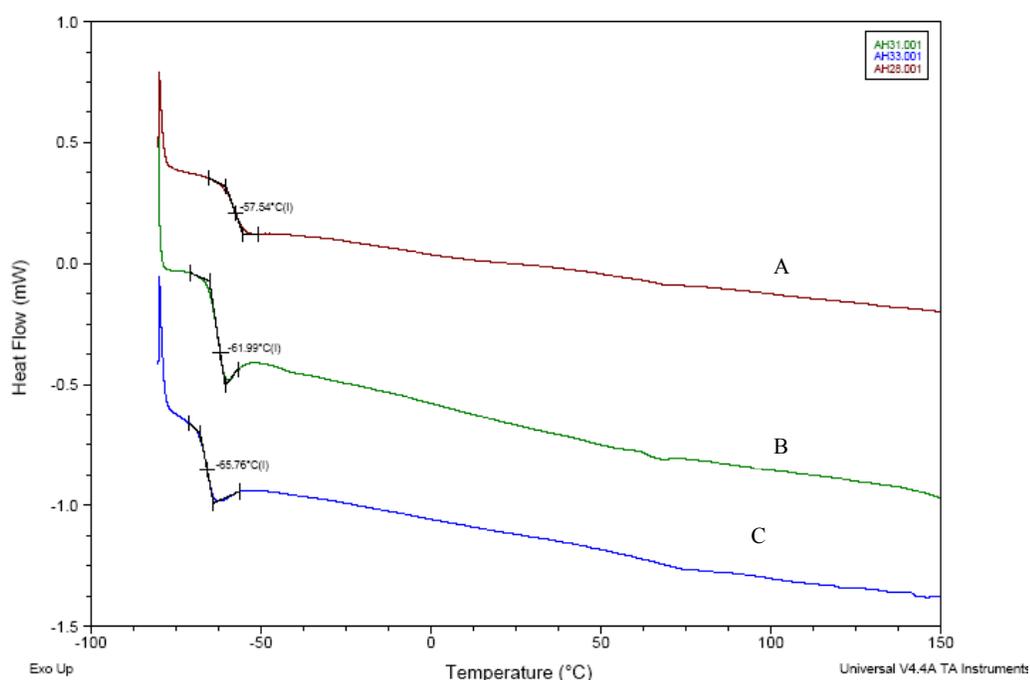
Viscosity is an important property of precursors in polyurethane foam processing and final product properties. Good dispersion of precursors with other low viscosity product depends on their viscosity, high energy mixing may be required. It may be difficult to control density of foams. The viscosity of HTNRs precursors is variable and is usually a function of the molecular weight and of the average number of hydroxyl groups per molecule. Therefore, this section shows the viscosities of precursors (HTNRs and commercial polyether polyol) that were the starting materials in preparation of polyurethane foams in **Table 5.3** and **Figure 5.29**.



**Figure 5.29** Viscosity of precursors

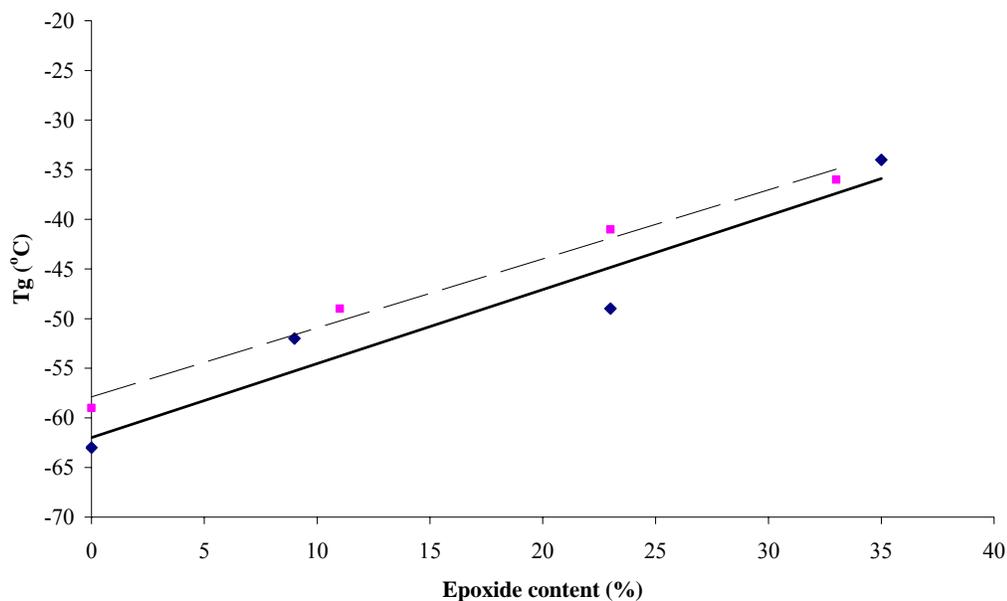
**Figure 5.29** shows the viscosity of precursors both from HTNR and commercial polyols that have different in molecular weights and microstructures between 1000 to 3400  $\text{g mol}^{-1}$ . Brookfield viscometer according to ASTM D 4878-03 was used at room temperature ( $30\text{ }^{\circ}\text{C}$ ). We observed that the viscosity of natural rubber precursors (HTNR) increases with increasing molecular weight. In addition, the higher level of epoxide contents in molecular chain gives the higher viscosity due to increasing interactions of oxirane rings between chains. In comparison with commercial precursors, it was found that HTNR1000 based precursors are more

viscous than commercial precursors (Raypol1010, 1020 and 3003) equal to about 10 times at 30 °C. It is clear that the more viscous the raw material is, the more difficult is to obtain homogenous mixture or good dispersed chemical products and to expand good foams. Therefore, a small amount of dichloromethane was added to HTNR based polyurethane foam formulations to reduce the viscosity as shown in **Tables 4.3-4.5**. Moreover, this solvent can be a physical blowing agent to obtain softer foams.



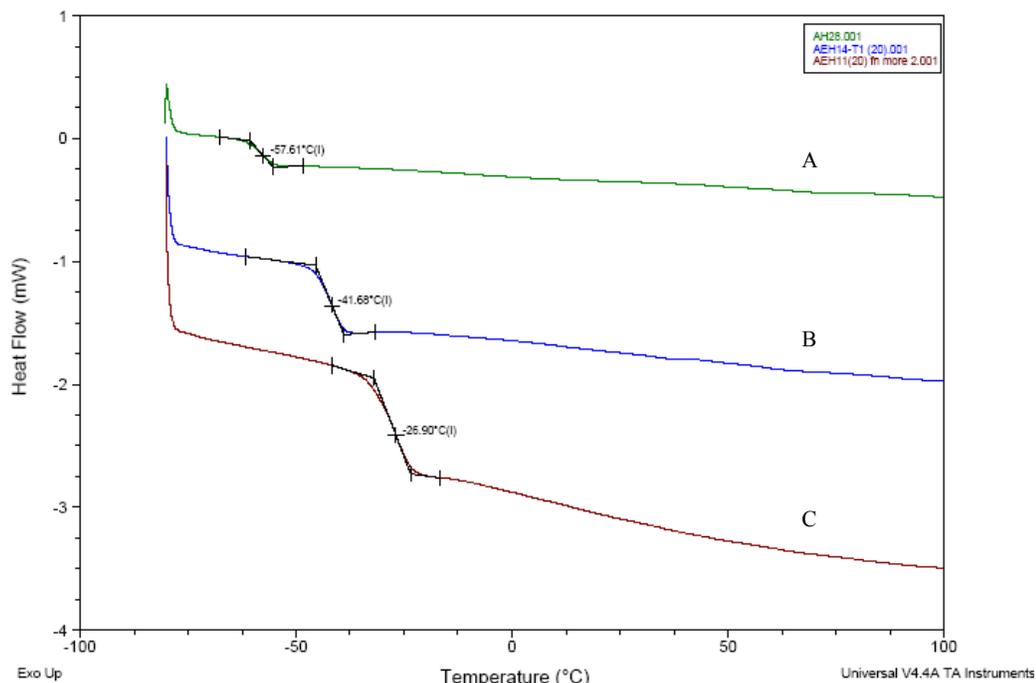
**Figure 5.30** DSC curves of the different molecular weight HTNR: A) HTNR1000, B) HTNR2000, and C) HTNR3400

All  $T_g$  results of oligomers (NR, HTNR 4, EHTNR 5, HHTNR 6 and HTNR( $\overline{fn} > 2$ ) 7) evaluated from the second heating thermogram at heating rate 10 °C min<sup>-1</sup> under nitrogen atmosphere were presented in the **Table 5.3** and it shows that  $T_g$  of HTNR1000, 2000 and 3400 g mol<sup>-1</sup> are slightly decreased compared with that of natural rubber (NR), respectively due to the decrease of molecular weight as shown in **Figure 5.30**. Raypol1020 and 3003 are commercial polyether precursors. Their  $T_g$  are about -70 °C due to the ether groups on the chain which increases flexibility of chains.



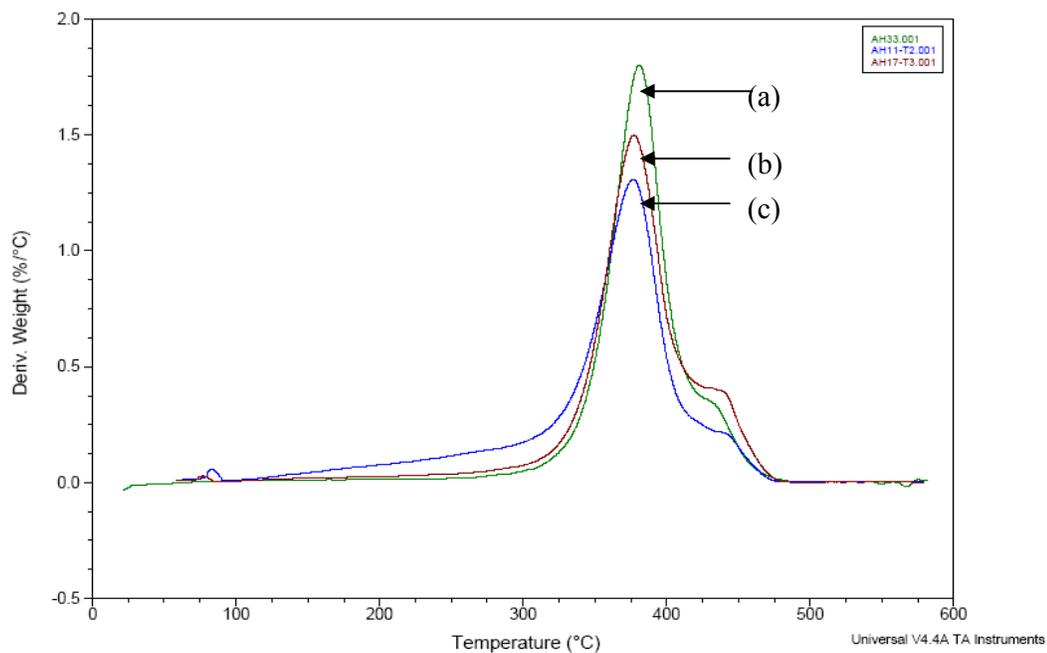
**Figure 5.31**  $T_g$  versus epoxide content on HTNR: ◆ based HTNR1000 and ■ based HTNR2000

Both epoxidized hydroxytelechelic natural rubbers (EHTNR) give an increasing  $T_g$  of oligomers depending on the increasing amount of epoxide groups (**Table 5.3**, **Figure 5.31** and **Appendix D (Figure 4D)**). For instance, 33% EHTNR1000 gives the highest  $T_g$  among all epoxidized oligoisoprenes derived from both HTNR1000 and 2000  $\text{g mol}^{-1}$ . The increasing of epoxide on main chain gives higher rigid backbone, inducing a decrease of backbone movement and an occurrence of chain interactions. This hypothesis was again supported by an increased of  $T_g$  of HTNR( $\bar{f}_n > 2$ ) **7** which was reduced from EHTNR **6** when compared with the starting material (EHTNR **6**). These results are caused by chain interactions which increase with hydroxyl groups on polymer chain as shown in **Figure 5.32**.

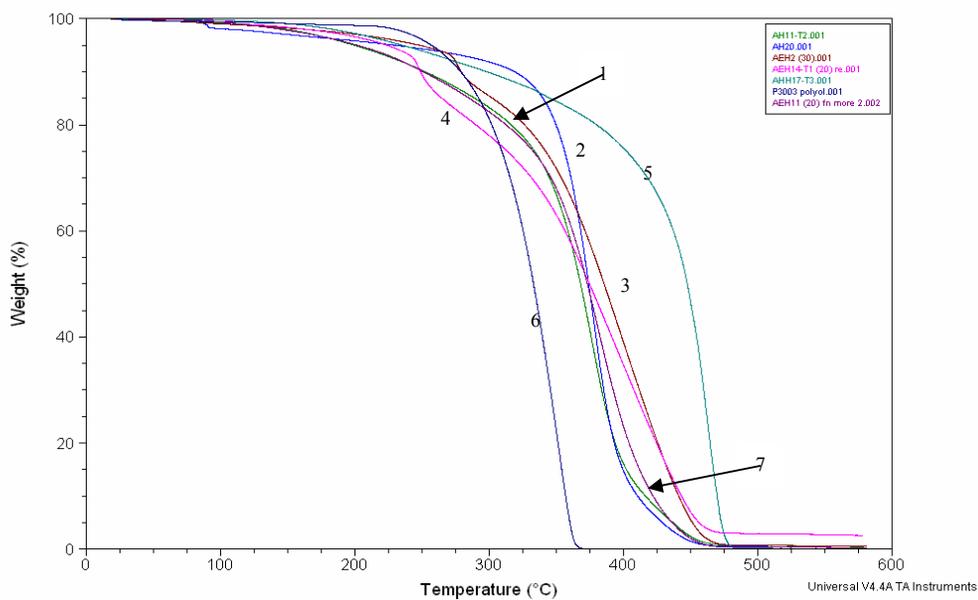


**Figure 5.32** DSC curves of the different molecular weight of HTNR: A) HTNR1000, B) 23%EHTNR1000, and C) HTNR1000( $\overline{M}_n > 2$ ) (23)

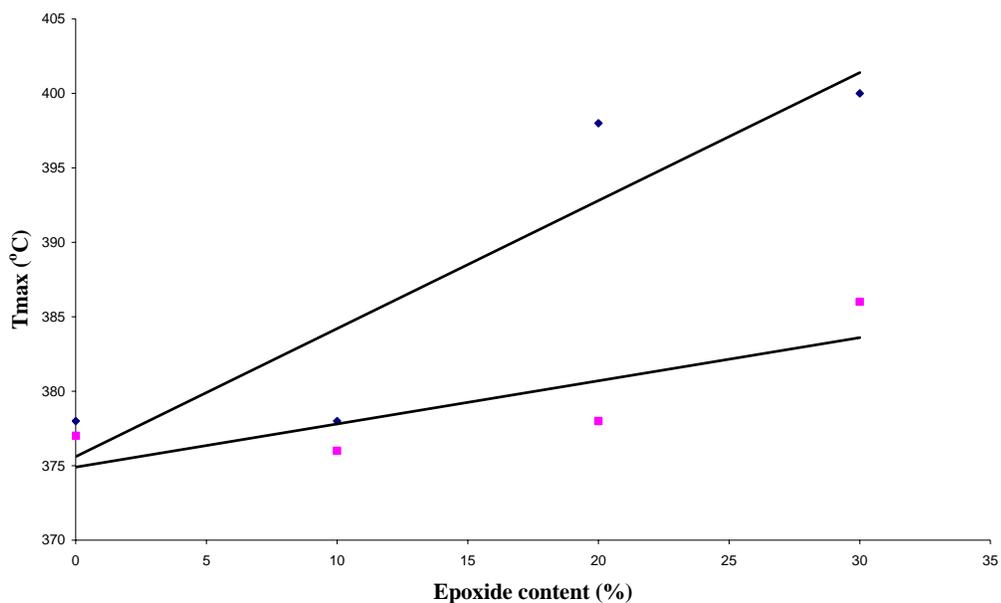
The study of the thermal stability of oligomers in different molecular weights and microstructures were carried out in nitrogen at  $10\text{ }^\circ\text{C min}^{-1}$  heating rate. Examples of TGA curves are presented in **Figure 5.33** and **Table 5.3**. Thermal stability of HTNR with different molecular weight was between  $378\text{--}382\text{ }^\circ\text{C}$ . It is noteworthy that there is no influence of molecular weight on thermal degradation of HTNR. Same curves are observed for the three studied HTNR. However, the lower molecular weight gave trend to lower the initial degradation temperature compared with the larger molecule.



**Figure 5.33** Derivation TGA curve of HTNR precursors: (a) HTNR1000, (b) HTNR2000, (c) HTNR3400



**Figure 5.34** TGA curves of oligomers under nitrogen atmosphere: (1) HTNR1000, (2) HTNR2000, (3) 36%EHTNR1000, (4) 23%EHTNR1000, (5) HHTNR, (6) 3003, (7) HTNR( $\bar{f}_n > 2$ ) (23)



**Figure 5.35** Tmax in the second step versus epoxide content on HTNR: ■ based HTNR1000 and ◆ based HTNR2000

The thermal degradation of HHTNR shows also one step (**Figure 5.34**, curve 5). Its Tmax of more than 460 °C is the noticeably highest compared with those of the other oligoisoprenes studied. This degradation step is due to the oxidation which its contribution is higher than HTNR and other modified HTNRs. It is clear that the better thermal stability of HHTNR is caused by the increasing of saturated unit (98%) in main polyisoprene chain. In this case, the thermal stability of hydroxytelechelic natural rubber can be improved by hydrogenation process.

In the case of EHTNR series in both HTNR1000 and 2000, the thermal degradation curves show two step of weight loss. The first step (i.e, 11%EHTNR1000 curve 3 and 33%EHTNR1000 curve 4) which probably corresponds to the degradation of epoxidized moieties located near the end-group of the oligomer chains or to the degradation of small molecules. Intermolecular reactions between the remaining epoxide moieties can possibly occur to lead to the increase in thermal stability observed in the second step as shown in **Figure 5.35**.

### **5.3 Preparation of polyurethane foams**

In this work, the novel renewable source precursors from natural rubber were used to prepare polyurethane foams by one shot technique. The influence of mixing speed during the process on, the effect of molecular weight and microstructure of precursors as well as the effect of type and amount of chain extenders on their physico-mechanical, thermal and acoustic properties compared with commercial precursor analogues were discussed. Their formulas are shown in **Tables 4.3-4.5**.

#### **5.3.1 Synthesis and characterization of HTNR and commercial precursors based polyurethane foams**

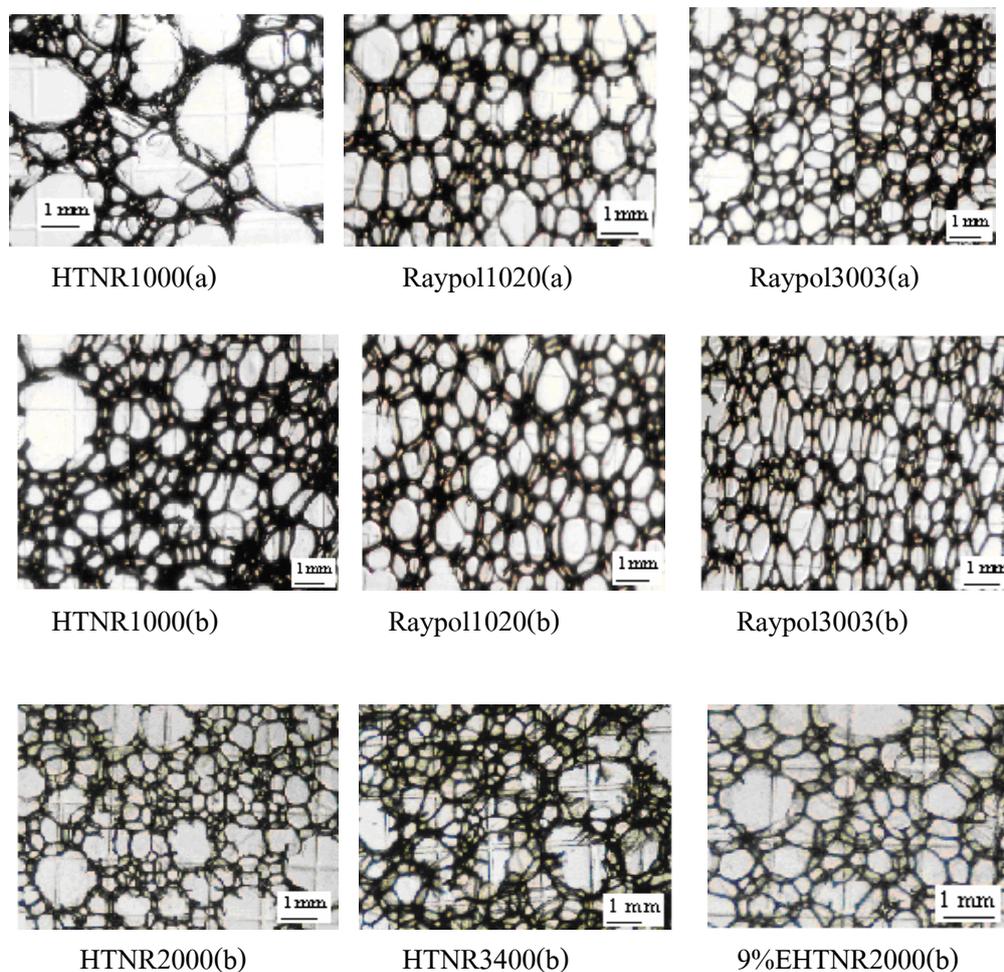
##### **5.3.1.1 Effect of mixing speed on the morphological properties of polyurethane foams**

In this topic, the effect of mixing speed in polyurethane foam synthesis process on the morphological properties of foams was studied. The mixing speed of mixer was used in two level speeds (i.e. 1000 and 11000 rpm). Cell counts, cell sizes, densities and light micrographs are collected in **Table 5.4** and **Figure 5.36**.

**Table 5.4** Physical properties of polyurethane foams prepared by the different mixing speeds for foams synthesis process

Speed (rpm)	Samples	Precursors	Appearance	Cell count (cells)	Cell size (mm)	Density (Kg m <sup>-3</sup> )
1000	PUF9	Raypol1020	L-y, F	22 ± 1.5	0.45	40.0 ± 1.9
	PUF5	Raypol3003	L-y, F	25 ± 2.4	0.40	42.2 ± 2.2
	PUF1	HTNR1000	Y, S-f	11 ± 1.6	0.91	66.5 ± 3.5
11000	PUF4	Raypol1010	L-y, F	24 ± 1.1	0.42	28.7 ± 3.1
	PUF9	Raypol1020	L-y, F	22 ± 1.7	0.46	33.9 ± 2.8
	PUF5	Raypol3003	L-y, F	25 ± 1.9	0.38	29.4 ± 2.2
	PUF14	Raypol3003 (Gly)	L-y, F	27 ± 1.3	0.38	30.8 ± 2.6
	PUF1	HTNR1000	L-y, F	24 ± 1.8	0.42	28.7 ± 4.3
	PUF2	HTNR2000	L-y, F	23 ± 0.7	0.42	20.0 ± 3.7
	PUF13	HTNR2000 (Gly)	L-y, F	25 ± 1.3	0.40	20.9 ± 2.9
	PUF3	HTNR3400	L-y, F	26 ± 0.6	0.38	24.5 ± 2.6
	PUF6	9%EHTNR2000	L-y, F	26 ± 1.2	0.38	18.6 ± 1.7
	PUF7	23%EHTNR2000	L-y, F	23 ± 1.9	0.43	23.5 ± 2.6
	PUF8	35%EHTNR2000	L-y, F	26 ± 2.0	0.38	22.8 ± 2.9
	PUF11	HTNR1000(2BD)	L-y, S-f	21 ± 1.9	0.47	32.6 ± 5.0
PUF12	HTNR1000(4BD)	L-y, S-f	22 ± 0.6	0.45	38.8 ± 2.0	

L= light-yellowish, Y = yellowish, F = flexible, S-f = semi-flexible



**Figure 5.36** Photographs of samples of polyurethane foams from different precursors at speed (a) 1000 rpm and (b) 11000 rpm ( $\times 22$ )

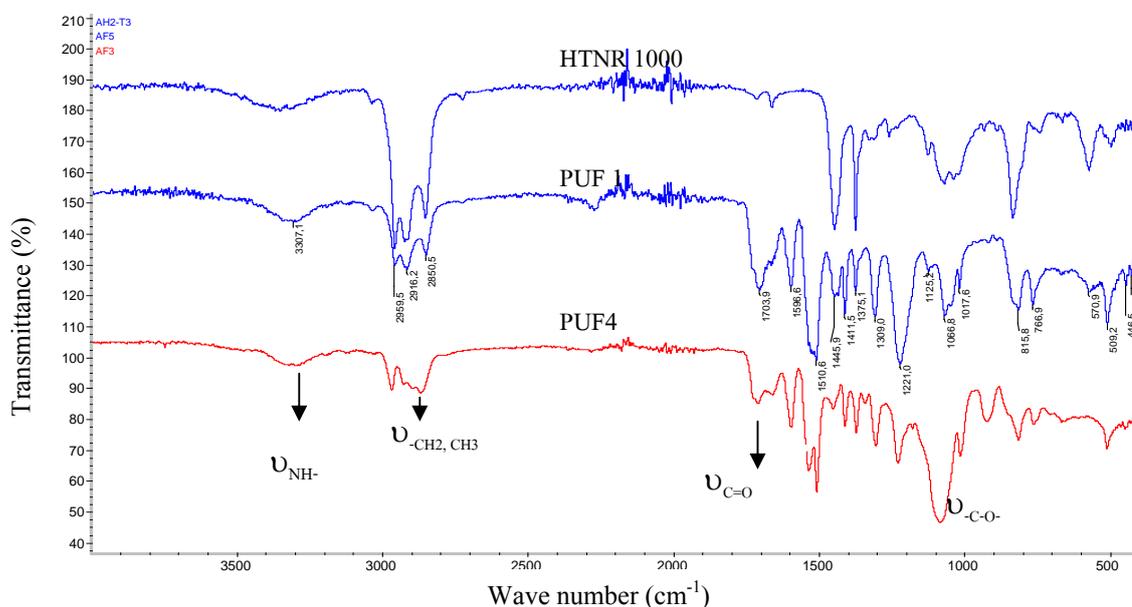
Densities of HTNR1000 or commercial polyols based polyurethane foams in **Table 5.4** prepared with a mixing speed of 1000 rpm are approximately  $66 \text{ kg m}^{-3}$  and  $36\text{-}42 \text{ kg m}^{-3}$ , respectively. The cell sizes of foams based from HTNR are bigger and less homogenous as well as with thicker cell wall than the others based from commercial precursors as shown in **Figure 5.36** and **Table 5.4**. It was clearly seen that the high viscosity and hydrophobicity of HTNR as well as the too slow a speed of mixer caused to be less the amount of nuclei (the starting of cells) or promote a good dispersion of all additives. Therefore, large cells and low consistency dimensions cells foam with high density were obtained. However, this problem with HTNR can be solved by increasing speed of mixer during process. It facts that a silicone surfactant can improve the mixing of the viscous and hydrophobic (HTNR) with hydrophilic additives such as

water. However, morphology and density of the other foams were slightly affected by an increasing of the speed mixing.

Evidently the cell dimensions are shown in **Figure 5.36** and **Table 5.4**. It was observed that the cell sizes of foams based on HTNR and commercial polyols were not significantly different. Spherical cells and regular size distributions are observed. Their cell sizes are between 0.38 and 0.47 mm. Moreover, it was also indicated that the obtained foams based on HTNR exhibited open cell structure.

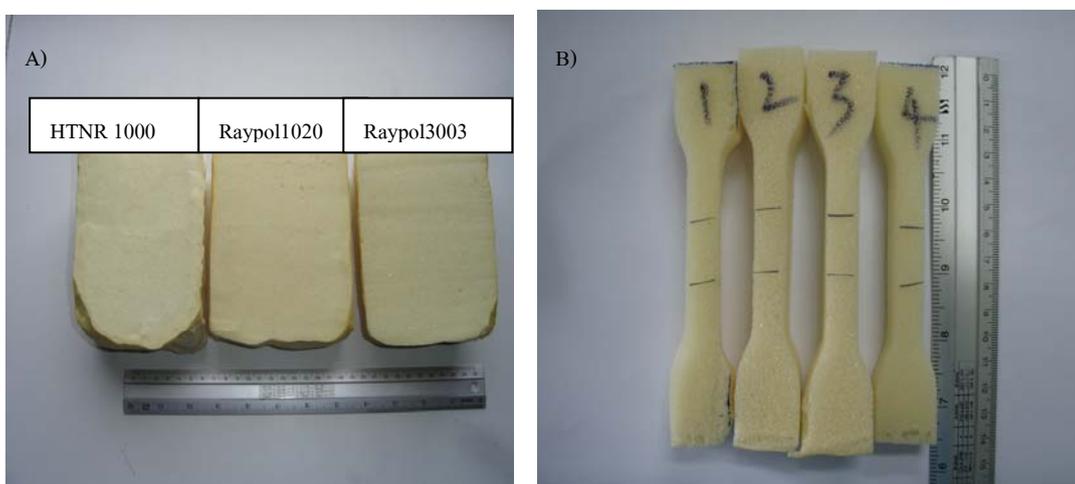
### 5.3.1.2 Characterization of polyurethane foams

HTNR based polyurethane foams were performed using the formulations ingredients as shown in **Table 4.3**, with constant isocyanate index of 100 in each formula. All polyurethane foams were synthesized by the one-shot process using a speed mixing at 11000 rpm until whiten color occurred at room temperature. The mixture was then poured into moulds and put in the oven at 40 °C. The samples were continued to stand for curing for 48 h at 40 °C before characterization and physico-mechanical, thermal and acoustic testing



**Figure 5.37** IR spectra of polyurethane foams based HTNR1000 (PUF1) compared with commercial precursor Raypol1010 (PUF4)

Chemical structure of all polyurethane foams was determined by ATR technique. Examples of obtained spectra are given in **Figure 5.37**. The IR spectrum of all the polyurethanes confirmed their chemical structure by the existence of absorptions at nearly  $3300$  and  $1700\text{ cm}^{-1}$  corresponding to N–H and C=O stretching vibrations of urethane functions respectively. Polyurethane foams prepared from commercial precursor (polyether polyols) show the stronger absorption peak at  $1100\text{ cm}^{-1}$  corresponding to C–O- stretching vibration. The disappearance of absorption peak at  $2270\text{ cm}^{-1}$  presents the absence of residual NCO in all foams. Samples of polyurethane foam buns and tensile specimens are shown in **Figure 5.38**.



**Figure 5.39** Photographs of polyurethane foam: (A) buns and (B) tensile specimens

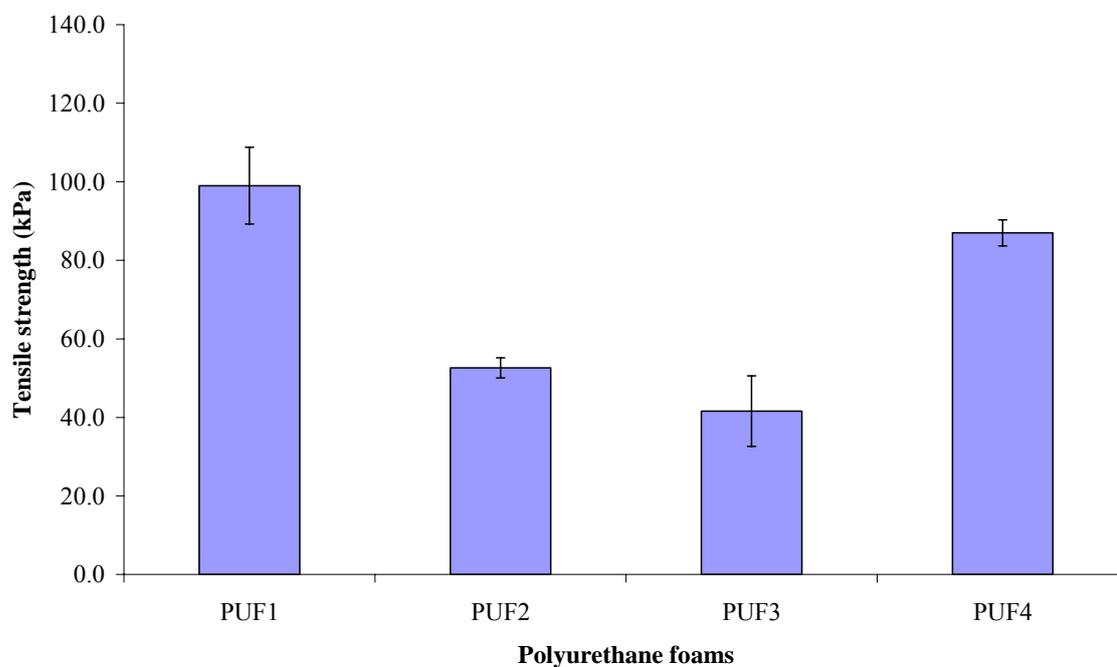
### 5.3.2 Physico-mechanical properties of polyurethane foams

#### 5.3.2.1 Effect of molecular weight of precursors

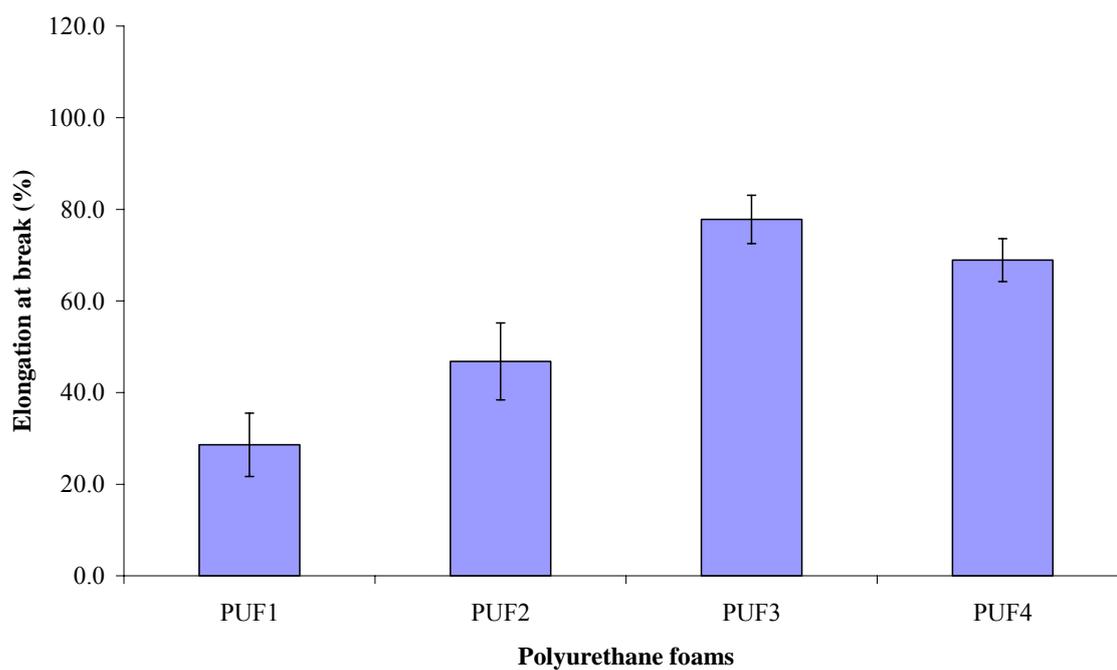
In this part, the effect of molecular weight of HTNR precursors on the physico-mechanical properties of polyurethane foams were studied in comparison with those of foams based on commercial polyol (Raypol1010) following the formulations in **Table 4.3**. The molecular weights were varied at 1000, 2000, and  $3400\text{ g mol}^{-1}$ . These results are shown in **Table 5.5** and **Figures 5.39-5.42**.

**Table 5.5** Effect of molecular weight of precursors on physico-mechanical properties of polyurethane foams

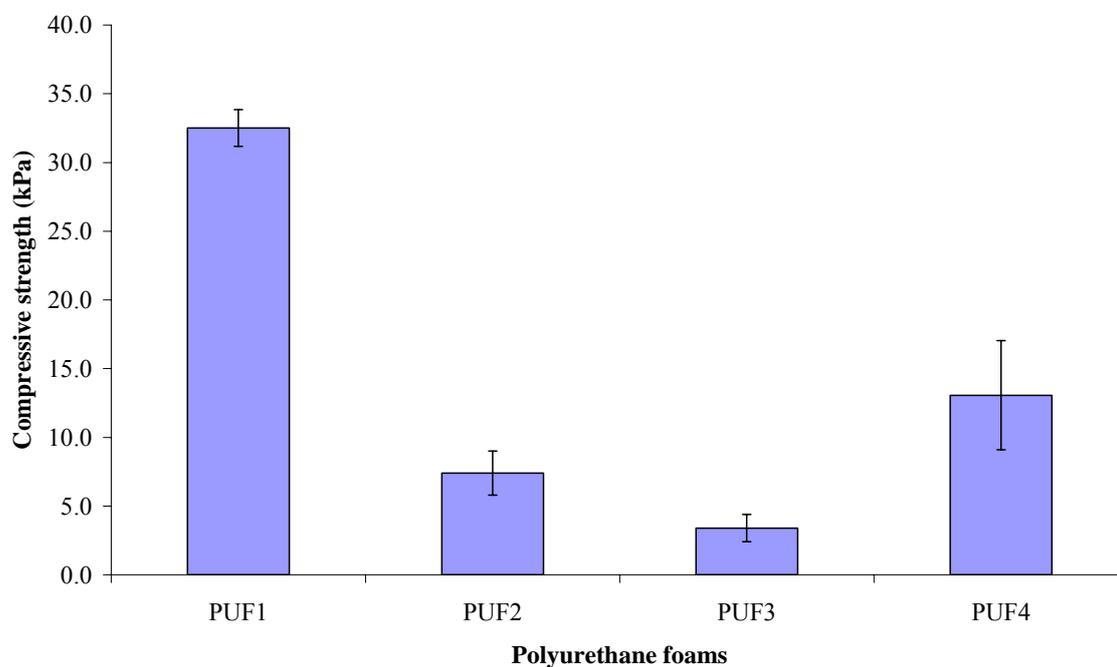
Samples	Precursors	Hard segment (%)	Density (Kg m <sup>-3</sup> )	Tensile strength (kPa)	Elongation at break (%)	Compressive strength (kPa)	Compression set (%)
PUF1	HTNR1000	48.6	28.7 ± 4.3	99.0 ± 9.8	28.6 ± 6.9	32.5 ± 1.3	46.0 ± 0.8
PUF2	HTNR2000	43.7	20.0 ± 3.7	52.6 ± 2.5	46.8 ± 8.4	7.4 ± 1.6	36.5 ± 1.8
PUF3	HTNR3400	42.6	24.5 ± 2.6	41.6 ± 9.0	77.8 ± 5.3	3.4 ± 1.0	9.5 ± 0.7
PUF4	Raypol1010	48.2	28.7 ± 3.1	87.0 ± 3.3	68.9 ± 4.7	13.1 ± 4.0	45.9 ± 0.4



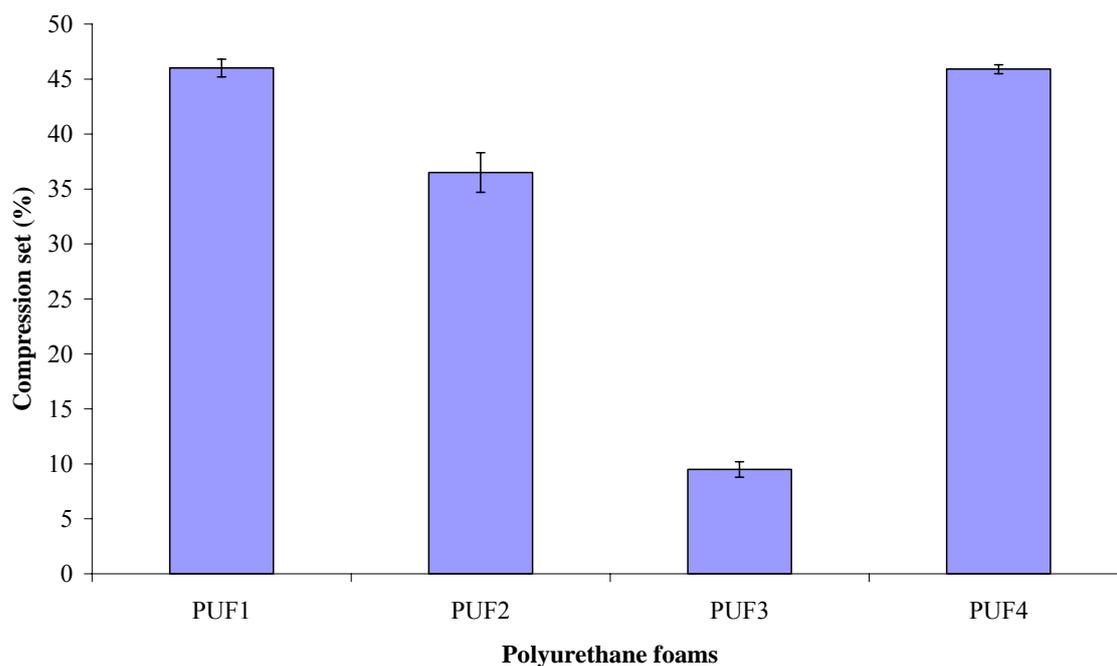
**Figure 5.39** Effect of molecular weight of precursors on tensile strength of polyurethane foams



**Figure 5.40** Effect of molecular weight of precursors on elongation at break of polyurethane foams



**Figure 5.41** Effect of molecular weight of precursors on compressive strength of polyurethane foams



**Figure 5.42** Effect of molecular weight of precursors on compression set of polyurethane foams

Densities of flexible polyurethane foams were determined according to ASTM D 3574 and are shown in **Table 5.5**. The densities of polyurethane foams based on HTNR were in the range of  $20\text{--}28\text{ kg m}^{-3}$ , whereas the densities of commercial precursors based polyurethane foams are varied from  $28\text{--}34\text{ kg m}^{-3}$ .

The physico-mechanical properties of HTNR based polyurethane foams (PUF1, PUF2, and PUF3) with varied molecular weights precursors ( $1000$ ,  $2000$ , and  $3400\text{ g mol}^{-1}$ ) were compared with those of the commercial analogue as shown in **Table 5.5** and **Figures 5.39–5.42**. It was found that PUF1 gives the highest tensile strength and compressive strength in all of HTNR based polyurethane foams (PUF2 and PUF3) (**Figure 5.39** and **5.41**). These results were influenced by the molecular weight of the precursor HTNR1000 which evidently has a shorter length between two hydroxyl end groups resulting in an increase of percentage of hard segments in the polyurethane foam. The results are in agreement with the previous work which studied polyisobutylene isoprene triol (Ako and Kennedy, 1989), in which the mechanical properties (tensile and compressive strengths) of polyurethane based elastomers were increased with decreasing molecular weight of triol. In the same manner, increasing amount of hard segments in hydroxyl polybutadienes (HTPB) and hydroxyl terminated natural rubber based polyurethanes led to an increase of tensile and compressive strengths (Huang and Lai, 1997; Paul *et al.*, 1998). Thus, we have obtained much tensile and compressive

strengths, when we used a lower molecular weight HTNR. On the contrary, the flexibility of foams was decreased with a lower molecular weight. The elongation at break (**Figure 5.40**) and compression set (**Figure 5.42**) of PUF1 was poorer than that of PUF2 and PUF3, respectively.

The physico-mechanical properties are markedly dependent on foam density. Generally, tensile and compressive strengths increase with increasing density. Even though it is very difficult to compare the influence of microstructure of precursors on properties of foams, fortunately, the density in both HTNR1000 and commercial polyol (Raypol1010) based polyurethane foams are similar, i.e., approximately  $28 \text{ kg m}^{-3}$ . Therefore, the mechanical properties of both polyurethane foams based on HTNR1000 and commercial polyols (Raypol1010) can be compared without the influence of density.

**Figure 5.39** and **5.41** show the tensile and compressive strengths of polyurethane foams, respectively. It was investigated that the polyurethane foam based on HTNR1000 has higher than those of the foam based on commercial polyol due to the different structure of precursors. The HTNR is isoprenic structure which has stronger tensile and compressive strengths of PUF1 were higher but elongation at break was lower. This is agreement with the results of Ako and Kennedy, which reported the preparation of polyurethane foam based on polyisobutylene isoprene (PIB) triol comparing with those based on polyether triol in the same range of molecular weight at isocyanate index 105. Their results revealed that the mechanical properties of polyurethane foams based PIB triol were superior to those of polyether triol based polyurethane foams (Ako and Kennedy, 1989).

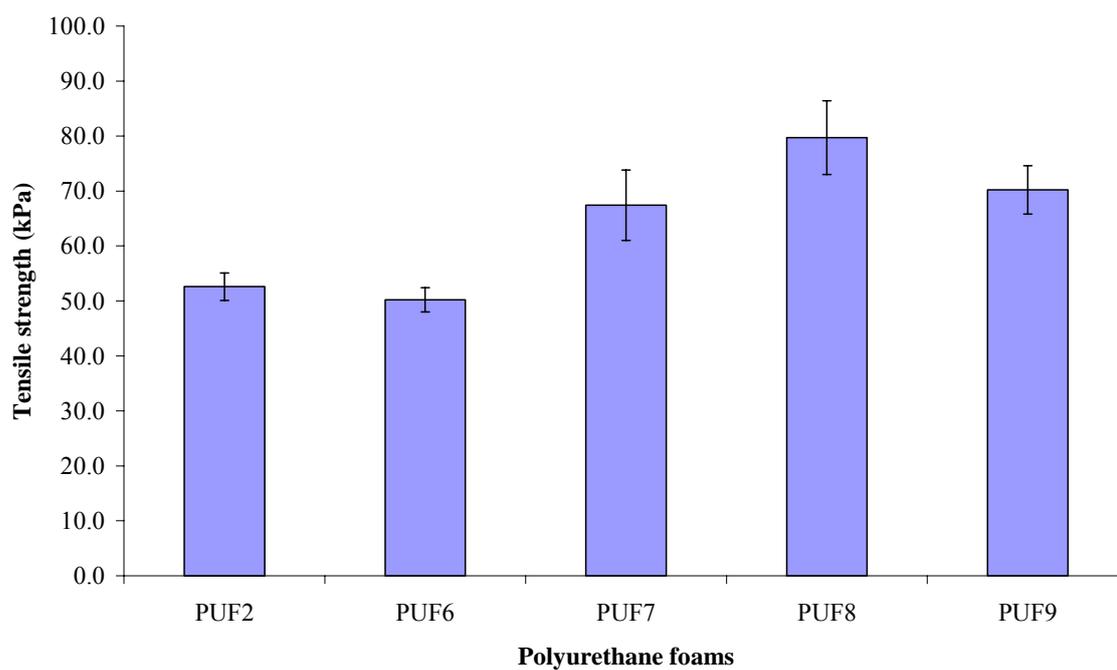
The compression set test was performed by deflecting the foam specimen to 50% initial thickness, exposing it to  $70 \text{ }^{\circ}\text{C}$  for 22 h and finally measuring the change in the thickness of specimen after recovery at room temperature for 30 min. A lower compression set indicates that the foam is more flexible or high elasticity i.e., it can recover better to its original shape after deformation. It was found that both foams types (HTNR based PUF1 and commercial polyol based PUF4) have poor thickness recovery. The inferior compression set of PUF1 and PUF4 foams is attributed to the effect of high amount of hard segment (Schoor *et al.*, 2004). On the other hand, PUF3 based on HTNR3400 with longer soft segment has excellent flexibility properties or elastic behavior as shown in **Figure 5.42**.

### 5.3.2.2 Effect of epoxide content

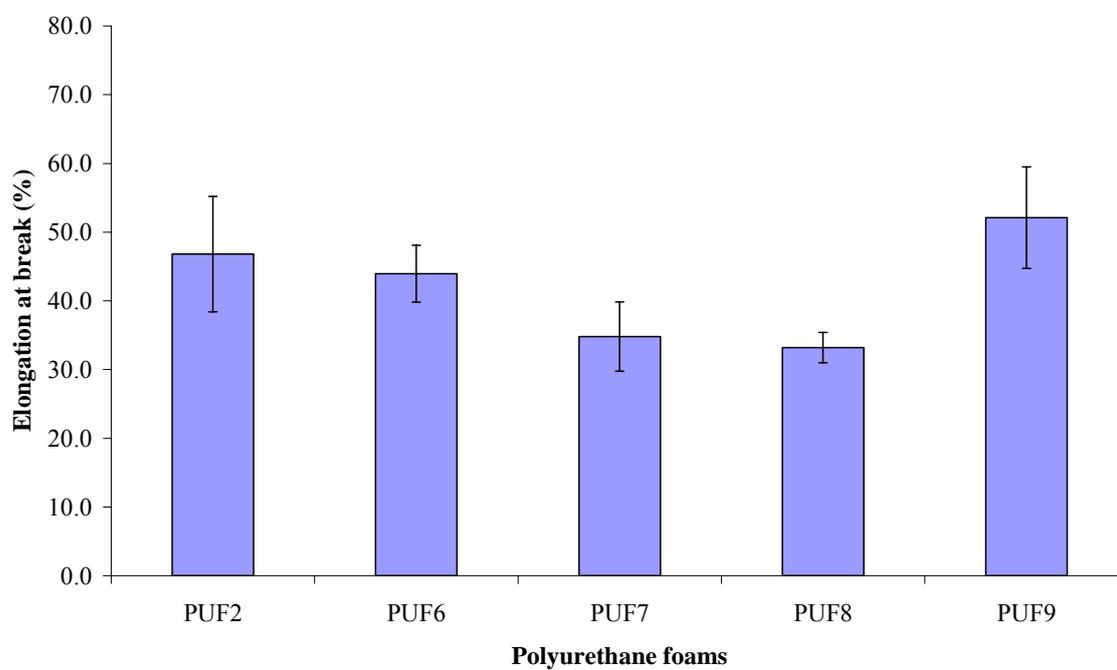
The effect of epoxide content on physico-mechanical properties of polyurethane foams were studied by using various three epoxide contents 0%, 9%, 23% and 35% to prepare with HTNR2000 based PUF2, PUF6, PUF7 and PUF8, respectively. The commercial polyol (Raypol1020 based PUF9) was also prepare for comparison purpose. The formations are shown in **Table 4.4**. The results are shown in **Table 5.6** and **Figures 5.43-5.46**.

**Table 5.6** Effect of epoxide content on HTNR on physico-mechanical properties of polyurethane foams

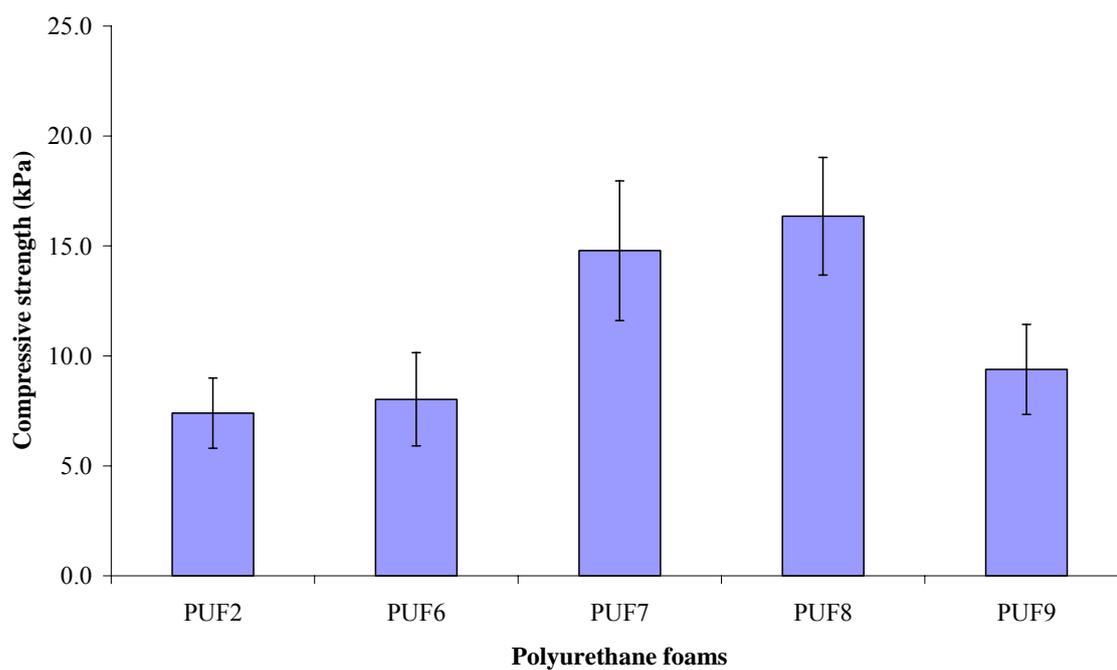
Samples	Precursors	Hard segment (%)	Density (Kg m <sup>-3</sup> )	Tensile strength (kPa)	Elongation at break (%)	Compressive strength (kPa)	Compression set (%)
PUF2	HTNR 2000	43.7	20.0 ± 3.7	52.6 ± 2.5	46.8 ± 8.4	7.4 ± 1.6	36.5 ± 1.8
PUF6	9%EHTNR 2000	43.7	18.6 ± 1.7	50.2 ± 2.2	44.0 ± 4.2	8.0 ± 2.1	42.9 ± 2.0
PUF7	23%EHTNR 2000	44.3	23.5 ± 2.6	67.4 ± 6.4	34.8 ± 5.0	14.8 ± 3.2	46.6 ± 0.8
PUF8	35%EHTNR 2000	44.6	22.8 ± 2.9	79.7 ± 6.7	33.2 ± 2.2	16.4 ± 2.7	47.0 ± 1.8
PUF9	Raypol 1020	44.0	33.9 ± 2.8	70.2 ± 4.4	52.1 ± 7.4	9.4 ± 2.0	40.1 ± 1.2



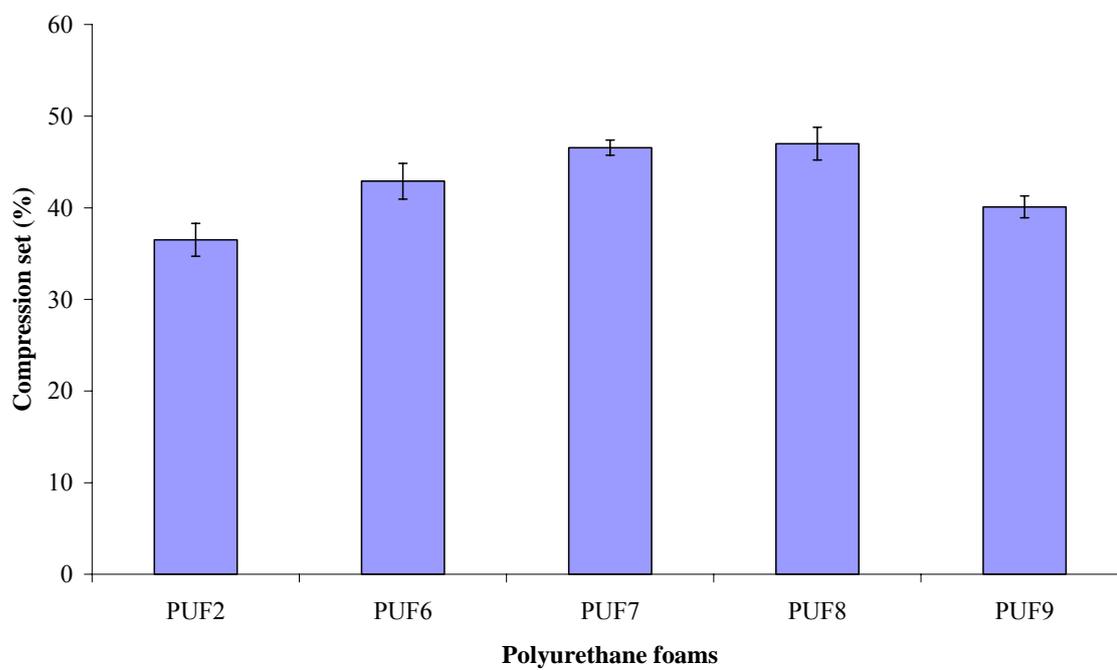
**Figure 5.43** Effect of epoxide content on tensile strength of polyurethane foams



**Figure 5.44** Effect of epoxide content on elongation at break of polyurethane foams



**Figure 5.45** Effect of epoxide content on compressive strength of polyurethane foams



**Figure 5.46** Effect of epoxide content on compression set of polyurethane foams

The physico-mechanical properties of HTNR2000 based polyurethane foams with various epoxide contents (PUF6; 9%, PUF7; 23% and PUF8; 35%) and those of commercial precursors based foam (PUF9; Raypol1020) are shown in **Table 5.6** and **Figures 5.43–5.46**. It was clear that tensile and compressive strengths of polyurethane foams based on HTNR are better but elongation at break and compression set are worse with an increasing amount of epoxide on precursors. It is possible that the cell wall and struts in polyurethane foams become more rigid and damage under compression leading to poor recovery after testing. Tu and coworkers (2008) reported the similar effect of epoxidized precursor on properties of flexible polyurethane foam. They found that the replacing up to 20% of polyether polyol by epoxidized soybean oil in flexible foams led to a better compressive strength but inferior compression set.

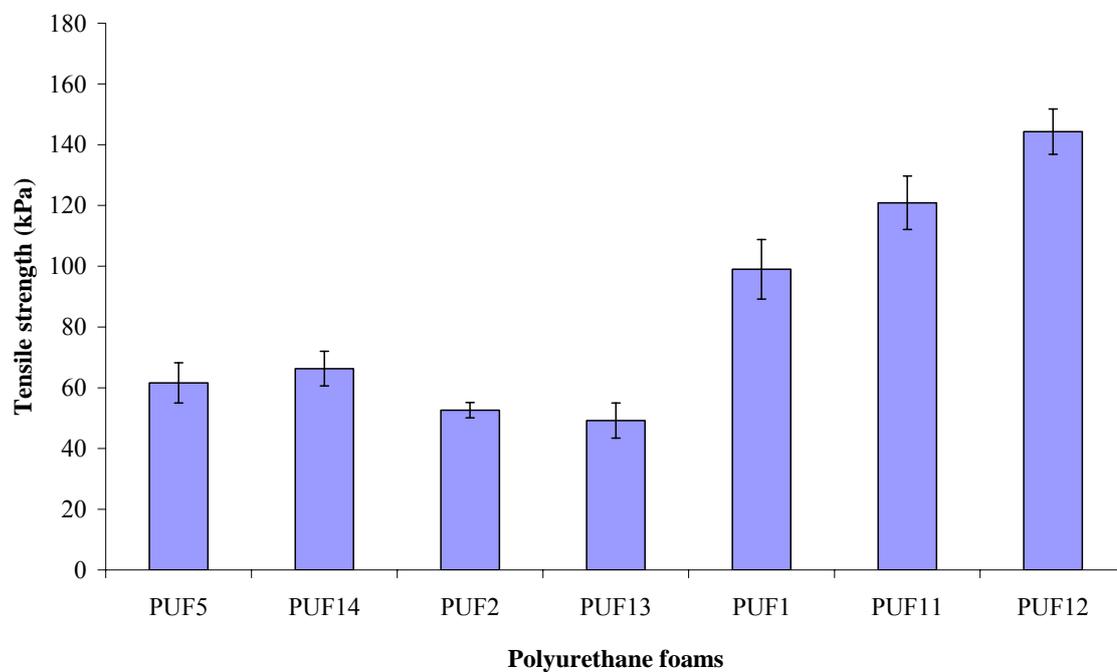
The influence of microstructure on the mechanical properties of PUF2 (HTNR2000) and PUF9 (Raypol1020) was difficult to analyze due to their difference in densities (approximately 20 and 34 kg m<sup>-3</sup>). However, the lower density PUF7 and PUF8 (23% and 35% EHTNR2000 based polyurethane foams) have better mechanical properties i.e., higher tensile and compressive strengths than PUF9 based on Raypol1020.

### 5.3.2.3 Effect of type and amount of chain extenders

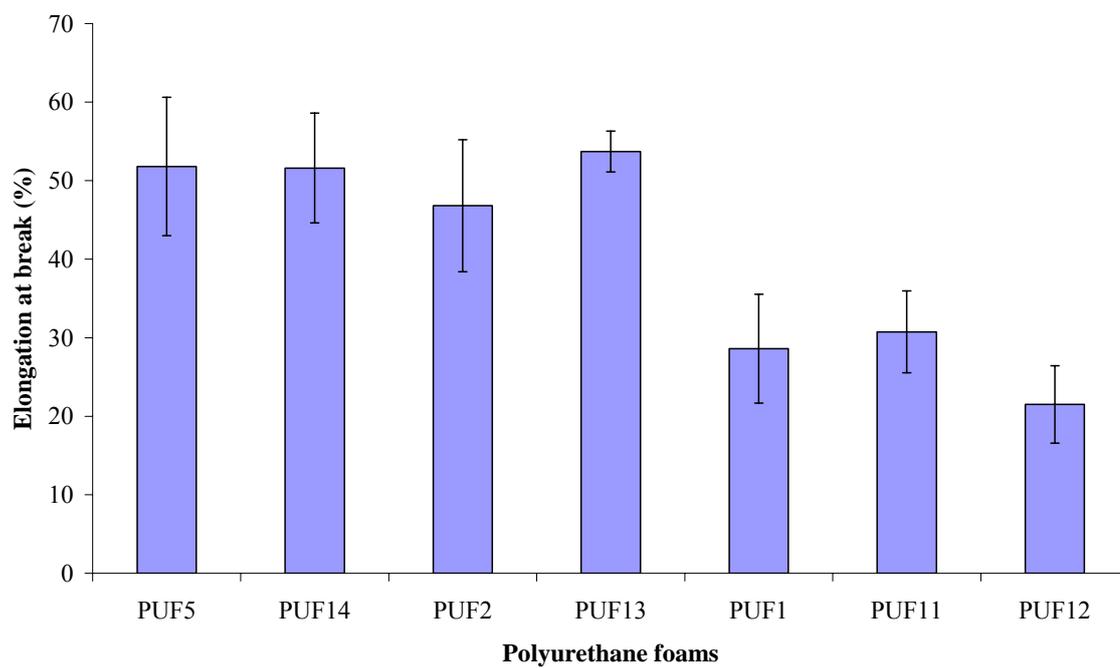
Polyurethane foams were studied on the effect of type and amount of chain extenders on physico-mechanical properties. The effect of two types of chain extenders (difunctional chain extender (1,4-butanediol, BD) and trifunctional chain extender (Glycerol, Gly)) was studied in HTNR2000 based polyurethane foam and in commercial precursor (Raypol3003) polyurethane foam. The influence of the amount of 1,4-butanediol (0.19, 0.38 and 0.78 g) in HTNR1000 based polyurethane foams was also studied. These results are showed in **Table 5.7** and **Figures 5.47-5.50**.

**Table 5.7** Effect of type and chain extenders content on physico-mechanical properties of polyurethane foams

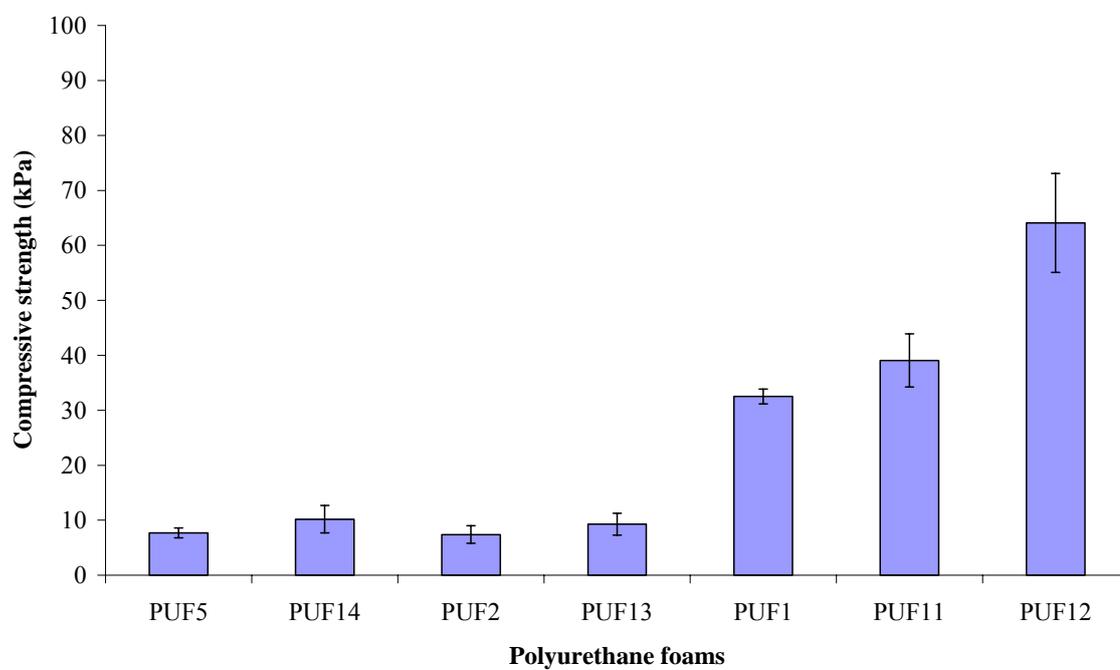
Samples	Precursors and chain extenders	Hard segment (%)	Density ( $\text{Kg m}^{-3}$ )	Tensile strength (kPa)	Elongation at break (%)	Compressive strength (kPa)	Compression set (%)
PUF5	Raypol3003 BD	44.0	$29.4 \pm 2.2$	$61.6 \pm 6.6$	$51.0 \pm 8.8$	$7.7 \pm 0.9$	$26.0 \pm 1.1$
PUF14	Raypol3003 Gly	44.2	$30.8 \pm 2.6$	$66.3 \pm 5.7$	$51.6 \pm 7.0$	$10.2 \pm 2.5$	$26.9 \pm 0.2$
PUF2	HTNR2000 BD	43.7	$20.0 \pm 3.7$	$52.6 \pm 2.5$	$46.8 \pm 8.4$	$7.4 \pm 1.6$	$36.5 \pm 1.8$
PUF13	HTNR2000 Gly	43.9	$20.9 \pm 2.9$	$49.2 \pm 5.8$	$53.7 \pm 2.6$	$9.3 \pm 2.0$	$38.0 \pm 1.4$
PUF1	HTNR1000 BD	48.6	$28.7 \pm 4.3$	$99.0 \pm 9.8$	$28.6 \pm 6.9$	$32.5 \pm 1.3$	$46.0 \pm 0.8$
PUF11	HTNR1000 2BD	49.0	$32.6 \pm 5.0$	$120.9 \pm 8.8$	$30.7 \pm 5.2$	$39.1 \pm 4.8$	$47.0 \pm 0.5$
PUF12	HTNR1000 4BD	49.7	$38.8 \pm 2.0$	$144.3 \pm 7.5$	$21.5 \pm 4.9$	$64.1 \pm 9.0$	$47.0 \pm 0.7$



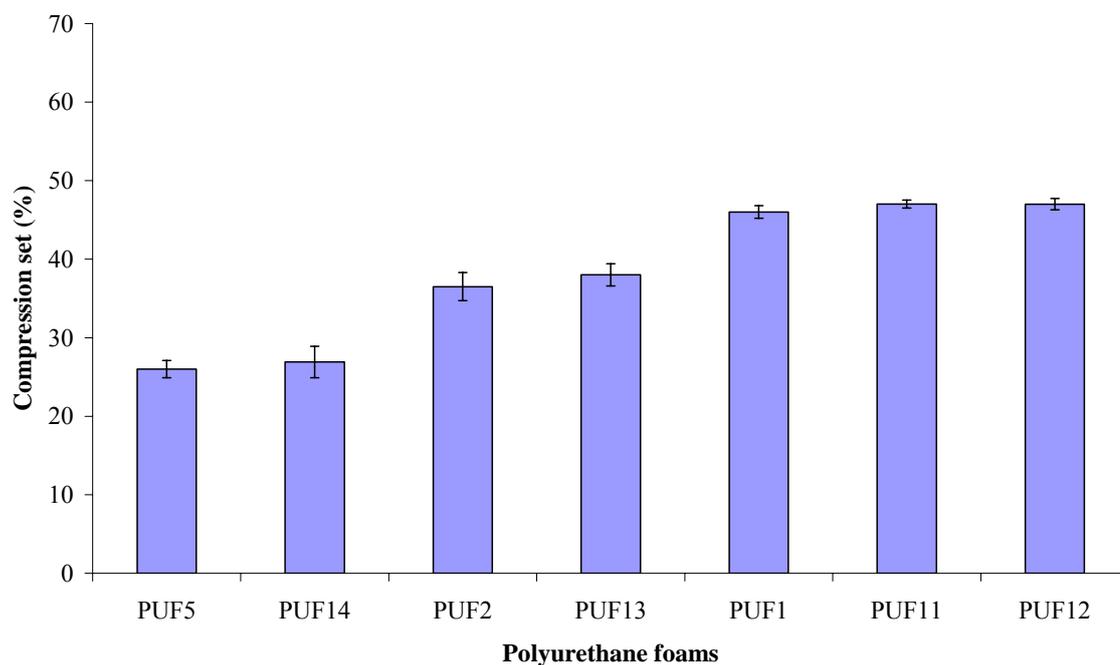
**Figure 5.47** Effect of type and chain extender content on tensile strength of polyurethane foams



**Figure 5.48** Effect of type and chain extender content on elongation at break of polyurethane foams



**Figure 5.49** Effect of type and chain extender content on compressive strength of polyurethane foams



**Figure 5.50** Effect of type and chain extender content on compression set of polyurethane foams

The results of influence of type of chain extender on physico-mechanical properties of polyurethane foam based on HTNR2000 and Raypol3003 and of the amount of chain extender 1,4-butanediol in foams based on HTNR1000 with isocyanate index equal to 100 are shown in **Table 5.7** and **Figures 5.47-5.50**. The properties of foams that used hydroxyl difunctional compound as chain extender (1,4-butanediol) and of that they used hydroxyl trifunctional compound as chain extender (glycerol) were compared. We observed that the tensile strength and compressive strength of foams using glycerol (PUF14 and PUF13) have a slightly higher values than those using 1,4-butanediol (PUF5 and PUF2). This phenomenon may be explained by the slight crosslink in the secondary alcohol position of glycerol. However, the effect of this trifunctional chain extender in foams on their properties is not clear. It seems to be the same effect than that observed with isocyanates (P-MDI) having functionality about 2.7 acting also as crosslinking agent. Elongation at break and compression set of foams using both 1,4-butanediol and glycerol give no different values as shown in **Figure 5.48** and **5.50**.

The amount of 1,4-butanediol (PUF1, 0.19g; PUF11, 0.38g; PUF12, 0.78g) on physico-mechanical properties of polyurethane foams on HTNR1000 was studied. This effect has more influence on the mechanical properties of foam than the type of chain extender. It was

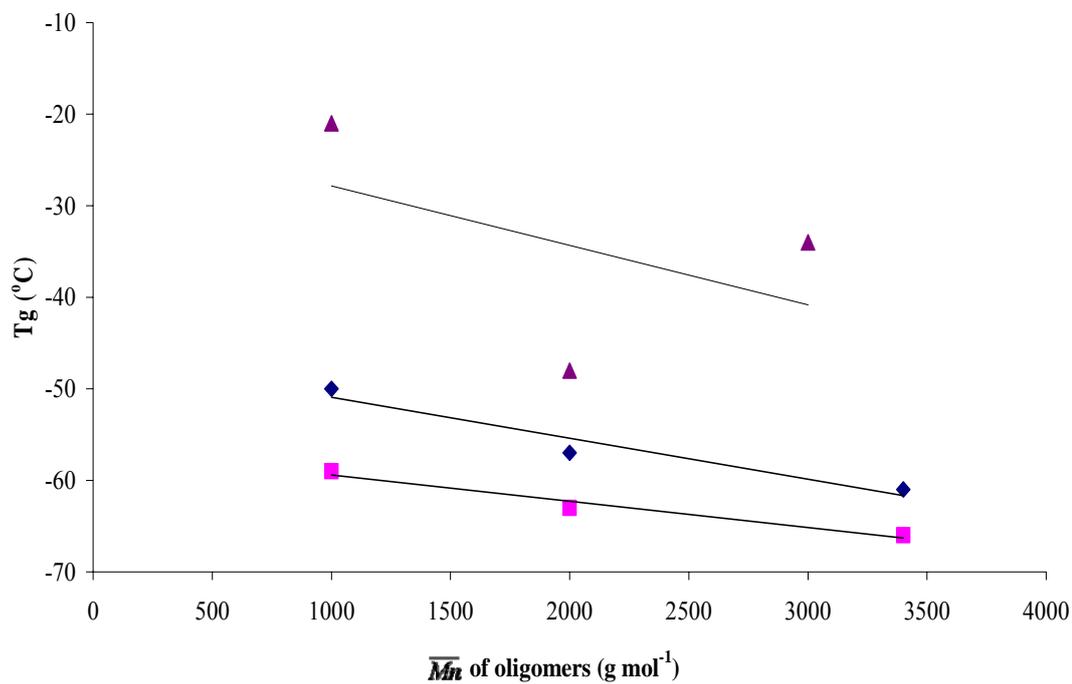
clearly shown that the tensile strength and the compressive strength of foams increased with increasing amount of 1,4-butanediol in foams with isocyanate index equal to 100. PUF12 has the highest values of tensile and compressive strengths. The increasing of mechanical properties is probably the result of both increased density and increased hard segment content. However, PUF12 shows no difference in elongation at break and compression set properties of foams.

### 5.3.3 Thermal properties of polyurethane foams

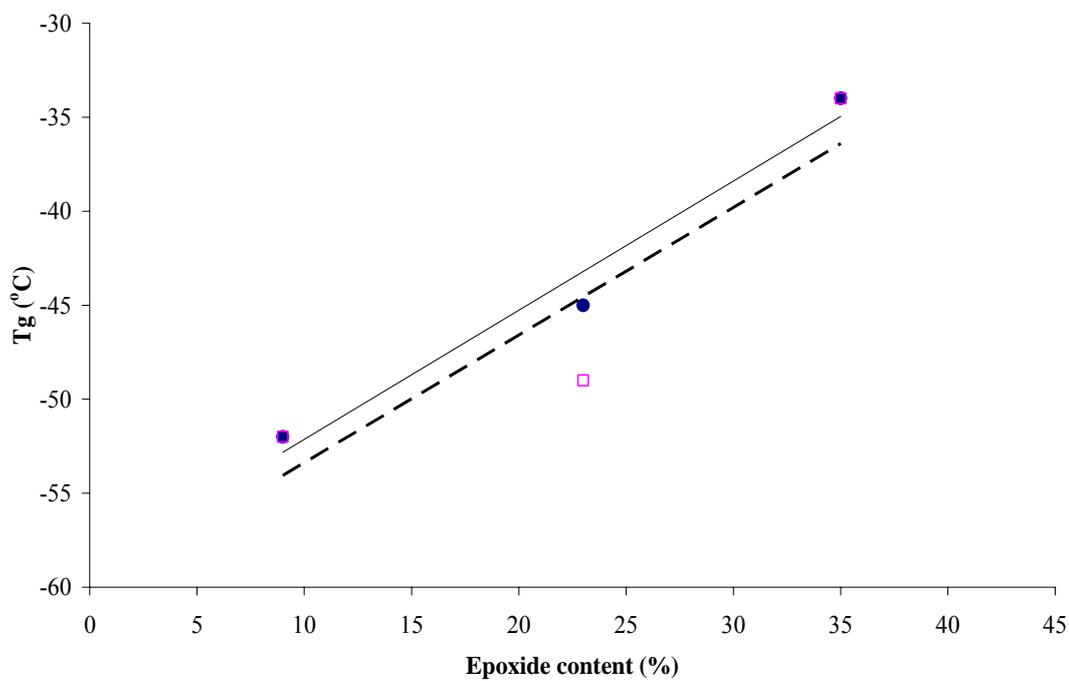
All thermal properties of polyurethane foams were studied by TGA and DSC. The results are showed in **Table 5.8**, **Appendix C** and **Appendix D**.

**Table 5.8** Thermal properties of polyurethane foams

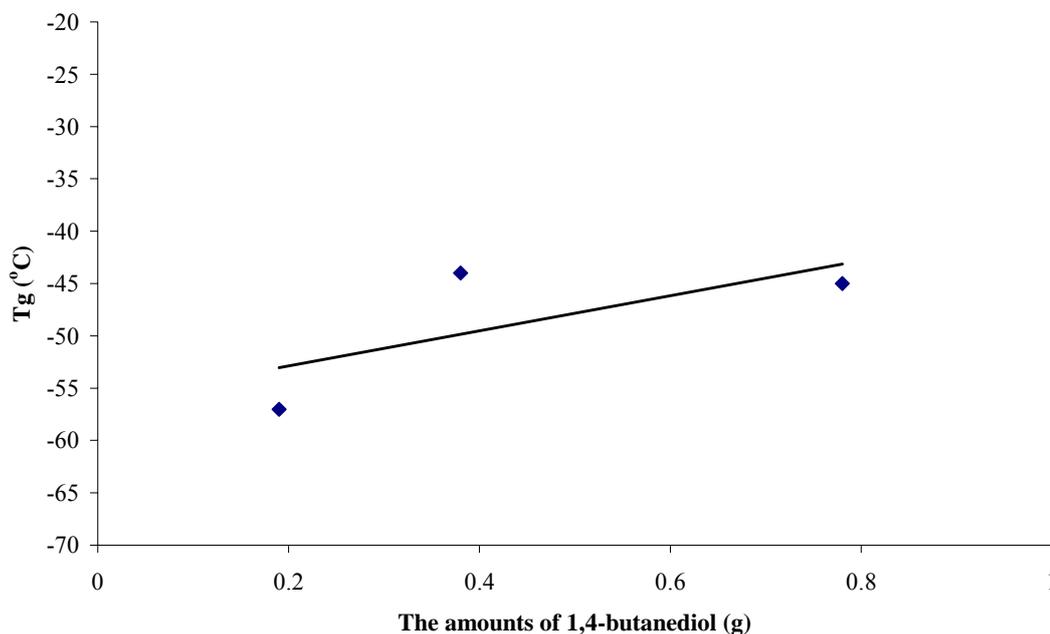
Samples	Precursors	T <sub>g</sub> (°C)	Thermal degradation steps			
			1 <sup>st</sup> step		2 <sup>nd</sup> step	
			T max (°C)	weight loss (%)	T max (°C)	weight loss (%)
PUF1	HTNR1000 (BD)	-50	306	43.8	372	48.7
PUF2	HTNR2000 (BD)	-57	301	32.1	378	52.0
PUF3	HTNR3400 (BD)	-61	293	14.2	380	76.5
PUF4	Raypol1010 (BD)	-21	309	36.0	375	54.4
PUF5	Raypol3003 (BD)	-34	292	24.8	385	67.3
PUF6	9%EHTNR2000 (BD)	-52	290	25.7	375	65.4
PUF7	23%EHTNR2000 (BD)	-45	302	27.4	381	66.9
PUF8	35%EHTNR2000 (BD)	-34	297	28.5	393	67.2
PUF9	Raypol1020 (BD)	-48	298	26.0	376	64.4
PUF11	HTNR1000 (2BD)	-44	302	41.6	371	51.0
PUF12	HTNR1000 (4BD)	-45	307	41.9	375	49.7
PUF13	HTNR2000 (Gly)	-56	296	25.0	378	68.3
PUF14	Raypol3003 (Gly)	-33	292	24.2	385	68.7



**Figure 5.51** T<sub>g</sub> (°C) versus  $\overline{Mn}$  of oligomers (g mol<sup>-1</sup>) (■ HTNR, ◆ HTNR based PUF, ▲ commercial oligomers based PUF)



**Figure 5.52** T<sub>g</sub> (°C) versus epoxide content (%) (□ EHTNR oligomers, ● EHTNRs based PUF)



**Figure 5.53** T<sub>g</sub> (°C) versus the amounts of 1,4-butanediol (g)

T<sub>g</sub> of all different polyurethane foams were evaluated from the second heating thermograms at heating rate 10 °C min<sup>-1</sup> under nitrogen atmosphere and the results are summarized in **Table 5.8** and **Figures 5.51-5.53**. All polyurethane foams showed only glass transition temperature (T<sub>g</sub>) of soft segments which is either HTNR or commercial precursors.

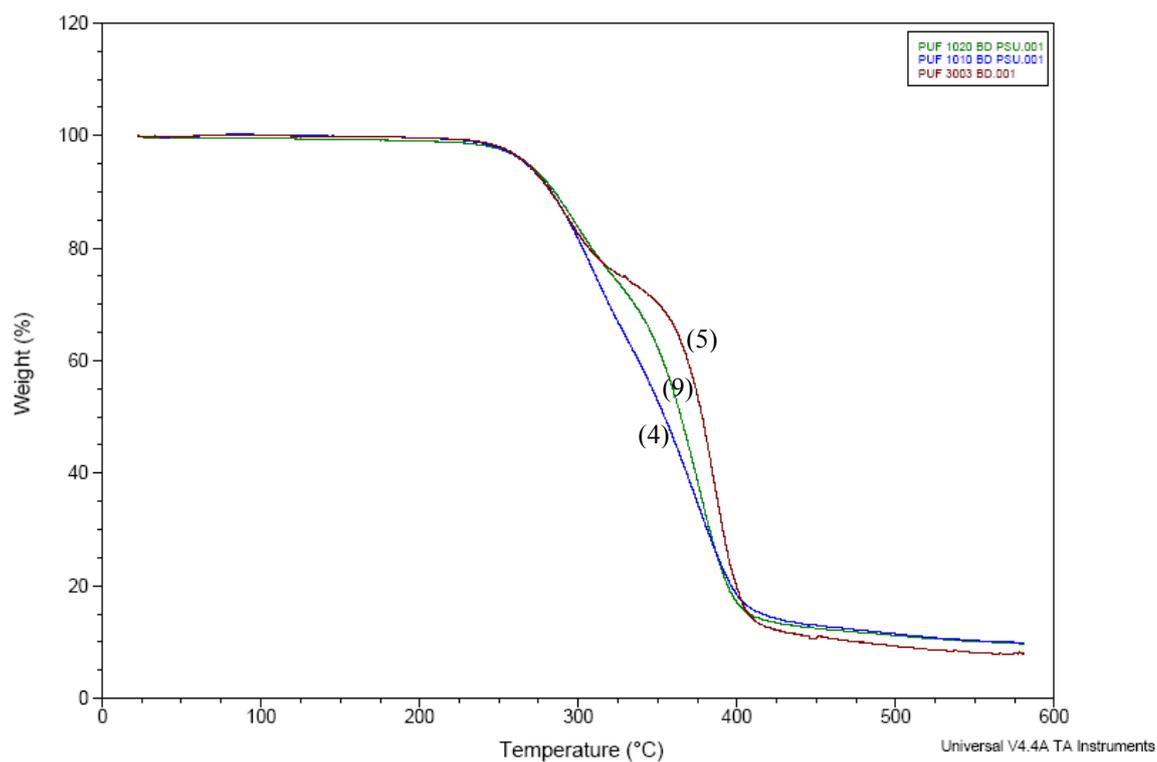
**Figure 5.51** shows the influence of molecular weight of soft segment on T<sub>g</sub> of all polyurethane foams examined. It was found that the observed T<sub>g</sub> of the foams based on both HTNR and on commercial precursors decreases with increasing length of soft segment due to an increase of the molecular chain flexibility in foams. In addition, the HTNRs based foams (PUF1, PUF2, and PUF3) exhibited lower T<sub>g</sub> (between -50 and -61 °C) than those of commercial precursors based foams (PUF4, -21 °C and PUF9, -48 °C). It indicated that HTNR based foams show excellent low temperature flexibility property. It can be explained by the interactions of the ether groups of the commercial polyols with urethane or urea linkage that reduce flexibility of polyurethane chains and therefore T<sub>g</sub> of commercial polyols based foams are higher when compared with T<sub>g</sub> of HTNR based foams.

The effect of epoxide content on T<sub>g</sub> of both oligomer and foams was also discussed. It was shown that their T<sub>g</sub> increased with increasing epoxide contents due to higher backbone

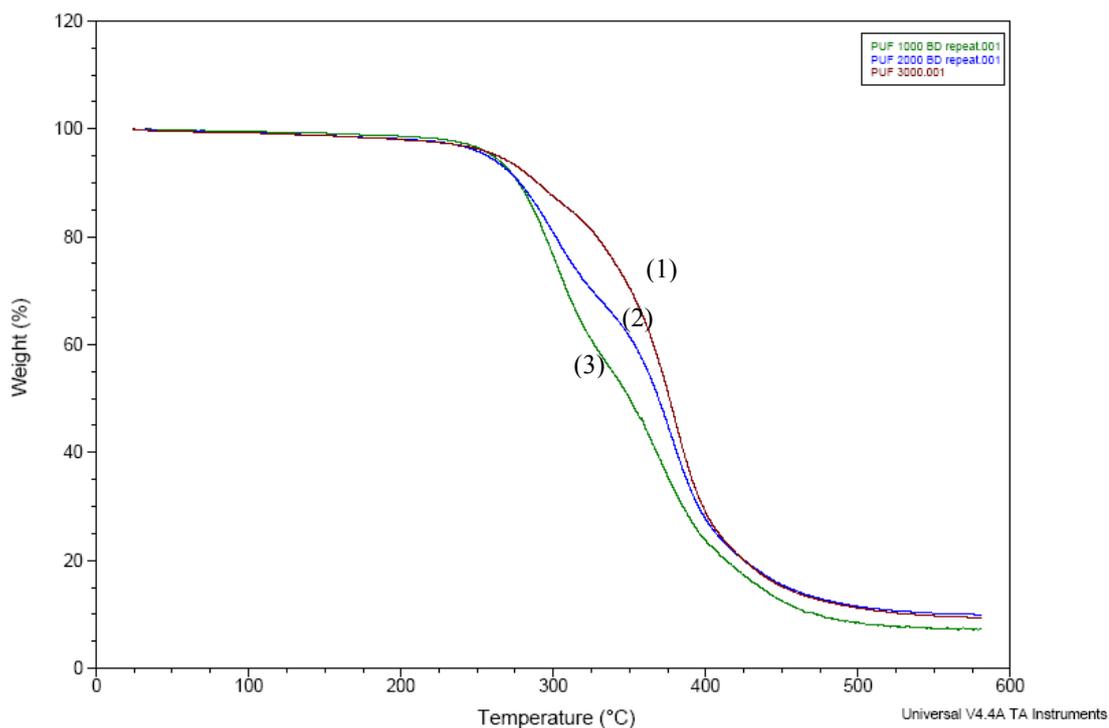
rigidity and higher chain interactions. The linear relationship of epoxide content and  $T_g$  is shown in **Figure 5.52**.

In addition, the effect of the amount of the chain extender (1,4-butanediol) in foams on  $T_g$  is showed in **Figure 5.53**. The amount of 1,4-butanediol was varied at 1, 2 and 4 times of 1,4-butanediol in the formulations (PUF1, PUF11, and PUF12 in **Table 4.5**). It can be seen that the  $T_g$  increases with increasing amount of chain extender due to an increase of backbone rigidity (urethane segments) and also due to occurring interactions between chains.

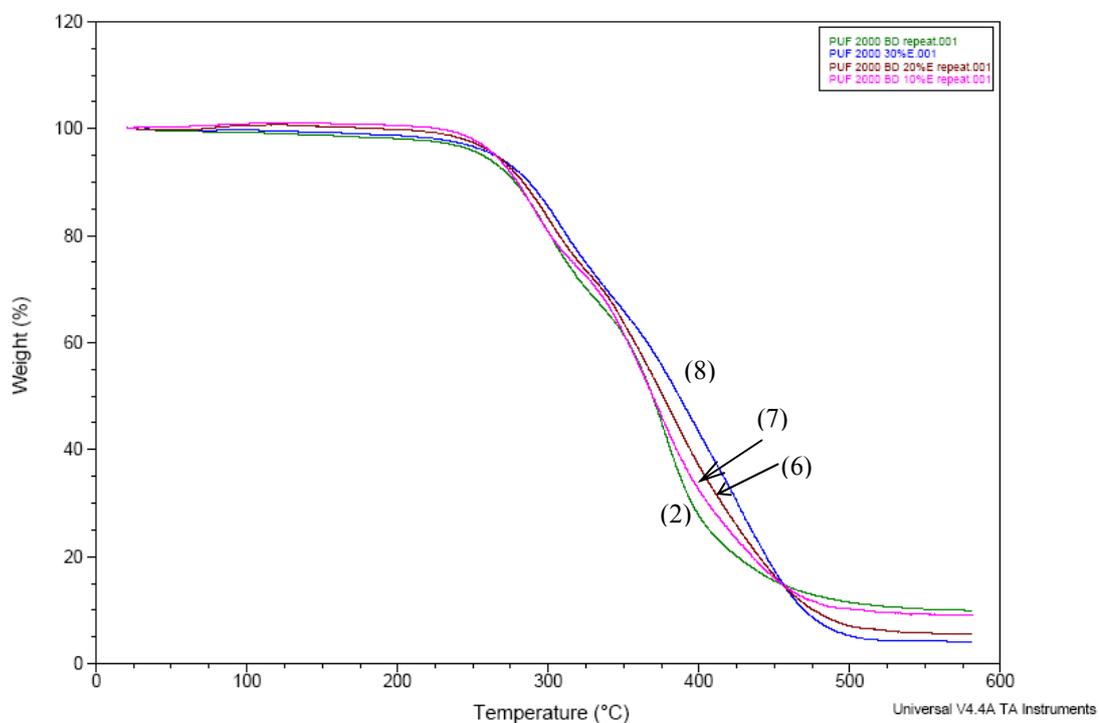
All TGA curves are showed in **Figures 5.54-5.58** were obtained at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ , from room temperature to  $600\text{ }^\circ\text{C}$ , under nitrogen atmosphere.



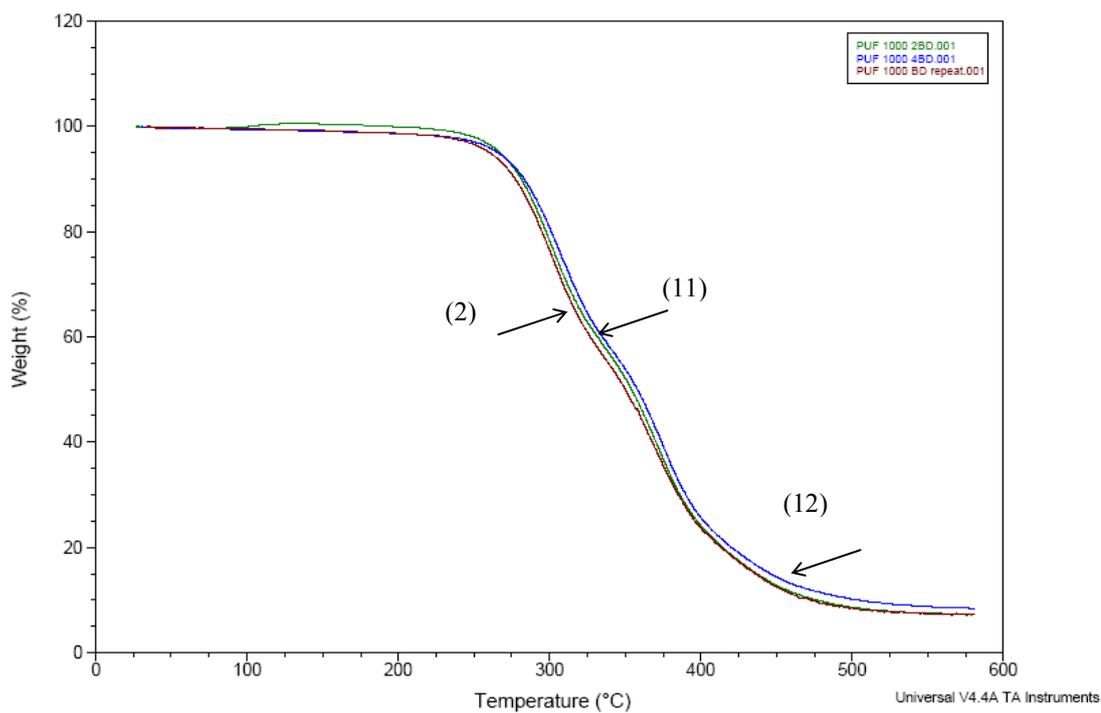
**Figure 5.54** TGA curves of polyurethane foams from commercial precursors: (4) (PUF4, Raypol1010), (9) (PUF9, Raypol1020) and (5) (PUF5, Raypol3003)



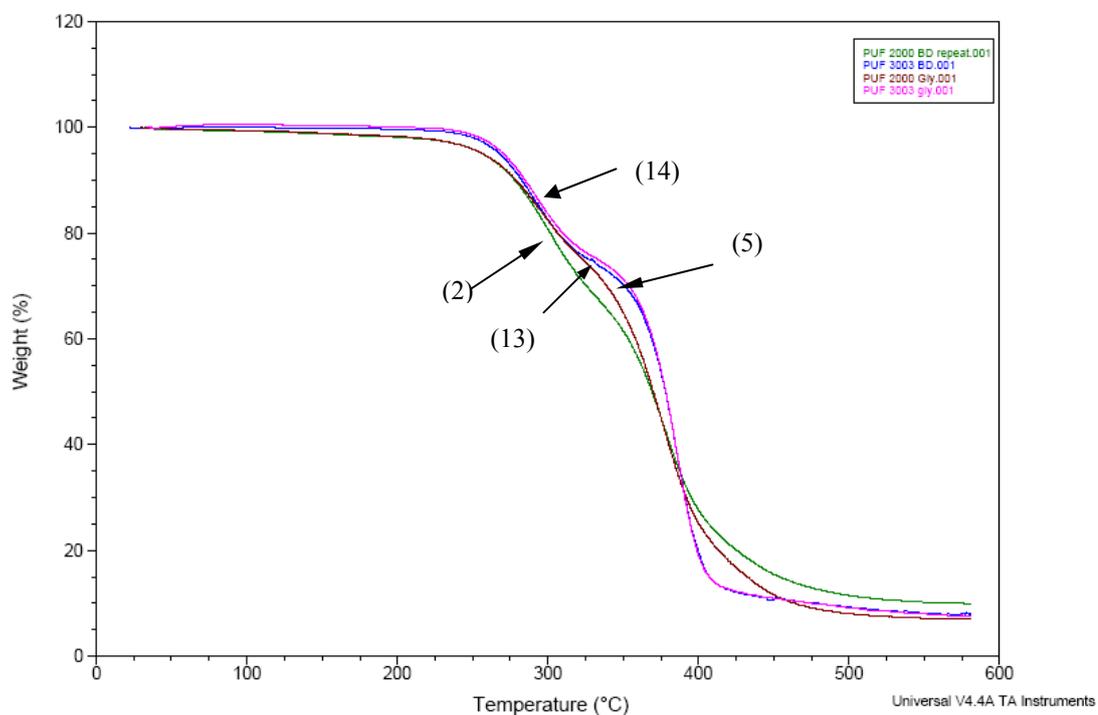
**Figure 5.55** TGA curves of polyurethane foams from HTNR: (1) (PUF1, 1000) (2) (PUF2, 2000) and (3) (PUF3, 3400)



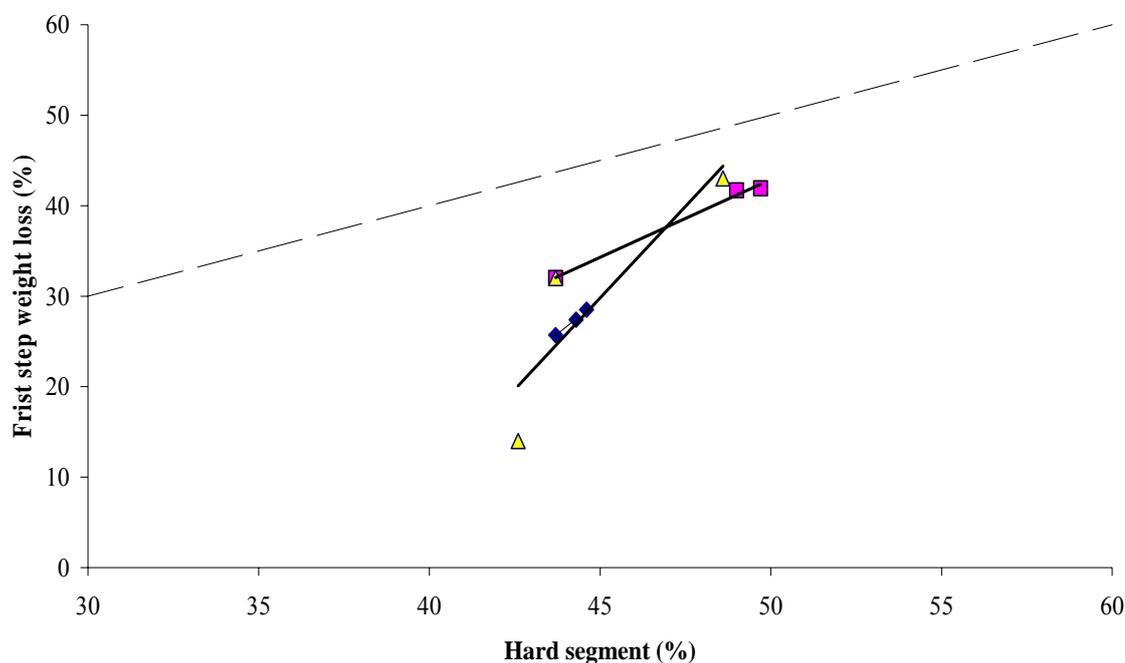
**Figure 5.56** TGA curves of polyurethane foams from EHTNR2000: (2) (PUF2, 0%), (6) (PUF6, 9%), (7) (PUF7, 23%) and (8) (PUF8, 35%)



**Figure 5.57** TGA curves of polyurethane foams from HTNR1000: (1) (PUF1, 0.19g), (11) (PUF11, 0.38g) and (12) (PUF12, 0.78g)



**Figure 5.58** TGA curves of polyurethane foams from HTNR2000 and Raypol3003: (2) (PUF2, HTNR(BD)), (5) (PUF5, Raypol(BD)), (13) (PUF13, HTNR(Gly)) and (14) (PUF14, Raypol(Gly))



**Figure 5.59** Weight loss in first step (%) versus hard segment content (%) in polyurethane foams (▲ varied on  $\overline{Mn}$  of oligomers, ◆ varied on the epoxide content on oligomers molecule, ■ varied on the amount of 1,4-butanediol, ---- theoretical linear)

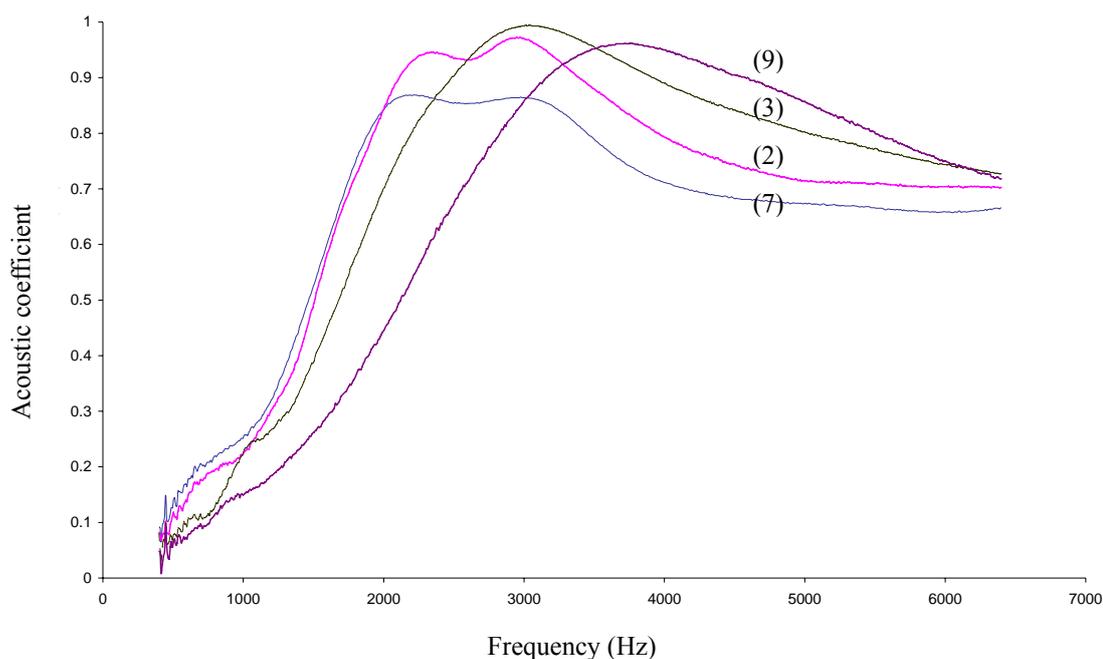
For all polyurethane foams tested, a two step thermal degradation was observed. Weight losses and characteristic temperatures determined from the maximum of the derived curve ( $T_{max}$ ) were analyzed. The first stage degradation at 290-309 °C corresponds to urethane bond breakage, while the second stage at 371-393 °C corresponds to a decomposition of precursors (soft segment). These results are in agreement with the study of thermal stability of polyurethane solid and polyurethane foam (Kébir *et. al.*, 2005 and Zhang *et. al.*, 2009).

All the foams have approximately the same degradation temperature (**Table 5.8** and **Figure 5.54** and **5.56-5.58**). We observed that the increase hard segment content by varying both of  $\overline{Mn}$  of oligomers (**Figure 5.55**) and the amount of 1,4-butanediol (**Figure 5.57**) lead to an increase of first step weight loss(%). This means that the increasing of hard segment leads to decrease of thermal stability in term of weight loss. Theoretically, the degradation of urethane functional group in the first step should display a linear relationship between theoretical weight loss (%) and hard segment (%). As shown in **Figure 5.59**, the first step weight losses are linearly

increasing hard segment contents by varying oligomer molecular weights, epoxide content and the amount of 1,4-butanediol, but the values obtained practically are lower than the theoretical values. This results can be explained by a higher stability of urethane linkage that occur from an influence of aromatic isocyanate structure of P-MDI and some crosslink in the foam due to a functionality of NCO which is equal to 2.7.

### 5.3.4 Acoustic properties of polyurethane foams

Acoustic property of polyurethane foams was studied with impedance tube test, Kunt's tube, according to ASTM E 1050 with variable frequencies from 400 to 6400 Hz at room temperature. The diameter of cylinder specimens was 29 mm and thickness was about 13 mm.



**Figure 5.60** Acoustic coefficient of polyurethane foams: (2) (PUF2, HTNR2000), (3) (PUF3, HTNR3400), (7) (PUF7, 23%HTNR2000), (9) (PUF9, Raypol1020)

**Figure 5.60** shows the experimental results for the acoustic absorption coefficient of the samples, as a function of frequency. HTNR (PUF2, PUF3 and PUF7) and commercial polyol (PUF9) based on polyurethane foams show a clear absorption peak over the range of 2000-5000 Hz. At higher frequencies, the absorption coefficient decreases. This behavior is characteristic of

open cell foams. However, the observed shift of the absorption peak toward higher frequencies may be related to the increase in density (Verdejo *et al.*, 2008).

Sound wave are absorbed by two main mechanisms: noise contacts the open cell foam structure in the form of sound pressure wave, such that the sound energy of the incident sound wave within the porous structure is partially converted to heat energy due to the effect of air friction, and part of the sound energy is dissipated in the form of heat energy due to the molecular chain damping effect of the polymer (Chen *et al.*, 1990; Verdejo *et al.*, 2008).

The absorption peaks of polyurethane foam based HTNR show dramatically more than 80%. It was indicated that these foams presented excellent acoustic property in the same level of the absorption coefficient of polyurethane foam based commercial precursor (PUF9). As a general rule, polyurethane foams absorb approximately 68% air borne sound, across the range of frequency (Global urethane service, 2009)

However, polyurethane foam based HTNR3400 (PUF3) and HTNR2000 (PUF2) shows the better acoustic coefficient than that based 23%EHTNR2000 (PUF7). This may be due to high degree of rigidity at 23% epoxidation level of polyol chain which increase the reflect effect to interior the sound absorption coefficient of foam. This is agreement with the results of Suhawati and coworker, (2008) which reported the studied a sound absorption of foamed rubber composites from wood and calcium carbonate. Their results revealed that the low sound absorption coefficient of foam rubber was observed, with increasing the high degree of hardness at a very high filler loading.

The sound absorption coefficients (average) of the example polyurethane foam spray are used as acoustic foams at various frequencies and thickness as shown in Appendix E.

## CHAPTER 6

### CONCLUSIONS

Controlled selective degradation of natural rubber was carried out both in latex phase and solvent phase. The degradation reaction of natural rubber, led to different carbonyltelechelic natural rubbers with different selected average molecular weights. Hydroxytelechelic natural rubber was later synthesized by selective reduction of carbonyl end-groups. The molecular weights, microstructure and functionality were determined by SEC,  $^1\text{H-NMR}$ , MALDI-TOF MS and FT-IR. Their chemical modifications were then performed *via* epoxidation, hydrogenation and ring opening reaction and their structure were characterized. The thermal properties of these telechelic natural rubbers were also investigated by DSC and TGA.

In addition, hydroxytelechelic natural rubbers (HTNRs) with three different molecular weights and with three degrees of epoxidation were used as starting material in preparation of polyurethane foams. Their physico-mechanical, thermal, acoustic properties, their cell morphology and chemical structure were investigated and compared to those of commercial precursor (polyether polyol) based polyurethane foams. The influences of the amount and type of chain extenders on their physico-mechanical and thermal properties were also studied. Conclusions could be drawn as the following:

1. The degradation of epoxidized natural rubber latex from field natural rubber latex having epoxidation level of 16.7% was performed with periodic acid using the specific mole ratio of [periodic acid]:[ENR] equal to 1.1 at 30 °C for 24 h. The analysis by SEC confirmed the decreasing of molecular weight in the level of 50000 g mol<sup>-1</sup>, but the degraded NR had the same level of epoxidation.

2. The degradation of field natural rubber latex with periodic acid (8% mole) including a N-iodosuccinimide ( $1.7 \times 10^{-2}$  mole) was performed at 30 °C for 24 h. The analysis by SEC confirmed the decreasing molecular weight in the level of 9000 g mol<sup>-1</sup>. In addition,  $^1\text{H-NMR}$

spectroscopy shows the signals of protons adjacent to ketone and aldehyde end-chain groups and few amounts of residual epoxide groups. However, the latex destabilization occurred at the end of the reaction.

3. Different degrees of epoxidation of field natural rubber (NR **1**) were obtained by varying reaction times (1.30, 3 and 8 h). The reaction was performed by performic acid generated *in situ* by reaction between formic acid and hydrogen peroxide at 60 °C. The molar ratio of hydrogen peroxide and natural rubber was equal to 0.30 and the molar ratio of hydrogen peroxide and formic acid was equal to 1. The obtained (ENR **2**) had epoxidation levels of 2.5, 4 and 10%, respectively

4. The degradation of partially epoxidized natural rubber having epoxidation levels of 2.5, 4 and 10% in THF solution was performed with the specific periodic acid using the mole ratio of periodic acid and ENR **2** equal to 1.1 at 30 °C for 6 h. Different molecular weights of carbonyltelechelic natural rubber (CTNR **3**) were obtained. In addition, the <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MALDI-TOF MS, SEC and FT-IR showed the carbonyl structures at the chain-ends (aldehyde and ketone) and that there were no residues of epoxide groups. Moreover, this process gave the high yield and was reproducible.

5. The hydroxytelechelic natural rubber (HTNR **4**) was prepared by the reduction of carbonyltelechelic natural rubber (CTNR **3**) with NaBH<sub>4</sub> in THF at 60 °C. The HTNR **4** structure was proved by NMR, FT-IR spectroscopies and MALDI-TOF MS techniques. Its functionality was equal to 2. The average molecular weights were evaluated by SEC, <sup>1</sup>H-NMR and MALDI-TOF MS. The molecular weights of HTNR were obtained in order: 1000, 2000, and 3400 g mol<sup>-1</sup>.

6. Epoxidized hydroxytelechelic natural rubber ( $\overline{Mn}$  1000 and 2000 g mol<sup>-1</sup>) (EHTNR **5**) were also prepared by *m*-chloroperbenzoic acid in solvent medium. The different epoxidized oligomers (approximately 10, 20 and 30% epoxidation) included isoprene units together and had two hydroxyl groups at the chain-ends.

The modification of HTNR **4** *via* hydrogenation, epoxidation and ring opening reaction was studied. Hydrogenated hydroxytelechelic natural rubber (HHTNR **6**) was prepared by hydrogenation process with hydrogen pressure including catalyst for 24 h. The HHTNR **6** was nearly completely hydrogenated (98%) and had two hydroxyl groups at the chain-ends.

The oxirane ring opening of 11% and 23%EHTNR (HTNR( $\overline{fn} > 2$ ) **7**) was also performed by  $\text{LiAlH}_4$  in ether solution. By this modification method, their functionalities in hydroxyl groups were increased to be 2.7 and 4.3, respectively in both the chain-ends and the backbone chains. The backbone chain was isoprene unit and the oxirane ring was also disappeared.

7. The viscosity of HTNRs was dependent on their molecular weight and on their degree of epoxidation. HTNR3400 was more viscous than HTNR2000 whereas 9%EHTNR was less viscous than 23% and 35%EHTNR2000, respectively.

8. The glass transition temperature ( $T_g$ ) of telechelic natural rubber were observed. The lower molecular weight was the slightly higher  $T_g$  of oligomers. On the other hand, with increasing of epoxidation levels or of functionality, higher  $T_g$  were showed. There was no influence of different molecular weights of HTNR on thermal degradation on the maximum rate of degradation ( $T_{\text{max}}$  about 380 °C). HHTNR **6** presented the highest thermal stability with having  $T_{\text{max}}$  up to 460 °C. In the case of EHTNR **5** series in both HTNR1000 and 2000, slight degradation in the first step was observed, but the thermal stability was increased in the second step.

9. Polyurethane foams were successfully prepared from the different molecular weights and the different epoxidation levels HTNRs. These HTNRs based foams had regularly open cells and had cell sizes between 0.38 and 0.47. Density (20-39  $\text{kg m}^{-3}$ ) depended on the variation of ingredients amounts in each formula, whereas commercial precursor analogues had cell sizes between 0.38 and 0.46, and density (29-34  $\text{kg m}^{-3}$ ).

10. For mechanical properties, the HTNR with the lower molecular weight gave a trend to increase strength properties (tensile and compressive strengths), but the elastic properties

(compression set and elongation at break) were decreased compared to higher molecular weight HTNRs. In the series of the epoxidized HTNR an increasing of strength properties, but had a decreasing of elastic properties were observed with the increasing of the epoxidation level. Similar trend was observed in the case of the increasing of amount of 1,4-butanediol that the tensile and compressive strengths of foams increased with increasing the amount of 1,4-butanediol by controlling of isocyanate index equal to 100, whereas the type of chain extenders had slightly affect on foams properties.

11. For thermal properties,  $T_g$  of foams based on HTNR and commercial precursors decreased with increasing molecular weights of precursors. It was indicated that polyurethane foams based on HTNR showed the better low temperature flexibility than commercial precursor analogues. For the series of EHTNR based foams, it shows that their  $T_g$  increased with an increasing of the epoxide content. Also, the increasing of amount of 1,4-butanediol gave an increasing of  $T_g$ . The different types of chain extenders (diol and triol) had no influence on  $T_g$ . The thermal degradation of all foams was occurred in two steps. The first step corresponds to the degradation of the urethane segment (290-309 °C), whereas the second step corresponds to soft segment (371-393 °C). The weight loss of polyurethane foam in first step was dependent on the amount of hard segment in each formulation.

12. For acoustic properties, the experimental results for the acoustic absorption coefficient of the samples, as a function of frequency. HTNR and commercial polyol based on polyurethane foams showed a clear absorption peak over the range of 2000-5000 Hz. At higher frequencies, the absorption coefficient consistently increases. The absorption peaks of polyurethane foam based HTNR showed dramatically more than 80%. It was indicated that these foams presented excellent acoustic property in the same level of the absorption coefficient of polyurethane foam based commercial precursor. However, polyurethane foam based HTNR3400 and HTNR2000 showed the better acoustic coefficient than that based 23%EHTNR2000.

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## **APPENDICES**

**Appendix A****A. MALDI-TOF MS****Table 1A** The theoretical and observed mass and calculated of CTNR 3

<b>n</b>	<b>Mass observed</b>	<b>Mass calculated</b>
7	616.1	615.6
8	686.1	683.6
9	752.5	751.7
10	820.7	819.8
11	888.8	887.9
12	957.0	956.0
13	1025.2	1024.1
14	1093.4	1092.1
15	1161.5	1160.2
16	1229.7	1228.3
17	1297.0	1296.4
18	1366.9	1364.4
19	1436.2	1432.5

**Table 2A** The theoretical and observed mass and calculated of HTNR1000

n	Mass observed	Mass calculated
7	620.2	619.6
8	688.4	687.6
9	756.5	755.7
10	824.7	823.8
11	892.9	891.9
12	961.1	960.0
13	1028.6	1028.0
14	1097.4	1096.1
15	1165.5	1164.2
16	1233.7	1232.3
17	1301.9	1300.4
18	1370.0	1368.4
19	1436.0	1436.5
20	1506.4	1504.6
21	1574.1	1572.7
22	1642.5	1640.8
23	1710.4	1708.8

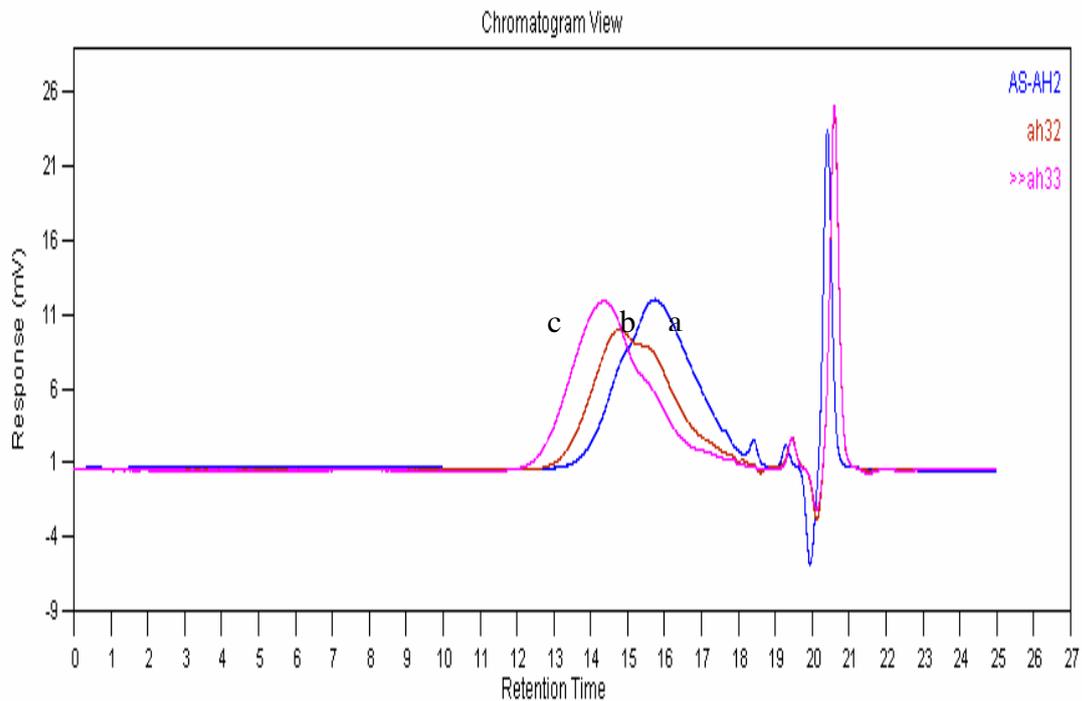
**Table 3A** The theoretical and observed mass and calculated of 11%EHTNR1000

n	Mass observed			Mass calculated		
	16	32	48	16	32	48
8	/	/	653.6	619.6	635.6	651.6
9	691.9	707.4	719.5	687.7	703.7	719.7
10	/	/	786.8	755.8	771.8	787.8
11	825.4	839.5	855.6	823.9	839.9	855.9
12	895.1	911.0	927.0	892.0	908.0	924.0
13	963.0	978.9	994.9	960.0	976.0	992.0
14	1031.2	1046.9	1062.9	1028.1	1044.1	1060.1
15	1098.9	1114.9	1130.9	1096.2	1112.2	1128.2
16	1166.9	1182.9	1198.9	1164.3	1180.3	1196.3
17	1235.0	1251.0	1267.0	1232.4	1248.4	1264.4
18	1301.0	1319.0	1335.0	1300.4	1316.4	1332.4
19	1369.0	1387.1	1403.1	1368.5	1384.5	1400.5
20	1437.2	1455.3	1471.3	1436.6	1452.6	1468.6
21	1503.3	1523.4	1539.5	1504.7	1520.7	1536.7
22	1573.7	1591.6	1607.7	1572.8	1588.8	1604.8
23	1639.7	1660.4	1675.8	1640.8	1656.8	1672.8
24	1710.6	1727.8	1744.0	1708.9	1724.9	1740.9
25	1776.1	1796.2	1812.9	1777.0	1793.0	1809.0

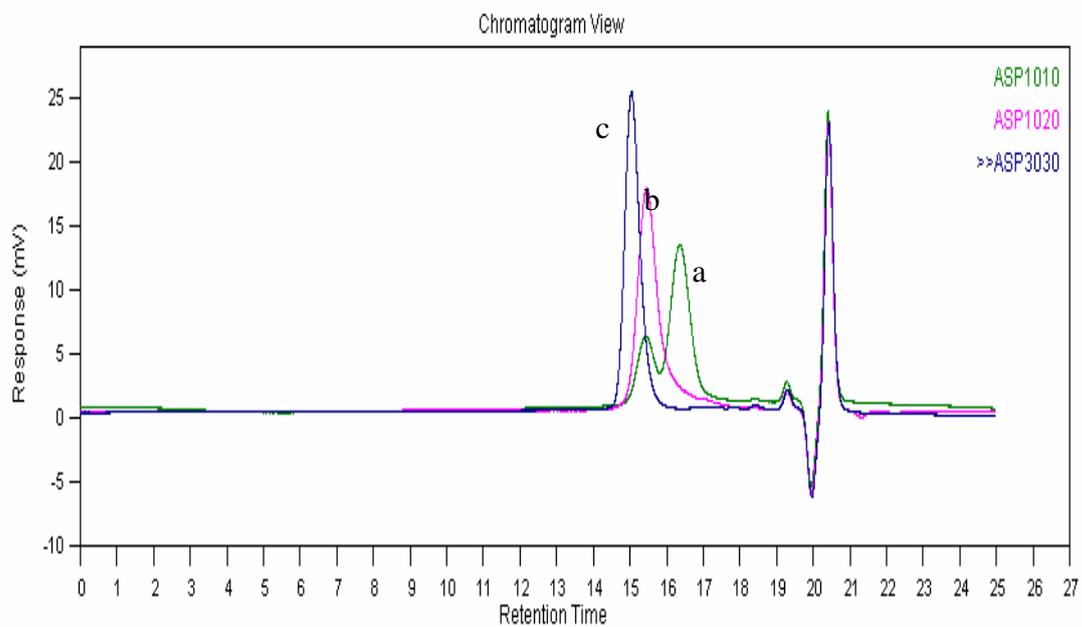
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## Appendix B

### B. SEC chromatograms



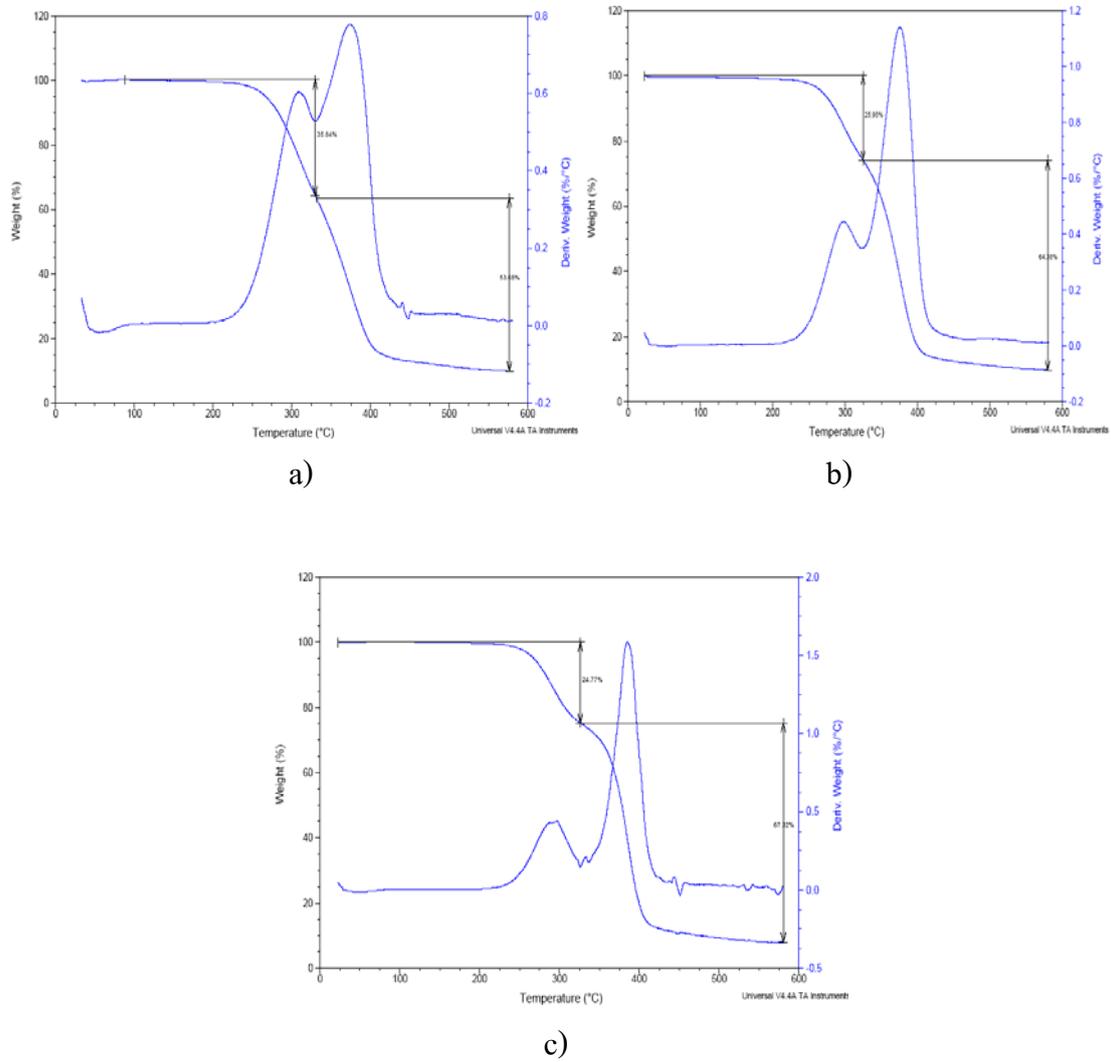
**Figure 1B** Chromatogram of HTNR a) HTNR1000, b) HTNR2000, c) HTNR3400



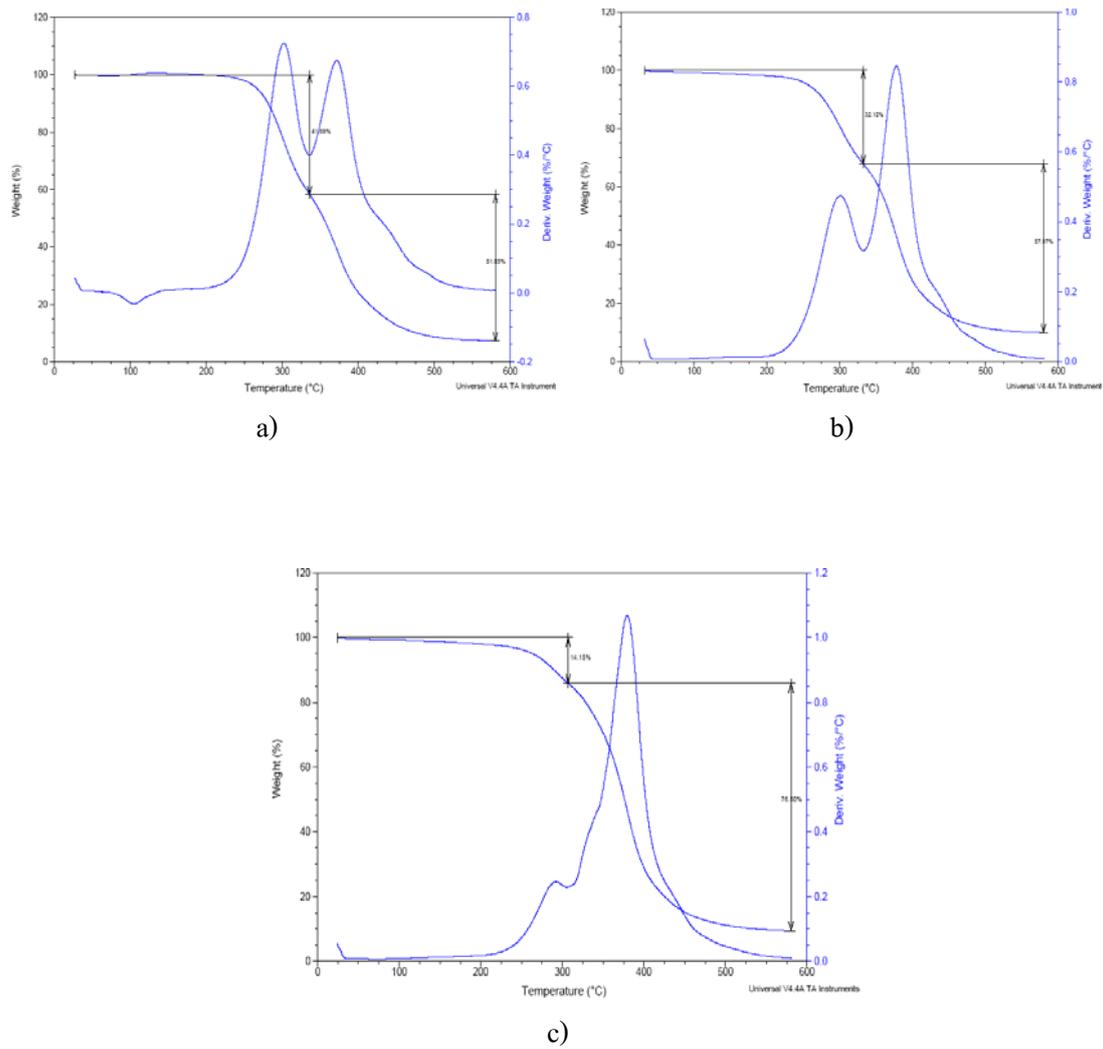
**Figure 2B** Chromatogram of Commercial polyol a) Raypol1010, b) 1Raypol020, c) Raypol3003

## Appendix C

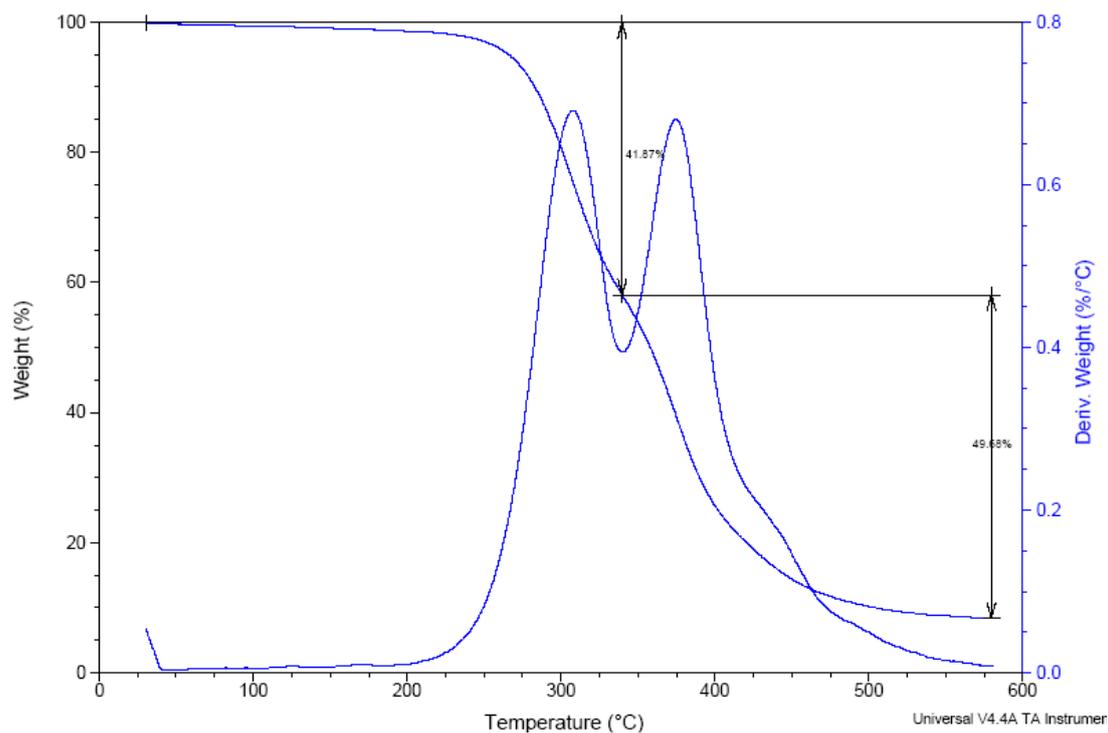
### C. Example of TGA curves of some polyurethane foams



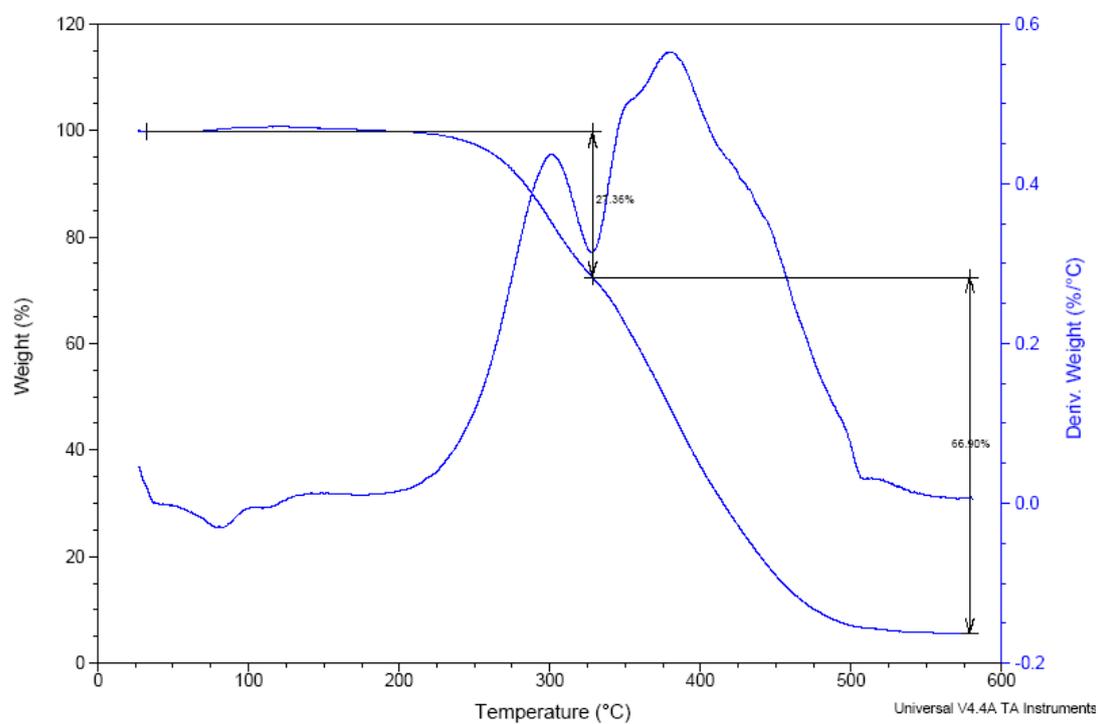
**Figure 1C** Thermograms of polyurethane foam based on difference of molecular weight of commercial polyether precursors: a) Raypol1010, b) Raypol1020, c) Raypol3003



**Figure 2C** Thermograms of polyurethane foam based on difference of molecular weight of HTNR: a) HTNR1000, b) HTNR2000, c) HTNR3400



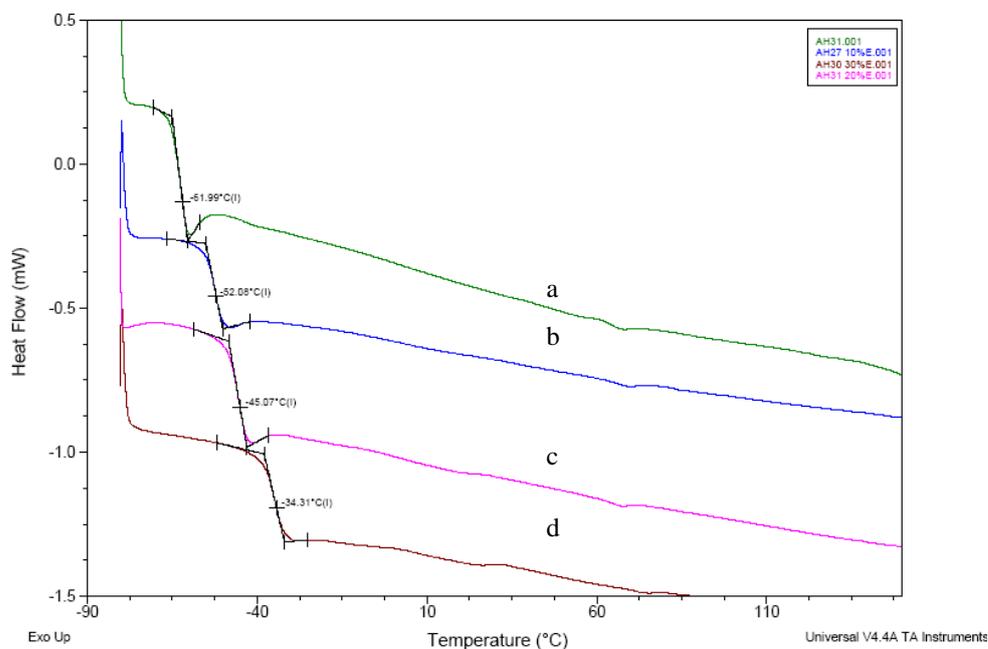
**Figure 3C** Thermograms of polyurethane foam based on HTNR1000 (4BD)



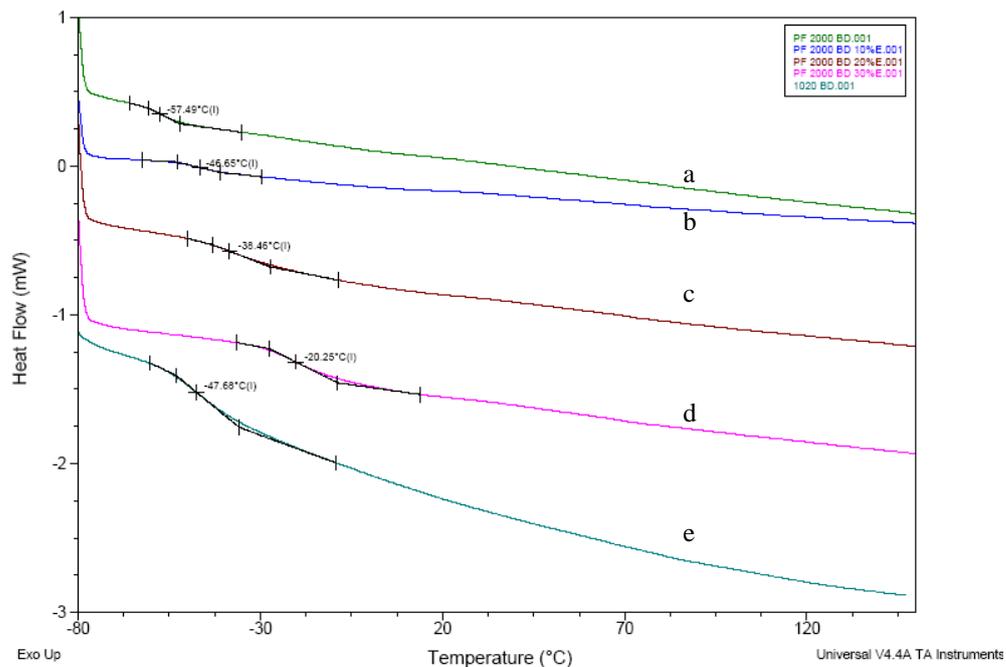
**Figure 4C** Thermograms of polyurethane foam based on 23%HTNR2000 (BD)

## Appendix D

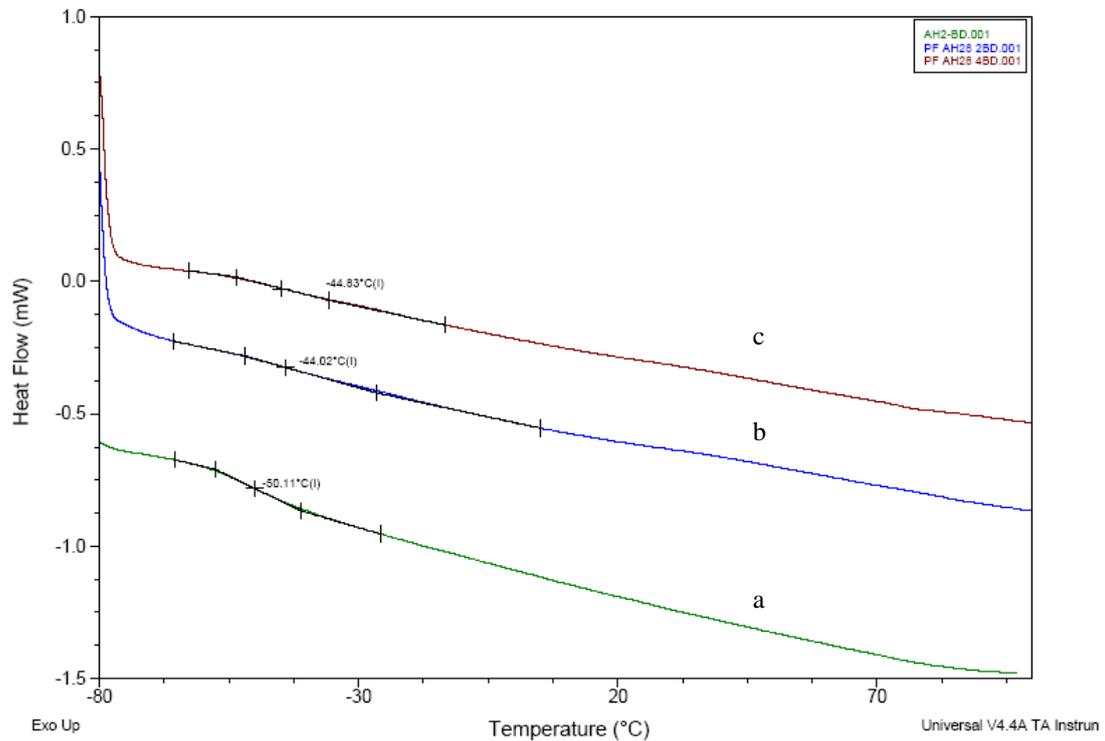
### D. Example of DSC curve of precursors and polyurethane foams



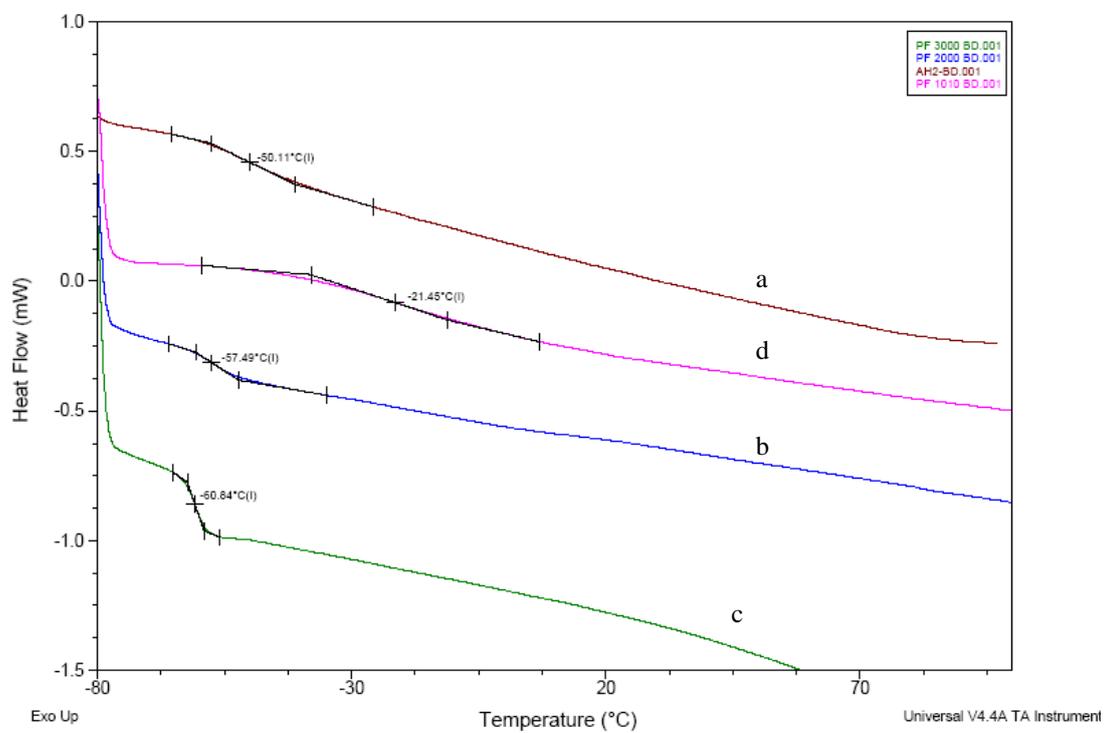
**Figure 1D** DSC curves of HTNR: a)2000, b)9%E2000, c)23%E2000 and d)35%E2000



**Figure 2D** DSC curves of PUF based on: a)HTNR2000, b)9%E2000, c)23%E2000, d)35%E2000 and e)Raypol1020



**Figure 3D** DSC curves of PUF based on HTNR1000: a) BD, b) 2BD, c) 4BD



**Figure 4D** DSC curves of PUF based on: a)HTNR1000, b)HTNR2000, c)HTNR3400 and d)Raypol1010

## Appendix E

**Table E** The sound absorption coefficients (average) of the example polyurethane foam spray are used as acoustic foams at various frequencies and thickness of samples (Global urethane service, 2009).

Frequency (Hz)	Thickness (inch)				
	¼"	3/8"	½"	¾"	1"
125	0.04	0.05	0.06	0.06	0.07
250	0.05	0.07	0.08	0.10	0.15
500	0.10	0.13	0.17	0.27	0.41
1000	0.28	0.33	0.46	0.54	0.76
1600	0.28	0.43	0.55	0.70	0.80
2000	0.31	0.59	0.70	0.89	0.74
2500	0.40	0.73	0.76	0.85	0.67
3150	0.50	0.76	0.77	0.82	0.72
4000	0.63	0.80	0.75	0.75	0.70
5000	0.73	0.73	0.76	0.78	0.77
6300	0.80	0.66	0.77	0.82	0.75

## CURRICULUM VITAE

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#### **Publications:**

Anuwat Saetung, Adisai Rungvichaniwat, Irène Campistron, Pairote Klinpituksa, Albert Laguerre, Pranee Phinyocheep and Jean-François Pilard. 2009. Controlled degradation of natural rubber and modification of the obtained telechelic oligoisoprenes: Preliminary study of their potentiality as polyurethane foam precursors, *Polymer*, On submitted.

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