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Preparation and Properties of Bio-based Polyurethane Made from Natural Rubber and Poly(ε-caprolactone)

Wannarat Panwiriyarat

A Thesis Submitted in Fulfillment of the Requirements for
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and

Le Grade de Docteur de l'Université du Maine
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Thesis Title Preparation and Properties of Bio-based Polyurethane Made from Natural Rubber and Poly(ε-caprolactone)

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The Graduate School, Prince of Songkla University, Thailand and Faculté des Sciences et Techniques, Université du Maine, Le Mans, France have approved this thesis as fulfillment of the requirements for the Degree of Doctor of Philosophy (Polymer Science and Technology) and the Doctor degree of Université du Maine (Chimie et Physicochimie des Polymères).

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This is to certify that the work here submitted is the result of the candidate's own investigations. Due acknowledgement has been made of any assistance received.

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ABSTRACT

The aim of this research work was to prepare a novel bio-based polyurethane (PU) composed by chemically modified natural rubber (NR) and poly(ε-caprolactone) diol (PCL), with and without isocyanate. Hydroxyl telechelic natural rubber (HTNR) was synthesized via epoxidized and carbonyl telechelic natural rubber. The parameters studied included type and relative amount of diisocyanate, molar ratio between diisocyante and diol (NCO:OH), molecular weight of HTNR and PCL diol, 1,4-butane diol (BDO, chain extender) content and molar ratio between HTNR:PCL diols. Three types of diisocyanate were employed: isophorone diisocyanate (IPDI), toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HDI). The number average molecular weights of HTNR and PCL diol were selected: 1700, 2800 and 2900 g/mol for HTNR and 530 and 2000 g/mol for PCL diol. The NCO:OH molar ratio was in the range 0.75:1.00 – 2.85:1.00. PU was prepared by one-shot method. The chemical structure of HTNR, PCL and PU were identified by ^{1}H-NMR FTIR and Raman spectroscopy. Tensile properties and tear resistance of PU were investigated. Characterization of mechanical and thermal properties was carried out using DSC, DMTA and TGA. A preliminary study showed that the molecular weight of PU increased with increasing NCO:OH molar ratio and reaction time, and chloroform was not a good solvent for polymer casting. Tetrahydrofuran was an appropriate solvent as it allowed film formation and it was used in all the other experiments. The NCO:OH molar ratio of 1.25:1.00 was suitable for preparing good PU films. FTIR analysis verified the presence of urethane linkages and crosslinking or chain branching. PU demonstrated excellent mechanical properties, which depended on the chemical composition. Excluding the use of PCL_{2000} and HDI, the tensile behavior seemed to have typical elastomeric characteristics. PU became amorphous except in the case of HDI, which was able to crystallize leading to the crystalline PU. The crystallinity increased the Young's modulus, the tear strength, the hardness and the thermal stability of PU. PU showed a phase separation between the PCL and HTNR segments. The longer and more flexible chain and non-polarity of HTNR were responsible of a decrease of the mechanical properties and transition temperatures. The very high molar ratio of NCO:OH (2.85:1.00) changed the tensile characteristics from an elastomer to a plastic. The high crosslinking was attributed to there being no phase separation between the hard and the soft segment. Hydrogen bonding between the PCL diol and the hard segment produced a high T_g. Raman spectra were able to identify the urethane linkage of PU containing different diisocyanates by showing the relative absorbance peaks. Synthesis of PU without isocyanate was successfully obtained via a polyaddition polymerization between a cyclic carbonate telechelic PCL/NR and 1,4-butylenediamine. The cyclic carbonate telechelic NR and cyclic carbonate telechelic PCL were prepared via the modification of the hydroxyl end groups of HTNR and PCL diols to carboxylic acid end groups by reacting with succinic anhydride. Then, the carboxylic acid end groups were changed to the cyclic carbonate end groups by using glycerol carbonate.

Keyword: Bio-based polymers, bioplastics, natural rubber, polyurethane, poly(ε-caprolactone), renewable resources

Titre de la thèse	Synthèse et étude des propriétés d'un polyuréthane biosourcé obtenu du caoutchouc naturel et du poly(ε-caprolactone)
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RESUME

L'objectif de ce travail de thèse était la synthèse d'un nouveau matériau polyuréthane biorsourcé composé par du caoutchouc naturel modifié chimiquement et par du poly(ε-caprolactone), (PCL), en présence ou absence d'isocyanates. Des oligoisoprènes téléchéliques hydroxylés (HTNR) ont été obtenus après époxidation du caoutchouc naturel et réduction des oligomères carbonyles. Plusieurs paramètres ont été étudiés comme la nature et la quantité relative de diisocyanate, le rapport molaire entre diisocyanate et diol (NCO:OH), l'influence de la masse molaire des diols HTNR et PCL, le pourcentage de 1,4-butane diol (BDO, extenseur de chaîne), et le rapport molaire entre les diols HTNR:PCL. Trois types de diisocyanate ont été employés : isophorone diisocyanate (IPDI), toluène-2,4-diisocyanate (TDI) et hexaméthylène diisocyanate (HDI). Masses molaires différentes ont été utilisées pour les diols HTNR et PCL: 1700, 2800 et 2900 g/mol pour HTNR et 530 et 2000 g/mol pour PCL. Le rapport molaire entre NCO:OH était entre 0,75:1,00 – 2,85:1,00. Les PU ont été préparés par la méthode « one shot » et les structures chimiques des HTNR et PU ont été identifiées par ^{1}H-NMR et FTIR. La résistance à la traction et à la rupture ont été étudiées. La caractérisation a été conduite par DSC, DMTA, ATG et spectroscopie Raman. Une étude préliminaire a montré que la masse molaire du PU augmentait avec le rapport NCO:OH et le temps de réaction, et que le chloroforme n'était pas un bon solvant pour obtenir des films. Le tetrahydrofurane était le solvant le plus approprié et il a été utilisé par la suite pour toutes les polymérisations. Le rapport NCO:OH = 1,25:1,00 s'est révélé optimal pour obtenir des films. L'analyse FTIR a permis de vérifier la présence de liaisons uréthane, de points de réticulation et de branchements. Le polyuréthane a montré des propriétés mécaniques excellentes dépendantes de la composition chimique. Si on exclue l'utilisation de PCL_{2000} et de HDI, le comportement à la traction était caractéristique des élastomères. Les PU étaient amorphes sauf quand HDI a été employé : en ce cas un PU semi cristallin a été obtenu. Cette cristallinité augmente le module de Young, la résistance à la rupture, la dureté et la stabilité thermique du PU. Pour ce PU une séparation de phase entre les segments du PCL et du HTNR a été observée. Les chaînes plus longues et plus flexibles du HTNR et leur non polarité sont responsables de la diminution des propriétés mécaniques et des températures de transition. Le materiau passe d'un comportement élastomère a un comportement plastique pour un rapport NCO:OH élevé (2,85 :1,00). Le dégréé de réticulation élevé a été retenu comme la cause pour laquelle il n'y avait pas de séparation de phase entre les segments souples et durs. La liaison hydrogène entre le diol PCL et le segment hard a généré des Tg élevées. Les spectres Raman ont montré la formation de la liaison uréthane du PU contenant différents diisocyanates. La synthèse de PU sans diisocyanate a été obtenue grâce à une réaction de polyaddition entre des carbonates cycliques téléchéliques dérivés du PCL et du caoutchouc naturel, et la 1,4-butylène diamine. Les structures contenant des carbonates cycliques ont été obtenues grâce à la modification des groupes OH sur le HTNR et le PCL à groupes carboxyle, utilisant l'anhydride succinique, et a la réaction successive avec le glycérol carbonate.

Mots clés: polymères biosourcés, bioplastiques, caoutchouc naturel, polyuréthane, poly(ε-caprolactone), ressources renouvelables

ชื่อวิทยานิพนธ์ การเตรียมและสมบัติพอลิยูรีเทนชีวภาพเตรียมจากยางธรรมชาติและพอลิคาโปรแลคโทน
ผู้เขียน นางสาววรรณรัตน์ พันธุ์วิริยรัตน์
สาขาวิชา วิทยาศาสตร์และเทคโนโลยีพอลิเมอร์
ปีการศึกษา 2555

บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้เพื่อเตรียมและศึกษาสมบัติของพอลิยูรีเทนชีวภาพชนิดใหม่ที่ได้จากยางธรรมชาติที่ผ่านการดัดแปรโมเลกุลและพอลิคาโปรแลคโทน (PCL) ผ่านวิธีการสังเคราะห์ที่ใช้และไม่ใช้ไอโซไซยาเนตเป็นสารตั้งต้น สำหรับยางธรรมชาติโมเลกุลต่ำที่มีหมู่ปลายสายโซ่เป็นหมู่ไฮดรอกซิล (HTNR) ที่ใช้เป็นสารตั้งต้นในการเตรียมพอลิยูรีเทนชีวภาพนี้ เตรียมผ่านปฏิกิริยาอิพ๊อกซิเดชันของยางธรรมชาติ ตามด้วยปฏิกิริยาการตัดสายโซ่และดัดแปรหมู่ปลายสายโซ่จากหมู่คาร์บอนิลกลายเป็นหมู่ไฮดรอกซิล ปัจจัยที่ใช้ในการศึกษาประกอบด้วยชนิดของไอโซไซยาเนต อัตราส่วนโดยโมลระหว่างไอโซไซยาเนตต่อไฮดรอกซิล (NCO:OH) และน้ำหนักโมเลกุลของไดออล ปริมาณตัวขยายสายโซ่ และอัตราส่วนระหว่าง HTNT:PCL ชนิดของไอโซไซยาเนตที่ใช้ประกอบด้วยไอโซโฟโรนไดไอโซไซยาเนต (IPDI) ทูโลอีน-2,4-ไดไอโซไซยาเนต (TDI) และเฮกซะเมทิลีนไดไอโซไซยาเนต (HDI) น้ำหนักโมเลกุลเฉลี่ยโดยจำนวนของ HTNR ที่ใช้คือ 1700, 2800 และ 2900 g/mol ในขณะที่น้ำหนักโมเลกุลเฉลี่ยโดยจำนวนของ PCL ที่ใช้เท่ากับ 530 และ 2000 g/mol และแปรอัตราส่วนโดยโมลของ NCO:OH ตั้งแต่ 0.75:1.00 ถึง 2.85:1.00 พอลิยูรีเทนเตรียมโดยใช้เทคนิคผสมสารแบบขั้นตอนเดียว (one-shot method) เป็นตัวขยายสายโซ่ ยืนยันโครงสร้างทางเคมีของ HTNR และพอลิยูรีเทน โดยใช้เทคนิค ^{1}H-NMR, FTIR และรามานสเปกโตรสโกปี ทำการศึกษาสมบัติความทนต่อแรงดึงและความต้านทานต่อการฉีกขาด และทดสอบลักษณะของพอลิยูรีเทนที่เตรียมได้โดยใช้เทคนิค DSC DMTA และ TGA ในการศึกษาขั้นต้นทำการเตรียมพอลิยูรีเทนโดยใช้คลอโรฟอร์มเป็นตัวทำละลาย พบว่าน้ำหนักโมเลกุลของพอลิยูรีเทนเพิ่มสูงขึ้น เมื่ออัตราส่วนโดยโมลของ NCO:OH และระยะเวลาในการทำปฏิกิริยาเพิ่มขึ้น แต่อย่างไรก็ตามไม่สามารถเตรียมฟิล์มพอลิยูรีเทนที่ดีจากระบบที่ใช้คลอโรฟอร์มเป็นตัวทำละลายได้ ดังนั้นเตตระไฮโดรฟูรานถูกนำมาใช้เป็นตัวทำละลายสำหรับการเตรียม

พอลิยูรีเทนเพราะสามารถเตรียมขึ้นรูปเป็นพอลิยูรีเทนฟิล์มได้ และสัดส่วนของ NCO:OH ที่มีค่าน้อยที่สุดที่สามารถเตรียมฟิล์มพอลิยูรีเทนเท่ากับ 1.25:1.00 ทำการวิเคราะห์พันธะยูรีเทนและการเชื่อมขวางอันเนื่องมาจากการเกิดพันธะอะโลฟาเนตโดยใช้เทคนิค FTIR พอลิยูรีเทนที่ได้แสดงสมบัติเชิงกลที่ดีขึ้นอยู่กับองค์ประกอบที่ใช้ พฤติกรรมของพอลิยูรีเทนส่วนใหญ่แสดงสมบัติคล้ายยาง ยกเว้นกรณีที่ใช้ PCL_{2000} และ HDI ที่แสดงพฤติกรรมการเสียรูปเป็นพฤติกรรมแบบพลาสติก นอกจากนี้ พอลิยูรีเทนที่เตรียมได้เหล่านี้ล้วนเป็นพอลิเมอร์อสัณฐาน ยกเว้นในกรณีที่ใช้ HDI เป็นสารตั้งต้นให้พอลิยูรีเทนที่เป็นผลึก ผลึกที่เกิดขึ้นนี้ส่งผลให้ยังมอดุลัสของยัง ค่าความต้านทานต่อการฉีกขาด ค่าความแข็งและเสถียรภาพทางความร้อนของพอลิยูรีเทนเพิ่มสูงขึ้น และมีการแยกเฟสระหว่างไดออลสองชนิดคือระหว่าง HTNR และ PCL เมื่อศึกษาอิทธิพลของ HTNR ต่อสมบัติเชิงกลและอุณหภูมิเปลี่ยนแปลงสถานะคล้ายแก้ว (T_g) ของพอลิยูรีเทน พบว่า HTNR ส่งผลให้สมบัติเชิงกลและ T_g ลดลงเป็นผลอันเนื่องจาก HTNR มีสายโซ่โมเลกุลยาว โครงสร้างยืดหยุ่นและไม่สามารถเกิดพันธะไฮโดรเจนในโมเลกุลของพอลิยูรีเทนได้ และเมื่อทำการศึกษาสมบัติของ พอลิยูรีเทนที่ใช้สัดส่วนของ NCO:OH ในปริมาณสูงมาก (2.85:1.00) พบว่าทำให้ลักษณะการเสียรูปจากการดึงยืดเปลี่ยนจากลักษณะคล้ายยางเป็นพลาสติก นอกจากนี้ปริมาณการเชื่อมขวางที่สูงส่งผลให้ไม่เกิดการแยกเฟสระหว่างส่วนแข็งกับส่วนยืดหยุ่น อีกทั้งส่งผลให้ T_g มีค่าสูงขึ้น ด้านการวิเคราะห์โครงสร้างและหมู่ฟังก์ชันของพอลิยูรีเทนโดยใช้เทคนิครามานสเปกโตรสโกปีสามารถตรวจสอบพันธะยูรีเทนที่เกิดขึ้นได้โดยปรากฏตำแหน่งการดูดกลืนที่แตกต่างกันขึ้นอยู่กับชนิดของไอโซไซยาเนตที่ใช้ และในส่วนสุดท้ายเป็นศึกษาเบื้องต้นในการเตรียมพอลิยูรีเทนผ่านกระบวนการสังเคราะห์ที่ไม่ใช้ไอโซไซยาเนตเป็นสารตั้งต้น โดยผ่านการทำปฏิกิริยาระหว่างพอลิคาโปรแลคโทนหรือยางธรรมชาติที่มีหมู่ไซคลิกคาร์บอเนตเป็นหมู่ปลายสายโซ่กับ 1,4-บิวทิลีนไดอะมีน ซึ่งเตรียมโอลิโกเมอร์ที่มีหมู่ปลายสายโซ่เป็นไซคลิกคาร์บอเนตดังกล่าวนี้ผ่านสองขั้นตอน เริ่มต้นจากการเปลี่ยนหมู่ไฮดรอกซิลของ PCL diol หรือ HTNR ให้กลายเป็นกรดคาร์บอกซิลิกโดยใช้ซัคซินิคแอนไฮไดร์ด จากนั้นเปลี่ยนหมู่กรดคาร์บอกซิลิกให้กลายเป็นไซคลิกคาร์บอเนตโดยใช้กลีเซอรอลคาร์บอเนต

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Wannarat Panwiriyarat

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LIST OF ABBREVIATIONS

BDO	1,4-butanediol
CBTNR	Carboxyl telechelic natural rubber
CCTNR	Cyclic carbonate telechelic natural rubber
CL	ε-Caprolactone
CTNR	Carbonyl telechelic natural rubber
DCC	N,N’-dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
ENR	Epoxidized natural rubber
FTIR	Fourier Transform Infrared Spectrometer
H_{12}MDI	4,4’-dicyclohexylmethane diisocyanate
HDI	1,6-hexamethylene diisocyanate
HS	Hard segment
HTNR	Hydroxyl telechelic natural rubber
IPDI	Isophorone diisocyanate
m-CPBA	m-chloroperbenzoic acid
MDI	Methylene diphenyl diisocyanate
NDI	Naphthalene 1,5-diisocyanate
NR	Natural rubber
PCL	Poly(e-caprolactone)
PDI	Phenylene diisocyanate
PEA	Poly(ethylene adipate) glycol
PHU	Polyhydroxylurethane
POP	Poly(oxypropylene) glycol
POTM	Poly(oxytetramethylene) glycol
PU	Polyurethane
SEC	Size exclusion chromatography
SS	Soft segment
TDI	Toluene diisocyanate
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TLNR	Telechelic liquid natural rubber
T_m	Melt transition temperature
XDI	Xylene diisocyanate

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Polyurethane (PU) is generally synthesized by polyaddition polymerization between polyisocyanates and polyols. Its molecular structure and properties vary over a broad range of stiffness or flexibility, hardness, and density [1]. There are many applications of polyurethane such as flexible or rigid foams, chemical resistant coatings, rigid and flexible plastics, specialty adhesives and sealants, and elastomers [2]. We can distinguish two types of polyurethane, depending on the polyol used: polyester polyurethane and polyether polyurethane.

Typical synthetic polymers have caused serious environmental problems because they are not easy to degrade in the natural environment. Polyurethane based materials also present this drawback and moreover they are high resistant to microbial attack. Generally, the ester-type polyurethane is more easily degraded than the ether-type polyurethane: the degradation is considered to be initiated by hydrolysis of the ester bond by some hydrolytic enzyme(s), such as esterase [3]. This explains why recently the development of biodegradable polyurethanes has generated increasing interested. One of the possible ways to address the problem is to insert a fragment of a known easily biodegradable polymer in the polyurethane backbone. Poly(ε-caprolactone) (PCL), for instance, a biodegradable aliphatic polyester, has been used as a diol to synthesize biodegradable polyurethanes for many applications [4-19]. PCL is synthesized via the ring-opening polymerization (ROP) of ε-caprolactone (CL) (which is petrochemical based monomer) using a diol as initiator/chain-transfer agent in the presence of a catalyst. Another issue of great concern in polymer synthesis is to conceive novel materials from renewable resources.

Natural rubber (NR) is an interesting renewable monomer feedstock because it is obtained by the collection the latex of the *Hevea Brasiliensis* tree and it can be easily chemically modified. Containing-double bonds with a stereoregular configuration on its backbone. If the polymer chain is cut into smaller oligomers, telechelic liquid natural rubber (TLNR) is obtained and it can be prepared using various methodologies such as photochemical [20-21], oxidative chemical [22-25], methathesis [22, 26], and anionic methods [27]. If hydroxyl functional groups are introduced as the oligomers chain ends, hydroxyl telechelic natural rubber (HTNR) is generated and it can be used as a soft segment (diol) in polyurethane synthesis [21, 23-24, 28-35].

To resume, PCL-based polyurethanes are biodegradable polymers whereas the HTNR-based polyurethanes are bio-based polymers, not easy to biodegrade. Therefore, if a biodegradable segment, for instant PCL is introduced into the HTNR-based polyurethanes, novel biobased-biodegradable materials should be obtained.

There have been many attempts to develop non-phosgene and non-diisocyanate routes for the synthesis of polyurethanes because isocyanate normally used to provide the NCO groups are highly hazardous and cause respiratory diseases. Therefore, non-isocyanate polymerization routes have been developed for polyurethane polymerization [1]. These “next generation” polyurethanes should also be readily biodegradable and recyclable [36]. The non-isocyanate route can be realized, for instance, via a reaction between cyclic carbonate oligomers and primary amine oligomers [37-46]. The synthesis of a cyclic carbonate by an environmentally friendly method can be carried out via the cycloaddition of carbon dioxide to epoxide groups in the presence of a catalyst and under high pressure [40, 45-47]. Recently, the cyclic carbonate end functional group has been prepared by chemical modification of glycerol carbonate [48-49], which is a biodegradable and non-toxic material derived from a renewable resource and it has been already used as a source of new polymeric materials [20, 21]. In this research work, cyclic carbonate telechelic natural rubber and cyclic carbonate telechelic polycaprolactone have been generated by the reaction with glycerol carbonate: the introduction of this new function both in PCL and NR oligomers offers the opportunity of expanding the applications of these raw materials, and the first synthesis of PU without isocyanate was achieved by a polyaddition polymerization between a cyclic carbonate and a diamine.

This study reported the preparation of bio-based polyurethane from telechelic natural rubber and poly(ε-caprolactone) using an isocyanate and a non-isocyanate route.

1.2 OBJECTIVES

The objectives of this Ph.D. research work were to synthesize novel bio-based polyurethane (PU) films containing fragments derived from the natural rubber (NR) polyisoprene chains and from poly(ε-caprolactone) (PCL) oligomers, following two alternative routes, with and without isocyanate, and to determine the mechanical and thermal properties of the resulting materials. Hydroxyl telechelic natural rubber (HTNR), cyclic carbonate telechelic natural rubber (CCTNR) and cyclic carbonate telechelic polycaprolactone (CCTPCL) have been prepared and used as precursors. The parameters as NCO:OH molar ratio, chain extender content, PCL:HTNR molar ratio, diisocyanate structure and molecular weight of diols were investigated.

The scope of work was divided into 6 parts.

Part I: Synthesis and characterization of polyurethane using chloroform as solvent.

This part concerned the preliminary study of the optimal NCO:OH ratio to use to obtain thin films and to investigate how the reaction time affected the molecular weight and properties of polyurethane when chloroform was used as solvent. ^{1}H-NMR and FTIR were used to determine the presence of the functional groups in order to verify the preparation HTNR and PU. Glass transition temperature, thermal decomposition and molecular weight of PU samples were investigated by using DSC, TGA and SEC, respectively.

Part II: Synthesis and characterization of polyurethane by using THF as solvent.

In this part, it was studied the effect of the NCO:OH molar ratio, chain extender content and PCL:HTNR molar ratio by using THF as solvent. The characterization was carried out by FTIR, DSC, TGA and DMTA.

Part III: Preparation and properties of polyurethane containing different diisocyanate molecules and different molecular weight of diols.

In this part, the effect of diisocyanate structure and molecular weight of diols on the thermal and mechanical properties of polyurethane by using THF as solvent were studied. The characterization of the PU was carried out by using FTIR, DSC, TGA and DMTA.

Part IV: Preparation and properties of polyurethane containing of NCO:OH ratio at 2.85:1.00.

This part involved with the preparation and properties of polyurethane containing molar ratio of NCO:OH (2.85:1.00). The effects of chain extender and diols content on the thermal and mechanical properties of PUs were investigated. The characterization was carried out by using FTIR, DSC, TGA and DMTA.

Part V: Characterization of polyurethane films by Raman spectroscopy.

This section was studied of the polyurethane surface by using Raman spectroscopy. Samples containing of different isocyanate type (TDI, IPDI and HDI) and diol type (PCL and HTNR) were examined.

Part VI: Synthesis and characterization of cyclic carbonate telechelic natural rubber and cyclic carbonate telechelic polycaprolactone for synthesizing polyurethane via non-isocyanate route.

This part concerned the synthesis of PU without diisocyanate via a polyaddition polymerization between a cyclic carbonate telechelic PCL, a cyclic carbonate telechelic NR and 1,4-butylenediamine. Their chemical structures were investigated by ^{1}H-NMR, ^{13}C-NMR and FTIR.

1.3 REFERENCES

1. Hepburn, C. Polyurethane elastomers, 2nd edition; Elsevier Science Publishers LTD: New York, 1992; pp 1-256.
2. Prisacariu, C. Polyurethane elastomers from morphology to mechanical aspects; SpingerWienNew York: New York, 2011; pp 10-107.
3. Zia, K.M., Bhatti, H.N., Bhatti, I.A. 2007. Methods for polyurethane and polyurethane composites, recycling and recovery: A review. React. Funct. Polym. 67, 675–692.
4. Gorna, K., Gogolewski., S. 2002. In vitro degradation of novel medical biodegradable aliphatic polyurethane based on ε-caprolactone and pluronics with various hydrophilicities. Polym. Degrad. Stabil. 75, 113–122.
5. Kim, S.C., Kim, Y.H., Lee, H., Yoon, D.Y., Song, B.K. 2007. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification. J. Mol. Catal. B-Enzym. 49, 75–78.
6. Younes, H.M., Grimaldo, E.B., Amsden., B.G. 2004. Synthesis, characterization and in vitro degradation of a biodegradable elastomer. Biomaterials. 25, 5261–5269.
7. Heijkants, R.G.J.C., Calck, R.V., Tienen, T.G., Groot, J.H., Buma, P., Pennings, A.J., Veth, R.P.H., Schouten, A.J. 2005. Uncatalyzed synthesis, thermal and mechanical properties of polyurethane based on poly(ε-caprolactone) and 1,4-butane diisocyanate with uniform hard segment. Biomaterials. 26, 4219–4228.
8. Heijkants, R.G.J.C., Schwab, L.W., Calck, R.V., Groot, J.H., Pennings, A.J., Schouten, A.J. 2005 (1). Extruder synthesis of a new class of polyurethane: Polyacylurethanes based on poly(ε-caprolactone) oligomers. Polymer. 46, 8981–8989.
9. Liu, C.B., Qian, Z.Y., Gu, Y.C., Fan, L.Y., Li, J., Chao, G.T., Jia, W.J., Tu, M.J. 2006. Synthesis, characterization, and thermal properties of biodegradable aliphatic copolyester based on ε-caprolactone, adipic acid, and 1,6-hexanediol. Mater. Lett. 60, 31 – 38.

10. Xie, Z., Lu, C., Chen, X., Chen, L., Hu, X., Shi, Q., Jing. X. 2007. A facile approach to biodegradable poly(ε-caprolactone)-poly(ethylene glycol)-based polyurethane containing pendant amino groups. Eur. Polym. J. 43, 2080–2087.
11. Hong, J.H., Jeon, H.J., Yoo, J.H., Yu, W.R., Youk, J.H. 2007. Synthesis and characterization of biodegradable poly(ε-caprolactone-co-β-butyrolactone)-based polyurethane. Polym. Degrad. Stabil. 92, 1186-1192.
12. Jiang, X., Li, J., Ding, M., Tan, H., Ling, Q., Zhong, Y., Fu, Q. 2007. Synthesis and degradation of nontoxic biodegradable waterborne polyurethane elastomer with poly(ε-caprolactone) and poly(ethylene glycol) as soft segment. Eur. Polym. J. 43, 1838–1846.
13. Tatai, L., Moore, T.G., Adhikari, R., Malherbe, F., Jayasekara, R., Griffiths, I., Gunatillake, P.A. 2007. Thermoplastic biodegradable polyurethane: The effect of chain extender structure on properties and in-vitro degradation. Biomaterials. 28, 5407–5417.
14. Jeon, H.J., Kim, J.S., Kim, T.G., Kim, J.H., Yu, W.R., Youk, J.H. 2008. Preparation of poly(ε-caprolactone)-based polyurethane nanofibers containing silver nanoparticles. Appl. Surf. Sci. 254, 5886–5890.
15. Zia, K.M., Zuber, M., Bhatti, I.A., Barikani, M., Sheikh. M.A. 2009. Evaluation of biocompatibility and mechanical behavior of chitin-based polyurethane elastomers. Part-II: Effect of diisocyanate structure. Int. J. Biol. Macromol. 44, 23–28.
16. Han, J., Chen, B., Ye, L., Zhang, A.Y., Zhang, J., Feng, Z.G. 2009. Synthesis and characterization of biodegradable polyurethane based on poly(ε-caprolactone) and L-lysine ethyl ester diisocyanate. Front. Mater. Sci. China. 3(1), 25–32.
17. Larraz, L.R., Fernandez d'Arlas, B., Tercjak, A., Ribes, A., Mondragon, I., Eceiza, A. 2009. Synthesis and microstructure–mechanical property relationships of segmented polyurethane based on a PCL–PTHF–PCL block copolymer as soft segment. Eur. Polym. J. 45, 2096–2109.

18. Sivakumar, C., Nasar, A.S. 2009. Poly(ε-caprolactone)-based hyperbranched polyurethane prepared via A2 + B3 approach and its shape-memory behavior. Eur. Polym. J. 45, 2329–2337.
19. Zhu, Y., Hu, J., Yeung, K. 2009. Effect of soft segment crystallization and hard segment physical crosslink on shape memory function in antibacterial segmented polyurethane ionomers. Acta Biomater. 5(9), 3346-3357.
20. Decker, C., Le Xuan, H., Nguyen Thi Viet, T. 1996. Photocrosslinking of functionalized rubber. III. Polymerization of multifunctional monomers in epoxidized liquid natural rubber. J. Polym. Sci. Pol. Chem. 34, 1771-1781.
21. Gopakumar, S., Paul, C.J., Nair, M.R.G. 2005. Segmented block copolymers of natural rubber and 1,4-butanediol-toluene diisocyanate oligomers. Mater. Sci. Poland. 23(1), 228-245.
22. Reyx, D., Compistron, I. 1997. Controlled degradation in tailor-made macromolecular elaboration: controlled chain-cleavages of polydienes by oxidation and by metathesis. Appl. Macromol. Chem. Phys. Angew. 247, 197-211.
23. Gopakumar, S., Nair, M.R.G. 2005. Determination of molecular parameters of NR/PU block copolymers by transport studies. Eur. Polym. J. 41, 2002–2009.
24. Kebir, N., Campistron, I., Lagurerre, A., Pilard, J.F, Bunel, C., Couvercelle, J.P., Gondard, C. 2005. Use of hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of polyurethane (PUs). Part 1. Influence of molecular weight and chemical modification of HTPI on the mechanical and thermal properties of PUs. Polymer. 46, 6869-6877.
25. Kebir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunal, C., Jouenne, T. 2007. Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of antibacterial ionic polyurethane and copolyurethane bearing ammonium groups. Biomaterials. 28, 4200-4208.
26. Solanky, S.S., Campistron, I., Laguerre, A., Pilard, J.F. 2005. Metathelic selective degradation of polyisoprene : Low-molecular-weight telechelic oligomer obtained from both synthetic and natural rubber. Macromal. Chem. Phys. 206, 1057-1063.

27. Paul, C.J., Gopinathan Nair, M.R., Koshy, P., Idage, B.B. 1999. Segmented block copolymer of natural rubber and bisphenol A-toluene diisocyanate oligomer. J. Appl. Polym. Sci. 74, 706-721.
28. Flandrin, F.R., Widmaief, J.M., Flat, J.J. 1996. Thermal ageing of polyurethane with hydrogenated polyisoprene soft segments. Polym. Degrad. Stabil. 57, 59-67.
29. Paul, C.J., Gorpinathan Nair, M.R. 1998. Segmented block copolymers of natural rubber and propylene glycol-toluene diisocyanate oligomers. Polym. Eng. Sci. 38(3), 440-451.
30. Paul, C.J., Gopinathan Nair, M.R., Koshy, P., Idage, B.B. 1999. Segmented block copolymer of natural rubber and bisphenol A-toluene diisocyanate oligomer. J. Appl. Polym. Sci. 74, 706-721.
31. Gopakumar, S., Gopinathan Nair, M.R. 2006. Natural rubber-polyurethane block copolymers: Nonlinear structural variations with NCO/OH ratio. Polym. Eng.Sci. 46(12), 1812-1821.
32. Gopakumar, S., Gopinathan Nair, M.R. 2006(1). Solution properties of NR/PU block copolymer by size-exclusion chromatography and viscometry. J. Polym. Sci. Phys. 44, 2104-2111.
33. Radhakrishnan Nair, M.N., Gopinathan Nair, M.R. 2008. Synthesis and characterization of soluble block copolymers from NR and TDI based polyurethane. J. Mater. Sci. 43, 738–747.
34. Sukumar, P., Jayashree, V., Gopinathan Nair, M.R., Radhakrishnan Nair, M.N. 2009. Synthesis and thermal studies of block copolymers from NR and MDI-based polyurethane. J. Appl. Polym. Sci. 111, 19-28.
35. Maier, G., Knopfova, V., Voit, B., Ly, P.H., Dung, B.T., Thanh, D.B. 2004. Synthesis and characterization of segmented block copolymers based on hydroxyl-terminated liquid natural rubber and α,ω-diisocyanate telechelics. Mactomol. Mater. Eng. 289, 927-923.
36. Matsumura, S., Soeda, Y., Toshima, K. 2006. Perspectives for synthesis and production of polyurethane and related polymers by enzymes directed toward green and sustainable chemistry. Appl. Microbiol. Biotechnol. 70, 12–20.

37. Tomita, H., Sanda, F., Endo, T. 2001. Polyaddition of bis(seven-membered cyclic carbonate) with diamines: A novel and efficient synthetic method for polyhydroxyurethanes. J. Polym. Sci. Pol. Chem. 39, 4091-4100.
38. Ochiai, B., Nakayama, J., Mashiko, M., Kaneko, Y., Nagasawa, T., Endo, T. 2005. Synthesis and crosslinking reaction of poly(hydroxyurethane) bearing a secondary amine structure in the main chain. J. Polym. Sci. Pol. Chem. 43, 5899–5905.
39. Tomita, H., Sanda, F., Endo, T. 2001. Reactivity comparison of five- and six-member cyclic carbonate with amine: Basic evaluation for synthesis of poly(hydroxyurethane). J. Polym. Sci. A: Polym. Chem. 39, 162–168.
40. Javni, I., Hong, D.P., Petrovic, Z.S.2008. Soy-based polyurethane by nonisocyanate route. J. Appl. Polym. Sci. 108, 3867–3875.
41. Tomita, H., Sanda, F., Endo, T. 2005. One-pot non-isocyanate synthesis of polyurethane from bisepoxide, carbon dioxide, and diamine. J. Polym. Sci. Pol. Chem. 43, 6613–6618.
42. Ochiai, B., Sato, S., Endo, T. 2007. Synthesis and properties of polyurethane bearing urethane moieties in the side chain. J. Polym. Sci. Pol. Chem. 45, 3408–3414.
43. Rokicki, G., Piotrowska, A. 2002. A new route to polyurethane from ethylene carbonate, diamines and diols. Polymer. 43, 2927-2935.
44. Kim, M.R., Kim, H.S., Ha, C.S., Park, D.W., Lee, J.K. 2001. Syntheses and thermal properties of poly(hydroxyl)urethanes by polyaddition reaction of bis(cyclic carbonate) and diamines. J. Appl. Polym. Sci. 81, 2735–2743.
45. Parzuchowski, P.G., Kowalska, M.J., Joanna Ryszkowska, J., Rokicki, G. 2006. Epoxy resin modified with soybean oil containing cyclic carbonate groups. J. Appl. Polym. Sci. 102, 2904–2914.
46. Ochiai, B., Inoue, S., Endo, T. 2006. One-pot non-isocyanate synthesis of polyurethane from bisepoxide, carbon dioxide, and diamine. J. Polym. Sci. A Polym. Chem., 43, 5899–5905.
47. Sun, J., Fujita, S., Arai, M. 2005. Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids. J. Organomet. Chem. 690, 3490-3497.

48. Helou, Carpentier, J.F., Guillaume, S.M. 2011. Poly(carbonate-urethane): an isocyanate-free procedure from α,ω-di(cyclic carbonate) telechelic poly(trimethylene carbonate)s. Green. Chem. 13, 266-271.

49. Kim, S.C., Kim, Y.H., Lee, H., Yoon, D.Y., Song, B.K. 2007. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification. J. Mol. Catal. B-Enzym. 49, 75–78.

CHAPTER 2

LITERATURE REVIEW

2.1 POLYURETHANE VIA ISOCYANATE ROUTE

2.1.1 General information

Polyurethane (PU) polymerized by a polyisocyanate-polyaddition process was discovered and developed by Otto Bayer and his coworkers in 1937 at I.G. Farben laboratories, in Leverkusen, Germany. PU can be synthesized to obtain a wide range of formats with tunable properties i.e. stiffness, hardness and density, which depend on the formulation, as shown in Figure 2.1. There are many applications of PU such as automotive parts, paints and coatings, footwear, flexible plastics, etc. The diversity of applications depends on the possibility to tailor the chemical composition of polyurethane. In addition, different raw materials and processing conditions can be chosen, to satisfy many specific requirements [1]. Polyurethane chain consists of organic molecules units joined by urethane links (carbamate, -NHCOO-). It is formed through polyaddition polymerization by a reaction between a monomer containing at least two isocyanate functional groups (-N=C=O) and another monomer containing at least two hydroxyl groups (alcohol, -OH) in the presence of a catalyst as illustrated in Figure 2.2. Polyurethane can be divided into two types, named according to the polyol used in the synthesis: polyester PU and polyether PU. PU is a material which is resistant to microbial attack, but generally, the ester-type PU is more easily degraded than the ether-type PU [2].

The polyol, diisocyanate and chain extender are the three basic components of the polyurethane chain. Normally, the chemical structure of polyurethane is considered a copolymer of the polyol and isocyanate-chain extender sequences in the term of the soft segment (SS) and hard segment (HS) [3-4], respectively, as shown in Figure 2.3. The HS is associated into hard domains which act as physical crosslinks and as filler particles within the rubbery SS matrix (Figure 2.4). Owing to rigidity and hydrogen bonding of the HS, the glass transition of the HS domains is above ambient temperature, while the SS domain usually has the glass transition temperature below ambient temperature [3].

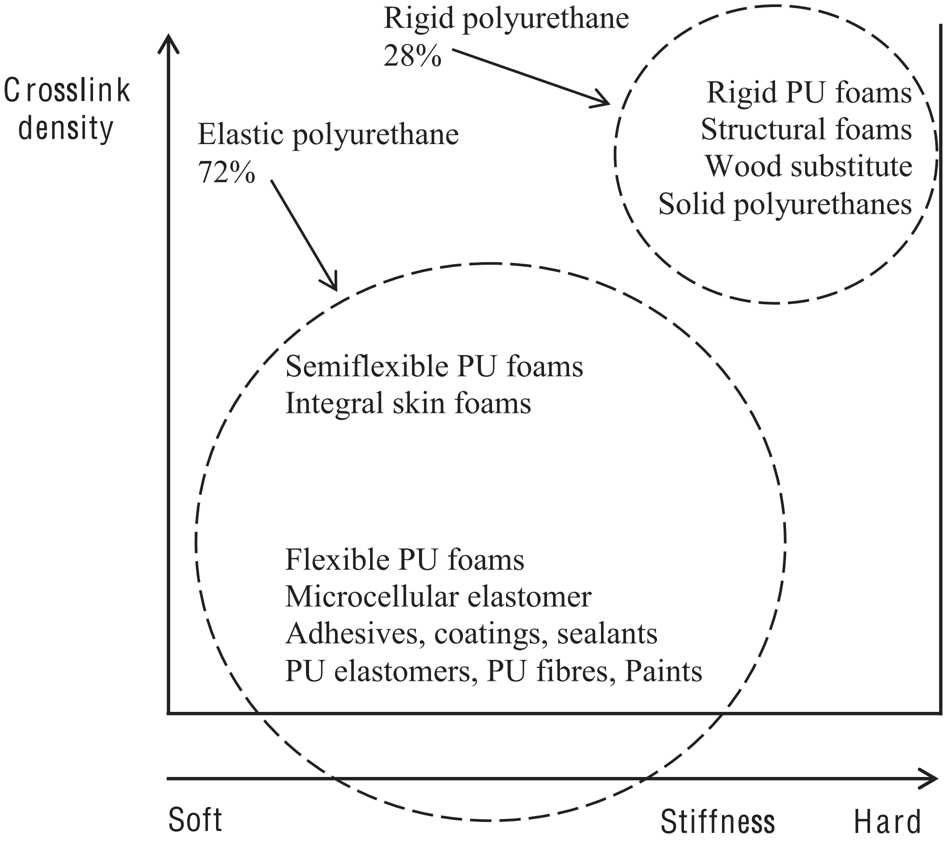
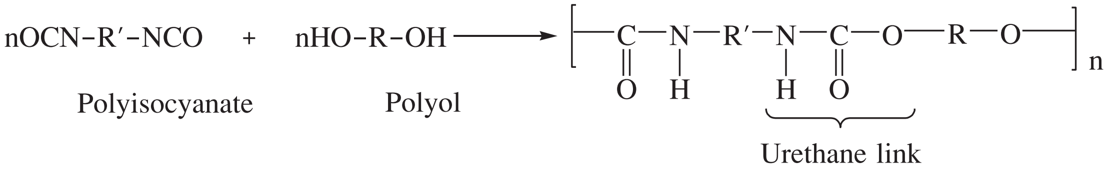


Figure 2.1 Classification of polyurethane as function of crosslink density and stiffness [5].



$$n\,OCN{-}R'{-}NCO + n\,HO{-}R{-}OH \longrightarrow \left[\underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} - R' - \underbrace{\underset{\underset{H}{|}}{N} - \underset{\underset{O}{\|}}{C} - O}_{\text{Urethane link}} - R - O - \right]_n$$

Figure 2.2 Chemical structure of polyurethane [2].

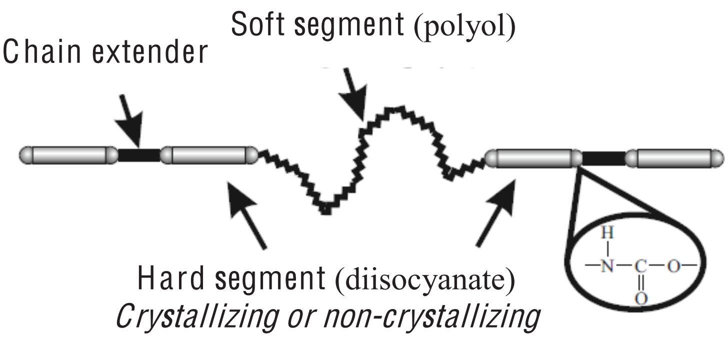


Figure 2.3 Structure of hard domains and soft domains of polyurethane [3].

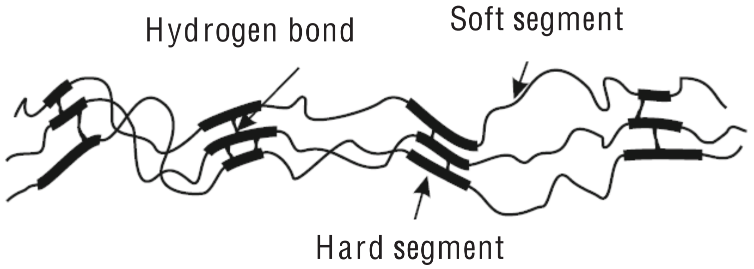


Figure 2.4 Association of the hard segments due to hydrogen bonding [3].

2.1.2 Polyurethane building blocks

The main starting materials for the synthesis of polyurethane are a diisocyanate, a polyol, a chain extender and a catalyst. The chemical and physical nature of these components affects the properties of the resulting polyurethane.

(a) Isocyanate

Both aromatic and aliphatic diisocyanates have been used in polyurethane formulations and few of the most widely used structures are showed in Figure 2.5 [toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), xylene diisocyanate (XDI), naphthalene 1,5-diisocyanate (NDI), 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 4,4’-dicyclohexylmethane diisocyanate (H_{12}MDI), norbornane diisocyanate (NDI)]. Figure 2.6 represents the resonance forms in the aliphatic isocyanate; the reactivity of the -N=C=O group is explained by the positive character of the carbon atom, which is attacked by nucleophiles, and by the negative character of the nitrogen and oxygen atom, which will be attacked by electrophiles [4]. Electron withdrawing groups in R increase the reactivity of the -NCO groups and, on the contrary, electron donating groups in R decrease the reactivity. When R is an aromatic group, the negative charge gets delocalized into the aromatic ring, providing the electron withdrawing character (Figure 2.7) [5]. Therefore, the aromatic isocyanates are more reactive than the aliphatic or the cycloaliphatic isocyanates. The reactivity of the different isocyanate types is showed in Table 2.1. The –NCO groups of a diisocyanate have different reactivities, despite of the perfect symmetry of the molecule. K_1 is the reactivity of the first –NCO groups in a diisocyanate which react with the first molecule of the hydrogen active compound to transform into a urethane isocyanate and K_2 means the reactivity of the second isocyanate group which has a much lower reactivity than the first –NCO group [5].

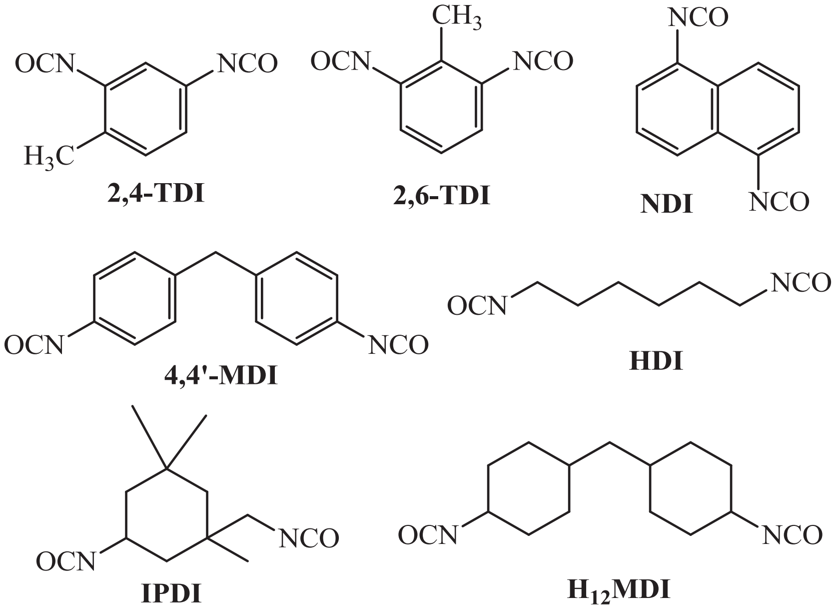
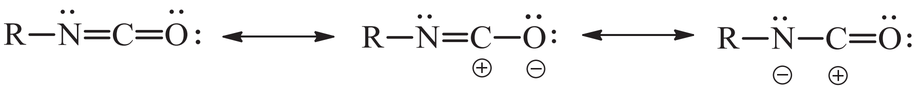


Figure 2.5 Chemical structures of different diisocyanates [4].



$$R-\ddot{N}=C=\ddot{O}: \longleftrightarrow R-\ddot{N}=\underset{\oplus}{C}-\underset{\ominus}{\ddot{O}}: \longleftrightarrow R-\underset{\ominus}{\ddot{N}}-C=\underset{\oplus}{\ddot{O}}:$$

Figure 2.6 Resonance in aliphatic isocyanates [4].

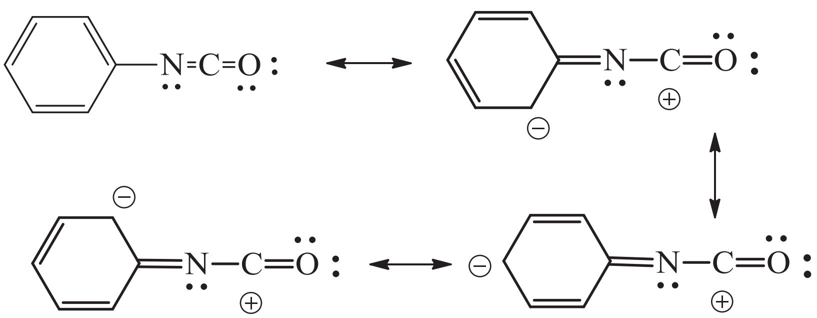
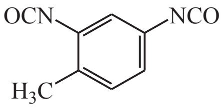
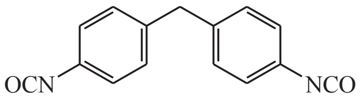
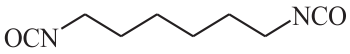
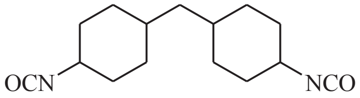
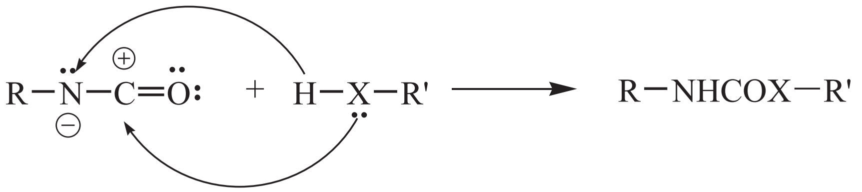


Figure 2.7 Resonance in aromatic isocyanates [4].

Table 2.1 The different reactivity of –NCO groups in some aromatic and aliphatic diisocyanate with hydroxyl group [5]

Diisocyanate	R	K_1	K_1 / K_2
2,4-TDI		400	12.121
Pure MDI		320	2.909
HDI		1	2.000
H_{12}MDI		0.57	1.425

The resonance structure of isocyanate group is responsible of the high reactivity of the isocyanates with hydrogen active compounds, through an addition on the carbon and nitrogen atom (Scheme 1) [5]. In polyurethane preparation, the HXR is HO-R. The nucleophilic center of the oxygen atom in OH group attacks the electrophilic carbon atom of NCO and the hydrogen atom of OH group interacts with the nitrogen atom.



Scheme 1 Reaction between isocyanate group and hydrogen active compounds [5].

The -NCO group can react with different compounds containing active hydrogen atoms to give the structures shown in Scheme 2 [6]:

$$RNCO + R'OH \longrightarrow RNHCOOR'$$ Urethane

$$RNCO + R'NH_2 \longrightarrow RNHCONHR'$$ Urea

$$RNCO + R'COOH \longrightarrow RNHCOR' + CO_2$$ Amide

$$\begin{tikzcd} RNCO + H_2O \arrow[r] & {[RNHCOOH]} \arrow[r] & RNH_2 + CO_2 \arrow[d, "RNCO"'] \\ & & RNHCONHR \end{tikzcd}$$

Amine

Urea

Scheme 2 Reaction between isocyanate group and hydrogen active compounds [5].

The –N-H groups of urethane and urea are also hydrogen active compounds due to the hydrogen atom connected to the nitrogen atom. Thus the reaction between the isocyanate and urea or urethane produces biuret and allophanate links onto the main chain. Formation of allophanates and biurets leads to branched chains or crosslinked structures (Figure 2.8). As a result the synthesis with an excess isocyanate generates crosslinked polyurethanes.

Comparing the relative reaction rates of isocyanates with different hydrogen active compounds, it can be noticed that all amines are much more reactive than the hydroxyl compounds (Table 2.2). Furthermore, a primary alcohol is more reactive than a secondary alcohol and much more reactive than tertiary or phenolic hydroxyl groups (Table 2.2).

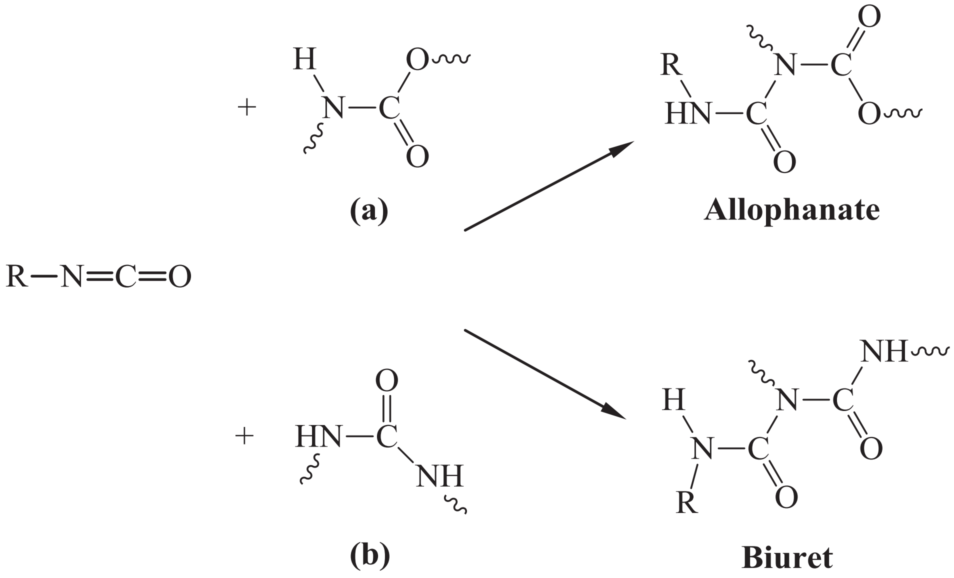


Figure 2.8 Secondary addition reactions of isocyanate with (a) polyurethane, (b) polyurea [4].

Table 2.2 The relative reaction rate of isocyanates with different hydrogen active compounds [5]

Hydrogen active compound	Formula	Reactive reaction rate (non-catalyzed, 25°C)
Primary aliphatic amine	$R\text{-}NH_2$	2500
Secondary aliphatic amine	$R_2\text{-}NH$	500-1250
Primary aromatic amine	$Ar\text{-}NH_2$	5-7.5
Primary alcohol	$R\text{-}CH_2\text{-}OH$	2.5
Water	HOH	2.5
Carboxylic acid	R-COOH	1
Secondary hydroxyl	$R_2\text{-}CH\text{-}OH$	0.75
Urea	R-NH-CO-NH-R	0.375
Tertiary hydroxyl	$R_3\text{-}C\text{-}OH$	0.0125
Phenolic hydroxyl	Ar-OH	0.0025-0.0125
Urethane	R-NH-COOR	0.0025

(b) Polyol

A polyol is a chemical compound containing hydroxyl groups. A polyol containing two hydroxyl groups (HO-R-OH) is referred to as diol. The molecular weight of the polyol is normally in the range of a few hundred to a few thousand. Polyols are classified into 2 types: polyether polyol and polyester polyol. The polyether polyol has a repeating structure of –R-O-R- and is synthesized by the reaction of epoxides (oxiranes) with an active hydrogen containing starting compound. The polyester polyol (–R-COO-R′-) is synthesized by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. Polyether diols have lower intermolecular attraction than polyester ones resulting in inferior mechanical properties [6]. In contrast, the polyether diol provides higher hydrolysis resistance than the polyester diol.

(c) Chain extender

Chain extender is a common chemical added in polyurethane. It is a low molecular weight chemical (< 400 g/mol) containing hydroxyl or amine end groups [3]. Normally, the functionality of the chain extender is two. Due to its functional groups, the chain extender can react directly with the isocyanate group. As a result, the chain extender is generally added in order to increase the mechanical properties and the glass transition temperature of the polyurethane, because it enlarges the hard segment. Although the chain extender has hydroxyl end groups similarly to the diol, it is considered as a part of the hard segment [1]. The polyurethane from diisocyanate and diol without the chain extender, the polyurethane may be a soft gum rubber with poor mechanical strength; therefore, it is necessary to use very high NCO:OH molar ratio or to add the chain extender to obtain high mechanical properties. Chain extender in polyurethane can be categorized into two classes: (i) aromatic diols and diamines and (ii) aliphatic diols and diamines. The most common used chain extenders are ethylene glycol, 1,4-butanediol (1,4-BDO or BDO), 1,6-hexanediol, cyclohexane dimethanol and hydroquinone bis(2-hydroxyethyl) ether (HQEE).

(d) Catalyst

There are two main categories of polyurethane catalysts: amine compounds and organometallic complexes. Tertiary amines and organotin compounds are widely used. Tertiary amine catalysts can be used both in the linear system (NCO + OH) than in the preparation of foams, using water (NCO+H_2O), while the organotin catalyst cannot be used for foam preparation. Dibutyltin dilaurate and tin octoate are two of the most widely used among the organotin catalysts because they are soluble in the reaction mixture, have low volatility and little smell. Unlike the strong bases as the tertiary amine, the organotin promotes the formation of branching and crosslinking via allophanate, biuret and trimer formation [6]. The reaction of an isocyanate with active hydrogen compounds takes place with or without a catalyst. The mechanisms of these reactions are depicted in Figure 2.9[4].

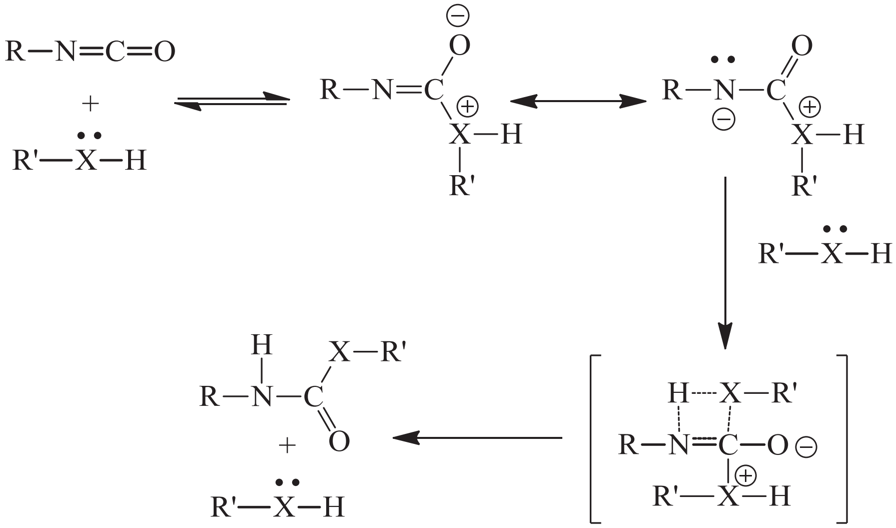


Figure 2.9 The mechanism of reaction between isocyanate group and hydrogen active compound in the absence of a catalyst [4].

The mechanism of reaction in the presence of amine and metal salt catalyst is shown in Figure 2.10 and 2.11, respectively.

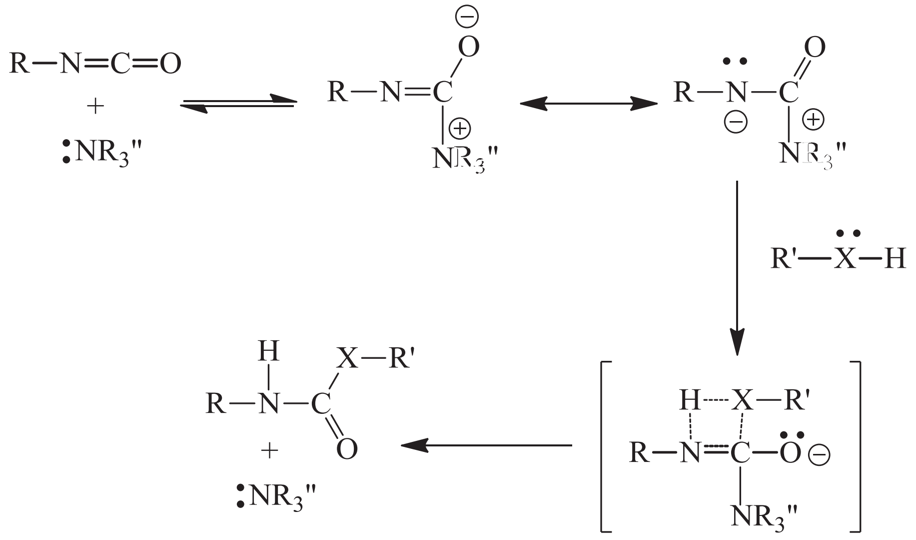


Figure 2.10 The mechanism of reaction between isocyanate group and hydrogen active compound in tertiary amine catalyst [4].

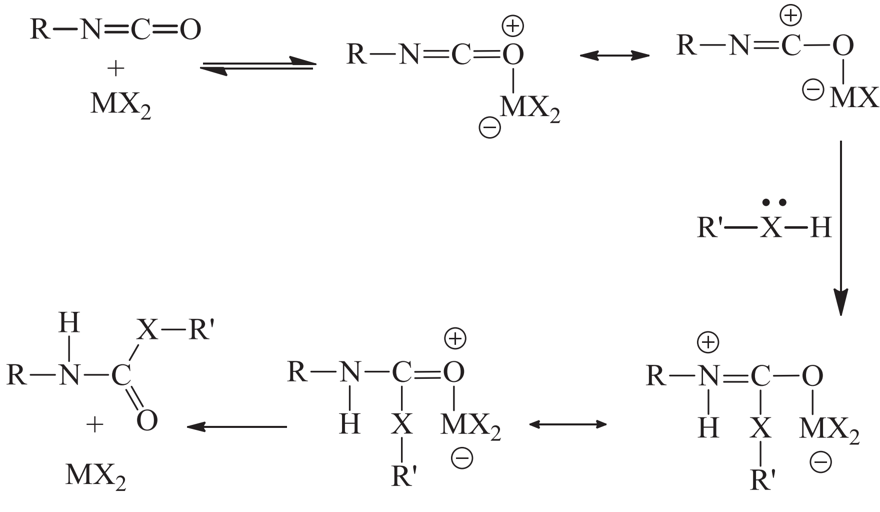


Figure 2.11 The mechanism of reaction between isocyanate group and hydrogen active compound in metal salts catalyst [4].

2.1.3 Structure –Property relation in polyurethane

(a) Effects of diisocyanate type

Each type of diisocyanate has its own intrinsic properties thus the selection of its structure is an important parameter affecting on the properties of the resulting polyurethane. Aliphatic isocyanates provide a superior light stability and show an increase of phase separation behavior over aromatic isocyanates [6].

The effect of diisocyanate type on the variation of the modulus at 300% elongation was investigated [1], as shown in Table 2.3. Polyurethane containing 1,4-PDI showed the highest 300% modulus. This result may be attributed to the compact, rigid, and highly symmetric nature of 1,4-PDI. The 4,4'-MDI shows a structure very similar to the 1,4-PDI, except the methylene group joining the two aromatic rings which results in free rotation of the two phenyl moieties. A three-dimensional structure of 4,4'-MDI obstructs efficient molecular packing so it provides the 300% modulus of PU lower than 1,4-PDI. The symmetry of 1,3-PDI is lower than 1,4-PDI due to the position of substitutes leading to less efficient molecular packing. Finally, the structure of 2,4-TDI is similar to that of 1,3-PDI with the exception of the addition of one methyl group. The asymmetrical structure of 2,4-TDI caused by this additional moiety leads to steric hindrance between polyurethane chains and less efficient packing [1].

Table 2.3 Effect of diisocyanate structure on the 300% modulus of polyurethane [1]

Diisocyanate	300% modulus (MPa)
1,4-phenylene diisocyanate (1,4-PDI)	23.4
4,4’-diphenylmethane diisocyanate (4,4’-MDI)	13.1
1,3-phynylene diisocyanate (1,3-PDI)	9.7
2,4-toluene diisocyanate (2,4-TDI)	2.1

*The molar ratio of diisocyanate:poly(tetramethylene adipate):1,4-bis(2-hydroxyethoxy) benzene of 2.5:1:1.5

(b) Effects of polyol structure

The influence of the polyol structure on the properties of polyurethane is illustrated by an example reported in Table 2.4[6]. It was found that the replacement of polyester (PEA) by polyethers (POTM, POP) in polyurethane structure leads to a lower tensile strength and modulus. In the case of polyethers, POTM gave higher tensile strength, 300% modulus and hardness than POP due to the regularity of its chain structure. In addition, the methyl group side-chain in POP prevents the crystallization of the flexible segment [6].

Table 2.4 Comparative effects of polyether and polyester polyol on the properties of polyurethane elastomer [6]

Polyol	σ_b (MPa)	ε_b (%)	300% Modulus (MPa)	Hardness (IRHD)
Poly(ethylene adipate) glycol (PEA)	50	620	20	86
Poly(oxytetramethylene) glycol (POTM)	40	500	15	90
Poly(oxypropylene) glycol (POP)	25	600	11	85

Molar ratio polyol: MDI: 1,4-BDO = 1: 4: 3

(c) Effects of chain extender

Diols and diamines are the two main types of chain extenders. The use of diamines results in higher physical properties with respect to the use of diols because the obtained urea linkages give strong hydrogen bonding interactions [6]. Moreover, increasing the ratio of chain extender results to an increase of hard segment content, thus the hardness, modulus and transition temperature of the final PU increase while the elongation at break decreases [1,6].

(d) Effects of the molecular weight of polyol

The optimal molecular weight of the polyol depends on the required final properties. How the diol molecular weight influences the properties of polyurethane is shown in Table 2.5. An increase in the molecular weight of the polyol leads to the reduction of the hard segment (weight fraction of isocyanate plus chain extender), resulting in a fall in hardness and an increase in the elongation. In addition, this table shows that the T_g of the soft segment shifts to higher temperature with a decrease in the molecular weight of polycaprolactone. The low molecular weight of PCL increases restriction of mobility of the soft segment because the hard segment and the soft segment become more compatible at the lower molecular weight [6].

Table 2.5 The effect of soft segment molecular weight on the properties of polyurethane from polycaprolactone (PCL):MDI:1,4-butane diol (BDO) at a 1:2:1 molar ratio [6]

M_n of PCL (g/mol)	530	1250	2100
Weight Fraction MDI/BDO	0.53	0.32	0.22
Hardness, (Shore A)	95	80	65
100% tensile stress (MN/m^2)	14	3	2
Ultimate elongation (%)	250	500	600
T_g from tan δ (°C)	35	-20	-35

2.1.4 Polymerization procedures for polyurethane

Two methods can be used for polyurethane synthesis: prepolymer technique (Figure 2.12) and a one shot technique (Figure 2.13).

(a) Prepolymer technique

A structure with -NCO groups at the chain ends, called prepolymer, is produced from the reaction of a diisocyanate with a polyol in the first step. A high molecular weight polyurethane is prepared by the reaction of a prepolymer with chain extender (diamine or diol) in the final step. This technique is normally used in the manufacture of polyurethane elastomer, coatings, sealants, flexible foam [5].

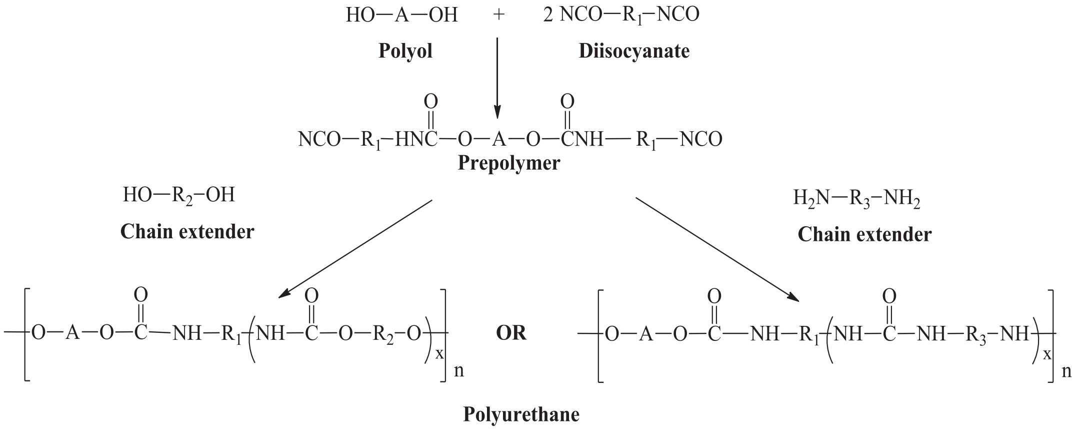


Figure 2.12 Synthesis of polyurethane by prepolymer technique [6].

(b) One shot technique

The one shot technique is one of the most used to prepare polyurethane because all the starting materials are mixed simultaneously: the evident advantages are that there is only one step so that the procedure is quicker [5].

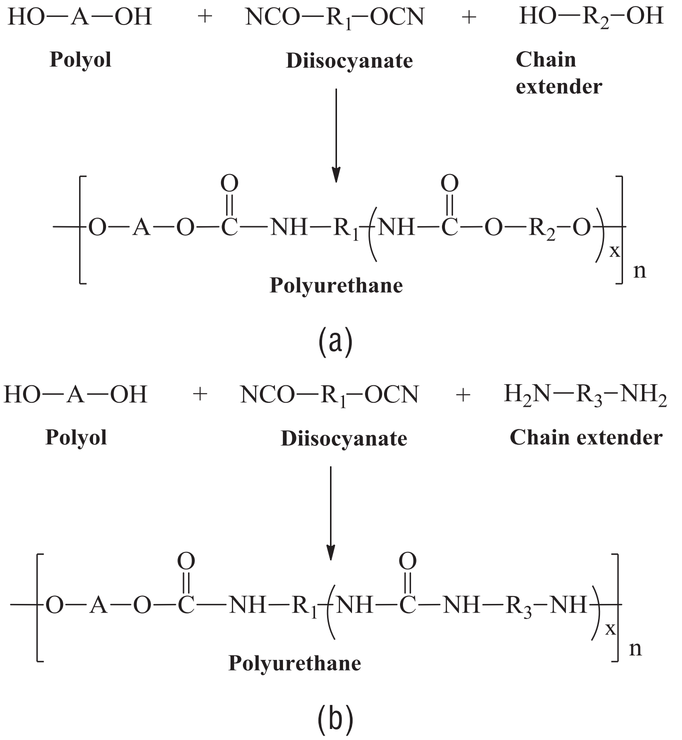


Figure 2.13 Synthesis of polyurethane by one shot technique (a) diol chain extender (b) amine chain extender [6].

2.1.5 Polyurethane containing poly(ε-caprolactone)

(a) General information

Polycaprolactone (PCL) is widely used to synthesize biodegradable polyurethane [7-23] because it is a biodegradable polyester with a low melting point of approximately 60°C, and a glass transition temperature of −60°C. PCL is prepared by ring opening polymerization of ε-caprolactone using a catalyst such as stannous octanoate (Figure 2.14).

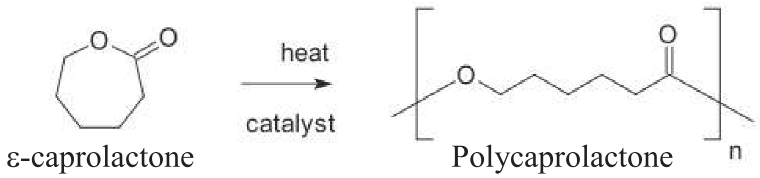
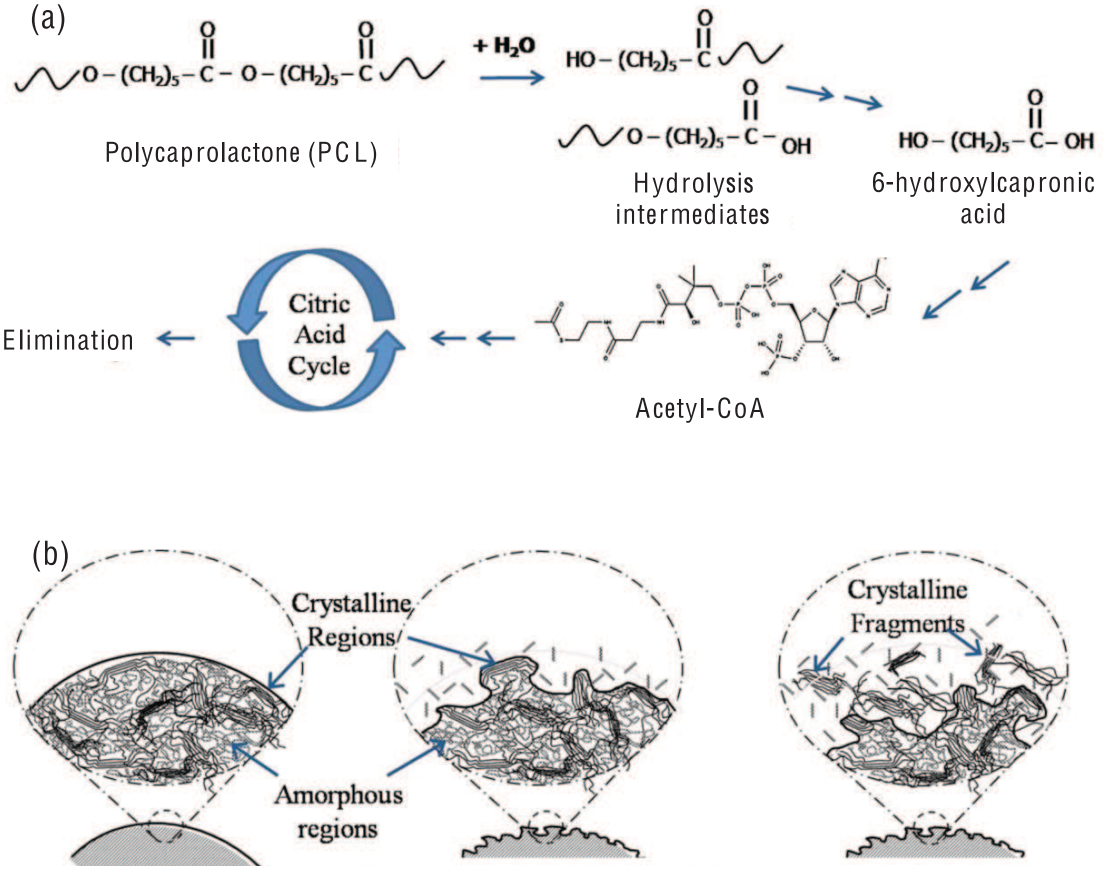


Figure 2.14 Ring opening polymerization of ε-caprolactone to polycaprolactone.

PCL can be degraded by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and has, therefore, received a great deal of attention for use as an implantable biomaterial. In particular it is especially interesting for the preparation of long term implantable devices, because its biodegradation is even slower than that of polylactide. The hydrolytically biodegradable mechanism of PCL is illustrated in Figure 2.15(a). Firstly, intermediate 6-hydroxyl caproic acid and acetyl coenzyme A are formed by hydrolysis reaction between PCL and water. Then, acetyl coenzyme A is transformed into the citric acid cycle and finally it is eliminated from the body. Figure 2.15(b) shows surface erosion of PCL in crystalline and amorphous phase. The initial surface erosion degradation of PCL occurs in amorphous phase which can lead to cyclic increasing and decreasing crystallinities throughout the degradation period [24].



PCL surface

Surface of the PCL during initial surface erosion degradation of amorphous regions

Fragmentation of crystalline regions during surface erosion degradation

Figure 2.15 (a) The degradation of PCL via hydrolysis and (b) Schematic visualization of how crystalline fragmentation could have taken place [24].

(b) The related publications

In order to our research work in the present contest, the publications of biodegradable polyurethanes based on polycaprolactone are reported in this chapter.

Gorna and Gogolewski [7] prepared linear biodegradable polyurethane with varying ratios of the hydrophilic-to-hydrophobic segment. The hydrophilic segment was constituted by the triblock polyol of poly(ethylene-propylene-ethylene oxide) (Pluronic®). The hydrophobic segment was based on poly(ε-caprolactone) diol. The molecular weight of polyurethane was determined by using viscosity measurements and size exclusion chromatography. It was found that the viscosity-average molecular weights and the polydispersity index of the polyurethane were 38,000–85,000 g/mol and 1.2–3.2, respectively. The less hydrophobic polyurethane can be absorbed up to 3.9% of water. The tensile strength, the Young's modulus and the elongation at break of polyurethane were in the range of 11–46 MPa, 4.5–91 MPa and 370–960%, respectively. The polyurethane showed the glass transition in the range of -60 to -21.5°C and the soft segment melting temperatures in the range of 30–55°C. Degradation of polyurethane samples was carried out at 37°C for 4, 12, 24 and 48 weeks using phosphate buffer solution (pH=7.4), containing sodium azide as bacteriostatic agent. It was found that the mass loss of all polyurethane samples did not exceed of 2% and the reduction of molecular weight was 15–80%. The extent of degradation was dependent on the polymer composition and the hydrophilic segment content.

Heijkants *et al.* [10] synthesized polyurethane based on poly(ε-caprolactone) (PCL) (750–2,800 g/mol) and 1,4-butane diisocyanate (BDI) with different soft segment lengths and constant uniform hard segment length, in the absence of catalysts, for the production of a degradable meniscus scaffold. First the polyester diols were endcapped with BDI yielding a macrodiisocyanate with a minimal amount of side reactions and a functionality of 2.0. Subsequently, the macrodiisocyanates were extended with 1,4-butanediol in order to obtain the corresponding polyurethanes with molecular weights between 78 and 160 kg/mol. A molar mass of the polyesterdiol crystalline PCL > 1,900 g/mol was found. The hard segment showed an increase in melting point from 78 to 122°C with the increasing of the hard segment content. It was estimated that the percentage crystallinity of the hard segment varied between 92 and 26%. The Young's modulus varied between 30 and 264 MPa, the strain at break varied between 870 and 1200% and tear-strengths varied between 97 and 237 kJ/m.

Yeganeh *et al.* [12] synthesized biodegradable polyurethane elastomers for medical implant application. The polyurethane elastomer was prepared from the reaction of epoxy terminated polyurethanes (EUP) and 1,6-hexamethylene diamine (HMDA), a curing agent. The EPU was initially synthesized from poly(ε-caprolactone) (PCL) or poly(ethylene glycol) (PEG) which reacted with 1,6-

hexamethylene diisocyanate (HDI) to obtain isocyanate terminated polyurethanes, which were subsequently reacted with glycidol to prepare EUPs. The biodegradation test showed that the elastomers based on PEG exhibited superior degradation rate and inferior mechanical properties in comparison to the elastomers based on PCL. The optimal degradation rate and mechanical properties were obtained from the elastomers prepared from the mixture of PCL and PEG.

Liu *et al.* [13] synthesized biodegradable aliphatic copolyesters from ε-caprolactone, adipic acid, and 1,6-hexanediol by melt polycondensation method. The pentaerythritol was used as the crosslinking agent. The chemical structure and thermal properties of these copolymers were studied. The water absorption behavior and hydrolytic degradation behavior of this copolyester were also investigated. This copolymer was amorphous because there were no crystallization and melting peak by DSC observation. The water absorption behavior of the copolymers increased with the increase in pentaerythritol content, but the water absorption did not change distinctly with the content of caprolactone. The degradation rate of the copolymers increased with the increase in pentaerythritol and the caprolactone content.

Xie *et al.* [14] synthesized a novel biodegradable poly(ε-caprolactone)-poly(ethylene glycol)-based polyurethane (PCL-PEG-PU) with pendant amino groups. The PCL-PEG-PU was prepared by direct coupling of PEG ester of NH_2-protected-(aspartic acid) (PEG-Asp-PEG) diols and poly(ε-caprolactone) (PCL) diols with hexamethylene diisocyanate (HDI) under mild reaction conditions. The pendant amino groups were then reacted with the chemical or bioactive reagent for biomedical applications. The polymer structures and the complete deprotection were confirmed by GPC, ^{1}H-NMR, and ^{13}C-NMR. DSC and WXRD results indicated that the crystallinity of the copolymer was enhanced with increasing PCL diol content in the copolymer. The content of amino group in the polymer could be adjusted by changing the molar ratio of PEG-Asp-PEG diol to PCL diol. This study explored an effective method to prepare polyurethanes bearing hydrophilic PEG segments and reactive amino groups.

Hong *et al.* [15] synthesized a poly(ε-caprolactone-co-β-butyrolactone) (PCLBL)-based polyurethane (PCLBL-PU) to improve the degradability of poly(ε-caprolactone)-based polyurethane (PCL-PU). PCLBL was synthesized by the ring-opening polymerization of ε-caprolactone (CL) and β-butyrolactone (BL) with stannous octanoate as catalyst. The introduction of a small amount of BL units significantly decreased the crystallinity of PCLBL. The crystallinity of the soft segment of PCLBLPU also decreased with increasing BL content. PCLBL-PU polymerized with PCLBL containing 5.7 mol% of BL units showed similar tensile properties to PCL-PU.

Jiang *et al.* [16] synthesized a series of non-toxic cross-linked waterborne polyurethanes from isophorone diisocyanate (IPDI), poly(ε-caprolactone) (PCL), poly(ethylene glycol) (PEG), 1,4-butandiol (BDO) and L-lysine without any other organic agent, mainly focusing on the effect of the amount of PEG, to obtain waterborne polyurethanes (WBPUs). The bulk structures and properties were characterized by DSC and IR. The modulus, tensile strength and elongation at break were in a range of 2.6-4.8 MPa, 16-21 MPa and 1100-1480 %, respectively. The change of tensile properties with the increasing amount of PEG in the polymers could be ascribed to the change of microphase separation. The corresponding biodegradability was tested with the enzyme Lipase AK. Tensile properties were determined before and after biodegradation test. It was found that tensile strength and elongation at break of these polyurethanes decrease in the course of degradation. An increased degradation of WBPU was observed when the amount of PEG in soft segment of WBPU decreased.

Jeon *et al.* [18] prepared poly(ε-caprolactone)-based polyurethane (PCL-PU) nanofibers containing silver (Ag) nanoparticles by electrospinning. The electrospinning solution was prepared from 8 g of PCL-PU and various amount of $AgNO_3$ in a mixed solvent system containing 7g of DMF and 3 g of THF, for use in antimicrobial nanofilter applications. The average diameter of the PCL-PU nanofibers was 560 nm and decreased with increasing concentration of $AgNO_3$. The PCL-PU nanofiber containing $AgNO_3$ exhibited higher tensile strength, tensile modulus, and lower elongation than the sample without $AgNO_3$. Small Ag nanoparticles were produced by the reduction of Ag^+ ions in the PCL-PU solutions. The average size and number of the Ag nanoparticles in the PCL-PU nanofibers were considerably increased after being annealed at 100°C for 24 h. They were all sphere-shaped and evenly distributed in the PCL-PU nanofibers, indicating that the PCL-PU chains well stabilized the Ag nanoparticles.

Han *et al.* [20] prepared biocompatible diisocyanate, lysine ethyl ester diisocyanate. Afterwards, biodegradable polyurethane (PU) was synthesized by the step growth polymerization of this diisocyanate with hydroxy terminated poly(ε-caprolactone) in the presence of 1,4- butanediol as a chain extender. The resulting PU was characterized by GPC, IR and DSC. Mechanical properties revealed that the maximum tensile strength was 23 MPa and the ultimate elongation was 1700 %. Both the tensile strength and the ultimate elongation were increased with the increase of the hard segment content. DSC measurements showed that the exothermic crystalline forming peak of the soft segment shifted to the high temperature when the hard segment content increased. The microfiber meshes with high porosity were obtained by solution electrospinning technique with the diameter of fibers of about 2 μm. The hydrolytic mass loss of PU films decreased with increasing PCL fraction, whereas the enzymatic degradation of PU films increased with increasing PCL fraction.

2.1.6 Polyurethane from telechelic liquid natural rubber

(a) General information

Natural rubber (NR) is usually obtained from the latex of the *Hevea Brasiliensis* tree, and it has an entirely *cis*-1,4-polyisoprene structure (Figure 2.16). Due to an irregular conformation in the solid state, NR is unable to crystallize under normal conditions and, therefore, exists as an amorphous, rubbery material.

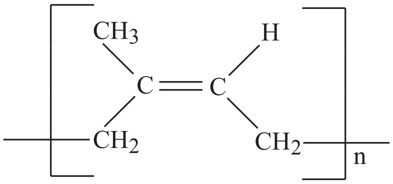


Figure 2.16 Structure of cis-1,4-polyisoprene.

NR is easily chemically modified due to the presence of the double bonds in the polymer backbone. When the long polymeric chains are selectively cut into low molecular weight NR ($M_n \leq 20000$) [25], liquid natural rubber (LNR) is obtained and it is constituted of oligomers bearing reactive terminal groups, which are referred to as telechelic liquid natural rubber (TLNR), and they can be used as new starting materials. Degradation or depolymerization of the NR leading to a formation of TLNR can be performed using different methods such as photochemical [26-27], oxidative chemical [28-31], metathesis [28, 32] and anionic [33]. Hydroxyl telechelic natural rubber (HTNR) is a TLNR used in the synthesis of polyurethane [27, 29-30, 34-41]. The schematic diagram for the preparation of HTNR [31] is shown in Figure 2.17.

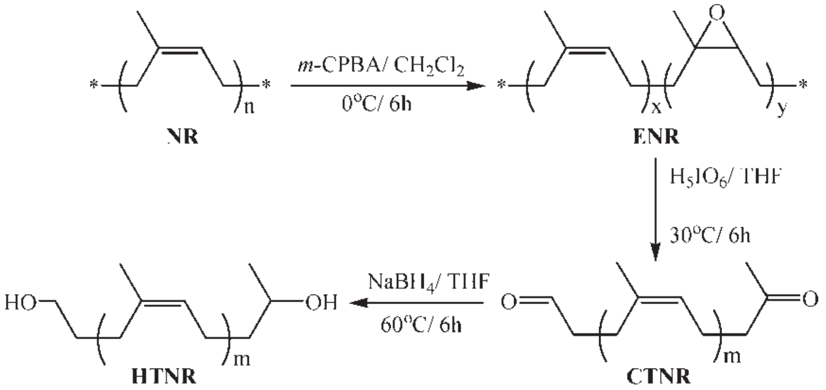


Figure 2.17 Schematic diagram of Hydroxyl telechelic natural rubber (HTNR) preparation.

Firstly, natural rubber is epoxidized by using m-chloroperbenzoic acid (m-CPBA), at 0°C, for 6 h, to form epoxy groups in NR chains (Figure 2.18). The m-CPBA has an electrophilic oxygen atom (II) on the peracid group, which initiates the reaction attacking the nucleophilic carbon-carbon double bond (I). This electropositive oxygen atom becomes part of the epoxy ring. Chain cleavage of the epoxidized natural rubber (ENR) is carried out using periodic acid and carbonyl telechelic natural rubber (CTNR) is obtained. Phinyocheep, *et al.* [42] reported that generally periodic acid is effectively employed for carbon–carbon scission of organic compounds containing a vic-diol structure. In the case of chain degradation of ENR latex, the periodic acid cleaves the ENR directly through the transformation of the epoxide ring into vic-diol, to produce low molecular weight oligomers containing an aldehyde and a ketone group at the chain-ends (Figure 2.19).

Finally, the carbonyl end-groups of CTNR are reduced to hydroxyl groups by using sodium borohydride ($NaBH_4$), at 60°C, for 6 h, followed by addition of ice to perform the reduction step. The mechanism of reduction of ketones and aldehydes to alcohols is shown in Figure 2.20.

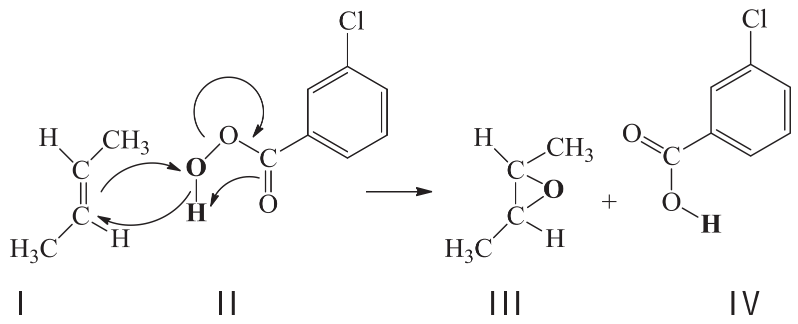


Figure 2.18 The mechanism of epoxy ring formation by using m-chloroperbenzoic acid as an oxidant [44].

(b) Related publications

In this chapter some examples of natural rubber based polyurethanes are reported.

Frandin, *et al.* [35] studied the effect of thermal aging at 150°C on the properties of polyurethane elastomer. The polyurethane elastomer was prepared by the classical one-shot method using 4,4’-diphenylmethane diisocyanate, hydrogenated hydroxyterminated polyisoprene (HHTPI), hydroxy terminated polybutadiene (HTPB), and 2-ethyl-1,3-hexane diol. The effect of different diols (HHTPI and HTPB) on the mechanical properties of polyurethane elastomers was investigated. The T_g of the soft segment in polyurethane remained constant before and after aging when HHTPI was used. A decrease in the modulus, tensile strength, tear resistance and hardness was in HHTPI based polyurethane found after ageing for 240 h, while HTPB based polyurethane showed an increase in the rigidity due to degradation of the soft segment and subsequent occurrence of crosslinking. It was concluded that the

HHTPI based polyurethanes were more resistant to degradation than the HTPB based polyurethane.

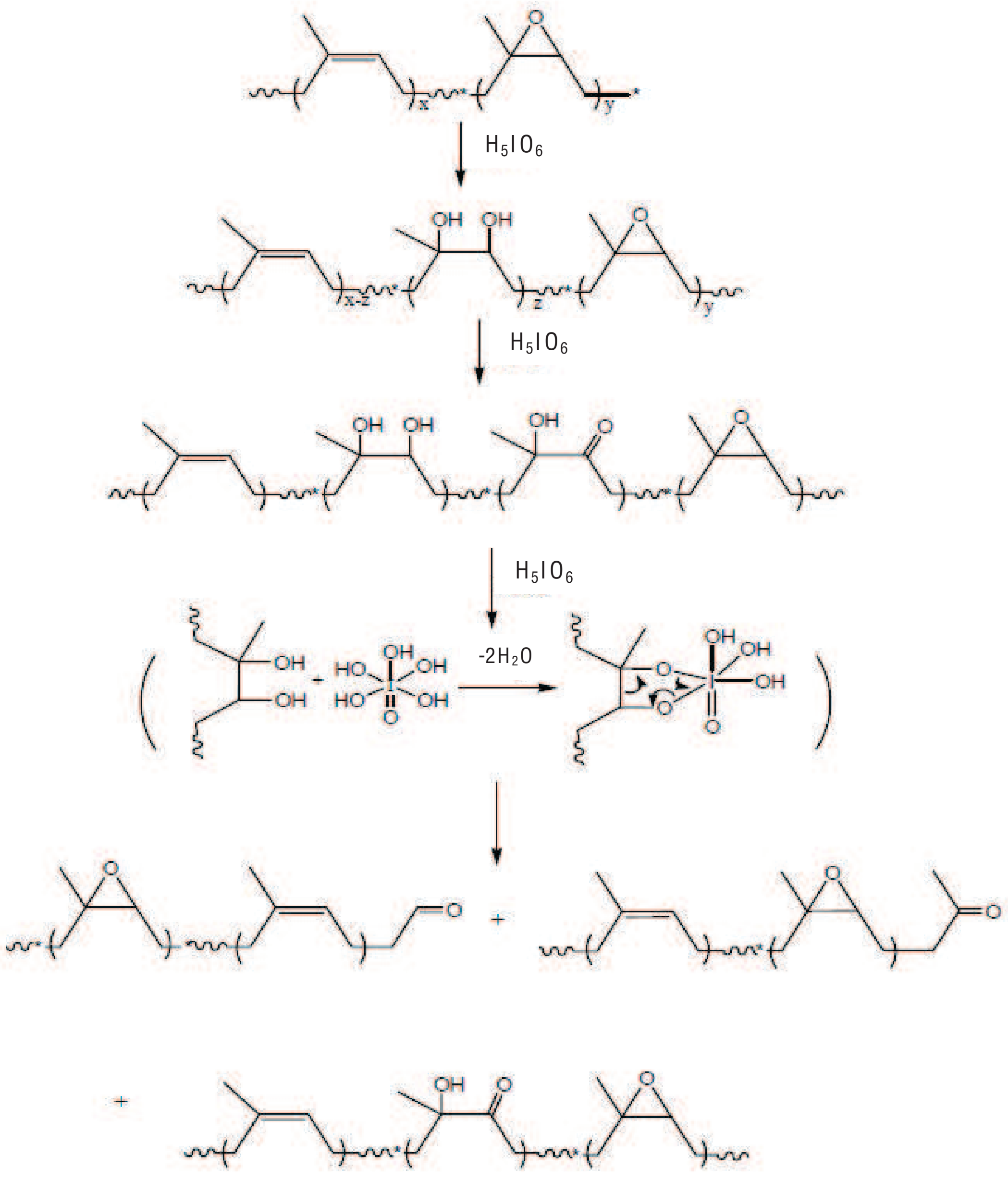


Figure 2.19 The degradation mechanism of epoxidized natural rubber latex by periodic acid [42].

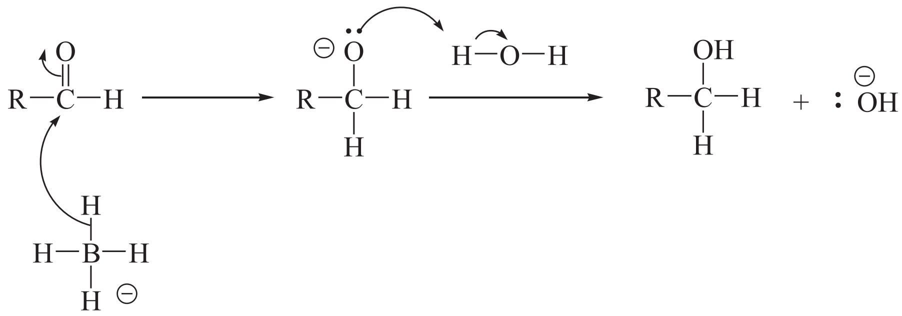


Figure 2.20 The reduction reaction mechanism of aldehyde to alcohol by using sodium borohydride as reducing agent [45].

Paul and Gorpinathan [36] synthesized polyurethane from hydroxyl-terminated liquid natural rubber (HTNR), Bisphenol A and toluene diisocyanate by one-shot and prepolymer processes in solution. Structural features were characterized by FTIR and NMR analysis: both processes provided similar spectra indicating a similar chemical structure. The polyurethane was amorphous; it showed the glass transition of the soft segment at approximately -64°C and of the hard segment in the range 75-105°C depending on the hard segment content. The two-stage thermal decomposition observed in TGA confirmed phase segregation in these materials. The scanning electron microscopy and optical micrographs showed well-defined domains dispersed in a matrix, indicating the two-phase morphology. Systematic changes in hardness and tensile properties with hard segment content were also observed. The samples behaved like soft elastomers at low hard segment content. They became toughened plastics at high hard segment content and rigid elastomers at intermediate compositions.

Kebir, *et al.* [30] prepared various telechelic *cis*-1,4-oligoisoprenes. The carbonyl telechelic *cis*-1,4-oligoisoprene (CTPI) was obtained from high molecular weight polyisoprene through an oxidative chain cleavage reaction. The CTPI was used as a starting material to obtain other telechelic oligomers via modification of the end groups. The amino telechelic cis-1,4-oligoisoprenes have been obtained in a mass range of 1600–2300 g/mol according to the pathway described in Figure 2.21. NMR experiments were used to confirm functionality and chemical structure after each chemical modification.

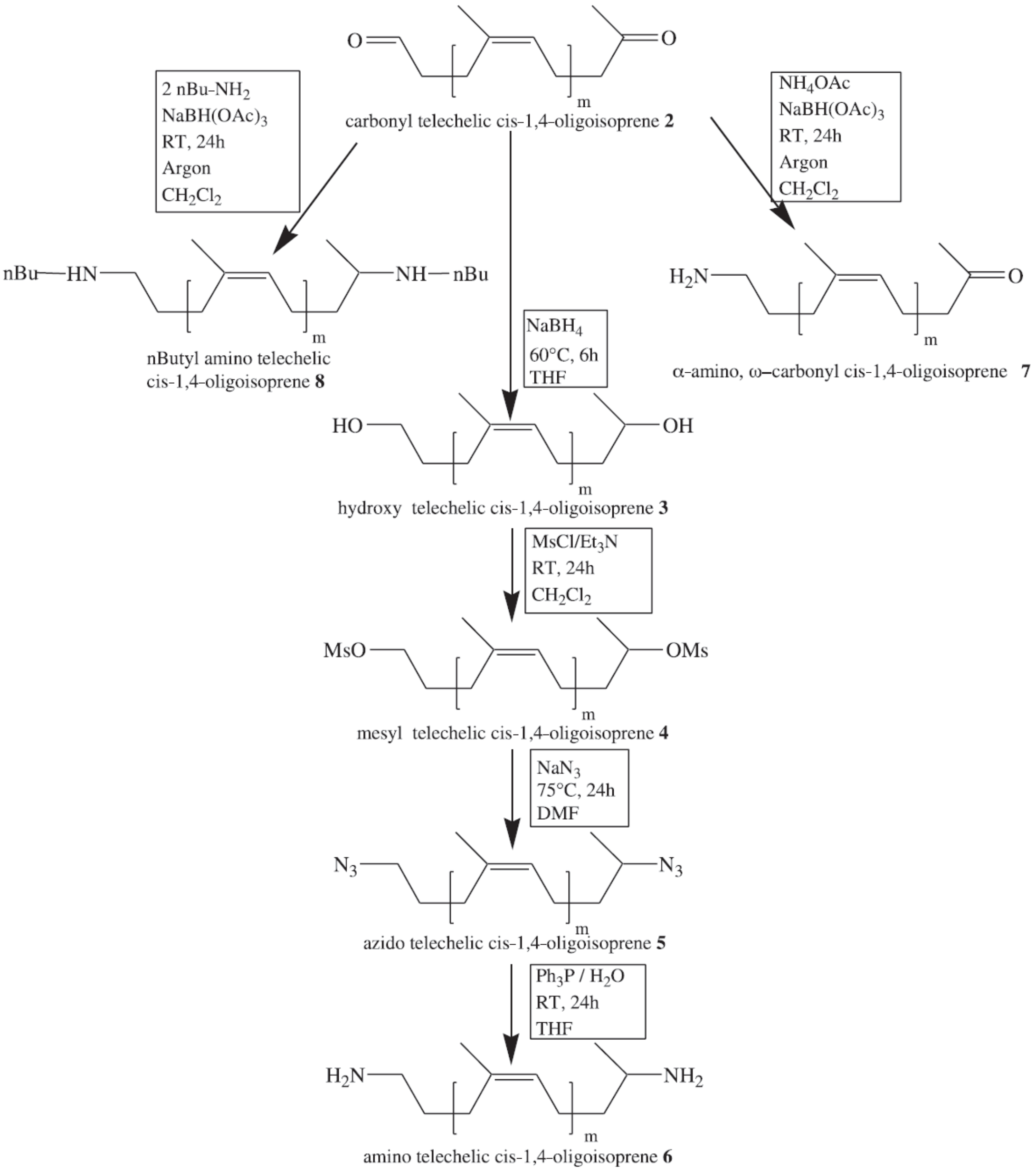


Figure 2.21 Synthesis of various amino telechelic cis-1,4-oligoisoprenes from carbonyl telechelic precursor [31].

Radhakrishnan Nair and Gopinathan Nair [40] prepared hydroxyl terminated liquid natural rubber (HTNR) with number average molecular weight of 4,600 g/mol, by the photochemical degradation of natural rubber. HTNR was successively used as a precursor for the preparation of polyurethane together with toluene diisocyanate

(TDI) and different chain extenders, such as propylene glycol (PG), 1,4-butane diol (1,4-BDO) and 1,3-butane diol (1,3-BDO) by solution polymerization. IR and NMR analyses showed the phase separation between soft segment and hard segment. T_g of the soft segment appeared at -59°C and a hard segment was in the range of 70-75°C. TGA observation showed two-stage thermal decomposition, which indicated that the block copolymers were completely phase-segregated systems. SEM images showed the amorphous heterophase morphology of the samples.

Sukumar, *et al.* [41] prepared five series of polyurethane based on hydroxy terminated liquid natural rubber (HTNR) and diphenyl methane-4,4'-diisocyanate (MDI). Different types of chain extender were used such as ethylene glycol (EG), propylene glycol (PG), 1,4-butane diol (1,4-BDO), 1,3-butane diol (1,3-BDO) and bisphenol A (BPA). In the generated polyurethanes a two phase separation occurred, as shown by the two-stage degradation TGA thermograms. The first-stage degradation was due to the hard segment and the second stage was caused by the NR phase. The polyurethane from BPA provided the lowest temperature with respect to the other chain extenders. The phase separation of polyurethane was observed also by DSC. The polyurethane exhibited two T_gs due to soft segment (NR phase) at -60 °C to -65°C and the hard segment at 76 to 110°C.

2.2 POLYURETHANE VIA NON-ISOCYANATE ROUTE

2.2.1 General information

Polyurethane can be produced also via an isocyanate-free synthesis. For example, the cationic ring opening polymerization of trimethylene urethane and tetramethylene urethane (Figure 2.22(a)), the copolymerization of 2,2-dimethyltrimethylene carbonate with tetramethylene urea (Figure 2.22(b)), the synthesis of thermoresponsive polyurethane from 2-methylaziridine and supercritical carbon dioxide (Figure 2.22(c)) and the reaction between cyclic carbonate and diamine (Figure 2.23).

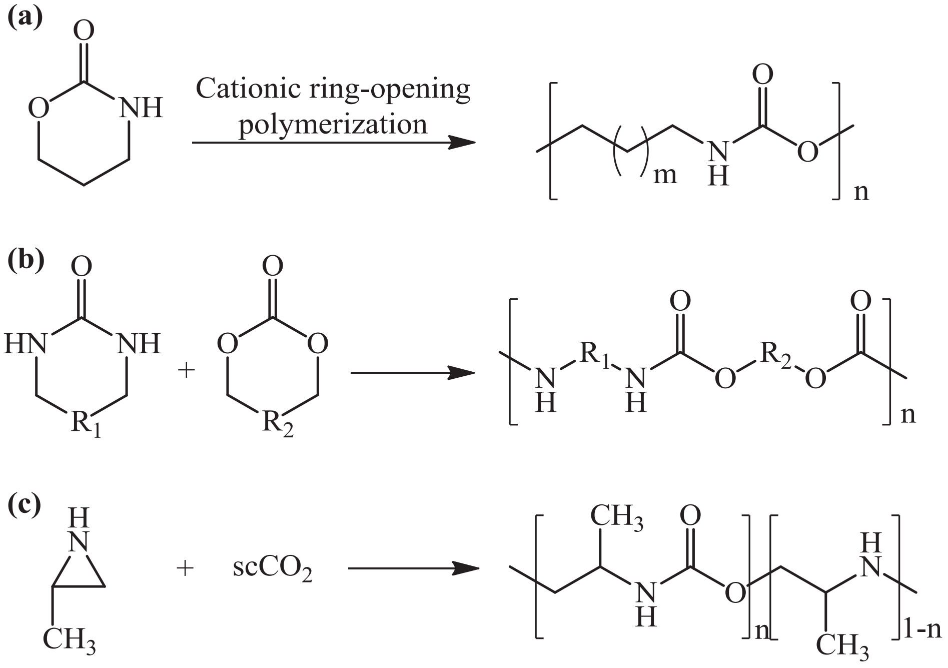


Figure 2.22 The non-isocyanate preparation route for polyurethane [46].

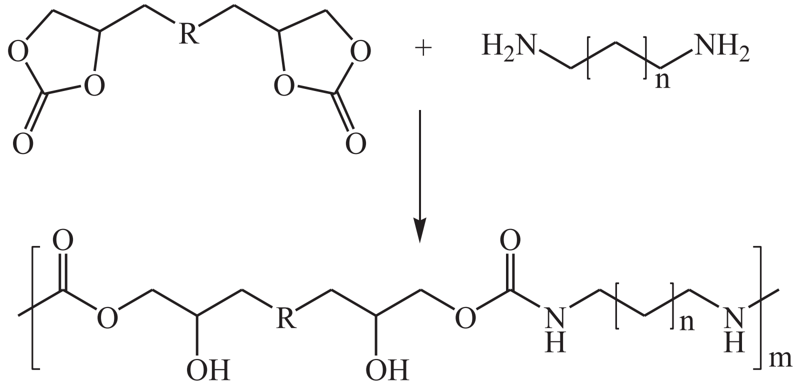


Figure 2.23 Polyurethane from cyclic carbonate group reacted with diamine [47].

2.2.2 The related publications

A representative choice of examples of polyurethane synthesis via non-isocyanate routes is presented in this paragraph.

Steblyanko, *et al.* [48] synthesized a bifunctional five-membered cyclic carbonate from carbon dioxide and diglycidyl terephthalate, and its polyaddition with alkyl diamines was carried out in dimethyl formamide, at room temperature, to obtain the corresponding poly(hydroxyurethane) with M_n in the range of 6,300–13,200 g/mol. The structure of the obtained polymers were identified by FTIR and NMR spectroscopy and their glass transition and decomposition temperatures were observed at 3–29°C and 182–277°C, respectively.

Tomita, *et al.* [49] prepared polyurethane from 1,2-bis[3-(1,3-dioxan-2-one-5-yl)-propylthio]ethane (B6CC) and 1,2-bis[4-(1,3-dioxolan-2-one-4-yl)-butylthio] ethane (B5CC) with 4,9-dioxadodecane-1,12-diamine. The reactivity of B6CC with the diamine was higher than that of B5CC. Additionally, B6CC provided a higher molecular weight polymer than B5CC. The reaction-rate constants in *N,N*-dimethylacetamide (initial reagent concentration 0.5 M) of B6CC and B5CC at 30, 50, and 70 °C were 0.70, 0.89, and 1.07 L/mol.h and 0.03, 0.06, and 0.10 L/mol.h, respectively. The activation energies were estimated to be 9.2 and 24.9 kJ/mol in the reactions with the diamine of B6CC and B5CC, respectively.

Tamami, *et al.* [50] studied epoxidized soybean oil, which was effectively converted to carbonated soybean oil (CSBO) containing five-membered cyclic carbonates by reaction with carbon dioxide in the presence of tetrabutylammonium bromide as catalyst, at 110°C. The non-isocyanate polyurethanes (NIPUs) were prepared from the reaction between CSBO and diamine and triamine. The diamines included ethylenediamine (ED) and hexamethylenediamine (HMD) and the triamine was tis(2-aminoethyl)amine (TA). NIPUs were further characterized by solvent extraction, dynamical mechanical analysis, and tensile testing. The network formation of all materials was verified. The sample from TA showed the lowest soluble fraction and elongation at break as well as the highest T_g.

Ochiai, *et al.* [51] studied the polyaddition between bifunctional five-membered cyclic carbonates and diethylenetriamine. The polyaddition proceeded via the selective addition of the primary amino group to the cyclic carbonates to give poly(hydroxyurethane) bearing a secondary amine structure in the main chain. The resulting poly(hydroxyurethane) having a secondary amine structure was crosslinked by a reaction with a bifunctional dithiocarbonate to give a networked poly(hydroxyurethane mercaptothiourethane).

Javni, *et al.* [52] synthesized polyurethane via a non-isocyanate route by reacting carbonated soybean oil with different diamines. The effect of amine structure and carbonate to amine ratio on polyurethane structure and mechanical, physical, and swelling properties was studied. The reactants 1,2-ethylene diamine, 1,4-butylene diamine, and 1,6-hexamethylene diamine were used. The carbonate and amine ratios were 1:0.5, 1:1, and 1:2. It was found that along with urethane formation, the amine group reacted with ester groups to form amides. All amines produced elastomeric polyurethane having the glass transition temperature between 0 and 40°C and having the hardness between 40 and 90 Shore A. The reaction of epoxidized soybean oil with carbon dioxide was optimized resulting in the complete conversion of epoxy to cyclic carbonate groups and gave polyurethane with higher crosslinking density and much higher tensile strength than the previously reported examples. Swelling in toluene and water depended on crosslink density and the polarity of polyurethane networks was controlled by the cyclic carbonate-to-amine ratio.

Deepa and Jayakannan [53] developed a melt transurethane polycondensation route under solvent-free and non-isocyanate condition for soluble and thermally stable aliphatic or aromatic polyurethane. Monomers consisted of the primary and secondary urethane or hydroxyl functionalities such as diurethane monomers and diols. The derived polyurethane was characterized by ^{1}H-NMR and ^{13}C-NMR. The molecular weights of the polyurethanes were 10–15 x 10^3 and 15–45 x 10^3 g/mol for M_n and M_w, respectively. The mechanistic aspects of the melt transurethane process and role of the catalyst were investigated using the model reactions, ^{1}H-NMR, and MALDI-TOF-MS. The model reactions indicated that 97% conversion was obtained in the presence of catalyst, whereas less than 2% conversion was observed in the absence of catalyst. The polymer samples were subjected to the end-group analysis using MALDI-TOFMS, which proved that the Ti-catalyst mediated non-isocyanate pathway in the melt transurethane process. The polyurethanes were stable up to 280°C, and their T_g was in the range from -30 to 120°C by using appropriate diols.

2.2.3 Cyclic carbonate preparation

There are several methods for synthesizing five member cyclic carbonates. The usual method is the reaction between an oxirane and carbon dioxide. This reaction is simple and can be conducted at both atmospheric and elevated pressures with high yields. Recently, glycerol carbonate has been used as a cyclic carbonate for synthesizing polyurethane.

(a) The reaction of an oxirane with carbon dioxide

The most abundant greenhouse gas from human activities is carbon dioxide (CO_2). It is a naturally abundant, cheap and recyclable carbon source. A cycloaddition between carbon dioxide and epoxide group produces the cyclic carbonate (Figure 2.24) [54].

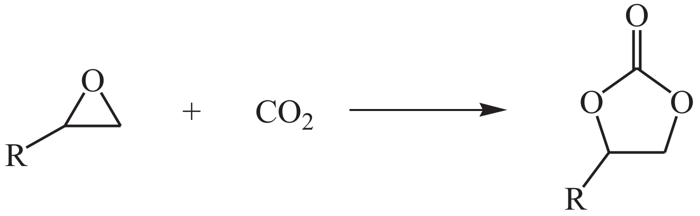


Figure 2.24 Cycloaddition of carbon dioxide to an epoxide to give a cyclic carbonate [54].

Carbonated natural rubber (Figure 2.25) can be prepared from epoxidized natural rubber (ENR) and carbon dioxide in the presence of lithium bromide (LiBr) as catalyst [55]. The mechanism of the carbonation of alkyl oxiranes by using LiBr as catalyst is exhibited in Figure 2.26.

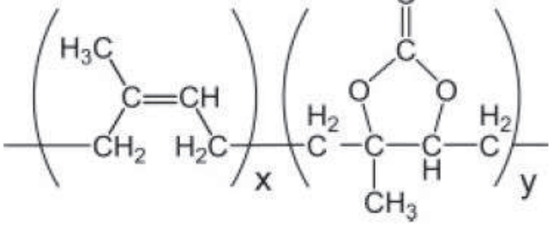


Figure 2.25 Chemical structure of carbonated natural rubber [55].

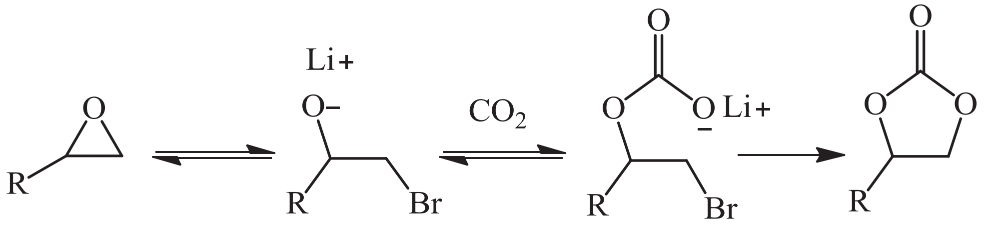


Figure 2.26 Mechanism of the carbonation of alkyl oxiranes by using LiBr as catalyst [55].

Several researchers have added CO_2 to bisphenol-A-based epoxy resin to provide the cyclic carbonated end functional groups (Figure 2.27) and these were successively used as starting materials for synthesizing polyurethane. Kim, *et al.* [56] synthesized poly(hydroxy)urethanes by the polyaddition reaction of bis(cyclic carbonate) and diamine. Bis(cyclic carbonate) was prepared from diglycidyl ether based on bisphenol A and carbon dioxide. Thermal properties and solubilities of the poly(hydroxy)urethanes containing different diamines were compared. The thermal properties of the poly(hydroxy)urethanes depended on the structure of the diamine as well as the structure of the monomer. These poly(hydroxy)urethanes were soluble only in aprotic solvents because of the hydrophilic character of the hydroxyl group.

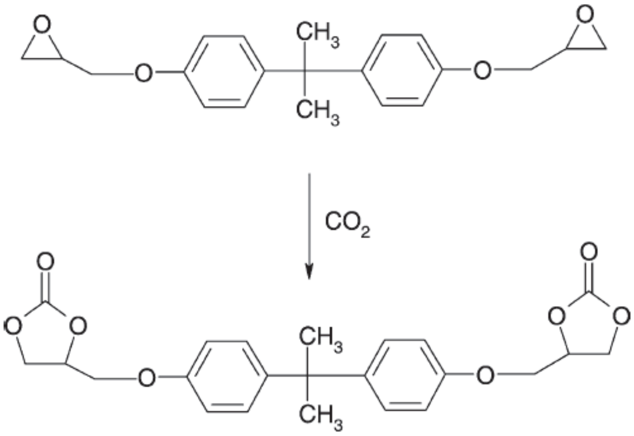


Figure 2.27 Synthesis of bis(cyclic carbonate) from bisphenol-A epoxy resin [57].

(b) The reaction of glycerol carbonate

Previously, glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) (Figure 2.28) was prepared from the reaction between glycerol and phosgene or carbon monoxide, which is a non-environmentally friendly method. Recently, it was prepared from the reaction between glycerol and dimethyl carbonate (DMC) or diethyl carbonate [58-60] as shown in Figure 2.29.

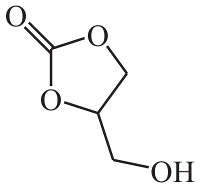


Figure 2.28 Chemical structure of glycerol carbonate.

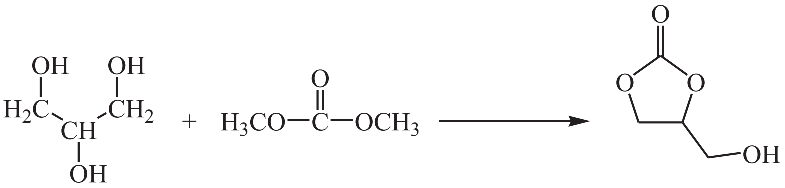


Figure 2.29 Trans-esterification of glycerol and dimethyl carbonate to glycerol carbonate [58].

The conversion processes of glycerol to useful materials have received an increasing attention because it is a renewable and inexpensive raw material. A large amount of glycerol is obtained as by-product of the plant oil methanolysis (Figure 2.30). Glycerol carbonate is a stable and colorless liquid that offers useful applications as a novel component of gas separation membranes, a surfactant, a new solvent for several types of materials or a nonvolatile solvent in the paint industry, a component in coatings, and a component of detergents. Also glycerol carbonate can be utilized as a source of new polymeric materials [59, 61]. Glycerol carbonate has two reactive sites (carbonate and pendant hydroxyl group) and can react with anhydrides, acyl chlorides etc. [62].

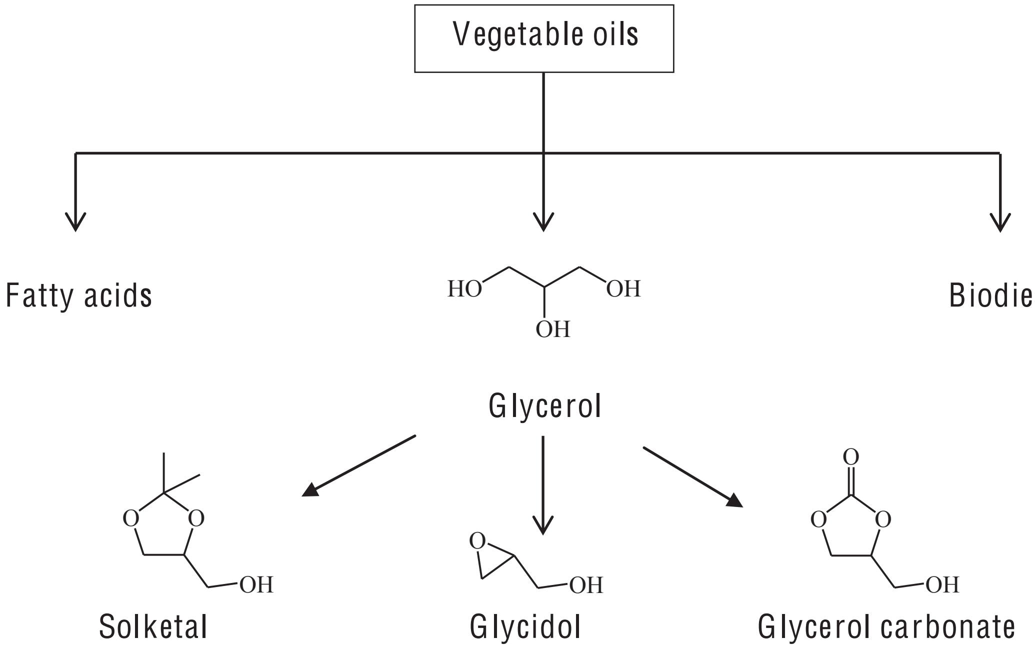


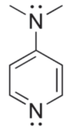
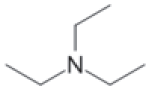
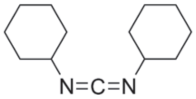
Figure 2.30 Chemical regents from glycerol [61].

Due to its functional groups, glycerol carbonate is used as a precursor for the preparation of starting materials for polymerization, i.e., preparation of α,ω-di(cyclic carbonate) telechelic polycarbonate precursor (Figure 2.31). The beginning is the reaction between PTMC-$(OH)_2$ and succinic anhydride using triethylamine and 4-dimethylaminopyridine (DMAP) as catalyst, resulting in carboxylic groups. Then, the carbonate-end functional groups in PTMC $(OCH_2DMC)_2$ were prepared from the reaction of the carboxyl chain-end groups of PTMC-$(COOH)_2$ and glycerol carbonate ($DMCCH_2OH$), in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and DMAP. The chemical structure of the three catalysts is reported in Table 2.6.

4-Dimethylaminopyridine (4-DMAP or DMAP) is a derivative of pyridine which is commercial and has a moderate price. It is used as a catalyst in the fields of organic, polymer, analytical and biochemistry [64]. DMAP is well known as a catalyst for the esterification of alcohols by acid anhydrides and acylation; in Figure 2.32 the acrylation mechanism of acetic anhydride and alcohol is illustrated [65]. The mechanism involves a pre-equilibrium formation of an acylpyridinium cation-carboxylate ion pair. The alcohol reacts with the carbonyl group of the acylpyridinium species in the rate determining step, to form the ester and the inactive protonated

DMAP. The inactive protonated DMAP is regenerated by using a tertiary base, such as triethylamine.

Table 2.6 Chemical name and structure of 4-DMAP, TEA and DCC.

Chemical Name	Chemical structure
4-Dimethylaminopyridine (4-DMAP)	
Triethylamine (TEA or Et_3N)	
N,N'-Dicyclohexylcarbodiimide (DCC)	

N,N'-Dicyclohexylcarbodiimide (DCC) is quite inexpensive. It is a powerful dehydrating agent commonly used for the preparation of amides, esters and anhydrides [66]. An esterification with DCC as a coupling reagent and 4-DMAP as an acyl-transfer catalyst is called the Steglich esterification. This reaction normally takes place at room temperature in dichloromethane; the mechanism is shown in Figure 2.33. DMAP is a strong base and it reacts with the hydrogen atom in carboxylic group due to its electron donating characteristic. Then this carboxylic acid reacts with DCC to form a O-acyl isourea. The alcohol attacks this intermediate, forming the corresponding ester and dicyclohexyl urea (DCU), which is insoluble in most solvents and sometimes very difficult to completely remove from the product. If the esterification is slow, a side-reaction occurs, diminishing the final yield or complicating purification of the product. This side-reaction is a 1,3-rearrangement of the O-acyl intermediate to a N-acyl urea which is unable to further react with the alcohol. To suppress this reaction, DMAP is added, acting as an acyl transfer-reagent [67].

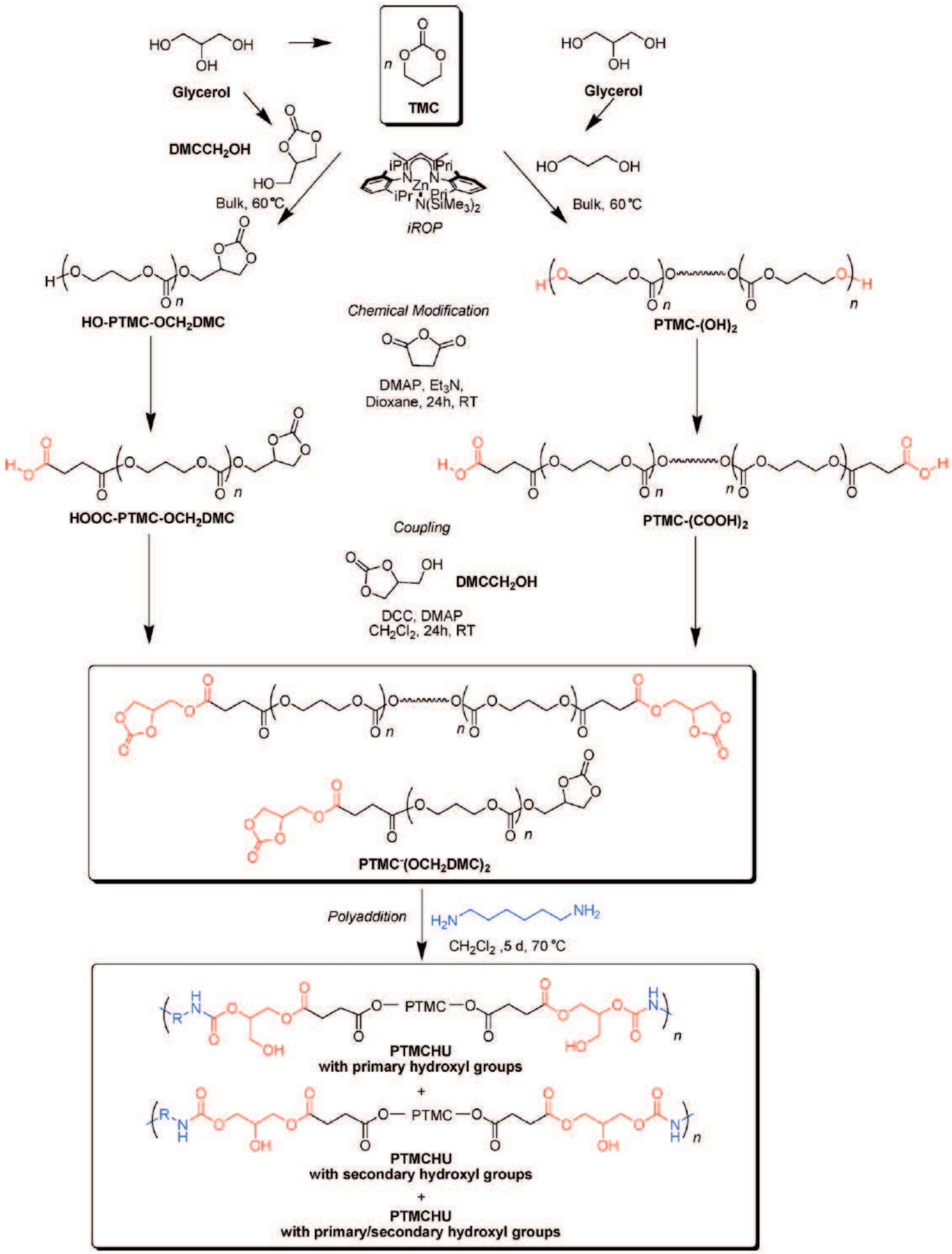


Figure 2.31 The schematic diagram for the synthesis of α,ω-di(cyclic carbonate) telechelic polycarbonate precursor [63].

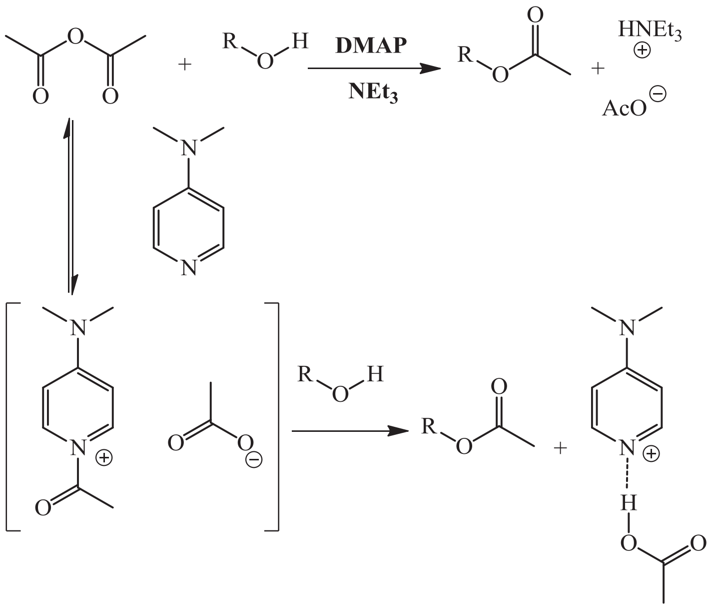


Figure 2.32 The mechanism for acylation using DMTA and Et_3N as catalysts [65].

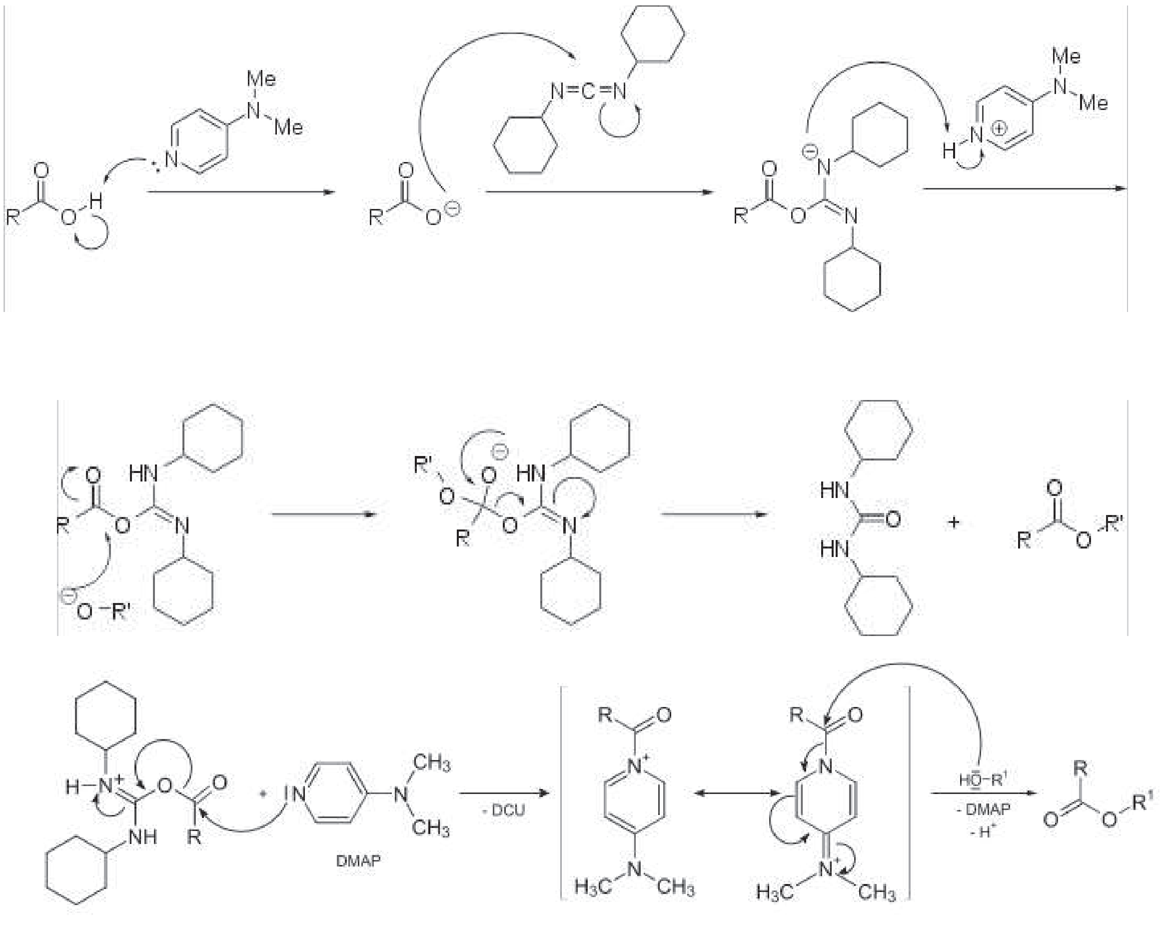


Figure 2.33 The mechanism of Steglich esterification [67].

2.3 CHARACTERIZATIONS

2.3.1 Mechanical properties

The general characteristics of different behavioral patterns of polymers in terms of their response to internal variables, such as molecular weight, chain topology, cross-linking, and crystallinity, will be monitored from external parameters such as mechanical properties and thermal properties. The mechanical properties are used to utilize for a specific purpose and to control whether an obtained polymeric material which are significant for their applications [66].

(a) Tensile testing

The mode of tensile deformation will be used to explain some of the essential parameters telling the mechanical properties of a material. The typical tensile specimen is shown in Figure 2.34. It has enlarged shoulder for gripping. The gage section is that deformation and failure will be occurred in this region [69].

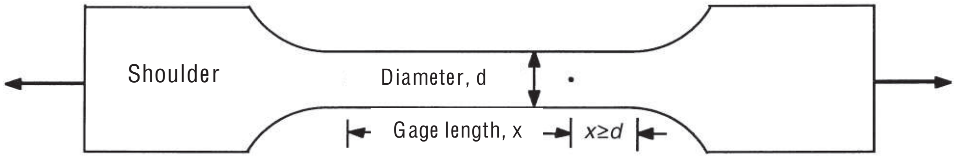


Figure 2.34 Typical tensile specimen [69].

The stress is defined as;

$$\sigma = F/A_0$$

Where F is the tensile force and A_0 is the initial cross-sectional area of the gage section.

The stain is defined as;

$$\varepsilon = (\Delta L/L_0) \times 100$$

Where L_0 is the initial gage length and ΔL is the change in gage length ($L-L_0$).

When force-elongation data are converted to stress and strain, the stress-strain curve can be plotted. A typical stress-strain curve of ductile polymers is depicted in Figure 2.35. The σ_b and ε_b are related to the stress at break and strain at break, respectively. In the case of the yield stress (σ_y) and yield strain (ε_y), they indicate the stress and strain after which a material will no longer return to its initial dimensions, this position is called yield point and this is a plastic deformation. The initial slope of the stress-strain curve is called the Young's modulus. The tensile modulus or modulus of elasticity is symbolized by "E". It is an index of the stiffness of the material since it represents the stress generated in the limit of a small deformation [68].

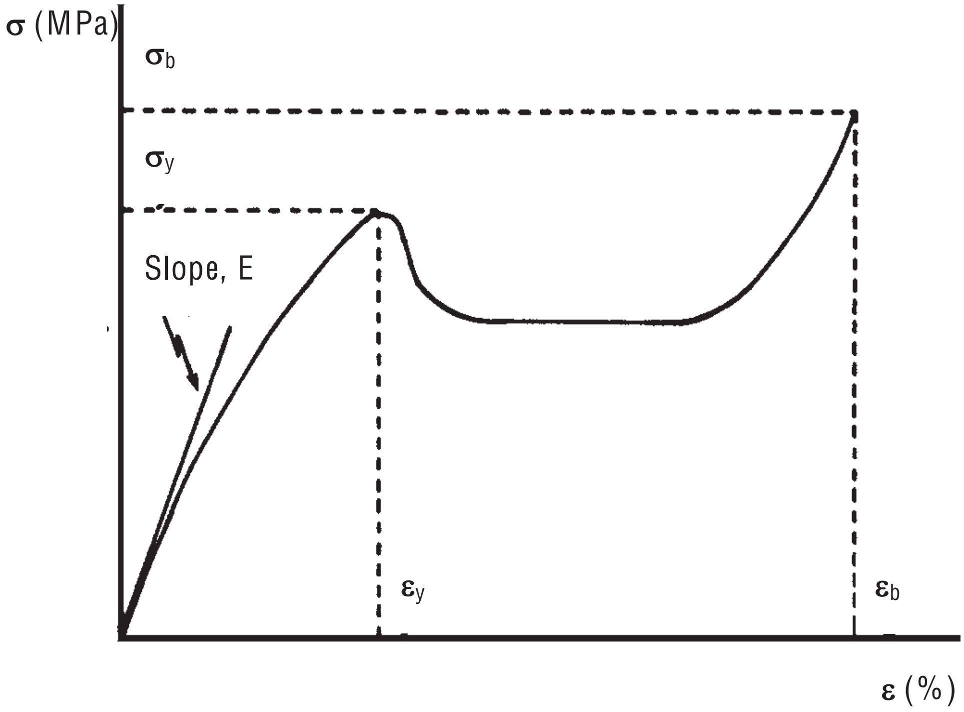


Figure 2.35 Typical stress-strain curve of ductile material [68].

The temperature has a strong effect on the modulus of polymers (Figure 2.36). Polymers exhibit some of the properties of both viscous liquid and elastic solids because they are viscoelastic. A polymer may be glass-like with a value of the Young's modulus in the range of 10^9-10^{10} Pa and it will break or yield at strains with a few percent at low temperatures or high frequencies. On the other hand, it may be rubber-like with the modulus in the range of 10^5-10^6 Pa and large extension. The glass-transition range is in an intermediate temperature range in which polymers are neither glassy nor rubber-like [70]. The stress-strain curve of different polymer is shown in Figure 2.37. The brittle materials give the curve "a". They are hard because there is little strain for high stress and they suddenly break with no plastic deformation. The curve "b" corresponds to a strong material and shows yield point before breaking. The yield point phenomena of necking and cold-drawing appear in the curve "c". The cold drawing is caused by this strain force induced to molecular orientation. In the case of curve "d" and "e", they show the stress-strain curve of homogeneous deformation with indistinct yield and rubber-like behavior, respectively. Curve "a" is a brittle polymer and curve "c", "d" and "e" is ductile. Brittle-to-ductile transition is shown in curve "b".

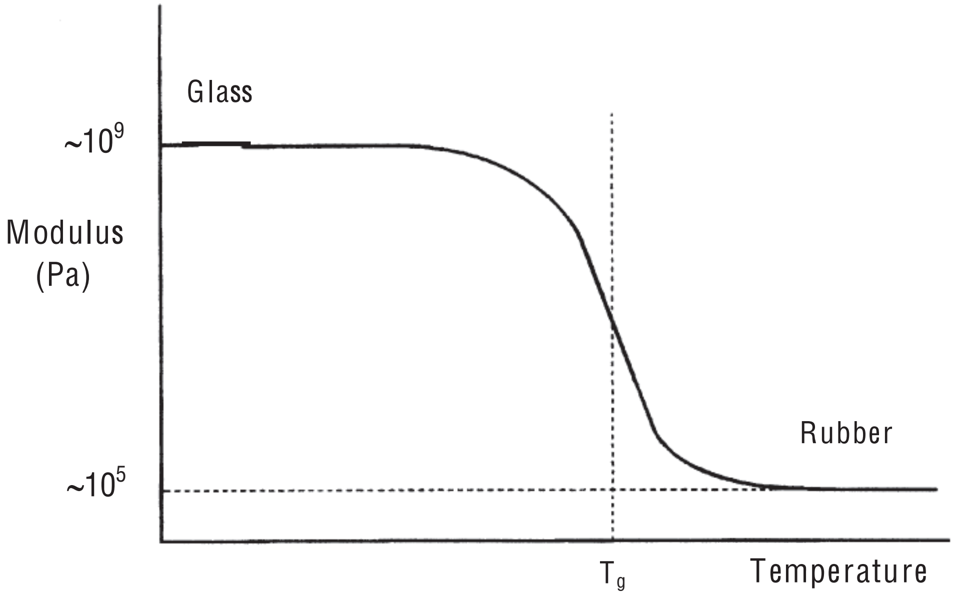


Figure 2.36 Young's modulus versus temperature [71].

(b) Tear strength [71]

This testing performed by pulling specimens apart using a tensile test machine operated without interruption at a constant rate of crosshead traverse until the specimen is completely torn. The maximum force required to tear a specimen is used to calculate the tear strength of the Die A, B and C specimens while the mean force is used for the T and CP specimens according to ASTM D624 (Table 2.7).

The tear strength calculates in Newton per meter of thickness by this equation:

$$\text{Tear strength} = F/d$$

Where F is the force in Newton and d is the median thickness of each sample in mm.

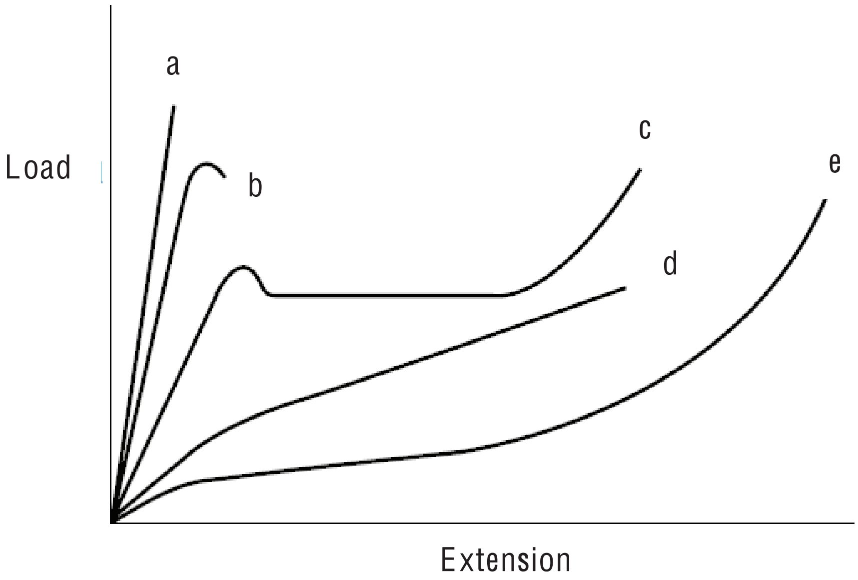
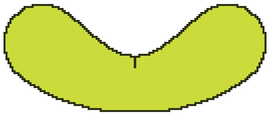
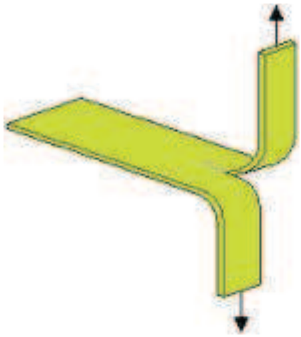


Figure 2.37 Possible forms of the load-extension curve for polymer [70].

(c) Hardness

Hardness is the resistance of polymers to compression and indentation. Brinnel hardness and Shore hardness are major methods of testing this property. Hardness of polymer is usually measured by Shore scales. Shore hardness is defined as the resistance to penetration by an indenter of specified shape under a defined load. The soft elastomers provide the hardness of between 10 and 90 Shore A. The hard elastomer and plastics is suitably tested by Shore D.

Table 2.7 The sample shapes and a standard testing according to ASTM D624 [72].

Type		Diagram	Test
Die A	Nicked crescent		 500 mm/min
Die B	Nicked tab end		
Die C	Right angle		
T	Trouser		
CP	Constrained path		

2.3.2 Thermal properties

(a) Differential scanning calorimetry (DSC)

The DSC is used to measure the difference of power (heat energy per unit time) between a polymer sample and the reference. The sample is in a sealed pan and an empty pan is used as a reference in order to maintain a zero temperature difference between them during heating and cooling temperature scan [73]. Figure 2.38 shows a schematic diagram of DSC apparatus. S is the sample pan and R is the reference pan. Figure 2.39 shows a typical DSC thermogram of polymer. The first feature is a relatively sudden change the value of heat capacity (C_p). This is the simplest case of the glass transition temperature (T_g). The second feature is an exothermic peak due to the crystallization of a polymer during heating scan which called cold crystallization temperature. The last feature is melting peak which is an endothermic peak. Amorphous polymers do not show cold crystallization and melting temperature.

(b) Thermogravimetric analysis (TGA)

The weight loss versus temperature of the sample is recorded in TGA technique. The basic instrument is shown in Figure 2.40. It consists of a precision balance, a programmable finance and a recorder. In addition, provisions are made for surrounding the sample with an air, nitrogen or an oxygen atmosphere. A small sample is continuously weighted in a controlled atmosphere as the temperature is increased at a constant heating rate. The weight loss is due to the volatilization of liquids and the decomposition and evolution of gases from solids. The onset of volatilization is proportional to the boiling point. The percent ash content of the sample verifies from the residue remaining at high temperature [74].

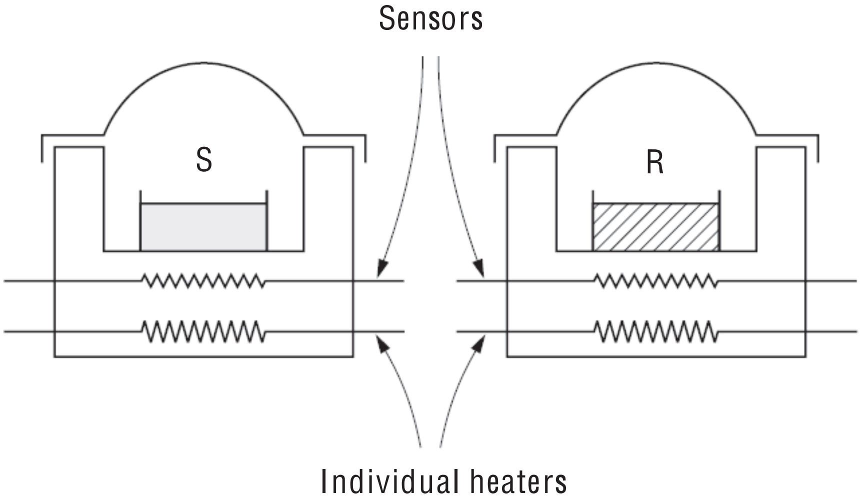


Figure 2.38 A schematic diagram of a DSC apparatus [73].

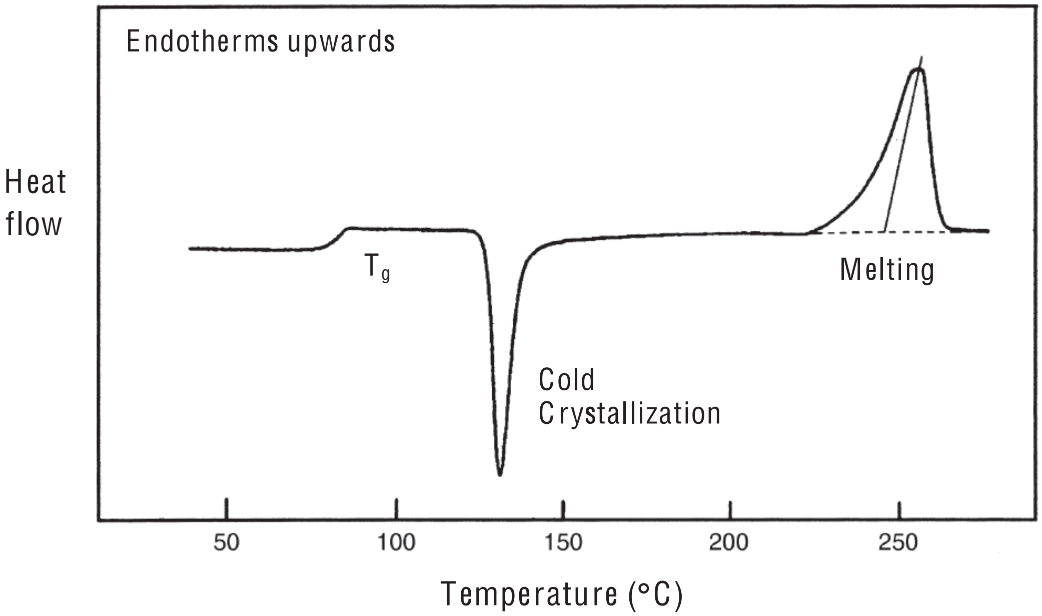


Figure 2.39 A typical DSC thermogram of polymer [73].

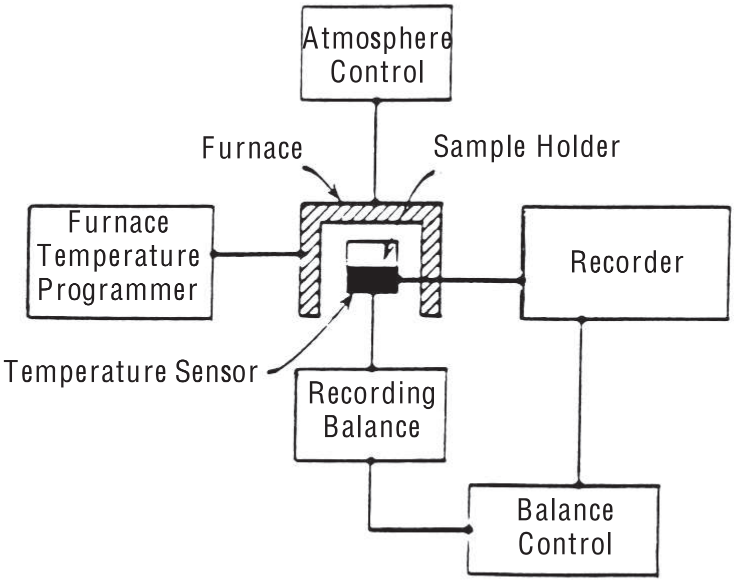


Figure 2.40 Typical components of a TGA instrument [74].

(c) Dynamic mechanical thermal analysis (DMTA)

DMTA is a measurement of the dynamic modulus in an oscillatory mechanical deformation experiment during a programmed temperature scan at controlled frequency. Thermograms are normally plotted to show the storage modulus and tan δ versus temperature (Figure 2.41). The peak of tan δ is a particularly measure of T_g [74].

2.3.3 IR and Raman spectroscopy

IR and Raman spectroscopy techniques belong to the vibrational spectroscopy. They are used for the determination and identification of molecular structure. Raman and IR spectroscopy are complementary techniques. Generally, IR spectroscopy is used for a measurement of the asymmetric vibrations of polar groups while Raman spectroscopy is suitable for the symmetric vibrations of non-polar groups [75]. In the IR active mode an oscillating electric dipole moment in polymeric molecules must take place. In the Raman active mode, the molecules must have an oscillating electrical polarisability. Figure 2.42 expresses the modes of vibration of the CO_2 molecule and their IR and Raman activities. The plus and minus signs indicate the partial charges on atoms and the arrows means the direction of motion [73]. The some differences of both techniques show in Figure 2.43 and Table 2.8.

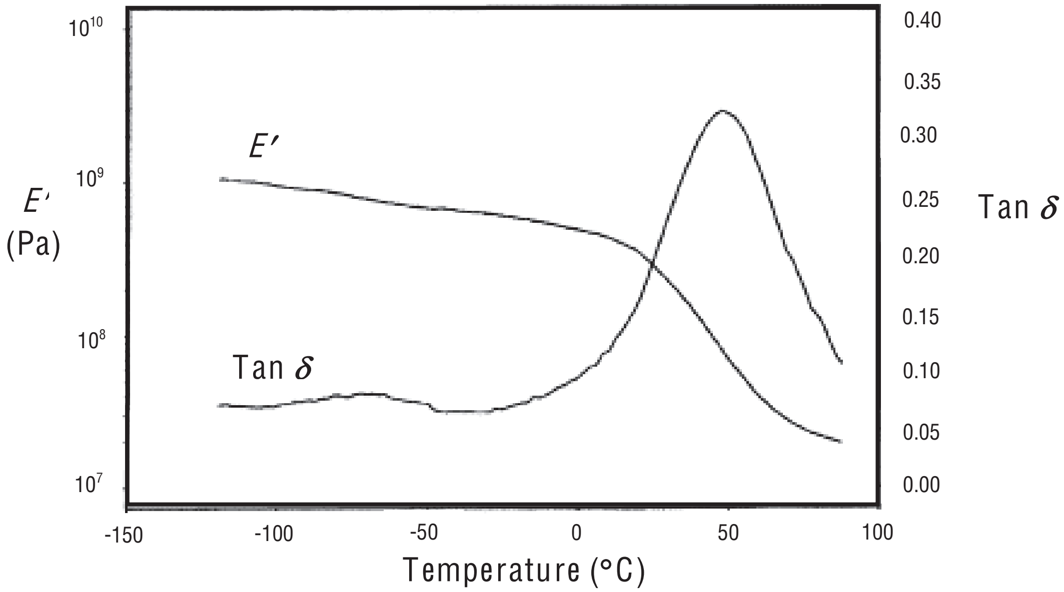


Figure 2.41 The storage modulus and tan δ versus temperature [76].

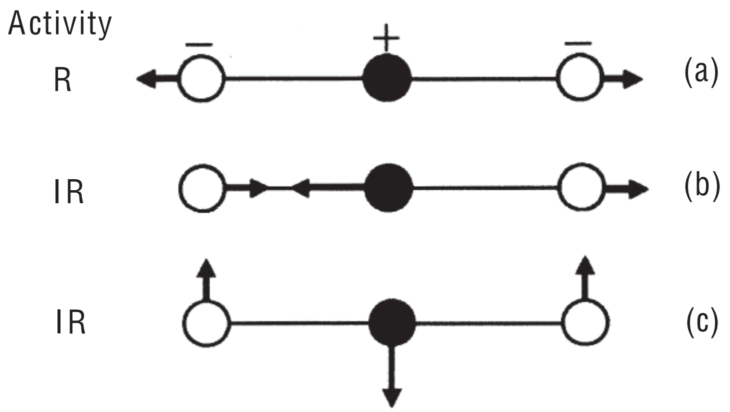


Figure 2.42 Vibrations of the CO_2 molecule (a) the symmetric stretching mode (b) the anti-symmetric stretching mode and (c) the bending mode [73].

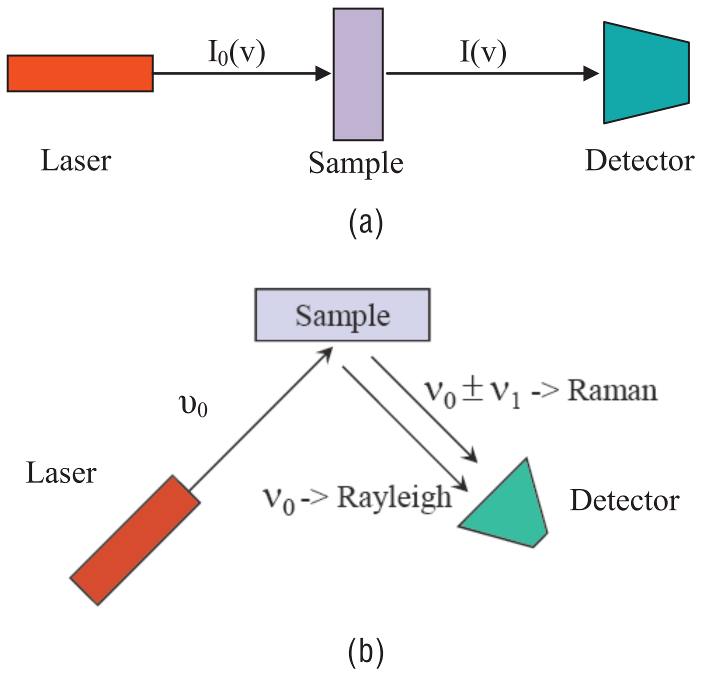


Figure 2.43 A typical of (a) IR and (b) Raman system.

Table 2.8 Comparison of Raman and IR spectroscopy [75].

Parameters	Raman	Infrared
Ease of sample preparation	Very simple	Variable
Liquids	Very simple	Very simple
Powders	Very simple	Simple
Polymer	Very simple	Simple
Gases	Simple	Very simple
Best vibrations	Symmetric	Asymmetric
Group Frequencies	Excellent	Excellent
Aqueous solutions	Very good	Very difficult
Quantitative analysis	Good	Good
Low frequency modes	Excellent	Difficult

The simple IR spectrometer consists of a source of radiation, a means of dispersing the radiation, an arrangement for allowing the radiation to pass through the sample or be reflected from its surface, a means of measuring intensities using a detector and a method of displaying and performing calculations on the spectrum. The Raman spectrometer contains a source of high-intensity monochromatic light used to irradiate the sample, a lens system to collect scattered radiation and a spectrometer to disperse it into its component wavelengths and record the intensity as a function of wavelength or wavenumber [73].

2.4 REFERENCES

1. Vermette, P., Grieseer, H.J., Laroche, G., Guidoin, R. 2001. Biomedical application of polyurethane: Tissue engineering intelligence unit; Eurekah.com: Texas, USA. 1-48.
2. Akutsu, Y., Kambe, T.N., Nomura, N., Nakahara, T. 1998. PUification and properties of a polyester polyurethane-degrading enzyme from *Comamonas acidovorans* TB-35. Appl. Environ.l Microb. Jan, 62-67.

3. Prisacariu, C. 2011. Polyurethane elastomers from morphology to mechanical aspects; SpingerWienNew York: New York, USA. 10-107.
4. Zafar, F., Sharmin, E. 2012. Polyurethane; In Tech: Rijeka, Croatia. 1-25
5. Inoescu, M. 2005. Chemistry and technology of polyols for polyurethane; Papra Technology: Shropshire, UK. 1-44.
6. Hepburn, C. 1992. Polyurethane elastomers, 2nd edition; Elsevier Science Publishers LTD: New York, USA. 1-256.
7. Gorna, K., Gogolewski., S. 2002. In vitro degradation of novel medical biodegradable aliphatic Polyurethane based on ε-caprolactone and Pluronics with various hydrophilicities. Polym. Degrad. Stabil. 75, 113–122.
8. Kim, S.C., Kim, Y.H., Lee, H., Yoon, D.Y., Song, B.K. 2007. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification. J. Mol. Catal. B-Enzym. 49, 75–78.
9. Younes, H.M., Grimaldo, E.B., Amsden., B.G. 2004. Synthesis, characterization and in vitro degradation of a biodegradable elastomer. Biomaterials. 25, 5261–5269.
10. Heijkants, R.G.J.C., Calck, R.V., Tienen, T.G., Groot, J.H., Buma, P., Pennings, A.J., Veth, R.P.H., Schouten, A.J. 2005. Uncatalyzed synthesis, thermal and mechanical properties of polyurethane based on poly(ε-caprolactone) and 1,4-butane diisocyanate with uniform hard segment. Biomaterials. 26, 4219–4228.
11. Heijkants, R.G.J.C., Schwab, L.W., van Calck, R.V., de Groot, J.H., Pennings, A.J., Schouten, A.J. 2005 (1). Extruder synthesis of a new class of Polyurethane: Polyacylurethanes based on poly(ε-caprolactone) oligomers. Polymer. 46, 8981–8989.
12. Yeganeh, H., Lakouraj, M.M., Jamshidi, S. 2005. Synthesis and properties of biodegradable elastomeric epoxy modified polyurethane based on poly(ε-caprolactone) and poly(ethylene glycol). Eur. Polym. J. 41, 2370–2379.
13. Liu, C.B., Qian, Z.Y., Gu, Y.C., Fan, L.Y., Li, J., Chao, G.T., Jia, W.J., Tu, M.J. 2006. Synthesis, characterization, and thermal properties of

biodegradable aliphatic copolyester based on ε-caprolactone, adipic acid, and 1,6-hexanediol. Mater. Lett. 60, 31 – 38.

14. Xie, Z., Lu, C., Chen, X., Chen, L., Hu, X., Shi, Q., Jing. X. 2007. A facile approach to biodegradable poly(ε-caprolactone)-poly(ethylene glycol)-based polyurethane containing pendant amino groups. Eur. Polym. J. 43, 2080–2087.
15. Hong, J.H., Jeon, H.J., Yoo, J.H., Yu, W.R., Youk, J.H. 2007. Synthesis and characterization of biodegradable poly(ε-caprolactone-co-β-butyrolactone)-based polyurethane. Polym. Degrad. Stabil. 92, 1186-1192.
16. Jiang, X., Li, J., Ding, M., Tan, H., Ling, Q., Zhong, Y., Fu, Q. 2007. Synthesis and degradation of nontoxic biodegradable waterborne polyurethane elastomer with poly(ε-caprolactone) and poly(ethylene glycol) as soft segment. Eur. Polym. J. 43, 1838–1846.
17. Tatai, L., Moore, T.G., Adhikari, R., Malherbe, F., Jayasekara, R., Griffiths, I., Gunatillake, P.A. 2007. Thermoplastic biodegradable Polyurethane: The effect of chain extender structure on properties and in-vitro degradation. Biomaterials. 28, 5407–5417.
18. Jeon, H.J., Kim, J.S., Kim, T.G., Kim, J.H., Yu, W.R., Youk, J.H. 2008. Preparation of poly(ε-caprolactone)-based polyurethane nanofibers containing silver nanoparticles. Appl. Surf. Sci. 254, 5886–5890.
19. Zia, K.M., Zuber, M., Bhatti, I.A., Barikani, M., Sheikh. M.A. 2009. Evaluation of biocompatibility and mechanical behavior of chitin-based polyurethane elastomers. Part-II: Effect of diisocyanate structure. Int. J. Biol. Macromol. 44, 23–28.
20. Han, J., Chen, B., Ye, L., Zhang, A.Y., Zhang, J., Feng, Z.G. 2009. Synthesis and characterization of biodegradable polyurethane based on poly(ε-caprolactone) and L-lysine ethyl ester diisocyanate. Front. Mater. Sci. China. 3(1), 25–32.
21. Larraz, L.R., Fernandez d’Arlas, B., Tercjak, A., Ribes, A., Mondragon, I., Eceiza, A. 2009. Synthesis and microstructure–mechanical property relationships of segmented polyurethane based on a PCL–PTHF–PCL block copolymer as soft segment. Eur. Polym. J. 45, 2096–2109.

22. Sivakumar, C., Nasar, A.S. 2009. Poly(ε-caprolactone)-based hyperbranched polyurethane prepared via A2 + B3 approach and its shape-memory behavior. Eur. Polym. J. 45, 2329–2337.
23. Zhu, Y., Hu, J., Yeung, K. 2009. Effect of soft segment crystallization and hard segment physical crosslink on shape memory function in antibacterial segmented polyurethane ionomers. Acta Biomater. 5(9), 3346-3357.
24. Woodruff, M.A., Hutmacher, D.W. 2010. The return of a forgotten polymer-polycaprolactone in the 21st century. Progress in Polymer Science. 35, 1217-1256.
25. Nor, H.M., Ebdon, J.B. 1998. Telechelic liquid natural rubber: A review. Prog. Polym. Sci. 23, 143-177.
26. Decker, C., Le Xuan, H., Nguyen Thi Viet, T. 1996. Photocrosslinking of functionalized rubber. III. Polymerization of multifunctional monomers in epoxidized liquid natural rubber. J. Polym. Sci. Pol. Chem. 34, 1771-1781.
27. Gopakumar, S., Paul, C.J., Nair, M.R.G. 2005. Segmented block copolymers of natural rubber and 1,4-butanediol-toluene diisocyanate oligomers. Mater. Sci. Poland. 23(1), 228-245.
28. Reyx, D., Compistron, I. 1997. Controlled degradation in tailor-made macromolecular elaboration: controlled chain-cleavages of polydienes by oxidation and by metathesis. Appl. Macromol. Chem. Phys. Angew. 247, 197-211.
29. Gopakumar, S., Nair, M.R.G. 2005. Determination of molecular parameters of NR/PU block copolymers by transport studies. Eur. Polym. J. 41, 2002–2009.
30. Kebir, N., Morandi, G., Campistron, I., Lagurerre, A., Pilard, J.F. 2005. Synthesis of defined amino telechelic *cis*-1,4-oligoisoprenes from carbonyl telechelic oligomers; first studies of their potentialities as polyurethane or polyuria materials precursors. Polymer. 46, 6844-6854.
31. Kebir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunal, C., Jouenne, T. 2007. Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of antibacterial ionic polyurethane and copolyurethane bearing ammonium groups. Biomaterials. 28, 4200-4208.

32. Solanky, S.S., Campistron, I., Laguerre, A., Pilard, J.F. 2005. Metathelic selective degradation of polyisoprene: Low-molecular-weight telechelic oligomer obtained from both synthetic and natural rubber. Macromal. Chem. Phys. 206, 1057-1063.
33. Paul, C.J., Gopinathan Nair, M.R., Koshy, P., Idage, B.B. 1999. Segmented block copolymer of natural rubber and bisphenol A-toluene diisocyanate oligomer. J. Appl. Polym. Sci. 74, 706-721.
34. Flandrin, F.R., Widmaief, J.M., Flat, J.J. 1996. Thermal ageing of polyurethane with hydrogenated polyisoprene soft segments. Polym. Degrad. Stabil. 57, 59-67.
35. Paul, C.J., Gorpinathan Nair, M.R. 1998. Segmented block copolymers of natural rubber and propylene glycol-toluene diisocyanate oligomers. Polym. Eng. Sci. 38(3), 440-451.
36. Paul, C.J., Gopinathan Nair, M.R., Koshy, P., Idage, B.B. 1999. Segmented block copolymer of natural rubber and bisphenol A-toluene diisocyanate oligomer. J. Appl. Polym. Sci. 74, 706-721.
37. Gopakumar, S., Gopinathan Nair, M.R. 2006. Natural rubber-polyurethane block copolymers: Nonlinear structural variations with NCO/OH ratio. Polym. Eng.Sci. 46(12), 1812-1821.
38. Gopakumar, S., Gopinathan Nair, M.R. 2006(1). Solution properties of NR/PU block copolymer by size-exclusion chromatography and viscometry. J. Polym. Sci. Phys. 44, 2104-2111.
39. Radhakrishnan Nair, M.N., Gopinathan Nair, M.R. 2008. Synthesis and characterisation of soluble block copolymers from NR and TDI based Polyurethane. J. Mater. Sci. 43, 738–747.
40. Sukumar, P., Jayashree, V., Gopinathan Nair, M.R., Radhakrishnan Nair, M.N. 2009. Synthesis and thermal studies of block copolymers from NR and MDI-based Polyurethane. J. Appl. Polym. Sci. 111, 19-28.
41. Maier, G., Knopfova, V., Voit, B., Ly, P.H., Dung, B.T., Thanh, D.B. 2004. Synthesis and characterization of segmented block copolymers based on

hydroxyl-terminated liquid natural rubber and α,ω-diisocyanato telechelics. Macromol. Mater. Eng. 289, 927-923.

42. Phinyocheep, P. Phetphaisit, W., Derouet, D. Campistron, I., Brosse, J.C. 2005. Chemical degradation of epoxidized natural rubber using periodic acid: preparation of epoxidized liquid natural rubber. J. Appl. Polym. Sci. 95, 6-15.
43. Kilway, K.V., Clevenge. R. 2007. Epoxidation of cholesterol: Experiment 2. Departmetn of Chemistry, University of Missouri, USA. 1-3
44. Saetung, A. 2009. Preparation of polyurethane foams from hydroxyltelechelic oligoisoprenes obtained by controlled degradation of natural rubber: study of their physic-mechanical, thermal, and acoustic properties. Thesis report; Prince of Songkla University, Pattani, Thailand, 1-67.
45. Internet access http://chemistry2.csudh.edu/rpendarvis/OxRed.html#redmech 23/10/2012
46. Matsumura, S., Soeda, Y., Toshima, K. 2006. Perspectives for synthesis and production of polyurethane and related polymers by enzymes directed toward green and sustainable chemistry. Appl. Microbiol. Biotechnol. 70, 12–20.
47. Rokicki, G., Piotrowska, A. 2002. A new route to polyurethane from ethylene carbonate, diamines and diols. Polymer. 43, 2927-2935.
48. Steblyanko, A., Choi, W., Sanda, F., Endo, T. 2000. Addition of five-membered cyclic carbonate with amine and its application to polymer synthesis. J. Polym. Sci. Pol. Chem. 38(13), 2375-2380.
49. Tomita, H., Sanda, F., Endo, T. 2001. Polyaddition behavior of bis(five- and six-membered cyclic carbonate)s with diamine. J. Polym. Sci. Pol. Chem. 39(6), 860-867.
50. Tamami, B., Sohn, S., Wilkes, G.L. 2004. Incorporation of carbon dioxide into soybean oil and subsequent preparation and studies of nonisocyanate polyurethane networks. J. Appl. Polym. Sci. 92, 883–891.
51. Ochiai, B., Nakayama, J.I., Mashiko, M., Kaneko, Y., Nagasawa, T., Endo, T. 2005. Synthesis and crosslinking reaction of poly(hydroxyurethane) bearing a secondary amine structure in the main chain. J. Polym. Sci. Pol. Chem. 43, 5899–5905.

52. Javni, I., Hong, D.P., Petrovic, Z.S., 2008. Soy-based polyurethane by nonisocyanate route. J. Appl. Polym. Sci. 108, 3867-3875.
53. Deepa, P., Jayakannan, M. 2008. Solvent-free and nonisocyanate melt transurethane reaction for aliphatic polyurethane and mechanistic aspects. J. Polym. Sci. Pol. Chem. 46, 2445–2458.
54. Sun, J., Fujita, S., Arai, M. 2005. Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids. J. Organomet. Chem. 690, 3490-3497.
55. Kawahara, S., Saito, T. 2006. Preparation of carbonated natural rubber. J. Polym. Sci. Pol. Chem. 44, 1561-1567.
56. Kim, M.R., Kim, H.S., Ha, C.S., Park, D.W., Lee, J.K. 2001. Syntheses and thermal properties of poly(hydroxy)urethanes by polyaddition reaction of bis(cyclic carbonate) and diamines. J. Appl. Polym. Sci. 81, 2735–2743.
57. Webster, D. 2003. Cyclic carbonate functional polymers and their application. Prog. Org. Coat. 47. 77-86.
58. Li, J., Wang, T. 2010. Coupling reaction and azoeotropic distillation for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. Chem. Eng. Process. 49, 530–535.
59. Kim, S.C., Kim, Y.H., Lee, H., Yoon, D.Y., Song, B.K. 2007. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification. J. Mol. Catal. B- Enzym. 49, 75-78.
60. Rockicki, G., Rakoczy, P., Parzuchowski, P., Sobiecki, M. 2005. Hyperbranced aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate. Green. Chem. 7, 529-539.
61. Giardi, C., Lapinte, V., Nielloud, F., Deviosselle, J.M., Robin, J.J. 2010. Synthesis of polyoxazolines using glycerol carbonate derivative and end chains functionalization via carbonate and isocyanate routes. J. Polym. Sci. Pol. Chem. 48, 4027-4035.
62. Clements, J.H. 2003. Reactive applications of cyclic alkylene carbonates; American Chemical Society: January 15.

63. Helou, M., Carpentier, J.F., Guillaume, S.M. 2001. Poly(carbonate-urethane): an isocyanate-free procedure from α,ω-di(cyclic carbonate) telechelic poly(trimethylene carbonate)s. Green. Chem. 13, 266-271.
64. Berry, D.J., Digiovanna, C.V., Metrick, S.S., Murgugan, R. 2001. Catalysis by 4-dialkylaminopyridines; ARKIVOC: 201-226.
65. Xu, S., Held, I., Kempf, B., Mayr, H., Steglich, W., Zipse, H. 2005. The DMAP-catalyzed acelylation of alcohols-A mechanistic study (DMAP=4-(Dimethylamino)pyridine). Chem. Eur. J. 11, 4751-4757.
66. Kvasnica, M. 2007. Dicylohexylcarbodiimide (DCC). Synlett. 14, 2306-2307.
67. Neises, B., Steglich, W. 1978. Simple method for the esterification of carboxylic acids. Angew. Chem. Int. Ed. 17(7), 522-524.
68. Wilkes, G.L. Encyclopedia of physical science and technology 3rd edition: in chapter of polymers, mechanical behavior. Polymer. 697-722.
69. Tensile testing 2nd edition; ASM International, Ohio USA. Accessed in www.asminternational.org.
70. Bower, D.I. 2002. An introduction to polymer physic: Cambridge University Press; Cambridge, UK, 162-185.
71. ASTM D 624: Standard test method for tear strength of convertional vulcanized rubber and thermoplastic elastomers; Annual Book of ASTM standard; 2000, Vol 09.01, West Conshohocken, USA.
72. Internet access http://www.simtec-silicone.com/high-tear-strength-makes-lsr-chewable/ 23/10/2012
73. Bower, D.I. 2002. An introduction to polymer physics. Cambridege University Press; New York, USA, 27-312.
74. Cheremisinoff, N.P. 1996. Polymer characterization: Laboratory techniques and analysis: Noyes Publications; New Jersey, USA, 17-64.
75. Larkin, P.J. IR and Raman spectroscopy: Principles and spectral interpretation: Elsevier; San Diego, USA, 1-5.
76. Gianni, A.D., Bongiovanni, R., Priola, A., Turri, S. 2004. UV-cured fluorinated coatings for plastics: effect of the photoinitiator and of the substrate filler on adhesion. Int. J. Adhes. Adhes. 24(6), 513-518.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF BLOCK COPOLYMER FROM NATURAL RUBBER, TOLUENE-2,4-DIISOCYANATE AND POLY(ε-CAPROLACTONE) DIOL-BASED POLYURETHANE

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ABSTRACT: A new type of polyurethane (PU) has been synthesized by using hydroxyl terminated liquid natural rubber (HTNR) and poly(ε-caprolactone) diol (PCL diol) as a soft segment and toluene-2,4 diisocyanate (TDI) as a hard segment. This PU is supposed to be a biodegradable and recyclable polymer. The PU samples were synthesized by solution polymerization. TDI/PCL diol polymerization was monitored in order to determine the appropriate NCO:OH ratio to obtain a molecular weight of the derived PU sufficient to form a polymeric film. The optimal NCO:OH ratios were 0.84:1 – 1.20:1 and the M_n of the derived PUs was 3000-8000 g/mol, as determined by GPC. PU from PCL diol-HTNR block copolymer was synthesized by varying molar ratio between PCL diol and HTNR. HTNR has been synthesized by epoxidation reaction and chain cleavage of natural rubber. The M_n of HTNR was in the range of 1700-8000 g/mol and M_n of 2900 g/mol was selected for preparing PU. ^{1}H-NMR and FTIR were used to determine the presence of the functional groups at the chain ends of the prepared HTNR and PU. Glass transition temperature and thermal decomposition of PU samples were investigated by using DSC and TGA, respectively.

Keywords: Biodegradable polyurethane, Poly(ε-caprolactone), Hydroxyl telechelic natural rubber

3.1 INTRODUCTION

Recently, the scientific and technological issues have been addressed to the use of renewable resources as raw materials in order to avoid problems from plastic waste management and greenhouse gases. Natural rubber (NR) is an interesting material for chemical modification as it is a renewable resource, and it is an abundant natural material, especially in Thailand. Natural rubber consists of double bonds on the polymeric backbone, which are able to be chemically modified to give new polymeric materials. Chain cleavages of NR and synthetic rubber for producing HTNR (hydroxytelechelic natural rubber) in order to be a precursor of polyurethane (PU) have been reported [1-4]. Nevertheless, PU prepared form HTNR has a low rate of degradation due to the resistance to biological attack, its hydrophobicity, and its lack of functional group recognizable by any microbial enzymatic system. Poly(ε-caprolactone) (PCL) is a biodegradable aliphatic polyester. It has already been used to synthesize biodegradable polyurethanes [5-7]. The objective of this work is to synthesize a biodegradable NR-based polyurethane by using HTNR and PCL as a soft segment and toluene diisocyanate (TDI) as a hard segment. This novel PU will likely be attacked by microorganisms on the PCL block resulting in biodegradation of the material.

3.2 EXPERIMENTAL

3.2.1 Preparation of hydroxyl telechelic natural rubber

Natural rubber (STR 5L) was epoxidized by using *m*-chloroperbenzoic acid at 0°C for 6 h, and then chain cleavage of the epoxidazed natural rubber (ENR) was obtained by addition of periodic acid to obtain carbonyl telechelic NR (CTNR). The carbonyl end group of CTNR was transformed in hydroxyl group by using sodium borohydride. The schematic diagram for preparation of HTNR is shown in Figure 3.1.

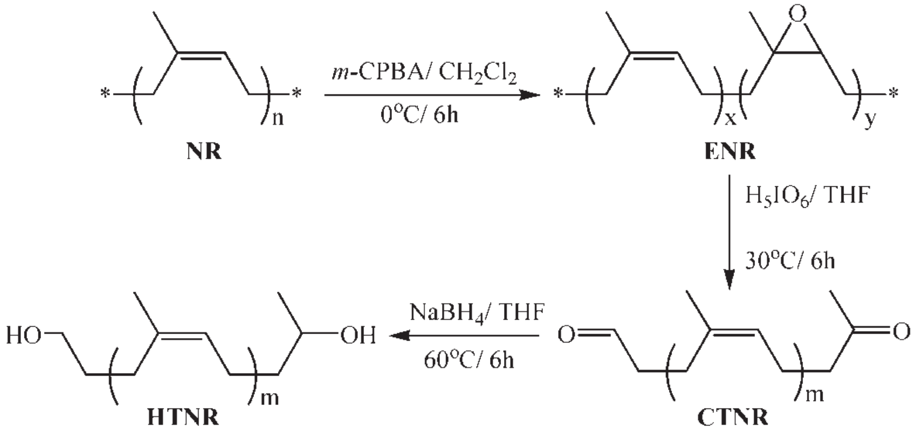

Figure 3.1 Schematic diagram of HTNR preparation.

3.2.2 Synthesis of polyurethane

PCL diol or/and HTNR were dissolved in chloroform. Dibutyl tin dilaurate acted as catalyst and it was added to the solution at 50°C. A known amount of TDI in chloroform was also added. The reaction time was varied from 1-5 h. The molecular weight of PCL diol was 530 g/mol. The molecular weight of resulting PUs was investigated by using GPC.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Effect of NCO:OH ratio and reaction time

GPC analysis was used to investigate the effect of NCO:OH ratio and reaction time of polymerization on the molecular weight of polyurethane prepared from TDI and PCL diol. The NCO:OH ratio was varied from 0.55:1 – 1.20:1 and reaction time was 5 h. The molecular weight tended to increase with increasing NCO:OH ratio (Figure 3.2). Generally, high NCO contents produce faster chain extension reaction rate. For ratios lower than 0.84, it was not possible to form a polymeric film. The highest M_n of PU was achieved for the ratio of 1.08 and 1.20, while the highest M_w of PU was for the ratio 1.08. Hence, this ratio (1.08:1) was selected to study the effect of reaction time on molecular weight of PU. The reaction time was varied from 1-5 h. It was found that the molecular weight increased when the reaction time increased as illustrated in Figure 3.3.

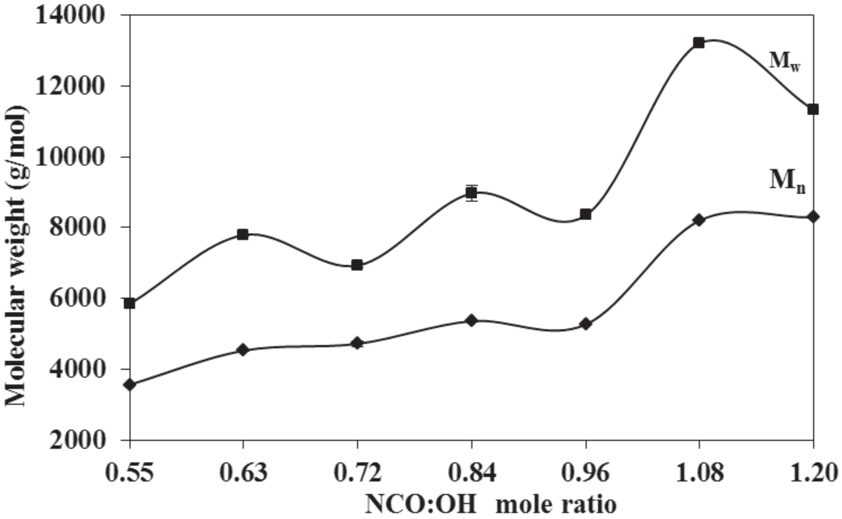

Figure 3.2 Effect of NCO:OH ratio on molecular weight of PU (TDI+PCL diol).

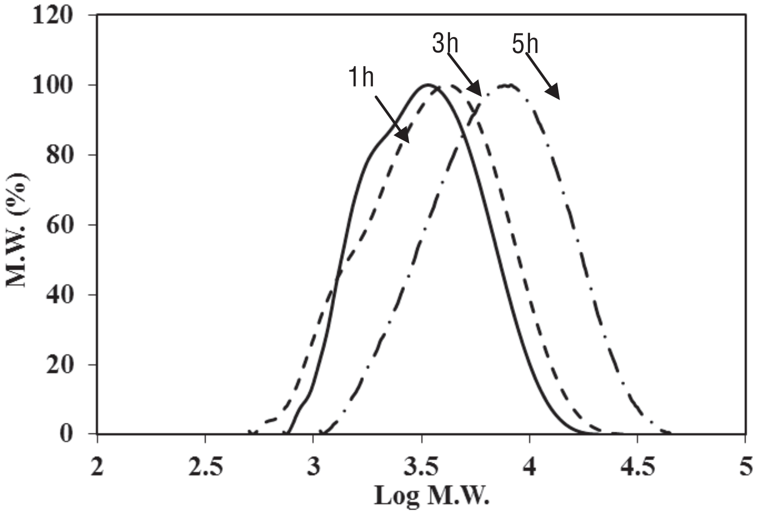

Figure 3.3 Effect of reaction time on molecular weight of PU (TDI+PCL diol).

3.3.2 Characterization of NR and telechelic NR

Samples were characterized by NMR and FTIR techniques. Figure 3.4 represents ^{1}H-NMR spectra of NR, ENR CTNR and HTNR. All samples were dissolved in $CDCl_3$. The chemical shift (δ) at 5.10 ppm (=CH), 2.05 ppm (CH_2) and 1.70 ppm (CH_3) appeared in all samples. The proton relative to the epoxy group in ENR appeared at 2.70 ppm. This peak disappeared in the CTNR spectrum and the proton of carbonyl group (CH=O) at 9.77 ppm became visible. The HTNR spectra did not show the signal at 9.77 ppm but the signals of the CH_2 and CH protons in α position with respect to the hydroxyl end group were displayed at 3.65 and 3.80 ppm, respectively. Figure 3.5 shows FTIR spectra of NR, CTNR and HTNR. The NR spectrum showed the absorption bands at 3035 and 835 cm^{-1} representing asymmetric stretching and C-H out of plane bending in =CHR, respectively. The bands at 1448 and 1376 cm^{-1} were assigned to C-H bending of CH_2 and CH_3 *cis*-1,4-isoprene, respectively. The absorption of C=C stretching was observed at 1664 cm^{-1}. The absorption band of carbonyl group at 1721 cm^{-1} appeared in the CTNR spectrum. The absorption band at 3352 cm^{-1} for O-H stretching from hydroxyl group was revealed in the HTNR spectrum while the absorption band of the carbonyl group at 1721 cm^{-1} was disappeared. This result confirmed that the carbonyl group in CTNR was completely changed to hydroxyl group in HTNR. Figure 3.6 demonstrates FTIR spectra of TDI, PCL and PUs (TDI+PCL and TDI+PCL+HTNR). The TDI spectrum illustrated the band of N=C=O stretching of isocyanate group at 2258 cm^{-1} and overtone of trisubstituted benzene at 1781 and 1721 cm^{-1}. The PCL spectrum showed O-H stretching at 3442 cm^{-1}, C=O stretching at 1731 cm^{-1} and asymmetric and symmetric C-O-C stretching at 1234 and 1167, respectively. The spectra of two PUs showed an absorption band at 3348 cm^{-1} representing the N-H stretching in urethane linkage and the band of C=N=O stretching of isocynate group was disappeared.

3.3.3 Thermal properties of biodegradable polyurethane

Biodegradable PUs were synthesized at 50°C for 5 h by varying TDI content and PCL:HTNR ratio as listed in Table 3.1. M_n of HTNR was 2900 g/mol. Sample 1 and 2 remained liquid indicating too low TDI content. It was found that to obtain the PU film, TDI content should be $\geq$ 1.17 mol and the HTNR content should be $\leq$ 0.07 mol. T_g of biodegradable PU increased with increasing TDI content. The derived PUs showed low T_g as an elastomer, as expected. Thermal properties of PUs depended on the TDI and HTNR content as shown in Figure 3.7 and 3.8, respectively.

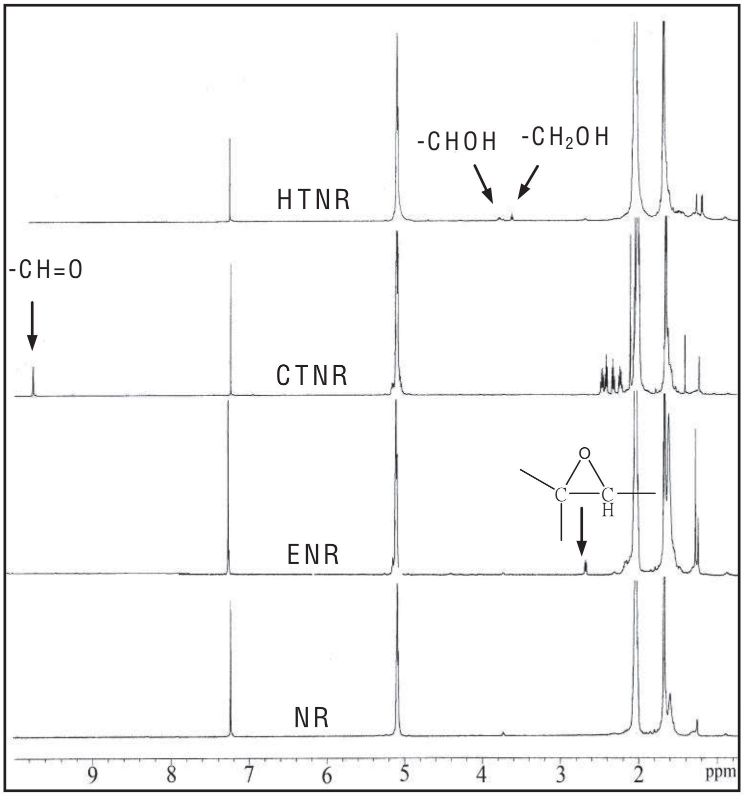

Figure 3.4 ^{1}H-NMR spectra of NR, ENR,CTNR and HTNR.

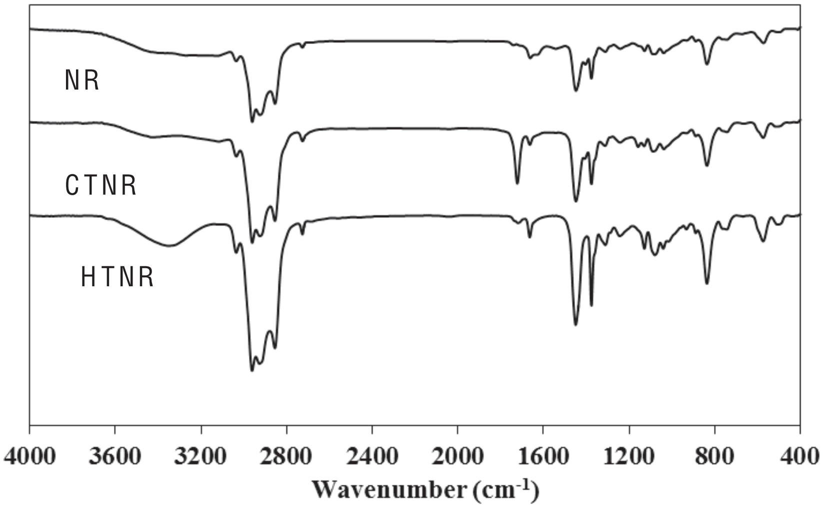

Figure 3.5 FTIR spectra of NR, CTNR and HTNR.

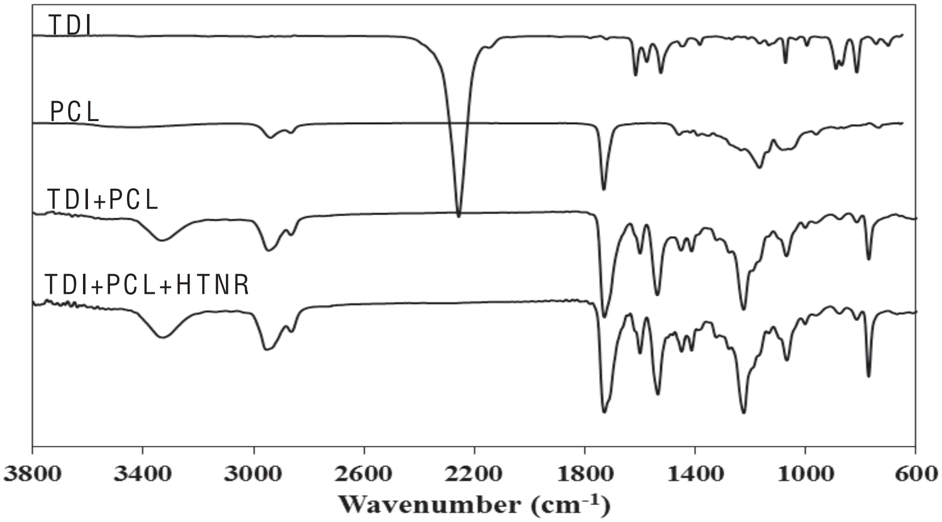

Figure 3.6 FTIR spectra of TDI, PCL and PU.

Table 3.1 Composition and glass transition temperature (T_g) and appearance of biodegradable PU.

Sample	TDI:PCL:HTNR (mol)	T_g (°C)	Appearance
1	1.17 : 0.86 : 0.14	-	Sticky soft solid
2	1.17 : 0.93 : 0.07	9.9	Yellow solid
3	1.30 : 0.93 : 0.07	14.9	Yellow solid
4	1.41 : 0.93 : 0.07	-	Yellow solid

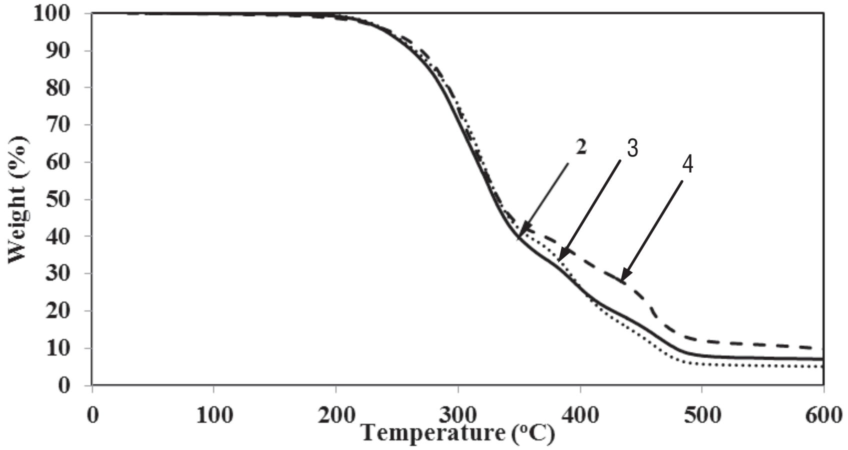

Figure 3.7 Effect of TDI content on thermal degradation of different PUs (TDI+PCL diol+HTNR, samples 2, 3, 4).

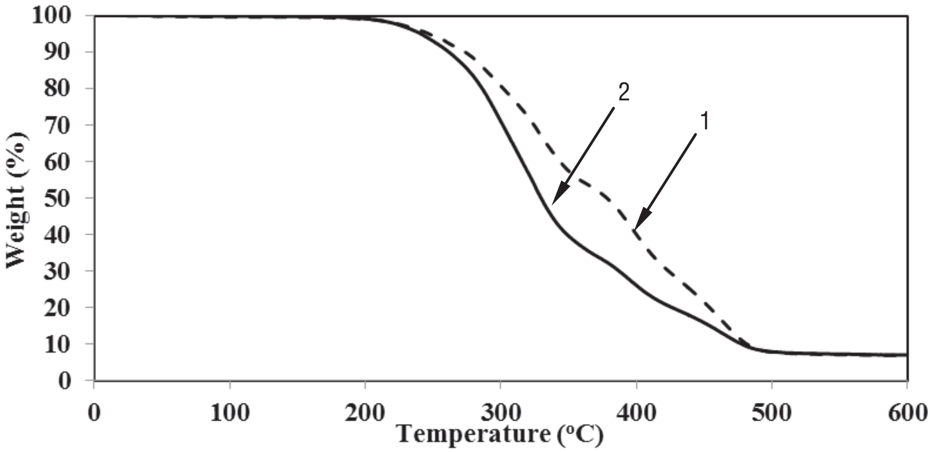

Figure 3.8 Effect of HTNR content on thermal degradation of PUs (TDI+PCL diol+HTNR samples 1 and 2).

3.4 CONCLUSION

A new type of polyurethane has been synthesized using polycaprolactone, toluene diisocyanate and hydroxytelechelic natural rubber derived oligomers. ^{1}H NMR and FTIR analyses were performed to confirm chemical structures and GPC analysis to obtain molecular weights. Thermal properties of the obtained polymeric films were also studied. After optimization of the parameters to obtain flexible films, the perspective is to perform biodegradation tests with bacteria and enzymes in order to investigate the biodegradation rate and extent.

3.5 ACKNOWLEDGEMENTS

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3.6 REFERENCES

1. Flandrin, F.R., Widmaief, J.M., Flat, J.J. 1996. Thermal ageing of polyurethane with hydrogenated polyisoprene soft segments. Polym. Degrad. Stabil. 57, 59-67.
2. Paul, C.J., Gorpinathan Nair, M.R. 1998. Segmented block copolymers of natural rubber and propylene glycol-toluene diisocyanate oligomers. Polym. Eng. Sci. 38, 440-451.
3. Kebir, N., Campistron, I., Lagurerre, A., Pilard, J.F., Bunel, C., Couvercelle, J.P., Gondard, C. 2005. Use of hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes (PUs). Part 1. Influence of molecular weight and chemical modification of HTPI on the mechanical and thermal properties of PUs. Polymer. 46, 6869-6877.
4. Sukumar, P., Jayashree, V., Gopinathan Nair, M.R., Radhakrishnan Nair, M.N. J. 2009. Synthesis and Thermal studies of block copolymers from NR and MDI-based polyurethanes. J. Appl. Polym. Sci. 111, 19-28.
5. Gorna, K., Gogolewski., S. 2002. In vitro degradation of novel medical biodegradable aliphatic polyurethanes based on ε-caprolactone and Pluronics with various hydrophilicities. Polym. Degrad. Stabil. 75, 113-122.
6. Younes, H.M., Grimaldo, E.B., Amsden, B.G. 2004. Synthesis, characterization and in vitro degradation of a biodegradable elastomer. Biomaterials. 25, 5261-5269.
7. Heijkants, R.G.J.C., Calck, R.V., Tienen, T.G., Groot, J.H., Buma, P., Pennings, A.J., Veth, R.P.H., Schouten, A.J. 2005. Uncatalyzed synthesis, thermal and mechanical properties of polyurethanes based on poly(ε-caprolactone) and 1,4-butane diisocyanate with uniform hard segment. Biomaterials, 26, 4219-4228.

CHAPTER 4

PREPARATION AND PROPERTIES OF BIO-BASED POLYURETHANE CONTAINING POLYCAPROLACTONE AND NATURAL RUBBER

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ABSTRACT: Novel polyurethanes were successfully synthesized by a one-shot polymerization. They contained poly(ε-caprolactone) diol (PCL diol) and hydroxyl telechelic natural rubber (HTNR) as the soft segment. The effect of the NCO:OH molar ratio (0.75:1.00 – 2.25:1.00), chain extender content and PCL:HTNR molar ratio (1:1, 0.7:0.3 and 0.3:0.7) on the thermal and mechanical properties of the resulting polyurethane were investigated. FTIR analysis showed the presence of urethane linkages and crosslinking or chain branching. The derived polyurethanes demonstrated excellent mechanical properties, which depended on their chemical composition. Their tensile behavior seemed to have typical elastomeric characteristics. Polyurethanes became amorphous and showed a phase separation between the PCL diol and HTNR segments. The phase separation between the soft and the hard segments was observed by the DMTA technique whereas DSC results showed only the glass transition temperatures of the soft segment. The longer and more flexible chain and non-polarity of HTNR was responsible of a decrease in the mechanical properties and transition temperatures.

Key words: polyurethane, natural rubber, poly(caprolactone), bio-based plastic, elastomer, renewable resources

4.1 INTRODUCTION

Polyurethane (PU) is widely employed in many applications such as elastomers, thermoplastics, thermosets, foams, coatings and adhesives. Polyurethane can be classified into 2 types according to the polyol used: polyester polyurethane and polyether polyurethane. It is a material not readily subject to microbial attack, but generally, the ester-type polyurethane is more easily degraded than the ether-type. In a case where some microbial degradation has occurred, it was considered to be initiated by hydrolysis of the ester bond by some hydrolytic enzyme(s), such as an esterase, lipase AK [1] etc. At present there is a growing demand for developing environmentally friendly products because of the great concern for controlling environmental pollution and global warming. There is consequently much scientific and technological interest in the use of renewable resources as raw materials in order to avoid problems from plastic waste management and green house gas emission. We are also facing the problem of the replacement of the monomers derived from petroleum sources, which are being consumed much faster than their natural replacements.

Natural rubber (NR) is an interesting material that can be used in the synthesis of novel bio-based polymers as it is a natural, abundant, renewable resource and it is possible to chemically modify its structure by a selective cleavage of the *cis*-1,4-polyisoprene chain or by the reaction of the double bonds in the repeating unit. Telechelic liquid natural rubber (TLNR) is prepared by chain cleavages of NR by photochemical [2,3] and oxidative chemical [4-6] methods. Such liquid natural rubber containing hydroxyl end functional group (HTNR) has been used as a polyol for the synthesis of polyurethane [3-9]. Due to the non-polarity of HTNR, there is no hydrogen bonding between the soft and the hard segments resulting in a lower tensile strength, modulus and water resistance than PU containing polar polyols [10]. Polyurethane prepared using HTNR as a precursor has a low rate of degradation due to its high resistance to biological attack and its hydrophobicity.

Polycaprolactone (PCL) is a biodegradable aliphatic polyester. It is a hydrophobic, semi-crystalline polymer. Polycaprolactone is synthesized by a ring-opening polymerization of ε-caprolactone derived from a petrochemical product using a diol as initiator/chain-transfer agent in the presence of a catalyst. PCL has been used as a diol for the synthesis of biodegradable polyurethanes [1,11-24]. Assuming that an addition of PCL segment in the HTNR-based polyurethane enhances the degradation, polyurethane containing HTNR and PCL diol as a soft segment has been synthesized during this research work.

To the best of our knowledge, there has been no previous report on the preparation of polyurethane consisting of HTNR and poly(ε-caprolactone) diol as the soft segment. The present study investigated the influence of the molar ratio between isocyanate (NCO) and the diol (OH), the chain extender content and the HTNR/PCL diols content on the mechanical and thermal properties of such novel bio-based polyurethanes. The polyurethane characteristics such as phase separation and glass transition were determined and described. Biodegradation experiments with soil bacterial, lipase enzymes and bacterial slurry from a waste water plant are currently being carried out on the obtained polyurethanes.

4.2 EXPERIMENTAL

4.2.1 Materials

Block natural rubber (NR), STR5 CV60 grade, was produced by Jana Concentrated Latex Co. Ltd., Thailand. Dibutyl tin dilaurate (Aldrich®), *m*-chloroperbenzoic acid (*m*-CPBA, Fluka®), prepolymer of poly(ε-caprolactone) diol (PCL diol, Fluka®) having a number-average molecular weight of 530 g/mol and isophorone diisocyanate (IPDI, Fluka®) were supplied by SIGMA-ALDRICH Inc., Missouri, USA. Periodic acid (Himedia®) and sodium borohydride (Rankem®) were manufactured by HiMedia Laboratories Pvt. Ltd. (Mumbai, India) and RFCL Ltd. (New Delhi, India), respectively. Dichloromethane and tetrahydrofuran (THF) were supplied by Fisher Scientific UK Limited (Leicestershire, UK) and 1,4-Butanediol (BDO, Merck®) was produced by Merck (Hohenbrunn, Germany). Molecular weight of IPDI and BDO was 222.3 and 90 g/mol, respectively. All chemicals were used as received.

4.2.2 Synthesis of the hydroxyl telechelic natural rubber (HTNR)

Natural rubber was dissolved in tetrahydrofuran and then reacted with periodic acid at 30°C for 6 h to obtain a carbonyl telechelic natural rubber (CTNR). CTNR solution was filtered to remove a by-product (iodic acid) and purified by using saturated sodium bicarbonate solution, 20 w/v% of sodium thiosulphate solution and saturated sodium chloride solution. Those organic solvents were removed by using an evaporator. The dried CTNR was dissolved in tetrahydrofuran and reacted with sodium borohydride. The reaction was carried out at 60°C for 6 h. The obtained HTNR was purified by saturated sodium chloride. The chemical structures of the ENR, CTNR and HTNR were identified by their ^{1}H-NMR spectra.

4.2.3 Synthesis of polyurethane (PU)

Polyurethane was synthesized by a one-shot method. The PCL diol and HTNR acted as a diol while the BDO was used as a chain extender. The diols and the chain extender were dissolved in THF (30 w/v%) before mixing with the isocyanate. Dibutyl tin dilaurate acting as a catalyst was added to the solution followed by a dropwise addition of a known amount of IPDI dissolved in THF. The reaction temperature was 60°C and the reaction time was 3 h. The resulting mixture was poured into a glass mold and heated continuously in an oven at 40°C for 3 h and 60°C for 24 h to obtain a sheet. The sample thickness was approximately 0.3-0.5 mm. The molar ratios of IPDI:PCL:HTNR:BDO were varied as shown in Table 4.1.

4.2.4 Sample characterization

The Fourier Transform Infrared Spectrometer (BRUKER® EQUINOX 55) was used to determine the functional group in the obtained PU. The samples were scanned at a frequency range of 650-4000 cm^{-1} with an attenuated total reflection (ATR). The presence of epoxide ring, the carbonyl and hydroxyl groups in the chemically modified NR were investigated by ^{1}H-NMR spectroscopy (Fourrier BRUKER® AC 400). The d-chloroform was used as a solvent. Differential scanning calorimetry analysis was performed on a TA Instruments® DSC Q 100. The DSC thermograms were recorded with a scan rate of 10°C/min for the heating scan and -10°C/min for the cooling scan in the temperature range of -80 to 200°C in a nitrogen atmosphere. Thermogravimetric analysis was performed on a TA Instruments®TGA Q 100 with a heating rate of 10°C/min from 30 to 600°C in a nitrogen atmosphere. Dynamic mechanical thermal analysis was investigated by using a Rheometric Scientific® DMTA V. The experiment was carried out in the dual-cantilever bending mode at a frequency of 1 Hz with a strain control of 0.01%, and the heating rate was 3°C/min. The temperature range was -80 to 200°C.

Table 4.1 Composition and appearance of polyurethanes

Code	Molar ratio				HS[(a)] (%)	Appearances[(b)]
	IPDI	PCL	HTNR	BDO		
PU1	0.75	1.00	-	-	23.9	Viscous liquid
PU2	1.00	1.00	-	-	29.6	Sticky and weak
PU3	1.25	1.00	-	-	34.4	C, S, T
PU4	1.50	1.00	-	-	38.6	C, S, T
PU5	2.00	1.00	-	-	45.6	C, H, T
PU6	2.25	1.00	-	-	48.6	C, H, T
PU7	1.25	0.50	0.50	-	20.0	Y, S, ST
PU8	1.25	0.35	0.35	0.30	28.1	Y, S, ST
PU9	1.25	0.25	0.25	0.50	36.7	Y, H, ST
PU10	1.25	0.50	-	0.50	54.9	C, H, T
PU11	1.25	0.35	0.15	0.50	42.3	Y, S, ST
PU12	1.25	0.15	0.35	0.50	32.4	Y, S, ST
PU13	1.25	-	0.50	0.50	27.5	Y, S, T

(a) Hard segment (%) = 100 [weight of (isocyanate+chain extender)]/ total weight

(b) C: colorless; Y: yellowish; H: hard; S: soft; O: opaque; ST: semi-transparent; T: transparent

4.2.5 Testing of mechanical properties

The tensile properties (ASTM D 412C) and tear strength (ASTM D 624 for the right-angle specimen) were determined by a universal testing machine (Lloyd®LR10K) at a crosshead speed of 500 mm/min. Testing was performed at 25±2°C. The casted polyurethane sheets were die-cut to obtain test specimens. At least 4 specimens were tested and the average values and standard deviations were reported. Young's modulus was determined from the slope of the linear portion of the stress–strain curves. The hardness Shore A (ASTM D2240) was determined by a Shore Durometer® PTC 408.

4.3 RESULTS AND DISCUSSION

4.3.1 Polyurethane characteristics

The synthesis of oligomers derived from natural rubber has been already described [4, 5]: the methodology allows the synthesis of oligoisoprenes with targeted molecular weight, a small polydispersity, and a functionality equal to two. The synthesis of the polyurethane sheets was then carried out seeking flexible and potentially biodegradable polymeric films to use in different applications.

The novel PUs were synthesized by varying the molar ratios between isocyanate and the diol (NCO:OH) or the IPDI content, the chain extender (BDO) content and the molar ratio between PCL diol and HTNR. IPDI and BDO were considered to be the hard segment. The physical appearances observed by eye of each formula are described in Table 4.1. The expected chemical structure of the novel polyurethane is shown in Figure 4.1. The first set of samples, PU1-PU6, was a preliminary study in order to seek an appropriate formula that could provide for good film. When the NCO:OH ratio was 0.75:1.0 (PU1), film formation did not occur and a viscous liquid was obtained because of inadequate amounts of NCO. Increasing the NCO:OH ratio to 1.00:1.00 produced a very sticky film with no mechanical integrity. This was due to the use of an asymmetric isocyanate with no chain extender leading to low hydrogen bonding [25]. Colorless and transparent sheets were generated when the NCO:OH ratio was superior to 1.25 (PU3-PU6). Increasing the NCO:OH ratio provided the different percentages of the hard segment as listed in Table 4.1. The excess of isocyanate seemed to be necessary in the present study and the ratio of 1.25:1.00 was selected for the successive preparation of the novel PU, owing to its ability to form satisfactory films. The PU sheets became yellowish and semi-transparent after blending HTNR with PCL diol as the soft segment. As expected, a higher content of the chain extender (BDO) increased the hardness of the PU sheets and the higher content of HTNR reduced the hardness of the PUs.

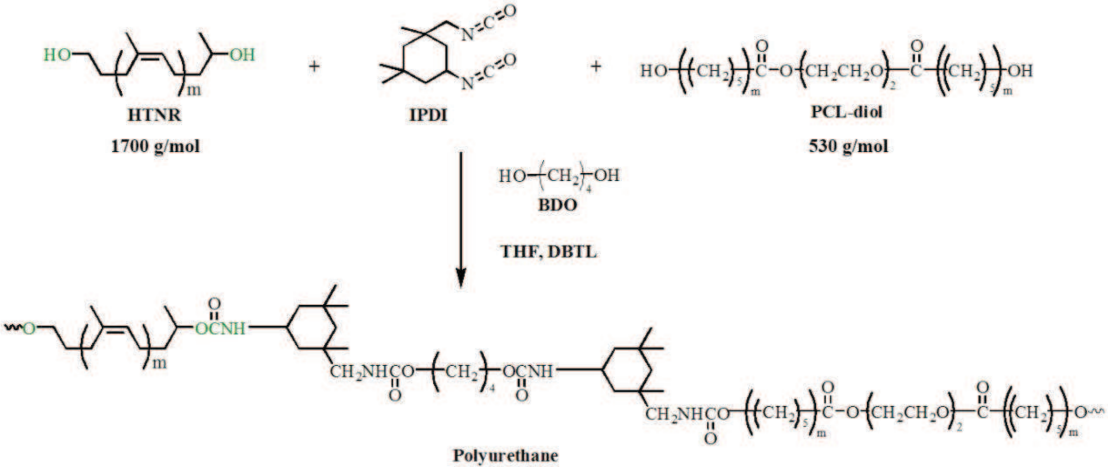


Figure 4.1 Chemical structure and reaction route of the novel PU.

The obtained sheets were characterized by FTIR. Figure 4.2 represents the FTIR spectra of PU3-PU6. The bands observed at 2948 and 2866 cm^{-1} were assigned to the asymmetrical and symmetrical -CH_2 stretching, respectively. The -CH_2 vibration also appeared at 1460, 1418 and 1362 cm^{-1}. The formation of polyurethane was evident because of the disappearance of the –OH and -N=C=O absorption band of the PCL diol and IPDI at 3442 and 2259 cm^{-1}, respectively. Four new absorption bands assigned to the urethane linkage were observed: the non-hydrogen bonded –C=O stretching at 1728 cm^{-1}; the carbonyl stretching of the C=O, which was hydrogen bonded with the NH group of the hard segment at 1715 cm^{-1}; the NH stretching at 3360-3365 cm^{-1}, and the NH bending vibration 1525-1550 cm^{-1}. An excess NCO caused crosslinking in PU that was observable from the allophanate group and the acylurea linkage. The characteristic peak of the allophanate group is a triplet of bands at the wave numbers of 1220, 1280 and 1310 cm^{-1} as well as the skeletal vibration of the allophanate group at 3298, 3267 and 3233 cm^{-1} [25,28]. The obtained PU showed the characteristic bands of the allophanate group at 1234, 1276 and 1304 cm^{-1}, whereas the absorption bands at 3233-3298 cm^{-1} were overlapped with the band at 3361 cm^{-1} (NH stretching). With an increase of the NCO:OH ratio, the new absorption bands appeared at 1640-1645 cm^{-1} (the left arrow in Figure 4.2) and a shoulder at 1551 cm^{-1} (the right arrow in Figure 4.2). The former corresponded to the C=O stretching of the amide group and the latter has been assigned to the C-N vibration of the urea functional group [26]. It was noticeable that the intensity at 1715 cm^{-1} and 1640-1645 cm^{-1} increased with the increasing NCO content, indicating more hydrogen bonding. This may be the cause of the ability to form a film in the presence of an excess of NCO. The presence of crosslinks was also the reason of the inability of the films to dissolve in the polar solvents such as tetrahydrofuran, chloroform, dichloromethane, methanol and ethanol. The other samples (PU7-PU13) also showed the main PU characteristic peaks similar to those in Figure 4.2 (not shown here).

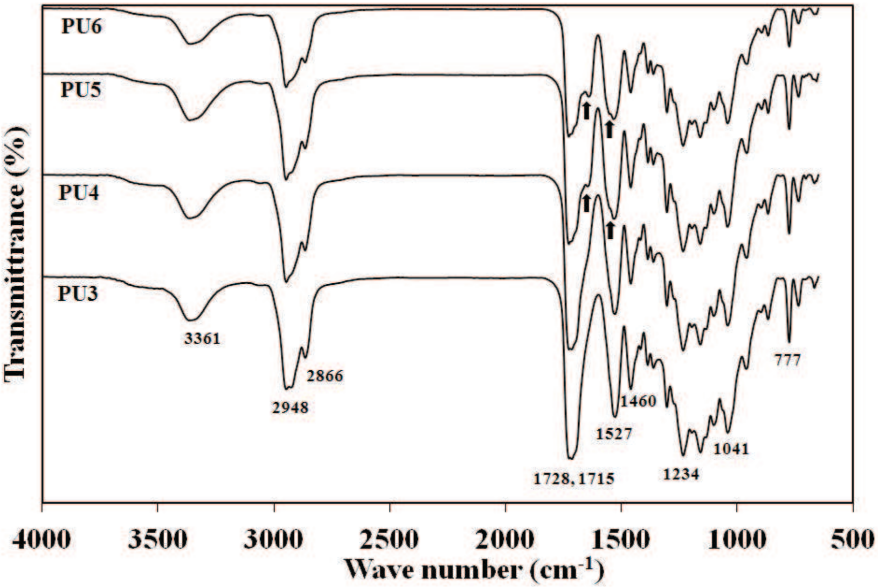


Figure 4.2 Infrared spectra of PU3-PU6.

4.3.2 Mechanical properties

After the optimization of the formulation and the chemical analyses to investigated theses composition, a study of their mechanical properties was carried out. The stress-strain curves of the PU samples are shown in Figure 4.3. No plastic yielding was observed in any sample. Excluding PU5 and PU6, all PUs exhibited sigmoidal shapes characteristic of rubber-like elastomers. The tensile properties of the polyurethane samples are displayed in Table 4.2. They had a typical elastomeric characteristic, i.e. low modulus and high elongation at break. Considering PU without HTNR and BDO (PU3-PU6), the Young's modulus, the tensile strength and the tear strength increased while the elongation at break decreased with an increasing NCO:OH ratio. The Young's modulus generally increases with the hard segment because the microdomain in the hard segment acts as a reinforcing filler [27]. The enhancement in the intermolecular and intramolecular attraction between the hard segments through hydrogen bonding and the higher crosslink density increased the tensile and tear strength and decreased the ductility of PU. The IPDI content (NCO:OH ratio) had slight effect on the hardness of PU (PU3-PU6) as it fell in the same range, i.e. ± 5 Shore A (Table 4.2).

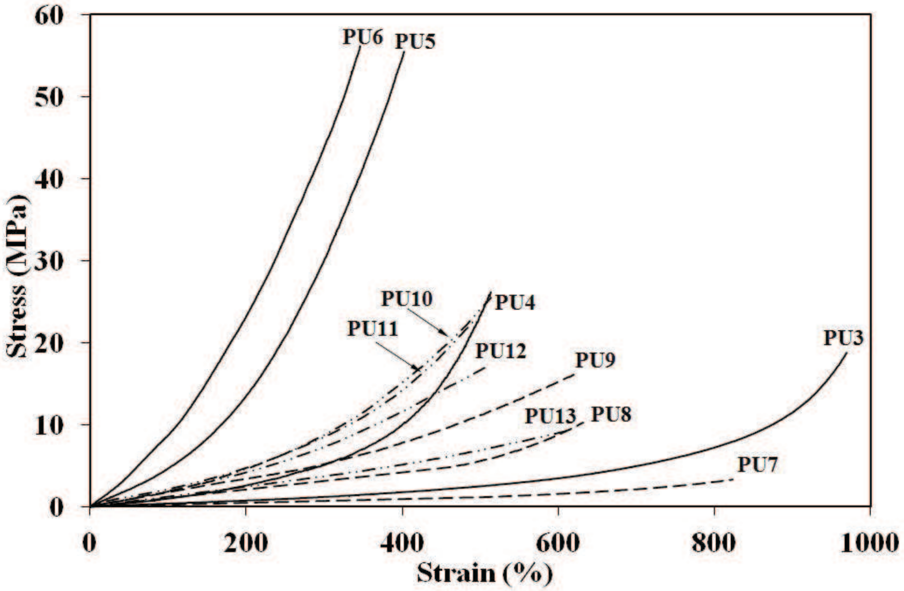


Figure 4.3 The stress-strain curves of PU3-PU13.

The incorporation of HTNR in the PCL-based PU, i.e. PU7, caused a reduction in mechanical properties when compared with PU3. PU7 behaved as a weak and soft polymer. In contrast, the addition of BDO (PU10) produced a higher modulus and tensile strength but a lower elongation at break than those of the PU3 and PU7. It seemed that BDO was essential in order to improve the mechanical properties of PU and this was confirmed by using HTNR and BDO without PCL diol as in PU13. This polymer exhibited a higher modulus and tensile strength than PU7 (which consisted of PCL diol and HTNR). At the same time, BDO reduced the elongation at break of PU13.

Table 4.2 The mechanical and physical properties of the PUs

Code	Tensile Properties			Tear strength (N/mm)	Hardness (Shore A)
	Young's modulus	Tensile strength	Elongation at break (%)		
PU3	0.5±0.1	18.9±0.2	916±75	16.9±0.5	42±2
PU4	1.2±0.4	22.6±3.3	488±73	22.8±0.8	42±4
PU5	3.9±0.4	54.5±1.4	392±15	56.2±7.1	45±2
PU6	7.9±1.3	53.6±3.6	351±6	109.1±20.9	48±2
PU7	0.3±0.1	3.5±0.3	824±39	7.5±0.7	21±2
PU8	1.0±0.1	14.1±1.1	703±35	13.8±1.1	32±3
PU9	1.4±0.3	14.9±1.6	590±48	38.6±1.1	47±1
PU10	2.5±0.9	21.7±1.9	493±1	65.4±0.4	57±1
PU11	2.2±0.4	24.3±1.2	506±9	38.3±1.2	56±1
PU12	1.9±0.0	14.2±0.1	518±3	30.8±2.1	51±2
PU13	1.2±0.0	9.1±0.2	605±8	20.9±1.4	40±3

Concerning the role of BDO, it has been used as the chain extender and also provided hydroxyl groups for polymerization. Therefore, it was considered as a part of the diol for stoichiometry calculations. In order to keep the constant NCO:OH ratio, the PCL diol and HTNR content had to be adjusted. The effect of the BDO content is shown in PU7-PU9. The modulus, tensile strength, hardness and tear strength of PU increased whereas the elongation at break decreased with the increasing BDO content. The contribution of BDO could be explained in terms of an increase in size of the rigid block or the hard segment. The modulus and tensile strength of PU8 and PU9 were slightly different but their elongation at break, tear strength and hardness displayed significant differences. The tensile properties of PU8 and PU9 were in the range of typical elastomers, for example vulcanized SBR and vulcanized BR [28].

In order to optimize the tensile properties, comparisons were made between PU9, PU11 and PU12. The PCL diol:HTNR ratio in PU9, PU11 and PU12 was 0.25:0.25, 0.35:0.15 and 0.15:0.35, respectively. All of them contained the same quantity of IPDI (1.25) and BDO (0.5). The PCL-rich PU (PU11) provided a higher modulus, tensile strength and tear strength than the HTNR-rich PU (PU12). The elongation at break and the hardness of both samples were in the same range. PU9 showed the highest elongation at break and lowest hardness. Its tensile strength was close to that of PU12 whereas its tear strength was similar to that of PU11. It could be explained that an increasing HTNR content reduced the opportunity of hydrogen bonding between the soft and hard segments resulting in a decrease in the modulus, tensile strength and tear strength.

Another parameter has been considered, the hard segment content, which also influences the mechanical properties of PU. In the present study, the molecular weight of HTNR was higher than that of PCL diol; therefore, the addition of HTNR decreased the hard segment content as shown in Table 4.1. Furthermore, HTNR would provide more flexibility than PCL diol. These brought about a decrease in the tensile strength and an increase in the elongation at break. PU10 containing the highest hard segment content showed the highest tear strength and hardness whereas PU13 containing the lowest hard segment content showed the lowest values of both properties. This behavior was similar to the results obtained in literature from another PCL-based PU [13] and HTNR-based PU [29]. The relationship between the tear strength and the hard segment content of PCL-based PU (PU1-PU6) has been observed to have a similar trend to the other published rresults [13].

4.3.3 Thermal properties

The study of the thermal properties was carried out in order to get complementary information about the film composition. The phase separation between the hard segment and the soft segment of PU can be determined from the thermal transitions. Table 4.3 represents the glass transition temperature (T_g) of PU3-PU13 obtained from DSC thermograms. The hard segment was prepared by using only IPDI and BDO at molar ratio of 1.25:1.00, and it showed T_g at 109°C. The virgin

PCL diol and HTNR showed a T_g at -36°C and -60°C, respectively. PU3-PU6, the PCL-based PUs, exhibited a single T_g indicating a non-phase separation between the hard segment and the soft segment, similar to other PCL-based PUs [11, 30-32]. The absence of the phase separation between the hard segment and the soft segment may be due to the hydrogen bonding between the PCL diol and the urethane linkage. The presence of the single T_g indicated the miscibility between the hard segment and soft segment as reported in the PCL-based PU using MDI [25]. The T_g increased from -7°C to 5°C when the NCO:OH ratio increased from 1.25 to 2.25. The higher NCO:OH ratio led to the formation of more branched chains or more crosslinking causing the increase in T_g.

The addition of the chain extender (BDO) provided a significant increase in T_{g2}. PU3 showed a T_g at -7°C whereas the T_g of PU10 was 30°C. BDO showed little effect on T_g of the HTNR-based PU, i.e., T_g of PU13 was -52°C, owing to no hydrogen bonding between HTNR and BDO.

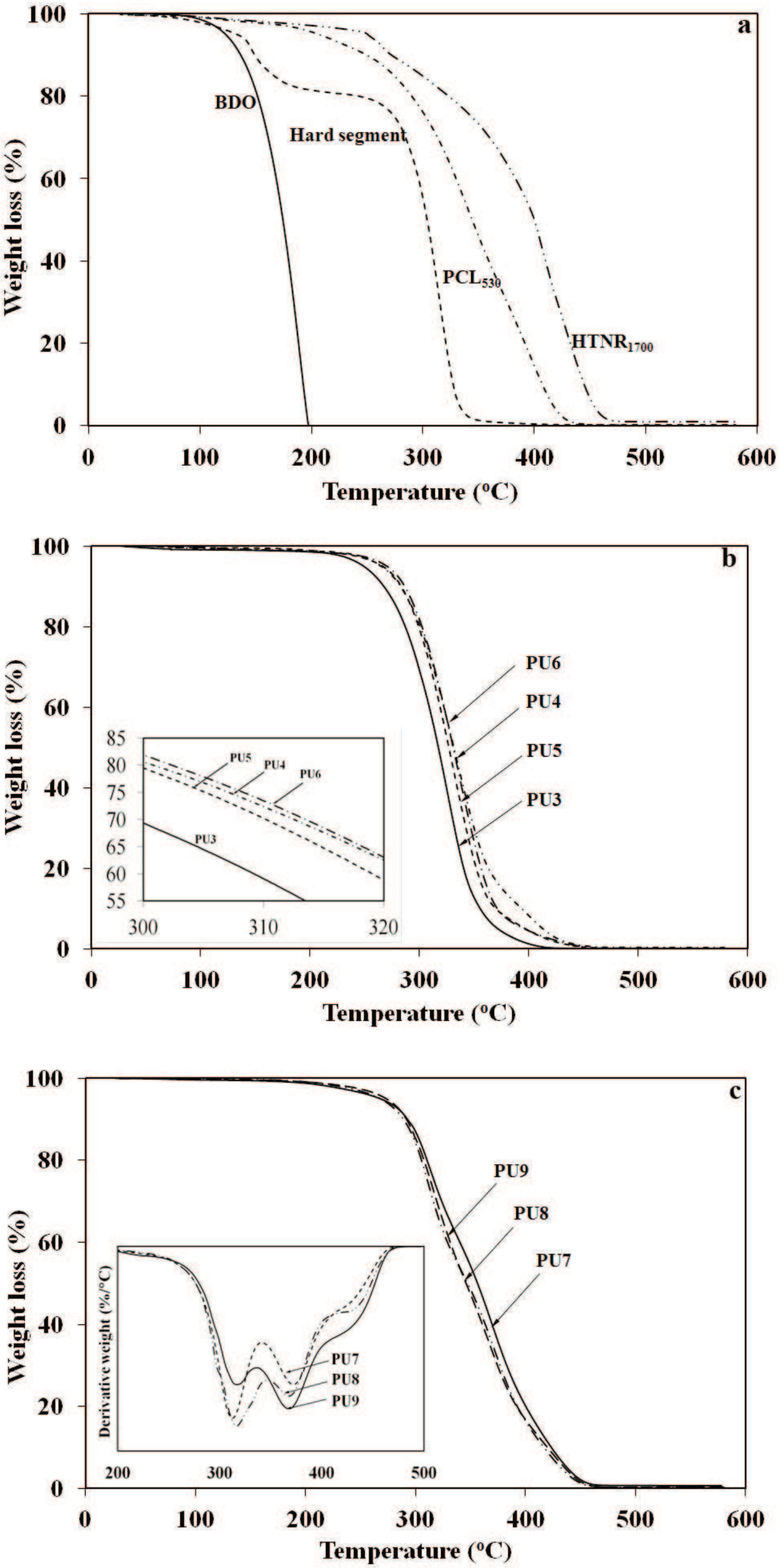
Table 4.3 Glass transition temperature of PU3-PU13 obtained from DSC

Code	2nd Heating scan		1st Cooling scan	
	T_{g1} (C°)	T_{g2} (C°)	T_{g1} (C°)	T_{g2} (C°)
PU3	-	-7	-	-9
PU4	-	0	-	-6
PU5	-	5	-	0
PU6	-	6	-	2
PU7	-54	-19	-60	-41
PU8	-55	-4	-59	0
PU9	-55	7	-60	2
PU10	-	30	-	22
PU11	-55	25	-61	20
PU12	-52	-8	-64	-12
PU13	-52	-	-61	-

The addition of HTNR segments (PU7-PU9, PU11 and PU12) revealed 2 T_gs: the lower-T_g (T_{g1}) and the higher-T_g (T_{g2}). The lower-T_g belonged to HTNR segment and changed slightly as changing HTNR content, i.e., -55°C to -52°C. Gopakumar and Nair [33] reported the T_g of the HTNR segment in the HTNR-based PU at -55°C. The higher-T_g (-19°C to 30°C) arose from the PCL diol and increased when HTNR content decreased. This is because more PCL diol content donated more hydrogen bonding with the hard segment. The insignificant change in T_{g1} indicated no hydrogen bonding between HTNR and the hard segment which should be due to the non-polarity of HTNR. T_g of the hard segment was not observed, similarly to the PCL-based PU (PU3-PU6), indicating no phase separation between the hard segment and the soft segment owing to the hydrogen bonding between the PCL diol and the hard segment. Although the phase separation between the hard segment and the soft segment could not be detected in the DSC experiment, it could be found in the DMTA experiment as described below.

No melting temperature was observed in all PU samples implying that no crystalline region. This can be justified by 3 different factors; firstly, concerning the PCL diol segment, the M_n of the PCL diol was 530 g/mol, which is too short for crystallization [28]. Secondly, the IPDI has an asymmetrical structure and it is referred to a conventional non-crystallizing diisocyanate. Another factor was the amorphous nature of HTNR. It was found in literature that HTNR-based PUs do not show crystallization [29,34].

The results of the thermogravimetric analyses are shown in Figure 4.4 for all PUs and precursors. Thermal degradation of the precursors depended on their molecular weight (Figure 4.4a). HTNR having the highest molecular weight (1700 g/mol) provided the highest thermal stability while the BDO showed the minor thermal stability due to its lowest molecular weight (90 g/mol). The hard segment sample was the same PU sample used in the DSC characterization. It contained only IPDI and BDO. The thermal degradation stability of the hard segment was lower than that of the PCL diol and HTNR. This result substantiated the previous assumption that the hard segment was shorter than the soft segment and this contributed to the dissolution of the hard segment and PCL diol. The thermal degradation stability increased with the increasing IPDI content as shown in Figure 4.4b (PU3-PU6) which can be the consequence of more chain branching or crosslinking. The addition of HTNR in the PCL-based PU yielded a higher thermal degradation (Figure 4.4c-4.4d). Two maximal rates of decomposition were found in PU9-PU12 (the inserted figure in Figure 4.4c) corresponding to PCL diol and HTNR.


a
BDO
Hard segment
PCL$_{530}$
HTNR$_{1700}$
Weight loss (%)
Temperature (°C)
0
20
40
60
80
100
0
100
200
300
400
500
600
b
PU6
PU4
PU5
PU3
55
60
65
70
75
80
85
300
310
320
c
PU9
PU8
PU7
Derivative weight (%/°C)
200
300
400
500

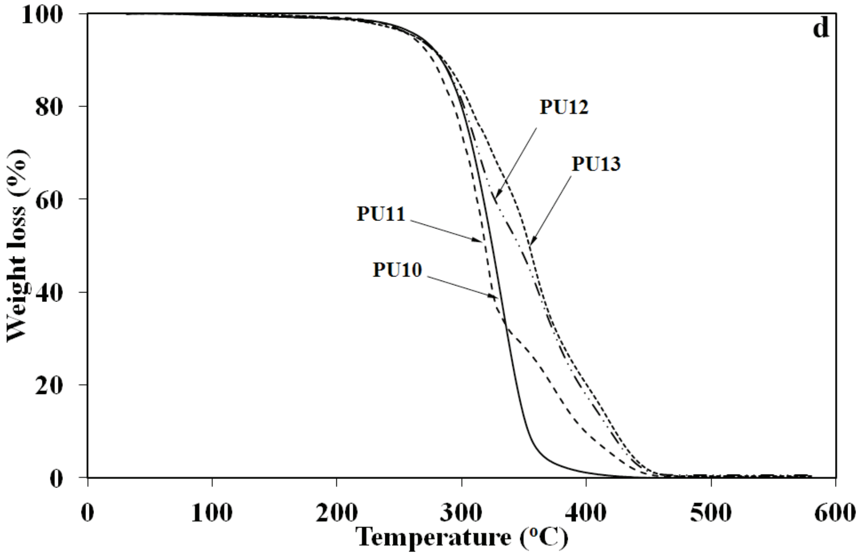


Figure 4.4 TGA thermogras of precursors and PU3-PU13: a precursors, b PU3-PU6, c PU7-PU9 and d PU10-PU13.

4.3.4 Dynamic mechanical thermal property

The dynamic mechanical thermal properties of PUs have been investigated in terms of the storage modulus, the loss modulus and the tan δ. The storage modulus at the glassy state of PUs was ranked in the same order as the Young's modulus and increased with the increasing NCO:OH molar ratio (IPDI content), in conformity with the Young's modulus (data not shown here). The addition of HTNR decreased the storage modulus, in agreement with the measured Young's modulus, because of a reduction in the interaction between the ester group in the soft segment and the urethane linkage in the hard segment. The loss modulus curves looked similar to the tan delta curves which are not shown here. The loss tangent maximum is usually used to determine the T_g while its position and shape can provide information about the degree of phase separation. In general, the T_g obtained from the maximum loss tangent occur at a higher temperature than the T_g determined by the DSC due to the dynamic nature of the DMTA. Two and three transition temperatures were observed (Figure 4.5); they are listed in Table 4.4 and defined as the transition temperature of three parts: PCL diol, HTNR and hard segment.

Table 4.4 Transition temperature of PU3-PU13obtained from DMTA

Code	Transition temperature (°C)		
	PCL segment	HTNR segment	Hard Segment
PU3	14	-	108
PU4	26	-	132
PU5	51	-	135
PU6	65	-	140
PU7	13	-32	-
PU8	29	-53	-
PU9	50	-40	-
PU10	54	-	129
PU11	52	-50	-
PU12	54	-31	-
PU13	-	-31	49

The effect of the NCO:OH ratio (PU3-PU6 in Figure 4.5a) agreed with the DSC data, which showed an increasing T_g when the IPDI content increased. Two transitions can be observed: a low transition temperature at 14-65°C that was assigned to the T_g of the PCL soft segment while the relatively low intensity at the higher transition temperature, >100°C, was believed to be the T_g of the hard segment, due to the restricted mobility of the hard segment [35]. The T_g of the hard segment was approximately 70°C. The enhancement of the T_g of PCL diol and the hard segment in PU3-PU6 arising from the increasing NCO:OH ratio should be due to the formation of more urethane linkages and more crosslinks resulting in more restriction of chain mobility. The amplitude of the tan δ peak decreased with the increase of the NCO:OH ratio. This indicated that the motion of the soft segment was hindered and the damping ability decreased. The half-width of the tan δ peak increased as the NCO:OH ratio increased; this implied that the microphase separation in the polymer was greatly increased [36].

The effect of the BDO on the T_g of the PCL-based PU was determined from PU3 and PU10. The transition temperatures were shifted to higher temperature. After adding BDO, the transition of the PCL segment shifted from 14°C (PU3) to 54°C (PU10) and the transition temperature of the hard segment also increased by approximately to 21°C. The effect of the BDO content was also clearly observed in the PU7-PU9. The transition of the PCL segment was remarkably increased due to the higher hard segment content and the greater rigidity of the molecular chain. The amplitude of the tan δ peak obviously decreased as the BDO content increased, to indicate that the ability of the soft segment motion decreased.

The addition of HTNR (PU7-PU9 and PU11-PU12) was responsible of the non-existence of the transition temperature above 100°C as demonstrated in Figure 4.5b and 5c. Two transition temperatures remained: -53°C to -31°C and 13 to 54°C and the transition temperature above 100°C disappeared as listed in Table 4.4. Certainly, the very low transition temperature, at subzero, was due to the HTNR segment. The sample without PCL (PU13) had to be evaluated in order to identify the relatively high transition temperature. PU13 showed a T_g of the HTNR segment and the hard segment at -31°C and 49°C, respectively. The T_g of the hard segment, consisting of only IPDI and BDO, was 70°C. It was assumed that the more flexible and non-polar characteristics of the HTNR reduced the rigidity of the hard segment in PU13; therefore, the hard segment of PU13 showed a low T_g. Unexpectedly, the transition temperature of the hard segment in PU13 was in the same range as the transition temperature of the PCL segment in the PCL-based PU containing BDO (PU10). As a result, the transition temperatures at 13-53°C of PUs containing PCL and HTNR were referred to as the transition temperatures of the PCL diol and the hard segment.

The effect of HTNR and BDO on the PCL-based PU was compared between PU3, PU7 and PU10. By adding BDO the T_gs increased from 14°C and 108°C (PU3) to 54°C and 129°C (PU10). By adding HTNR the T_gs decreased to -32°C and 13°C (PU7). The transition temperatures obtained from DMTA agreed with those derived from DSC. The T_g of the PCL segment seemed to be unchanged after adding HTNR and the two soft segments showed a phase separation. A strong interaction between the PCL diol and the hard segment was observed. However, the dynamic mechanical thermal analysis showed a phase separation between the soft and the hard segment. This may be due to the difference in the viscoelastic behavior of each segment that responded to the dynamic force in a different manner.

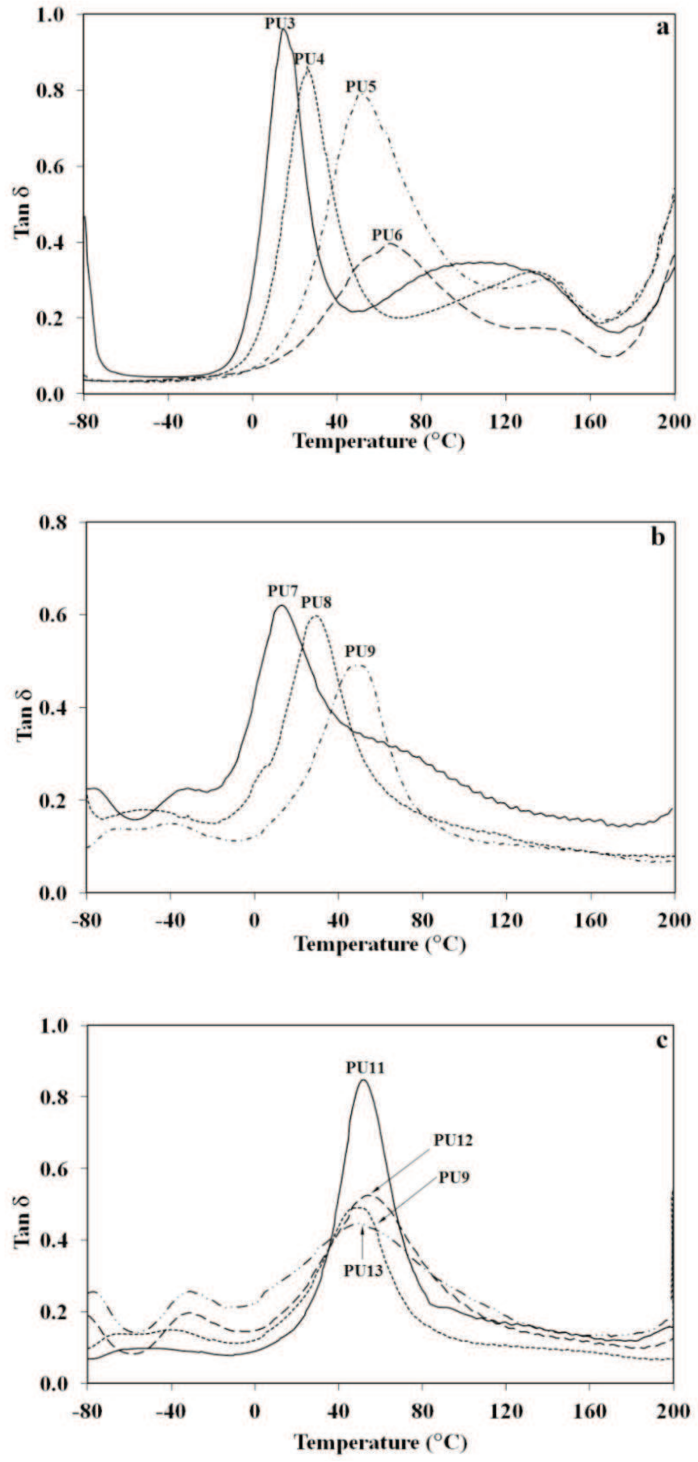


Figure 4.5 Tan δ versus temperature of PU3-PU13: a PU3-PU6, b PU7-PU9, c PU10-PU13.

4.4 CONCLUSIONS

Novel bio-based polyurethanes were successfully synthesized by a one-step solution polymerization using a poly(ε-caprolactone) diol (PCL diol) and hydroxyl telechelic natural rubber (HTNR) as the soft segment. The effect of the NCO:OH molar ratio (isophorone diisocyanate content) and the chain extender (1,4-butane diol) content on the mechanical and thermal properties was studied in order to seek the optimal conditions for forming polyurethane films. It was found that an excess diisocyanate was required for film formation and the chain extender increased the mechanical properties of polyurethane. Concerning the HTNR-based polyurethane, it had relatively low mechanical properties compared with the PCL-based polyurethane. A combination of PCL diol and HTNR provided good mechanical properties. All polyurethanes became crosslinked materials as identified by the Fourier transform infra red analysis and their tensile characteristics were similar to rubber-like materials. Two soft segments, PCL diol and HTNR, showed a phase separation as indicated by the results from the differential scanning calorimetry ananlysis (DSC) and dynamic mechanical thermal analysis (DMTA). Phase separation between the soft and the hard segment was not observed in the DSC analysis but it was observed when the dynamic force was applied in the DMTA. No crystallization was detected for any polyurethane. Molecular interactions were expected to be found only between the PCL diol and the hard segment, but not between the HTNR and the hard segment. The longer and more flexible chain and the non-polarity of HTNR offered a reduction in hydrogen bonding between the soft and the hard segments, which resulted in a decrease in the mechanical properties and the transition temperatures of polyurethane.

4.5 ACKNOWLEDGEMENTS

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4.6 REFERENCES

1. Jiang, X., Li, J., Ding, M., Tan, H., Ling, Q., Zhong, Y., Fu, Q. 2007. Synthesis and degradation of nontoxic biodegradable waterborne polyurethanes elastomer with poly(ε-caprolactone) and poly(ethylene glycol) as soft segment. Eur. Polym. J. 43,1838–1846.
2. Decker, C., Le, X.H., Nguyen, T.V.T. 1996. Photocrosslinking of functionalized rubber. III. Polymerization of multifunctional monomers in epoxidized liquid natural rubber. J. Polym. Sci. Pol. Chem.34,1771-1781.
3. Gopakumar, S., Nair, M.R.G. 2005. Swelling characteristics of NR/PU block copolymers and the effect of NCO/OH ratio on swelling behavior. Polymer. 46,10419-10430.
4. Kebir, N., Morandi, G., Campistron, I., Laguerre, A., Pilard, J.F. 2005. Synthesis of well defined amino telechelic cis-1,4-oligoisoprenes from carbonyl telechelic oligomers; first studies of their potentialities as polyurethane or polyurea materials precursors. Polymer. 46, 6844-6854.
5. Kebir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunal, C., Jouenne, T. 2007. Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of antibacterial ionic polyurethanes and copolyurethanes bearing ammonium groups. Biomaterials. 28, 4200-4208.
6. Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Pilard, J.F. 2010. Controlled degradation of natural rubber and modification of the obtained telechelic oligoisoprenes: Preliminary study of their potentiality as polyurethane foam precursors. J. Appl. Polym. Sci. 117, 1279–1289.
7. Paul, C.J., Gopinathan, N.M.R., Koshy, P., Idage, B.B. 1999. Segmented block copolymer of natural rubber and bisphenol A-toluene diisocyanate oligomer. J. Appl. Polym. Sci. 74, 706-721.
8. Radhakrishnan, N.M.N., Gopinathan, N.M.R. 2008. Synthesis and characterisation of soluble block copolymers from NR and TDI based polyurethanes. J. Mater. Sci. 43, 738–747.

9. Maier, G., Knopfova, V., Voit, B., Ly, P.H., Dung, B.T., Thanh, D.B. 2004. Synthesis andcharacterization of segmented block copolymers based on hydroxyl-terminated liquid natural rubber and α,ω-diisocyanato telechelics. Mactomol. Mater. Eng. 289, 927-923.
10. Sun, X., Ni, X. 2004. Block copolymer of trans-polyisoprene and urethane segment: crystallization behavior and morphology. J. Appl. Polym. Sci. 94, 2286-2294.
11. Gorna, K., Gogolewski, S. 2002. In vitro degradation of novel medical biodegradable aliphatic polyurethanes based on ε-caprolactone and Pluronics with various hydrophilicities. Polym. Degrad. Stabil. 75, 113–122.
12. Younes, H.M., Grimaldo, E.B., Amsden, B.G. 2004. Synthesis, characterization and in vitro degradation of a biodegradable elastomer. Biomaterials. 25, 5261–5269.
13. Heijkants, R.G.J.C., Calck, R.V., Tienen, T.G., Groot, J.H., Buma, P., Pennings, A.J., Veth, R.P.H., Schouten, A.J. 2005. Uncatalyzed synthesis, thermal and mechanical properties of polyurethanes based on poly(ε-caprolactone) and 1,4-butane diisocyanate with uniform hard segment. Biomaterials. 26, 4219–4228.
14. Heijkants, R.G.J.C., Schwab, L.W., Calck, R.V., Groot, J.H., Pennings, A.J., Schouten, A.J. 2005. Extruder synthesis of a new class of polyurethanes: Polyacylurethanes based on poly(ε-caprolactone) oligomers. Polymer. 46, 8981–8989.
15. Yeganeh, H., Lakouraj, M.M., Jamshidi, S. 2005. Synthesis and properties of biodegradable elastomeric epoxy modified polyurethanes based on poly(ε-caprolactone) and poly(ethylene glycol). Eur. Polym. J. 41, 2370–2379.
16. Liu, C.B., Qian, Z.Y., Gu, Y.C., Fan, L.Y., Li, J., Chao, G.T., Jia, W.J., Tu, M.J. 2006. Synthesis, characterization, and thermal properties of biodegradable aliphatic copolyester based on ε-caprolactone, adipic acid, and 1,6-hexanediol. Mater. Lett. 60, 31–38.
17. Xie, Z., Lu, C., Chen, X., Chen, L., Hu, X., Shi, Q., Jing, X. 2007. A facile approach to biodegradable poly(ε-caprolactone)-poly(ethylene glycol)-based

polyurethanes containing pendant amino groups. Eur. Polym. J. 43, 2080–2087.

18. Hong, J.H., Jeon, H.J., Yoo, J.H., Yu, W.R., Youk, J.H. 2007. Synthesis and characterization of biodegradable poly(ε-caprolactone-co-β-butyrolactone)-based polyurethane. Polym. Degrad. Stabil. 92, 1186-1192.
19. Tatai, L., Moore, T.G., Adhikari, R., Malherbe, F., Jayasekara, R., Griffiths, I., Gunatillake, P.A. 2007. Thermoplastic biodegradable polyurethanes: The effect of chain extender structure on properties and in-vitro degradation. Biomaterials. 28, 5407–5417.
20. Jeon, H.J., Kim, J.S., Kim, T.G., Kim, J.H., Yu, W.R., Youk, J.H. 2008. Preparation of poly(ε-caprolactone)-based polyurethane nanofibers containing silver nanoparticles. Appl. Surf. Sci. 254, 5886–5890.
21. Zia, K.M., Zuber, M., Bhatti, I.A., Barikani, M., Sheikh, M.A. 2009. Evaluation of biocompatibility and mechanical behavior of chitin-based polyurethane elastomers. Part-II: Effect of diisocyanate structure. Int. J. Biol. Macromol. 44, 23–28.
22. Han, J., Chen, B., Ye, L., Zhang, A.Y., Zhang, J., Feng, Z.G. 2009. Synthesis and characterization of biodegradable polyurethane based on poly(ε-caprolactone) and L-lysine ethyl ester diisocyanate. Front. Mater. Sci. China. 3(1), 25–32.
23. Larraz, L.R., Fernandez, A.B., Tercjak, A., Ribes, A., Mondragon, I., Eceiza, A. 2009. Synthesis and microstructure–mechanical property relationships of segmented polyurethanes based on a PCL–PTHF–PCL block copolymer as soft segment. Eur. Polym. J. 45, 2096–2109.
24. Sivakumar, C., Nasar, A.S. 2009. Poly(ε-caprolactone)-based hyperbranched polyurethanes prepared via A2 + B3 approach and its shape-memory behavior. Eur. Polym. J. 45, 2329–2337.
25. Prisacariu, C. 2011. Polyurethane elastomers from morphology to mechanical aspects, New York: SpingerWienNewYork, USA, 75-108.
26. Thomas, V., Muthu, J. 2008. Biomechanical studies on aliphatic physically crosslinked poly(urethane urea) for blood contact applications. J. Mater. Sci: Mater. Med. 19, 2721–2733.

27. Durrieu, V., Gandini, A., Belgacem, M.N., Blayo, A., Eisele, G., Putaux, J.L. 2004. Preparation of aqueous anionic poly(urethane-urea) dispersions: Influence of the nature and proportion of the urethane groups on the dispersion and polymer properties. J. Appl. Polym. Sci. 94, 700-710.
28. Biemond, G.J.E., Braspenning, K., Gaymans, R.J. 2008. Polyurethane with monodisperse rigid segments based on a diamine-diamide chain extender. J. Appl. Polym. Sci. 107, 2180-2189.
29. Hepburn, C. 1991. Polyurethane elastomer, 2nd edition. New York: Elsevier Applied Science LTD., USA, 56.
30. Kebir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunal, C., Jouenne, T. 2006. Use of new hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes (PUs): Influence of isocyanate and chain extender nature and their equivalent ratios on the mechanical and thermal properties of PUs. E-polymer. 48, 1-14.
31. Mondal, S., Hu, J. 2006. Structural characterization and mass transfer properties of polyurethane block copolymer: influence of mixed soft segment block and crystal melting temperature. Polym. Int. 55, 1013-1020.
32. Wang, W., Ping, P., Yu, H., Chen, X., Jing, X. 2006. Synthesis and characterization of a novel biodegradable, thermoplastic polyurethane elastomer. J. Polym. Sci. Pol. Chem. 44, 5505-5512.
33. Ping, P., Wang, W., Chen, X., Jing, X. 2007. The influence of hard-segments on two-phase structure and shape memory properties of PCL-based segmented polyurethanes. J. Polym. Sci. Pol. Phys. 45(5), 557-570.
34. Gopakumar, G., Nair, G. 2006. Natural rubber–polyurethane block copolymers: Nonlinear structural variations with NCO/OH ratio. Polym. Eng. Sci. 23(1): 227-245.
35. Gopakumar, S., Paul, C.J., Nair, M.R.G. 2005. Segmented block copolymers of natural rubber and 1,4-butanediol-toluene diisocyanate oligomers. Mater. Sci.-Poland. 23(1), 227-245.
36. Bagdi, K., Molnar, K., Wacha, A., Bota, A., Pukanszky, B. 2011. Hierarchical structure of phase-separated segmented polyurethane elastomers and its effect on properties. Polym. Int. 60, 529-536.

37. Jiang, H., Zheng. Z., Song, W., Wang, X. 2008. Moisture-cured polyurethane/polysiloxane copolymers: Effects of the structure of polyester diol and NCO/OH ratio. J. Appl. Polym. Sci. 108, 3644-3651

CHAPTER 5

EFFECT OF THE DIISOCYANATE STRUCTURE AND THE MOLECULAR WEIGHT OF DIOLS ON BIO-BASED POLYURETHANES

Manuscript submitted in *Journal of Applied Polymer Science*

ABSTRACT: Bio-based polyurethanes (PU) containing poly(ε-caprolactone) diol (PCL) and hydroxyl telechelic natural rubber (HTNR) were synthesized. The effect of the diisocyanate structure and the molecular weights of diols on the mechanical properties of PU were investigated. Three different molecular structures of diisocyanate were employed: an aliphatic diisocyanate (hexamethylene diisocyanate, HDI), an aromatic diisocyanate (toluene-2,4-diisocyanate, TDI) and a cycloalkane diisocyanate (isophorone diisocyanate, IPDI). Two molecular weights of each diol were selected. When HDI was employed, a crystalline PU was generated while asymmetrical structures of TDI and IPDI provided an amorphous PU. The presence of crystalline domains was responsible of a change in tensile behavior and physical properties. PU containing TDI and IPDI showed a rubber-like behavior: low Young's modulus and high elongation at break. The crystalline domains in PU containing HDI acted as physical crosslinks, enhancing the Young's modulus and reducing the elongation at break, and they are responsible of the plastic yielding. The crystallinity increased the tear strength, the hardness and the thermal stability of PU. There was no significant difference between the TDI and IPDI on the mechanical properties and the physical characteristics. Higher molecular weight of PCL diol changed tensile behavior from the rubber-like materials to the plastic yielding. Thermal and dynamic mechanical properties were determined by using DSC, TGA and DMTA.

Key words: Polyurethane, natural rubber, polycaprolactone, bio-based polymer

5.1 INTRODUCTION

Polyurethane is generally prepared via a polyaddition reaction between a diisocyanate and a polyol to form urethane linkages. Its molecular structure and its properties vary over a broad range of stiffness or flexibility, hardness, and density [1], consequently there are many applications of polyurethane such as flexible or rigid foams, chemical resistant coatings, rigid and flexible plastics, specialty adhesives and sealants, and elastomers [2], all of which lead to an increase in polyurethane consumption. At the end of their life cycle, these synthetic polymers so widely used do not degrade naturally leading to a considerable amount of waste and, as consequence, to environmental issues. In this context, the development of biodegradable polyurethane is a topic of interest. Among the commercial biodegradable polymers, such as polyhydroxyalkanoates, poly(lactic acid), and polyesteramide, poly(ε-caprolactone) (PCL) diol has been widely used as a starting material for synthesizing biodegradable polyurethane, which can now be found in many applications [3-18].

The synthesis of bio-based polyurethanes in general has gained interest as well. In order to find alternative renewable monomer feedstocks and to promote sustainable development, many bio-based polyols from renewable resources, such as plant oil [19-23] sugar [24], chitosan [25], natural rubber [26-39], chitin [40-41], glucan [42] and heparin [43] have been explored for polyurethane synthesis. Natural rubber can be easily chemically modified to give a functionalized rubber, such as epoxidized natural rubber (ENR), carbonyl telechelic natural rubber (CTNR) and hydroxyl telechelic natural rubber (HTNR). In principle, a PCL-based polyurethane is a biodegradable polyurethane, whereas a HTNR-based polyurethane is a bio-based polymer and does not easily degrade; although NR is a biopolymer, its biodegradation has not been widely studied, we found just one article reporting the biodegradation of NR/starch blend by bacteria isolated from soil [44]. Therefore, if a biodegradable segment, for instance PCL, were introduced into HTNR-based polyurethane, biodegradation should occur in the PCL segment and the HTNR segment could be recovered and reused.

Recently, a new bio-based polyurethane made from HTNR and PCL diol was reported by Panwiriyarat and coworkers [45]. In this work polyurethane containing a high amount of isophorone diisocyanate was prepared and the effect of the HTNR amount on the mechanical properties of the resulting polymer was investigated. The NCO:OH molar ratio equaled to 2.85:1.00 and 1,4-butanediol (BDO) was used as chain extender. The formation of the urethane linkage and of allophanate groups was observed by FTIR analysis. The material resulted highly crosslinked and this was attributed to no phase separation between the hard and the soft segment. The hydrogen bonding between the PCL diol and the diisocyanate fragments was considered responsible of the high T_g observed. By addition of a small amount of HTNR in the formulation, the tensile properties and tear strength of PU increased significantly. With a further increase of the HTNR content, the tensile behavior of PU was changed from a tough to a soft polymer.

Generally, the mechanical and thermal properties of polyurethane directly depend on the chemical composition, type and molecular weights of the soft and hard segments [3-4, 46]. Consequently in the present work we aimed at completing the previous study and we investigated the effect of the diisocyanate type and the molecular weights of the HTNR and the PCL diol on the mechanical and thermal properties of polyurethane containing a lower isocyanate content.

5.2 EXPERIMENTAL

5.2.1 Materials

Three types of diisocyanate were employed: isophorone diisocyanate (IPDI), toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HDI). Two commercial PCL diols were selected and their molecular weights were 530 and 2000 g/mol. HTNR was synthesized from solid NR and their molecular weights were 1700 and 2800 g/mol. All chemicals used are listed in Table 5.1 and their chemical structures are shown in Figure 5.1. The PCL diol was vacuum dried at 40°C for 24 h prior to use. Other chemicals were used as received.

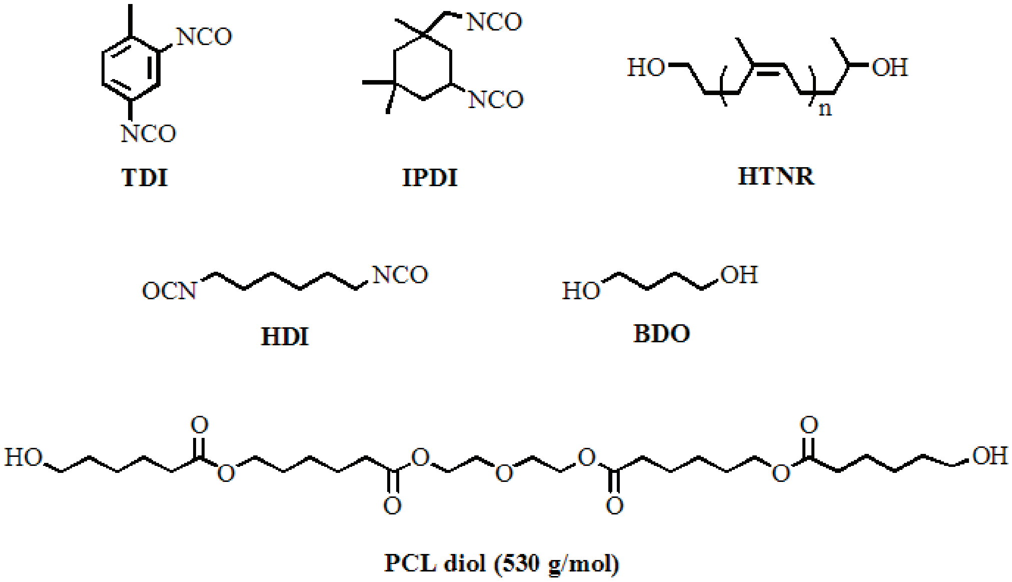
Table 5.1 List of chemicals

Chemical	Tradename/Producer	Specification
Natural rubber	Jana Concentrated Latex Co., Thailand	STR5 CV60 grade
Dibutyl tin dilaurate	Aldrich	Analytical grade (95%)
m-chloroperbenzoic acid	Fluka	Analytical grade (70%)
Poly(ε-caprolactone) diol*	Aldrich	Laboratory grade $\bar{M}_n$ = 530/2000 g/mol T_m: 36-48°C, relative density at 25°C: 1073 g/cm^3
Isophorone diisocyanate	Fluka	Analytical grade (98.0%)
Toluene-2,4-diisocyanate	Fluka	Analytical grade (90.0%)
Hexamethylene diisocyanate	Fluka	Analytical grade (98.0%)
Periodic acid	Himedia	Analytical grade (99.5%)
Sodium borohydride	Rankem	Analytical grade (98.0%)
Tetrahydrofuran	Fisher Scientific UK Limited	Analytical grade (99.8%)
1,4-Butanediol	Merck	Analytical grade (99.0%)

* two grades: $\bar{M}_n$ = 530 g/mol (liquid) and 2000 g/mol (wax).

5.2.2 Synthesis of hydroxyl telechelic natural rubber (HTNR)

Hydroxyl telechelic natural rubber (HTNR) was prepared by an oxidative chain cleavage reaction of natural rubber. The double bonds of NR were cleaved by using periodic acid at 30°C for 6 h in tetrahydrofuran to obtain a carbonyl telechelic natural rubber (CTNR). The carbonyl end-group in CTNR became hydroxyl end-group by using sodium borohydride. The reaction was carried out at 60°C for 6 h in tetrahydrofuran. All chemical structures were verified by ^{1}H-NMR spectroscopy and molar masses by gel permeation chromatography. Two number average molecular weights (M_n) of HTNR were prepared: 1700 and 2800 g/mol (referred to HTNR$_{1700}$ and HTNR$_{2800}$, respectively).



TDI IPDI HTNR

HDI BDO

PCL diol (530 g/mol)

Figure 5.1 Chemical structure of HTNR, PCL diol, BDO, TDI, HDI and IPDI.

5.2.3 Synthesis of polyurethane

Polyurethane (PU) was synthesized by a one-shot method. Three parameters were investigated: the molecular weight of the PCL diol (530 and 2000 g/mol), of HTNR (1700 and 2800 g/mol), and the diisocyanate structure. Three types of diisocyanate were employed (in this paper the abbreviation NCO will be used to indicate a diisocyanate molecule, not a single group): IPDI, TDI and HDI. The total diol content (OH) came from PCL diol, HTNR and 1,4-butanediol (BDO). Generally BDO acts as a chain extender and contains hydroxyl groups; therefore, BDO content was taken into account in the diol calculation of chemical components. Chemical composition of the resulting PUs is listed in Table 5.2. The molar ratio of NCO:OH was 1.25:1.00 while the molar ratio of PCL:HTNR:BDO was 0.35: 0.15: 0.50. A mixture of these diols was dissolved in THF (30 w/v%) and mixed with dibutyl tin dilaurate as a catalyst. A known amount of diisocyanate in THF was slowly added and the reaction temperature maintained at 60°C for 3 h. At the end of the reaction, the viscous polymer solution was poured into a glass mold and heated at 40°C for 3 h and at 60°C for 24 h to evaporate the solvent. The obtained square PU sheets were 15 cm x 15 cm with a thickness of 0.3-0.5 mm.

5.2.4 Testing of the mechanical properties

The die-cut specimens were prepared from the polyurethane sheets. The tensile properties (ASTM D 412C) and tear strength (ASTM D 624) were determined by a tensile testing machine (Lloyd®LR10K) at a crosshead speed of 500 mm/min. Eight specimens were tested for every sample. The average value and standard deviations were reported. The Young's modulus was determined from the initial slope of the linear portion of the stress–strain curves. The hardness shore A was carried out according to ASTM D2240 by a Shore Durometer® PTC 408.

5.2.5 Polymer characterization

Thermogravimetric analysis (TGA) was carried out on a TA Instruments® TGA Q 100 with a heating rate of 10°C/min from room temperature to 600°C, under nitrogen atmosphere. TGA curves were recorded. The temperature at which a certain amount of weight loss occurred, e.g. 5%, 10% and 50%, was determined from the TGA curves. A characteristic temperature (T_{peak}) that corresponds to the maximum rate of degradation was determined from the derivative thermogravimetric curves (DTG).

Differential scanning calorimetry (DSC) was performed on a TA Instruments® DSC Q 100 under nitrogen atmosphere. In order to eliminate the effect of the thermal history, all samples were first heated from 20°C to 200°C and then, were slowly cooled with a heating/ cooling rate of 10°C/min and -10°C/min, respectively. Glass transition temperature (T_g) was recorded from the second heating scan in the range of -80 to 200°C.

The storage modulus (E'), the loss modulus (E'') and the loss tangent ($\tan \delta$) were measured by a Rheometric Scientific® DMTA V. The experiments were carried out in the tension mode at a frequency of 1 Hz with a strain control of 0.01%, and the heating rate was 3°C/min. The temperature range was -80 to 200°C.

5.3 RESULTS AND DISCUSSION

The aim of this research study was to expand and complete the initial investigation of the synthesis of new bio-based and potentially biodegradable polyurethanes, based on polycaprolactone and natural rubber precursors. The attention was focused on the influence of the diisocyanate structure and on the diol molecular weight on the physical and thermal properties of the generated polyurethane sheets.

The molar ratio of precursors NCO:PCL:HTNR:BDO (NCO refers to a diisocyanate molecule, containing 2 isocyanate groups) to use in the formulations was selected from the preliminary study carried out. It was found that when the NCO:OH ratio was 0.75:1.00, film formation did not occur and a viscous liquid was obtained because of inadequate amounts of NCO groups. The higher ratio (1.00:1.00) produced a very sticky film with no mechanical integrity. The desired films were finally generated when the NCO:OH ratio was 1.25:1.00.

The obtained PUs contained 25-42% of the hard segment (i.e. diisocyanate plus chain extender) as shown in Table 5.2. The percentage of the hard segment depended also on the molecular weights of the starting materials. The physical appearances of PU by visual observation are described in Table 5.2; the yellow color of PU derived from the presence of HTNR, while soft and semi-transparent sheets were given by the samples containing TDI and IPDI. On the contrary PU2 prepared from HDI was hard and opaque.

Table 5.2 Chemical composition and physical properties of PU1-PU5

Code	Molar ratio				HS$^{(a)}$ (%)	Physical Appearances$^{(b)}$
	1.25 NCO	0.35 PCL	0.15 HTNR	0.5		
PU1	TDI	PCL$_{530}$	HTNR$_{1700}$	✓	37.4	Y, S, ST
PU2	HDI	PCL$_{530}$	HTNR$_{1700}$	✓	36.7	Y, H, O
PU3	IPDI	PCL$_{530}$	HTNR$_{1700}$	✓	42.3	Y, S, ST
PU4	IPDI	PCL$_{530}$	HTNR$_{2800}$	✓	34.8	Y, S, ST
PU5	IPDI	PCL$_{2000}$	HTNR$_{1700}$	✓	25.3	Y, S, O

(a) Hard segment (%) = 100 [weight of (isocyanate+chain extender)]/ total weight

(b) Y: yellowish; H: hard; S: soft; O: opaque; ST: semi-transparent

The formation of a crosslinked network in PU due to the excess of isocyanate was investigated by performing solubility tests and FTIR analyses. No sample dissolved in chloroform and tetrahydrofuran which are the solvents used for the polymerization of PU.

Infrared spectra of the polyurethane films were carried out to check the formation of the urethane bonds: Figure 5.2 shows FTIR spectra of PCL diol, HTNR, TDI and PU1 and in Table 5.3 the FTIR assignment of the precursors and PU are listed [47-49]. The –OH absorption band of PCL diol and HTNR and the -N=C=O absorption band of diisocyanate were not observed in PU1, which showed new absorption bands in 4 regions: (1) at 1728 cm^{-1}, corresponding to the non-hydrogen bonded –C=O stretching; (2) at 1715 cm^{-1}, corresponding to the carbonyl stretching of the C=O hydrogen bonded with the NH group in the urethane linkage; (3) at 3360-3365 cm^{-1}, corresponding to the NH stretching vibration; (4) at 1525-1550 cm^{-1}, corresponding to the bending vibration. It was found that an excess of isocyanate generates allophanate groups and acylurea linkages that cause crosslinking in PU [2, 50]. The characteristic peaks of the allophanate group fall in 2 regions: (1) stretching vibrations at 1220, 1280 and 1310 cm^{-1} and (2) bending vibrations at 3298, 3267 and 3233 cm^{-1} [51]. The present PUs showed the characteristic bands of the allophanate group at 1234, 1276 and 1304 cm^{-1}, and the absorption bands at 3233-3298 cm^{-1} were overlapped with the band of NH stretching at 3361 cm^{-1}. Generally, the excess of diisocyanate can react with water and generate an urea linkage before forming a biuret later. The wavenumbers of the signals of the biuret and the allophanate groups fall in the same region so it was believed that the allophanate was formed in our case because the samples were in a dry environment.

The effect of the diisocyanate (NCO) type was determined from the samples called PU1-PU3 and the effect of the molecular weight of PCL and HTNR was determined from samples PU3-PU5.

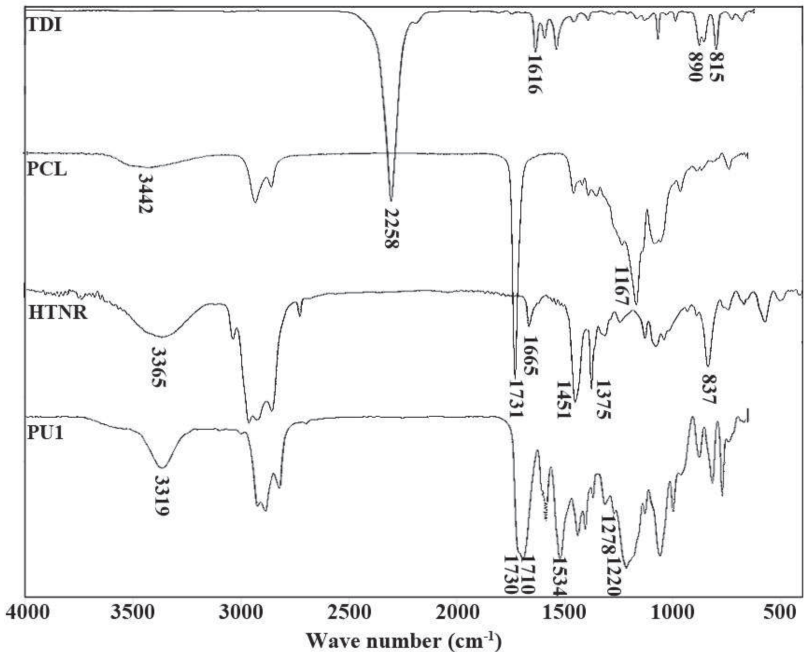


Figure 5.2 FTIR spectrum of TDI, HTNR, PCL diol and PU1.

Table 5.3 FTIR assignment of precursors and polyurethane

	Wavenumber	Assignment
PCL	3442 cm^{-1}	υ (O-H)
	1731 cm^{-1}	υ (C=O) of ester
	1167 cm^{-1}	υ (C-O) of ester
HTNR	3365 cm^{-1}	υ (O-H)
	2730-2900 cm^{-1}	υ (CH_2, CH_3)
	1664 cm^{-1}	υ (C=C)
	1448, 1376 cm^{-1}	δ (CH_2, CH_3)
	834 cm^{-1}	δ (C=C-H)
TDI	2258 cm^{-1}	υ (N=C=O)
	1721, 1781 cm^{-1}	Overtone of aromatic substitution
	1600-1500 cm^{-1}	υ (C=C) in aromatic compound
	815- 890 cm^{-1}	δ (C=C-H)
PU	3319 cm^{-1}	υ (N-H), H-bonded
	1730 cm^{-1}	υ (C=O)
	1710 cm^{-1}	υ (C=O), H-bonded
	1534 cm^{-1}	δ (N-H) + υ (C-N)
	1310 cm^{-1}	δ (N-H) + υ (C-N)
	1220 cm^{-1}	Amide III + υ (C-O)

(υ = stretching, δ = bending)

5.3.1 Effect of the diisocyanate type

(a) On the mechanical properties

Three different molecular architectures of diisocyanate were employed: a linear aliphatic diisocyanate (HDI), an aromatic diisocyanate (TDI) and a cycloalkane diisocyanate (IPDI). The molecular weight of the PCL and HTNR used in this case was 530 g/mol and 1700 g/mol, respectively. Mechanical tests were carried out and the stress-strain curves of the polyurethanes (Figure 5.3) and their tensile properties (Table 5.4) have been obtained. It was observed that PU1 and PU3 showed rubber-like behavior with no plastic yielding. An elastic deformation followed by yielding and a plastic deformation was observed in the PU2. The polyurethane derived from HDI (PU2) showed the highest Young's modulus (E) and the lowest elongation at break (ε_b). HDI is claimed to be a crystallizing diisocyanate [2] due to its linear structure; therefore, PU2 was expected to be a crystalline PU. Furthermore, its opacity should be the result of the crystallization of the hard segment. This assumption was verified by DSC analysis, as described later. The crystalline region of the hard segment acted as a physical crosslink providing a higher modulus and a lower elongation at break. The low tensile strength (σ_b) of PU2 was due to the relatively low ductility compared to PU1 and PU3. The effect of the crystallization of HDI was also responsible of the highest tear strength and hardness values (Table 5.4). Found for PU2.

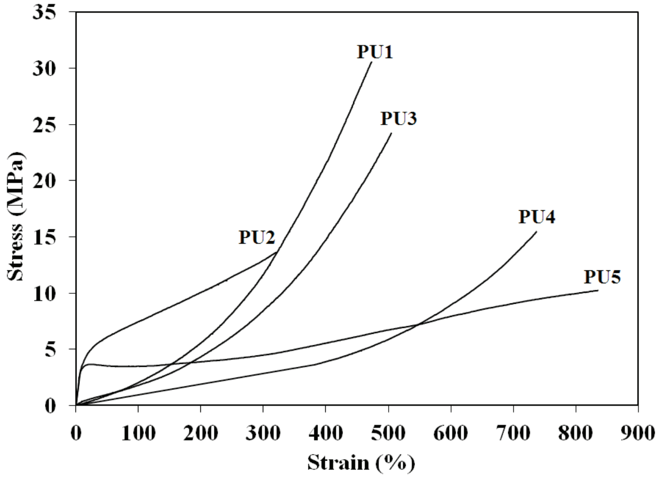


Figure 5.3 Stress-strain curves of PU1-PU5.

Table 5.4 Effect of various type of diisocyanate and molecular weight of diol on the mechanical properties of PU1-PU5

Code	Tensile Properties				Tear strength (N/mm)	Hardness (Shore A)
	E (MPa)	$E_{300\%}$ (MPa)	σ_b (MPa)	ε_b (%)		
PU1	1.9±0.4	11.6±1.0	28.4±1.9	447±52	32.0±3.5	49±3
PU2	37.1±4.1	12.9±1.1	15.0±1.9	329±21	57.7±6.2	77±3
PU3	2.2±0.4	8.4±1.0	24.3±1.2	506±10	38.3±1.2	56±1
PU4	0.9±0.0	3.5±0.5	15.6±0.6	753±14	29.9±1.8	37±2
PU5	49.0±4.0	4.4±0.6	10.0±1.3	867±44	45.0±4.2	31±2

According to Hepburn[1], the effect of the methyl substituent in TDI and IPDI is dominant, and causes an asymmetrical structure leading to amorphous domains. This results in a large drop in the Young's modulus and tear strength and an increase in the flexibility. This phenomenon has been also observed in the present study. The tensile behavior of PU1 and PU3 looked like a typical rubber: very low Young's modulus, high tensile strength and high elongation at break. Their hardness and tear strength were ranked in the following order: PU1 < PU3 < PU2 (Table 5.4). We could observe that the molecular structure of the diisocyanate played a major role on the mechanical properties of PU. The linear diisocyanate showed a remarkable difference in the tensile behavior and the mechanical properties from the cyclic one, but TDI and IPDI did not show significant difference in those properties, except that the elongation at break of PU3 was higher than that of PU1. The modulus at 300% ($E_{300\%}$), an important property of elastomers, is the stress at a 300% strain. All PUs showed a high $E_{300\%}$, i.e., in the range of 8-13 MPa, indicating a strong elastomer. Furukawa et al. [52] reported the structure-properties relationship of caprolactone-based PU with 2 types of diisocyanates: 1,2-bis(isocyanate)ethoxyethane (TEGDI) and HDI. The polyurethane elastomer was prepared by using a two-shots method and the ratio of NCO:OH was 1.05:1.00. They found that the Young's modulus was in the range of 0.8-15 MPa, which was lower than that of the present study, and the tensile strength was 1.0-42 MPa, which was a larger range than the present study. The elongation at break of those PUs was in the same range as found in the present study, while the The

TEGDI-based PU showed a larger strain at break and lower Young's modulus than the HDI ones.

(b) On the thermal properties

The thermal behavior of the polyurethanes was investigated by DSC and TGA. The DSC thermograms of the soft segments (the diol precursors) and the hard segment (the diisocyanate plus chain extender) recorded from the second heating scan are illustrated in Figure 5.4a and 5.4b, respectively. The hard segment model was obtained from the polyurethane sheet containing only diisocyanate and the chain extender (BDO), in the molar ratio of 1.25:1.00. PCL diols had a double melting peak (T_m): at -9/15 °C for the low molecular weight (PCL_{530}) and 44/49 °C for the high molecular weight (PCL_{2000}), similar to the observations by Kim et al. [17]. There was an unclear transition temperature at -78 °C in the PCL_{530} sample (Figure 5.4a). This transition occurred at the beginning of the investigation, and it could be due to a shift of the base line. Unfortunately, the T_g of PCL_{530} was not detectable from the cooling scan. The crystallization temperature (T_c) obtained from a cooling scan was noticeable in PCL diols (data not shown here). The HTNRs were amorphous and their T_g values were in the same range, -60 °C to -58 °C. The differences in molecular weight between both HTNRs were not so high as that of the PCL diols, and this led to a similar T_g. the crystallization behavior of the hard segment strongly depended on diisocyanate structure as showed in Figure 5.4b. A melting peak was observed in HDI-based hard segment: it displayed relatively low T_g at 28 °C and T_m at 175 °C, whereas the IPDI-based and TDI-based hard segment showed only T_g in the same range: at 109 °C and 107 °C, respectively.

The DSC results of samples PU1-PU3 are shown in Figure 5.4c. PU1 and PU3 were amorphous whereas PU2 was a semi-crystalline polymer because of the crystallinity of the HDI hard segment. PU2 showed T_m at 126 °C (Figure 5.4c) and T_c, obtained from a cooling scan, at 63 °C. The presence of the endothermic peak in PU at ~ 130°C due to HDI is reported by Furukawa et al. [52]. Although the PCL diol was a crystallizable material, it could not be crystallized in the present PUs. This phenomenon was verified by PU5 containing PCL_{2000} in which no melting peak was observed. As a result, the crystalline PU (PU2) had a different tensile behavior from the amorphous PU (PU1 and PU3) and, at the same time, it had the highest Young's modulus.

PU1-PU3 had double T_g; in particular, T_gs of PU1 and PU3 were similar, -55 °C and 25 °C. Although the T_gs of the TDI and IPDI hard segment were high, 107 °C and 109 °C, respectively, they did not appear in PU1 and PU3. Undoubtedly, the T_g at -55 °C was due to the HTNR segment. It was believed that the T_g at 25 °C belonged to the PCL diol segment that had hydrogen bonds with the hard segment. Only the PCL diol, but not the HTNR, in the polyurethane is able to form hydrogen bonding with the hard segment [45]. Therefore, this T_g (25 °C) was higher than the T_g of the virgin PCL_{530} and lower than the T_g of the TDI and IPDI. The analysis of PU2 showed that it had two T_gs at -58 °C and -25 °C; the lower T_g was assigned to the HTNR segment and the higher one to the PCL diol, hydrogen bonded with the HDI hard segment. We can assume that the lowest T_g in PU2 is due to the segmental hexamethylene contribution [2]. No phase separation between the PCL diol and the IPDI hard segment in the polyurethane was observed [45], consequently, a phase separation between the hard segment and the soft segment in the present PUs was not found.

The transition temperatures of the PUs were also determined by using dynamic mechanical thermal analysis (DMTA). Figure 5.5 shows the dynamic mechanical curve of PU1-PU3 including the storage modulus, the loss modulus and the loss tangent as a function of temperature. The molecular architecture of the diisocyanate also played a major role in the dynamic mechanical thermal properties. The more flexible, linear structure of the HDI was responsible of a low storage modulus and a low α transition temperature of PU2. The rise in E' of PU2 may be due to its crystallinity or its sensitivity in microphase separation. Furukawa, et al. [52] reported that the rise in E' of PCL-based PU is due to the recrystallization of the soft segment. According to Samy et al. [53], the rise in E' of polyurethane relates to the microphase separation. TDI (PU1) and IPDI (PU3) provided similar DMTA curves. The loss modulus shown in Figure 5.5b was also strongly dependent on the molecular structure of the diisocyanate. The flexible structure of HDI in PU2 caused a sudden drop in E″ at approximately -23 °C, whereas the rigidity of TDI and IPDI contributed to the higher E″ at this temperature. Figure 5.5c represents the tan δ of PU1-PU5. As found from the DSC results, PU1-PU3 showed multiple transition temperatures with no significant differences between PU1 and PU3. PU1 and PU3 showed α transition temperature at 49 °C, which arose from the relaxation of the PCL diol that hydrogen bonded with the diisocyanate. The α transition temperature of the TDI and IPDI hard segment was 56 °C and 70 °C, respectively. A subglass transition temperature (β relaxation) of PU1 and PU3 was detected at -50 °C, and it derived from the HTNR segment. PU2 instead exhibited 3 transition temperatures: 65, -15 and -76°C; it was assumed the α and β transition temperatures were at -15°C and -76 °C, respectively, while the relaxation temperature at 65 °C (> T_g) might be associated with the crystallinity.

Thermo gravimetric analysis of the samples was carried out. The thermal stability of the diol precursors (PCL diols, HTNRs and BDO), the hard segments (diisocyanate+BDO) and PUs are illustrated in Figure 5.6 (A weight loss at a certain temperature from the TGA thermogram is also listed in Table 5.5). A T_{peak} in Table 5.5 was the temperature at which a rapid drop in weight loss took place. The thermal stability of the diols depended on their chemical structure and molecular weight (Figure 5.6a). The lowest thermal degradation temperature appeared in the BDO due to its lowest molecular weight. PCL_{2000} showed higher thermal stability than $PCL_{530,}$ whereas both HTNRs had similar thermal degradation temperatures. Figure 5.6b illustrates TGA curves of the hard segment (diisocyanate and BDO): a slight difference in the thermal stability between the TDI and the IPDI hard segment was observed, therefore there was an insignificant difference in the thermal stability between PU1 and PU3 (Figure 5.6c). The HDI hard segment had a higher thermal stability than the TDI and IPDI, even though the HDI has a linear molecular structure and can form crystalline domains. As a result, PU2 had the highest thermal stability. These results reasonably agree with those from the study of Wei, et al. [54].

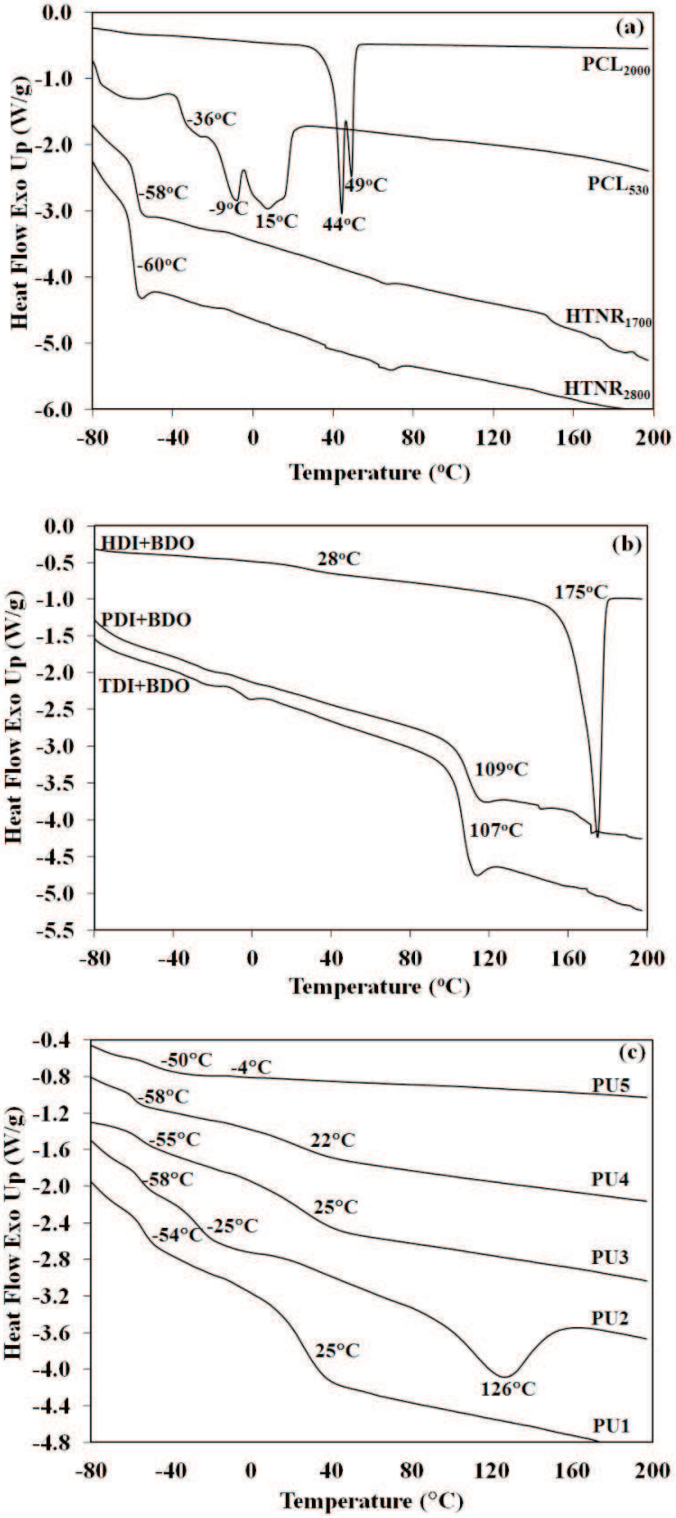


Figure 5.4 DSC thermograms recorded from the 2nd heating scan: (a) diol precursors; (b) hard segments and (c) PU1-PU5.

Table 5.5 TGA data of the precursors, hard segment (NCO+BDO) and PU1-PU5

Materials	T_5[a] (°C)	T_{10}[a] (°C)	T_{50}[a] (°C)	T_{90}[a] (°C)	T_{peak}[b] (°C)
BDO	123	136	174	192	189
PCL_{530}	206	249	344	407	339, 398
PCL_{2000}	308	350	399	422	407
$HTNR_{1700}$	250	272	400	445	263, 407
$HTNR_{2800}$	253	287	390	441	439
TDI+BDO	110	124	293	450	124, 306, 452
HDI+BDO	270	283	314	388	304, 365, 460
IPDI+BDO	132	149	304	327	146, 314
PU1	257	272	318	425	304, 378
PU2	256	273	342	415	305, 374
PU3	260	276	318	399	320, 377
PU4	261	279	331	404	315, 375
PU5	242	259	301	379	304, 378

a = data obtained from the TGA curve b = data obtained from the DTG curve

5.3.2 Effect of the molecular weight of the diols

(a) On the mechanical properties

The use of polyols with different molecular weights allowed an investigation of the effect of the polyol chain length. The synthesized polymers had different hard segment contents that depended on the polyol molecular weight: 42.3, 34.8 and 25.3% for PCL_{530}-$HTNR_{1700}$ (PU3), PCL_{530}-$HTNR_{2800}$ (PU4) and PCL_{2000}-$HTNR_{1700}$ (PU5), respectively. The physical appearances of the films are described in Table 5.2: PU5 was opaque although it consisted of IPDI, the non-crystallizing diisocyanate. We hypothesized that the opacity was not due to crystallization as occurred in PU2, but it might arise from the high phase segregation because by the high molecular weight of PCL_{2000}: when the DSC thermogram (Figure 5.4c) was examined, no T_m was detected and this confirmed the assumption.

The influence of the molecular weight on the stress-strain curves is illustrated in Figure 5.3. PU3 and PU4 exhibited a typical rubbery characteristic with a high elongation at break and a low modulus. PU5 initially underwent an elastic deformation followed by a yielding and a plastic deformation. The molecular weight of the PCL diol influenced the tensile behavior of PU more than that of the HTNR. The effect of the molecular weight of the diols on the tensile properties, tear strength and hardness is listed in Table 5.4. By increasing the molecular weight of the PCL diol (PU3 vs. PU5), the Young's modulus and the elongation at break increased but the tensile strength decreased. It may be assumed that the crystallinity of the PCL_{2000} give a major contribution to the higher modulus in PU5. In addition, there would be a higher tensile strength and lower elongation at break if the crystallinity of PCL_{2000} was dominant. However, PU5 had an amorphous nature as determined by the DSC characterization. This inconsistency could be explained in terms of the content of the hard segment that was associated with the crosslink density. The hard segment content was calculated based on the weight of the chemicals. By using a constant molar ratio, the concentration of chemicals changed owing to their different molecular weight, thus, PU3 had a greater hard segment content than PU5. If the higher molecular weight of the PCL diol exerted a major influence on the Young's modulus, the hard segment content may exert a major influence on the tensile strength and elongation at break. The higher molecular weight of the PCL diol increased the tear strength, which agreed with the increase in the Young's modulus. Concerning PU5, a decrease in the hardness may be due to the higher flexibility of the longer chain of the soft segment (PCL_{2000}) and the low hard segment content: in fact it was noticed that PU5 had the lowest hard segment content among the PU1-PU5 samples, and this led it to have the lowest hardness and the highest elongation at break.

The higher molecular weight of HTNR decreased the mechanical properties, except for the elongation at break, as seen comparing PU3 and PU4. These differences may result from an increase in the chain flexibility and a decrease in the hard segment content due to the longer chain length of the HTNR.

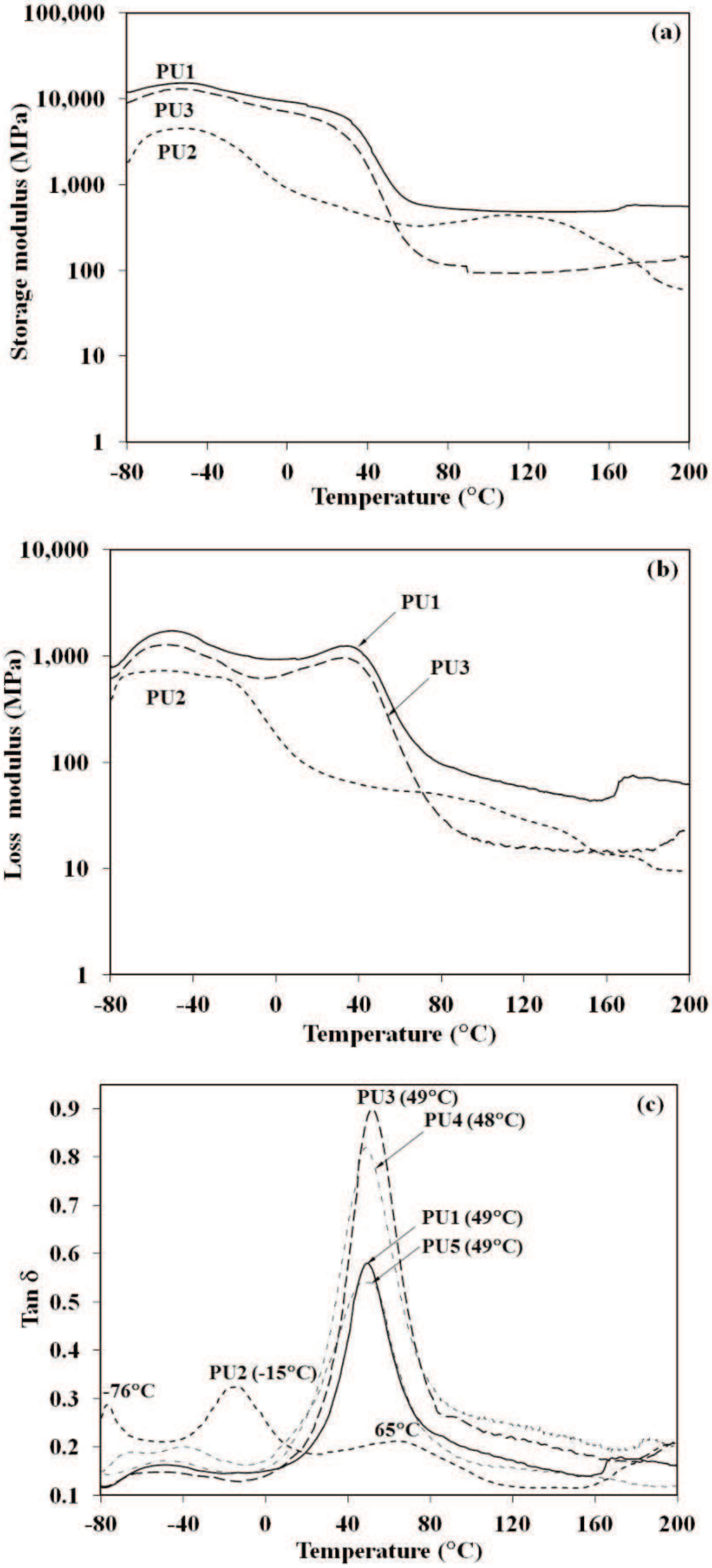


Figure 5.5 Dynamic mechanical curves as a function of temperature of: (a) the storage modulus of PU1-PU3, (b) the loss modulus of of PU1-PU3and (c) the tan δ of PU1-PU5.

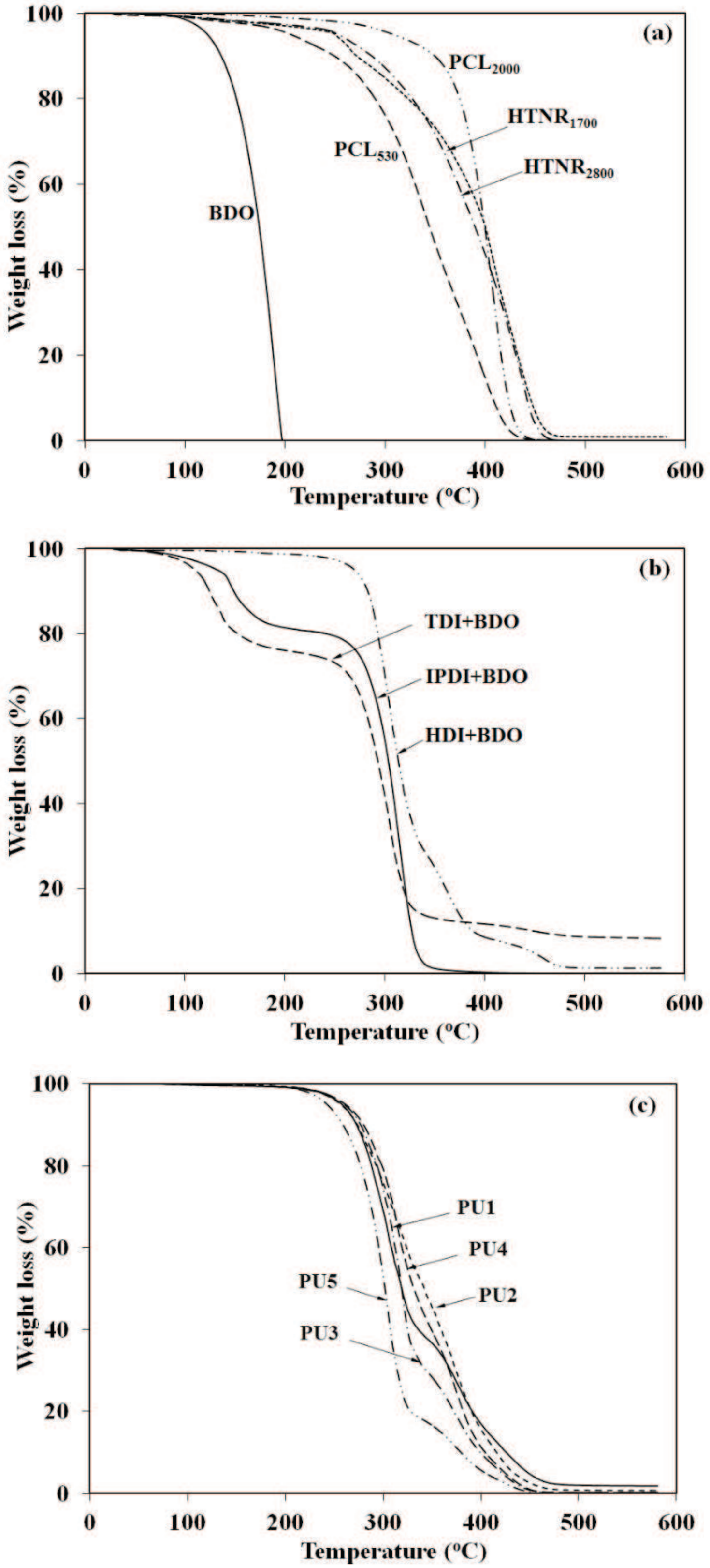


Figure 5.6 TGA thermograms of (a) diol precursors (b) hard segments and (c) PU1-PU5.

(b) On the thermal properties

The influence of the molecular weight of the diols on the thermal properties is shown in Figure 5.4c. PU3-PU5 showed amorphous characteristics, which is not surprising as crystallization of the soft segment rarely occurs at molecular weights inferior to 2000 g/mol [1]. Considering the molecular weight of the PCL diol used, PU3 and PU5 showed 2 T_gs (the low-T_g and the high-T_g): -55 °C and 25 °C in PU3 and -50 °C and -4 °C in PU5. It appeared that the higher molecular weight of the PCL diol was responsible of the lower T_g, e.g., from 25 °C in PU3 to be -4 °C in PU5. The effect of the molecular weight of the PCL diol on the T_g may be related to the hard segment content: a lower crosslink density, due to a lower hard segment content, could have produced a lower T_g in PU5 than in PU3. This phenomenon could be explained by the fact that when chain length between the crosslinks increases, a higher flexibility of the material is obtained. This same observation was also clearly found in the cooling scan (data not shown here). The HTNR chain length induced a little change in T_g, with PU3 having slightly higher T_gs than PU4, therefore, in conclusion, it was observed that the molecular weight of the PCL diol had more influence on the T_g value than that of the HTNR.

In contrast to the DSC results, the α transition temperatures derived from the DMTA of the PU3-PU5 were in the same range (49 °C), and their DMTA curves were similar (Figure 5.6c). The thermal stability of PU4 seemed to be the lowest (Table 5.5) but generally the thermal degradation temperatures of PU3-PU5 were in the same range.

5.4 CONCLUSION

The aim of this research work was to synthesize novel bio-based and potentially biodegradable polyurethanes. Different formulations were conceived and conditions were optimized in order to obtain thin, flexible films. A study of the influence of selected parameters on the mechanical and thermal properties of the resulting materials was carried out. It was found that the molecular architecture of diisocyanate and molecular weight of diol played an important role on the mechanical properties and materials characteristics. The linear structure of hexamethylene diisocyanate (HDI) was able to crystallize leading to a crystalline PU (PU2), whereas the asymmetrical cyclic structure of toluene-2,4-diisocyanate (TDI), and isophorone diisocyanate (IPDI) produced amorphous PU (PU1 and PU3). This morphology affected the tensile behavior and the mechanical properties. The crystalline region acted as physical crosslink enhancing the Young's modulus and reducing the elongation at break, and it was responsible of the plastic yielding during tensile testing. In contrast, the amorphous characteristic of PU1 and PU3 was the cause of the rubber-like behavior, i.e., very low Young's modulus and high elongation at break. The crystallinity also increased the tear strength, the hardness and the thermal stability of PU. There was no significant difference between TDI and IPDI on the mechanical properties and the materials characteristics. Although PCL diols could crystallize, they could not provide crystallization in the generated PU. The increase in the molecular weight of PCL diol changed tensile performance of PU from the rubber-like to the plastic-like behavior. Another factor that controlled the mechanical properties and features of PU was the hard segment content, which was related to the crosslink density. No phase separation between the hard and the soft segment was observed because of the hydrogen bonding formed between PCL diol and diisocyanate; T_g values determined from DSC and DMTA substantiated this assumption.

5.5 ACKNOWLEDGEMENT

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5.6 REFERENCES

1. Hepburn, C. Polyurethane elastomers, 2nd edition; Elsevier Science Publishers LTD: New York, 1992; pp 1-2.

2. Prisacariu, C. 2011. Polyurethane elastomers from morphology to mechanical aspects; SpingerWienNew York: New York, 10-107.
3. Li, F., Hou, J., Zhu, W., Zhang, X., Xu, M., Luo, X., Ma, D., Kim, B.K. 1996. Crystallinity and morphology of segmented polyurethanes with different soft-segment length. J. Appl. Polym. Sci. 62, 631-638.
4. Lan, P.N., Corneillie, S., Schacht, E., Davies, M., Shard, A. 1996. Synthesis and characterization of segmented polyurethanes based on amphiphilic polyether diols. Biomaterials. 17, 2273-2280.
5. Wang, W., Ping, P., Yu, H., Chen, X., Jing, X. 2006. Synthesis and characterization of a novel biodegradable, thermoplastic polyurethane elastomer. J. Polym. Sci. A Polym. Chem. 44, 5505-5512.
6. Ping, P., Wang, W., Chen, X., Jing, X. 2007. The influence of hard-segments on two-phase structure and shape memory properties of PCL-based segmented polyurethane. J. Polym. Sci. B Polym. Phys. 45, 557-570.
7. Skarja, G.A., Woodhouse, K.A. 2000. Structrue-property relationships of degradable polyurethane elastomers containing an amino acid-based chain extender. J. Appl. Polym. Sci. 75, 1522-1534.
8. Chiou, B.S., Schoen, P.E. 2002. Effects of crosslinking on thermal and mechanical properties of polyurethane. J. Appl. Polym. Sci. 83,212-223.
9. Rogulska, M., Kultys, A., Pikus, S. 2008. Studies on thermoplastic polyurethanes based on new diphenylethane-derivative diols. III. The effect of molecular weight and structure of soft segment on some properties of segmented polyurethanes. J. Appl. Polym. Sci. 110, 1677-1689.
10. D’Arlas, B.F., Rueda, L., Caba, K., Mondragon, I., Eceiza, A. 2008. Microdomain Composition and properties differences of biodegradable polyurethanes based on MDI and HDI. Polym. Eng. Sci. 48(3), 519-529.
11. Maafi, E.M., Malek, F., Tighzert, L. 2010. Synthesis and characterization of new polyurethane based on polycaprolactone. J. Appl. Polym. Sci. 115, 3651-3658.
12. Gorna, K., Gogolewski, S. 2002. In vitro degradation of novel medical biodegradable aliphatic polyurethanes based on ε-caprolactone and Pluronics® with various hydrophilicities. Polym. Degrad. Stab. 75, 113-122.

13. Gorna, K., Polowinski, S., Gogolewski, S. 2002. Synthesis and characterization of biodegradable poly(ε-caprolactone urethane)s. I. Effect of the polyol molecular weight, catalyst, and chain extender on the molecular and physical characteristics. J. Polym. Sci. A Polym. Chem. 40, 156-170.
14. Sarkar, D., Yang, J. C., Gupta, A. S., Lopina, S. T. 2009. Synthesis and characterization of L-tyrosine based polyurethanes for biomaterial applications. J. Biomed. Mater. Res. A. 90(1), 263-271.
15. Watnabe, A., Takebayashi, Y., Ohtsubo, T., Furukawa, M. 2009. Dependence of biodegradation and release behavior on physical properties of poly(caprolactone)-based polyurethanes. J. Appl. Polym. Sci. 114, 246-253.
16. Gong, C.Y., Fu, S.Z., Gu, Y.C., Liu, C.B., Kan, B., Deng, H.X., Luo, F., Qian, Z. Y. 2009. Synthesis, characterization, and hydrolytic degradation of biodegradable poly(ether ester)-urethane copolymers based on ε-caprolactone and poly(ethylene glycol). J. Appl. Polym. Sci. 113, 1111-1119.
17. Kim, B.K., Lee, S. ., Xu, M. 1996. Polyurethanes having shape memory effects. Polymer. 37(26), 5781-5793.
18. Bogdanov, B., Toncheva, V., Schacht, E., Finelli, L., Sarti, B., Scandola, M. 1999. Physical properties of poly(ester-urethanes) prepared from different molar mass polycaprolactone-diols. Polymer. 40, 3171-3182.
19. Bakare, I.O., Pavithran, C., Okieimen, F.E., Pillai, C.K. 2008. Synthesis and characterization of rubber-seed-oil-based polyurethanes. J. Appl. Polym. Sci. 109, 3292-3301.
20. Tu, Y.C., Suppes, G.J., Hsieh, F. H. 2009. Thermal and mechanical behavior of flexible polyurethane-molded plastic films and water-blown foams with epoxidized soybean oil. J. Appl. Polym. Sci. 111, 1311-1317.
21. Chian, K.S., Gan, L.H. 1998. Development of a rigid polyurethane foam from palm oil. J. Appl. Polym. Sci. 68, 509-515.
22. Jalilian, M., Yeganeh, H., Haghighi, M.N. 2008. Synthesis and properties of polyurethane networks derived from new soybean oil-based polyol and a bulky blocked polyisocyanate. Polym. Int. 57, 1385-1394.
23. Lligadas, G., Ronda, J.C, Galia, M., Biermann, U., Metzer, J.O. 2006. Synthesis and characterization of polyurethane from epoxidized methyl oleate

based polyetherpolyols as renewable resources. J. Polym. Sci. A Polym. Chem. 44, 634-645.

24. Begines, B., Zamora, F., Roffe, I., Mancera, Galbis, J.A. 2011. Sugar-based hydrophilic polyurethanes and polyurea. J. Polym. Sci. A Polym. Chem. 49, 1953–1961.
25. Barikani, M., Honarkar, H., Barikani, M. 2009. Synthesis and characterization of polyurethane based on chitosan and Poly(ε-caprolactone). J. Appl. Polym. Sci. 112, 3157-3165.
26. Paul, C.J., Gopinathan Nair, M.R. 1998. Segmented block copolymer of natural rubber and propylene glycol-toluene diisocyanate oligomer. Polym. Eng. Sci. 38(3), 440-451.
27. Cherian, A. B., Thachil, E. T. 2004. Block copolymers of unsaturated polyesters and functional elastomers. J. Appl. Polym. Sci. 94, 1956-1964.
28. Sun, X., Ni, X. 2004. Block copolymer of trans-polyisoprene and urethane segment: crystallization behavior and morphology. J. Appl. Polym. Sci. 94, 2286-2294.
29. Gopakumar, S., Paul, C.J., Nair, M.R.G. 2005. Segmented block copolymers of natural rubber and 1,4-butanediol-toluene diisocyanate oligomers. Mater. Sci.-Poland. 23(1), 227-245.
30. Cherian, A.B., Abraham, B.T., Thachil, E.T. 2006. Modification of unsaturated polyester resin by polyurethane pre polymers. J. Appl. Polym. Sci. 100, 449-456.
31. Kébir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunel, C., Couvercelle, J.P. 2006. Use of new hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes (PUs): Influence of isocyanate and chain extender nature and their equivalent ratios on the mechanical and thermal properties of PUs. E-polymers. 48, 1-14.
32. Kébir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunel, C., Jouenne, T. 2007. Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of antibacterial ionic polyurethanes and copolyurethanes bearing ammonium groups. Biomatherials. 28, 4200-4208.

33. Radhakrishnan Nair, M.N, Gopinathan Nair, M.R. 2008. Synthesis and characterization of soluble block copolymers from NR and TDI based polyurethanes. J. Mater. Sci. 43, 738-747.
34. Chandrasekharan Nair, R., Gopakumar, S., Gopinathan Nair, M.R. 2007. Synthesis and characterization of block copolymers based on natural rubber and polypropylene oxide. J. Appl. Polym. Sci. 103, 955-962.
35. Sukumar, P., Jayashree, V., Gopinathan Nair, M.R., Radhakrishnan Nair, M.N. 2009. Synthesis and thermal studies of block copolymers from NR and MDI-based polyurethane. J. Appl. Polym. Sci. 111, 19-28.
36. Radhakrishnan Nair, M.N., Sukumar, P., Jayashree, V., Gopinathan Nair, M.R. 2010. Mechanical properties and fractography of block copolymers based on NR and MDI-based polyurethanes. Polym. Bull. 65, 83-96.
37. Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Doutres, O., Pilard, J.F. 2010. Preparation and physic-mechanical, thermal and acoustic properties of flexible polyurethane foams based on hydroxytelechelic natural rubber. J. Appl. Polym. Sci. 117, 828-837.
38. Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Doutres, O., Pilard, J.F. 2010. Controlled degradation of natural rubber and modification of the obtained telechelic oligoisoprenes: Preliminary study of their potentiality as polyurethane foam precursors. J. Appl. Polym. Sci. 117, 1279-1289.
39. Kébir, N., Campistron, I., Laguerre, A., Pilard, J. F., Bunel, C. 2011. New crosslinked polyurethane elastomers with various physical properties from natural rubber derivatives. J. Appl. Polym. Sci. 122, 1677-1687.
40. Matsui, M., Munaro, M., Akcelrud, L.C. 2011. Chitin-polyurethane networks: correlations between physical properties and composition. J. Polym. Res., 18(6), 2255-2264.
41. Zia, K.M., Zuber, M., Barikani, M., Bhatti I.A., Khan, M.B. 2009. Surface characteristics of chitin-based shape memory polyurethane elastomers. Coll. Surf B Biointer. 72(2), 248-252.

42. Wang, Y,. Xu, W., Chen, Y. 2010. Surface modification on polyurethanes by using bioactive cdarboxymethylated fungal glucan from Poria cocos. Coll. Surf B Biointer. 81(2), 629-633.
43. Wan, M., Baek, D.K., Cho, J.H., Kang, I.K. 2004. In vitro blood compatibility of heparin-immobilized polyurethane containing ester groups in the side chain. J. Mater. Sci.: Mater. Med. 15, 1079-1087.
44. Watcharakul S, Umsakul K, Hodgson B, Chumeka W, Tanrattanakul V. 2012. Biodegradation of a blended starch/natural rubber foam biopolymer and rubber gloves by Streptomyces coelicolor CH13. Electron. J. Biotechnol. 15(1), DOI: 10.2225.
45. Panwiriyarat, W., Tanrattanakul, V., Pilard, J.F., Pasetto, P., Khaokong, C. 201X. Physical and thermal properties of polyurthane from isophorone diisocyanate, natural rubber and poly(ε-caprolactone) with high NCO:OH content. Adv. Sci. Lett. 19, 1016-1020.
46. Mondal, S., Hu, J.L. 2006. Structural characterization and mass transfer properties of polyurethane block copolymer: influence of mixed soft segment block and crystal melting temperature. Polym. Int. 55, 1013–1020.
47. Khan, A.S., Ahmed, Z., Edirisinghe, M.J., Wong, F.S.L., Rehman, I.U. 2008. Preparation and characterization of a novel bioactive restorative composition based on covalently coupled polyurethane-nanohydroxyaptite fibres. Acta. Biomaterialia. 4, 1275–1287.
48. Romanova, V., Begishev, V., Karmanov, V., Kondyurin, A., Maitz, M.F. 2002. Fourier transform Raman and Fourier transform infrared spectra of cross-linked polyurethaneurea films synthesized from solutions. J. Raman. Spectrosc. 33, 769-777.
49. Hercule, K.M., Yan, Z., Christophe, M.M. 2011. Preparation and characterization of waterborne polyurethane crosslinked by urea brideges. Int. J. Chem. 3(2), 88-96.
50. Hepburn C. Polyurethane elastomer, 2nd edition; Elsevier Applied Science LT: New York, 1991; pp 58.

51. Thomas, V., Muthu, J. 2008. Biomechanical studies on aliphatic physically crosslinked poly(urethane urea) for blood contact applications. J. Mater. Sci. Mater. Med. 19, 2721–2733.
52. Furukawa, M., Mitsui, Y., Fukumaru, T., Kojio, K. 2005. Microphase-separated structure and mechanical properties of novel polyurethane elastomers prepared with ether based diisocyanate. *Polymer*. 46(24), 10817-10822.
53. Samy, A. M., Joshua U. O. 2009. Recent advances in synthesis, characterization and rheologic properties of polyurethanes and POSS/polyurethane nanocomposites dispersions and films. Prog. Polym. Sci. 34, 1283–1332.
54. Wei, Y., Cheng, F., Li, H., Yu, J. 2005. Thermal properties and micromorphology of polyurethane resins based on liquefied benzylated wood. J. Sci. Ind. Res. 64, 435-439.

CHAPTER 6

PHYSICAL AND THERMAL PROPERTIES OF POLYURETHANE FROM ISOPHORONE DIISOCYANATE, NATURAL RUBBER AND POLY(ε-CAPROLACTONE) WITH HIGH NCO:OH CONTENT

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ABSTRACT: A series of polyurethane (PU) polymers have been synthesized using poly(ε-caprolactone) diol (PCL diol) and hydroxyl telechelic natural rubber (HTNR) as a soft segment. The hard segment included isophorone diisocyanate and 1,4-butanediol (BDO) that was added as a chain extender. The effect of the BDO and HTNR content was investigated in terms of the mechanical and thermal properties of the obtained PU. The presence of urethane linkage was verified by FTIR and found that crosslinked PU was obtained. The addition of BDO in the PCL diol-based PU increased the Young's modulus and tear strength but decreased the elongation at break resulting in a decrease in the tensile strength. By addition of a small amount of HTNR, the tensile properties and tear strength of PU increased significantly. With a further increase in the HTNR content, the tensile behavior of PU was changed from a tough to a soft polymer. The mixture of the PCL diol and HTNR used as the soft segment produced a promising bioplastic material with regard to an enhancement of biodegrability. The high crosslinking was attributed to there being no phase separation between the hard and the soft segment according to the results of the DSC and DMTA analysis. Hydrogen bonding between the PCL diol and the hard segment produced a high T_g.

Keywords: Polyurethane, Natural Rubber, Polycaprolactone, Bio-based polymer, Bioplastic

6.1 INTRODUCTION

Polyurethane (PU) is synthesized by the polyaddition reaction of polyisocyanate with polyol. PU can be used in various applications because it can be polymerized as a thermoplastic, a thermoset or an elastomer. The numerous molecular structures of PU can be attributed to the three components in its chemical structure: polyol, diisocyanate and chain extender [1]. Due to the environmental problems of plastic waste, the greenhouse effect and the loss of petroleum sources, many research efforts have been devoted to the use of renewable resources as raw materials. Natural rubber (NR) is one of the most interesting materials for chemical modification as it contains reactive double bonds in its backbone and is a renewable resource. Low molecular weight NR was modified to have reactive hydroxyl endgroups for use as a polyol for synthesizing PU [2-8]. In addition, PU prepared from biodegradable polymers have also been of interest, especially, PU prepared from poly(ε-caprolactone) (PCL).

PCL is one of the biodegradable polyesters. The low molecular weight PCL is used as a polyol to synthesize a biodegradable PU [9-13]. The aim of this study was to investigate the mechanical and thermal properties of PU consisting of different amount of PCL diol and HTNR.

6.2 EXPERIMENTAL

6.2.1 Materials

Natural rubber (STR 5L) was produced by Jana Concentrated Latex Co. Ltd. Songkhla, Thailand. All chemicals used were analytical grade and used as received, including isophorone diisocyanate (IPDI, Fluka®), m-chloroperbenzoic acid (mCPBA, 70%, Fluka®), dibutyl tin dilaurate (DBTL, 95%, Aldrich®), polycaprolactone diol (PCL diol, $\overline{M}n$ = 530 g/mol), periodic acid (H_5IO_6, 99.5%, Himedia®), sodium borohydride ($NaBH_4$, 98.0%, Rankem®) and 1,4-Butanediol (BDO, 99.0%min. Merck®).

6.2.2 Synthesis of hydroxyl telechelic natural rubber

Hydroxyl telechelic natural rubber (HTNR) was synthesized according to previous work [3-5]. The purified product was identified by nuclear magnetic resonance spectroscopy (^{1}H-NMR) [3-5]. These reaction conditions provided HTNR with the number average molecular weight ($\bar{M}_n$) of 1,700 g/mol as determined by gel permeation chromatography and ^{1}H-NMR.

6.2.3 Synthesis of polyurethane

Polyurethane was synthesized by a one-shot method. The PCL diol and HTNR were the diol substrate while the BDO was used as a chain extender. The PCL diol, HTNR diol and BDO were dissolved in THF (30 w/v%) before mixing with the IPDI. Dibutyl tin dilaurate acting as a catalyst was added to the solution followed by the dropwise addition of a known amount of IPDI dissolved in THF. The reaction temperature and time was 60°C and 3 h, respectively. The mixture was casted on a glass mold and heated in an oven at 40°C for 3 h followed by 60°C for 24 h. The NCO:OH molar ratio was constant at 2.85:1.00. The prepared PU was designed as PU1 to PU6 based on its formula listed in Table 6.1. PU4 and PU5 contained a mixture of PCL diol and HTNR.

Table 6.1 Composition and physical appearance of PU

Sample	Molar ratio				HS[a] (%)	Features[b]
	IPDI	PCL_{530}	$HTNR_{1700}$	BDO		
PU1	2.85	1.00	-	-	54.5	H, C, T
PU2	2.85	0.90	-	0.10	57.5	H, C, T
PU3	2.85	0.50	-	0.50	72.0	H, C, T
PU4	2.85	0.90	0.10	-	50.0	SH, Y T
PU5	2.85	0.50	0.50	-	36.3	S, Y, T
PU6	2.85	-	1.00	-	27.2	S, Y, T

[a] HS (%) = 100 [weight of (isocyanate+chain extender)]/ total weight

[b] C: colorless; Y: yellowish; H: hard; S: soft; SH: semi-hard; T: transparent

6.2.4 Testing of mechanical properties

The tensile properties (ASTM D 412C) and tear strength for the right-angle specimen (ASTM D 624) were determined by a universal testing machine (Lloyd®LR10K) at a crosshead speed of 500 mm/min. The Young's modulus was obtained from the initial modulus. The hardness Shore A (ASTM D2240) was investigated by a Shore Durometer® PTC 408.

6.2.5 Materials characterization

The chemical characteristics and functional group analysis were determined by ^{1}H-NMR (Varian Unity Inova® 500MHz) and Fourier transform infrared spectroscopy (FTIR, BRUKER® EQUINOX 55). Thermal properties were evaluated by thermogravimetric analysis (PerkinElmer® TGA 7) and differential scanning calorimetry (PerkinElmer® DSC 7 at a heating rate of 10°C/min under N_2 gas. Dynamic mechanical thermal analysis (Rheometric Scientific®DMTA V) was carried out between -80 and 150°C in the dual-cantilever bending mode at a frequency of 1 Hz with a strain control of 0.1% and the heating rate of 3°C/min.

6.3 RESULTS AND DISCUSSION

6.3.1 Polyurethane characteristics

Films were produced from all compositions (PU1-PU6) because of the high isocyanate (NCO) content. The physical appearance of PU1-PU6 observed by eye is listed in Table 6.1. In the absence of HTNR (PU1-PU3), colorless and transparent sheet were produced. The addition of HTNR caused yellowish and softer sheet. The decrease in hardness with an increasing HTNR content was related to the hard segment content. Changing the BDO and HTNR content provided a different percentage of the hard segment. Although BDO is a chain extender, it is a part of the hard segment. PU6 had the lowest amount of hard segment. The percentage of the hard segment was calculated based on the weight of chemicals; therefore, a higher molecular weight of HTNR yielded more weight for the soft segment. Due to the excess of the NCO content, it was expected that a crosslinked PU would be formed with a chemical structure as shown in Figure 6.1. The solubility test using common solvents, i.e., dichloromethane, chloroform, tetrahydrofuran, methanol and ethanol, showed that no solvent could dissolve PU1-PU6, implying them and a dominant crosslinking characteristic.

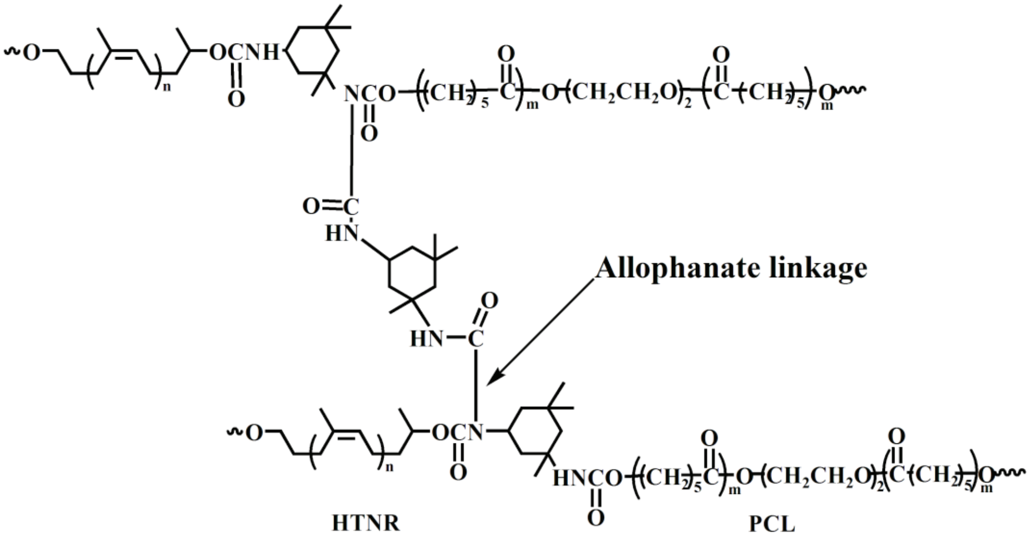

Figure 6.1 Chemical structure of PU.

The functional groups of PU were verified by FTIR. Figure 6.2 shows the FTIR spectrum of PU1, PU6, PCL diol, HTNR and IPDI. PU1 and PU6 had the new absorption bands resulting from NH stretching and a bending vibration appeared at 3325-3340 cm^{-1} and 1525-1550 cm^{-1}, respectively, and the absorption band of the amide group (NH) was at 1640-1645 cm^{-1}. With a high NCO:OH ratio it was possible to produce allophanate links (Figure 6.1) leading to chain branching or crosslinking. The characteristic peaks of the allphanate linkage [14] showed as a triplet band around the wave number of 1220, 1280 and 1310 cm^{-1}, that was easily observed in PU6, and a skeletal vibration of allophanate group at 3298, 3267 and 3233 cm^{-1} that overlapped with the peak of NH stretching. The new absorption band at 1728 cm^{-1} was assigned to the non-hydrogen bond of C=O stretching while the hydrogen bonded with the NH group of C=O appeared at the wave number of 1715 cm^{-1}. Furthermore, the formation of PU was evident by the disappearance of –OH absorbance band of the PCL diol at 3445 cm^{-1} and the HTNR at 3365 cm^{-1} as well as -N=C=O absorbance band of IPDI (2260 cm^{-1}).

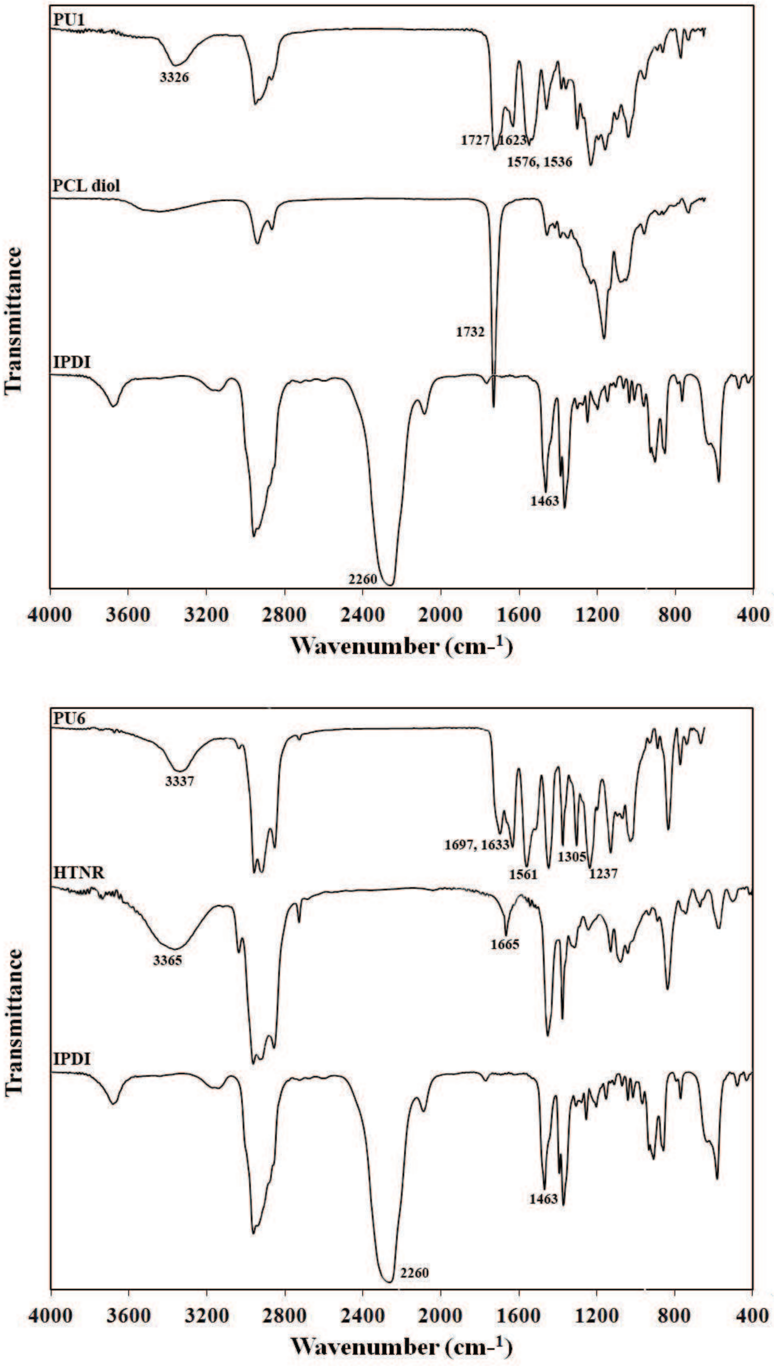

Figure 6.2 FTIR spectra of precursors (PCL diol, HTNR and IPDI), PU1 and PU6.

6.3.2 Mechanical properties

The stress-strain curves of PU are shown in Figure 6.3 and the tensile properties listed in Table 6.2. Three types of tensile behavior were observed in Figure 6.1. First, the PU1-PU4 exhibited a high modulus (E) and yield stress (σ_b). Secondly, PU5 exhibited a low modulus and yield stress. The third type, PU6, had no plastic yielding, and its shape looked similar to a typical elastomer. The incorporation of BDO acting as a chain extender resulted in an increase in the modulus, the tear strength and the hardness (PU2-PU3) because of an increase in the physical crosslink and the size of the rigid block. In contrast, these decreased the elongation at break which was attributed to the reduction in the tensile strength. Generally the tear strength is related to the hard segment content [12].

The small amount of HTNR in PU4, compared to that in PU1, enhanced the tensile properties and the tear strength but reduced the hardness of the PU. The composition of PU4 was very interesting due to its very high mechanical properties and relatively low hardness. When compared to PU2, PU4 had higher mechanical properties and was softer although its hard segment content was lower. This result also indicated that using a small amount of HTNR was better than using BDO. A further increase in the amount of HTNR, tensile behavior changed from a tough polymer to a soft polymer as found in PU5. The elongation at break was much increased whereas the modulus, the tensile strength and the tear strength decreased. With 100% of the HTNR, PU6 had the characteristics as a typical elastomer, i.e. a low modulus and high elongation at break. An increasing HTNR content reduced the opportunity for hydrogen bonding between the soft and hard segments. In addition, the mechanical properties of the polyurethane depended primarily on their hard segment content. When the HTNR increased, the hard segment of the polyurethane decreased. Consequently, PU4-PU6 displayed different tensile behavior.

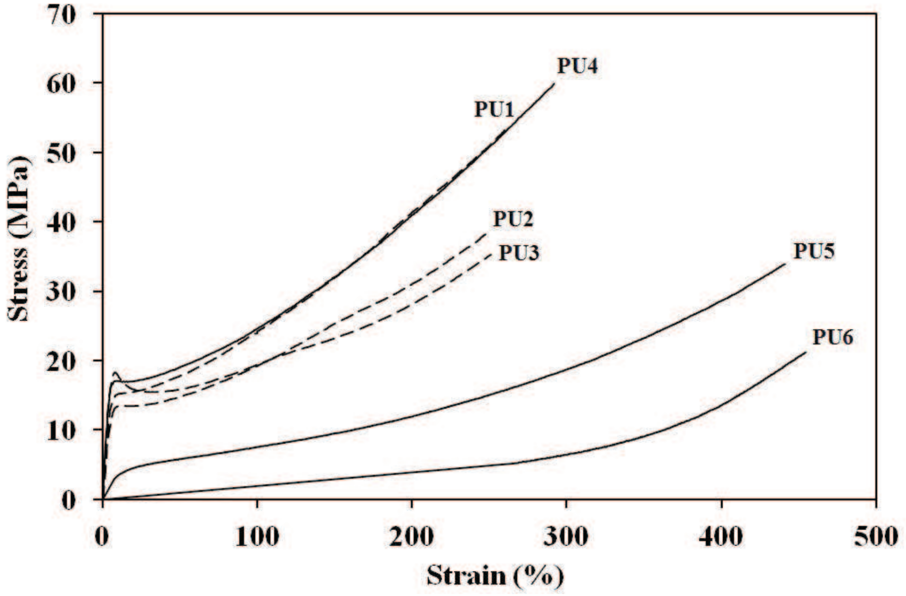

Figure 6.3 The stress-strain curve of PU1-PU6.

Table 6.2 The mechanical properties of PU1-PU6.

Sample	Tensile Properties			Tear strength (N/mm)	Hardness (Shore1A)
	E (MPa)	σ_b (MPa)	ε_b (%)		
PU1	249±7	54±1	262±1	102±16	83±3
PU2	270±29	35±5	267±21	113±4	92±3
PU3	339±53	37±3	236±14	131±10	99±1
PU4	337±43	56±5	278±19	120±6	63±2
PU5	42±3	33±2	439±3	56±1	57±2
PU6	3±1	21±7	415±88	35±3	38±1

6.3.3 Thermal properties

Figure 6.4 shows the DSC thermograms of PU1-PU6 recorded from the second heating scan. No sample showed a melting temperature indicating that they were amorphous polymers. It was believed that the very high NCO content brought about a high crosslinking. Moreover, the PCL diol had a low molecular weight so it was not easy to form crystals between its molecular chains. The non-polar and long chains of HTNR obstructed the production of crystals in the polyurethane.

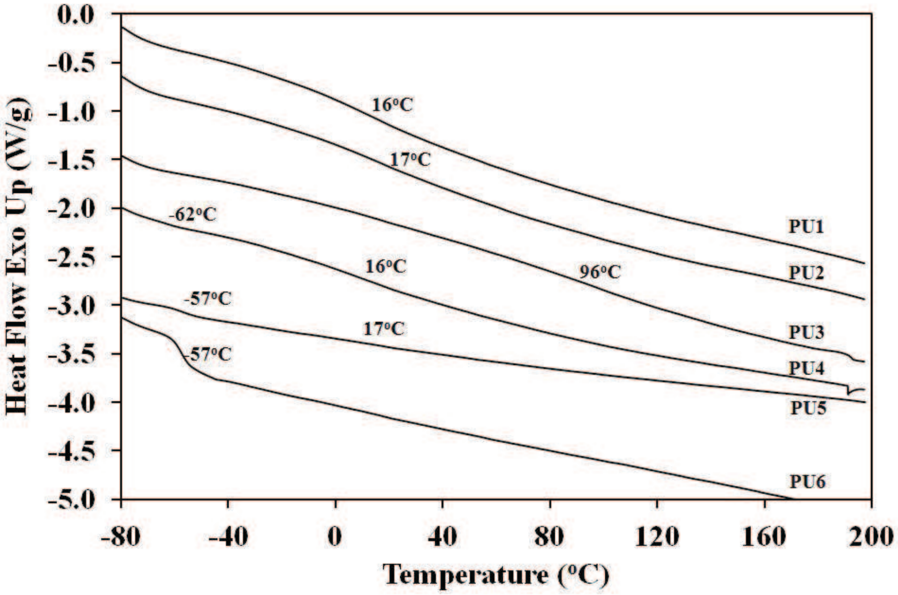

Figure 6.4 DSC thermograms of PUs.

PU containing a single soft segment, PU1-PU3, exhibited one glass transition (T_g) listed in Table 6.3. There was no phase separation between the hard and soft segment, to imply a high degree of mixing between both segments that may be due to the intermolecular hydrogen bonding and chemical crosslinking [15]. Noticeably, a very high T_g occurred with a high BDO content (PU3) while little change was observed in the one with a low content (PU2). As the BDO content increased the physical crosslinking (hydrogen bonding) and the hard segment content increased, resulting in an increase in T_g. PU6 had a single T_g at a subzero temperature. This was due to the non-polar nature of HTNR so there was no hydrogen bonding between the hard and soft segment attributed to a very low T_g, and the high crosslinks caused no phase separation. PU4 and PU5 containing a dual soft segment exhibited two T_gs. The lower T_g arose from the HTNR segment and the higher one came from the PCL diol. There was little effect of the HTNR content on both T_gs. It can be explained that the effect of crosslinking was bigger than the effect of the chain length of HTNR. The molecular movement of HTNR was controlled by crosslinks; more crosslinks contributed to less molecular movement. The effect of the chemical composition of PU on the transition temperature was clearly seen from the DMTA results in Figure 6.5 and Table 6.3. All samples showed one T_g to indicate that there was no phase separation between the hard and soft segments. PU1-PU3 showed a very broad peak that shifted towards the higher temperature as the BDO content increased. Hydrogen bonding might be attributed to the broadness of these peaks. The addition of HTNR decreased the T_g significantly. The transition temperature of PU5 and PU6 was in the same range.

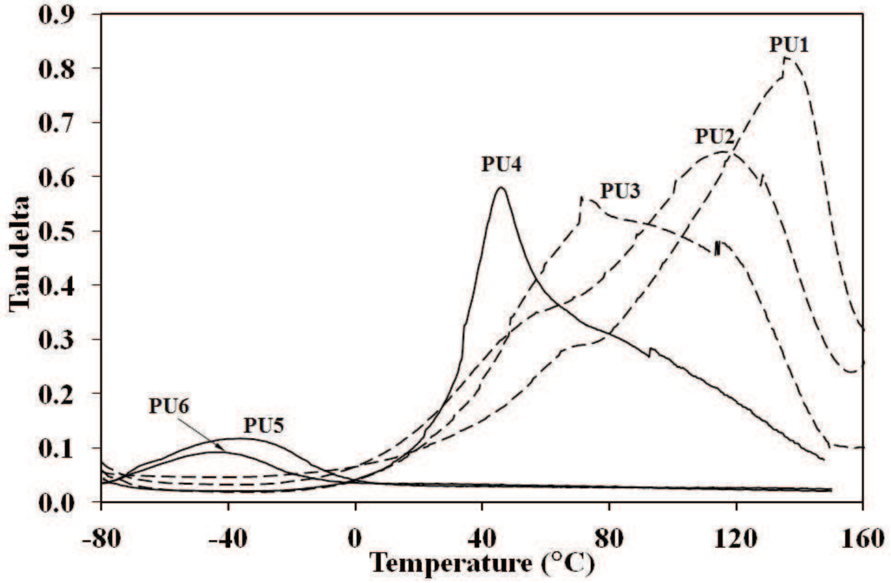

Figure 6.5 DMTA spectra of PUs showing loss tangent peaks.

Table 6.3 T_g of PUs obtained from DSC and DMTA.

Sample	T_g (°C) from	
	DSC	DMTA
PU1	16	71
PU2	17	115
PU3	96	135
PU4	-62, 16	46
PU5	-57, 17	-36
PU6	-57	-43

The TGA thermograms of PUs are shown in Figure 6.6. An increasing BDO content caused a small decrease of the thermal stability of PUs because of the increase of BDO content resulted in a decrease of the content of diols. The PCL diol had a degradation temperature in the range of 270-350°C whereas the degradation temperature of the BDO was 180°C. The influence of the HTNR content on the thermal stability of PUs showed that the thermal stability of PUs increased with an increasing HTNR content. This was due to the higher molecular weight and higher stability of the HTNR. The degradation temperature of HTNR was ~407°C that contributed to the higher degradation temperature in PU4-PU6.

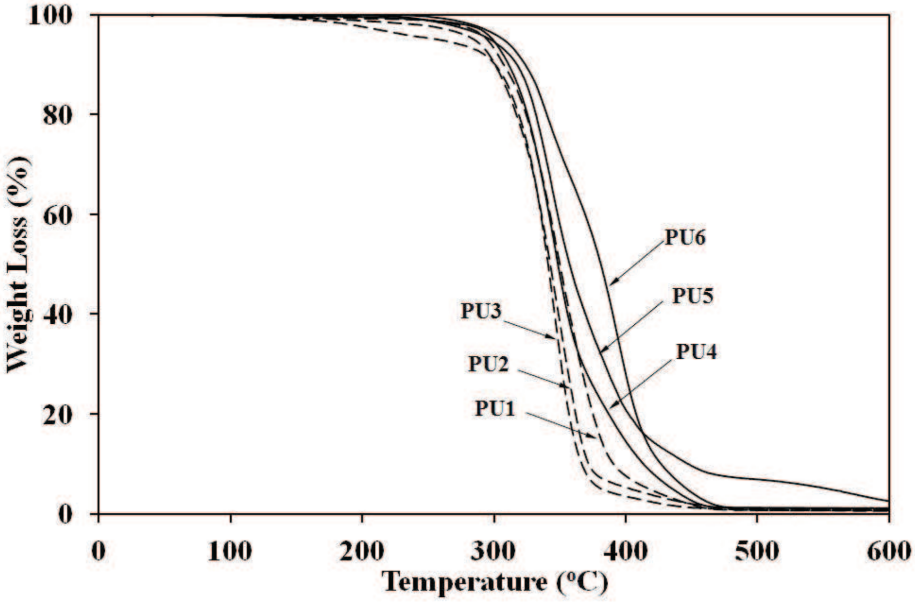

Figure 6.6 TGA thermograms of PU.

6.4 CONCLUSIONS

The new bio-based polyurethanes were successfully synthesized by a one-step solution polymerization using a PCL diol and HTNR as a soft segment. Due to the high molar ratio of NCO:OH, a high degree of crosslinking was obtained resulting in an amorphous PU. The low molecular weight of the PCL diol and HTNR also contributed to the amorphous behavior. Crosslinking in PU was substantiated by the formation of allophanate linkages as seen from the FTIR result and solubility test. As the BDO content increased, the Young's modulus and tear strength increased but the elongation at break and hardness decreased. The reduction of the tensile strength was related to the decrease in the elongation at break. The incorporation of HTNR to the PCL diol produced significant changes in the mechanical properties and hardness of

PU. Addition of a small quantity of HTNR increased the tensile properties and tear strength and made for a softer PU. However the tensile behavior did not change, and the sample (PU4) still a tough polymer. By increasing the HTNR content equal to that of the PCL diol (PU5), the tensile behavior changed to be a soft polymer and finally without the PCL diol (PU6), the sample behaved as a typical elastomer: with a very low modulus, no plastic yielding and a high elongation at break. The phase separation between the hard and the soft segment was not observed in the DMTA results; the samples showed only one T_g. In contrast, the DSC exhibited 2 T_gs (PU4 and PU5) while the rest exhibited only one T_g.

6.5 ACKNOWLEDGEMENTS

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6.6 REFERENCES

1. Hepburn, C. 1991. Polyurethane elastomer. Elsevier Applied Science LTD., New York, USA.
2. Gopakumar, S., Nair, M.R.G. 2005. Swelling characteristics of NR/PU block copolymers and the effect of NCO/OH ratio on swelling behavior. Polymer. 46, 10419-10430.
3. Kebir, N., Morandi, G., Campistron, I., Laguerre, A., Pilard. J.F. 2005. Synthesis of well defined amino telechelic cis-1,4-oligoisoprenes from carbonyl telechelic oligomers; first studies of their potentialities as polyurethane or polyurea materials precursors. Polymer, 46, 6844-6854.
4. Kebir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunal, C., Jouenne. T. 2007. Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of

antibacterial ionic polyurethanes and copolyurethanes bearing ammonium groups. Biomaterials. 28, 4200-4208.

5. Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Pilard. J.F. 2010. Controlled degradation of natural rubber and modification of the obtained telechelic oligoisoprenes: Preliminary study of their potentiality as polyurethane foam precursors. J. Appl. Polym. Sci. 117, 1279–1289.
6. Paul, C.J., Gopinathan Nair, M.R., Koshy, P., Idage. B.B. 1999. Segmented block copolymer of natural rubber and bisphenol A-toluene diisocyanate oligomer. J. Appl. Polym. Sci. 74, 706-721.
7. Radhakrishnan Nair, M.N., Gopinathan Nair, M.R. 2008. Synthesis and characterisation of soluble block copolymers from NR and TDI based polyurethanes. J. Mater. Sci. 43, 738–747.
8. Maier, G., Knopfova, V., Voit, B., Ly, P.H., Dung, B.T., Thanh D.B. 2004. Synthesis andcharacterization of segmented block copolymers based on hydroxyl-terminated liquid natural rubber and α,ω-diisocyanato telechelics. Macromol. Mater. Eng. 289, 927-923.
9. Gorna, K., Gogolewski, S. 2002. In vitro degradation of novel medical biodegradable aliphatic polyurethanes based on ε-caprolactone and Pluronics with various hydrophilicities. Polym. Degrad. Stabil. 75, 113–122.
10. Younes, H.M., Grimaldo, E.B., Amsden, B.G. 2004. Synthesis, characterization and in vitro degradation of a biodegradable elastomer. Biomaterials. 25, 5261–5269.
11. Heijkants, R.G.J.C., Calck, R.V., Tienen, T.G., Groot, J.H., Buma, P., Pennings, A.J., Veth, R.P.H., Schouten, A.J. 2005. Uncatalyzed synthesis, thermal and mechanical properties of polyurethanes based on poly(ε-caprolactone) and 1,4-butane diisocyanate with uniform hard segment. Biomaterials. 26, 4219–4228.
12. Heijkants, R.G.J.C., Schwab, L.W., van Calck, R.V., de Groot, J.H., Pennings, A.J., Schouten, A.J. 2005. Extruder synthesis of a new class of polyurethanes: Polyacylurethanes based on poly(ε-caprolactone) oligomers. Polymer. 46, 8981–8989.

13. Yeganeh, H., Lakouraj, M.M., Jamshidi. S. 2005. Synthesis and properties of biodegradable elastomeric epoxy modified polyurethanes based on poly(ε-caprolactone) and poly(ethylene glycol). Eur. Polym. J. 41, 2370–2379.
14. Thomas, V., Muthu. J. 2008. Biomechanical studies on aliphatic physically crosslinked poly(urethane urea) for blood contact applications. J. Mater. Sci.-Mater. Med. 19, 2721–2733.
15. Lu, Y., Zhang, L. 2003. Effects of NCO/OH molar ratio on miscibility and properities of simi interpenetrating polymer network polyurethane and benzyl konjec Glucommanan. J. Appl. Polym. Sci. 88, 1304-1310.

CHAPTER 7

RAMAN SPECTROSCOPY OF POLYURETHANE

7.1 INTRODUCTION

Infrared (IR) and Raman spectroscopy are both vibrational spectroscopy, they give characteristic spectra of a molecule. They are employed to examine the molecular structure via the vibrational mode of a molecule. Although some vibrations may be active in both Raman and IR spectroscopy, there are different selection rules between both methods. Generally, symmetric vibrations of non-polar groups are active in Raman spectroscopy while IR spectroscopy is suitable for the asymmetric vibrations of polar groups [1]. There are some advantages associated to the use of Raman spectroscopy: it is a non-contact and non-destructive analysis technique, it does not require sample preparation, Raman signal originates from the small, focused zone of the excitation of the laser. Besides, it is suitable to characterize heterogeneous materials. Raman spectroscopy was discovered in 1928 by Chandrashehara Venkata Raman in a phenomenon of inelastic scattering of light called Raman Effect. Raman spectroscopy has been used to characterize the structure, environment and dynamics of polymeric materials [2], such as natural rubber [3-6], polyamide and poly(phenylene oxide) [7], polyolefins [8], poly(vinyl methyl ether) [9], and polyurethane [10-15].

Polyurethane is used in many applications, depending on its composition and chemical structure, such as coatings, adhesives, sealants, elastomers, foams and plastics. Thus, an understanding of its molecular structure and properties is essential. The present study describes the Raman characterization of polyurethane containing PCL (polycraprolactone, containing a polar ester linkage) and HTNR (hydroxytelechelic natural rubber, non-polar structure). The previous chapters described the structure of these PU materials by using FTIR and NMR. In this chapter the preliminary investigation of the structure of these PU by using Raman spectroscopy is presented.

7.2 EXPERIMENTAL

Raman spectra of all samples were recorded with a Jobin-Yvon® T64000 multichannel spectrometer. Samples were illuminated with a Coherent argon–krypton ion laser, selecting the red 647.1 nm line in order to minimize the contribution of luminescence to the spectra. Each spectrum was accumulated 20 times in order to improve the signal-to-noise ratio. The samples were analyzed in the wave number range of 400–3200 cm^{-1}. Calibration of the spectrometer was precisely checked on the silicon band at 520.2 cm^{-1}. All experiments were performed at room temperature under an optical microscope using a x100 long work distance objective. The polyurethane used in this experiment contained high NCO:OH molar ratio. The formula and composition of polyurethane samples are exhibited in Table 7.1.

Table 7.1 Formula and composition of polyurethane

Formula	Composition	Molar ratio
TP	TDI / PCL	2.25 / 1
TH	TDI / HTNR	2.25 / 1
TPB	TDI / PCL / BDO	2.25 / 0.9 / 0.1
TPH	TDI / PCL / HTNR	2.25 / 0.5 / 0.5
IP	IPDI / PCL	2.85 / 1
HP	HDI / PCL	2.20 / 1

7.3 RESULTS AND DISCUSSION

7.3.1 Characterization of precursors

To begin the study, the building blocks of the PU were investigated: polyols (PCL diol and HTNR), chain extender (BDO) and diisocyanates (TDI, IPDI and HDI) spectra were taken. Figure 7.1 illustrates Raman spectrum of HTNR, PCL diol and BDO. The observed bands of HTNR can be assigned on the basis of NR because HTNR is composed of cis-1,4-polyisoprene units and its assignment bands are shown in Table 7.2 [3-6]. The CH_2 asymmetric stretching and CH_3 symmetric stretching vibration appeared at 2931 and 2912 cm^{-1}, respectively. The strong band at the wave number of 1665 cm^{-1} can be identified as the C=C stretching. In addition, the bands at 1449, 1312 and 1284 cm^{-1} can be attributed to CH_3 asymmetric stretching, CH_2 twisting and CH bending, respectively. The bands of C-CH_2 stretching and =CC_2 rocking and scissoring occurred at the wave number of 997 and 493 cm^{-1}, respectively. The O-H stretching at 3200-3500 cm^{-1} was not clearly observed in the Raman spectrum; consequently, Raman spectroscopy is unable to verify the presence of the hydroxyl group in HTNR under the operating conditions.

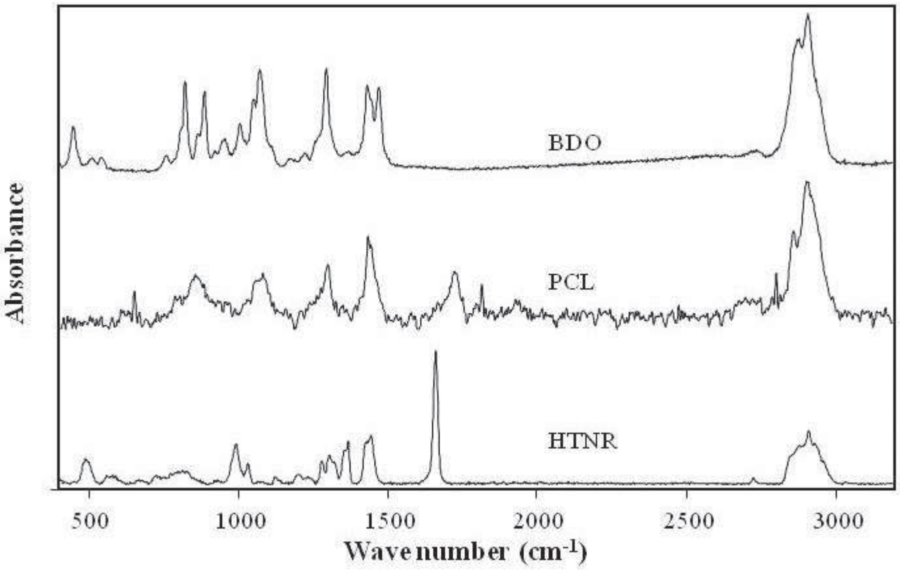

Figure 7.1 Raman spectra of BDO, PCL diol and HTNR.

The repeating units of PCL contain aliphatic ester jointed together with diethylene glycol segment. Therefore, ester was characterized by a carbonyl bond at the wave number of 1728 cm^{-1} (Table 7.3). The asymmetric and symmetric CH_2 stretching generated strong peaks at 2912 and 2867 cm^{-1}, respectively. The bending vibration of the CH_2 group gave a band at 1437 cm^{-1} while CH bending was at 1302 cm^{-1}. The two groups of medium bands in asymmetric and symmetric CCC stretching were at 1061 and 847 cm^{-1}, respectively. Nevertheless, the bands of O-H stretching in hydroxyl group in the range of 3200-3600 cm^{-1} were not shown. The band at 1437 cm^{-1} could be assigned to the CH_2 bending or C-O-H bending, or probably the sum of their contributions. The band at 1437 cm^{-1} was verified from the characterization of the polyurethane sample prepared from PCL and TDI so it can be assigned to CH_2 bending [10]. The bands at 1061 and 847 cm^{-1} belonged to out of phase and in phase C-C-O stretching [15] because they disappeared in PU spectrum resulting from the reaction between OH group and NCO group to form the urethane linkage.

Table 7.2 Band assignment of Raman spectrum of HTNR [3-6]

Wave number (cm^{-1})	Assignment
2931	CH_2 asymmetric stretching
2912	CH_3 symmetric stretching
2883	*
2727	*
1665	C=C stretching
1449	CH_3 asymmetric stretching
1372	*
1312	CH_2 twisting
1284	CH bending
1206	=C-H in-plane deformation
1038	CH_3 rocking
997	C-CH_2 stretching
810	CH wagging
579	*
493	=CC_2 rocking and scissoring

* No assignment in the literature.

The assignment of peaks in the Raman spectrum of BDO is listed in Table 7.4. Four distinct bands appeared at 2912, 2887, 1473 and 1296 cm^{-1} and they were assigned to CH_2 asymmetric and symmetric stretching, CH_2 symmetric scissoring and -$(CH_2)_n$- in-phase twisting, respectively. The bands assigned to hydroxyl groups appeared in the wave number of 1072, 866 and 446 cm^{-1}, which were out of phase C-C-O stretching, in of phase C-C-O stretching, and C-O-H bending of primary alcohol, respectively. These bands disappeared in PU spectrum due to the reaction between hydroxyl group and isocyanate group. A band at 1433 cm^{-1} was due to CH_2 bending similarly to the bands from PCL found in the polyurethane spectrum.

Table 7.3 Band assignment of PCL

Wave number (cm^{-1})	Assignment
2912	CH_2 asymmetric stretching
2867	CH_2 symmetric stretching
1728	C=O stretching
1437	CH_2 bending
1302	CH bending
1061	Out of phase C-C-O stretching
847	In of phase C-C-O stretching

Table 7.4 Band assignment of BDO

Wave number (cm^{-1})	Assignment
2916	CH_2 asymmetric stretching
2887	CH_2 symmetric stretching
1473	CH_2 symmetric scissoring
1433	CH_2 bending
1296	$-(CH_2)_n-$ in-phase twisting
1072	Out of phase C-C-O stretching
1007	C-CH_2 stretching
866	In of phase C-C-O stretching
822	-C-C-C- symmetric stretching
446	Primary alcohol C-C-O bending

Similarly to PCL, BDO is a low molecular weight entity containing 2 hydroxyl groups; therefore, the Raman spectrum clearly showed the absorbance of C-O vibration at 1061 and 847 cm^{-1} for PCL and at 1072, 866 and 446 cm^{-1} for BDO. Similarly to HTNR, BDO and PCL diol did not show the O-H stretching in the range of 3400-3600 cm^{-1} because the O-H stretching band was very weak in Raman spectrum [16].

Figure 7.2 shows the Raman spectra of 3 diisocyanates: TDI, IPDI and HDI which are aromatic, cycloalkane and alkane diisocyanate, respectively. Normally, the out-of-phase N=C=O stretching mode is clearly observed in an IR spectrum at 2300-2250 cm^{-1}, but this vibration mode becomes weak or undetectable in a Raman spectrum. These diisocyanates showed the in-phase N=C=O stretching mode in the wave number of 1499, 1439 and 1431 cm^{-1}, for TDI, IPDI and HDI (Table 7.5), respectively. In Raman spectroscopy, the intensity of the peaks relies to the polarisability of the molecule or compound and then it means that a band intensity or position can depend of the orientation of the molecule relatively to the incident laser polarisation. The band position can also be related to the electronic environment of the bond. Consequently, because the 3 molecular structures are different, the N=C=O stretching mode exhibit distinct band positions for the 3 compounds. Moreover, because the structures of these diisocyanates are different: aromatic, cycloalkane and alkane structure for TDI, IPDI and HDI, Raman spectrum bands display different patterns. Raman spectrum for TDI contained the wave number of 1615, 1573, 1206 and 698 cm^{-1} assigned to benzene ring stretching [10, 13, 15-16], trisubstituted benzene vibration, ring vibration and ring deformation of 1,2,4-trisubstitued benzene [15-16]. IPDI showed the ring vibration of alkyl cyclohexane at 752 cm^{-1} [16] and HDI the CH_2 bending at 796 cm^{-1}.

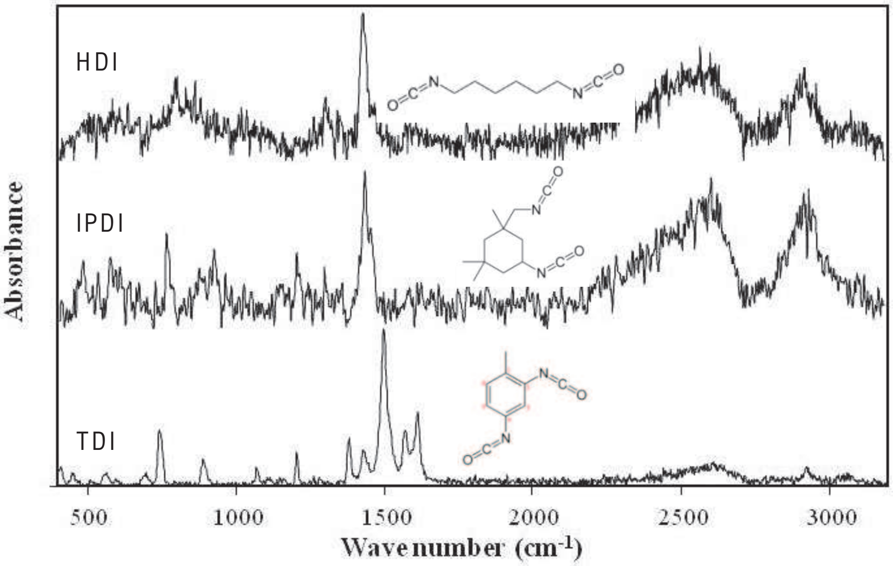

Figure 7.2 Comparison Raman spectra of TDI, IPDI and HDI.

Table 7.5 Band assignments of TDI, IPDI and HDI

Wave number (cm^{-1})			Assignment
TDI	IPDI	HDI	
	2944		CH_3 asymmetric stretching
2927		2925	CH_2 asymmetric stretching
1615			Benzene ring stretching
1573			Trisubstituted benzene
1499	1439	1431	N=C=O in-phase stretching
1429			CH_3 asymmetric bending
1384			CH_3 symmetric bending
1206			Ring vibration
1062			CH_3 rocking
	928		C-C skeletal vibration
		796	CH_2 bending
	752		Ring vibration of alkyl cyclohaxane
742			C-H bending vibration
698			Ring deformation of 1,2,4-trisubstitued benzene

7.3.2 Characterization of polyurethane containing different diols

This section examined the vibration bands of polyurethane prepared from TDI containing the different types of diol component: TDI+PCL, TDI+HTNR, TDI+PCL+BDO and TDI+PCL+HTNR. Raman spectrum of the TDI+PCL polyurethane is illustrated in Figure 7.3 and its peak assignment is listed in Table 7.6. The absence of –N=C=O absorption at 1499 cm^{-1} was observed. The new peak appeared at 1534, 1324 and 1272 cm^{-1} corresponding to C-N-H bending in amide II [10, 13, 15], C-N-H bending in amide III and the C-N stretching [13], respectively. This indicated the formation of urethane linkage.

Raman spectrum of the polyurethane prepared from TDI and HTNR is shown in Figure 7.4 and the wave number and assignment is shown in Table 7.7. The spectrum of this polyurethane looked similar to that of TDI and HTNR, except the band at 1499 cm^{-1} correspondinc to N=C=O in-phase stretching disappeared. And it demonstrated the new band at 1324 cm^{-1} for C-N-H bending in amide III (-C(=O)-NHR) like PU prepared from TDI and PCL. The C-N stretching showed an overlapped shoulder at 1284 cm^{-1} band, which is CH bending band of HTNR.

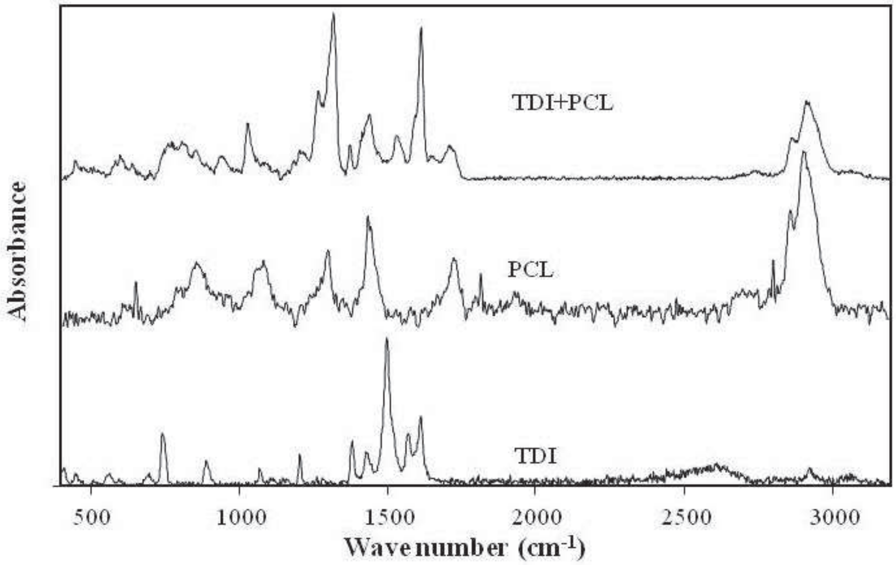

Figure 7.3 Comparison Raman spectra of TDI, PCL and PU from TDI+PCL.

Table 7.6 Raman spectrum of the TDI+PCL polyurethane

Wave number (cm^{-1})	Assignment
2925	CH_2 asymmetric stretching
2896	CH_2 symmetric stretching
1722	C=O stretching
1619	Benzene ring stretching
1534	C-N-H bending in amide II (-C(=O)-NHR)
1444	CH_2 bending [10, 13]
1379	CH_3 symmetric bending
1324	C-N-H bending in amide III (-C(=O)-NHR)
1272	C-N stretching
1034	CH_3 rocking

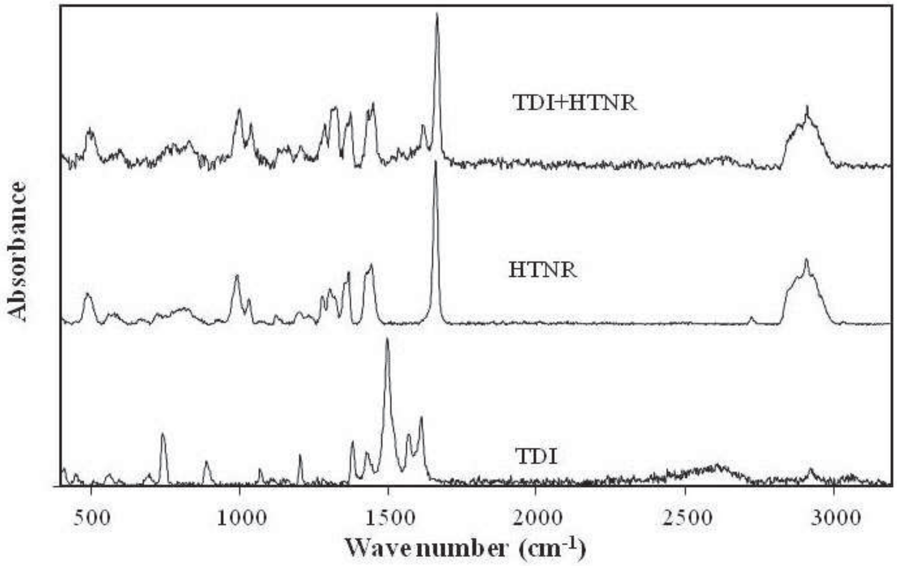

Figure 7.4 Comparison Raman spectra of TDI, HTNR and PU from TDI+HTNR.

Raman spectrum and assignment of PU which prepared from TDI+PCL+BDO is reported in Figure 7.5 and Table 7.8, respectively. The BDO content was 10 % mol based on PCL content. This spectrum displayed the main peaks of the urethane linkages which were similar to the PU prepared from TDI and PCL. It illustrated the C-N-H bending in amide II, C-N-H bending in amide III and C-N stretching at 1533, 1326 and 1272 cm^{-1}, respectively. The isocyanate peak of TDI (1499 cm^{-1}) and hydroxyl vibration bands of BDO (1072, 866 and 446 cm^{-1}) completely disappeared after polymerization reaction.

Raman spectra of PU prepared from TDI with various diols are shown in Figure 7.6. The new Raman bands were observed in the PU prepared from TDI+PCL and TDI+PCL+BDO at 1534, 1324 and 1272 cm^{-1} coresponding to C-N-H bending in amide II, C-N-H bending in amide III and C-N stretching, respectively. PU containing HTNR demonstrated only one new peak at 1324 cm^{-1}, and the C-N stretching at 1272 cm^{-1} showed an overlapped shoulder with the peak of 1284 cm^{-1} corresponding to CH bending band of HTNR structure. The wave number of 1499 cm^{-1} which is N=C=O in-phase stretching disappear in all polyurethane samples.

Table 7.7 Band assignment of PU from TDI+HTNR

Wave number (cm^{-1})	Assignment
2925	CH_2 asymmetric stretching
2913	CH_3 symmetric stretching
2871	_
1667	_*
1620	C=C stretching
1452	N=C=O in-phase stretching
1435	CH_3 asymmetric stretching
1375	CH_3 symmetric bending
1324	C-N-H bending in amide III (-C(=O)-NHR)
1289	CH_2 twisting
1210	CH bending
1041	Ring vibration, =C-H in-plane deformation
1004	CH_3 rocking
831	-
498	-

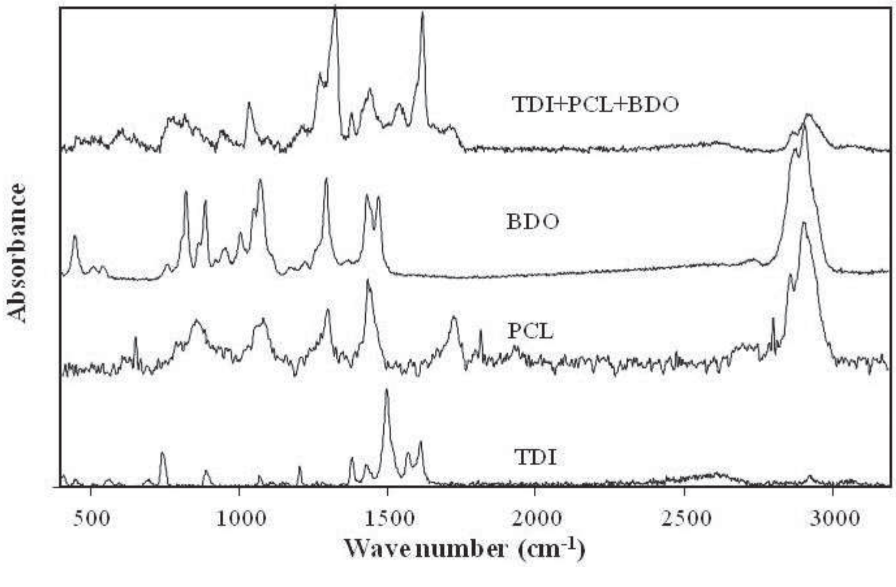

Figure 7.5 Comparison Raman spectra of TDI, PCL, BDO and PU from TDI+PCL+BDO.

Table 7.8 Band assignment of PU from TDI+PCL+BDO

Wave number (cm^{-1})	Assignment
2931	CH_2 asymmetric stretching
2868	CH_2 symmetric stretching
1731	C=O stretching
1621	Benzene ring stretching
1533	C-N-H bending in amide II (-C(=O)-NHR)
1431	CH_2 bending
1384	CH_3 symmetric bending
1326	C-N-H bending in amide III (-C(=O)-NHR)
1276	C-N stretching
1036	CH_3 rocking
829	-C-C-C- symmetric stretching

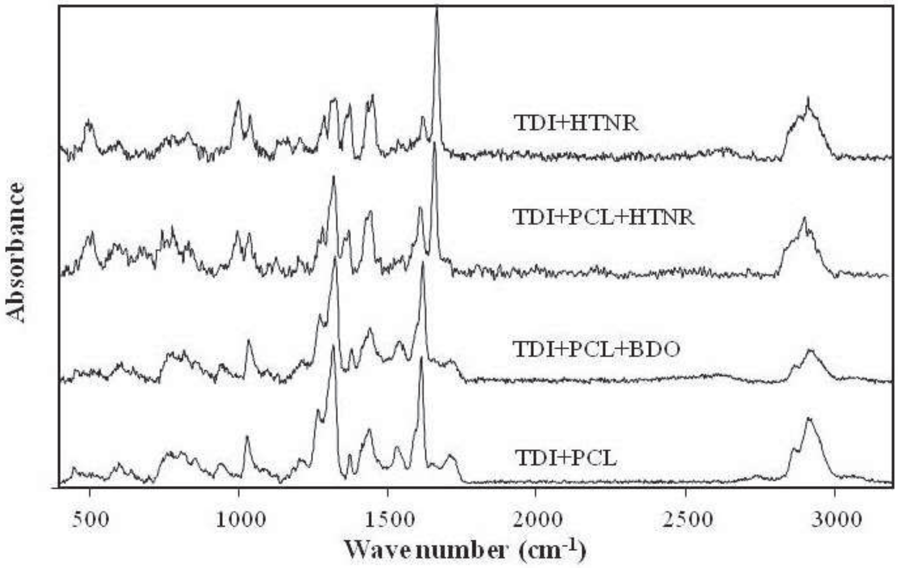

Figure 7.6 Comparison Raman spectra of PU from TDI and various diols.

7.3.3 Characterization of polyurethane containing different diisocyanate

This part investigated Raman spectra and the assignment of the PU prepared from PCL diol and different diisocyanate (TDI+PCL, IPDI+PCL and HDI+PCL). The wave number of 1533, 1326 and 1272 cm^{-1} corresponding to C-N-H bending amide II, C-N-H bending in amide III and C-N stretching, respectively, were demonstrated in the PU from TDI+PCL as displayed in Figure 7.3 and Table 7.6.

The spectrum of the PU prepared from IPDI+PCL is shown in Figure 7.7. The isocyanate peak at 1439 cm^{-1} was not observed. This suggested that there was no unreacted isocyanate (no free-isocyanate). The PU showed the new characteristic peak of C-N-H bending in amide III (-C(=O)-NHR) which was observed at 1251 cm^{-1} [10]. The absorbance peak at 1304 cm^{-1} was assigned to CH bending and urethane amide III [10]. The peak at 1732 cm^{-1} was the C=O stretching of PCL and the peak at 777 cm^{-1} was the ring vibration of alkyl cyclohaxane from IPDI structure. The new bands at 1226 and 1203 cm^{-1} cannot be assigned.

Raman spectrum and the assignment of the PU prepared from HDI+PCL is showed in Figure 7.8 and Table 7.10, respectively. The carbonyl absorption band of the secondary amide was observed at the wave number of 1615 cm^{-1}. This peak was not observed in the PU containing TDI because it overlapped with the benzene ring stretching peak at 1615 cm^{-1}. The peak assigned to the urethane amide III was detected at the wave number of 1302 cm^{-1} and the isocyanate absoption band at 1431 cm^{-1} cannot be detected.

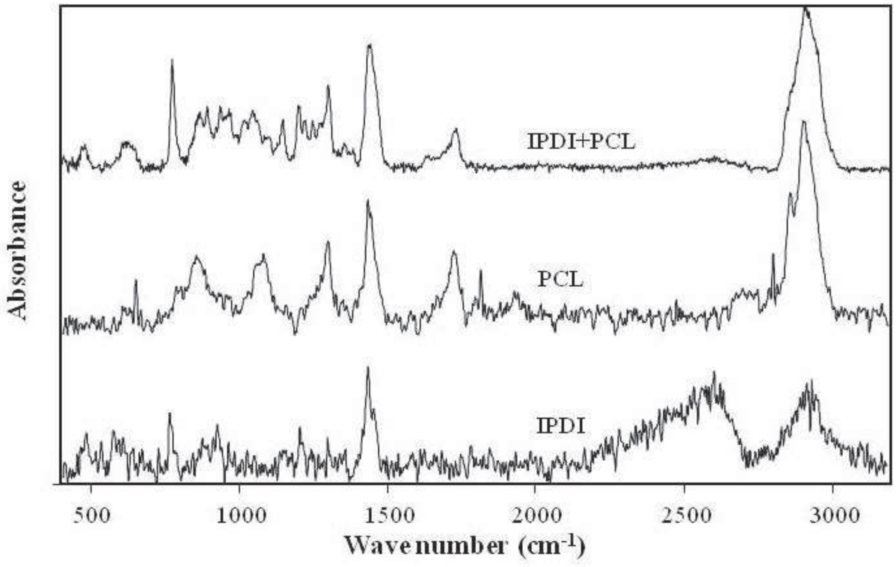

Figure 7.7 Comparison Raman spectra of IPDI, PCL and PU from IPDI+PCL.

Table 7.9 Band assignment of PU from IPDI+PCL

Wave number(cm^{-1})	Assignment
2921	CH_2 asymmetric stretching
1730	C=O stretching
1446	CH_2 bending
1304	CH bending and urethane amide III
1251	C-N-H bending in amide III (-C(=O)-NHR)
1226	-
1203	-
1152	C-O-C stretching
896	(C–C), wag(CH_2), twist(CH_2)
777	Ring vibration of alkyl cyclohaxane

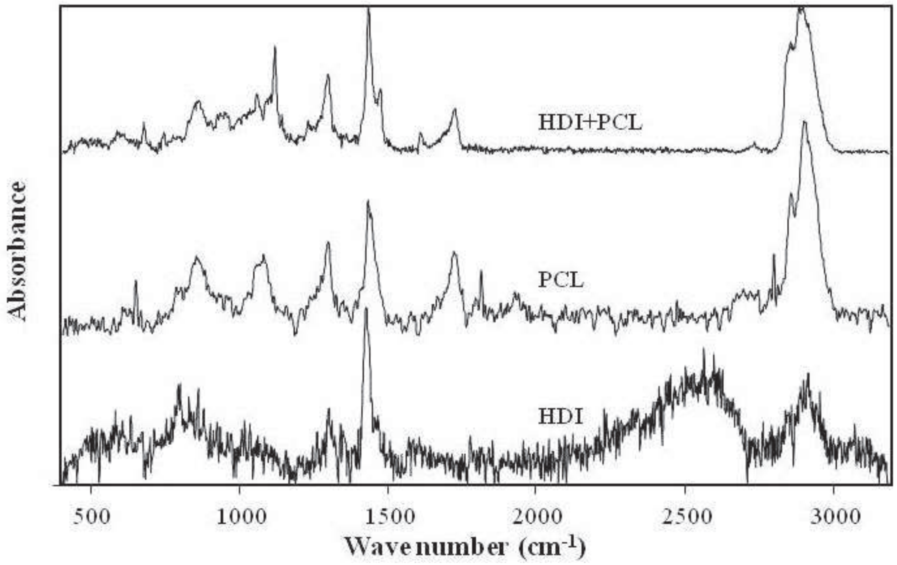

Figure 7.8 Comparison Raman spectra of HDI, PCL and PU from IPDI+PCL.

Table 7.10 Band assignment of PU from HDI+PCL

Wave number (cm^{-1})	Assignment
2907	CH_2 asymmetric stretching
1733	C=O stretching of PCL
1615	C=O stretching of amide II
1481	CH_2 stretching [15]
1440	CH_2 bending
1302	CH bending and urethane amide III
1123	C-O-C stretching
1060	Out of phase C-C-O stretching
853	C–C–C bending

7.4 CONCLUSION

Raman spectroscopy was used to characterize precursors as well as polyurethane coatings. Peaks have been assigned based on literature data or experimental observation of samples with different formulations. The formation of the urethane linkage was observed confirming that Raman spectroscopy is a suitable method to characterize this kind of compounds. Nevertheless, the positions of the urethane characteristic peaks were found to be dependent on the composition of polyurethane, with important shifts for CN in amide III for example. Moreover the assigned peaks of hydroxy telechelic natural rubber overlapped with the urethane peak. The characteristic peaks of PU showed the different wavenumber of urethane linkage by using the different diisocyanate.

This study constituted a first database collecting the peaks frequencies and relative assignments in polyurethane sheets derived from natural rubber and different polyols and diisocyanates, and it opens the perspective to use the Raman technique for further investigation, to gather information for example about the existence and distribution of crystalline and amorphous domains or to confirm or infirm the presence of small molecules coming from side reactions during the polymerization process.

7.5 REFERENCES

1. Larkin, P. 2011. Infrared and raman spectroscopy: priciples and spectral interpretation. Elsevier Inc. Waltham, USA. 1-5.
2. Das, R.S., Agrawal, Y.K. 2011. Raman spectroscopy: Recent advancements, techniques and applications. Vib. Spectrosc. 57, 163-176.
3. Samran, J., Phinyocheep, P., Daniel, P., Derouet, D., Buzare, J.Y. 2004. Raman spectroscopic study of non-catalytic hydrogenation of unsaturated rubbers. J. Raman Spectrosc. 35, 1073-1080.
4. Cormell, S.W., Koenig, J.L. 1969. Raman spectra of polyisoprene rubbers. Macromolecules. 2(5), 546-549.
5. Hendra, P.J., Jackson, K.D. . 1994. Application of Raman spectroscopy to the analysis of natural rubber. Spectrochimica. Acta. 50A(11), 1987-1997.
6. Jackson, K.D.O., Loadman, M.J.R., Jones, C.H., Ellis, G. 1990. Fourier transform raman spectroscopy of elastomers: an overview. Spectrochimica. Acta. 46A(2), 1987-1997.
7. Khulbe, K.C., Kruczek, B., Chowdhury, G., Gagne, S., Matsuura, T., Verma, S.P. 1996. Characterization of membranes prepared from PPO by Raman scattering and atomic force microscopy. J. Membr. Sci. 111, 57-70.
8. Rodriguez-Perez, M.A., Campo-Arnaiz, R.A., Aroca, R.R., Saja, J.A. 2005. Characterisation of the matrix polymer morphology of polyolefins foams by Raman spectroscopy. Polymer. 46, 12093-12102.
9. Pastorczak, M., Kozanecki, M., Ulanski, J. 2009. Water-polymer interactions in PVME hydrogels-Raman spectroscopy studies. Polymer. 50, 4535-4542.
10. Parnell, S., Min, K., Cakmak, M. 2003. Kinetic studies of polyurethane polymerization with Raman spectroscopy. Polymer. 44, 5137-5144.
11. Khan, A.S., Ahmed, Z., Edirisinghe, M.J., Wong, F.S.L., Rehman, I.U. 2008. Preparation and characterization of a novel bioactive restorative composite based on covalently coupled polyurethane–nanohydroxyapatite fibres. Acta. Biomaterialia. 4, 1275–1287.
12. Ferry, A., Jacobsson, P. 1996. Raman, infra-red, and d.s.c. studies of lithium coordination in a thermoplastic polyurethane. Polymer. 37(5), 737-744.

13. Romanova, V., Begishev, V., Karmanov, V., Kondyurin, A., Maitz, M.F. 2002. Fourier transform raman and fourier transform infrared spectra of cross-linked polyurethaneurea films synthesized from solutions. J. Raman. Spectrosc. 33, 769-777.
14. Liem, H., Yeung, L.Y. 2007. Segment self-orientational behavior in shape memory polymer thin films probed by Raman spectroscopy. J. appl. Polym. Sci. 105, 765-770.
15. Janik, H., Palys, B., Petrovic, Z.S. 2003. Multiphase-separated plyurethanes studied by micro-Raman spectroscopy. Macromol. Rapid. Commun. 24, 265-268.
16. Lin-Vien, D., Clothup, N.B., Fateley, W.G., Grasselli, J.G. The handbook of infrared and Raman characteristic frequencies of organic molecules. Academc Press, Inc. Harcourt Brace Jovanovich.

CHAPTER 8

A CONVENIENT PROCEDURE FOR THE SYNTHESIS OF BIS(CYCLIC CARBONATE)S-TERMINATED NATURAL RUBBER AND POLY(ε-CAPROLACTONE) FROM HYDROXYL-TERMINATED PRECURSORS

ABSTRACT: This study represented a preliminary investigation of the preparation of an isocyanate-free polyurethane via the reaction of cyclic carbonate terminated oligomers and diamines with an appropriate catalyst. Polycaprolactone diol (PCL diol) and hydroxyl telechelic natural rubber (HTNR) were used as starting materials in which the hydroxyl end-groups were transformed in carboxylic acid groups at first, and cyclic carbonate end-groups successively. Glycerol carbonate was employed for the preparation of the cyclic carbonate. The derived polyurethane was referred to polyhydroxylurethane (PHU) because it contained hydroxyl groups. ^{1}H-NMR, ^{13}C-NMR, and FTIR analyses were carried out for samples identification and they confirmed that novel interesting cyclic carbonate terminated polyisoprenes and cyclic carbonate terminated polycaprolactone were obtained and they were successively reacted with diamines to generated isocyanate free, biobased polyurethanes.

Key words: polycaprolactone; non-isocyanate polyurethane; natural rubber; renewable resource

8.1 INTRODUCTION

Polyurethane (PU) is a large family of polymeric materials which have various applications such as flexible or rigid foams, chemical resistant coatings, specialty adhesives and sealants, and elastomers. This is due to the chemical structure which is easily controlled by changing the monomers: polyol and diisocyanate. Recently, polyurethane prepared from renewable resources has been prepared using modified polyol from plant oil [1-4], sugar [5], chitosan [6] and natural rubber [7-20]. Typically, PU is synthesized by the polyaddition reaction of a diisocyanate and a polyol in the presence of catalyst [21]. Some chemicals used in isocyanate synthesis route are toxic such as phosgene, nitro compounds and aniline; and isocyanate is also harmful for the human body because it affects the respiratory system [22]. Therefore, there are attempts to synthesize polyurethane without isocyanate: these are called the non-isocyanate or non-phosgene synthetic routes [23].

Our group reported recently the synthesis of a bio-based polyurethane containing poly(ε-caprolactone) diol (PCL diol) and hydroxytelechelic natural rubber (HTNR) [24]. This novel polyurethane could be considered an environmentally friendly polymer because PCL is a biodegradable polymer and NR is a renewable resource, however different isocyanates were employed in the polymerization method. Therefore, the aim of the present study was to develop isocyanate-free bio-based polyurethane composed by similar building blocks.

There are many non-isocyanate preparation routes for polyurethane. For example, the cationic ring opening polymerization of trimethylene urethane and tetramethylene urethane [25], the copolymerization of 2,2-dimethyltrimethylene carbonate with tetramethylene urea [26], the synthesis of thermoresponsive polyurethane from 2-methylaziridine and supercritical carbon dioxide [27] and the reaction between cyclic carbonate and diamine [28-35]. The five member cyclic carbonates can be prepared following several methods. A common procedure is the reaction between an oxirane and carbon dioxide. This reaction is simple and can be conducted at both atmospheric and elevated pressures with high yields. Recently, glycerol carbonate has been used as a cyclic carbonate for synthesizing polyurethane. The “green” glycerol carbonate is prepared form the reaction between glycerol and dimethyl carbonate (DMC) or diethyl carbonate [36-38]. Helou, *et al.* [39] used the glycerol carbonate to prepare the cyclic carbonate-terminated polycarbonate.

Other groups synthesized the non-isocyanate polyurethane by using bis(cyclic carbonate) and diamine [28-35]. The hydroxyl end-groups appear in this polyurethane and they can be hydrogen bonded to the carbonyl group in the urethane linkage. Due to the presence of the hydroxyl end-groups, this non-isocyanate polyurethane (polyhydroxyurethane, PHU) showed higher water absorption with respect to the isocyanate-based one and it may have applications where water absorption and retention is desirable [32]. Moreover, the thermal stability of PHU is higher than the isocyanate-based polyurethane because the former does not contain allophanate or biuret units [31].

In this study, a procedure to introduce cyclic carbonate groups as chain ends in both polycaprolactone and natural rubber derived oligomers was described. These precursors have been used in the formulation of a novel PCL/NR based polyurethane without isocyanate. Characterization of chemical structure of precursors, intermediates and the final product by H^1- and ^{13}C-NMR and FTIR were described.

8.2 EXPERIMENTAL

8.2.1 Materials

Natural rubber (STR 5L) was produced by Jana Concentrated Latex Co. Ltd., Songkhla, Thailand. All chemicals used were analytical grade, included periodic acid (H_5IO_6, 99.5%, Himedia®) manufactured by HiMedia Laboratories Pvt. Ltd. (Mumbai, India), sodium borohydride ($NaBH_4$, 98.0%, Rankem®) produced by RFCL Ltd. (New Delhi, India) and low molecular weight polycaprolactone diol (PCL diol, PCL-OH) ($\bar{M}_n$ = 530 g/mol) produced by SIGMA-ALDRICH Inc., (Missouri, USA). Succinic anhydride, triethylamine (Et_3N), 1,4-butylenediamine, 4-dimethylaminopyridine (DMAP), and *N,N'*-dicyclohexylcarbodiimide (DCC) were produced by SIGMA-ALDRICH Inc. PCL diol was dried at 40°C in a vacuum oven for 24 h prior to using.

8.2.2 Characterization

^{1}H- and ^{13}C-NMR spectra were recorded by using the Varian® Unity Inova Fourier Transform Nuclear Magnetic Resonance Spectrometer at 400 MHz using tetramethylsilane (TMS) as an internal standard. Deuterated chloroform ($CDCl_3$) was used as a solvent. The BRUKER® EQUINOX 55 Fourier Transform Infrared Spectrometer was employed to determine the presence of functional groups. The samples were scanned in the frequency range of 4000-650 cm^{-1}.

8.2.3 Hydroxyl telechelic natural rubber (HTNR) preparation

Hydroxyl telechelic natural rubber (HTNR) was prepared by an oxidative chain cleavage reaction of natural rubber (Figure 8.1) with the molecular weight of 1700 g/mol. The double bonds of NR were cleaved by using periodic acid to obtain carbonyl telechelic natural rubber (CTNR). The ketone and aldehyde end-groups in CTNR were reduced to hydroxyl end-groups (HTNR) by sodium borohydride. The chemical structure of the products was identified by NMR and FTIR techniques according to data previously collected [12, 18-19, 24].

8.2.4 Synthesis of precursors with carboxylic acid chain ends

This step describes the preparation of the precursors (PCL and NR) having carboxylic acid end-groups. A solution of PCL diol or HTNR (x mol) in dichloromethane was stirred at ambient temperature in a round-bottomed flask, equipped with a magnetic stirrer bar. Then triethylamine (2x mol), DMAP (2x mol) and succinic anhydride (2.05x mol) was charged in to the reaction flask and continuously stirred at room temperature for 24 h. The reaction solution was washed with saturated $NaHCO_3$, followed by saturated NaCl solution, aqueous hydrochloric acid (5% v/v), and saturated NaCl solution. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum yielding a viscous liquid (90% yield). Pure carboxyl telechelic PCL (CBTPCL, M_n= 1300 g/mol, M_n/M_w=1.18) and carboxyl telechelic natural rubber (CBTNR, M_n= 2200 g/mol, M$_n$/M$_w$=2.11) were obtained. The chemical structure of the products was identified by using NMR and FTIR techniques, according to previously collected data [39-40]. Figure 8.1 and 8.2 display the synthesis route to obtain CBTNR and CBTPCL, respectively.

PCL-OH: ^{1}H-NMR (CDCl$_3$) δ (ppm): 1.4 (q, -CH$_2$C*H*$_2$CH$_2$CH$_2$-), 1.58 (q, -CH$_2$C*H*$_2$ CH$_2$O), 1.60 (m, O=C-CH$_2$C*H*$_2$CH$_2$-), 2.31 (t, O=C-C*H*$_2$CH$_2$-), 2.35 (t, O=C-C*H*$_2$CH$_2$-), 2.47 (s, -O*H*), 3.60 (t, CH2C*H*$_2$-OH), 3.70 (t, O-C*H*$_2$CH$_2$OC=O), 4.06 (t, CH2C*H*$_2$-OC=O) 4.23 (t, -O-CH$_2$C*H*$_2$-OC=O)

^{13}C-NMR(CDCl$_3$) δ (ppm): 24.6 (O=CCH$_2$*C*H$_2$CH$_2$CH$_2$-O), 25.2 (O=CCH$_2$*C*H$_2$CH$_2$ CH$_2$-OH), 25.5(O=CCH$_2$CH$_2$*C*H$_2$CH$_2$-O), 28.3 (O=CCH$_2$CH$_2$*C*H$_2$CH$_2$-O), 32.2 (O=CCH$_2$CH$_2$*C*H$_2$CH$_2$-OH), 34.0 (O=C*C*H$_2$CH$_2$CH$_2$CH$_2$-O), 62.3 (O=CCH$_2$CH$_2$CH$_2$ *C*H$_2$-OH), 63.3 (OCH$_2$*C*H$_2$-OC=O), 64.1(O=CCH$_2$CH$_2$CH$_2$*C*H$_2$-O), 69.1(O*C*H$_2$CH$_2$-OC=O), 173.6 (*C*=O)

FTIR: $\upsilon_{(OH)}$ = 3442 cm^{-1}, $\upsilon_{(CH2,\ CH3)}$ = 2940–2850 cm^{-1}, $\upsilon_{(C=O)}$ = 1731 cm^{-1}, $\upsilon_{(C-O)}$ = 1167 cm^{-1}

CBTPCL: ^{1}H-NMR (CDCl$_3$) δ (ppm): 1.39 (q, -CH$_2$C*H*$_2$CH$_2$CH$_2$-), 1.65 (q, O=C-CH$_2$C*H*$_2$CH$_2$-) and (q, -CH$_2$C*H*$_2$CH$_2$O), 2.34 (m, O=C-C*H*$_2$CH$_2$-), 2.67 (t, O=C CH$_2$C*H*$_2$ COOH), 2.63 t, O=CC*H*$_2$CH$_2$COOH), 3.70 (t, O-C*H*$_2$CH$_2$OC=O), 4.07 (t, CH2C*H*$_2$-OC=O) 4.27 (t, -O-CH$_2$C*H*$_2$-OC=O), 8.58 (bs, -COO*H*) and disappearance of 2.47 (s, -O*H*)

^{13}C-NMR (CDCl$_3$) δ (ppm): 24.5 (O=CCH$_2$*C*H$_2$CH$_2$CH$_2$-O), 25.5 (O=CCH$_2$CH$_2$*C*H$_2$ CH$_2$-O), 28.3 (O=CCH$_2$CH$_2$*C*H$_2$CH$_2$-O), 29.2 (OC=O*C*H$_2$CH$_2$COOH), 30.3 (OC=O CH$_2$ *C*H$_2$COOH), 34.1 (O=C*C*H$_2$CH$_2$CH$_2$CH$_2$-O), 63.0 (OCH$_2$*C*H$_2$-OC=O), 63.7, 64.6 (O=CCH$_2$CH$_2$CH$_2$*C*H$_2$-O), 69.0 (O*C*H$_2$CH$_2$-OC=O), 172.2 (*C*=O), 173.6 (*C*=O), 177 (*C*OOH) and disappearance 25.2 (O=CCH$_2$*C*H$_2$CH$_2$CH$_2$-OH), 32.2 (O=CCH$_2$CH$_2$*C*H$_2$ CH$_2$-OH), 62.3(O=CCH$_2$CH$_2$CH$_2$*C*H$_2$-OH),

FTIR: $\upsilon_{(COOH)}$ = 3200-3500 cm^{-1}, $\upsilon_{(CH2,\ CH3)}$ = 2940–2850 cm^{-1}, $\upsilon_{(C=O)}$ = 1723 cm^{-1}, $\upsilon_{(C-O)}$ = 1167, 1259cm^{-1}

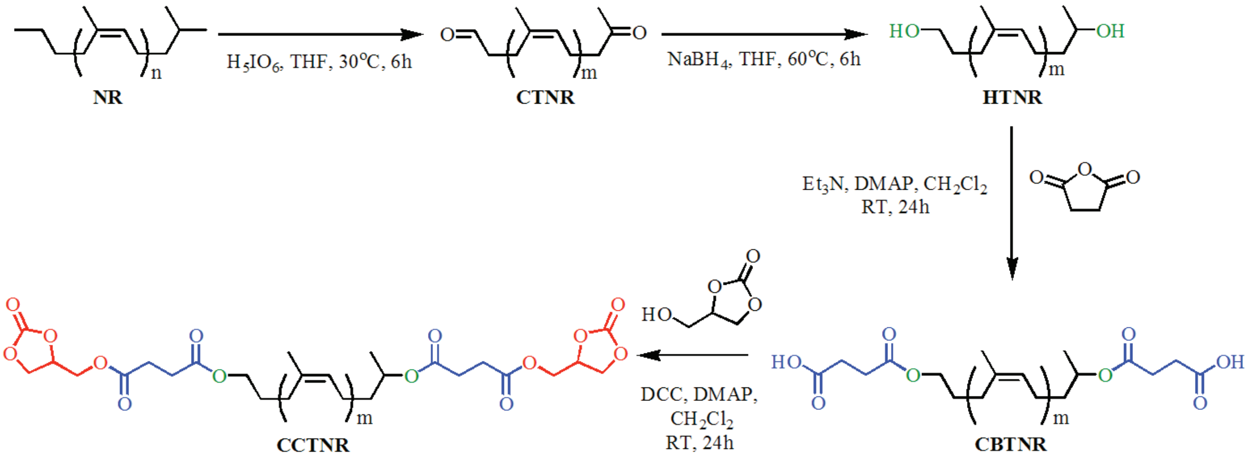

Figure 8.1 The synthesis of cyclic carbonate telechelic natural rubber (CCTNR).

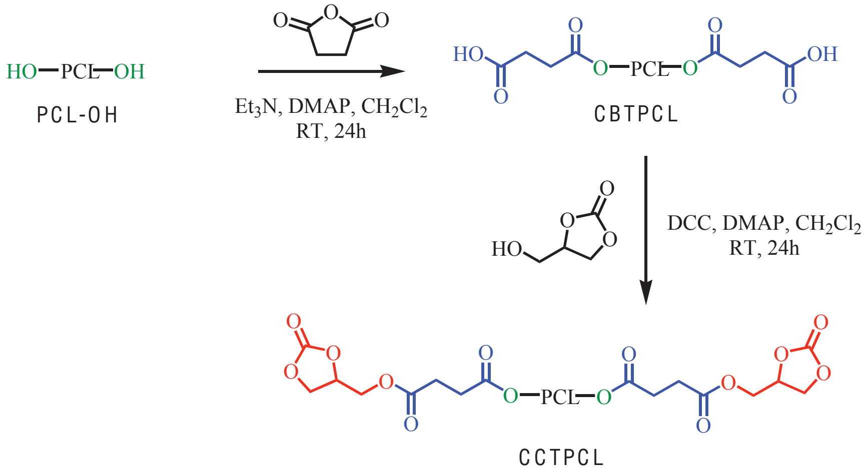

Figure 8.2 The synthesis procedure of cyclic carbonate telechelic PCL (CCTPCL).

CBTNR: ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.22 (d, $CH_3CHOC{=}O$), 1.67 (s,-CH_3 isoprenic), 2.04 (m, -CH_2 isoprenic), 2.63 (m, $OC{=}OCH_2CH_2COOH$) 4.07 (t, $CH_2OC{=}O$), 4.90 (m, $CHOC{=}O$), 5.10 (t, =CH isoprenic) and disappearance of 3.65 (t, CH_2OH), 3.80 (m, $CHOH$)

^{13}C-NMR ($CDCl_3$) δ (ppm): 19.85 ($CH_2CH_2C(CH_3)$-$OC{=}O$), 22.3 (CH_3CH-$OC{=}O$), 23.4 ($CH_3C{=}CH$), 26.4 ($CH_2CH{=}C$ isoprenic), 29.7 ((CH_2CH_2COOH)) 30.9 (CH_2 COOH), 33.2 (CH_2-$C{=}CH$ isoprenic), 36.1 ($CH_2CH(OC{=}O)CH_3$), 64.6 (CH_2CHO $C{=}O$), 71.4 ($CH_3CHOC{=}O$), 125 ($C{=}CH$ isoprenic), 135.2 ($C{=}CH$ isoprenic) 172 ($C{=}O$)

FTIR: $\upsilon_{(COOH)}$ = 3200-3500 cm^{-1}, $\upsilon_{(CH2,\ CH3)}$ = 2940–2850 cm^{-1}, $\upsilon_{(C=O)}$ = 1729 cm^{-1}, $\upsilon_{(C=C)}$ = 1661 cm^{-1}; $\upsilon_{(CH2\ ,CH3)}$ *cis*-1,4-isoprene =1448, 1376 cm^{-1}; $\upsilon_{(C\text{-}O)}$ = 1259, 1167cm^{-1}, $\upsilon_{(C=C\text{–}H)}$ = 834 cm^{-1},

8.2.5 Synthesis of cyclic carbonate-end functional group

Solution of CBTPCL or CBTNR (x mol) in dichloromethane were prepared. DMAP (2x mol), DCC (2x mol) and glycerol carbonate (2.2x mol) were added to the DCM solution, which was left stirring for 24h, at room temperature [39]. The reaction mixture was successively filtered and then washed with aqueous hydrochloric acid (5% v/v), followed by a saturated NaCl solution. Finally, the product was precipitated in ethanol to obtain a cyclic carbonate telechelic PCL (CCTPCL M_n= 1900 g/mol, M_n/M_w=1.20) or a cyclic carbonate telechelic natural rubber (CCTNR, M_n= 4000 g/mol, M_n/M_w=2.27), as viscous liquids (70-80% yield). The chemical structure of the products was identified by NMR and FTIR. Figure 8.1 and 8.2 show the synthesis route to obtain CCTNR and CCTPCL, respectively

CCTPCL: **^{1}H-NMR** ($CDCl_3$) δ (ppm): 1.34 (q, $\text{-}CH_2C\mathit{H_2}CH_2CH_2\text{-}$), 1.65 (q, $O{=}C\text{-}CH_2C\mathit{H_2}CH_2\text{-}$) and (q, $\text{-}CH_2C\mathit{H_2}CH_2O$), 2.35 (t, $O{=}C\text{-}C\mathit{H_2}CH_2\text{-}$), 2.30 (t, $O{=}CC\mathit{H_2}\ CH_2\text{-}$), 2.65 (m, $O{=}CC\mathit{H_2}C\mathit{H_2}C{=}O$), 3.70 (t, $O\text{-}C\mathit{H_2}CH_2OC{=}O$), 4.07 (q, $CH_2C\mathit{H_2}\text{-}OC{=}O$, $\text{-}CH\text{-}C\mathit{H_2}\text{-}O$) 4.27 (t, $\text{-}O\text{-}CH_2C\mathit{H_2}\text{-}OC{=}O$), 4.34, (m, $\text{-}OC\mathit{H_2}CH(O)CH2\text{-}$), 4.56 (t, $OC\mathit{H_2}CH\text{-}$), 4.93 (m, $C\mathit{H}$) and disappearance of 8.58 (bs, $\text{-}COO\mathit{H}$)

^{13}C-NMR ($CDCl_3$) δ (ppm): 24.5 ($O{=}CCH_2\mathit{C}H_2CH_2CH_2\text{-}O$), 25.5($O{=}CCH_2CH_2\mathit{C}H_2CH_2\text{-}O$), 28.3 ($O{=}CCH_2CH_2\mathit{C}H_2CH_2\text{-}O$), 28.9 ($OC{=}O\mathit{C}H_2\mathit{C}H_2C{=}OO$), 34.1($O{=}C\mathit{C}H_2CH_2CH_2CH_2\text{-}O$), 63.3($OCH_2\mathit{C}H_2\text{-}OC{=}O$), 64.1 ($(O)O{=}CO\mathit{C}H_2CH$), 64.7 ($O{=}CCH_2CH_2CH_2\mathit{C}H_2\text{-}O$), 66.0 ($O{=}CO\mathit{C}H_2CH$), 69.1($O\mathit{C}H_2CH_2\text{-}OC{=}O$), 73.6 ($\mathit{C}HO$), 154.3($\text{-}O\mathit{C}{=}O(O)$), 171.8($\mathit{C}{=}O$), 172.1($\mathit{C}{=}O$), 173.5($\mathit{C}{=}O$) and disappearance of 29.2 ($OC{=}O\mathit{C}H_2CH_2COOH$), 30.3 ($OC{=}OCH_2\mathit{C}H_2COOH$), 177 ($\mathit{C}OOH$)

FTIR: $\upsilon_{(CH2,\ CH3)}$ = 2940–2850 cm^{-1}, $\upsilon_{(C=O)}$ = 1817 cm^{-1}, $\upsilon_{(C=O)}$ = 1723 cm^{-1}, $\upsilon_{(OCH3)}$=1451 cm^{-1}, $\upsilon_{(C\text{-}O)}$ = 1271, 1158, 1094 and 1058 cm^{-1}

CCTNR: **^{1}H-NMR** ($CDCl_3$) δ (ppm): 1.22 (d, $C\mathit{H_3}CHOC{=}O$), 1.67 (s,$\text{-}C\mathit{H_3}$ isoprenic), 2.04 (m, $\text{-}C\mathit{H_2}$ isoprenic), 2.63 (m, $OC{=}OC\mathit{H_2}C\mathit{H_2}COOH$) 4.07 (t, C*H*$_2$OC=O), 4.27-4.40 (m, -O-CH$_2$C*H*$_2$-OC=O and -OC*H*$_2$CH(O)CH2-), 4.54 (t, OC*H*$_2$CH-), 4.90 (m, C*H*OC=O), 5.10 (t, =C*H* isoprenic)

^{13}C-NMR (CDCl$_3$) δ (ppm): 19.85 (*C*H$_2$CH$_2$C(CH$_3$)-OC=O), 22.3 (*C*H$_3$CH-OC=O), 23.4 (*C*H$_3$C=CH), 26.4 (*C*H$_2$CH=C isoprenic), 29.2 (OC=O*C*H$_2$CH$_2$C=OO), 28.9 (OC=OCH$_2$ *C*H$_2$C=OO), 33.2 (*C*H$_2$-C=CH isoprenic), 36.1 (*C*H$_2$CH(OC=O)CH$_3$), 63.1(OCH$_2$*C*H$_2$-OC=O), 64.6 (CH$_2$*C*HOC=O), 66.0 (O=CO*C*H$_2$CH), 71.4 (*C*H$_3$CHOC=O), 73.6 (*C*HO), 125 (C=*C*H isoprenic), 135.2 (*C*=CH isoprenic), 154(-O*C*=O(O)), 172 (*C*=O) and disappearance of 29.7 ((*C*H$_2$CH$_2$COOH)) 30.9 (*C*H$_2$COOH)

FTIR: $\upsilon_{(CH2,\ CH3)}$ = 2940–2850 cm^{-1}, $\upsilon_{(C=O)}$ = 1818 cm^{-1}, $\upsilon_{(C=O)}$ = 1735 cm^{-1}, $\upsilon_{(C=C)}$ = 1663 cm^{-1}; $\upsilon_{(CH2\ ,CH3)}$ *cis*-1,4-isoprene =1449, 1376 cm^{-1}; $\upsilon_{(C\text{-}O)}$ = 1265, 1159cm^{-1}, $\upsilon_{(C=C\text{–}H)}$ = 837 cm^{-1}

8.2.6 Synthesis of polyurethane

The one equivalent of cyclic carbonate oligomer (CCTPCL or/and CCTNR), 1,4-butylenediamine and lithium chloride was well mixed in DMSO at 100°C, for 24 h under atmosphere [35]. The molar ratio of cyclic carbonate-terminated oligomer and diamine was 1:1. The reaction was purified by precipitation in water and washed thoroughtly with water and dried under vacuum to obtain the viscous yellow/brown liquid of polyhydroxylurethane (PHU, Yield=60-70%). The conversion of cyclic carbonates was followed by FTIR spectroscopy. Figure 8.3 represents the synthetic route to polyhydroxylurethane.

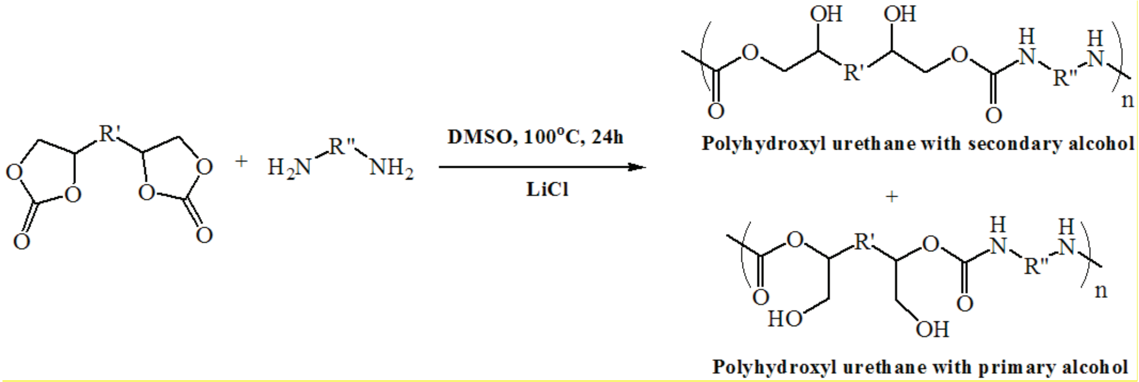

Figure 8.3 Polyaddition of cyclic carbonate and diamine in DMSO.

8.3 RESULTS AND DISCUSSIONS

The first achievement of this research work is the generation of new structures of oligomers derived by natural rubber or polycaprolactone, bearing carboxylic acid and cyclic carbonate moieties, which make them interesting building blocks in many synthetic pathways, leading to new materials.

The cyclic carbonate end functional group of PCL and NR was obtained in high yield, in a two steps procedure, which is illustrated in Figure 8.1 and 8.2 for NR and PCL, respectively. At first, the carboxylic telechelic oligomer (CBTPCL and CBTNR) was prepared from the reaction between hydroxyl end-functional group of PCL-OH or HTNR with succinic anhydride, at room temperature for 24 h, in CH_2Cl_2, by using DMAP and Et_3N as catalyst and auxiliary base, respectively. Then, the synthesis of cyclic carbonate end-capped PCL or NR involved the esterification of carboxylic telechelic oligomer with glycerol carbonate, in the presence of DMAP and DCC at room temperature for 24 h in CH_2Cl_2. The obtained products (CCTPCL and CCTNR) were investigated by ^{1}H-NMR, ^{13}C-NMR and FTIR as demonstrated in Figure 8.4-8.7. The polyhydroxylurethane (PHU) was prepared from the reaction between CCTPCL/CCTNR and 1,4-butylenediamine.

8.3.1 Characterization of carboxylic acid-end terminated oligomers

The different steps of the syntheses were followed performing ^{1}H-NMR and FTIR spectra. Figure 8.4 shows ^{1}H-NMR spectra of PCL derived structures. The signal corresponding to the protons of the hydroxyl groups at 2.47 ppm in the PCL-OH spectrum disappeared in the CBTPCL spectrum, because of the reaction of PCL-OH with succinic acid. The new signals of a triplet around 2.63 and 2.67 ppm as well as a broad singlet around 8.58 ppm can be assigned to the methylene proton ($-CH_2-$), which is connected to a carboxylic end group and to the proton of a carboxylic group (-COOH). The methylene group (proton *f* and *k*) in the PCL-OH at chemical shift of 1.58 ppm became 1.65 ppm in the CBTPCL, and the chemical shift of proton *l* was shifted from 3.60 ppm in the PCL-OH to 4.07 ppm in the CBTPCL. These results corresponded with ^{13}C-NMR results. The chemical shift of the methylene proton at

25.2, 32.2 and 62.3 ppm in the PCL-OH did not appear in the CBTPCL, and the CBTPCL showed the new peaks of methylene proton adjacent to carboxylic end group at 29.2 and 30.3 ppm. Furthermore, the carbon of the carboxylic group, a new peak in the CBTPCL, was observed at the chemical shift of 177 ppm.

The signals characteristic of methyl, methylene and unsaturated methane protons of *cis*-1,4-isoprene units (HTNR) appeared at 1.6, 2.1 and 5.1 ppm (Figure 8.5), respectively. In addition, three other signals at 1.2, 3.65 and 3.8 ppm were assigned to methyl, methylene and methine proton that were connected to hydroxyl group. After changing the hydroxyl end functional group (HTNR) into the carboxylic end functional group (CBTNR), the last 3 peaks shifted to 1.22, 4.07 and 4.90 ppm, respectively. The new signal at 2.63 ppm also appeared similarly to the case of CBTPCL. Nevertheless, all NR precursors showed the small peaks at 2.70, 1.43 and 1.29 ppm, which corresponded to the proton adjacent to oxirane ring, the methylene proton connected to epoxy group and the methylic protons adjacent to oxirane ring, respectively. This was evident that HTNR, CBTNR and CCTNR consisted of oxirane ring.

The FTIR spectra of PCL-OH in Figure 8.6 displayed the peak at 3442 cm^{-1} (O-H stretching vibration), 1731 cm^{-1} (C=O stretching vibration) and 1167 cm^{-1} (ether stretching vibration) indicating the hydroxyl group in the PCL-OH. After reaction of PCL-OH with succinic anhydride, the FTIR spectra of CBTPCL showed the broad peak at 3200-3500 cm^{-1} of COOH vibration and the ester vibration appeared at 1259 cm^{-1}. The spectrum of CBTNR showed 2 distinct new peaks at 1732 and 1265 cm^{-1}, which were assigned to C=O and ester stretching vibrations, respectively (Figure 8.7).

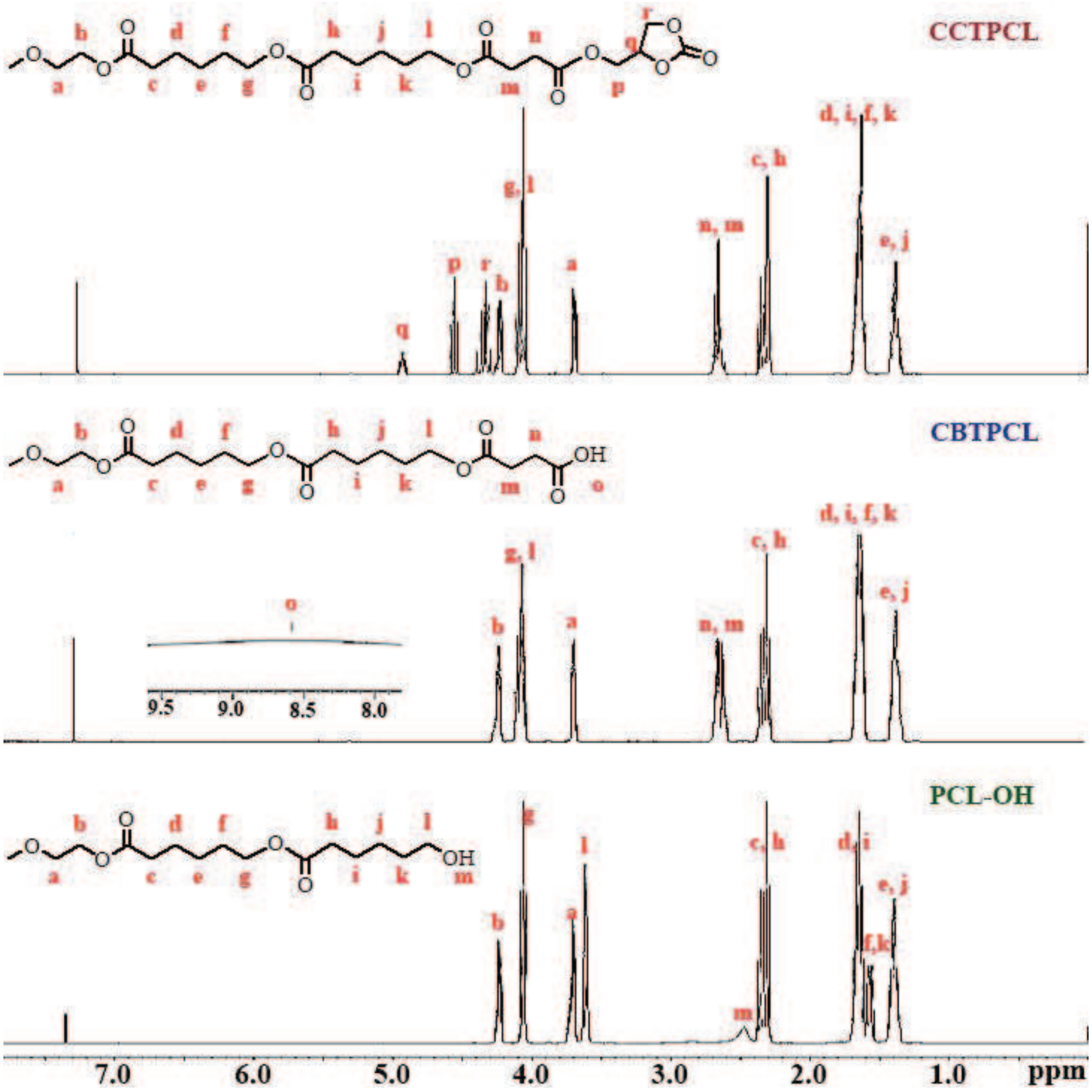

Figure 8.4 ^{1}H NMR spectra of PCL diol (PCL-OH), carboxyl telechelic PCL (CBTPCL) and cyclic carbonate telechelic PCL (CCTPCL).

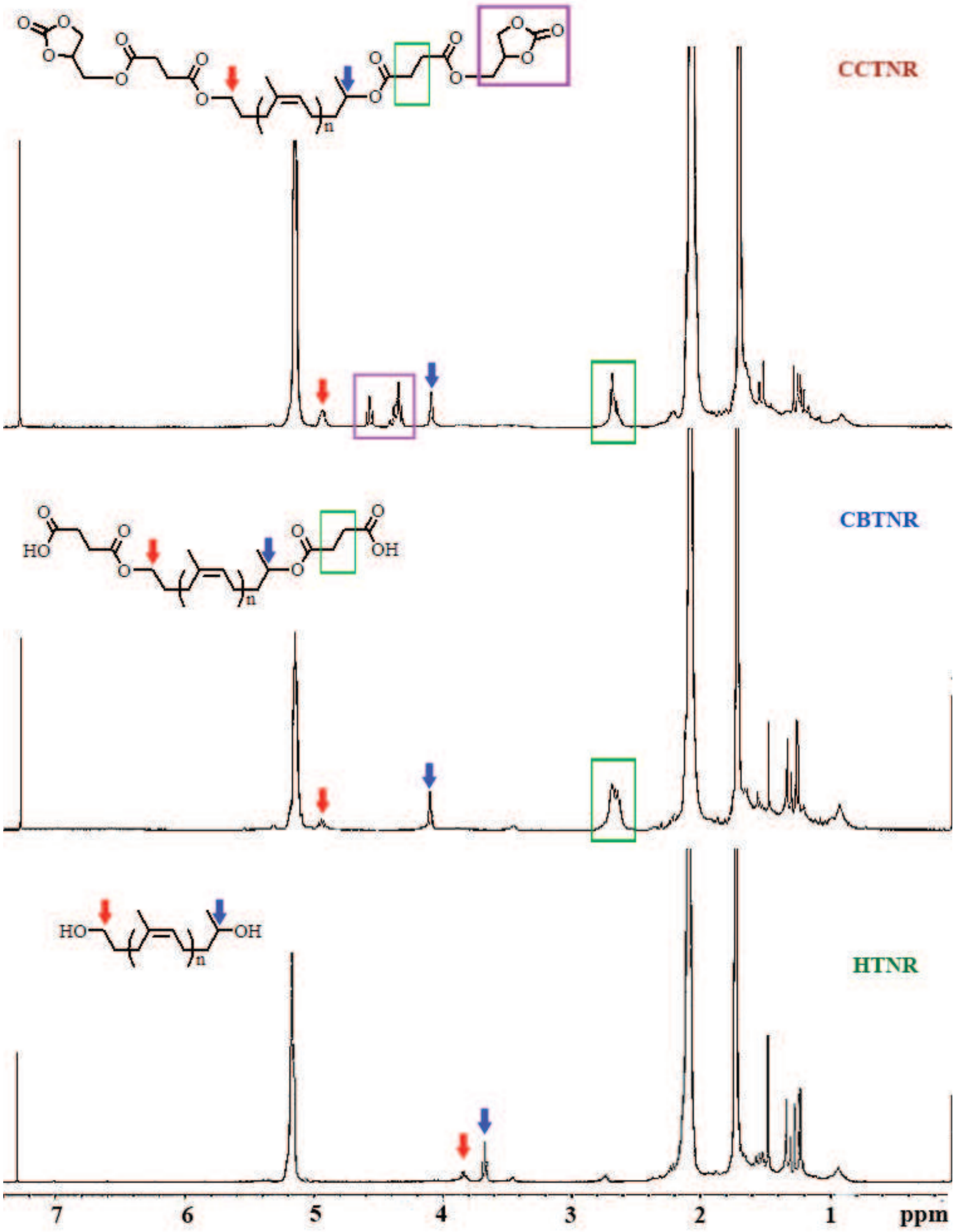

Figure 8.5 ^{1}H NMR spectra of hydroxyl telechelic natural rubber (HTNR), carboxyl telechelic natural rubber (CBTNR) and cyclic carbonate telechelic natural rubber (CCTNR).

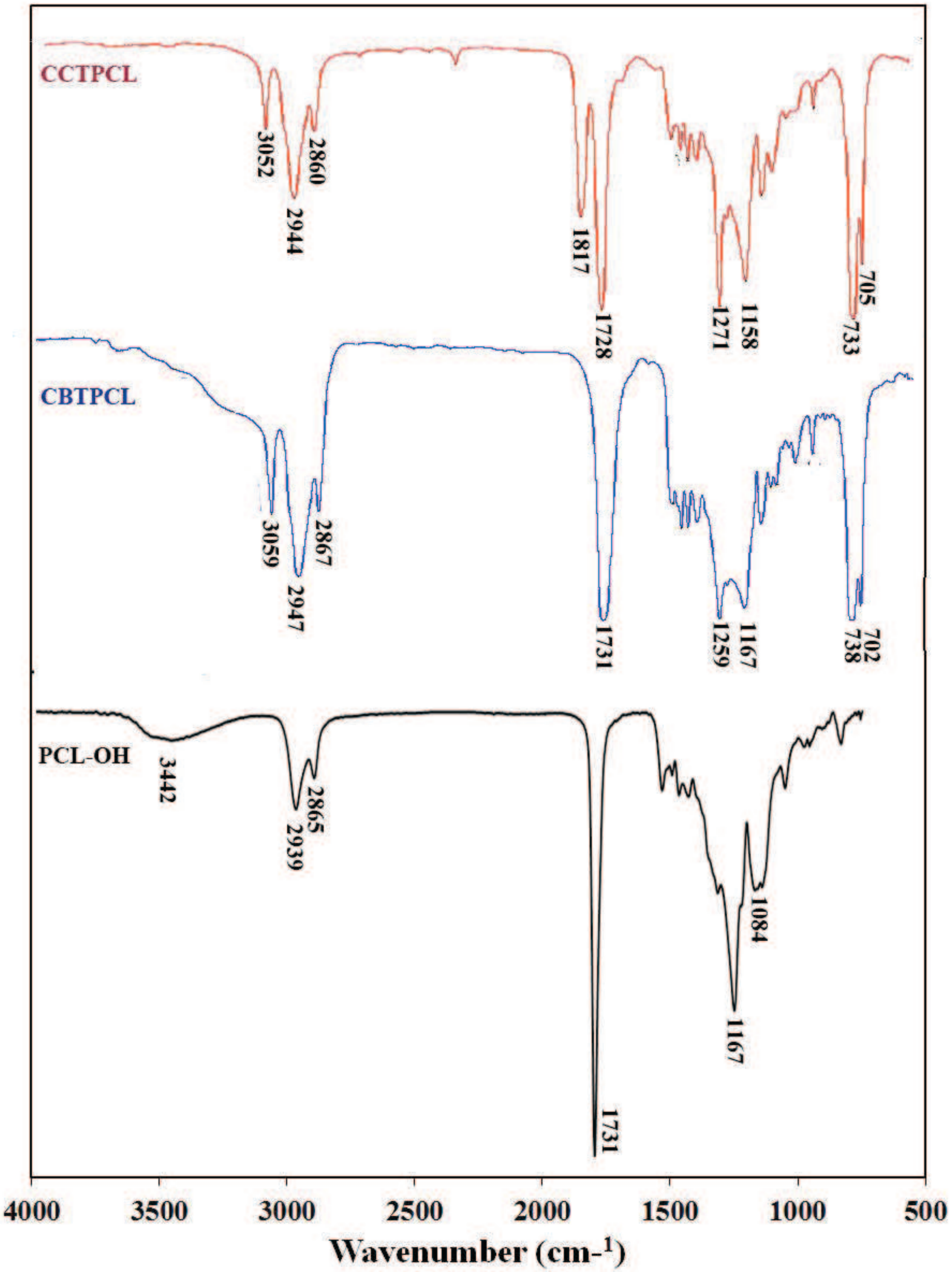

Figure 8.6 FTIR spectra of PCL diol (PCL-OH), carboxyl telechelic PCL (CBTPCL) and cyclic carbonate telechelic PCL (CCTPCL).

8.3.2 Synthesis of cyclic carbonate-end functional group

The esterification of carboxylic telechelic oligomers (CBTPCL or CBTNR) with glycerol carbonate in the presence of DMAP and DCC, at room temperature, for 24 h, in CH_2Cl_2 was performed to prepare the CCTPCL and CCTNR. The ^{1}H-NMR spectrum of CCTPCL is illustrated in Figure 8.4. The signal corresponding to the methane proton in the cyclic carbonate was observed at 4.93 and the methylene proton in cyclic carbonate appeared at 4.56 and 4.34 ppm. The proton signal of COO*H* at 8.58 ppm disappeared in CCTPCL. The ^{13}C-NMR spectrum of CCTPCL showed the new carbonyl carbon and the methine carbon peak of cyclic carbonate at 154.3 and 73.6 ppm, respectively, and the peak at 177 ppm due to *C*OOH disappeared indicating the presence of the cyclic carbonate in the sample.

CCTNR also showed a new peak in the range of 4.27-4.90 ppm due to the cyclic carbonate group (Figure 8.5). The chemical shift of methine proton in the cyclic carbonate ($(CH_2)C\underline{H}OC{=}O$) at 4.90 ppm was overlapped with the methine proton of isoprene chain ($CH_2(CH_3)C\underline{H}OC{=}O$).

Figure 8.6 and 8.7 illustrate FTIR spectra of CCTPCL and CCTNR, respectively. The absorption band of carbonyl group of cyclic carbonate was observed at 1818 cm^{-1} and there was no absorption band in the region 3200-3500 cm^{-1}, which was characteristic of hydroxyl vibration of the carboxylic group. All observations from NMR and FTIR confirmed the formation of the cyclic carbonate terminated oligomers (CCTPCL and CCTNR).

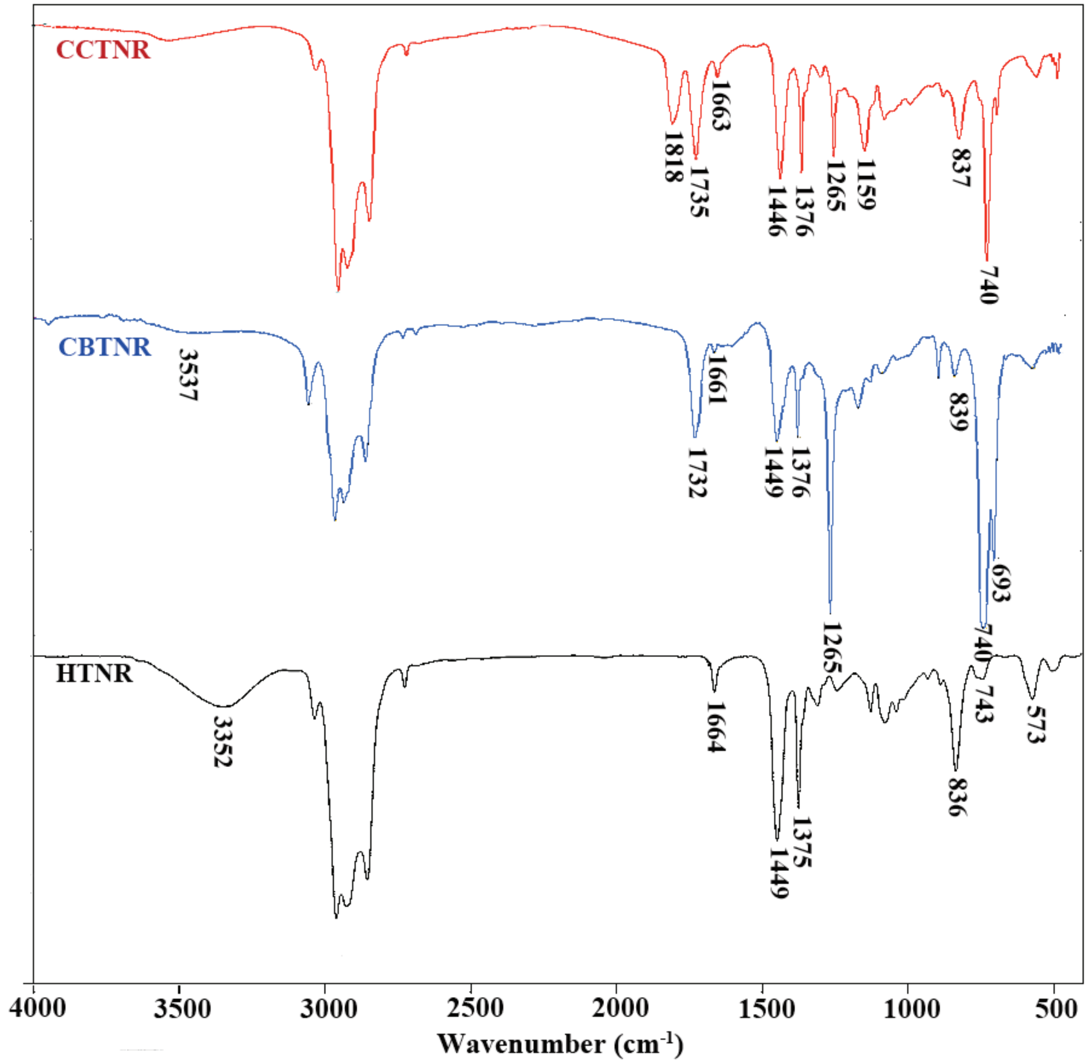

Figure 8.7 FTIR spectra of hydroxyl telechelic natural rubber (HTNR), carboxyl telechelic natural rubber (CBTNR) and cyclic carbonate telechelic natural rubber (CCTNR).

8.3.3 Reaction of cyclic carbonate oligomers with diamines

A preliminary study of polyhydroxylurethane (PHU) synthesis was carried out via the polyaddition reaction between cyclic carbonate oligomers (CCTPCL or/and CCTNR) and 1,4-butylenediamine. FTIR spectrum of CCTPCL and PHU is exhibited in Figure 8.8. PHU1 consisted of CCTPCL and diamine. PHU2 consisted of

CCTPCL, CCTNR and diamine, and the molar ratio of CCTPCL:CCTNR was 0.7:0.3. PHU1 did not show the peak at 1818 cm^{-1} assigned to the carbonyl vibration of the cyclic carbonate. The absorption peak at 1730 cm^{-1} in PHU1 was assigned to the C-N vibration of urethane carbonyl group, which overlapped to the C=O stretching vibration of the ester group in CCTPCL. The new absorption peaks found in PHU1 were at 1525 and 3440 cm^{-1} assigned to the C-N vibration of amide II and the O-H/N-H vibration, respectively. Therefore, the PHU was successfully synthesized by using the CCTPCL and 1,4-butylenediamine in the present study. All these observation agreed with the results reported previously [28-29, 39]. By using the CCTPCL and CCTNR as starting materials for PHU2, the residue of cyclic carbonate was observed at the wavenumber of 1818 cm^{-1}. This may be due to relatively low solubility of CCTNR in DMSO resulting in the lower reactivity than CCTPCL. The future study will be focused on selecting the good solvent of CCTNR and increasing molecular weight of the obtained thermoplastic PHU.

8.4 CONCLUSION

Novel cyclic carbonate telechelic PCL (CCTPCL) and cyclic carbonate telechelic natural rubber (CCTNR) were prepared from their hydroxy-terminated precursors (PCL-OH and HTNR) and glycerol carbonate, a renewable starting material. This synthesis method produced high yields of pure products (70-80%), which are useful intermediates in many synthetic pathways. One application of the obtained functional oligomers was the polyaddition polymerization between CCTPCL and 1,4-butylenediamine to form polyhydroxylurethane. The polyurethane structure was confirmed by FTIR spectra, which showed that the cyclic carbonate group disappeared after reaction with the amino groups and new peaks relative to a urethane bond (C-N, N-H, O-H) were observed.

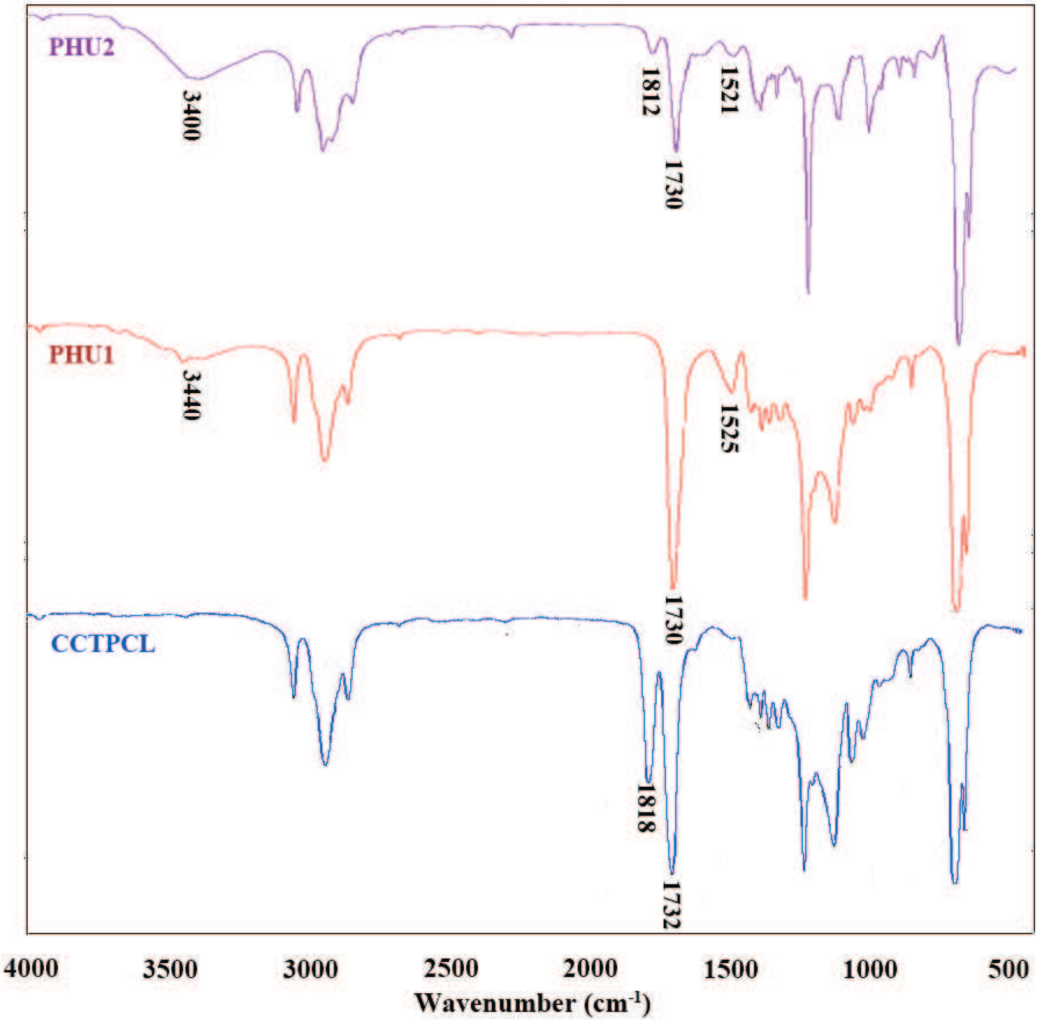

Figure 8.8 FTIR spectra of cyclic carbonate-terminated PCL (PCL-CC) and polyhydroxylurethane (PHU).

8.5 ACKNOWLEDGEMENTS

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8.6 REFERENCES

1. Tu, Y.C., Suppes, G.J., Hsieh, F.H. 2009. Thermal and mechanical behavior of flexible polyurethane-molded plastic films and water-blown foams with epoxidized soybean oil. J. Appl. Polym. Sci. 111, 1311-1317.
2. Chian, K.S., Gan, L.H. 1998. Development of a rigid polyurethane foam from palm oil. J. Appl. Polym. Sci. 68, 509-515.
3. Jalilian, M., Yeganeh, H., Haghighi, M.N. 2008. Synthesis and properties of polyurethane networks derived from new soybean oil-based polyol and a bulky blocked polyisocyanate. Polym. Int. 57, 1385-1394.
4. Ligadas, G., Ronda, J.C, Galia, M., Biermann, U., Metzer, J.O. 2006. Synthesis and characterization of polyurethane from epoxidized methyl oleate based polyetherpolyols as renewable resources. J. Polym. Sci. Pol. Chem. 44, 634-645.
5. Begines, B., Zamora, F., Roffe, I., Mancera, Galbis, J.A. 2011. Sugar-based hydrophilic polyurethanes and polyurea. J. Polym. Sci. Pol. Chem. 49, 1953–1961.
6. Barikani, M., Honarkar, H., Barikani, M. 2009. Synthesis and characterization of polyurethane based on chitosan and poly(ε-caprolactone). J. Appl. Polym. Sci. 112, 3157-3165.
7. Paul, C.J., Gopinathan Nair, M.R. 1998. Segmented block copolymer of natural rubber and propylene glycol-toluene diisocyanate oligomer. Polym. Eng. Sci. 38(3), 440-451.
8. Cherian, A.B., Thachil, E.T. 2004. Block copolymers of unsaturated polyesters and functional elastomers. J. Appl. Polym. Sci. 94, 1956-1964.
9. Sun, X., Ni, X. 2004. Block copolymer of trans-polyisoprene and urethane segment: crystallization behavior and morphology. J. Appl. Polym. Sci. 94, 2286-2294.
10. Gopakumar, S., Paul, C.J., Nair, M.R.G. 2005. Segmented block copolymers of natural rubber and 1,4-butanediol-toluene diisocyanate oligomers. Mater. Sci.-Poland. 23(1), 227-245.

11. Cherian, A.B., Abraham, B.T., Thachil, E.T. 2006. Modification of unsaturated polyester resin by polyurethane pre polymers. J. Appl. Polym. Sci. 100, 449-456.
12. Kébir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunel, C., Couvercelle, J.P. 2006. Use of new hydroxytelechelic cis-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes (PUs): Influence of isocyanate and chain extender nature and their equivalent ratios on the mechanical and thermal properties of PUs. E-polymers. 48, 1-14.
13. Kébir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunel, C., Jouenne, T. 2007. Use of telechelic cis-1,4-polyisoprene cationomers in the synthesis of antibacterial ionic polyurethanes and copolyurethanes bearing ammonium groups. Biomatherials. 28, 4200-4208.
14. Radhakrishnan Nair, M.N, Gopinathan Nair, M.R. 2008. Synthesis and characterization of soluble block copolymers from NR and TDI based polyurethanes. J. Mater. Sci. 43, 738-747.
15. Chandrasekharan Nair, R., Gopakumar, S., Gopinathan Nair, M.R. 2007. Synthesis and characterization of block copolymers based on natural rubber and polypropylene oxide. J. Appl. Polym. Sci. 103, 955-962.
16. Sukumar, P., Jayashree, V., Gopinathan Nair, M.R., Radhakrishnan Nair, M.N. 2009. Synthesis and thermal studies of block copolymers from NR and MDI-based polyurethane. J. Appl. Polym. Sci. 111, 19-28.
17. Radhakrishnan Nair, M.N., Sukumar, P., Jayashree, V., Gopinathan Nair, M.R. 2010. Mechanical properties and fractography of block copolymers based on NR and MDI-based polyurethanes. Polym. Bull. 65, 83-96.
18. Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Doutres, O., Pilard, J.F. 2010. Preparation and physic-mechanical, thermal and acoustic properties of flexible polyurethane foams based on hydroxytelechelic natural rubber. J. Appl. Polym. Sci. 117, 828-837.
19. Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Doutres, O., Pilard, J.F. 2010. Controlled degradation of natural rubber and modification of the obtained telechelic oligoisoprenes:

Preliminary study of their potentiality as polyurethane foam precursors. J. Appl. Polym. Sci. 117, 1279-1289.

20. Kébir, N., Campistron, I., Laguerre, A., Pilard, J.F., Bunel, C. 2011. New crosslinked polyurethane elastomers with various physical properties from natural rubber derivatives. J. Appl. Polym. Sci. 122, 1677-1687.
21. Prisacariu C. 2011. Polyurethane elastomers from morphology to mechanical aspects, New York: SpingerWienNewYork, USA, 75-108.
22. Hepburn C, 1991. Polyurethane elastomer, 2nd edition. New York: Elsevier Applied Science LTD., USA, 407.
23. Matsumura, S., Soeda, Y., Toshima, K. 2006. Perspectives for synthesis and production of polyurethanes and related polymers by enzymes directed toward green and sustainable chemistry. Appl. Microbiol. Biotechnol. 70, 12-20.
24. Panwiriyarat, W. Tanrattankul, V. Pilard, J.F., Pasetto, P., Khaokong, C. 2011. Synthesis and characterization of block copolymer from natural rubber, toluene-2,4-diisocyanate and poly(ε-caprolactone) diol-based polyurethane. Mater. Sci. Forum. 695, 316-319.
25. Kusan, J., Keul, H., Höcker, H. 2001. Cationic ring-opening polymerization of tetramethylene urethane. Macromolecules. 34, 389–395.
26. Schmitz, F., Keul, H., Höcker, H. 1998. Copolymerization of 2,2-dimethyltrimethylene carbonate with tetramethylene urea: a new route to the polyurethane. Polymer. 39, 3179–3186.
27. Ihata, O., Kayaki, Y., Ikariya, T. 2004. Synthesis of thermoresponsive polyurethane from 2-methylaziridine and supercritical carbon dioxide. Angew. Chem. Int. Ed. 43, 717–719.
28. Tomita, H., Sanda, F., Endo, T. 2001. Polyaddition of bis(seven-membered cyclic carbonate) with diamines: A novel and efficient synthetic method for polyhydroxyurethanes. J. Polym. Sci. Pol. Chem. 39, 4091-4100.
29. Ochiai, B., Nakayama, J., Mashiko, M., Kaneko, Y., Nagasawa, T., Endo, T. 2005. Synthesis and crosslinking reaction of poly(hydroxyurethane) bearing a secondary amine structure in the main chain. J. Polym. Sci. Pol. Chem. 43, 5899–5905.

30. Tomita, H., Sanda, F., Endo, T. 2001. Reactivity comparison of five- and six-member cyclic carbonate with amine: Basic evaluation for synthesis of poly(hydroxyurethane). J. Polym. Sci. Pol. Chem. 39, 162–168.
31. Javni, I., Hong, D.P., Petrovic, Z.S. 2008. Soy-based polyurethanes by nonisocyanate route. J. Appl. Polym. Sci. 108, 3867–3875.
32. Tomita, H., Sanda, F., Endo, T. 2005. One-pot non-isocyanate synthesis of polyurethanes from bisepoxide, carbon dioxide, and diamine. J. Polym. Sci. Pol. Chem. 43, 6613–6618.
33. Ochiai, B., Sato, S., Endo, T. 2007. Synthesis and properties of polyurethanes bearing urethane moieties in the side chain. J. Polym. Sci. Pol. Chem. 45, 3408–3414.
34. Rokicki, G., Piotrowska, A. 2002. A new route to polyurethanes from ethylene carbonate, diamines and diols. Polymer. 43, 2927-2935.
35. Kim, M.R., Kim, H.S., Ha, C.S., Park, D.W., Lee, J.K. 2001. Syntheses and thermal properties of poly(hydroxyl)urethanes by polyaddition reaction of bis(cyclic carbonate) and diamines. J. Appl. Polym. Sci. 81, 2735–2743.
36. Li, J., Wang, T. 2010. Coupling reaction and azoeotropic distillation for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. Chem. Eng. Process. 49, 530–535.
37. Kim, S.C., Kim, Y.H., Lee, H., Yoon, D.Y., Song, B.K. 2007. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification. J. Mol. Catal. B- Enzym. 49, 75-78.
38. Rockicki, G., Rakoczy, P., Parzuchowski, P., Sobiecki, M. 2005. Hyperbranced aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate. Green. Chem. 7, 529-539.
39. Helou, M., Carpentier, J.F., Guillaume, S.M. 2011. Poly(carbonate-urethane): an isocyanate-free procedure from α,ω-di(cyclic carbonate) telechelic poly(trimethylene carbonate)s. Green. Chem. 13, 266-271.
40. Ramos, M., Huang, S.J. 2002. Functional condensation polymer; Klumer Academic Publishers: New York. 185-196.

CHAPTER 9

CONCLUSIONS

The objectives of this research work were to prepare novel bio-based polyurethane (PU) composed by low molecular weight chemically modified natural rubber oligomers (NR) and low molecular weight poly(ε-caprolactone) (PCL diol), via isocyanate and non-isocyanate route, and to investigate their mechanical and thermal properties. The tensile properties, tear strength and hardness were determined as well. The full characterization of the precursors as well of the obtained PU films was carried out by ^{1}H- and ^{13}C-NMR, FTIR, Raman spectroscopy, DSC, TGA and DMTA. The PU formulation allowed the preparation of a range of polymers with different mechanical and thermal properties.

The PU prepared via the isocyanate route was obtained by a one-shot method. HTNR and PCL diols were used as a soft segment and 1,4-butanediol (BDO) acted as chain extender . HTNR is a low molecular weight NR containing hydroxyl end group. It is prepared from a reduction reaction between carbonyl telechelic natural rubber (CTNR) and sodium borohydride. CTNR is obtained from an oxidation cleavage reduction of epoxidized natural rubber (ENR) by using periodic acid. CTNR in the present study was prepared using 2 approaches. The first approach was a 2-step method: (1) synthesis of ENR via an epoxidation reaction of NR by using *m*-chloroperbenzoic acid and (2) ENR opening using periodic acid to give CTNR. The second approach was a 1-step method in which NR reacted directly with periodic acid. It was expected that epoxidation occurred and, then, chain cleavage followed. The molecular weight, chemical structure and functionality were determined by SEC, NMR and FTIR. HTNR were prepared having different molecular weight: $\overline{M}_n$ = 1700, 2800 and 2900 g/mol. The thermal properties of HTNR were investigated by DSC and TGA. Its glass transition temperature was -60°C and thermal degradation was in the range of 407-439 °C, respectively.

The first preliminary study was an investigation of the effect of NCO:OH molar ratio (0.84:1 – 1.20:1) and reaction time on film formation, on the molecular weight and the thermal properties of the obtained PU, using chloroform as reaction solvent. The PU was synthesized using HTNR and PCL diols as soft segment and toluene-2,4-diisocyante (TDI) as a hard segment. The molecular weight increased from ~3,000 to 8,000 g/mol by increasing of NCO:OH molar ratio (0.84:1 – 1.20:1) and by increasing reaction time from 1-5 h. Chloroform is a very volatile solvent consequently cracking of PU film was observed. In addition, chloroform provides a lower reactivity rate of polyurethane synthesis than THF, so that it was not possible to form a polymeric film at the same NCO:OH molar ratio and reaction time. Tetrahydrofuran (THF) was a good solvent for PU film preparation, and it was used in the rest of the experiments.

After assessing that THF was the best solvent, PU was prepared from isophorone diisocyanate (IPDI), HTNR, PCL diol and BDO. IPDI and BDO were considered to be the hard segment and HTNR and PCL diol acted as soft segment. The influences of the NCO:OH molar ratio, chain extender (BDO) content, PCL:HTNR molar ratio, diisocyanate structure and molecular weight of diol on the mechanical properties was investigated. The characterization was performed by FTIR, DSC, TGA and DMTA. The effect of the various parameters on PU properties are summarized in the following paragraphs.

The effect NCO:OH molar ratio was varied in the range 0.75:1.00 to 2.85:1.00. The lowest ratio that produced a good PU film was 1.25:1.00. The excess of isocyanate caused chain branching and crosslinking in PU which was observed by FTIR. The Young's modulus, tensile strength and tear strength increased while the elongation at break decreased with an increasing NCO:OH ratio. The T_g, observed from DSC thermograms, increased from -7°C to 5°C when the NCO:OH ratio increased from 1.25 to 2.25. The thermal stability of PU determined from TGA thermograms was increased with an increasing NCO:OH ratio. The properties of PU with very high NCO:OH ratio (2.85:1) were studied. The urethane linkage and crosslinking in PU were confirmed by FTIR. The high crosslinking was attributed to there being no phase separation between the hard and the soft segment according to the results of the DSC and DMTA analyses. Hydrogen bonding between the PCL diol and the hard segment produced a high T_g.

The BDO as the chain extender was important to improve the PU properties. A higher modulus and tensile strength were observed in PU containing BDO. The Young's modulus, tensile strength, elongation at break and tear strength were obtained in the range of 0.3-1.4 MPa, 3.5-15 MPa, 590-825% and 7.5-39 N/mm, respectively, from PU containing 0-30% BDO based on diol content. The addition of BDO gave an increase of T_g due to a higher hard segment content and rigidity.

The effect of PCL:HTNR ratio on PU properties was investigated. The HTNR content was 0, 30, 50, 70 and 100 mol%, based on PCL diol content. An increase of HTNR content reduced the degree of hydrogen bonding between the soft segment and the hard segment, leading to the reduction of the Young's modulus, tensile strength and tear strength. The addition of HTNR decreased the T_g of PU but provided a higher thermal degradation.

The molecular architecture of diisocyanate played an important role on the properties of PU. Three different molecular structures of diisocyanate were used: an aliphatic diisocyanate (HDI), an aromatic diisocyanate (TDI) and a cycloalkane diisocyanate (IPDI). The linear structure of HDI provided a crystalline PU. The crystalline region acted as physical crosslink enhancing the Young's modulus and reducing the elongation at break. In contrast, the asymmetric diisocyanate (TDI and IPDI) provided amorphous PUs, which showed a rubber-like behavior.

Two molecular weights of each diol (HTNR and PCL diol) were selected to study the effect of molar mass on PU properties. The molecular weights of PCL diol were 530 and 2000 g/mol. The molecular weights of HTNR were 1700 and 2800 g/mol. The higher molecular weight of PCL diol changed the tensile behavior of PU from the rubber-like materials to the plastic yielding. The higher molecular weight of PCL diol increased the tear strength and Young's modulus and decreased the hardness. The higher molecular weight of PCL diol provided the lower T_g while HTNR chain length did not show a significant effect on T_g of PU. In addition, the higher molecular weight of HTNR decreased the mechanical properties except the elongation at break. This was due to the higher flexibility of the longer chain of HTNR.

Raman spectroscopy was used to observe the formation of urethane linkage. The urethane characteristic peak depended on the compositions of polyurethane, in particular on the diisocyanate type.

Finally, the cyclic carbonate telechelic PCL (CCTPCL) and cyclic carbonate telechelic natural rubber (CCTNR) were synthesized for the first time and used as precursors to synthesize a PU via non-isocyanate route. CCTPCL and CCTNR were successfully prepared in two steps from their hydroxyl-terminated functional group (PCL-OH and HTNR). The polyhydroxylurethane was successfully prepared from the polyaddition polymerization between CCTPCL and 1,4-butylenediamine. The polyurethane structure was confirmed by its FTIR spectrum, which showed that the cyclic carbonate group disappeared due to the reaction with amine, and the new peaks of urethane characteristics were observed.

This research work produced novel bio-based polyurethane from natural rubber and poly(ε-caprolactone). The obtained PU featured mechanical properties in the same range of the commercial polyurethane. This PU exhibited both rubber-like and plastic-like behavior depending on its composition.

A possible extension of this work is the development of the novel bio-based polyurethane in other applications such as in foam formulations. Foam is widely used in the majority of polyurethane such as flexible, semiflexible and rigid foams. In addition, the synthesis method of non-isocyanate PU should be further developed and full characterization of mechanical and thermal properties of resulting PU should be carried out. Preliminary tests on the biodegradability of few selected PUs have been recently started, using lipase type enzymes or a bacteria slurry coming from a wastewater plant. The results are not reported in this PhD dissertation; however they show a slow degradation of the natural rubber-PCL based PU, which suggests applications in which a slowly degradable material is required. Further studies of the PU degradation in terms of biological, physical and chemical depolymerization will be carried out, with the objective to recover and reuse the fragments coming from the NR segments.

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Publications:

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Wannarat Panwiriyarat, Varaporn Tanrattanakul, Jean-françois Pilard, Pamela Pasetto and Chuanpit Khaokong. 2012. Effect of natural rubber and poly(ε-caprolactone) content on mechanical and thermal properties of novel biodegradable Polyurethane, Advance Science Letters 19(3), 1016-1020.

Wannarat Panwiriyarat, Varaporn Tanrattanakul, Jean-François Pilard, Pamela Pasetto and Chuanpit Khaokong. 2012. Preparation and properties of bio-based polyurethane containing polycaprolactone and natural rubber, the Journal of the Polymer and Environment, on accepted.

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Wannarat Panwiriyarat, Varaporn Tanrattanakul, Jean-François Pilard, Pamela Pasetto and Chuanpit Khaokong. 2012. Effect of natural rubber and poly(ε-caprolactone) content on mechanical and thermal properties of the novel biodegradable polyurethane. International Conference on Bio-based Polymers and Composites 2012, Lake Balaton, Siófox, Hungary, May 27-31. (Oral)

Wannarat Panwiriyarat, Varaporn Tanrattanakul, Jean-François Pilard, Pamela Pasetto and Chuanpit Khaokong. 2012. Bio-based polyurethane made from toluene-2,4-diisocyanate, natural rubber and poly(ε-caprolactone) with high NCO:OH content: physical and thermal properties. Journées de l'École Doctorale 3MPL, JED2012, École des Mines de Nantes (EMN), Nantes, France, June 20-21. (Oral)

Wannarat Panwiriyarat, Varaporn Tanrattanakul, Jean-françois Pilard, Pamela Pasetto and Chuanpit Khaokong. 2012. Effect of natural rubber and poly(ε-caprolactone) content on mechanical and thermal properties of novel biodegradable Polyurethane. 2012 International Conference on Advances in Materials Science and Engineering (AMSE 2012), President Palace Hotel, Bangkok, Thailand, September 27-28. (Oral)