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LE MANS UNIVERSITE ET PRINCE OF SONGKLA UNIVERSITY COMUE UNIVERSITE BRETAGNE LOIRE

ECOLE DOCTOBALE N° 596 Matière Molécules et Matériaux Spécialité : Sciences des Matériaux

# Par Nathapong SUKHAWIPAT

# Synthesis of Natural Rubber Based Cationic Waterborne Polyurethane **Dispersion for Adhesive Applications**

Thèse présentée et soutenue à Hat Yai, Songkhla, Thailand, le 20 Juillet 2018 Unité de recherche : Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University 15 Karnjanavanich Rd., Hat Yai, Songkhla 90110, Thailand

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propriétés adhésives sur support cuir

**Mots clés :** Caoutchouc naturel, Caoutchoucs liquides hydroxytéléchélique, Cationiques waterborne polyurethane, Adhésifs

Résumé : Synthèse de nouveaux WPU (waterborne polyurethane) cationiques à partir du caoutchouc naturel (NR), et évaluation de leurs propriétés adhésives pour des surfaces de type cuir. Ces WPU ont été obtenus par reaction du caoutchouc liquide hydroxy téléchélique (HTNR), de toluene-2.4diisocyanate (TDI), N-methyl diethanol amine (NMDEA, en tant qu'émulsifiant) et d'ethylene glycol (EG, extenseur de chaîne). Ces structures biosourcés sont développés comme alternatives aux WPU issus des ressources fossiles à fort impact environnemental.Les effets de cinq paramètres ont été étudiés, à savoir la quantité d''émulsifiant (de 0 à 2,25 mole), celle d'éthylène glycol (de 0 à 3 moles), le Mn du HTNR (de 100 à 3000 g.mole<sup>-1</sup>), l'indice NCO (de 100 à 150) et le taux d'époxydation des HTNR précurseurs (de 0 à 30%).

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Il a été en outre démontré que la stabilité des dispersions aqueuses pour les formulations optimales dépassait les 10 mois. La géométrie des particules dispersées a été étudiée, démontrant un aspect sphérique et une taille à l'échelle nanométrique. Ainsi, plusieurs facteurs ont été étudiés pour évaluer les propriétés adhésives optimales sur bandes de cuir (Mn, pourcentage d'époxyde). Des tests standard (Peel test et Lap Shear test) ont été utilisés et les valeurs obtenues comparées avec celles issus de formulations adhésives commerciales avec ou sans solvants. Au bilan, une formulation optimale a été déterminée (Mn = 3000 g.mole-1, LR epoxydation = 10%, NMDEA 5.67% wt, NCO index de 100 et 1 mole d'EG) avec cuisson préalable des systèmes à 70°C. Ce WPU a montré une force d'adhésion supérière à toutes les formulations commerciales testées.

Le Mans

Université

Title : Synthesis of natural rubber based cationic waterborne polyurethane dispersion for adhesive applications

Keywords : Natural rubber, liquid Natural rubber, Cationic waterborne polyurethane, Adhesive

**Abstract :** Novel cationic waterborne polyurethane (cWPU) based on natural rubber (NR) have been prepared by the polymerization reaction of hydroxyl telechelic natural rubber (HTNR), toluene-2,4diisocyanate (TDI), N-methyl diethanol amine (NMDEA, as emulsifier), and ethylene glycol (EG, chain extender). The polyol structures have been developed as alternative to produce cWPUs derived from a renewable resource. The effects of five parameters were studied - amount of NMDEA (0 -2.25 mole), amount of EG (0 - 3 mole), molecular weight of HTNR (~1000 – 3000 g.mole<sup>-1</sup>), NCO index (100 - 150), and epoxide content on eHTNR soft segment (0 - 30%). The appearance of cWPU dispersion was milky-blue with long shelf life time, more than 10 months.

Particle of prepared cWPU were spherical shape in the nano range size. The adhesive properties of cWPUs on the real leather surface, taking into account of the different molecular weights of HTNR and different degree of epoxide content on HTNR, were tested by lap shear test and 180 degree peel test and compared with commercial adhesives. Overall, to balance the stability and adhesive strength, the best conditions for preparing cWPU adhesive for leather application in this study was from the composition of HTNR3000 with epoxide content of 10%, NMDEA 5.67%wt, NCO index of 100 and 1 mole of EG. in condition of curing at 70 °C. In comparison to nonsolvent based and solvent based commercial adhesives. the adhesive strengths of these synthesized cWPU adhesive were superior.

Titre de la thèse	Elaboration de Waterborne Polyurethane cationiques à partir de
	caoutchouc naturel; évaluation de leurs propriétés adhésives sur
	support cuir
Auteur	Mr. Nathapong SUKHAWIPAT
Spécialité	Sciences des Matériaux

### ABSTRACT

L'objectif de ce travail concerne la synthèse de nouveaux WPU (waterborne polyurethane) cationiques à partir de caoutchouc naturel (NR), et l'évaluation de leurs propriétés adhésives pour des surfaces de type cuir. Ces WPU ont été obtenus par action de caoutchouc liquide hydroxy téléchélique (HTNR), de toluene-2,4-diisocyanate (TDI), *N*-methyl diethanol amine (NMDEA, en tant qu'émulsifiant) et d'ethylene glycol (EG, extenseur de chaîne). Ces structures biosourcés sont développés comme alternative aux WPU issus des ressources fossiles à fort impact environnemental.

La première étape de la synthèse a consisté à préparer les oligoisoprènes téléchéliques (HTNR), à partir de caoutchouc naturel de haute masse par coupure oxydante des insaturations, suivie dans une seconde étape de la réduction des fonctions carbonyles d'extrémité de chaine. Les structures chimiques différentes ont été obtenues de manière contrôlée grâce à la maîtrise du processus de scission oxydante des insaturations présentes dans la chaines des polymères de départ. Les caoutchouc liquides obtenus ont été caractérisés selon différentes méthodes spectroscopiques, spectrométriques (FTIR, NMR, MALDI-TOF MS) et chromatographique (SEC). Leurs propriétés thermiques ont été évaluées par TGA et DSC. Des oligomères HTNR de masse 1000, 2000 et 3000 g.mole<sup>-1</sup> on été ainsi obtenus

La seconde étape du travail a consisté à préparer les émulsions cWPU à partir des oligomères précédents avec un TSC contrôlé de 20%. Les effets de cinq paramètres ont été étudiés, à savoir la quantité d'émulsifiant (de 0 à 2,25 mole), celle d'éthylène glycol (de 0 à 3 moles), le Mn du HTNR (de 100 à 3000 g.mole<sup>-1</sup>), l'indice NCO (de 100 à 150) et le taux d'éposydation des HTNR précurseurs (de 0 à 30%). La microstructure des cWPU a été confirmée par RMN et FTIR. . Il a été en outre démontré que la stabilité des dispersions aqueuses pour les formulations optimales

dépassait les 10 mois. La géométrie des particules dispersées a été étudiée, démontrant un aspect sphérique et une taille d'une échelle nanométrique. Les propriétés de surface mais aussi mécaniques des films cWPU obtenus à partir de ces émulsions (balance hydrophile/hydrophobe, hydrophilie de surface, énergie de surface) ont été évaluées. Leur morphologie a été caractérisées par TEM et SEM. Les propriétés thermiques ont été par ailleurs étudiées par analyse TGA, DSC et DMTA. Enfin, les propriétés mécaniques des films ont pu être améliorées en augmentant le rapport segment dur/segment souple, l'indice NCO, la concentration en extenseur de chaîne et le pourcentage de fonction époxyde sur la chaîne oligoisoprénique.

La troisième étape du travail réalisé s'est particulièrement focalisée sur l'étude des propriétés d'adhésion des formulations. Ainsi, plusieurs facteurs ont été étudiés afin d'évaluer les propriétés adhésives optimales sur bandes de cuir (Mn, pourcentage d'époxyde). Deux tests spécifiques standardisés (Peel test et Lap Shear test) ont été utilisés et les valeurs obtenues comparées avec celles issus de formulations adhésives commerciales (adhésifs commerciaux avec ou sans solvants). En outre les effets de cuisson (à température ambiante et 70°C) ont aussi été étudiés. Au bilan, une formulation optimale a été déterminée (Mn = 2000 g.mole<sup>-1</sup>, LR epoxydation = 10%, NMDEA 5.67%wt, NCO index de 100 et 1 mole d'EG). De surcroît il apparaît qu'une cuisson préalable des systèmes à 70°C augmente considérablement la force d'adhésion, au-delà de ce que peuvent démontrer toutes les formulations commerciales testées.

Mots clés : Caoutchouc naturel, Caoutchoucs liquides hydroxytéléchéliques, cWPU, adhésifs.

Thesis Title Synthesis of natural rubber based cationic waterborne polyurethane dispersion for adhesive applications
Author Mr. Nathapong SUKHAWIPAT
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### ABSTRACT

The aim of this work is to synthesize novel cationic waterborne polyurethane (cWPU) based on natural rubber (NR) by the polymerization reaction of hydroxyl telechelic natural rubber (HTNR, soft segment), toluene-2,4-diisocyanate (TDI, hard segment), *N*-methyl diethanol amine (NMDEA, an emulsifier), and ethylene glycol (EG, chain extender). The main target application of this work is for real leather adhesive.

In the first approach, NR had been modified to prepare polyol substrates, named HTNR, for polyurethane preparation to reduce the use of fossil fuel based polyols. By the semi-solution process, HTNR was successfully prepared from NR by controlling epoxidation and selective cleavage oxidation reaction followed by reduction reaction. The different chemical structures and microstructure of these oligomers were defined by FTIR, NMR, MALDI-TOF MS and SEC. Their thermal properties were studied by TGA and DSC. The expected molecular weight of HTNR for 1000, 2000, and 3000 g.mole<sup>-1</sup> was calculated the molecular weight by <sup>1</sup>H NMR which was about 950, 1800, and 2820 g.mole<sup>-1</sup> with well-controlled reaction and reproducibility.

In the second approach, well-defined natural rubber based cWPU was synthesized by normal stepgrowth polymerization with controlled total solid content (TSC) about 20%. The effects of five parameters were studied – amount of NMDEA (0 – 2.25 mole), amount of EG (0 – 3 mole), molecular weight of HTNR (~1000 – 3000 g.mole<sup>-1</sup>), NCO index (100 – 150), and epoxide content on eHTNR soft segment (0 – 30%). The chemical structures of prepared cWPUs were confirmed by FTIR and NMR. Hydrophobic/hydrophilic properties, surface wetting, and surface energy of cWPU were measured by contact angle. The mechanical properties of the films were investigated by tensile testing machine. Also, morphology of cWPU were characterized by TEM and SEM. In addition, their thermal properties were studied by TGA, DSC and DMTA. In this work, the appearance of cWPU dispersion was milky-blue with long shelf life time more than 10 months. Particle size of prepared cWPU were spherical shape in nano range (70 - 300 nm). The mechanical properties were improved by increasing hard segment – decrease of molecular weight of HTNR, increase of NCO index, increase of epoxide content on HTNR backbone especially increase of EG content. Similarly, thermal properties of the cWPU were improved by increasing hard segment. Moreover, the surface energy and surface wetting values was also increased by increasing hard segment part.

Finally, the adhesive properties of cWPUs on the real leather surface in account of the different molecular weights of HTNR and different degree of epoxide content on HTNR were tested. Lap shear test and 180 degree peel test were investigated and compared with commercial adhesives – solvent, and non-solvent based adhesive. Also, temperatures of curing adhesive were also studied at room temperature and 70 °C. The best adhesive from the effects of molecular weight of HTNR was for cWPU from HTNR2000 and the best adhesive from the effects of epoxide content was cWPU from eHTNR10. In addition, adhesive strength in condition of curing at 70 °C is higher than adhesive strength in condition of curing at room temperature because of chemical bonding occurred during the assembly process was aroused. In comparison to non-solvent based commercial adhesive, the adhesive strengths of these synthesized cWPU adhesive were stronger than standard commercials. Overall, to balance the stability and adhesive strength, the best condition for preparing cWPU adhesive for leather application in this study is from the composition of HTNR3000 with epoxide content of 10%, NMDEA 5.67%wt, NCO index of 100 and 1 mole of EG.

**Keyword:** natural rubber, hydroxyl telechelic natural rubber, epoxide, cationic waterborne polyurethane, adhesive, lap shear test, peel test

ชื่อวิทยานิพนธ์	การสังเคราะห์น้ำยางพอลิยูริเทนชนิดประจุบวกจากยางธรรมชาติ
	สำหรับประยุกต์ใช้เป็นกาว
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สาขาวิชา	วิทยาศาสตร์และเทคโนโลยีพอลิเมอร์
ปีการศึกษา	2560

### บทคัดย่อ

วัตถุประสงค์ในงานวิจัยครั้งนี้ คือ การสังเคราะห์น้ำขางพอลิยูรีเทนประจุบวก ระบบน้ำชนิดใหม่จากขางธรรมชาติ โดยเตรียมจากปฏิกิริยาการเกิดพอลิเมอร์ระหว่างขางธรรมชาติ ที่มีหมู่ปลายสายโซ่เป็นไฮดรอกซิล (ส่วนนิ่ม) โทลูอีน-2,4-ไดไอโซไซขาเนต (ส่วนแข็ง) *เอ็น-*เมทิล ไดเอทานอลเอมีน (ตัวกระจายเนื้อเดียวกัน) และเอทิลีนไกลกอล (สารขยายสายโซ่) โดยน้ำขางพอลิ ยูรีเทนที่เตรียมได้ในงานวิจัยนี้ เพื่อใช้ประโยชน์เป็นกาวระบบน้ำสำหรับติดหนัง

งานวิจัยนี้ประสบความสำเร็จในการเครียมสารตั้งด้นพอลิออลจากขางธรรมชาติสำหรับสังเคราะห์ พอลิขูรีเทนเพื่อใช้ทดแทนพอลิออลจากแหล่งปีโตรเลียมด้วยวิธีการเตรียมแบบกึ่งสารละลายแบบ ควบคุมการตัดโมเลกุลของสายโซ่ขางธรรมชาติ โดยผ่านปฏิกิริยาอีพอกซิเดชันที่มีการควบคุมแล้ว ตัดสายโซ่ตำแหน่งหมู่อีพอกไซค์ ตามด้วยปฏิกิริยารีดักชันเพื่อให้ได้ขางธรรมชาติที่มีหมู่ปลายสาย โซ่เป็นไฮครอกซิล ผลิตภัณฑ์ที่เตรียมได้มีโครงสร้างทางเคมีและขนาดที่แตกต่างกัน โดยสามารถ วิเคราะห์ด้วยเทคนิลฟลูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปลโทรมิเตอร์ นิวเคลียร์แมกเนติกเร โซแนนซ์ โครมาโทกราฟีแบบคัดขนาด และมัลดิทอฟ-ทอฟ แมสสเปลโตรมิเตอร์ รวมทั้งวิเคราะห์ สมบัติทางความร้อนด้วยเครื่องวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยคุณสมบัติทาง ความร้อน และเครื่องดิฟเฟอเรนเซียลสแกนนิงแคลอริมิเตอร์ โดยน้ำหนักโมเลกุลของพอลิออลจาก ยางธรรมชาติที่ต้องการเตรียมที่ 1000 2000 และ 3000 กรัม/โมล สามารถเตรียมได้ที่ 950 1800 และ 2800 กรัม/โมล โดยสามารถทำการเตรียมซ้ำและมีเปอร์เซ็นต์ผลผลิตที่สง

นอกจากนี้ ยังประสบความสำเร็จในการเตรียมพอลิยูรีเทนประจุบวกระบบน้ำโดยใช้พอลิออลจาก ยางธรรมชาติโดยเตรียมจากปฏิกิริยาการเกิดพอลิเมอร์แบบขั้นและควบคุมปริมาณของแข็งทั้งหมด ที่ 20 เปอร์เซ็นต์ งานวิจัยนี้ได้ทำการศึกษาอิทธิพลของตัวแปรต่างๆ ดังนี้ ศึกษาปริมาณตัวกระจาย เนื้อเดียวกัน (0 – 2.25 โมล) ปริมาณของสารขยายสายโซ่ (0 – 3 โมล) อิทธิพลของน้ำหนักโมเลกุล ของยางธรรมชาติที่มีหมู่ปลายสายโซ่เป็นไฮครอกซิล (~1000 – 3000 กรัม/โมล) ดัชนีไอโซไซยา เนต (100 – 150) และปริมาณอีพอกไซด์ในโครงสร้างของยางธรรมชาติที่มีหมู่ปลายสายโซ่เป็นไฮ ครอกซิล (0 – 30 %) ผลิตภัณฑ์พอลิยูรีเทนประจุบวกระบบน้ำที่เตรียมได้นำไปวิเคราะห์ผลต่างๆ ในส่วนระบบน้ำยางและในส่วนของฟิล์ม ดังนี้ วิเคราะห์โครงสร้างทางเคมีด้วยเทคนิคฟลูเรียร์ ทรานส์ฟอร์ม อินฟราเรคสเปกโทรมิเตอร์ และนิวเคลียร์แมกเนดิกเรโซแนนซ์ สมบัติกวามชอบน้ำ/ ไม่ชอบน้ำ การเปียกผิว พลังงานพื้นผิวด้วยเทคนิกการวัดมุมสัมผัส ทคสอบแรงดึงของฟิล์มด้วย เกรื่องทคสอบแรงดึง ลักษณะทางสัณฐานวิทยาด้วยกล้องจุลทรรศน์แบบส่องกราคและกล้อง จุลทรรศน์แบบส่องผ่าน นอกจากนี้ยังศึกษาสมบัติทางความร้อนด้วยเกรื่องวิเคราะห์การ เปลี่ยนแปลงน้ำหนักของสารโดยอาศัยกุณสมบัติทางความร้อน ดิฟเฟอเรนเชียลสแกนนิงแคลอริ มิเตอร์ และเกรื่องวิเคราะห์สมบัติทางกวามร้อนของวัสดุเชิงกล พอลิยูรีเทนประจุบวกระบบน้ำที่ เศรียมได้ เป็นสีขาวน้ำนมขอบฟ้าลักษณะอนุภาคของสารที่เตรียมได้มีเป็นทรงกลม มีขนาดอยู่ ในช่วงนาโนเมตรและมีการกระจายตัวที่ดี รวมทั้งมีอายุการเก็บรักษามากกว่า 10 เดือน จากผลการ ทดลองพบว่า สมบัติเชิงกล สมบัติทางกวามร้อน รวมทั้งสมบัติความเปียกผิวจะเพิ่มขึ้นเมื่อเพิ่ม สัดส่วนของส่วนแข็งเพิ่มขึ้น โดยการลดน้ำหนักโมเลกุลของยางธรรมชาติที่มีหมู่ปลายสายไซ่ เป็นไฮดรอกซิล การเพิ่มดัชนีไอโซไซยาเนต การเพิ่มปริมาณหมู่อีพอกไซด์บนโครงสร้างของยาง ธรรมชาติที่มีหมู่ปลายสายไซ่เป็นไขลรอกซิล และดัวแปรที่มีอิทธิพลต่อสมบัติของพอลิยูรีเทนประ จุบวกระบบน้ำมากที่สุดคือ การเพิ่มปริมาณสารขยายสายไซ ่เต่อย่างไรก็ตามสัดส่วนที่เพิ่มขึ้นของ

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### LIST OF ABBREVIATIONS

### ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflection Fourier-transform Infrared
CTNR	Carbonyltelechelic Natural Rubber
cWPU	Cationic Waterborne Polyurethane
DMTA	Dynamic Mechanical Thermal Analysis
DRC	Dry Rubber Content
DSC	Differential Scanning Calorimeter
eHTNR	Epoxidized Hydroxytelechelic Natural Rubber
EG	Ethylene Glycol
ENR	Epoxidized Natural Rubber
GPC	Gel Permeation Chromatography
HTNR	Hydroxytelechelic Natural Rubber
MALDI-TOF MS	Matrix Assisted Laser Desorption Time of Fight Mass
	Spectroscopy
NCO index	Isocyanate Index (The ratio of NCO/OH)
NMDEA	N-Methyldiethanolamine
NMR	Nuclear magnetic resonance
NR	Natural rubber
PDI (Đ)	Polydispersity index
SEC	Size exclusion chromatography
TDI	Toluene-2,4-diisocyanate
TGA	Thermogravimetric Analyzer
$T_g$	Glass transition temperature
$T_{max}$	Maximum temperature
TSC	Total solid content
rpm	Round Per Minute

#### **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Introduction**

In general, polyurethane is materials that compose of the hard segment from the diisocyanate and the soft segment from polyols [1]. Polyol soft segment is one of a vital part in polyurethane adhesive and the properties of polyurethane can be decided by this part. Typically two sources of the polyol are used in cWPU work; natural [2-5] and petroleum source [6-9]. Most polyols used for polyurethane preparation come from petroleum sources in the class of polyether and polyester which are very stressed against the environment and body toxicity. To reduce the use of fossil fuel based polyols, there are many investigation trying to modify plant oil from natural based cWPU such as soybean oil suppress [2, 4], unfortunately physical and mechanical properties were limited due to low molecular weight that acquire polyure than foam or low-elastic polyure than [10] due to obtained short soft segment in polyurethane. To overcome drawback, our group focus is attention on other natural polymer source such as natural rubber, once of renewable and green material which was demonstrated to be modified via reactive double bond along the molecular chain of cis-1.4polyisoprene [11] which can be break to be hydroxyl group [12] and it has good elastic properties from *cis*-1,4-polyisoprene structure [13]. Moreover, this material possesses excellent physical properties, especially high mechanical and tear strength, remarkable elastic behavior, which have not yet been completed by synthetic elastomers [11, 14]. There are many works reported by our research group about WPU from natural rubber [15-18]. Several researches has been reported about telechelic cis-1,4-oligoisoprenes from NR, and there are many techniques on the degradation of synthesis and natural rubber such as redox method [19], ozonolysis oxidation method [20], oxidation at high temperature and pressure method [21], photochemical method [22], metathesis reaction [23], and chemical oxidation reaction [11, 24, 25]. With well-controlled method with high selectivity and repeatability, the chemical oxidation reaction was modified to prepare the natural rubber telechelic substrate for the further step of polyurethane preparation. The structures and properties of telechelic cis-1,4-oligoisoprenes, as well as additional chemical transformations resulting in isoprene oligomers that deserve to use as soft segment in good properties of polyurethane. Polyurethane base on natural rubber had been reported in many applications across

virtually all fields: flexible polyurethane foam [11], coatings [13], adhesives [13], sealants and elastomers [26], thermoplastic polyurethane (TPU) [27] and waterborne polyurethane dispersions (PUDs) [15, 16].

Presently, polyurethane adhesives are mostly found in household products and daily applications because of their distinctive adhesive properties on the account of strong physical bonding through Van der Waals forces, low surface energy, hydrogen bonding, and inter- and intrachain of polymer while chemical bonding through interaction of reactive functional group on PU structure and the substrates, low viscosity, and diffusion into porous substrates [28]. Conventionally, PU adhesives are contained with 40 - 60% volatile organic solvents, which is mostly used for stabilizing its system to be used for long shelf-life [1, 29, 30]. These solvents are hazardous and directly origin of irritation for eyes, nose, dizziness, throat, and headache. Moreover, it is the major cause of criteria air pollutant to environmental problems [31, 32]. In this decade, waterborne polyurethane (WPU) or polyurethane dispersion are found to be of high interest in replacing conventional PU adhesives because of environmentally friendly, easy to handle and nontoxic compared to the conventional polyurethane. There are three different classes of WPU cationic, anionic, and nonionic - depending on the neutralized charge of emulsifier inserted into the system. The main structures of polyurethane are similar but for the WPU there are specific emulsifiers. Meaning of cationic and anionic WPU is always composed of internal emulsifier while nonionic emulsifier is composed of external emulsifier. For example, anionic WPU (aWPU) is usually composed of 2,2-dimethylolpropionic acid (DMPA) [16, 33-35], cationic WPU (cWPU) is usually composed of N-methyldiethanolamine (NMDEA) [2, 3, 7, 15, 36], and nonionic WPU is mostly used glycol class such as poly(ethylene glycol) [37]. This work focused on the development of cWPU due to their high adhesive potential on various anionic substrates such as textiles, paper, leather, polymers and glass [8, 38]. High adhesion of cWPU adhesive can not only be explained from physical and mechanical bonding of WPU main chain but it can also be due to statistic force from anionic on the substrate surfaces and cationic charge in the main chain of cWPUs. Therefore, this work concentrates on the synthesis of cWPU added and study of its adhesive properties. In this decade, advance adhesive applications for the real leather product is attentive because real leather is widely used in many routine applications including shoes, garments, bags, furniture. In addition, real cow leather is a unique material and cannot be compromised with synthetic materials [39, 40]. Normally the assembly of leather products in the industrial sector is mostly used solvent based glue. To be better in cooperation and sustainable, this present work studies the possibility to replace of solvent based adhesive to water based adhesive by using synthesized cWPUs on real cow leather and maybe apply on other substrates.

Generally, good thermoset adhesives obtained from acrylates, epoxy resin and polyurethane [41]. Due to the reactive groups on the main structure, physical bonding between the polymer main chains and also chemical bonding occurred during adhesive application, many research groups try to insert acrylates and epoxy group into WPU structures to gain better adhesion. State-of-the-art, there are many processes to improve adhesive strength and mechanical properties of WPU adhesives. First of all, previous research had reported that one of the parameters having effects on PU film properties and adhesive properties is  $M_{\mu}$  of the polyol and polymer [42-46]. In addition, polymer main chain structure modified by grafting with reactive group effected for adhesive improvement is one of interesting. Acrylate is effective reactive group mostly used to be grafted agent on WPU adhesive. Alvarez et al. [47] reported that the adhesive properties of WPU were improved by grafting with bisphenol A-glicidylmethacrylate (Bis-GMA). The adhesion of the hybrid polyurethane improves by adding Bis-GMA, even in small amounts. Yong et al. [48] grafted WPU with hydroxypropyl acrylate to improve the adhesion. It was reported that the resultant WPU films possessed the good hardness and good adhesion strengths. However, grafting method is very complicated and use too much time and chemical agents are not environment friendly. Other techniques are added the nano scale reinforcing agents into the WPU system, but there is some limitations to use and storage time [49, 50]. For epoxy resin, it is a good adhesive by showing high elongation, high toughness, and high strain rate because of distinguishing structure and a reactive group, but it is mostly stable in only solvent based, difficult to handle and short lifetime [51-54].

Consequently, this research shed new light on the synthesis novel natural rubber based cationic waterborne polyurethane dispersion and to apply the prepared cWPU for adhesive applications to added-value of NR. The scopes of this work are divided into three main parts for studying covering all parameters. In the first part, hydroxyl telechelic natural rubber (HTNR) is prepared and characterized in three ranges of molecular weight; approximately 1000, 2000, and 3000 g.mole<sup>-1</sup>. In the second part, the parameters effected on cationic waterborne polyurethanes are studied. The amount of emulsifier (from 0 - 2.25 mole), the amount of chain extender (0 - 3

mole), molecular weight of HTNR ( $1000 - 3000 \text{ g.mole}^{-1}$ ), the isocyanate index (100 - 175), and amount of epoxide content on HTNR backbone (0 - 30%) are synthesized and investigated. In the third part, the cWPU adhesives are applied and corrected the result on real cow leather by Lap shear test and Peel test.

### **1.2 Objectives**

- 1.2.1 To synthesize the novel cationic waterborne polyurethane based on natural rubber
- 1.2.2 To study the preparation, characterization and properties of novel cationic waterborne polyurethane based on natural rubber
- 1.2.3 To apply cationic waterborne polyurethane based on natural rubber for adhesive applications

### 1.3 Scope of this work

1.3.1 Preparation and structural characterization of hydroxyl telechelic natural rubber (HTNR) effected of its molecular weight on polyurethane waterborne properties

1.3.2 Investigation on effects of parameters of the amount of emulsifier, the amount of chain extender, molecular weight of HTNR, isocyanate index, and epoxide content on HTNR substrates

1.3.3 Adhesive properties to be investigated; Peel test and Lap shear test

#### **CHAPTER 2**

#### LITURATURE REVIEW

#### 2.1 Introduction of Natural Rubber

Natural rubber (NR) contains about 94% polyisoprene in almost 100% cis-1,4-configuration. Additionally, the remainder consists of protein and lipids in a series of phospholipids, esters of higher fatty acids and sterols. Recent evidence suggest that NR has been known as highly cis-1,4polyisoprenic structure which is easily oxidized due to having reactive double bond along the molecular chain [11]. The structure of natural rubber is shown Figure 2.1. Considering all of this evidence, this material possesses excellent physical properties, especially high tensile and tear strength, remarkable elastic behavior, which have not yet been competed by synthetic elastomers because natural rubber is normally composed of regular cis-1,4- configuration structure and semicrystallize when this isoprenic polymer is drawn. Consequently, natural rubber is used in over 40,000 products, including more than 400 medical devices, surgical gloves, aircraft tires and countless engineering and consumer products [55, 56]. There are many novel applications of natural rubber based such as adhesive, coating, additive or substrate for novel polymer. Over 90% of natural rubber is produced in Asia, particularly in Malaysia, Indonesia and Thailand [57]. Especially, the static data of the natural rubber of world static collected by Malaysia Rubber Board show that raw natural rubber was exported from Thailand more than 50% of all [58]. From this data, Thailand is the country that can produce mass raw natural rubber and export to many countries that can produce products. However, the exported values are too low. Therefore, we interested to use natural rubber to added-value, so we need to prepare them to be the product before export them into the world trade. Extensive research has shown that rubber give better value compared with raw natural rubber. One of the interesting is to produce cationic waterborne polyurethane base on natural rubber.

To reduce polyols segment in polyurethane manufacture from petroleum resource, many research groups are interested in materials come from natural. They found that natural rubber is an interesting source that can be modified to become a reactive hydroxyl polymer [11] because it has the reactive double bond which can be break to obtain hydroxyl group [12] and it has good elastic

properties from *cis*-1,4-polyisoprene structure to improve mechanical properties of polyurethane [13].

In this research provides new insights into synthesis cWPU based on natural rubber for the adhesive applications.



Figure 2.1 Structure of natural rubber (cis-1,4-polyisoprene).

### 2.2 Telechelic natural rubber (TNR)

Liquid NR produced by *Hevea brasiliensis* tree is an important renewable natural polymer and can be modified to be the telechelic polymer that use as novel polymer based. In term of "telechelic polymer", Uraneck *et al.* [59] originally defined that oligomer having two functional terminal groups. From definition of telechelic polymer, "telechelic natural rubber" can be referred to oligomer natural rubber with range of molecular weight from 100 to 10000 g.mole<sup>-1</sup> and having two or more functional reactive end-group terminated on oligomolecule [56]. They were obtained from degradation process of natural rubber by cleavage of *cis*-1,4-polyisoprene double bond. This degradation technique is not deteriorated the nature of *cis*-1,4-polyisoprene structure but only reduces the molecular weight of natural rubber and made the new reactive group on the chain side after breaking the chain. There are two TNRs: example of hydroxyl telechelic natural rubber (HTNR) and carbonyl telechelic natural rubber (CTNR). The structure of telechelic natural rubber is shown in **Figure 2.2.** When **X** and **Y** are reactive end group on *cis*-1,4-polyisoprenic chain, and **n** is in the range of 2 to 150 with low molecular weight, respectively.

To prepare polyurethane, HTNR is interesting to prepare as the soft segment having reactive terminal group.


Figure 2.2 Structure of telechelic natural rubber.

## 2.2.1 Preparation of TLNR

To prepare telechelic *cis*-1,4- oligoisoprenes, many researchers use both of natural rubber and synthetic rubber to prepare them. In the interesting point of all researchers, they bring together the key information in the published literature on the degradation of synthesis and natural rubber, emphasizing metathesis reactions, oxidative damage and break of the double bonds.

### 2.2.1.1 Redox method

Nor and Ebdon [19] have collected the redox method to produce the telechelic natural rubber. This method is mostly used mixture of the couple of oxidizing agent and reducing agent to cleavage the double bond of natural rubber and introduces the terminal chain of the back bone. Such oxidizing agents are organic peroxide, hydrogen peroxide, oxygen atmosphere or ferric chloride-oxygen that couple with aromatic hydrazine or sulphanillic acid as reducing agent. The terminals of product are obtained with carbonyl or hydroxyl group that depend on the types of redox system with the molecular weight of 3000-35000 g.mole<sup>-1</sup> and polydispersity index less than 2. The mechanism of example of couple of oxygen and phenylhydrazine is shown in **Figure 2.3**.



Figure 2.3 The mechanism of redox reaction of natural rubber by the couple of oxygen and phenylhydrazine [19].

## 2.2.1.2 Oxidation reactions by ozone

Ozonolysis is used to break bond of NR to reduce it molar mass by ozone. In 2000, Nor and Ebdon [20] used an oxygen/ozone stream from ozonizer passed NR solution in chloroform at  $0^{\circ}$ C for process of degradation on NR structure. After the 1 minute of reaction, molar mass decreased to 5,390 g.mole<sup>-1</sup>, and it will be decreased close to 840 g.mole<sup>-1</sup> with the reaction time of 20 minutes.

From the FTIR results, they confirm the formation of hydroxyl, carbonyl and ester group in the products.

### 2.2.1.3 Oxidation reactions by chemical degradation

The structures and properties as well as additional chemical transformations resulting in isoprene oligomers, functionalized oligomers and polymers base on both are also described following the reaction in the **Figure 2.4** and **Figure 2.5**. In the last 2013, the whole oxidative degradations of NR were collected by Fainleib [12]. Basically interested in many research groups, they used acid and per acid to degrade NR. There are many methods can be prepared the degraded natural rubber by oxidation degradation. In 2000, Nor and Ebdon [20] prepared HTNR by using oxygen/ozone. Gillier-Ritoit *et al.* [24] compared the preparing oxidation degradation of H<sub>5</sub>IO<sub>6</sub> and *m*-chlorobenzoic acid/H<sub>3</sub>IO<sub>6</sub>. In 2003, LTNR from latex was prepared by CH<sub>3</sub>COOOH/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with catalyst of propanol by Klinklai *et al.* [14]. Degradation agent, *m*-chlorobenzoic acid/H<sub>5</sub>IO<sub>6</sub> was used as oxidative degradation agent in latex by Phinyocheep *et al.* [60]. H<sub>2</sub>O<sub>2</sub>/HCOOH/H<sub>5</sub>IO<sub>6</sub> was used as oxidative degradation agent in latex by Phinyocheep *et al.* [61] and Saetung *et al.* [11]. In all the studies reviewed here, the temperature, the time, and the mechanism of reaction are effected on degraded NR to be reactive end group on the chain of oligoisoprene. Collectively, these studies indicate that longer reaction and high temperature provided formation of lower molar mass product. The whole data are summarized in Table 1.



Figure 2.4 Oxidation process of NR latex by H<sub>5</sub>IO<sub>6</sub> [61].



Figure 2.5 Oxidation process of NR in dichloromethane by  $H_5IO_6$  [25].

# 2.2.1.4 Oxidation at high temperature and pressure

In the other methods for prepare telechelic natural rubber, Nor and Ebdon [19] have collected the method and result of Gupta *et al.* High temperature at 150  $^{\circ}$ C and high pressure at 200-300 psi containing 30-40% hydrogen peroxide were also used in the methods' Gupta *et al.* (1985) [21] to prepare HTNR. The results of these conditions are having a molecular weight in the range of 2500 and 3000 g.mole<sup>-1</sup> and average functionality of 1.4. This method was purposed mechanism as the **Figure 2.6**.



**Figure 2.6** The mechanism of natural rubber cleavage reaction by hydrogen peroxide under high pressure and high temperature [21].

## 2.2.1.5 Photochemical method

To cleavage covalent double bond of natural rubber, they need equivalent energy that leads to bond cleavage. In this point, natural rubber can be cleavage out and decreased the molecular weight of it by the energy of 200-400 kJ/mole under the light of ultraviolet in the range wavelength of 600-300 nm.

In 1998, Nor and Ebdon [19] have collected the results of the method's Cunnen that using the photochemical chain scission for preparation of telechelic natural rubber by irradiating with ultraviolet light composed with nitrobenzene as photosensitizer to obtain carbonyl telechelic oligomer having molecular weight about 3000 g.mole<sup>-1</sup>. The suggestion reaction was shown in **Figure 2.7**, but there was no more detail about the mechanism. After Ravindran *et al.* (1988) [22] reported that they prepared HTNR in toluene by ultraviolet light composed of hydrogen peroxide

as oxidizing agent and methanol or tetrahydrofuran media. The result showed that molecular weight of product in range of 5,000-8,700 g.mole<sup>-1</sup> with polydispersity index of methanol was less than tetrahydrofuran and the mechanism of this method was suggested in the **Figure 2.8**.



**Figure 2.7** The suggest reaction of cleavage natural rubber in the presence of nitrobenzene and irradiate with ultraviolet [19].



**Figure 2.8** Mechanism of natural rubber cleavage reaction by hydrogen peroxide under ultra violet light [22].

#### 2.2.1.6 Metathesis reactions

Metathesis reaction is the reaction with process of carbon-carbon double bond cleavage and reforming the structure by catalytically induced reaction. The reaction is widely induced by transition metal complexes. For the practical metal, catalyst of metathesis is mostly based on complex of tungsten, molybdenum or rhenium with co-catalyst of tin or aluminum alkyl compound. There are a few reports exist on this technique on natural rubber. For examples, bis(tricyclohexylphosphine) benzylidine ruthenium(IV) dichloride (first generation Grubbs catalyst) and tricyclohexylphosphine [1,3 - bis(2,4,6-trimethylphenyl) - 4,5 - dihydroimidazol - 2-ylidene] benzylidine ruthenium(IV) dichloride (second generation Grubbs catalyst) that were widely used to reduce the molar mass of natural rubber. In 2005, Solanky et al. [62] investigated a model polymer degradation reaction of Grubb's catalysts. The result of this study show the lowest molecular weight of oligomeric isoprene in range of 4,700-5,500 g.mole<sup>-1</sup> in case of second generation of Grubb's catalysts. To obtain lower molar mass of oligomeric isoprene from Grubb's catalysts, Gutiérrez et al. (2011) [63] used second generation of Grubb's catalysts cross-metathesis with  $\beta$ -pinene. The studies presented that their molar mass can be changed by the ratio of NR to eta-pinene and reaction time. The molar mass of oligomer was obtained in the range of 700-3000 g.mole<sup>-1</sup> and its reaction was shown in **Figure 2.9.** After the reducing molar mass, the product will be reacted to compose it as HTNR.



Figure 2.9 Metathesis degradation of NR using  $\beta$ -pinene as chain transfer agent [63].

In 2011, Saetung *et al.* [23] prepared  $\alpha, \omega$ -bistrithiocarbonyl-end functionalized telechelic *cis*-1,4-polyisoprene as TLNR by using new Ruthenium complex as the Grubbs II catalyst for the metathesis degradation reaction and using bistrithiocarbonyl-end functionalized olefin as chain transfer agent. This results showed that the degradation reaction occurred rapidly in a single step

and obtained the TLNR with the molecular weight of 8,200 g.mole<sup>-1</sup>. The purpose this TLNR product from the reaction with new Ruthenium complex is shown in **Figure 2.10**.



**Figure 2.10** Synthesis of  $\alpha$ , $\omega$ - bistrithiocarbonyl- end functionalized telechelic *cis*- 1,4- polyisoprene from NR *via* metathesis degradation with new Ruthenium complex [23].

The degradation of natural rubber is summarized in **Table 2.1**. In this research, we interested in the chemical oxidation degradation to prepare the HTNR in the combination of latex system and solution system for polyols based polyurethane.

Rubber	Degradation agent	Catalyst	Temperature of degradation, <sup>°</sup> C	Time of degradation	Highest molecular mass reached	Lowest molecular mass reached	Chemical structure and functional groups	Reference
NR	oxygen/ozone		0	20 min	5390	840	ozonide, peroxide, di- peroxide group	[20]
NR	H <sub>5</sub> IO <sub>6</sub>	-	30	6 h	9,032	4,135	isoprene unit, -OH, - C=O	[24]
	m-chlorobenzoic acid $/H_5IO_6$	-	30	6 h +6 h	7,760	3,320		
NR latex	H <sub>2</sub> O <sub>2</sub> /HCOOH/ H <sub>5</sub> IO <sub>6</sub>	-	30-60	30 h	11,000	4,500	isoprene unit, epoxy,- OH, -C=O, aldehyde	[11, 61]
NR latex	Peracetic acid/ (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Propanol	10	3 h	337,000	23,000	isoprene unit, epoxy group	[14]
NR	<i>m</i> -chlorobenzoic acid / $H_5IO_6$ and then reduce with NaBH <sub>4</sub>	-	30 - 60	6 h +6 h	5,350	2,900	isoprene unit, -OH, - C=O	[64]

**Table 2.1** Degradation processes by various methods and telechelic *cis*-1,4-oligoisoprene products obtained from natural rubber.

## 2.3 Hydroxyl telechelic natural rubber (HTNR)

In the period of polyurethane timeline, many researchers are finding out the new soft segment prototypes, polyols materials, to prepare novel structures and properties of polyurethane from natural resources replacing of polyols from petroleum resources. Therefore, in this period, new-oil and used-oil from vegetables or plants which are available hydroxyl polyols in the structure of its fatty acid [65, 66] and synthesis or natural rubber which can be modified by oxidation degradation to be HTNR are interested. The lower molecular mass of the oil limited the properties and performances of the polyurethane. Contrary, higher molecular mass of natural rubber can be varied the properties and performance of prepared polyurethane. From these reasons, natural rubber is an extensive interesting choice of natural polymer that can modify to become a reactive functional polymer before using it in part of polyurethane as soft segment. Many reactions on the reactive double bonds of isoprene structure along the molecular chain such as epoxidation, hydrogenation, graft copolymerization and oxidative degradation reaction as describe in the section of TLNR.

### 2.4 Polyurethane

### 2.4.1 History of polyurethane

Bayer *et al.* discovered first polyurethane since 1937 [10, 67]. The reaction between toluene diisocyanate and dihydric alcohol were used as early prototypes to obtain first crystalline polyurethane fibers. Polyurethane elastomers are developed to find the way for rubber replacement during the period of World War II and they were succeeded in 1940 that these materials could be used as alternative rubber [67].

Basically, polyurethanes are linear thermoplastic polymers that have to two sections, soft segment and hard segment. These polymers were usually formed by the polymerization reaction of two main block components: diisocyanate block and long chain diol block. In general, the formation reaction of the urethane group is shown in **Figure 2.11**.





From the nature structures of polyurethane, they are formed linear blocks polymeric chain, alternating two different segments in other main chain linked together by covalent bond forming a block copolymer to be polyurethane.

### 2.4.2 Raw material and resources

There are 3 main parts included in polyurethane preparation.

### 2.4.2.1 Isocyanate

There are specific class of diisocyanates that can be aromatic, aliphatic, cycloaliphatic or polycyclic such as xylene diisocyanate (XDI), *m*-tetramethylxylylene diisocyanate (TMXDI), hydrogenated xylene diisocyanate (HXDI), naphthalene 1,5-diisocyanate (NDI), *p*-phenylene diisocyanate (PPDI), 3,3' - dimethyldiphenyl- 4,4' - diisocyanate (DDDI), 1,6- hexamethylene diisocyanate (HDI), 2,2,4-trimethylhexamethylene diisocyanate (TMDI), isophorone diisocyanate (IPDI), 4,4'-dicyclohexylmethane diisocyanate (H12MDI), norbornane diisocyanate (NDI), 4,4'-dibenzyl diisocyanate (DBDI). Diisocyanate that mostly used for hard segment is in class of toluene

diisocyanate (TDI) and in class of polymeric diisocyanate (PMDI) [29, 30]. The structures of popular isocyanate are shown in Figure 2.12.



Figure 2.12 Common used diisocyanate in polyurethane synthesis.

## 2.4.2.2 Polyols

Polyols in polyurethane component can be used polyfunctional polyether, polyester polyols and others. These are form to be the soft segment in a part of polyurethane. These segments are formed by long-chain diols. Therefore, they are flexible at room temperature. Polyols from polyester and polyether are mostly used as soft segment.

In the present, many research groups are finding out to apply new polyols into the polyurethane synthesis process to replace of petroleum based polyols such as vegetable oil [2, 68] and telechelic natural rubber [23, 56, 60, 69]. In this research, we are interested in hydroxyl telechelic natural rubber or HTNR as soft segment in polyurethane synthesis process. The structure of HTNR isshown in **Figure 2.13**.



Figure 2.13 HTNR for polyurethane based natural rubber.

## 2.4.2.3 Additives

Some of polyurethane preparation, reactions are composed of additive that may be required during the production of polyurethane such as used to control the reaction, used to modify the reaction condition, and also used to modify the final properties of the product. These additive agents may be consisted of catalysts, fillers, crosslinkers, chain extenders, moisture scavengers, color agents and others.

### (1) Catalysts

Amine catalysts	<b>Property and Application</b>		
	Solid, soluble in water, glycols and		
Diaminobicyclooctane (DABCO)	polyethers. May be used in most types of		
	polyurethanes.		
N N N N N N Dentemathyldiathylana triamina	Liquid (light yellow). Flexible foams and		
	semi-rigid foams.		
	Liquid (an intense odour). Rigid foams,		
N,N-Dimethylcyclohexylamine	polyester-based flexible foams and some		
	semi-rigid foams.		
	Liquid. Polyester-based flexible foams, semi-		
<i>N,N</i> -Dimethylcetylamine	rigid foams and for prepolymer making		

Table 2.2 Available commercial amine catalysts and applications [70].

There are many mechanisms of added-catalyst system which are used to describe how the reactions go on and how the catalysts work on. The reaction with tertiary amine is shown in **Figure 2.14.** The reaction with metal salts is shown in **Figure 2.15.** In case of tin, there are two formed of tin which are tin (II) and tin (IV), and the mechanisms of all tins are shown in **Figures 2.16** and **2.17**, respectively.

Organometallic catalysts	<b>Property and Application</b>		
Starra a starta	Slabstock polyether-based flexible foams,		
Stannous octoate	moulded flexible foams.		
	Colorless solid, RIM, two-pot moulding		
Dibutyitin dilaurate	systems, elastomers.		
Dibutultin managati da	Excellent hydrolysis resistant catalyst for		
Dibutyitin mercaptide	storage stables two-pot systems.		
Dibutyltin thiocarboxylates and Dioctyltin	Delayed action (i.e.hindered) catalysts for RIM		
thiocarboxylates	and high resilience foams.		
Dhanylan anoysis anonismoto	Potting compounds, and can be used as a		
Phenylmercuric propionate	delayed action catalyst		
Lead octoate	Urethane chain extension catalyst		
	General catalysts for urethane reactions and for		
Alkali metal salts (e.g. potassium ethanoate	isocyanate polymerisation. Calcium carbonate		
and sodium carbonate)	catalyze urethane reaction and also increase cure		
	rate of polyurethane		

Table 2.3 Available commercial organometallic and metal salt catalysts and applications [70].



Figure 2.14 Mechanism of tertiary amine catalysed reaction [71].



Figure 2.15 Mechanism of metal salt catalysed reaction [71].



Figure 2.16 Mechanism for tin II salts catalyzed reaction [71].



Figure 2.17 Mechanism for tin IV salts catalyzed reaction [71].

## (2) Chain extenders

Chain extenders are difunctional substances, glycols, diamines or hydroxyl amine, short chain diols or amine such as ethylene glycol and ethylene diamine while cross linking agents have a functionality of three or more such as diethylene triamine and triethylene tetramine. The chain extender reacts with diisocyanates to form a polyurethane or polyurea to obtain the higher molecular weight of polymer [33].

In 2014, Lei *et al.* [34] prepared waterborne polyurethane dispersions with different chain extenders including ethylene diamine (EDA), diethylene triamine (DETA), and triethylene tetramine (TETA) for potential application in waterborne ink. Waterborne ink from polyurethane was revealed that the NCO/OH molar ratio of 1.6 was appropriate for the preparation of stable waterborne polyurethane dispersion with solid content of about 40 wt% and organic solvent content of 5 wt%. The chain extended polyurethane by EDA and DETA with a mole ratio of 2:3 showed excellent properties. EDA shows only effective chain extender while DETA and TETA show effective in both of chain extender and crosslinker.

### (3) Emulsifiers

Emulsifier is a molecule in which one end likes to be in an apart of one environment (soft segment) and the other part environment (hard segment) to make it as emulsion. By the theory, polyurethane backbone with the repeat units contains acid or tertiary nitrogen groups, which are completely neutralized or quarternized to form salts [32].

In case of waterborne polyurethane we interested, their structures are usually formed by the reaction of excess isocyanates and polyols or mixture of polyols to form prepolymer. The fact of polar functional groups capped in the polyurethane chain aids water solubility or water dispersibility of polyurethane that best known in the group of carboxylic acid, sulfonic acid and tertiary amine. The concentration of functional groups in the polyurethane backbone is highly effective in solubility or dispersibility potentials in water.

Waterborne polyurethane divided by emulsifier substitution can be divided into two classes. The first class consists of polymers stabilized by external emulsifiers and the second one consists of internal emulsifier, achieved stabilization by including hydrophilic centers in the polymer. There are three classes of hydrophilic group: non-ionic, cationic groups and anionic groups. These groups are as emulsifiers and produce stable water based emulsions. In principle may be used one from 3 groups [32]:

Nonionic groups: for example; polyethylene oxide chains Cationic groups: for example; alkylated or protonated tertiary amines Anionic groups: for example; carboxylate or sulfonate groups

Surprisingly, there is little published data on cationic polyurethane dispersion. In the first group, Lu and Larock (2010) [2] synthesized aqueous cationic polyurethane dispersions from soybean oil as polyols and diphenyl 4,4-diisocyanate as diisocyanate. In this research, they used *N*-Methyl diethanol amine (NMDEA) as cationic internal emulsifier and used acetic acid to stabilize cationic salt.

The second group, Xin *et al.* [8] prepared cationic polyurethane dispersed in water by using polytetramethylene ether glycol as soft segment and Isophorone diisocyanate as hard segment. As the well dispersing agent, they used *N*- methyl diethanol amine (NMDEA) neutralized by perfluoroalkyl acrylate.

Data from the two research groups indicate that NMDEA is used as good as stable cationic polyurethane dispersion, so in this project we choose NMDEA as the cationic dispersion agent for run on the synthesis process.

For other additives, they are used specific additive to prepare specific polyurethane application such as moisture scavengers, color agents and fillers.

### 2.4.3 Chemistry of polyurethane

There are many reactions to preparation of polyurethane. They are formed by various polymerization reactions: the condensation polymerization reaction and the addition polymerization reaction. In the industrial point, addition polymerization reaction was interested because it was no by product in the final product that sometime hardly to eliminate from the reaction.

1. The reaction between bischloroformate and diamine (condensation reaction)

$$\begin{array}{c} O \\ CI \\ \hline C \\ \hline$$

2. The reaction between diisocyanate and di or polyhydroxy compound (addition reaction)

$$O=C=N-R-N=C=O + HO-R'-OH \longrightarrow \begin{bmatrix} O & H & H & O \\ -C & N-R-N-C-O-R'-O \end{bmatrix}$$

Furthermore, isocyanate was used as a precursor to prepare as-polyurethane with various methods. In the primary reaction, iscocyanate will be reacted with compound containing active hydrogen as show in **Figure 2.18**.



Figure 2.18 Primary addition reaction of isocyanate [70].

From the result of above reactions, it was found that some reaction released carbon dioxide as by product used in case of polyurethane foam.

In addition, the secondary reactions of isocyanate as-polyurethane are shown in Figure 2.19.



Figure 2.19 Secondary addition reactions of isocyanate [70].

From the reaction, it is normally observed that linear polyurethane is formed after diisocyanate reacts with diols while crosslinked polyurethanes or branched polyurethanes are also formed when the polyurethane containing excess isocyanate groups (three or more groups in the compound) reacts with polyols. Excess isocyanate groups can undergo two possible reactions as shown in **Figures 2.20-2.21**.



Figure 2.20 Self-addition reaction of isocyanate 2 equivalents [70].



isocyanurate

Figure 2.21 Self-addition reaction of isocyanate 3 equivalents [70].

## 2.5 Waterborne polyurethane

### 2.5.1 Introduction of waterborne polyurethane

The volatile organic solvent in polyurethane is not only potential hazards associated body toxic that leads to skin allergy, cancer, and many diseases but also environmental toxic that cause of waste from processes bring to air toxic. To avoid the effect of hazard solvent, waterborne polyurethanes or aqueous polyurethanes dispersion formed with ionic emulsifier have been extensively studied to avoid these hazard organic solvent. As the concept of waterborne polyurethane, it is the polyurethane that stable to disperse in aqueous media without solvent. These polyurethanes are anionic, cationic or non-ionic waterborne polyurethane. Therefore, waterborne polyurethane is extensive materials that need to use in daily life.

Waterborne polyurethanes have been gaining increasing importance in a wide range of application because of their excellent properties. These properties are [1]:

- 1). Adhesion to various substrates
- 2). Resistance to chemicals, solvents and water
- 3). Abrasion resistance
- 4). Flexibility and toughness

There are advantages of waterborne. Examples of these advantages are fast dry, outstanding flexibility and impact resistance, excellent abrasion resistance, nonflammable, easy water clean-up and low volatile organic content (less pollution) [1]. The waterborne polyurethane can apply to wood floor coatings and finishes, vinyl upholstery topcoats, automotive base coats, coatings for plastics, printing inks, fiberglass finishes, leather finishes and adhesives.

For decade years, there are many improvements of waterborne polyurethane. Their improvement details can be summarized with the significant characteristic of manufacturing and composing of [1]:

- Most waterborne polyurethane contains N-methyl pyrrolidone solvent
- This solvent used to maintain viscosity of prepolymer intermediate
- Some solvent-free waterborne polyurethane made in acetone or MEK, followed by solvent removal
- Special equipment required to recover low-boiling solvents
- Use of tetramethylxylene diisocyanate (TMXDI) produces low-viscosity prepolyurethane
- Solvent-free polyurethanes sometime exhibit poor water resistance upon air drying
- Water resistance can be improved by: addition of co-solvent, use of aziridine crosslinker, baking the dried coating, using ammonia as the neutralizer

The possible to obtain aqueous emulsion stable depend on introduction of these hydrophilic groups, which function as internal emulsifiers, and achieve the particle size in range of 0.01-0.2 µm. The results of waterborne polyurethane can be obtained from a wide range of different morphologies and physical properties because there are many synthetic routes available for waterborne preparing can differ widely in term of:

(1) Natural and concentration of the polar solubilizing group

- (2) Molecular weight of polyurethane
- (3) Hydrophobic or hydrophilic characteristics of other parts in polyurethane chain

The functional groups of waterborne polyurethane can be classified into 3 categories with the most commonly used conferring water solubility including weak acids (carboxylic), strong acids (sulfonic), weak bases (amine), strong bases (tertiary and quaternary ammonium compounds) and nonionizable groups ( ethylene oxide, vinyl pyrrolidonre) . For the water soluble of polyurethane, their habituation depends on pH region over which their groups are substantially unionized in case of ionizable solubilizing groups. In case of the polymer containing weak carboxylic acid groups (e.g. acrylic acid form) are often water soluble which depend on the concentration of acrylic acid at pH above 4.2 ( $pK_a$  of acrylic acid ~4.2) so that the polymer soluble in water when the environmental pH lower than this pH value. In the other hands, basic polyurethane containing for example tertiary amine groups with sufficient concentration of the functional group are soluble at low pH (below  $pK_b$  of basic group), but it is insoluble in pH above  $pK_b$  of its [1].

### 2.5.2 Preparation of waterborne polyurethane

There are several synthetic processes for high molecular weight waterborne polyurethanes which include of 4 processes: acetone process, melt-dispersion process, prepolymer mixing process and ketimine process [1]. Commonly, all processes start with the first step by diols or polyols react with diisocyanate and then involves dispersion in water. The polyurethane with low viscosity is achieved by one of the following methods. There are: (1). In case of obtained low molecular polyurethane, the chain extender is required to chain extension step at the system to achieve the high molecular weight. This case will occur when in process of ketamine and prepolymer mixing.

(2). The polyurethane is dissolved in solvent and solvent will be removed after the aqueous dispersion step. This technique will appear in the process of acetone.

(3). The polyurethane is heated to facilitate dispersion in water which technique is found in case of melt dispersion process.

In the present cationic preparation in this research, the main step used to prepare the waterborne polyurethane is shown in **Figure 2.22**.



**Figure 2.22** Preparation of cationic polyurethane, by final reaction with acid or alkalyting agent [1].

In 2012, Lu *et al.* [72] synthesized cationic waterborne polyurethane using diisocyanate and polyester diol and *N*-methyl diethanolamine (NMDEA) as cationic emulsifier agent in an emulsion system. Waterborne cationic polyurethane is stable with the emulsifier that composes in range of

mass fraction is 7.0% - 9.5%. The mechanical properties of emulsion polyurethane cast films show that tensile strength increases and elongation at break decrease with the NMDEA content increasing.

In 2013, Lai *et al.* [6] synthesized cationic blocked waterborne polyurethane by the reaction of *N*-[(1,1-dimethyl-2-acetyl)ethyl]- $\beta$ -dihydroxyethylamino propanamide, isophorone diisocyanate, polycaprolactone glycol and bisphenol A, with imidazole as blocking agent and NMDEA as cationic emulsifier agent. In this work, they fixed the NCO index = 100 that all substrate in this ratio can be reacted completely. The application of the polyurethane was applied to improve strength of paper. The result showed that the strength of paper can be increased with increasing part of waterborne polyurethane.

In 2014, Li *et al.* [73] prepared high stability cationic waterborne polyurethane with high solid content using polyoxyethylene alkyl amine derivative as cationic emulsifier agent. The optimal conditions for preparing cationic polyurethane are [polyoxyethylene alkyl amine]/[polyol] = 1.9 and [NCO]/[OH] = 1.2 with the solid content of 51.28%. For the properties of prepared polyurethane, elongation at break of cast film increase, thermal stability increase and tensile strength slight downtrend with increasing hydrophilic agent.

In 2015, Li *et al.* [7] prepared cationic waterborne polyurethane containing side chain aromatic azo groups with low polydispersity applied for pH and light sensitive work. The polyurethane was synthesized by step- growth addition polymerization from polyether polylol, isophorone diisocyanate, NMDEA and a new aromatic azo- containing monomer by fix the NCO index = 100. It showed good thermodynamic properties of polyurethane, excellent adhesions to polymeric and glass surfaces and thin film forming ability.

In 2018, Laing *et al.* [3] studied cationic water polyurethane (cWPU) dispersion from castor oil and its derivative with isocyanate and NMDEA as emulsifier agent. The cWPU based on castor oil presents with good mechanical properties and antibacterial properties which can potentially be used as the coating in medical instruments, food processing, or added into paints for pathogen control.

## 2.6 Adhesive

### 2.6.1 Introduction of adhesive

An adhesive is a material, applied to the surfaces of substrates to join them permanently by an adhesive bonding process. The strength of adhesion depends on the type of adhesive and surface preparation.

Basically, there are 5 requirements for the good adhesive bonding [74].

### 2.6.1.1 Proper choice of adhesive

There are several different types of adhesive provided the best adhesive strengths. Choosing the correct adhesive for application is very important. There is a various factor into the choice of adhesive, depending on processing condition, nature of substrate surfaces and surface preparation techniques.

### 2.6.1.2. Good join design

A carefully designed joint can yield a better bonding by combination of the advantages of mechanical design with adhesive bond strength to the end use requirements of the part of bonding. Therefore, it is possible to impart the good strength to joint by design.

## 2.6.1.3 Cleanliness

Clean surface is very important to obtain a good adhesive bond by start with clean material surface (adherend). Impurity or contaminated matters such as dirt, oils, oxide layer, and moisture, lead to weak boundary layer, must be removed. Therefore, surface treatments generally involve reactive physical bonding and chemical bonding.

### 2.6.1.4 Wettability

Wettability is presented on the surface of adherend materials by using a liquid phase. The good wettability results lead to greater contact area between adhesive and adherends. High wettability is the reason of the possibility of adhesion force occurred.

#### 2.6.1.5. Adhesive bonding process

The appropriation process is one of successful bonding of materials. The process after applying adhesive on the adherends is very important. The adhesive applied on the adherend must be turned to solid by the solidification methods. It can be subjected to the proper temperature, pressure, and time-holding. There are three different ways to convert liquid adhesive to solid.

- 1) Chemical reaction by any combination of heat, pressure, and curing agents
- 2) Cooling from a molten liquid
- 3) Drying by solvent evaporation

#### 2.6.2 Theory of Adhesion

The mechanisms of adhesion have been postulated to describe by 6 theories, for instance, Mechanical interlocking, electrostatic force, diffusion, wettability, chemical bonding, weak boundary layer [74].

## 2.6.2.1 Mechanical interlocking

Adhesion occurs by penetration of adhesives into irregularity surface such as pores and cavities on substrate surfaces caused of bonding two roughness surfaces. Frequently, it form stronger bonds to porous abraded surfaces than smooth surfaces. This theory, however, is not widely used to describe since smooth surfaces can take a good adhesion results. After abrading the surface of an adherend, it can be enhanced the adhesion because of mechanical interlocking, clean surface, high reactive surface, and increase in contact area.

### 2.6.2.2 Electrostatic

The good adhesion of adhesive and adherends can be improved by electrostatic forces. Electrostatic forces in electrical double layer are formed at adhesive and adherend surface in account for resistance to separation. This force gains support from the electrical discharges have been noticed when an adhesive is separated from an adherend surfaces. However, in case of nonmetal surfaces materials, the contribution of electronic mechanism has been calculated and found in small when compared with chemical bonding occurred.

## 2.6.2.3 Diffusion

The molecule inter- diffusion develops adhesion between the adherend surfaces and adhesive. It is primarily applicable in using both adhesive and adherend are polymers with relatively long chain molecules capable of mobility. The nature of materials and condition of bonding will influence to what extent diffusion apply to. Typically, the diffusion interfacial layer has a thickness in range of 1 - 100 nm. Solvent joining and heat welding of thermoplastics is first regarded to molecule diffusions. Normally, diffusion bonding can be interpreted by cohesive energy density. The bond strength is maximum value when balancing of the adhesive and the adherend solubility.

#### 2.6.2.4 Wettability

Adhesion forces resulting from molecular contact between both material surfaces is developed. It is the first step to expand interfacial forces of adhesives and adherend. Wettability is the process of establishing serialized contact of interfacial between adhesive and adherend. High wettability Adhesive is the adhesive with lower surface tension than critical surface tension of the applied solid. The good and poor wettability are present in **Figure 2.23**. This is the reason that the surface treatment of plastic can increase their surface energy and polarity to get more wettability.



Figure 2.23. Wettability of adhesive spreading across surface (a) good and (b) poor [74].

### 2.6.2.5 Chemical bonding

Chemical bonding such as hydrogen, covalent, and ionic bonds formed between the surface of adhesive and adherends or molecules are stronger than the dispersion's attractive forces (mechanical interlocking, electrostatic, diffusion and wettability). Generally, there are four types of interactions occurred during chemical bonding such as covalent bonds, hydrogen bonds, Van der Waals forces, and acid-base interactions. The precious nature of the interactions for giving adhesive bond depends on the chemical structure and its composition of the interface between adhesive and adherend. Covalent and ionic bonds are the chemical bonding with high adhesion values. It is more than secondary valence bonding based on weaker physical bonding provided by hydrogen bonding, Van der Waals, and acid-base interaction.

#### 2.6.2.6 Weak boundary layer

Weak boundary layer is used for describing the bond failure at cohesive break or a weak layer of boundary. It can be found with three factors: adhesive, adherend, the environment or the combination of all factors. It occur in case of having impurity or defect concentrates close to bonding surface and forms a very weak attachment to the adherend and adhesive.

In 2014, Zain *et al.* [75] studied the effects of surface treatments on the system of polyurethane adhesive bonded aluminium alloy. It was reported that adhesive bonding depend on surface treatment and roughness. The chemicals used and methods of surface treatment are main factors in contributing a good adhesion between adhesive resin and substrate. These factors influenced the wettability of liquid/substrate surface. Moreover, the investigation showed that the adhesion between adhesive and substrates after treatment is durable bond with PU adhesive.

In 2015, Yu *et al.* [76] studied interface reaction in ultrasonic vibration-assisted brazing of aluminum to graphite using Sn–Ag–Ti solder foil. It was confirmed that ultrasonic vibration could enhance the wettability of liquid solder on the surface of base metals and accelerate the diffusion rates of interfacial reactions. Therefore, improving the wetting and spreading behavior of the liquid solder and reducing the energy required to initiate interfacial reactions.

In 2016, Matsuzaki *et al.* [77] studied the surface modification by undercut micropatterns on PP plates using a roll-imprinting process in order to improve the adhesive joint strength of PP with epoxy adhesive by introducing mechanical interlocking. It was reported that the tensile adhesive

strength was found to increase with increasing undercut angle and roughness because of higher mechanical interlocking.

In 2017, Haldar *et al.* [78] studied the simulation of an interlocking micro-architecture for a polymer composite material consisted of PMMA building and PU layer. The performance of the proposed interlocking design has been performed under different loading configurations. The simulations results were reported that the geometric interlocking works well without any use of adhesive for holding the blocks together.

In 2017, Wang *et al.* [79] studied the adhesive interfacial characteristics and the related bonding performance of four self-etching adhesives with different functional monomers applied to dentin. Two types of bonding mechanisms–micromechanical and chemical bonding–have been established. It was reported that chemical bonding can significantly improve both bonding strength and bonding durability.

In 2018, Alvarez *et al.* [47] studied about grafting the hybrid waterborne polyurethane/acrylate dispersion synthesized with bisphenol A-glicidylmethacrylate (Bis-GMA) and used it for stainless adhesive. The evidences found that high surface free energy was investigated in case of high wettability, chemical bonding between substrates and hybrid polymer, and adequate crosslinking degree between the polyurethane and acrylate chains.

#### 2.6.3 Definition of failure modes

There are three different possibilities for adhesive failure occurred after pulling apart in a direction perpendicular to bond. The first adhesive failure is structural failure or cohesive failure in adherend as shown in **Figure 2.24(a)**. The failure in adherend can be occur when the adhesive is stronger than adherend. Secondly, adhesive failure, the failure occur between the adhesive layer and one of adherends. This failure can be occurred in case of lower adhesive forces between the interfacial forces of substrates as shown in **Figure 2.24(b)**. For the last, cohesive failure, the adhesive remains covered aherend, adhesive bond between adhesive and adherend is stronger than the interaction of adhesive-adhesive. The failure image is presented in **Figure 2.24(c)**.



Figure 2.24. Three types of adhesive failure [80].

### 2.7 Adhesive polyurethane

### 2.7.1 Information of adhesive polyurethane

Polyurethanes are widely used as adhesive in various industrial and household sectors. Because of their high polarity and hydrogen bonding of polyurethane in side between isocyanate and adhered surface, there are high performances to bond to bond diverse substrates: plastics, rubbers, metals, glass or other ceramics and woods, so using polyurethane adhesives have expanded to include bonding of numerous substrates. These glues are cured by addition reactions of polyols into polyisocyante. In addition, other advantages of the adhesive, there are excellent low temperature resistance, low cure temperature, good flexibility and impact strength and good wetting to surface variety as good adhesion. In the past, polyurethane were used to bond leather, fabric and rubber composite and then two components polyurethane were used as adhesive for metal-to-metal. For decade period of improvement, waterborne polyurethane adhesive is discovered in the same period of reactive hot melt adhesive development and try to replace solvent based polyurethane in market shared.

For many years we found polyurethane adhesive, this adhesive type is known in the potential of their good potentials; adhesion, flexibility, low temperature performance, high cohesive strength and cure speed can be controlled by the manufacturing's process. Polyurethane is good choice to use as adhesive because:

1) Low surface energy and high wetting lead to high adhesion.

2) A very small size of them can permeate into the porous of substrate.

3) Hydrogen bonding is formed with the substrate rapidly.

4) Covalent bonds is formed with active hydroxyl substrate.

### 2.7.2 Types of Polyurethane adhesive

There are two common main types of polyurethane adhesive consisting of one component and two component polyurethane adhesive [1].

#### 2.7.2.1 One-component adhesive

### 1) Prepolymer based adhesive

For the oldest type of one-component, moisture-cured adhesive, the polyurethane is cured by di- or triisocyanates react with active hydrogen on adhered surface or moisture present in the air. After the reaction of isocyanate group side chain, the formation of urea and biuret linkages occurred and the molecular weight, strength, and adhesive properties are increased. Prepolymers are use either for 100% solids polyurethane or solvent based one-component adhesives. Recently, isocyanates were added to increase adhesion force and other physical properties of moisture-cured polyurethanes. This polyurethane is used today in rebounded foam, tire cord and vehicle maintenance application.

The concept of this adhesive: resin/hardener is prepolymer with isocyanate group endings. The polyreaction of isocyanates is occurred by polyaddition in the humidity environment, resulting in a lattice structure of polyurethane structure.

### 2) Thermoplastic adhesive

For these types, hot melt adhesives, these polyurethanes are hydroxyl polymers based on the reaction products of isocyanate (such as MDI) with linear polyester polyols and chain extenders. Several suppliers divide these in group of thermoplastic polyurethanes. The polymers are produce by isocyanate group and hydroxyl group interaction in the ratio of them (NCO/OH) at slightly less than 1:1 that use to limit molecular weight build in range of 50,000-200,000 g.mole<sup>-1</sup> (hydroxyl content approximately 0.05%-0.1%). These are typically dispersed in solvent for apply to the surface where we will adhere. After solvent evaporation, the adhesive was heated to be melted in state of soft, rubbery, and amorphous (normally, at temperature of 50-70 °C). After cooling, recrystallize to stronger and more flexible bond. The application of this polyurethane is used in shoe sole, the shoe upper fit to the sole.

### 3) Water based polyurethane

With growing in the recent year, environmentally friendly, waterborne polyurethane is replace of solvent based polyurethane adhesive in a number of application fields. The systems of water based are fully reacted with linear prepolymer or polymer, emulsifier or dispersing in water agent. This polyurethane is accomplished by building hydrophilicity into main chain polymer with either cationic or anionic molecules or hydrophilic polyols or external emulsifiers in some case. Shoe soles, packaging laminates, textile laminates, and binder in particle board industry replacing solvent based adhesives are covered.

### 4) Blocked di- and polyisocyanate adhesive

As in the structure of isocyanate, they may contain more than two isocyanate group on its molecule that can be blocked. It is reversible reaction and commonly temperature more than 140 °C the isocyanate block will be deblocked and then obtain reactive group to react with other components. In deblocking of isocyanate process, it can make in the lower generally temperature by using deblocking catalyst such as organotin/or zinc or tertiary amine. Also, blocked isocyanates can be not only used with polyols, hydroxyl- terminated urethane polymer, but also with any molecules that are consisted of active hydrogen containing polymer, such as hydroxyl- or carboxyl containing, cellulosic surface, and others. These blocked polymer system can be applied for adhesive application in the form of 100% solid, solvent based or water based system and then deblocked it to react with the other components.

#### 2.7.2.2 Two-components adhesive

This type of polyurethane adhesive is widely used due to the fast curing work or critical work, equipment manufacturer line require fixture of part rapidly, especially fix at ambient environment or bake at low temperature. Laminating applications that it surface without moisture or moisture cannot penetrate into bonding of them require two-component polyurethane adhesives to bond the substrate. The two- component consists of isocyanate low equivalent weight or prepolymer and polyols/ or polyamine low equivalent weight in the solvent or 100% solid form. These two-component must be kept separated until before expense. The bonding will be occurred rapidly by polyaddition reaction after these two components were mated. Polyisocyanate such as

PMDI, TTI and others may be reacted with hydroxyl-terminate polymer as well as hydroxyl in polyurethane prepolymer. The crosslinking density of the adhesive is appointed by the ratio of polyols to polyisocyanate.

For the part of waterborne polyurethane adhesive, it contains high molecular weight dispersed in aqueous media and sets to be adhesive film due to water evaporation or migration from polyurethane matrix. Because water based adhesive polyurethane is lower viscosity and high solid content, it obtains better than solvent based adhesive polyurethane. The dominant of products designed is heat activated bonding on their surface. The linear chains are mostly found and crystallize segment are normally found in the polyester segment.

## 2.8 Adhesive testing

Firstly, the adhesive materials are used to bond materials together firmly. In this point, the following primary performances are required [81].

1) Good manufacturability: because manufacturability is the general evaluation of the bonding operation of adhesives. Sufficient fluidity to make sure the surface of adherents adequately wetting-treated is required for good manufacturability of adhesives.

2) Bonding strength is the main performance index to evaluate the adequate quality of adhesives.

3) Good durability and weather resistance, less likely to get aged are also required.

4) Good stability, less swelling or shrinkage deformation is also required.

5) No harm to human health and less effect to environmental use are required.

6) Other performances such as thermal stability, chemical stability and storage stability are required for the specific application.

To test the adhesive, there are many methods to apply for adhesive testing for examples, lap shear test and peel and adhesion test.

#### 2.8.1 Lap shear testing

Lap shear is once of tensile test method for testing adhesion by pulling bonded layers apart along the plane adhesion to test the adhesive performance. By the test results, it can be clearly
described by breakup behavior of the adhesive layer from the substrate, or more likely a breakaway in the cohesion of either the substrate or the self of adhesive layer (glue), or both. Tensile force can accuracy applies along the plane to give rise configuration that minimum distortion away or breakup from the plane, including the substrate to make them up thickness in dark part or adhesive layer (glue) in light part. The settings up of these techniques are shown in **Figure 2.25.** In the process testing, each terminal of the sample is held by vice grips and pulled apart with varying controlled rate, and the force applied is expressed proportion to the total adhesive surface area, or shear area [82].



Figure 2.25 Shear lap test characteristic types [82].

## 2.8.2 Peel testing

Measurement of adhesive strength is used as peel test and adhesive test for many purposes. The adhesive bonding can be measured by tensile testing, shear testing or compression testing, but peel test is appropriated where there is flexibility in a jointed layer. Peel test is measured by a universal tester. The advantage of using a universal tester can also be used for adhesive shear and compression tests, or coatings pull-off tests [83]. There are many types of peel test that were shown in **Figure 2.26**.

Standard peel test method results are depended on speed and angle of separation in test. If a peel-able lid packaging is typically opened by hand with  $45^{\circ}$  testing, that may be a better internal standard. One bonded layer is significantly more flexible than the other, a  $90^{\circ}$  test may be most

appropriate. For  $90^{\circ}$ , a friction-free wheel fixture may be used, or at  $115^{\circ}$  (ASTM D3167 and equivalents) using a specified floating roller. Both of  $90^{\circ}$  and  $115^{\circ}$  ensure a constant angle of separation test. For another angle test,  $180^{\circ}$  peel tests, this peel can be achieved by pulling the sample against a supporting plate and it can be applied to a vertical metal plate which is pulled away from the end tab of the tape. The prepared adhesives are intended for clinical application, a special substrate are required to test them on [83].



Figure 2.26 Peel and adhesive test characteristic types [83].

Moreover, there are many other adhesion tests. Adhesion is also measured by pencil hardness test, gravelometer, impact for falling dart or mandrel bend that can be evaluated. In addition, loss of adhesion can be received during some chemical resistance tests. ASTM D2370 describes the testing result of elongation, tensile strength, and stiffness of organic/water solvent films [84].

## 2.9 Adhesive applications

There are many applications of adhesive materials that are used in many fields to fix the two or more parts of materials together and many selections of commonly used adhesives.

### 2.9.1 Adhesive for wall and floor

For wall application of adhesives, due to the convenient for brush coating, less consumption and good and strong bonding power, polyvinyl acetate is normally used. In the account of floor application, the adhesive have to adequate strength that applies to use so that adopt polyvinyl acetate latex as basic material, sometime tertiary-butyl phenol- formaldehyde resin and a certain amount of rubber ingredients and solvent are also used. A kind of mono- or bi-components adhesive can be used, there are both based on water or solution with high bonding strength. In General, the adhesive for wood application are non-toxic and odorless, fast drying, anti-ageing, and oil resistant. Moreover, low price, convenient and safe for construction, stable storage and others are also required [81].

#### 2.9.2 Adhesive for wood

The wood adhesive is commonly used in building construction. Urea formaldehyde condensate, added with curing agent ammonium chloride has features such as normal temperature curing, strong bonding power and low price [81].

Phenolic resin is one of the important adhesives that is used as adhesive for wood construction. There are many advantages of this material such as room temperature curing and strong bonding power, but its film that created after use is crisp.

Moreover, vinyl acetate-polyacrylate emulsion and additives are one more types of water based adhesive. The features of them are room temperature drying, convenient application and good initial bonding power and good brush ability that became to their advantages.

## 2.9.3 Adhesives for ceramic tile

Their applications on ceramic tile and marble are commonly used for laying and pasting and for pointing joints. Normally, ceramic tile adhesive is a powder made of cement modified by polymer and that also has many features - strong water resistance, good durability, convenient operation and inexpensive [81].

## 2.9.4 Adhesive for glass and organic glass

Nowadays, glasses were mainly used as main materials to construct the building and apart of decorating materials, which are composed of inorganic and organic glasses. For inorganic glasses, silica glasses, a colorless transparent sticky liquid, and cures fast at room temperature, generally cures completely within 4-8 hours were required to use in this work type. In the part of the organic glass, poly(methyl methacrylate) is a colorless transparent, colloidal liquid adhesive and intensive properties. This adhesive is resistant to water, oil, weak acid and spray as an adhesive material. The acrylic ester adhesive is the adequate adhesive material that has many features such as strong bonding strength, high transparency and simple operation for glass work [81].

In addition, there are many special adhesive applications on adhesive materials such as medical adhesive, food adhesive supplication and marine adhesive.

## 2.9.5 Adhesives for medical application

Medical adhesives are applied and removed many times a day that comprises an integral part of healthcare delivery in the Neonatal Intensive Care Unit (NICU) for patients as a component of a variety of products, including tapes, wound dressings, electrodes and others [85]. There are many types of adhesive for medical application, for example, acrylates, hydrocolloid, silicone and others [85].

Acrylate is one type of adhesive to use in secure medical devices such as tube and oxygen cannula. The backings are used with acrylate adhesive are silk, cloth, polyester, paper, plastic and polyurethane film.

Hydrocolloid adhesive is used with films as backing for ostomy care, platform underneath the tape, integrated into adhesive products such as endotracheal tube holder, umbilical catheter securement.

Silicone is adhesive materials used with woven polyester and plastic as a platform between skin and tape and the border of wound dressings.

## 2.9.6 Adhesives for food application

Food and Drug Administration (FDA) requires adhesive that bonding filter end caps and other filter components properly as well as bonding mesh filter gauze and separating sieves. Because of these advantages, many food and drug companies have been formulated and developed the epoxy based adhesive introduced to food production application, using FDA approved raw materials. The properties of this field adhesive include a high level toughness and good shock and impact resistance as well as good environmental durability. Moreover, curing at room temperature or heated for a fast cure with high shear and peel strength are normally found [86].

### 2.9.7 Adhesives for marine application

For marine applications, part of boating's ongoing popularity is thanks to improvements in boating technology which adhesive materials make an important contribution. Their materials were chosen as sealing on the boat hulls from water, weather, corrosion and element that increase the effect of hydrodynamic and durability property. Many adhesive products are interested in two high performance modified epoxy adhesives designed for bonding large production boats. Those are easily designed bonding polyester in work line with increase working time and capable of providing consistently high strength and durable bonds to a variety of substrates [87].

## **CHAPTER 3**

## **MATERIALS AND METHODS**

## **3.1 Materials**

## 3.1.1 High ammonia concentrated latex

Concentrated natural rubber latex with high ammonia (0.7% ammonia) used as raw material for Hydroxyl Telechelic Natural rubber was purchased from Yala Latex Industry co., Ltd. (Thailand).

## 3.1.2 Hydrogen peroxide

Hydrogen peroxide (35%,  $H_2O_2$ ), used as a couple chemical reagent for epoxidized natural rubber synthesis, were purchased from Ajax Finechem (Unilab®) (Australia).

#### 3.1.3 Formic acid

Formic acid (99%, HCOOH), used as a couple chemical reagent for epoxidized natural rubber synthesis, was purchased from BASF-YPC Company Limited (China).

## 3.1.4 Periodic acid

Periodic acid (99%,  $H_5IO_6$ ), used as a chemical reagent for degradation of epoxidized natural rubber to be carbonyl telechelic natural rubber, was purchased from Sigma-Aldrich (Germany).

### 3.1.5 Sodium borohydride

Sodium borohydride (99%, NaBH<sub>4</sub>), used as a chemical reagent for reduction of carbonyl telechelic natural rubber, was purchased from Ajax Finechem (Unilab®) (Australia).

#### 3.1.6 m-Chloroperbenzoic acid

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

## 3.1.7 Acetic acid

Acetic acid (95%, CH<sub>3</sub>COOH), used as neutralizer the system of cationic waterborne polyurethane, was purchased from Carlo Erba (Italy).

### 3.1.8 Methyl ethyl ketone

Methyl ethyl ketone (95%, MEK), used as solvent of cationic waterborne polyurethane synthesis, was purchased from Fisher Scientific UK Limited (England).

#### 3.1.9 N-methyl diethanolamine

*N*-methyl diethanolamine (98%, NMDEA), used as internal emulsifier for cationic waterborne polyurethane synthesis, was purchased from Sigma-Aldrich (Germany).

### 3.1.10 Dibutyltin dilaurate

Dibutyltin dilaurate (95%, DBTL), used as a catalyst for the cationic waterborne polyurethane synthesis, was purchased from Aldrich chemical (Germany).

#### 3.1.11 Toluene diisocyanates

2,4-Toluene diisocyanates (98%, TDI), used as a chemical for cationic waterborne polyurethane synthesis, was purchased from Sigma-Aldrich (Germany).

#### 3.1.12 Ethylene Glycol

Ethylene glycol (99.5%,  $C_2H_6O_2$ , EG), used as chain extender for cationic waterborne polyurethane synthesis, was purchased from Carlo Erba (Italy).

#### 3.1.13 Deionized water

Deionized water, used as purity and non-charges water media for cationic waterborne polyurethane synthesis, was prepared by water purifier from ELGA pure labflex (model LC134).

#### 3.1.14 Sodium hydrogencarbonate

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

#### 3.1.15 Sodium thiosulfate

Sodium thiosulfate (99%,  $Na_2S_2O_3$ ), used as a purified agent, was purchased from Acros organics (Belgium).

### 3.1.16 Magnesium sulfate

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

## 3.1.17 Deuterated chloroform

Deuterated chloroform (99.8%,  $CDCl_3$ ) with tetramethylsilane (0.03%, TMS) as internal standard, used as a solvent in NMR analysis, was purchased from Merck (Germany).

#### 3.1.18 Sodium Chloride

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

#### 3.1.19 Tetrahydrofuran

Tetrahydrofuran ( $C_4H_8O$ , THF), used as solvent for hydroxyl telechelic natural rubber preparation, was purchased from Acros organics (Belgium).

## 3.2 Instruments

The instruments were used in this research were listed in the **Table 3.1**.

Table 3.1 Instruments lists were used for characterization in the experiments.
--

Instruments	Model	Manufacturer
	Tensor 207	Bruker
Fourier transform infrared (FT-IR)	1750	Perkin-Elmer
	Unity Inova500	Varian
Nuclear magnetic resonance (NMR)	400	Bruker <sup>®</sup>
Nano-ZS	ZEN3600	Malvern Instruments Company
	DSA100	KRUSS
Contact angle	OCA 15EC	Data physics
Size Exclusion Chromatography	Chain 2707	Waters®
	JSM-5900LV	JEOL
Scanning electron microscope (SEM)	JSM-6510LV	JEOL
	JEM-2010	JEOL
Transmission electron microscope (TEM)	JSM-5900	JEOL
	DSC 200F3	NETZSCH
Differential scanning calorimeter (DSC)	DSC Q100	TA
	STA 449F3	NETZSCH
Thermogravimetric analysis (TGA)	TGA Q500	TA
	DMTA V	Rheometric Scientific
Dynamic mechanical analyses (DMA)	MCR 302	Anton Paar
	3365	Instron
i ensile testing machine	Model M500-30AT	Universal Testing Machine
Mass spectrometer (MALDI-TOF MS)	Biflex III	Bruker
pH meter	HI83141	HANNA instrument

### 3.3 Experimental

3.3.1 Preparation of polyol base on natural rubber by controlled chemical degradation

## **3.3.1.1 Preparation of epoxidized natural rubber (ENR)**

ENR was first prepared by epoxidation reaction of NR. Details of the preparation process of ENR to be used were according to Seatung *et al.* [11]. NR latex was first diluted to 20% DRC and stabilized by 3 phr of 10% Teric N 30 as nonionic surfactant. They were stirred overnight at room temperature and open system to de-ammonium (about 12-16 hours). The epoxidation system was carried out in a reactor glass equipped on water bath with temperature controller. After that, the latex was heated to 60 °C and then HCOOH was slowly dropped into the latex with the ratio of [HCOOH]: [isoprene unit] = 0.3 mole.mole<sup>-1</sup> for about 15 minutes. The reaction was continuous stirred for 15 minutes in the reactor before drop  $H_2O_2$  with ratio of 0.3 mole.mole<sup>-1</sup>. The reaction was kept at 60 °C and continuously stirred for 1, 4 and 8 hours. The reaction was stopped by adding of saturated sodium bicarbonate (NaHCO<sub>3</sub>) immediately in ENR latex. The ENR solution was coagulated in 98% methanol sheeted out and washed the sheet with flow water for several times until the surface of ENR was not soapy. The clean sheet was kept into the air flow oven at 40 °C until drying. Chemical structure and molecular weight of ENR was characterized by NMR while its functional groups was also determined by FTIR spectroscopy.

## 3.3.1.2 Preparation of carbonyl telechelic natural rubber (CTNR)

CTNR was prepared followed the methodology of Seatung *et al.* [11]. ENR was dissolved in THF with concentration of 0.4 mole.L<sup>-1</sup>. After that, 0.5 mole.L<sup>-1</sup> of  $H_3IO_6$  was drop wised into the reaction with constant stirring at 30 °C. The oxidation degradation was run for 6 hours and then iodate salt from the reaction was filtered out before evaporated THF. CTNR was trans-media to DCM before wash with saturated NaHCO<sub>3</sub>, 20% sodium thiosulfate solution to eliminate residual iodate salts and saturated NaCl, respectively. CTNR was then separated and removed residual water by MgSO<sub>4</sub> anhydrous and filter the CTNR. Finally DMC was evaporated. Chemical structure and molecular weight of CTNR was characterized by NMR while its functional groups were also determined by FTIR spectroscopy.

#### **3.3.1.3 Preparation of hydroxyl telechelic natural rubber (HTNR)**

 $NaBH_4$  excess with 7 times of CTNR mole was first dissolved into the reactor and then drop wise the solution of CTNR in THF into the solution of  $NaBH_4$ . The CTNR was reduced at 60 °C for 6 hours. The solution was then cooled down before hydrolyzing the reaction with distilled water to eliminate the residual  $NaBH_4$  The solution was washed with saturated NaCl and dried on  $MgSO_4$ anhydrous. The HTNR was filtered and evaporated out of THF. Chemical structure and molecular weight of HTNR was characterized by NMR while its functional groups was also determined by FTIR spectroscopy. The molecular weight was also investigated by NMR and SEC.

# **3.3.1.4 Preparation of epoxidized hydroxyl telechelic natural rubber**

## (eHTNR)

According to the method of Kébir et *al.* [27] and Saetung et *al.* [11], eHTNR was prepared from HTNR3000. The reaction was set with three-necked round bottom flask with magnetic stirrer at 0 °C under Argon gas atmosphere. HTNR3000 (10 g, 3.33 mmol) was dissolved in dried DMC (0.067 mol.L<sup>-1</sup>) in the reactor and then mCPBA (2.538g, 14.7 mmol for 10% epoxide; 5.08 g, 29.4 mmol for 20% epoxide; 7.61 g, 44.10 mmol for epoxide 30%) in dried DMC (50mL) was added dropwise into the reaction. The equivalent mole ratios of mCPBA to isoprene unit in HTNR3000 were 0.1, 0.2 and 0.3 for epoxide percentage content of 10, 20 and 30, respectively. The reaction was run for 3 hours. After reaction, the mixture was suddenly stopped with saturated NaHCO<sub>3</sub> twice time, and followed by washing with saturated NaCl aqueous solution. Separated organic solvent was kept and dried with MgSO<sub>4</sub> anhydrous. The DMC was removed out with vacuum evaporator and vacuum oven in 40 °C for 3 hours to give the product yield of 92, 91 and 95% for 10, 20 and 30% epoxide, respectively. Chemical structure and molecular weight of HTNR was characterized by NMR while its functional groups was also determined by FTIR spectroscopy. The molecular weight was also investigated by NMR and SEC. The summary reaction of polyol base on natural rubber is demonstrated in **Scheme 3.1**.



Scheme 3.1. Preparation of epoxidized hydroxyl telechelic natural rubber (eHTNR).

## 3.3.2 Preparation of waterborne cationic polyurethane (cWPU)

Waterborne cationic polyurethanes based on natural rubber was prepared by prepolymer mixing process with various many conditions by adjustment the methodology of Lu *et al.* [2]. For common condition, HTNR, *N*-methyl dimethanol amine (NMDEA) and methyl ethyl ketone (MEK) were added into the reactor equipped with stirrer set, nitrogen inlet, condenser and thermal controller. Diisocyanate was dropwised into the mixture at 70°C with mechanical stirring. The reaction was run on 70 °C for 4 hours. After that, the polymer solutions were cooled to room temperature, and then neutralize by acid (1.5 equivalents of NMDEA), followed by dispersion at high speed with distilled water to produce the cationic polyurethane with solid content in water after remove MEK by vacuum evaporation. The cationic waterborne polyurethane was prepared and studied with various conditions (i.e. emulsifier contents, molecular weight of HTNR, concentration of ethylenediamine, isocyanate index) that effect on the properties of cationic

waterborne polyurethane. The reactions of prepared cationic waterborne polyurethane are presented in **Scheme 3.2**.



Scheme 3.2 Cationic waterborne polyurethane from hydroxyl telechelic natural rubber preparation.

## 3.3.2.1 Effects of NMDEA on cWPU properties

Effect of NMDEA on the properties of the polyurethane with various concentration of NMDEA 0.75, 1.50 and 2.00 equivalent mole, respectively were investigated. The molecular weight of HTNR was approximately 3000 g.mole<sup>-1</sup> and fix the type of diisocyanate with the NCO index = 100. The recipes of the cWPU in this series are presented **Table 3.2**. The obtained polyurethane was carried out to determine acid-based, solid content, particle size and stable of cationic waterborne polyurethane. Then, cationic waterborne polyurethanes were cast as film and investigated the tensile, swelling ratio, chemical structure characterization, and also thermal stability of film.

		Recipe (1	mole)					
Code	(NCO index = 100)							
	HTNR	NMDEA	TDI	EG				
cWPU1	1	0	1	0				
cWPU2	1	0.75	1.75	0				
cWPU3	1	1.5	2.5	0				
cWPU4	1	1.75	2.75	0				
cWPU5	1	2	3	0				
cWPU6	1	2.25	3.25	0				

Table 3.2 Ingredients of cWPU in effects of emulsifier (NMDEA) content.

Note: HTNR3000

## 3.3.2.2 Effects of concentration of ethylene glycol (chain extender) on

## **cWPU** properties

The effect of ethylene glycol (EG) on the properties of the polyurethane with various concentrations of EG are 0, 0.5, 1.00, 1.50, and 2.00 equivalent mole respectively. NMDEA was fixed the concentration while type diisocyanate with the constant concentration and molecular weight of HTNR with approximately 3000 g.mole<sup>-1</sup> were fixed with the NCO index = 100. The recipes of the cWPU in this series are presented **Table 3.3**. The obtained polyurethane was carried out to determine acid-based, solid content, particle size and stable of cationic waterborne polyurethane. Then, cationic waterborne polyurethanes were cast as film and investigated the tensile, swelling ratio, chemical structure characterization, and also thermal stability of film.

		Reci	pe (mole)	
Code		(NCO i	ndex = 100)	
	HTNR	NMDEA	EG	TDI
cWPU6	1	2.25	0	3.25
cWPU7	1	2.42	1	4.42
cWPU8	1	2.51	1.5	5.01
cWPU9	1	2.60	2	5.60
cWPU10	1	2.77	3	6.77

Table 3.3 Ingredients of cWPU in effects of chain extender (EG) content.

Note: Controlled NMDEA concentration of 5.67%wt, HTNR3000 and NCO index of 100

## 3.3.2.3 Effects of molecular weight of HTNR on cWPU properties

The effect of molecular weight of HTNR on the properties of the polyurethane with various molecular weight of HTNR are approximately 1000, 2000 and 3000 g.mole<sup>-1</sup>, respectively. The diisocyanate and NMDEA were fixed with the NCO index = 100. The recipes of the cWPU in this series are presented **Table 3.4**. The obtained polyurethane was carried out to determine acid-based, solid content, particle size and stable of cationic waterborne polyurethane. Then, cationic waterborne polyurethanes were cast as film and investigated the tensile, swelling ratio, chemical structure characterization, and also thermal stability of film.

Code		ND		Recipe	(mole)			
	HI	NK	(NCO index = 100)					
	$M_n$ (g.mole <sup>-1</sup> )	Code	HTNR	NMDEA	EG	TDI		
cWPU7	~ 3000	HTNR3000	1	2.42	1	4.25		
cWPU17	~ 2000	HTNR2000	1	1.91	1	3.91		
cWPU18	~ 1000	HTNR1000	1	1.02	1	2.02		

**Table 3.4** Ingredients of cWPU in effects of Molecular weight  $(M_n)$  of HTNR.

Note: Controlled NMDEA concentration of 5.67%wt and NCO index of 100

## 3.3.2.4 Effects of concentration of Isocyanate index (NCO index) on

## **cWPU** properties

The effect of diisocyanate on the properties of the polyurethane with various NCO index = 100, 125, 150, and 175 respectively. NMDEA and type of diisocyanate were fixed. Molecular weight of HTNR was also fixed at approximately 3000 g.mole<sup>-1</sup>. The recipes of the cWPU in this series are presented **Table 3.5**. The obtained polyurethane was carried out to determine acid-based, solid content, particle size and stable of cationic waterborne polyurethane. Then, cationic waterborne polyurethanes were cast as film and investigated the tensile, swelling ratio, chemical structure characterization, and also thermal stability of film.

Code	NCO index	Recipe (mole)					
	-	HTNR	NMDEA	EG	TDI		
cWPU6	100	1	2.25	0	3.25		
cWPU7	100	1	2.42	1	4.25		
cWPU19	125	1	2.42	0	4.60		
cWPU20	150	1	2.25	0	4.88		
cWPU21	175	1	2.25	0	6.5		
cWPU22	125	1	2.42	1	5.31		
cWPU23	150	1	2.42	1	6.38		

Table 3.5 Ingredients of cWPU in effects of NCO index.

Note: Controlled NMDEA concentration of 5.67%wt, HTNR3000

## 3.3.2.5 Effects of eHTNR on cWPU properties

The reaction was used with the same conditions as the previous work for comparing the results [15]. eHTNR was dissolved in dried THF before mixing into the mixture of NMDEA and DBTL within the reactor equipped with stirrer set, argon inlet, condenser and thermal controller. Under the temperature of 70 °C with stirrer rate of 100 rpm, TDI was added dropwise into the reaction of chemical mixture. After the stable condition for 4 hours, EG was gentle dropped into the system for 30 minutes with stirring rate of 100 rpm, then the system was cooled and neutralized by acetic acid for 1 hour with stirring rate of 100 rpm followed by slowly dropping deionized water with the reaction time of 30 minutes with speed of 400 rpm, respectively. Finally, THF solvent was removed out by vacuum rotary evaporator to obtain only eHTNR based cWPU in water medium. The summary process was shown in **scheme 3.3.** The recipes of the cWPU are presented **Table 3.6**.



Scheme 3.3. Preparation of eHTNR based Cationic waterborne polyurethane.

		Recipe (m	ole)				
Code	(NCO index = 100)						
	HTNR	NMDEA	EG	TDI			
cWPU-HTNR	1	2.55	1	4.55			
cWPU-eHTNR10	1	2.65	1	4.65			
cWPU-eHTNR20	1	2.70	1	4.70			
cWPU-eHTNR30	1	2.76	1	4.76			

Table 3.6 Ingredients of cWPU in effect of different eHTNR.

Note: Controlled NMDEA concentration of 5.67%wt and NCO index of 100

After preparation, the cWPU films were formed by casting into Teflon mold (11 cm x 5 cm) with the cavity depth of 0.3 mm. After mold casting, emulsion solution was left at room temperature for 7 days. Then emulsion solution was dried in an oven at 70  $^{\circ}$ C for 24 hours. The cast films were kept in desiccator for further characterizations.

## 3.3.3 Adhesive preparation

## 3.3.3.1 Lap shear test

Before bonding, cow leather was degreased with a rag containing acetone [88]. Then, samples were stored open to the atmosphere in dust proof boxes to dry for overnight. All cWPU adhesive latexes with a controlled solid amount of 75 mg for lap shear test were directly applied on real cow leather surface. After applying cWPU on the adhered surfaces, the substrate was subjected to hot air blowing to remove water out and pressed for setting overnight. The assembly was pressed with 1 kg/3.125 cm<sup>2</sup> of adhesive area/sample. A comparison between curing at 70 °C overnight and curing samples at room temperature was performed. For one experiment, 5 reproducibility for one sample was assembly.

## 3.3.3.2 180 degree peel test

The process was similar to the process of lap shear test for drying the leather surfaces. All cWPU adhesive latexes with a controlled solid content of 500 mg for T-peel test were directly applied on cow leather surface. After applying cWPU on the adhered surfaces, the substrates were subjected to hot air blowing to remove water out and pressed for setting overnight. The assembly was pressed with 1 kg/50 cm<sup>2</sup> of adhesive area/sample. A comparison between curing at 70 °C overnight and curing samples at room temperature was performed. For one experiment, 5 reproducibility for one sample was assembly.

#### 3.3.4 Analysis of HTNR and cWPU

The oligomers from natural rubber and cWPU were investigated their chemical structure, molecular weight, and physical properties as well as thermal properties.

## 3.3.4.1 Chemical structure

Fourier transform infrared (FT-IR) spectra of oligomer natural rubber and cWPUs were corrected in the range of wave numbers from  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  in transmission of ATR mode.

Nuclear magnetic resonance (NMR) spectra of oligomer natural rubber and cWPUs were recorded on Fourier Transform NMR Spectrometer 500 MHz for <sup>1</sup>H NMR by diluting sample in

CDCl<sub>3</sub>. The results were analyzed with flip angle of 3.150, scan number of 16 and pulse delay time of 1.00 and non-set relaxation time. NMR Chemical shifts were reported in ppm relative to the deuterated solvent resonances.

From NMR results, epoxide percentages on were calculated by the as follow:

Epoxide (%) = 
$$\frac{I_{2.69}}{I_{2.69}+I_{5.14}}$$
 x 100

Where  $I_{2.69}$  is integration value of peak 2.69 ppm (C*H* epoxide)  $I_{5.14}$  is integration value of peak 5.14 ppm (C=C*H* isoprene)

Molecular weights  $(M_n)$  of HTNR were calculated as follow:

$$M_n$$
 (g.mole<sup>-1</sup>) =  $\left(\frac{I_{5.14}}{\frac{I_{3.69}}{2}}\right) \ge 68 + 104$ 

Where  $I_{3.69}$  is the integration value of the peak at 2.69 ppm (CHOH)

 $I_{5.14}$  is the integration value of the peak at 5.14 ppm (C=CH isoprene)

Molecular weights  $(M_n)$  of eHTNR were calculated as followed:

$$M_n$$
 (g.mole<sup>-1</sup>) =  $\left(\frac{I_{5,14}}{I_{3,69}}\right) \ge 68 + \left(\frac{I_{2,69}}{I_{3,69}} \ge 84\right) + 104$ 

Where  $I_{2.69}$  is the integration value of the peak at 2.69 ppm (CH epoxide)  $I_{3.69}$  is the integration value of the peak at 2.69 ppm (CHOH)  $I_{5.14}$  is the integration value of the peak at 5.14 ppm (C=CH isoprene) MALDI-TOF mass spectrometry analysis was performed on a Bruker UltraFlex II instrument equipped with a nitrogen laser operating a 337 nm, pulsed ion extraction source and reflection. Spectra were recorded in the reflection mode with an acceleration voltage of 19 kV and a delay of 200 ns. 1000 single shot acquisitions were summed to give the spectra and the data were analyzed using Bruker FlexAnalysis and Polytools softwares. Samples were prepared by dissolving the matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in the solvent dichloromethane and mixing with the polymer (10 mg/mL) and the cationizing agent silver trifluoroacetate (AgTFA) in the ratio of 1:20:1.

### 3.3.4.2 Physical Properties

Viscosity of eHTNR was carried out by AR 2000 of TA Instruments with cone geometry of 20 mm and 3°58'. The viscosity was measured by using flow ramp with 5 min time to adjust temperature, then 5 points per decade from 0.01 to 100 s<sup>-1</sup> during 120 second.

Total solid content of cWPUs suspension were calculated by differential weight before and after drying. To identify them, cWPU about 1 g was placed in aluminium tray and drying in air oven under the temperature of 100  $^{\circ}$ C until there is constant weight. The solid content (%TSC) is calculated as average of 3 sample of each formulation as follows:

$$\% TSC = \frac{(W_i - W_x)}{W_i} \times 100$$

Where  $W_i$  is the weight of the initial weight of cWPU dispersion and  $W_x$  is the weight after drying sample.

Particle size and size distribution of synthesized cWPU suspension were characterized by Nano-ZS particle sizer (Malvern Instruments Company, UK).

Wettablity properties were determined by Contact angle measurements with sessile drop method. Average water (hydrophilic liquid) contact angle with individual droplet volume of 2  $\mu$ l was determined in 5 separate measurements at different locations for each sample. Average

Diiodomethane (hydrophobic liquid) contact angle for with volume of  $1.5 \ \mu$ l was determined in 5 separate measurements with locations for each sample.

Swelling ratio in solvents was characterized by immersing the circular cWPU films in DMF, Toluene and THF for 24 hours in Petri dish. After that, the diameter of each swollen sample was measured using graph-paper. The swelling properties were compared between the swollen and original specimens. The result of one formula was reported by average of five specimens. The area of cWPU circular film is calculated as follows:

$$A = \pi r^2$$

Where *r* is the radius of the circular film

The swelling percentage of cWPU films (%S) is calculated as follows:

$$\%S = \frac{(A_i - A_0)}{A_0} \times 100$$

Where  $A_i$  is the area of the immersion treated film and  $A_0$  is the area of initial film Water absorption behaviors of cWPU films were assessed with weight each dried sample film (1 cm × 1 cm) before and after immersing in distilled water with 5 replicates for each sample. It was monitored daily day for 7 days to weigh and calculate the percentage exchanging of the sample. The absorption percentage (%) is calculated as follows:

Water adsorption (%) = 
$$\frac{(W_i - W_0)}{W_0} \times 100$$

Where  $W_i$  is the weight of the immersion treated film and  $W_0$  is the weight of initial film The stability of cWPU suspension was observed by keeping the cWPUs in the storage vial at room temperature. The appearance of cWPUs was observed and collected. pH value of cWPU suspension was measured by pH meter. The calibration curve was fitted with 3 points of pH buffers; pH 4, pH 7, and pH 10. The reported pH was collected for 3 times with average value.

## 3.3.5.3 Morphology

The morphology confirmation of synthesized cWPU dispersion was determined by transmission electron microscope (TEM) with 160 kV. The samples were diluted by DI water and strained by 2% Osmium tetraoxide on the coated side of a 200-mesh Nickel grid. Then, the samples were imaged by TEM after drying.

The fracture surface photographs synthesized cWPU films corrected from tensile testing fracture were observed by scanning electron microscope (SEM) with condition of high vacuum and high voltage at 20.00 kV. All samples were coated with gold.

Optical microscope (OM) images of adhesive surface after testing were observed by Olympus Statif BX51 with magnification of x50.

#### **3.3.4.4 Mechanical properties**

Tensile properties of cWPU film were prepared following ISO37 with die type 2. The apparatus was equipped with 100 N load cell and extensor grip included laser sensor for checking their elongation with cross head speed of 100 mm.min<sup>-1</sup>.

## 3.3.4.5 Thermal properties

DSC analysis of the cWPU films was collected. The process using alumina pan with starting sample weight of about 10 mg was run under nitrogen atmosphere (nitrogen rate = 100 mL.min<sup>-1</sup>) with heating rate of 10 °C.min<sup>-1</sup> from -100 °C to 100 °C. The data was corrected after clearing their thermal history by first time running, and then second heating scan was used to correct glass transition temperature ( $T_o$ ) of synthesized cWPU.

TGA analysis of the cWPU films was performed. Weight loss of cWPU film was measured under nitrogen atmosphere with starting weight of about 10 mg. The samples of thermogravimetric analysis were gradually heated from room temperature to 600  $^{\circ}$ C with heating rate of 10  $^{\circ}$ C.min<sup>-1</sup>.

Dynamic mechanical analyses of the cWPU films were carried out by DMTA in tensile mode at a frequency of 1 Hz and 0.01% strain with a heating rate of 3 °C.min<sup>-1</sup> by scanning heating temperature of -100 °C to 150 °C. Tensile storage modulus (G'), loss modulus (G''), and the loss factor (tan  $\delta$ ) as the ratio of loss modulus to storage modulus (G''/G') are used to quantify the elastic and viscous behavior of a viscoelastic material under deformation.

## 3.3.4.6 Adhesive properties

## (a) Lap shear test

Tensile lap shear tests were carried out using a tensile machine in tensile mode by applied standard of ISO 4587 testing. The specimens were prepared with  $25 \pm 0.25$  mm of width and 100  $\pm 0.25$  mm of length as shown in **Figure 3.1**. The length of overlap were 12.5 mm  $\pm 0.25$  mm and test with constant speed 10 mm.min<sup>-1</sup>. The results of the tests are expressed as the arithmetic mean of the breaking force, in newton (N). The lap shear strength was calculated by Equation as follwed. The results were corrected and calculated from 5 times reproducibility for one sample before reporting the mean values.

Lap shear strength 
$$(MPa) = \frac{Max \text{ force } (N)}{Area (mm^2)}$$



**Figure 3.1** (a) Specimens of cow leather for lap shear test and (b) Lap shear testing according to ISO4587 (2003).

## (b) 180 degree Peel Test

180 degree peel tests were carried out using a tensile machine in tensile mode as ISO 11339 testing. The specimens were prepared with  $25 \pm 0.5$  mm of width and  $200 \pm 0.5$  mm of length as shown in **Figure 3.2** by repeating five times for each measurement. The test was carried out at constant speed of 10 mm.min<sup>-1</sup>. To separate the specimens, the average peeling force curves (maximum and minimum) were determined for about 100 mm of peeling (disregarding the first 25 mm and the last 25 mm) in newtons with a function of time.



**Figure 3.2** Specimens of cow leather for 180 degree peel test and (b) 180 degree test according to ISO 11339 (2010).

Adhesive tests also performed on commercial adhesives for comparison: suppliers

Commercial A: Nouveau SADER (Non-solvent adhesive), Bostik Commercial B: Pattex (Non-Solvent adhesive), Henkel Commercial C: Movi Multikol Transparent (Solvent based adhesive)

## **CHAPTER 4**

## **RESULTS AND DISCUSSION**

### 4.1 Modification of NR by selective degradation

Hydroxyl telechelic natural rubber (HTNR) have been prepared from natural rubber (NR). Firstly, epoxidized NR (ENR) was prepared by epoxidation reaction from NR. ENR was then selective oxidation degradation reaction to obtain carboxyl telechelic NR (CTNR) and followed by reduction reaction of CTNR to obtain HTNR. The resulting HTNR was characterized by FT-IR spectroscopy as shown in **Figure 4.1**. The results showed that the absorption band of *cis*-1,4 polyisoprene of natural rubber was revealed in the wave numbers about 2970, 1449, 1376, and 836 cm<sup>-1</sup> corresponding to -C-H stretching,  $-CH_2$ - deformation,  $-CH_3$  deformation, and =C-H out of plane deformation, respectively.

After epoxidation reaction, new peak of ENR were found at wavenumber of 870 cm<sup>-1</sup> corresponding to epoxide group (-C-O). In addition, peak at wavenumber of 1633 cm<sup>-1</sup> corresponding to C=C was reduced because of the present of epoxide in that position.

The selective cleavage of epoxide structure by periodic acid of ENR to be CTNR was also confirmed. New peak at the region of 1700 cm<sup>-1</sup> indicating to carbonyl (C=O), the new terminated functional group. The target product was carried from the reduction reaction of CTNR and the structure were also confirmed. Carbonyl peak at the region of 1700 cm<sup>-1</sup> disappeared and the band of hydroxyl group (-OH) were indicated at 3400 cm<sup>-1</sup>.



Figure 4.1 FTIR spectra of NR, ENR, CTNR, and HTNR.

Confirmation of successful HTNR was further provided by <sup>1</sup>H NMR spectroscopy as shown in **Figure 4.2** The results from <sup>1</sup>H NMR spectrum of isoprene unit from NR were observed the signal at 5. 12, 2. 07, and 1. 67 ppm corresponding to **3** ( $-CH_2(CH_3)C=CHCH_2-$ ), **1,4** ( $-CH_2(CH_3)C=CHCH_2-$ ), and **2**( $-CH_2(CH_3)C=CH-$ ), respectively.

After the epoxidation reaction, ENR was successfully prepared by controlling of chemical degradation with the yield of 99%. The confirmation structure was confirmed by <sup>1</sup>H NMR spectra showing the signal of 5. 12, 2. 69, 2. 07, 1. 67, and 1. 59 for **3** ( $-CH = C(CH_3) CH_2$ ), **7** ( $-CHOC(CH_3) CH_2$ ), **1,4** ( $=CH - CH_2CH_2C(CH_3) CH_2$ -), **2** ( $-CH = C(CH_3) CH_2$ ), and **6** ( $-CHOC(CH_3)CH_2$ ), respectively.

CTNR was then prepared from ENR by selective cleavage of epoxide structure by oxidation degradation with periodic acid and the yield result was about 95%. <sup>1</sup>H NMR spectrum confirmed the structure of CTNR with signal at 9.77, 5.12, 2.45, 2.35, 2.25, 2.07, 1.67 for 7 (-C $H_2$ CHO), 3 (-

 $CH = C(CH_3)CH_2$ -), 5 ( $CH_3COCH_2CH_2$ ), 6 (- $CH_2CHOCH_3$ ), 8 ( $CH_3COCH_2$ -), 1,4 (- $CH_2CH = C(CH_3)CH_2$ -) and 2 (- $CH = C(CH_3)CH_2$ ), respectively.

The last process of HTNR preparation was the reduction reaction of CTNR to be HTNR. In this step, the yield of HTNR preparation was about 95%. The result obtained from <sup>1</sup>H NMR showed that the important signals were found at 5. 12, 3. 80, 3. 65, 2. 07, 1. 67 1. 20 ppm for 3 (- $CH=C(CH_3)CH_2$ -), 8 (- $CHOHCH_3$ ), 7 (- $CH_2OH$ ), 1,4 (- $CH_2CH=C(CH_3)CH_2$ -) and 2 (- $CH=C(CH_3)CH_2$ ), and 9 ( $CH_3CHOH$ ), respectively.



**Figure 4.2** <sup>1</sup>H NMR spectra of NR, ENR, CTNR, and HTNR.

The FTIR spectroscopy and <sup>1</sup>H NMR spectroscopy confirm that HTNR has been successful which can further be used as polyol to prepare cationic waterborne polyurethane.

#### 4.2 Properties of cationic waterbornc polyurethane (cWPU)

Natural rubber based cWPU adhesives were synthesized by step-growth polymerization with controlled %TSC approximately 20 %. The effects of different parameter on the properties of cWPU were studied on emulsifier content (NMDEA), chain extender content (EG), molecular weight of HTNR, isocyanate index (NCO index), and epoxide content on HTNR backbone. The results were corrected and discussed as follow.

## 4.2.1 Effects of NMDEA (emulsifier) on cWPU properties

In this part, the effects of amount of emulsifier, NMDEA, on cWPU properties were studied by fixing the molecular weight of HTNR about 3000 g. mole<sup>-1</sup> and isocyanate index of 100. Chemical structure, physical properties and themal properties of cWPU were investigated.

The cWPU properties based on natural rubber in series of emulsifier effect, NMDEA content in range of 0 - 2.25 mole. All cWPUs were prepared with total solid content (TSC) in range of 21 -27 %. The stability of dispersion was clearly observed that the NMDEA content had significantly affected on stability and particle size distribution. For instance, the NMEDA content less than 1.50 mole (NMDEA contents of 0 - 1.00 mole) could not be stable and also coagulated because of emulsifier insufficiency in its system [32]. Notwithstanding, the system of prepared cWPU was stable with emulsifier content at least 1.50 mole (NMDEA contents of 1.50 - 2.25 mole). By the physical appearance, the dispersions of cWPU were milky blue as presented in **Figure 4.3**.



Figure 4.3 Appearances of cWPU latex with various NMDEA content.

The systems of emulsion were in acidic with pH in range of 4.31 - 4.37 by little or nonacetic acid odor. The results revealed that all acetic molecules neutralized tertiary amine position of NMDEA part of chain to obtain the complete cationic charge in cWPU chain. Apart from that, by observing its appearance, shelf-life with well dispersion is more than 10 months.

The particle size distribution of cWPUs with NMDEA content more than 1.5 mole were well-dispersed, and the particle sizes of dispersions were in range of 87.1 to 59.8 nm as shown in **Figure 4.4**. It might be that the Gibb's free energy of water-oil surface of cWPU containing hydrophilic, NMDEA, slightly decreased with increasing of NMDEA content in the cWPU emulsion particle [89].



Figure 4.4 Size distribution by intensity with various NMDEA content.

Zeta potential values of the cWPUs with different NMDEA content listed in **Table 4.1** were 51.2 mV, 57.1 mV, 64.1 mV, and 70.6 mV for cWPU3, cWPU4, cWPU5, and cWPU6, respectively. The previous study suggest that zeta potential values above + 30 mV may be considered a suitable threshold for particle stability [90]. The evidence showed that the particle of

synthesized cWPUs were stable and had a high density of positive charge on the surface area. The lower zeta potential can be explained by the slight up in stability which leads to a smaller dimensional particle size with higher NMDEA content. This work demonstrates zeta potential values in a higher range can be obtained by increasing the NMDEA due to a high chance of positive charges would be generated in position of NMDEA by neutralizing with acetic acid. Large particle size and low zeta potential in positive charges are usually agglomerated easier than smaller particle size that is directly affected in storage life time of cWPUs.

Also, to characterise the shape and size of cWPU dispersion, cWPU dispersion was studied by TEM. **Figure 4.5** presented the particles of cWPU base on natural rubber by magnification of 100K (a) and 300K (b) carried out by TEM. The showed dark point of cWPU phase in TEM images is generally presented with the stained  $OsO_4$  on carbon- carbon double bond of HTNR (isoprene unit) because the main part of cWPU is formed by natural rubber more than 70%. Clearly, the PU phase was mostly found in round shape and well dispersed. The result showed mostly regularly dispersed in water showing the particle size of approximately 20 nm agreed with the value from using zeta nanosizer technique. For this work, the particle sizes of prepared cWPUs were smaller than others because of the nature viscosity of long- chain HTNR is normally higher than naturalresource oils. The spherical size of particle was displayed because of shear force between the blade and polymer materials with properly charge in water media during the process of cWPU preparing. Therefore, TEM images can confirm the shape and the distribution of cWPU that can stable in water media by according the results of zeta nanosizer.



**Figure 4.5** TEM images of synthesized cWPU based on natural rubber (cWPU6) at magnification of a) x100K b) x300K.

From all of view shapes, TEM and zeta nanosizer results, the possible model of cWPU are offered as shape of round. For each well dispersed particle, it play with the regular shape of round that is stabilized of the cWPU shape by positive  $(N^+)$  charge affected in part of neutralized NMDEA by acetic acid. The stabilized charge is distributed in the process of synthesizing inserting NMDEA into the chain of PU containing HTNR and TDI as soft segment and hard segment, respectively. The chains of cWPU are rolled in the particle and try to have and get them stable by inserting positive charge out of their particle surfaces. In the particle size, the effect of physical crosslink and hydrogen bonding lead them to have more stable and disperse in water well. Beside, possible model of cWPU behavior in aqueous medium was presented as round shape as presented in **Figure 4.6**.



Figure 4.6 Possible model of cWPU behavior in aqueous medium.

The summary of cWPU properties based on natural rubber in series of emulsifier effect, NMDEA content in range of 0 - 2.25 mole, was shown in **Table 4.1**.

		Physical Properties									
Code	TSC (%)	Stability	Appearance	рН	Film	Particle size (nm)		Zeta Potential (mV)		Contact angle (theta)	
					appearance	size	PDI <sup>b</sup>	Value	SD <sup>c</sup>	Water	Oil
cWPU1	N/A	Unstable	Solid	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
cWPU2	N/A	Unstable	Solid	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
cWPU3	22.43	Stable <sup>a</sup>	Milky blue	4.31	could not form film	87.1	0.276	51.2	4.6	109	35
cWPU4	26.82	Stable <sup>a</sup>	Milky blue	4.32	could not form film	83.8	0.32	57.1	5.5	102	36
cWPU5	26.31	Stable <sup>a</sup>	Milky blue	4.34	very-yellowish soft film	73.8	0.149	64.1	6.2	96	37
cWPU6	21.02	Stable <sup>a</sup>	Milky blue	4.37	very-yellowish soft film	59.8	0.14	70.6	6.1	90	39
N/A : Not a	vailable		<sup>a</sup> more than 6 m	nonths							

**Table 4.1** Summary of physical properties of cWPU from different NMDEA content.

<sup>b</sup> Polydispersity index from nanosizer <sup>c</sup> Zeta Deviation from zeta potential

The cWPU were cast as film and the chemical structure was characterized by FT-IR spectroscopy and <sup>1</sup>H NMR spectroscopy. The FT-IR spectroscopy was the first method for indicating the functional group of cWPU film as shown in **Figure 4.7**. The chemical structures of polyurethane shown as important functional groups were observed at 3302, 1707, 1602, 1538 and 1224 cm<sup>-1</sup> assigned to -N-H stretching, -C=O ester stretching, N-H bending of urethane position, - N-C=O vibration of polyurethane linkage, and C-O acylstretching of urethane linkage, respectively [38, 91-94]. Moreover, the absorption band of *cis*-1,4 polyisoprene of natural rubber was revealed in the wave numbers of 2970, 1449, 1376, and 836 cm<sup>-1</sup> corresponding to -C-H stretching, -CH<sub>2</sub>-deformation, -CH<sub>3</sub> deformation, and =C-H out of plane deformation, respectively [11, 18]. From the results of all spectra, the region of isocyanate (-NCO) absorption peak at 2270 cm<sup>-1</sup> had disappeared showing that free active isocyanate had completely reacted in the last process by water.



Figure 4.7 FTIR spectra of cWPU films from different NMDEA content and HTNR.

The chemical structure of cWPU film was confirmed by <sup>1</sup>H NMR spectroscopy as shown in **Figure 4.8**. For the important peak, the signals of isoprene unit from polyol based on natural rubber were observed at 5.12, 2.07, 1.67, and 1.25 ppm corresponding to **3** (-CH<sub>2</sub>(CH<sub>3</sub>)C=C**H**CH<sub>2</sub>-), **1**(- $CH_2(CH_3)C=CHCH_2$ -), **2**(-CH<sub>2</sub>(CH<sub>3</sub>)C=CH-), and **9** (-CH<sub>2</sub>(CH<sub>3</sub>)CHO-), respectively. In addition, new signals were also observed at 7.23, 7.03, and 6.97 ppm corresponding to benzene ring protons **11-13** of TDI structure. [95, 96] Moreover, the important signal at 8.14 ppm corresponding to urethane linkage **10** (-C(O)N**H**-Ph-) was observed. This result was used as the basis confirmation that the cWPU synthesis is successfully synthesized from polyol based on natural rubber.



**Figure 4.8** <sup>1</sup>H NMR spectrum of synthesized cWPU.

Furthermore, their hydrophobic/hydrophilic properties of cWPU films have been tested by the contact angle measurement techniques that was described to reversible surface wettability. **Table 4.2** presented summary results of contact angle hydrophobicity and hydrophilicity of prepared cWPU films by casting on glass plates. For NMDEA effect results, water contact angle and oil contact angle were shown trendy of hydrophilicity increasing by increasing of NMDEA
content. As summary in the **Table 4.1**, the contact angle results of cWPU film with NMDEA contents of 1.50, 1.75, 2.00, and 2.25 mole were 109, 102, 96, and 90 degree for water contact angle and were 35, 36, 37, and 39 degree for oil contact angle, respectively. By the effect of neutralized NMDEA content by acetic acid, it made more positive-charge in system leading to more hydrophillicity property in the cWPU. However, water contact angle is quite high degree because of effect of non-polar natural rubber soft segment, but it still clearly showed the effect of NMDEA content with increasing of water-like property. It maybe concern that synthesized cWPU had more polar resulted from more concentrate of positive charge of NMDEA effect.

Code name	Water contact angle image	Oil contact angle image		
	109°	35°		
cWPU3				
	102°	36°		
cWPU4				
	96°	37°		
cWPU5				
cWPU6	90°	39°		

<b>Table 4.2</b> Water and Oil contact angle of cWPU	films.
--	--------

The appearance of cWPU films with a different NMDEA content containing presented that the content of NMDEA below 1.75 mole could not be formed film whereas the content of NMDEA 2 and 2.25 mole was able to form film and gave a yellowish and soft behavior but it could not be peel out of Teflon mold. However, the strength of cWPU film could increase by adding some chemical, chain extender or crosslinker, but they were still stable in the water with well dispersion. Therefore, in this work, cWPU containing NMDEA 2.25 mole (5.67%) was chosen to study the addition of chain extender to improve its all properties in the next step.

## 4.2.2 Effects of concentration of EG (chain extender) on cWPU properties

In this part, the effects of amount of chain extender, EG, on cWPU properties were studied by fixing the molecular weight of HTNR about 3000 g.mole<sup>-1</sup>, EG 1 mole, and isocyanate index of 100. Chemical structure, physical properties, mechanical properties and themal properties of cWPU were investigated.

# 4.2.2.1 cWPU latex

This study was to investigate the effect of chain extender with a concentration of 1.00 - 3.00 mole leading to the mechanical improvement of cWPU films. Extended cWPUs were in the range of acidic with pH value of 3.71 - 3.79 with none or less acetic acid odor with the appearance of very light yellowish milky blue as shown in **Table 4.3**. Because of the long extended cWPU chain affected from EG as a chain extender, the medium of extended cWPU system was prepared in aqueous with total solid content in the range of 17-20% to decrease the viscosity of the system.

cWPU6	cWPU7	cWPU8	cWPU9	cWPU10
Cannot form film		-		2

Table 4.3 Appearances of cWPU from different EG content latex and films.

The cWPUs with chain extender were studied the size distribution and zeta potential. These results showed that there were 2 ranges of size – small size range and a large size range as presented in **Figure 4.9**. The results suggested that the small range sizes were increased from 16.71 to 67.60 nm while, the large size of cWPUs presented in a range of 106.10 to 453.30 nm with increasing of EG content from 1.00 to 3.00, respectively. In the first size distribution, small particle size, the effect of residual short chain EG and NMDEA by reactive OH reacted with a free isocyanate in the system which was results of the small size range showed in size distribution display. Meanwhile, the large size distribution is that the extended main- chain cWPU from the plain reaction of NMDEA, HTNR and TDI prepolymer reacted with EG growing up to long chain cWPU and marking in the large size distribution display. These results are consistent with Saetung, *et al.* who reported that anionic WPU based on HTNR was increased an amount of chain extender with a higher particle size. [18, 91]. Similarly, the particle size distribution of WPU based on poly( $\alpha$ -caprolactone) was also increased by increasing amount of chain extender [97].



Figure 4.9 The result of size distribution by intensity in effect of EG.

Zeta potential values of the cWPUs with chain extender, EG, content listed in **Table 4.4** were +51.2, +57.1, +64.1, and +70.6 mV for cWPU3, cWPU4, cWPU5, and cWPU6, respectively. All of the studies reviewed here support the hypothesis that zeta potential values above +30 mV (for positive charge dispersion) and lower than -30 mV (for negative charge dispersion) may be considered a suitable threshold for particle stability [90]. The results indicated that the particle of synthesized cWPUs were stable and had a high density of positive charge on the surface area. The lower zeta potential can be explained by the slight up instability which leads to a smaller dimensional particle size with higher NMDEA content. This work demonstrates zeta potential values in a higher range can be obtained by increasing the NMDEA due to a high chance of positive charges would be generated in the position of NMDEA by neutralizing with acetic acid. Large particle size is usually agglomerated easier than smaller particle size that is directly affected by storage lifetime of cWPUs.

Moreover, all physical properties of cWPU were concluded and presented in Table 4.4.

Physical Properties								Contact angle				
- Code name	TSC (%)	%) Stability	Appearance	рН	Film appearance	Particle size (nm) (% Found)			Zeta Potential (mV)		(theta)	
						Peak 1 <sup>b</sup>	Peak 2 <sup>c</sup>	PDI <sup>d</sup>	Value	SD <sup>e</sup>	Water	Oil
cWPU6	21.02	Stable <sup>a</sup>	Milky blue	4.37	very- yellowish soft film	59.8 (100)	-	0.14	70.6	6.1	90	39
cWPU7	16.67	Stable <sup>a</sup>	Milky blue	3.73	very- yellowish film	76.46 (100)	-	0.438	71.1	10.5	91	35
cWPU8	16.34	Stable <sup>a</sup>	Milky blue	3.71	yellowish film	17.24 (10.4)	174.50 (89.6)	0.361	59.8	6.3	93	35
cWPU9	17.43	Stable <sup>a</sup>	Milky blue	3.79	yellowish film	41.51 (24.6)	214.30 (75.4)	0.585	55.9	7.5	94	33
cWPU10	17.14	Stable <sup>a</sup>	Milky blue	3.75	yellowish film	67.60 (8.5)	453.30 (91.5)	0.304	62.7	11.8	97	30
$N/\Lambda \cdot Not$ ave	ilabla				<sup>a</sup> mor	than 10 m	onthe					

**Table 4.4** Summary of physical properties of cWPU from different EG content.

N/A: Not available

<sup>b</sup> First size distribution (percentage found)

more than 10 months

<sup>c</sup> second size distribution (percentage found)

<sup>d</sup> Polydispersity index from nanosizer

<sup>e</sup> Zeta Deviation from zeta potential

# 4.2.2.2 cWPU films

The cWPUs were cast as a film and the film formation after adding chain extender into the main chain showed more strength and could be formed film as well and easily removed out from Teflon mold. This phenomenon was the first evidence that its mechanical properties were improved. Also, the chemical structure was indicated by FTIR.

To confirm the structure of cWPU, FTIR was the first technique to study the functional group of synthesized cWPU. FT-IR spectra of the cWPU film samples were shown in **Figure 4.10**. The chemical structures of polyurethane film shown as important functional groups were observed at 3302, 1707, 1602, 1538 and 1224 cm<sup>-1</sup> assigned to -N-H stretching, -C=O ester stretching, N-H bending of urethane position, -N-C=O vibration of polyurethane linkage, and C-O acylstretching of urethane linkage, respectively.[38, 91-94] Moreover, the absorption band of *cis*-1,4 polyisoprene of natural rubber was revealed in the wave numbers of 2970, 1449, 1376, and 836 cm<sup>-1</sup> corresponding to -C-H stretching, -CH<sub>2</sub>- deformation, -CH<sub>3</sub> deformation, and =C-H out of plane deformation, respectively [11, 18]. After adding EG into the active chain of cWPU to obtain the chain extender in the system, FTIR spectra showed a quite familiar spectrum of cWPU without EG, but there is a peak showed in the spectrum. With wavenumber of 1409 cm<sup>-1</sup>, it ascribed to symemetric stretching of glycolate bridge (-O-C=O) of ethylene glycol and isocyanate active site, respectively [98].

According to all spectra results, the region of isocyanate (-NCO) absorption peak at 2270 cm<sup>-1</sup> had disappeared showing that free active isocyanate had completely reacted in the last process by water. From the FTIR results, this result was used as the basis confirmation that the cWPU synthesis based on natural rubber was successfully synthesized with this technique and ethylene glycol could be used for chain extender as well in this work.



Figure 4.10 FTIR spectra of cWPU films compared to HTNR.

The effect of EG content on water uptake of cWPU films were also studied and presented in **Figure 4.11**. For instances, all cWPU films immersed into water for 7 days showed slightly increased with increasing of EG content as well as immersion time. In the day 7, the results showed that percentage of water uptake were 7.77, 12.75, 13.81 and 19.28 % with EG content of 1.00, 1.50, 2.00 and 3.00 mole, respectively. The results showed that increased percentage of water uptake with EG increasing contents clearly. Therefore, the more EG content, the more hydrophilic hard segment in the class of isocyanate because of the high possibility of reaction between isocyanate-terminted chain and active short chain hydroxyl group of EG. Like this, it can be assumed that the chain of cWPU has a more hydrophilic block in the chain because of EG content effect. However, its results were significantly different in comparison to other polyol based because of nature of

hydrocarbon natural rubber in their structure on this our cWPU. For the anionic WPU base on NR with an equal percentage of emulsifier amount (.5.6%), Saetung *et* al [18], reported that the water uptake results their cWPU films immerged for 7 days were in the range of 17 - 45% their work is higher than this work. Primarily, the result proves that cWPU base on NR is more properly in the field of adhesive, coating and all material sensitive to water than aWPU. It was assumed that because of the different interaction of intra-/inter chain of nature charge of anionic and cationic WPU.



Figure 4.11 Water absorption percentage of cWPU films with varying ethylene glycol content.

Also, the swelling properties of cWPU films in a chosen solvent of tetrahydrofuran (THF) were shown in **Table 4.6**. Normally, isocyanate hard segment was hardly dissolved in THF, while natural rubber soft segment is easily dissolved in THF. The results of cWPU with EG content of 1.00 mole was completely dissolved because of high non-polar nature of natural rubber and high linear structure content. Meanwhile, cWPU with EG content more than 1.50 mole had the more shape stable because of higher content of isocyanate hard segment in intra-chain. This result showed that swelling percentage of the film was decreased with increasing of EG content. The swelling percentages of cWPU film with EG containing 1.50, 2.00 and 3.00 mole were 236, 100 and 56%, respectively. What the supporting reason of these is the more hard segment promoting physical

bonding from intra-/inter-chain hydrogen bonding led to lower swelling values of cWPU films [18].

In addition, their hydrophobic/hydrophilic properties of cWPU films have been studied by the contact angle measurement techniques that were described to reversible surface wettability [99]. Table 4.5 presented summary results of contact angle hydrophobicity and hydrophilicity of prepared cWPU film. The contact angle resulted that film of cWPU with EG content of 0, 1.00, 1.50, 2.00, and 3.00 mole were 90, 91, 93, 94, and 95 degree, respectively for water drop testing, and were 39, 35, 35, 33, and 31 degree, respectively for oil drop testing. Although it seem that, the polarity of cWPU trends to decrease slightly with increasing EG content which might have resulted from during contact angle analysis, the time of contact is fast, and water has no time to penetrate inside the cWPU film. In addition, the EG content is increased, physical interactions between urethane groups can occur, and these polar groups are then less available to interact with the water drop at the surface. Therefore, contact angle results show more hydrophobic properties with increasing EG content.



Table 4.5 Water and Oil contact angle of cWPU films from different EG content.

The mechanical properties of cWPU films with a different EG content have been studied. Young's modulus, tensile strength and elongation at break of cWPU films based on polyol form NR (HTNR3000) with different amounts of EG varied from 1.00 to 3.00 mole are summarized in **Table 4.6**. The results exhibit tensile stress–strain behavior inversing from an elastomer to tough plastics as shown in **Figure 4.12**. The behaviors are clearly shown that is depending on the EG content that all show two functions of chain extender and diol. Without EG content, the appearance showed the very soft film, so there are no data of cWPU6. For the added EG system, EG content of 1.00 to 2.00 mole are observed for an elastomeric polymer with modulus increased slightly from 1.14 to 8.05 MPa.

Tensile strength and elongation at break increased slightly with a value of 1.70 to 2.70 MPa, and 116.64 to 118.89 %, respectively. Having more EG content, 3.00 mole, demonstrate toughplastic in the first period of measurement and then run the result as an elastomeric polymer with modulus, tensile strength, and elongation at break of 44.66 MPa, 4.73 MPa and 162.62 %, respectively. The modulus of cWPU10 was observed that there was increased 5 times compared with cWPU9. There were increase mechanical properties due to high physical bonding with hydrogen bonding and entanglement effect. In addition, urethane linkage was developed and contributed in inner particle between the same chain and particle surface of cWPU [100] that led to increasing mechanical properties of prepared cWPU by increasing of EG content. The results were in accord with recent anionic WPU based on HTNR studies indicating that mechanical properties of WPU films were improved by increased the amount of chain extender [18, 97].

All of these behaviors showed and related with SEM images of cross section film from tensile testing as shown in **Figure 4.13**. The effect of these behaviors is significantly depended on HTNR based that is used as the main soft segment in this work, so all samples of prepared cWPU showed elastomer behavior.

This result indicated that chain extender is associated with increased the mechanical properties of cWPU film.



Figure 4.12 Strength-strain curves of cWPU films with various EG content.

Code nome	Young's modulus	tensile strength	Elongation at break	Swelling in	
Coue name	(MPa)	(MPa)	(%)	<b>THF (%)</b>	
cWPU7	$1.14\pm0.23$	$1.70\pm0.19$	$116.64 \pm 1.38$	N/A	
cWPU8	$2.04\pm0.07$	$1.79\pm0.11$	$117.12 \pm 4.13$	236.11	
cWPU9	$8.05\pm0.04$	$2.70\pm0.02$	$118.89\pm0.75$	100.69	
cWPU10	$44.66\pm0.58$	$4.73\pm0.59$	$162.62 \pm 5.83$	56.25	

Table 4.6 Mechanical properties and swelling percentages of cWPU with different EG content.

Note: N/A = can not measure

Furthermore, the morphology of cWPUs were studied by SEM technique which used cWPU film specimens from the cross section of tensile testing. The roughs and fracture behaviors were shown in **Figure 4.13**.

By the cross section SEM images from tensile testing, the fracture showed the effect of chain extender addition with the roughness of cWPU film surface by the magnification of x500. The

material surfaces exhibited the trend of increasing roughness of surface with increasing of EG content from 1 to 3 mole. This result indicated that the matrix of specimen tearing contributed to higher tensile strength by slightly showing from brittle fraction to ductile fraction while it is tearing. With the EG content of 1.00 mole, it showed a quite smooth surface because of its brittle fraction property related to its mechanical property from tensile results that showed very low strain and stress. In addition, EG content more than 1.50 showed the tear of cWPU film matrix with higher ductile evidence by tearing as sheet-like and also pillar-like (higher rough surface) before it is tear apart. Sheet-like tear was the evidence showed that its matrix is extended and held until it broke. Meanwhile, pillar-like tear of cWPU film was the important part that showed more colonies in the surface with adding more EG content in cWPU system. Both of tear evidence would be important of tear behavior to improve the mechanical properties which affected chain extender of EG content. They were confirmed by tensile properties that slightly increased with increasing of EG into the system by 3.00 mole. For the highest content of EG in this work, the property was closely presented to plastic behavior.



Figure 4.13 SEM image of cWPU film resulted from cross section of tensile test (x500).

For the thermal properties, TGA, DSC, and DMTA were used to obtain and studied the results of cWPU films from different EG content series and polyol substrate. Thermal degradation of cWPU film showed in the TGA and DTG results as shown in **Figure 4.14 a** and **4.14 b**, respectively. The thermogravimetric curve of HTNR showed that the thermal degradation take place through only one step with a  $T_{max}$  at in temperature 377 °C with a weight loss of 92.90%. While cWPU film with EG (0, 1, 1.5, 2, and 3 mole) as used HTNR as polyol show a similar behavior that have two-step of the thermal decomposition. The first thermal degradation shows in the range of 205-215 °C that attributed to breaking of urethane linkage as EG, HTNR, isocyanate, and also loss of carbon dioxide from urethane deformation [18]. Closely, some of cracking part decomposition step, mass of sample was changed in the temperature range of 377-382 °C related to the decomposition of HTNR as indicated in pure polyols substrate. It provided the ship of temperature degradation because it had longer chain and more physical hydrogen bonding between those chains [27]. Besides, there are more stable in higher temperature.



Temperature (°C)



**Figure 4.14** Thermal gravimetric results of cWPU with various EG content - (a) TGA curves and (b) DTG curves.

In order to analyze mass percentage, the mass change of each step was applied to calculate the percentage content in that referred part after cWPU formation labeled as real content. Contrary, the amount of each composition before the reaction started was labeled as calculated content. For the hard segment calculation from TGA, the first decomposition was used to refer to hard segment decomposition that the mass change prefer to the summation content of TDI, NMDEA and EG part which are short chain segment, while, the soft segment was referred to HTNR part decomposed in the second step of TGA result. The results were shown in **Table 4.7.** Indicating the component of soft segment, the result showed calculated content was lower than real content because of the effect of more physical bonding like hydrogen bonding in the system by shifting from the higher temperature resistance of some part of hard segment. On the other hand, the hard segment in real content was lower than calculated content because adding EG into the system affected by the more hydrogen bonding. By the effect of these, the content of hard segment in real content was lost in the result of TGA, but their compositions were shifted into the part of soft segment content.

				rties					
		First ste	р		Second sto	ep			
Code		Mass			М	ass	Mass	Tan	
name	ame T <sub>max</sub> change/c		e/content	T <sub>max</sub>	change/	/content	residual	delta <sup>c</sup>	$T_g^{d}$
	(°C)	(	%)	(°C)	(%)		(%)		
		Cal <sup>a</sup>	Found <sup>b</sup>		Cal <sup>a</sup>	Found <sup>b</sup>			
HTNR	—	-	-	377.2	100.00	92.90	0.11	N/A	N/A
cWPU6	215.2	21.35	10.07	380.6	78.83	79.49	1.45	N/A	N/A
cWPU7	210.7	27.97	10.20	379.8	72.89	74.50	2.77	-54	-53.2
cWPU8	213.2	30.86	10.29	380.1	70.33	74.42	3.39	-53	-52.6
cWPU9	205.7	33.58	10.39	378.4	67.89	72.50	3.67	-54	-52.0
cWPU10	205	38.51	10.84	379.9	63.59	70.12	4.57	-55	-51.7

Table 4.7 Thermal properties of synthesized cWPU with different EG content.

N/A = cannot measure

<sup>a</sup> Cal. = percentage content added into the reaction

<sup>b</sup>Found = percentage content is found in TGA

<sup>c</sup> Tan delta from DMTA result  $^{d} T_{g}$  from DSC results

Thermal property from DSC technique is one main point to provide the important data as shown in **Figure 4.15**. It can be identified the part of amorphous, crystalize and also fusion behavior of cWPUs as well as show in  $T_g$  value which depend on main chain movement of polymer backbone. Normally,  $T_g$  of polymer will be shown in the part of amorphous that is a chain mobility and flexibility with lower  $T_g$  showed in the DSC thermogram. By the work, HTNR3000 obtained very low  $T_g$  in the temperature range of about -62 °C showing amorphous phase. It is strongly affected and constantly showed in all sample which confirmed that HTNR in the cWPU had more efficient in cWPU properties. All cWPU amorphous part showed  $T_g$  values in the quiet same temperature by slightly increasing in the range of -54 to -52 °C as varying EG.

Overall, DSC thermograms of cWPUs are observed the  $T_g$  of poly(ether urethane) linkage that normally were observed in the range 40 – 70 °C [101]. In this work, the linkage of urethane that had the effect of natural rubber and TDI were displayed in range of 41.6 – 41.9 °C by slightly increasing with increasing of EG content from 1.00 – 3.00 mole, respectively. However, the



ure than linkage  $T_g$  of cWPU without EG as chain extender was not clearly showed in DSC thermogram.

Figure 4.15 DSC thermograms of HTNR3000 and series of cWPU films with different EG content.

Also, to enter the molecular mobility of polymer sensitively DMTA was an offered equipment. As show in **Figure 4.16**, tan delta and storage modulus was presented with a function of temperature for observing the effect of EG content and all properties to defy them.  $T_g$ , glassy state of polymer, is normally defied by tan delta while the stiffness of prepared materials, extended cWPU, is determined by storage modulus of DMTA. As **Figure 4.16a**, tan delta of cWPU7-10; extended cWPU; was observed in the temperature of -53.98, -52.56, -54.10 and -54.97 °C for cWPU7, cWPU8, cWPU9 and cWPU10, respectively. The results show tan delta in the range of elastic properties of main part of natural rubber that normally found in range of about -60 °C. Comparing the results,  $T_g$  from DMTA and from DSC were quite similar trend because only one

glassy state with relating temperature was observed. The results could be proved that the most content in extended cWPU was natural rubber part and could describe as the reasons of DSC part. **Figure 4.16b** illustrated the storage modulus with clearly result. The obvious results from DMTA could describe clearly the effect of EG on storage modulus result because of more sensitive from molecular chain mobility. In the first period of graph,  $-100^{\circ}$ C to  $-60^{\circ}$ C, glass phase or hard plastic behavior was found in all samples by observing that the stiffness was gradually rose up with adding more EG content. This phenomenon was normally that the effect of chain extender on extended cWPU chain and high crosslink chance and hydrogen bonding from urethane linkage were that the following effect. For second state, all samples show the major relaxation found in temperature range about  $-60^{\circ}$ C to  $-40^{\circ}$ C determined by dramatically decreased in storage modulus. This state was in range of  $T_g$  of prepared cWPU by presenting major effect of HTNR on cWPU. The last phase found in curve was rubbery state or elastomer which observed at temperature above  $-40^{\circ}$ C. This phase was very clear the effect of EG on cWPU by showing highest stiffness materials in cWPU10 and lowest value in cWPU7. These can confirm the properly extended cWPU in the system *via* the normal reaction in this work.





Figure 4.16 DMTA curves of cWPU film – (a) Tan delta and (b) Storage modulus.

This work used ethylene glycol (EG) as a chain extender and the result showed that it worked well. The mechanical properties and thermal properties were increased by increasing EG content. However, the increasing of an amount of chain extender increase a particle size distribution and decrease their term stability. Therefor, the amounts of optimal EG would be 1 mole that obtained a small particle size and well stable with long-term stability.

# 4.2.3 Effects of molecular weight $(M_n)$ of HTNR on cWPU properties

In this part, the effects of molecular weight of polyol soft segment, HTNR, on cWPU properties were studied by fixing the NMDEA 5.67 %wt, the EG content of 1 mole, and isocyanate index of 100. Chemical structure, physical properties, mechanical properties, themal properties and adhesive properties of cWPU were also investigated.

#### 4.2.3.1 Characterization of HTNR substrates

The different molecular weights of HTNR (from 1000 to 3000 g.mole<sup>-1</sup>) results prepared by semi-solution process were monitored by <sup>1</sup>H-NMR and SEC as shown in **Table 4.8**. From the <sup>1</sup>H NMR, the molecular weight of HTNR could be calculated by integration of vital peaks at 5.14 ppm (C=C*H* isoprene) and at 3.65 ppm (CHO*H*) [11, 15, 27]. Molecular weights of prepared HTNR were 954, 1804, and 2824 g.mole<sup>-1</sup> as HTNR code of HTNR1000, HTN2000, and HTNR3000, respectively.

The overlaid of the SEC chromatograms of these HTNR were presented in Figure 4.17. Its shows that the traces were shifted from low retention time to higher retention time corresponding to lower molecular weight of HTNR when retention time increase. HTNR with different  $M_n$  were calculated and presented as 1058, 2099, and 3530 g. mole<sup>-1</sup> as HTNR code of HTNR1000, HTN2000, and HTNR3000, respectively. Moreover, polydispersity index ( $\mathbf{D}$ ) of all samples were in range of 1.6-1.9 which were low value and approached to 1 meaning the obtained HTNRs had very similar value of molecular weight. The results of this study indicated that well-controlled HTNRs could be prepared by semi-solution technique with very close to the expected molecular weights.



Fig 4.17 Retention times of GPC chromatogram of HTNR with different molecular weight

		Molecu	ht (g.mol	Thermal				
Expected	Code name		SI	SEC		$T_g^{b}$	Degradation <sup>c</sup>	
molecular weight (g.mole <sup>-1</sup> )		<sup>1</sup> H-MNR	м	м	$\mathbf{\tilde{H}}^{\mathrm{a}}$	(°C)	T <sub>ma</sub>	Weight loss
			IVI <sub>n</sub>	17 <b>1</b> W			(°C)	(%)
1000	HTNR1000	954	1058	1709	1.62	-58.7	372	99
2000	HTNR2000	1804	2099	3825	1.82	-60.1	368	99
3000	HTNR3000	2824	3530	6606	1.87	-62.1	366	99

Table 4.8 Summary of molecular weight of prepared HTNR

<sup>a</sup>  $\mathbf{D}$  = Polydispersity index from SEC (M<sub>w</sub>/M<sub>n</sub>)

<sup>b</sup> T<sub>g</sub> from DSC results

<sup>c</sup> Thermal degradation from TGA results

In addition, HTNR substrates with different molecular weight were investigated the thermal properties obtained from thermal gravimetric analysis (TGA and DTG) and the results were

presented in **Figure 4.18** and listed in **Table 4.8**. The decomposition of HTNR1000 were in high percentage in low temperature range than HTNR2000 and HTNR3000, but no significant differences were found for  $T_{max}$  value, about 370 °C. In this point, due to the main structure of HTNR is natural rubber  $T_{max}$  value of those were in the same range. These results corroborated the idea of Fernández and team research (2016) [102], who suggest that lower molecular weight polymer was easily decomposed more than higher molecular weight polymer and the idea of Fuensanta and Martín-Martínez (2018) [103], who suggested that the same structure of substrate with different molecular weight decompose at similar temperature.





**Figure 4.18** Thermal gravimetric results of HTNR with different molecular weight – (a) TGA curves and (b) DTG curves.

Moreover, three different molecular weight of HTNR substrates were also investigated glass transition temperature ( $T_g$ ) from DSC. As shown in **Figure 4.19**,  $T_g$  values of HTNR with different molecular weight were slightly increased from -62.1 to -58.7 °C by reducing the molecular weight of HTNR from 3000 to 1000 g.mole<sup>-1</sup>, respectively. With the same functional group, high molecular weight polymer usually have a long chain and high free space and volume which each molecules and chain can move freely [104]. In this point, the mobility of long chain of polymer will be occurred easier in low energy (low temperature) than short chain polymer. These factors might explain the relatively good correlation between high molecular weight and low  $T_g$  value. These results seem to be consistent with other research which found that low molecular weight of HTNR had higher  $T_g$  value than the high molecular weight of HTNR [11, 27].



Figure 4.19 DSC thermograms of HTNR with different molecular weight.

The FT-IR spectroscopy, <sup>1</sup>H-NMR spectroscopy, and SEC confirmed that HTNR with different molecular weight has been successfully synthesized which can further be used as polyol to prepare cationic waterborne polyurethane.

# 4.2.3.2 Characterization of cWPU

### 4.2.3.2.1 cWPU latex

The cWPUs with NCO index of 1.00 were successfully synthesized by normal step- growth having total solid content percentage of 16 - 19% and milky blue appearance and were stable in aqueous media as shown in **Table 4.9**. To introduce the cationic charge into the long chain WPU NMDEA was neutralized with acetic acid. "*N*" position of cWPU in the NMDEA sections was stabilized by overload 50% acetic acid to make sure that all amine positions were positively charged. Thus, pH values of the dispersion WPUs were in acidic ranges (pH 3.7 - 4.2)



Table 4.9 Appearance of WPU base on HTNR with different molecular weights latex and films.

The hydrodynamic diameter and zeta potential of the latexes was measured by dynamic light scattering. The particle size of cWPUs based on HTNR3000, HTNR2000 and HTNR1000 were 76, 168 and 591nm, respectively. As the molecular weight of the HTNR section used to make the cWPU increased the particle size decreased as shown in **Figure 4.20**. All cWPUs had a narrow polydispersity index ranging from 0.2-0.3 indicating uniform particle sizes and a controlled polyurethane synthesis. The trend in decreased particle size with increased molecular weight of HTNR is explained by the lower shear force required when low molecular weight HTNR was used to make the cWPU. By contrast the cWPU latex with high molecular weight HTNR has higher viscosity, meaning that a greater interfacial shear force was exerted during the formation of the latex and leading to a smaller particle size as a result.



Figure 4.20 Particle size dispersions of cWPUs based on different  $M_n$  of HTNR.

Zeta potential values of cWPUs with different  $M_n$  of HTNR with HTNR3000, HTNR2000 and HTNR1000 (cWPU7, cWPU17, and cWPU18) were +71.1 mV, +66.9 mV and +66.8 mV, respectively. Typically, zeta potential values above +30 mV may be considered a suitable threshold for particle stability [90]. These results could be assumed that the particle of synthesized cWPUs were stable and had a high density of positive charge on the surface area. The lower zeta potential can be explained by the slight drop in stability which leads to a larger dimensional particle size with low  $M_n$  HTNR. This work demonstrates zeta potential values in a higher range can be obtained by increasing the  $M_n$  of HTNR. Large particle size is usually sediment easier than smaller particle size that is directly affected in storage life time of cWPUs.

Moreover, the particle size of cWPUs based on different  $M_n$  of HTNR1000, HTNR2000, and HTNR3000 were observed by TEM. The evidence was demonstrated in **Figure 4.21**. With round of shape, dimension sizes of cWPUs with various  $M_n$  of HTNR of 1000, 2000, and 3000 g.mole<sup>-1</sup> were found in range of approximately of 240, 150, and 30 nm, respectively. Deep-dark points of stained natural rubber with OsO<sub>4</sub> were showed in main components of these cWPUs and others were found in less. It showed good dispersion of cWPU particles in its media with large particle size of cWPUs (based on  $M_n$  of HTNR1000 and HTNR2000). Contrary, HTNR3000 based cWPU was found in smallest particle size of dimension about 30 nm showing agglomeration, but the good dispersion in the water media with milky blue appearance were still observed.

In comparison of zeta nanosizer results, all particle size results from zeta nanosizer were larger than particle size from TEM by showing the compared results in **Figure 4.22**. Technically, the nature of zeta nanosizer detected with laser light through the applied sample dispersed in its media and monitored the light for proving the sample size. This technique could be easily detected the agglomerated sample side and calculated for presenting the average sizes of the sample, and it is usually reported the larger size more than the real one.

Overall, cWPUs were slightly dropped its dimension particle size by increasing  $M_n$  of HTNR. High  $M_n$  and long chain HTNR normally shows itself with higher viscosity than low  $M_n$  and short chain HTNR because of its chain entanglement and intra-/inter-chain physical interaction. Particle size was usually controlled by spinning and viscosity. Controlling blade spinning of round for stirring was fixed so that the effect of viscosity was able to discuss. Interfacial between blade and pre-cWPU mixture were faced. On the processing time, the spinning blade touched with the center of mixture, and flash them with high shear in condition of high viscosity (High  $M_n$  of HTNR) to get the small particle of cWPU. On the other hand, low viscosity components were tear with low shear to get large particle of cWPU.



Figure 4.21 TEM images of particle size of cWPUs based on different molecular weight of HTNR.



**Figure 4.22** Comparison of particle size of cWPU based on different molecular weight of HTNR resulting from nanosizer and TEM images.

The physical properties of cWPU with different molecular weight of HTNR  $(1000 - 3000 \text{ g.mole}^{-1})$  were concluded in **Table 4.10**.

	Physical Properties									Contact angle		
Code TSC (%) St	TSC (%)	Stability	Appearance	рН	Film appearance	Particle si	und)	Zeta Potential (mV)		(theta)		
					Peak 1 <sup>b</sup>	Peak 2 <sup>c</sup>	PDI <sup>d</sup>	Value	SD <sup>e</sup>	Water	Oil	
cWPU7	16.67	Stable <sup>a</sup>	Milky blue	3.73	very-yellowish film	76.46(100)	-	0.438	+71.1	10.5	91	35
cWPU17	17.66	Stable <sup>a</sup>	Milky blue	4.13	yellowish film	167.9(100)	-	0.239	+66.9	9.9	83	39
cWPU18	18.73	Stable <sup>a</sup>	Milky blue	4.22	brittle yellowish film	85.53(26.4)	590.5(73.6)	0.305	+66.8	14.5	44	43
N/A : Not a	vailable				8	<sup>a</sup> more than 6 m	onths					
<sup>b</sup> First size o	First size distribution (percentage found) <sup>c</sup> second size distribution (percentage found)											
<sup>d</sup> Polydisper	ydispersity index from nanosizer <sup>°</sup> Zeta Deviation from zeta potential											

**Table 4.10** Summary physical properties of cWPU with different molecular weight of HTNR.

### 4.2.3.2.2 cWPU films

The synthesized cWPUs with different  $M_n$  of HTNR were cast. The films appearance were in shade of yellow to yellowish brown. Due to the less transparent optical properties of the aromatic rings in the isocyanate used these films were yellow in appearance, with cWPU made from HTNR3000 being a light yellow whilst films from HTNR2000 and HTNR1000 were deep yellow and yellowish-brown respectively, shown in **Table 4.10**. The result showed that cWPU from HTNR1000 was brittle whilst that from HTNR3000 had the best elastomeric properties. Visual inspections of the films suggest that the viscoelastic and adhesive properties can be altered by changing the molecular weight of the HTNR depending on the application of the film.

To confirm the chemical structure, FTIR spectroscopy were studied the functional group of prepared cWPUs from different molecular weight. The FTIR spectra of cWPU films were shown in **Figure 4.23**. The adsorption peaks of HTNR was found in wave numbers of 3500 cm<sup>-1</sup>, broad peak, (-OH stretching), 3100 to 2800 cm<sup>-1</sup> (-C-H stretching), 1447 cm<sup>-1</sup> (-CH<sub>2</sub>- bending), 1378 cm<sup>-1</sup> (-CH<sub>3</sub> deformation), and 880 cm<sup>-1</sup> (=C-H out of plane) [11, 18]. Moreover, the characteristic functional groups of polyurethane were attributed in wavenumber of 3270 cm<sup>-1</sup> (-NH stretching), 1720 cm<sup>-1</sup> (-C=O stretching), 1667 cm<sup>-1</sup> (-NH bending), 1536 cm<sup>-1</sup> (-NCOO stretching), 1224 cm<sup>-1</sup> (C-O stretching of urethane), 1136 cm<sup>-1</sup> (-CN- stretching), and 1056 cm<sup>-1</sup> (-C-O-C- stretching) [38, 93, 105]. Another, the results could be noted that the absence of a peak at 2270 cm<sup>-1</sup> corresponding to free isocyanate were observed. Due to the reaction was complete there was no toxicity that could affect routine applications. The NH peak of HTNR1000 was sharpest, attributed to the higher ratio of NCO in the cWPU formulation because of the shorter chain length of HTNR [106]. However, there are no significantly different in peak because there is the same functional group but only difference in molecular weight of polyol.



Figure 4.23 FT-IR spectra of HTNR and cWPUs films.

In addition, the effects of  $M_n$  of HTNR substrate on water uptake percentage of cWPU films were monitored and corrected for 1 week. As can be seen in the graph in **Figure 4.24**, the water uptake of all cWPU films raised up. The results of cWPU7 (with HTNR3000) and cWPU17 (with HTNR2000) film were found in the low range from about 4 to 8% and 3 to 10%, respectively. Furthermore, the water uptake percentage of cWPU18 (with HTNR1000) was corrected from 16 to 35%. The most interesting aspect of this graph is short chain polyol substrate obtained high water uptake percentage because of in this study the ratio of the reactive group of hydroxyl from polyol and other substrates and cyanate group were fixed as one. These results were in agreement with that the amount of isocyantate (high polar group substrate) in case of low  $M_n$  of HTNR were normally used more than high  $M_n$  of HTNR by the calculation. In this point, the ratio of water-like increased while nonpolar in part of natural rubber decreased. Therefore, the cWPU films composed of high polar substrates (water-like) in the system is agreed in high percentage of water-like percentage from contact angle results.



Figure 4.24 Water uptake percentage of cWPU films from different molecular weight of HTNR.

Furthermore, their hydrophobic/hydrophilic properties of cWPU films have been studied by the contact angle measurement techniques that were described the surface wettability. Contact angle resulted from cWPU films with different  $M_n$  of HTNR were corrected in **Table 4.11**. The strong evidence of hydrophilic property was increased, when cWPU obtained with low  $M_n$  of HTNR. The contact angle values of cWPU7, cWPU17, and cWPU18 were 91°, 83°, and 44° for water and 35°, 39°, 43° for oil, respectively. The results were agreed with the arguments of water absorption and support the reason in the description. What a striking about the contact angle results in the table was that cWPU had low water contact angle, high surface wetting which was good adhesion for the further adhesive application.

Code name	Water contact angle image	Oil contact angle image		
	91°	35°		
cWPU7				
cWPU17	83°	39°		
cWPU18	<b>44</b> °	<b>43</b> °		

Table 4.11 Contact angle of cWPU films in effects of molecular weight of HTNR.

The mechanical properties of cWPU films based on HTNR with a different  $M_n$  were corrected and the results of the correlation analysis were summarized in **Table 4.12**. The most interesting aspect of the graph of stress-strain curves showed clearly turning from elastomeric polymer to tough and rigid plastic by reducing  $M_n$  of HTNR substrates from 3000 to 1000 g. mole<sup>1</sup> as can be seen from the **Figure 4.25**. The increase of Young's modulus values were found in case of reducing  $M_n$  of polyol substrates by rising up from 1.17 to 60.89 MPa. On the other hand, tensile strength and elongation at break of the cWPU films were slightly dropped. No significant difference were found for tensile strength by showing slightly dropped from 1.70, 1.67, and 1.66 MPa for cWPU7, cWPU17, and cWPU18, respectively. The elongation at break of these films were 116, 87, and 6 % for cWPU7, cWPU17, and cWPU18, respectively. High Young's modulus value in account of low  $M_n$  of HTNR was because of the short chain of polyol, soft segment part, in polyurethane main chain. Normally, elastic behavior of this PU is mainly from natural rubber consisted of *cis*-1,4- polyisoprene. The elastic behavior is decreased and dropped in condition of

short chain and low  $M_n$  [107]. Other reason is that the density of urethane linkage between cyanate group and reactive hydroxyl group. By fixing the isocyanate index and batch size, in case of low  $M_n$  of HTNR is normally composed of high density of urethane linkage led to high rigidity them. The most obvious finding to emerge from the analysis was that the polymer showed high stiffness and rigidity properties in case of low  $M_n$  of HTNR while high  $M_n$  of HTNR showed high elastic properties.



Figure 4.25 Stress-strain curves of cWPU films from different molecular weight of HTNR.

 Table 4.12 Mechanical properties and swelling percentages of cWPU with different molecular weight of HTNR.

Codo nomo	Young's modulus	Tensile strength	Elongation at break	Swelling in	
Coue name	(MPa)	(MPa)	(%)	<b>THF (%)</b>	
cWPU7	$1.14 \pm 0.23$	$1.70\pm0.19$	$116.64 \pm 1.38$	N/A	
cWPU17	$4.26\pm0.11$	$1.67\pm0.10$	$87.06\pm2.10$	N/A	
cWPU18	$60.89\pm0.33$	$1.66\pm0.07$	$6.33 \pm 0.13$	N/A	

Note: N/A = can not measure

Moreover, the morphology of roughs and fracture behaviors of cWPU film specimens from the cross section of tensile testing were imaged from SEM. **Figure 4.26** provided the results obtained from the SEM analysis of cWPU cross-section films from different  $M_n$  of HTNR resulted from tensile testing. The results of this study indicated that the matrix of sample tearing contributed to higher Young's modulus (in the account of high  $M_n$  of HTNR) by turning from ductile fraction to brittle fraction during tensile testing. In this point, in case of high  $M_n$  of HTNR, rougher surface and sheet-like after fraction showed that the films of cWPU were higher ductile properties than rigid properties while the smooth surface would occur in the brittle polymer in case of low  $M_n$  of HTNR. These results seem to be consistent with the idea of mechanical properties which found that cWPU films with low  $M_n$  had high brittle and rigid properties while high  $M_n$  had high elastic properties.



**Figure 4.26** SEM images of cWPU cross-section films from different molecular weight of HTNR resulted from tensile testing.

Furthermore, thermal properties of cWPU films with different  $M_n$  of HTNR series and polyol substrate were studied by TGA, DSC and DMTA. Thermal degradation of cWPU films demonstrated by TGA and DTG results were presented in **Figure 4. 27** and maximum decomposition temperature ( $T_{max}$ ) were listed in **Table 4.13**. The results of decomposition in each step and segment were also provided. In comparison to pure HTNR, all HTNR decomposed only one step in temperature about 370 °C. From the obtained results, there are same steps of decomposition by having 2 main decomposition steps. The range of 190-260 °C was the first step decomposition attributed to breaking of urethane linkage as EG, HTNR, isocyanate, and also loss of carbon dioxide from urethane deformation [18].  $T_{max}$  of cWPU7, cWPU17, and cWPU18 were about 210.7, 209.3, and 208.5 °C, respectively. For the second decomposition step, decomposed temperature of sample was changed into the higher temperature range of 340-460 °C related to the decomposition range of telechelic natural rubber part as indicated in pure polyols substrate. In this step,  $T_{max}$  cWPU7, cWPU17, and cWPU18 were about 379.8, 379.5, and 378.7°C, respectively. The evidences from TGA results suggested that the thermal stabilities of cWPU films were slightly increased by increasing the  $M_n$  of HTNR.


**Figure 4.27** Thermal gravimetric results of cWPUs film based on different molecular weight of HTNR – (a) TGA curves and (b) DTG curves.

		Thermal proper	rties	
Code name	First step <sup>a</sup>	Second step <sup>a</sup>	$T^{b}(^{0}C)$	Tan delta <sup>c</sup>
	$T_{max}$ (°C)	$T_{max}$ (°C)	$I_g$ (C)	(°C)
HTNR3000	-	372	-58.7	N/A
HTNR2000	_	368	-60.1	N/A
HTNR1000	-	366	-62.1	N/A
cWPU7	210.7	379.8	-52.7	-54
cWPU17	209.3	379.5	-47.8	-52
cWPU18	208.5	378.7	-43.9	-44

Table 4.13 Thermal properties of synthesized cWPU and HTNR with different molecular weight.

<sup>a</sup> Thermal degradation from TGA results

<sup>b</sup>  $T_{g}$  from DSC results

<sup>c</sup> Tan delta from DMTA

Moreover, to identify the part of amorphous and crystalline behavior, DSC technique was used to investigate these thermal properties. For this work, DSC thermograms were shown only amorphous phase indicated by  $T_g$  value, as shown in **Figure 2.28** and listed in **Table 4.13**. Data from this figure, cWPU with different  $M_n$  of HTNR, could be compared with the data in **Figure 4.19**, HTNR substrates with different molecular weight. It could be seen from the data that the  $T_g$  in cWPU group performed significantly higher than pure HTNR group. For the pure HTNR results,  $T_g$  values were -62.1, -60.1, -58.7 °C for HTNR3000, HTNR2000, and HTNR1000, respectively. In addition, for the group of cWPU,  $T_g$  values were -52.7, -47.8, and -43.8 °C for cWPU based on HTNR3000, HTNR2000, and HTNR1000, respectively. The increase of  $T_g$  was observed because of urethane linkage and more rigid short chain of polyol part in main chain of cWPU. Urethane linkage was formed after the reaction between isocyanate and reactive hydroxyl group leading to high density of hydrogen bonding then. Moreover, short chain polyol part in cWPU effected to rigidity and chain mobility. Therefore, low  $M_n$  of HTNR were had higher  $T_g$  value than high  $M_n$  of HTNR.



Figure 4.28 DSC thermograms of cWPU based on different molecular weight of HTNR.

Furthermore, thermo-mechanical properties was tested by DMTA which enter molecular mobility of polymer sensitively. Detailed examination of the storage modulus (G') and tan  $\delta$  of cWPU films different  $M_n$  of HTNR substrates presented with a function of temperature were shown in Figure 4.29. Two important themes emerge from the studies discussed so far: (1) glassy state of polymer,  $T_g$ , was defined by tan  $\delta$ , and (2) the stiffness of cWPU films was determined by G'. DMTA results presented clearly the effect of  $M_n$  of HTNR on storage modulus result of cWPU films. There were three steps demonstrated in the results. In the first period of graph, about -100 to - 60 °C, glass phase or hard plastic behavior was found in all cWPU films and the stiffness was increased rapidly with decrease of  $M_n$  of HTNR. The effect of rigid structure from chain length of polyol part on the polymer backbone and hydrogen bonding from urethane linkage were correlated. For second state, all samples results showed the major relaxation found in temperature approximately -60 to -25 °C presented by dramatically dropped in storage modulus, corresponding to the energy dissipation of the polymer that was shown as the peak maximum in the tan  $\delta$  curve [108]. This state was in range of  $T_g$  of synthesized cWPU by presenting major effect of natural rubber on the cWPU films. In difference, major relaxation was shifted into higher temperature by increasing epoxide on eHTNR backbone due to difference density of interaction of intra- and intermolecular chain. The last phase found in curve was rubbery state or elastomeric phase observed in

temperature above -40 °C. This phase was very clear the effect of molecular weight on cWPU films by showing highest stiffness materials in cWPU18 (from HTNR1000) and lowest value in cWPU7 (from HTNR3000). DMTA results confirmed that thermo-mechanical properties could be enhanced by decreasing  $M_n$  of HTNR substrates. However, in case of using HTNR1000 substrate, cWPU film was very brittle and directly affected to dynamic and testing with some defect points.

 $T_g$  values from DMTA results were listed in **Table 4.13**. For cWPU7, cWPU17, and cWPU18  $T_g$  values were of -54, 42, and -44 °C, respectively. The results show tan  $\delta$  related to relaxation temperature in the range of elastic properties natural rubber, main composition in cWPU, but the difference of  $T_g$  values affected from different density of hydrogen bonding and urethane linkage on cWPU main chain were discessed. In comparison, there were similar trend of  $T_g$  values from DMTA and from DSC because only one glassy state with relating temperature was found.





Figure 4.29 (a) Tan  $\delta$  and (b) Storage modulus as function of temperature for cWPU films from different molecular weight of HTNR.

This study has also shown that the molecular weight of HTNR has an effect on a particle size distribution and term stability. These results indicated that cWPU with the higher molecular weight of HTNR provided a well-defined dispersion having monomodal distribution with a small particle size (containing particle 74 nm) and good dispersion stability. Additionally, the increase in a molecular weight of HTNR leads to high visco- elastic properties, therefore, tensile strength and elongation at break are higher and include a highly hydrophobic. This result is according to  $T_g$  value that is shifted to a lower temperature with a higher molecular weight. Increasing a molecular weight of HTNR increase the mobility of polyurethane backbone leading to a low  $T_g$  value. Also, the thermal stability of cWPU films were slightly increased by increasing the molecular weight of HTNR.

# 4.2.4 Effects of Isocyanate index (NCO index) level on cWPU properties

In this part, the effects of NCO index on cWPU properties were studied by fixing the NMDEA 5.67 %wt, the EG content of 1 mole, and molecular weight of HTNR about 3000 g.mole<sup>-1</sup>. Chemical structure, physical properties, mechanical properties of cWPU were investigated.

## 4.2.4.1 cWPU latex

These cWPU showed well-dispersed with milky-blue appearance latex as shown in **Table 14 and 15** and the physical properties were summarized in **Table 4.16**. Shelf life was more than 10 months with the total solid content (TSC) about in range of 17 - 21%. pH values of these cWPUs were approximately 4 which indicated that overdose of acetic (acetic acid content was used 150% of NMDEA content) was neutralized into the amine functional group of NMDEA for making sure that all positions were cationic.

cWPU6	cWPU19	cWPU20
Cannot form film		s the state

Table 4.14 Appearance of cWPU base on natural rubber with different NCO index (without EG).



**Table 4.15** Appearance of cWPU base on natural rubber with different NCO index (with 1 mole of EG).

Stabled cWPU was found in NCO index of 100 - 150 for without EG content system while with EG content at 1 mole was stable in NCO index of 100 - 125. Coagulated cWPU was found in the unstable system with the increase of isocyanate index. This isocyanate could be reacted with water in cWPU latex to form the urea hard segments and carbon dioxide gas [18, 109, 110]. The **Scheme 4.1** shows the possible reaction of free isocyante in cWPU system.



Scheme 4.1 Reaction of free isocyanate in cWPU system.

The appearance of accessed urea would be gathered and coagulated due to insufficient emulsifier to stabilize in water. Figure 4.30 provided the results obtained from the preliminary particle size distribution of cWPU from different NCO levels. Dimensional particle sizes were increased by increasing level of NCO index. In case of non-EG content, presented in Figure 4.30a, the particles size of cWPU was slightly increased from 59.8 to 83.8 and 94.2 nm with NCO index levels of 100, 125 and 150, respectively. Similarly, the particles size distribution of cWPU with EG, presented in Figure 4.30b, was increased from 76.5 to 192.7 nm by NCO index levels of 100 and 125, respectively. But the particle size distribution is normally cause of prepolymer viscosity, ionic group position, chain rigidity and soft segment structure [18]. In this work, the reasons could be described by two points. The large particle size observed in side of folded main chain of cWPU with normal reaction in synthesis process while the smaller size range might be the reaction of excess isocyanate and short chain cWPU randomly or urea form in the system [18, 109, 110]. These results were related with the trend of anionic WPU based on NR result that the particle size increase with increasing NCO index level [18]. Because of the random copolymerization the reaction was run randomly to get long chain with active functional group to rise the particle size with higher NCO levels.

Zeta potential values of the cWPUs with different NCO index were listed in **Table 4.16**. The result provided two parts. Zeta potential of cWPU with EG 1 mole were about +71 and +60 mV for cWPU7 and cWPU22, respectively. In addition, the results from without EG condition were +70.6, +64, and +56 mV, respectively. All studies results suggest that zeta potential values above +30 mV (for positive charge dispersion) and lower than - 30 mV (for negative charge dispersion) may be considered a suitable threshold for particle stability [90]. The results of this study indicated that the particle of synthesized cWPUs were stable and had a high density of positive charge on the surface area. The lower zeta potential can be explained by the slight up in stability which leads to a smaller dimensional particle size with higher NMDEA content. This work demonstrates zeta potential values in a higher range can be obtained with low NCO index.



Figure 4.30 Size distribution chromatograms of cWPU with varying amount NCO index - (a) without chain extender and (b) with 1 mole of chain extender.

Furthermore, all physical properties of cWPU were concluded and presented in Table 4.16.

	Physical Properties									Contact angle			
Code name	TSC (%) Stability	G( 1 9)				Particle si	Particle size (nm) (% Found)			Zeta Potential		(theta)	
		Appearance	рн	1 Film appearance	Peak 1 <sup>b</sup>	Peak 2 <sup>c</sup>	PDI <sup>d</sup>	Value	SD	Water	Oil		
cWPU6	21.02	Stable <sup>a</sup>	Milky blue	4.37	very-yellowish film	59.8 (100)	-	0.14	+70.6	6.2	90	39	
cWPU7	16.67	Stable <sup>a</sup>	Milky blue	3.73	very-yellowish film	76.5 (100)	-	0.438	+71.1	10.5	91	35	
cWPU19	18.72	Stable <sup>a</sup>	Milky blue	3.92	yellowish film	83.8 (100)	-	0.224	+64.0	7.2	88	37	
cWPU20	19.23	Stable <sup>a</sup>	Milky blue	3.88	yellowish film	94.2 (100)	-	0.253	+56.1	6.1	76	36	
cWPU21	N/A	Unstable	Coagulation	N/A	N/A	N/A	-	N/A	N/A	N/A	N/A	N/A	
cWPU22	17.73	Stable <sup>a</sup>	Milky blue	4.02	yellowish film	36.1 (26.5)	192.7 (73.5)	0.428	+59.9	5.5	89	32	
cWPU23	N/A	Unstable	Coagulation	N/A	N/A	N/A	-	N/A	N/A	N/A	N/A	N/A	

 Table 4.16 Summary of physical properties of cWPU from different NCO index level.

N/A : Not available

<sup>b</sup> First size distribution (percentage found)

<sup>d</sup> Polydispersity index from nanosizer

<sup>a</sup> more than 10 months

<sup>c</sup> second size distribution (percentage found)

<sup>e</sup> Zeta Deviation from zeta potential

### 4.2.4.2 cWPU films

The cWPUs with different NCO index were cast as film. **Table 14 and 15** compared the physical appearances of film of cWPU with a different NCO index. The samples showed that the increasing level of NCO index or adding EG is able formed film whereas the NCO index of 100 and without EG could not be formed film. The increasing level of NCO index, would cause the color of film change from yellow to yellowish brown due to the optical properties [111]. Because the excess isocyanate amount produced the urea molecules by reaction with water and dispersed in films to be more strength and deeper color of shade [109, 112].

The chemical structure confirmation and hydrogen bonding were checked by FTIR spectroscopy. The spectra results of the cWPUs were demonstrated in Figure 4.31. For the substrate, HTNR, the adsorption peaks was found in wavenumbers about 3500 cm<sup>-1</sup> (broad peak), 3100 to 2800 cm<sup>-1</sup>, 1447 cm<sup>-1</sup>, 1378 cm<sup>-1</sup>, and 880 cm<sup>-1</sup> attributed to -OH stretching, -C-H vibration,  $-CH_2$ - bending,  $-CH_3$  deformation and =C-H out of plane, respectively [11, 18]. After reaction, cWPU with various NCO index, the chemical structures of all cWPU films shown as important functional groups were attributed in ranges of wavenumber 3270 cm<sup>-1</sup> (-NH stretching), 1720 cm<sup>-1</sup> (-C=O stretching of urethane), 1667 cm<sup>-1</sup> (-NH bending), 1536 cm<sup>-1</sup> (-NCOO of urethane linkage vibration), 1224 cm<sup>-1</sup> (C-O stretching of urethane), 1136 cm<sup>-1</sup> (-CN- vibration), and 1056 cm<sup>-1</sup> (-C-O-C- vibration of urethane linkage) [38, 91-94, 113]. In addition, the adsorption band of cis-1,4 polyisoprene of natural rubber was found in wavenumbers of about 2802 to 2950, 1447, 1378, and 880 cm<sup>-1</sup> corresponding to -C-H stretching, -CH<sub>2</sub>- bending, -CH<sub>3</sub> deformation, and =C-H out of plane deformation, respectively [11, 18]. Moreover, the results could be noted that free isocyanate peak of cWPU disappeared in wavenumber of 2270 cm<sup>-1</sup> because excess isocyanate reacted with water to obtain urea in cWPU system completely. Therefore, it had no toxic in our routine applications.

From the result of FTIR, cWPUs with different NCO index level were successfully prepared by normal step-growth polymerization.



**Figure 4.31** FTIR spectra of cWPU film with various NCO index and compared with HTNR3000 substrate.

Moreover, NH stretching (at wavenumber about 3270 cm<sup>-1</sup>) and carbonyl group (at wavenumber about 1700 cm<sup>-1</sup>) was shifted into red shift (lower wavenumber) by increasing level of isocyanate index in all sample results and the spectra results were demonstrated in **Figure 4.32**. These phenomena could be explained by influence of the hydrogen bonding between –NH of urethane and carbonyl of urethane with intra- and intermolecular of cWPU backbone and free urea molecules in the system [33, 114-116]. Also, this effect was one of the important parameter for improving the strength of films by increasing level of isocyanate index. Thus, in case of without chain extender, higher levels of NCO index could peel of the films from mold easier than lower level (NCO index 1.00 without chain extender cannot be formed film as well).



**Figure 4.32** FTIR spectra of cWPU film with various NCO index at wave number from  $3600 - 3000 \text{ cm}^{-1}$  and  $1800 - 1600 \text{ cm}^{-1}$  (a) with 1 mole EG and (b) without EG.

In addition, the effects of NCO index on the water uptake percentage of cWPU films were monitored for 7 days and calculated then. The results presented **in Figure 4.33**. These results showed that all water uptake results of cWPU films rose up by increasing level of NCO index. In case of non- chain extender water uptakes were slightly increased by immerging time from 1 to 7 days showing in range of 2 - 12 %. While series of adding 1 mole of EG showed the result in range of 2 - 25 %. The results could indicate that the system with EG had more water uptake than cWPU films without EG. One interesting finding was water uptake increased in condition of higher NCO index. The present of urea was the most effective in water uptake because by their chemical structure urea is high polar structure. In comparison, for the anionic WPU based on NR with the same percentage of emulsifier amount (-5.6%), Saetung *et* al [18], reported that the water uptake results of WPU film from different NCO index for 7 days were in range of 17 - 45 % and the water uptake was up by increasing NCO index level. Primarily, the result prove that cWPU base on NR is more properly in field of adhesive, coating and all material sensitive to water than aWPU. The results from this study could be assumed that because of the different interaction of intra-/inter chain of nature charge of anionic and cationic WPU.

Also, the swelling properties of cWPU in chosen solvent of tetrahydrofuran (THF) were shown in **Table 4.17**. Normally, isocyanate hard segment is hardly dissolved in THF, while natural rubber soft segment is easily dissolved in THF. Almost sample were dissolved in THF except cWPU22 (NCO index of 1.25 and adding chain extender for 1 mole) which found about 160% swelling. The result showed that was mostly dissolved because of high non-polar nature of natural rubber and high linear structure content. What the supporting reason of these is the more hard segment promoting physical bonding from intra-/inter-chain hydrogen bonding effected to swelling values of cWPU films [18]. For without EG, there were insufficient interaction of intra- and intramolecular interaction to overcome the dissolution of THF.





**Figure 4.33** Water uptake of cWPU films from different level of NCO index – (a) with 1 mole EG and (b) without EG.

Moreover, their hydrophobic/hydrophilic properties of cWPU films have been studied by the contact angle measurement techniques that was described to reversible surface wettability. **Table 4.18** showed figures of water contact angle and oil contact angle for hydrophobicity and hydrophilicity of cWPU films and the results were summarized in **Table 4.17**. Hydrophilicity was increased by increasing of NCO levels in both cases. In case of non-EG, water contact angle values were 90, 88, and 76 degree while oil contact angle values were 39, 37, and 36 degree for NCO index of 100, 125, and 150, respectively. In condition of adding EG, water contact angle values were 91 and 89 degree while oil contact angle values were 35 and 32 degree for NCO index of 100 and 125, respectively. There are gently different because most of the ingredients were natural rubber part which is non polar structure [15]. On the other hands, water contact angle value which was dramatically dropped in system of NCO index of 150 because of high polarity of urea in the presence system. These contact angle values were relatively hydrophilic and easier to wet many material surfaces [99]. That was a good parameter to pave the way for adhesive application.

Code name	Water Contact Angle	Oil Contact Angle
	90°	<b>39°</b>
cWPU6		
	88°	37°
cWPU19		
	76°	36°
cWPU20		
	91°	35°
cWPU7		
	89°	32°
cWPU22		

Table 4.17 Images of contact angle of cWPU films with various different NCO index.

To describe the strength and polymer behavior, mechanical properties of cWPU films with different EG content have been studied. Mechanical properties of cWPU films were indicated by stress-strain curves as shown in **Figure 4.34** and listed in **Table 4.18**. In case of non-EG, the properties of films were up by increasing NCO levels from 125 to 150. Tensile strength of films

were 0.32 and 0.82 MPa, Young's modulus values were 0.95 and 1.21 MPa, and Elongation at break values were 26.05 and 20.65 % for cWPU19 and cWPU20, respectively. In addition, adding EG series, it could be increased the mechanical properties. The tensile strength were 1.83 and 7.76 MPa, Young's modulus values were 1.14 and 20.52 MPa, and Elongation at break values were 116.64 and 72.32 % for cWPU7 and cWPU22, respectively. The evidence showed that they presented the same trend of mechanical properties when composing with higher NCO index. These results could be described by the present of urea in the system from excess NCO reacted with water. The influence of the hydrogen bonding between –NH of urethane and carbonyl of urethane with intra- and intermolecular of cWPU backbone and free urea molecules in the system were indicated and also described by FTIR results [33, 114-116]. Moreover, the comparison of strength in series of NCO index 125, non-EG content (cWPU19) and EG content (cWPU22), jumped into 7 fold times by adding EG as chain extender because of long chain and chain entanglement that was explained in our previous work [15]. From the mechanical properties results, the inversion of soft elastic to hard plastic behavior were indicated by increasing NCO index. However, in case of adding chain extender had more mechanical properties than without chain extender.



Figure 4.34 Stress vs strain curves of cWPU films with various different NCO index level.

Code	Young's modulus	Tensile Strength	Elongation at break	Swelling in
	(MPa)	(MPa)	(%)	<b>THF (%)</b>
cWPU6	N/A	N/A	N/A	N/A
cWPU7	$1.14\pm0.23$	$1.83\pm0.19$	$116.64 \pm 1.38$	N/A
cWPU19	$0.95\pm0.17$	$0.32\pm0.03$	$26.05 \pm 0.11$	N/A
cWPU20	$1.21 \pm 0.22$	$0.82 \pm 0.13$	$20.65 \pm 0.31$	N/A
cWPU22	$20.52 \pm 0.25$	$7.76 \pm 0.33$	$72.32 \pm 1.27$	159.55

Table 4.18 Mechanical properties of cWPU films with various NCO index level.

Note: N/A = can not measure

Moreover, the morphology of roughs and fracture behaviors of cWPU film specimens from the cross section of tensile testing were imaged from SEM. The surface of those materials were indicated into 2 parts – without EG and adding EG – presented in **Figure 4.35**. In case of without chain extender, NCO index 100 cannot formed as strength film and peeled out from mold, so there are no result of NCO index in case of cWPU6. However, in condition of good films, the fracture surfaces of cWPU19 were rougher than cWPU20 for NCO index of 125 and 150, respectively. Meanwhile, in case of adding chain extender cWPU, the results could well-stable in range of NCO index from 100 – 125 as showing before. It clearly demonstrated that smoother surface in condition of higher NCO index like in case of without chain extender.

In both cases, with and without chain extender, the fracture surface of higher NCO index was smoother than lower NCO index. The reason is that changing from elastic materials to hard plastic materials was indicated by increasing NCO index because of more physical bonding inter and intra molecular of polyurethane chains. SEM results were agreed with stress-strain curves by showing dropping strain percentage while stress was increased.



**Figure 4.35** SEM images of cWPU films with various NCO index – without chain extender (cWPU19 and cWPU 20) and with chain extender (cWPU7 and cWPU22).

Furthermore, thermal properties of cWPU films with different NCO index level series and polyol substrate were studied by TGA, DSC and DMTA. Thermogravimetric analysis results showed the thermal stability, decomposition and components determined by weight loss and its derivatives. For the substrates, HTNR3000, the result showed a single stage degradation in temperature about 377 °C. The thermogravimetric curve of cWPU with various isocyanate index without EG (cWPU6 (NCO index 100), cWPU19 (NCO index 125), and cWPU20 (NCO index 150)) has a similar behaviour that show two stages of the thermal detradation as shown in **Figure 4.36**. The first stage is mainly a decomposition. This stage can be observed that  $T_{max}$  of cWPU films are shifted to higher temperatures with increase isocyanate index [33]. Further, increase isocyanate index give rise to strong statistic force and hydrogen bonding. It was found that a mass of hard segment content is 15.73 wt%, 17.60 wt%, and 21.20 wt% for cWPU6, cWPU19, and cWPU20 respectively as shown in **Table 4.19**. The second stage show the thermal decomposition

at the same temperature with  $T_{max}$  at 379 °C that is associated with chain scission of HTNR3000 as soft segment. Also, long chain soft segment decreased in amount with increasing NCO index content that found a mass of soft content at 81.79 wt%, 78.54 wt%, and 75.75 wt% respectively.

In addition, cWPU with various isocyanate index and used 1 mole of EG (cWPU7 (NCO index 100) and cWPU22 (NCO index 125) show that thermal degradation takes place through two stages as shown in **Figure 4.37.** The first stage, it can be observed that are shifted to higher temperatures with increase isocyanate index by showing  $T_{max}$  from 210.7 to 217.1 °C for cWPU7 and cWPU22, respectively. This is due to chain extender react with isocyanate forming the rigid urethane linkage that provided higher the thermal stability. The second stage is also attributed to the degradation of HTNR3000 about 380 °C. Also, the mass loss found in first step were 27.11 and 29.67% by increasing NCO index from 100 to 125. The second step found the mass loss about 72.89 and 70.33% for cWPU7 and cWPU22, respectively.





**Figure 4.36** Thermogravimetric results of cWPUs films with various NCO index in case of without EG.





**Figure 4.37** Thermogravimetric results of cWPUs films with various NCO index in case of adding 1 mole of EG.

Code	Thermal properties								
	1 <sup>st</sup> step				2 <sup>nd</sup> step				
	Mass		ISS	Mass			Mass residual	Tan	<b>T</b> <sup>d</sup>
	max	change/co	ntent (%)	max	<sup>1</sup> <sub>max</sub> change/content (%)		(%)	delta <sup>c</sup>	g
	(C)	Theory <sup>a</sup>	Found <sup>b</sup>	(C)	Theory <sup>a</sup>	Found <sup>b</sup>	(70)		
HTNR	-	-	-	377	100	99.2	0.11	N/A	-54.7
cWPU6	215.2	21.17	15.73	380.6	78.83	81.79	2.08	N/A	-53.2
cWPU19	211.2	24.44	17.6	380.4	75.56	78.54	3.31	-65.1	-52.8
cWPU20	223.4	27.22	21.2	380.5	72.78	75.75	2.59	-64.3	-52.2
cWPU7	210.7	27.11	12.27	379.8	72.89	84.15	2.77	-54	-52.7
cWPU22	217.1	29.67	17.13	379.7	70.33	78.22	4.23	-53.4	-51.9

Table 4.19 Thermal properties of synthesized cWPU with different NCO index.

N/A = cannot measure

<sup>a</sup> Cal. = percentage content is added into the reaction

<sup>b</sup>Found = percentage content is found in TGA

<sup>c</sup> Tan delta from DMTA result  ${}^{d}T_{g}$  from DSC results

Thermal property from DSC was to provide the part of amorphous, crystallization and also fusion behavior of HTNR3000 and cWPUs backbone as well as showing in glass transition temperature ( $T_g$ ). The DSC curve of HTNR3000 and a series of cWPUs show a single glass transition temperature as shown in **Figure 4.38**. A comparison between  $T_g$  value of a series of cWPUs and HTNR3000 is shifted to a higher temperature than  $T_g$  value of HTNR at at -54.7 °C. With various NCO index in series - cWPU6 (NCO index 100), cWPU19 (NCO index 125), and cWPU20 (NCO index 150), trend of  $T_g$  values were slightly up from -53.2 °C, -52.8 °C and -52.2 °C respectively. The rise of  $T_g$  in increasing NCO level is because of the present of urea in the system. These presented urea were possibly formed the hydrogen bonding and interaction of intra- and inter-molecular chain between urea structures and cWPU main chain in order to additional glass transition [117]. In addition, higher NCO index lead to more free urea in system which can be reinforce and interact with main chain of cWPU to get more rigid in backbone chain increasing temperature to be mobilized. Likewise, the chain extender can be used to increase the  $T_g$  value of cWPU. This result is shown in the following comparison of cWPU without and with chain extender that presented in cWPU6, cWPU19 (without chain extender) and cWPU7, cWPU22 (with chain extender). The  $T_g$  value of cWPU6 is equal to -53.2 °C and cWPU7 is equal to -52.7 °C. Similarly,  $T_g$  values of cWPU7 and cWPU22 were rose up from - 52.8 °C and - 51.5 °C, respectively. This is due to chain extender react with isocyanate forming the rigid urethane linkage that provided more rigid polymer chain and giving entanglement and physical crosslink effect [15]. These results indicated that increased isocyanate index or chain extender gave rise to hard segment content caused the  $T_g$  value to increase.



**Figure 4.38** DSC thermograms of HTNR3000 and series of cWPU films with different NCO index.

**Table 4.19** shows  $T_g$  values obtained using DSC and DMTA measurement analyses. These results are actually not surprising. It was known that  $T_g$  value depends on the technique and the measurement mode.  $T_g$  value from DSC measure by modulation oscillation frequency and  $T_g$  value form DMTA measure by torsion and extension with oscillation frequency. In this part, the viscoelastic properties of cWPU with different levels of NCO index and the influence of chain extender were studied by DMTA analysis. Two important values emerge from the studies discussed so far: (1) glassy state of polymer,  $T_g$ , was defined by tan  $\delta$  (ratio of the loss modulus (not shown) to the storage modulus (G')), and (2) the stiffness of cWPU films was determined by G'.

The effect of isocyanate index on the tan  $\delta$  of cWPU cWPU19 (NCO index 125) and cWPU20 (NCO index150) showed a sharply dropped at -65. 1 °C and -64.1 °C of respectively, which corresponds to the  $T_g$  value as shown in **Figure 4.39**. Furthermore, increasing the isocyanate index led to increasing the hard segment content also increase energy dissipation that causes the tan  $\delta$  shifted to a higher temperature. The storage modulus (G') is reprented the elastic portion as shown in **Figure 4.40**. The curve of G' shift to higher value of G' with the increase of iscocyanate index because it occurs strong hydrogen bonding and more physical crosslink that decreased mobility of the chain. This result confirmed that the increasing the isocyanate enhanced the physical cross-links in PU matrix and improved the mechanical properties.

In addition, the influence of chain extender on cWPU was investigated by DMTA analysis. A comparison between the tan  $\delta$  and the value of G'of cWPU19 (NCO index 125) and cWPU22 (NCO index 125 and 1 mole of EG) as shown in Figure 4.39. The curves of tan  $\delta$  obviously shift to the higher temperature at -65. 1 °C and -53.4 °C of cWPU19 and cWPU22 respectively. This is due to the chain extender is to extend the chain length of hard segment and increase the crosslink density lead to higer values of tan  $\delta$  that is indicative of more energy dissipate and is correlated with chain stiffness. Figure 4.40 shows the storage modulus of cWPU22 shift to a higher storage modulus curve than cWPU19. This result clearly indicates that the using chain extender lead to chain extension and chemical crosslink, as evidenced in the mechanical properties study.

Moreover, it was found that both of the increasing isocyanate index content and the using chain extender increase the  $T_g$  value and a higher storage modulus. We observed that the chain extender strongly influences the visco-elastic properties more than the effect of isocyanate index

content. This result show in the tan  $\delta$  and the value of G'of cWPU22 (NCO index 125 and 1 mole of EG) shifts to the hightest value of the curve than a value of the curve for cWPU20 (NCO index 150 without EG), cWPU7 (NCO index 100 and 1 mole of EG), and cWPU19 (NCO index 125 without EG), respectively. It could be the using chain extender lead to a strong hydrogen bonding *via* physical and chemical crosslink while the increasing isocyante index content gives rise to a hydrogen bonding with increasing hard segment content. The physical crosslink occurs by hydrogen bonding and hard segment formation and the chemical crosslink occurs by chain extension. This results indicated that the thermodynamic and mechanical properties can be improved by increasing isocyanate index content and using chain extender [117].



Figure 4.39 Tan delta curves from DMTA of cWPU films with various NCO index.



Figure 4.40 Storage modulus curves from DMTA curves of cWPU films with various NCO index.

This work showed the effect of isocyanate index content and the using chain extender on the stability and particle size distribution, thermal properties and thermodynamic properties of cWPU. The results showed that well-dispersed cWPU with monodisperse particle size distribution is found at low isocyanate index content. In addition, the increasing isocyante index content leads to form a urea bond that give rise to a high surface wettability and a higher thermal properties and thermodynamic properties of cWPU film. Moreover, the using chain extender has strongly effected on the thermodynamic properties of cWPU films. This result indicated that the thermal stability and thermodynamic properties increased with increasing both of the isocyanate index content and the using chain extender.

#### 4.2.5 Effects of epoxide content on HTNR backbone on cWPU properties

In this part, the effects of epoxide content on HTNR backbone (0-30%) on cWPU properties were studied by fixing starting molecular weight of HTNR about 3000 g'mole<sup>-1</sup>, the NMDEA 5.67 % wt, the EG content of 1 mole, and isocyanate index of 100. Chemical structure, physical properties, mechanical properties, themal properties and adhesive properties of cWPU were also investigated.

### 4.2.5.1 Polyol substrates

To confirm the chemical structure, FTIR spectroscopy and NMR spectroscopy were used. The generation of functional groups was confirmed by FTIR and the spectra are shown in **Figure 4.41**. The characteristic peaks of the *cis*-1,4 isoprene unit from natural rubber were observed for the wavenumbers about 2970, 1449, 1376, and 836 cm<sup>-1</sup> corresponding to -C-H stretching, -CH<sub>2</sub>-deformation, -CH<sub>3</sub> deformation, and =C-H out of plane deformation, respectively [11, 15, 18]. There is another important peak at the wavenumber about 3100 - 3700 cm<sup>-1</sup> corresponding to -O-H stretching from hydroxyl group of HTNR polyol precursor. Another, for eHTNR precursor, new absorption band exhibited in the wavenumber about 890 cm<sup>-1</sup> corresponding to epoxide group on eHTNR backbone.

In addition, after polymerization, the new important peaks of cWPU were found at 3302, 1707, 1602, 1538 and 1224cm<sup>-1</sup> and assigned to -N-H stretching, -C=O ester stretching, N-H bending of urethane position, -N-C=O stretching of polyurethane linkage, and C-O acyl stretching of urethane linkage, respectively [38, 91-94].



Figure 4.41 FTIR spectra: comparison of HTNR, eHTNR30 and cWPU-eHTNR30.

Another technique confirming the chemical structure, epoxide content and molecular weight of eHTNR products is <sup>1</sup>H NMR. The spectra of products are shown in **Figure 4.42**. For the characteristic peaks, the signals of isoprene unit from polyol based on natural rubber were observed at 5.12, 2.07, 1.67, and 1.25 ppm corresponding to *d* (-CH<sub>2</sub>(CH<sub>3</sub>)C=CHCH<sub>2</sub>-), *b*<sub>3</sub>*f* (-CH<sub>2</sub>(CH<sub>3</sub>)C=CHCH<sub>2</sub>-), *c* (-CH<sub>2</sub>(CH<sub>3</sub>)C=CH-), and *h* (-CH<sub>2</sub>(CH<sub>3</sub>)CHO-), respectively [15, 95, 96]. As expected for eHTNR product, the new important peak appeared at chemical shift of 2.6-2.8 ppm and it was assigned to *k* (-CH<sub>2</sub>(CH<sub>3</sub>)C(O)CHCH<sub>2</sub>-). In this work a molecular weight of about 3000 g.mole<sup>-1</sup> was chosen for HTNR (HTNR3000). Also, the targeted epoxide content on the eHTNR backbone was 10, 20 and 30% named eHTNR10, eHTNR20 and eHTNR30, respectively. By the integration calculation, the epoxide content for eHTNR10, eHTNR20, and eHTNR30 were about 12, 22, and 32%, respectively, while the molecular weight were about 3050, 3150, and 3370 g.mole<sup>-1</sup>, respectively. The result confirmed that HTNR and eHTNR were well-controlled structures as well as in our previous work [15, 27]. After polymerization, the evidence of new signals were also observed at about 7.23, 7.03, 6.97, and 2.20 ppm corresponding to benzene ring protons *l*, *m*, *n*, and *o* of TDI structure [15, 95, 96]. Another important signal at 8.14 ppm corresponding to urethane linkage at position of *p* (-C(O)N*H*-Ph-) was observed.



Figure 4.42<sup>1</sup>H NMR spectra of comparison of HTNR, eHTNR30 and cWPU-eHTNR30.

Also, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) using DCTB and AgTFA as matrix and doping agent, respectively, was used to characterize eHTNR structure with hydroxyl chain end and epoxide content on eHTNR backbone. The zoomed MALDI TOF mass spectra of eHTNR polyols are shown in **Figure 4.43**. In all cases the difference between the main peaks is equal to m/z 68 which relates to the mass of the isoprene repeating unit (M = 68g.mole<sup>-1</sup>). In addition, families of peaks with the *m/z* difference of 16 (oxygen atom) were present in comparison to the main family, showing polymers chains containing one, three, four, and six epoxide units for HTNR, eHTNR10, eHTNR20, and eHTNR30, respectively. Therefore, structure and increasing number of epoxide units were confirmed by MALDI-TOF results and agreed with the epoxide percentage from <sup>1</sup>H NMR results.

Therefore, these eHTNR oligomers can be prepared with well-controlled molecular weight and chain ends and can be used as polyols precursor for the preparation of cWPU. Also, cWPU from natural rubber based oligomers can be prepared by the simple step-growth polymerization.



Figure 4.43 MALDI-TOF mass spectra of HTNR, eHTNR10, eHTNR20, and eHTNR30 (m/z zoom in range of 1500 – 1600).

Furthermore, average molecular weight  $(M_n)$  and dispersity index ( $\mathbf{D}$ ) from different epoxide contents on eHTNR oligomers were indicated by SEC and the chromatogram are depicted in **Figure 4.44** and the results are listed in **Table 4.20**. The  $M_n$  of HTNR, eHTNR10, eHTNR20, and eHTNR30 were 3650 ( $\mathbf{D} = 2.05$ ), 2880 ( $\mathbf{D} = 1.98$ ), 3920 ( $\mathbf{D} = 2.05$ ), and 4200 ( $\mathbf{D} = 1.95$ ) g.mole<sup>-1</sup>, respectively. The dispersity of eHTNRs was about 2 which shows that the molecular weights of oligomers were very similar in range. The results of NMR and SEC are in the same trend with higher  $M_n$  with increasing epoxide.



Figure 4.44 Size exclusion chromatograms and dispersity of eHTNR with different epoxide content.

Sample	E	NMR			SEC		
	Expected E (%)	Epoxide	$M_n$	$M_n$	$M_{w}$	Đ	
		100110 (70)	(g.mor)	(g.mor)	(g.mor)		
HTNR3000	0	0	3009	3642	7468	2.05	
eHTNR10	10	11.82	3147	3877	7684	1.98	
eHTNR20	20	21.86	3293	3921	8039	2.05	
eHTNR30	30	31.61	3366	4199	8181	1.95	

Table 4.20 Summary molecular weight of eHTNR with different epoxide content.

The viscoelasticity of the oligomer polyol precursors were also studied by viscosimeter. The viscosity results of eHTNRs at 50 °C with various shear rates are shown in **Figure 4.45**. It was observed that for HTNR, eHTNR10, eHTNR20 and eHTNR30 the constant viscosity was about 1.97, 3.82, 4.21 and 8.02 Pa.s, respectively. Increasing of viscosity was mainly caused by the increasing the rigidity of the backbone structures inferred by the epoxide content on the main chain,

because all the oligomers had the same length in chain. In addition, epoxides on the eHTNRs are effective for the interaction between chains and also intra-action by getting more dipole and hydrogen bonding between the epoxide positions in function of epoxide content. When shear forces are applied, they break the physical linkages due to the hydrogen bonding and other electrostatic interactions. Therefore, after applying shear force, the viscosity dropped and showed stable values.

The FTIR spectroscopy, <sup>1</sup>H NMR spectroscopy, SEC and MALDI-TOF confirmed that HTNR has been successful prepared and can further be used as polyol to prepare cationic waterborne polyurethane.



Figure 4.45 Viscosity of eHTNR with different epoxide content.

Thermal properties of polyol substrates were also studied by TGA and DSC. To identify the thermal stability of polyol substrates TGA and DTG were used to carry the thermal degradation of eHTNR substrates from different epoxide content. Weight loss of pristine polyol was represented by only one peak in the range of 300 - 480 °C. Indeed, the degradation temperature of substrates slightly shifted to higher range of 350 - 400 °C with increasing epoxide content in the backbone, as shown in **Figure 4.46(a)**. The maximum degradation temperature ( $T_{max}$ ) of eHTNRs were investigated by DTG and shown in **Figure 4.46(b)**. The data showed that  $T_{max}$  values were shifted

to higher temperature from 371, 372, 374, and 377 °C for epoxide content about 0, 10, 20 and 30%. This can be explained considering that increasing epoxide content leads to a more polar structure, more hydrogen bonding and so more interactions between polymer chains, and a higher rigid structure for which higher energy is needed to cleave the main chain [27]. Therefore, in this work the degradation temperature increased with increasing epoxide amount on the eHTNR backbone.





**Figure 4.46** Thermal gravimetric results of natural rubber based polyols – (a) TGA curves and (b) DTG curves.

To identify the part of amorphous, crystalline and fusion behavior, DSC technique was used to characterize and identify the thermal properties by demonstrating the existence of a glass transition temperature ( $T_g$ ) and a melting temperature ( $T_m$ ), depending on the polymer backbone movement. In this work, only a  $T_g$  value was detected, which means that these telechelic oligomers are amorphous and show chain mobility and flexibility in a low temperature range. DSC thermograms of different eHTNR precursors are shown in **Figure 4.47**.  $T_g$  of these polyols are dramatically up from -64.9, -59.8, -55.1, and -52.8 °C for HTNR (eHTNR0), eHTNR10, eHTNR20, and eHTNR30, respectively. Due to more epoxide moieties on the telechelic natural rubber backbone leading to more rigid structure, the energy and temperature for polymer backbone movement and rotation are also higher than for the lower epoxide content [27]. Therefore, the polyols are amorphous polymers and low  $T_g$  appeared in the viscous liquid oligomers precursors.



Figure 4.47 DSC thermograms of eHTNR series with different epoxide percentage.

## 4.2.5.2 cWPU latex

cWPUs were successfully synthesized by fixing the NMDEA percentage at 5.67% and the NCO index of 100. The formulations contained the different eHTNR in order to study the effect of epoxide content on oligomer from 0, 10, 20, and 30% (named HTNR (eHTNR0), eHTNR10, eHTNR20, and eHTNR30, respectively).

A summary of cWPU properties based on different epoxide content on oligomers precursor backbone is shown in **Table 4.22**. The stable cWPU emulsions were in an acidic range of pH 4.20 – 4.28, by little or non-acetic acid odor with milky-yellow appearance, as shown in **Table 4.21**. In this work, acetic acid was used as neutralizing agent for generating positive charges on the tertiary amine position of NMDEA molecule. Because of the overload of acetic acid still in the system, the latex is in the acid range. Total solid content (TSC) values of synthesized cWPU was in the range of 16 - 18%. Moreover, by visual observation, the shelf-life of the emulsions showing well-dispersed particles of cWPU from different eHTNR was more than 6 months.
**Table 4.21** Appearance of cWPU in latex form and films – cWPU-HTNR, cWPU-eHTNR10, cWPU-eHTNR20, and cWPU-eHTNR30.



Particle size distribution measure in emulsion state was carried out by nanosizer technique. The diameters of cWPUs particles based on different epoxide content on the backbone of natural rubber polyols were found in the nanometer range as shown in Figure 4.48. The particle size increased with increasing epoxide content on the telechelic oligomers precursors. Particle size distribution were 76, 79, 94, and 188 nm with polydispersity values of 0.438, 0.277, 0.122, and 0.528 for cWPU-HTNR, cWPU-eHTNR10, cWPU-eHTNR20, and cWPU-eHTNR30, respectively. In this work, cWPUs were prepared by well-controlled turbine speed, temperature and homogeneous stirring. The particle size of cWPUs slightly increased from 0 to 20% epoxide and jumped up with 30% epoxide, for which the dispersion curve was quite wide because of the appearance of different size of particles. The particle size could be related to the polarity of cWPUs chains, which become more hydrophilic containing more epoxide groups so that the particles "swelled" in water phase. The size could also depend on the viscosity of the hydroxyl oligomers starting materials. During the preparation process, the speed of the stirring blade is fixed; in case of epoxide content 0 to 20%, the viscosity was suited to be used with the speed for this work, while a very high viscosity was found in case of 30% epoxide, as shown in Figure 4.45. The shear force

between blade and starting materials is not well-controlled, so this over-viscosity led to big and different size of cWPU.

Therefore, in future work, the particle size distribution could be tuned in the same range having a narrow dispersion by adjusting the speed of the blade during the preparation.



Figure 4.48 Size distribution of cWPU dispersions based on different epoxidized HTNR polyols.

Zeta potential results of cWPUs formulated with different eHTNR precursors are displayed in **Figure 4.49** and listed in **Table 4.22**. The results of zeta potential values of cWPU-HTNR, cWPU-eHTNR10, cWPU-eHTNR20 and cWPU-eHTNR30 were +71, +57, +54, and +50 mV, respectively. Theoretically, nano particle dispersion with zeta potential values above +30 mV or lower than -30 mV depending on the type of materials may be considered a suitable threshold for nano particle dispersion with very high stability [90, 118]. Normally, the factors influencing zeta potential value are pH value, ionic strength, and nano particle concentration, but in this work the concentration of cWPU dispersion were controlled. Also, the positive charges from neutralizing NMDEA with acetic acid were similar in all systems. Therefore, the effects of pH and ionic strength were offered. From the results, it can be assumed that epoxide groups were protonated because the system was in the acid range. The number of epoxide 30% used more H<sup>+</sup> protonating than 10% epoxide. Thus, H<sup>+</sup> in the system of higher epoxide groups was detected in lower content relating to pH value of cWPU dispersion system and lower zeta potential values were measured. Although the decrease of zeta potential values was found by increasing number of epoxide on the backbone, the zeta potential values of the cWPUs were still higher than +30 mV relating to a very high stability of nano particle dispersion. Beside, from this technique, these synthesized cWPU were well-dispersed emulsion with positive charge.

Another, natural real cow leather is an anionic substrate [8, 119], so the high density of positive charge on the cWPUs particles surface will allow the establishment of electrostatic interactions responsible of the strength of the adhesion forces. With the particle size at the nanometer scale and zeta potential showing high positive surface charge the synthesized cWPUs revealed to be appropriated to use for the envisaged adhesive applications.



Figure 4.49 Zeta potential of cWPU dispersions based on different epoxidized HTNR polyols.

	<b>Physical Properties</b>								
Code			Destisle sin <sup>a</sup>		Zeta Potential		Swelling (%)		ng (%)
	TSC (%)	pН			Average Zeta	Zeta			
	Size D (nm)	Ð	(mV) Deviation	THF	DMF	Toluene			
cWPU-	16.67	4.20	76	0.438	+71	5.51	N/A	N/A	331
HTNR	10.07	4.20	10					1011	
cWPU-	17.76	4 22	79	0 277	+57	5 31	N/A	N/A	300
eHTNR10	17.70	7,22	1)	0.277	101	5.51	14/21	14/21	500
cWPU-	18.01	1 24	04	0.112	+54	3 55	NI/A	N/A	240
eHTNR20	10.01	4.24	74	0.112	194	5.55	1 <b>N</b> / A	IN/A	240
cWPU-	14 55	4 28	188	0 528	+50	3 13	N/A	N/A	138
eHTNR30	11,35	1.20	100	0.520	. 50	5.15	11/21	1 1/21	150

Table 4.22 Physical properties of cWPUs based on different eHTNR.

Note: N/A means that the polymer dissolved

<sup>a</sup> Size distribution peaks from Zeta nanosizer (dynamic light scattering)

Moreover, particle shape and particle size were also visualized by TEM. The TEM images present the cWPU particles with a scale bar of 200 nm as show in the **Figure 4.50**. The dark points of cWPU emulsion phases in TEM images are due to the staining with  $OsO_4$  and its interaction with the carbon-carbon double bond of the isoprene repeating unit. Synthesized cWPU particles are clearly displayed with spherical shape. Particle size agreed with the values found from dynamic light scattering results, by showing regularly dispersed spherical particles in water with the same trend of size. From TEM results, particle size of cWPUs from HTNR, eHTNR10, eHTNR20, and eHTNR30 were about 5, 70, 90, and 190 nm, respectively. For cWPU-HTNR, because it is very small size dispersed in water media the group of well-dispersed particle was detected by laser from zeta nanosizer showing bigger size than the size from TEM.



**Figure 4.50** TEM images of prepared cWPUs based on different eHTNR – (A) cWPU-HTNR, (B) cWPU-eHTNR10, (C) cWPU-eHTNR20, and (D) cWPU-eHTNR30.

# 4.2.5.3 cWPU films

cWPU liquid emulsions were cast into a Teflon mold and dried at 70 °C overnight to avoid the presence of bubbles in the films. The cWPU films were kept in desiccator and studied the physical properties, mechanical properties, and thermal properties.

# a) Water uptake

The effect of epoxide content in eHTNR based cWPU films on water uptake was monitored for 1 week and the data are presented in **Figure 4.51**. The water uptake curves clearly show the effect of epoxide content on different eHTNR based cWPU films. In the first five days, water uptake percentage raised from 0.5 to 3.7%, 0.8 to 4.9%, 1.1 to 7.1%, and 1.8 to 8.7, for cWPU film from HTNR, eHTNR10, eHTNR20, and eHTNR30, respectively, and seemed to reach a plateau towards the day 6 and 7. It is observed that water uptake percentage value of cWPU-HTNR films is the lowest one and cWPU film composed of 30% epoxide content on eHTNR backbone is highest one; this can be explained because of the different polarity and free volume of the polymer films. In this work, the polarity of the films surface is due to the urethane linkage and the epoxide groups on the backbone; of course increasing the number of epoxide groups on the long chain of the hydrophobic natural rubber, turns it is a more polar polymer and can explain the reason of the water uptake.

We wanted to study also the swelling ratios in three solvents with different polarity; THF, DMF and Toluene, after monitoring for 24 hours. The results showed that all polyurethane films were dissolved in THF and DMF, the polar solvents, and they just swelled in the non-polar Toluene. The swelling percentage of cWPU films were 331, 300, 240, and 138% for cWPU from HTNR, eHTNR10, eHTNR20, and eHTNR30, respectively. Percentage of swelling decreased with increasing epoxide content on cWPU backbone because increasing polarity of the polymer structures.



Figure 4.51 Water uptake percentage of cWPU films from different eHTNR.

# b) Surface wettability and surface energy

One of the techniques used to characterize the properties of adhesive materials is contact angle, for the determination of hydrophobicity/hydrophilicity, surface wettability and also surface energy of the materials. Both sides of the films of cWPU from different eHTNR were studied, polymer-air and polymer-Teflon interfaces, and the results are presented in **Table 23** - **25**. The surface energy was also calculated *via* two components; dispersion and nondispersion one by water ( $H_2O$ ) and diiodomethane ( $CH_2I_2$ ), respectively.



Table 4.23 Air-polymer interface contact angle of cWPU based on different eHTNR.



Table 4.24 Teflon-polymer interface contact angle of cWPU base on different eHTNR.

For the polymer-air interface, the contact angle of cWPUs from HTNR, eHTNR10, eHTNR20, and eHTNR30 was 92°, 85°, 54°, and 51° for water contact angle and 38°, 43°, 49°, and 66° degree for diiodomethane contact angle, respectively. For the other side, polymer-Teflon, contact angle of cWPUs from HTNR, eHTNR10, eHTNR20, and eHTNR30 were 106°, 104°, 88°, and 87° for water contact angle and 43°, 46°, 51°, and 53°, respectively. Overall, it was again confirmed that the hydrophilic properties of the prepared cWPU films increased with increasing epoxide content on the cWPU backbone. In addition, the water contact angle of air-polymer side is lower compared to the Teflon side, indicating a higher hydrophilic character. This can be due to a possible partial oxidation of some polymer chains in contact with air. PTFE chains could also be transferred on the cWPU surface during the demolding, inducing a higher hydrophobicity.

Surface energy is an important parameter for future adhesive applications because it describes the wettability of cWPU films through their surface energy. Total solid surface energy  $(\pmb{\gamma}_s)$  is calculated via Owen-Wendt theory by two components - dispersion  $(\pmb{\gamma}_s^{~D})$  and nondispersion component ( $\gamma_s^{P}$ ). Surface energy is calculated and corrected in Table 4.26 for both sides of the films. Total surface energy of cWPUs from HTNR, eHTNR10, eHTNR20, and eHTNR30 was 42.8, 42.1, 53.4, and 50.5 mJ/m<sup>2</sup> for polymer-air face and 40.1, 38.0, 37.0, and 36.6 mJ/m<sup>2</sup> for Polymer-teflon face. Theoretically, high surface energy values will induce a better wettability and adhesion with any material [120]. For comparison, in 2008, Lin Y. H. et al. synthesized fluorinated poly(urethane-acrylate)s and they reported that the surface energies were in the range of 19 - 38mJ/m<sup>2</sup> [121]. In 2011, Hwang H-D and Kim H-J studied fluorinated polycarbonate-based polyurethane dispersions of anionic type. The surface energy of those anionic WPU were in range of 20 – 50 mJ/m<sup>2</sup> [122]. In 2013, Çanak T. Ç. and Serhatlı I. E. synthesized fluorinated urethane acrylate based for coating application. Surface energy of their prepared polyurethane was in the range of 22 – 39 mJ/m<sup>2</sup> [123]. In 2017, Zheng G. et al. synthesized anionic waterborne polyurethane and studied the surface properties. It was reported that surface energy of WPU films were about 19  $-37 \text{ mJ/m}^2$  [124]. From the comparison with the literature data, it emerges that the surface energy values of the PU polymers were lower than the cWPUs in this work, therefore, our cWPUs are suitable to be used for adhesive applications because of their high surface energy, low surface tension, and high wettability.

Samula Nama	H <sub>2</sub> O Conta	ct Angle (theta)	CH <sub>2</sub> I <sub>2</sub> Contact Angle (theta)		
Sample Name	Polymer-Air	Polymer-Teflon	Polymer-Air	Polymer-Teflon	
cWPU-HTNR	$91.6\pm0.60$	$105.5\pm3.17$	$38.4 \pm 0.49$	$42.9 \pm 1.94$	
cWPU-eHTNR10	$84.5\pm2.40$	$103.6\pm6.21$	$42.9\pm6.18$	$46.3\pm3.33$	
cWPU-eHTNR20	$54.2\pm2.60$	$88.3\pm0.46$	$49.3 \pm 1.23$	$51.3\pm0.74$	
cWPU-eHTNR30	$51.3 \pm 5.02$	$87.4 \pm 2.01$	$66.1 \pm 0.53$	$52.6 \pm 4.13$	

Table 4.25 Contact angle values of cWPU with various epoxide in eHTNR.

_	Surface Energy (mJ/m <sup>2</sup> )					
Sample	Polymer - Air face			Polymer - Teflon face		
	$\gamma_s^p$	$\gamma_s^{D}$	$\mathbf{\gamma}_{\mathrm{s}}$	$\gamma_s^p$	$\gamma_s^{D}$	γ <sub>s</sub>
cWPU-HTNR	0.5	42.3	42.8	0.2	39.9	40.1
cWPU-eHTNR10	2.1	39.9	42.1	0	38.0	38.0
cWPU-eHTNR20	17.1	36.3	53.4	1.9	35.1	37.0
cWPU-eHTNR30	24.3	26.3	50.5	2.2	34.4	36.6

Table 4.26 Surface energy values of cWPU with various epoxide content in eHTNR.

# c) Mechanical properties

Mechanical properties of eHTNR based cWPU films with various epoxide percentages on eHTNR substrate are summarized in Table 4.27. Stress-strain curves of eHTNR based cWPUs clearly demonstrated that the switch from elastomeric properties to tough plastic was accentuated by increasing the epoxide percentage on the backbone of eHTNR substrates, as showed in Figure 4.52. Young's modulus of the cWPUs films rose up from 1.45 to 2.75 N/mm<sup>2</sup> with increasing epoxide percentage on substrate. On the contrary, strain at break of cWPUs films dropped from 740 to 189% by increasing epoxide on backbone of HTNR from 0 to 30. The stress at break values fluctuated from 7.32, 9.65, 4.34, and 2.35 N/mm<sup>2</sup> for cWPU films based on HTNR, eHTNR10, eHTNR20, and eHTNR30, respectively. The elastic behavior of cWPU films is due to the about 70 percentage of natural rubber as main component of the films. To reach a similar strain, it was required much more stress for eHTNR10 than for HTNR, which consists only of cis-1.4polyisoprene units. This can be explained by the interactions (hydrogen bonds) that are established by the donor epoxide groups, which require more energy to be broken in comparison to HTNR based films, where this contribution does not exist. However, the inter- and intra- molecular hydrogen bonds increase also the Young's modulus and the tensile strength, and the effect is more relevant for eHTNR20 and eHbTNR30. So, higher epoxide percentages on eHTNR substrate made cWPU films more tough and brittle.



Figure 4.52 Stress-strain curves of eHTNR based cWPU films with various epoxide percentages on the eHTNR substrate.

**Table 4.27** Mechanical properties of eHTNR based cWPU films with various epoxide percentages

 on eHTNR substrate.

	Average			
Code	Stress at Break	Strain at Break	Young's Modulus	
	(N/mm²)	(%)	(N/mm²)	
cWPU-HTNR	$7.32\pm0.54$	$740\pm27.31$	$1.45 \hspace{0.1 cm} \pm \hspace{0.1 cm} 0.21$	
cWPU-eHTNR10	$9.65 \pm 1.36$	$579\pm32.33$	$1.94\pm0.09$	
cWPU-eHTNR20	$4.34\pm0.43$	$301\pm24.21$	$1.98\pm0.08$	
cWPU-eHTNR30	$2.35 \pm 0.19$	$189 \pm 21.37$	$2.75 \pm 0.49$	

After the tensile testing, the surface of the cross section of the films was observed by SEM (**Figure 4.53**, magnification of x500). The effect of epoxide content on cWPU backbone was to infer a different roughness to the cWPU film surface: the trend showed a decreasing roughness of surface with increasing of epoxide content on cWPU backbone from 0 to 30%. The smooth surface is normally occurred in the brittle polymer because the cWPU film cannot stretch out during tensile testing. On the other hand, the rough fracture surface (with sheet-like surface) is usually found in

the ductile polymer because the matrix of cWPU film is stretched until breaking during tensile testing. Clearly, lower epoxide content based cWPU showed rougher surface than higher content of epoxide one. It is related with the results of mechanical by showing that cWPU-eHTNR30 film gives the highest Young's modulus and the lowest strain percentage, but cWPU-HTNR gives the lowest Young's modulus and the highest strain percentage. Therefore, these result confirmed that the properties of cWPU films were changed from ductile materials to brittle materials by increasing epoxide on HTNR backbone.



**Figure 4.53** SEM images of cWPU cross-section films from tensile testing – (A) cWPU-HTNR, (B) cWPU-eHTNR10, (C) cWPU-eHTNR20, and (D) cWPU-eHTNR30.

# d) Thermal properties

Thermal degradation results of cWPU films studied by TGA and DTG are presented in **Figure 4.54(a)** and **Figure 4.54(b)**, respectively, and the maximum decomposition temperatures  $(T_{max})$  are listed in **Table 4.28**. In the thermograms different decomposition steps were identified.

For the pristine HTNR and eHTR polyol substrates, the decomposition shows only one step at temperature about 370 - 377 °C. In this work, cWPU films decompositions were similar by showing 2 main degradation steps. The first in the range of 190-260 °C is attributed to the breaking of urethane linkage as EG, HTNR, eHTNR, isocyanate, and also to the loss of carbon dioxide from urethane deformation [18].  $T_{max}$  of cWPU-HTNR, cWPU-eHTNR10, cWPU-eHTNR20, and cWPU-eHTNR30 in this range were 211.1, 209.3, 222.1, and 208.7 °C, respectively. The second decomposition step was at a higher temperature range of 340-460 °C, and it was related to the degradation of the natural rubber part, as indicated in the pure polyols substrate. In this step,  $T_{max}$  of cWPU-HTNR, cWPU-eHTNR30 are 377.2, 379.47, 383.2, and 388.05 °C, respectively. It is observed that the shift of temperature degradation to a higher range was found by having higher epoxide content in the polymer backbone structure. This is because of the physical hydrogen bonding established from urethane linkages and epoxide groups in the main chain, leading to more intra- and intermolecular chain interactions [27] . Therefore, thermal resistances of the materials were improved by including epoxide groups on the cWPU backbone.



Figure 4.54 Thermograms of eHTNR based cWPUs – (a) TGA curves and (b) DTG curves.

In addition, DSC thermograms of synthesized cWPUs are presented in **Figure 4.55.** The results of  $T_g$  are dramatically increased with increasing epoxide content on the backbone of cWPUs.  $T_g$  values of cWPUs from HTNR, eHTNR10, eHTNR20, and eHTNR30 were -59.4, -44.9, -42.7, and -39.3 °C, respectively. Comparing to pure telechelic oligomer,  $T_g$  of polymers jumped into a higher temperature range. It is because of two reasons; urethane linkage and hydrogen bonding from epoxide structure. Urethane linkage was formed after reaction of cWPUs preparation. It is normally found that long chain polymer and high interaction of polymer chains need more energy to be mobilized and moved than pure oligomer substrates.



Figure 4.55 DSC thermograms of cWPU films.

Thermo-mechanical properties were evaluated by DMTA. Two important values emerged from the studies discussed so far : (1) the glass transition temperature (Tg), which corresponds to the maximum of the tan  $\delta$  peak.Tan  $\delta$  is equal to the ratio of the loss modulus (not shown) to the storage modulus (G'), and (2) the stiffness of cWPU films was determined by G' (elastic or storage modulus). The evolutions of G' and tan  $\delta$  of cWPU films from different eHTNR are presented in function of temperature. The epoxide content on eHTNR soft segment backbone strongly affected

the viscoelastic properties of cWPU films. The increase of epoxide on the backbone led to a higher density of rigid structure because of the epoxide groups on the polymer chain. Again, because hydrogen bonding occurrs between the urethane linkage and epoxide groups, this phenomenon directly affected the storage modulus, which represented the elastic behavior, as shown in **Figure 4.56(a)**. The curves of G' shift to higher value with the increase of epoxide content in part of soft segment because of rigid structure of eHTNR, multi-hydrogen bonding, and more physical crosslink and that decreased the chain mobility.

In addition, the effects of epoxide content on the  $T_g$  (temperature of the tan  $\delta$  peak) value of cWPU with eHTNR0, eHTNR10, eHTNR20, and eHTNR30 were dramatically increased at -55.2, 48.9, 41.2, and -39.6 °C, respectively, corresponding to a  $T_g$  value (as shown in **Figure 4.56(b)**). Moreover, the increase of epoxide content led to an increase of the rigid structure, to more interactions in the matrix, and also to an increase in the dissipation energy. Therefore, tan  $\delta$  value of cWPU shifted to higher temperatures. In comparison, the trend of  $T_g$  values from DMTA are related to  $T_g$  from DSC. All of the DMTA results show only one peak, determining the homogeneous properties of the cWPU from different eHTNR films [125]. This result indicated that the thermodynamic and mechanical properties of cWPU films can be improved by increasing epoxide content on eHTNR backbone.





Figure 4.56 (a) Storage modulus and (b) Tan delta (Tan  $\delta$ ) as function of temperature for cWPU films from different eHTNR.

	$T_{max}$ (°	C) from TGA		$T_g$ (°C)	
Samples	First step	Second step	DSC	DMTA	
cWPU-HTNR	211.1	377.2	-59.4	-55.2	
cWPU-eHTNR10	209.3	379.5	-49.9	-48.9	
cWPU-eHTNR20	222.1	381.2	-42.9	-41.2	
cWPU-eHTNR30	208.7	388.0	-39.3	-39.6	

Table. 4.28 Thermal properties results of cWPU films from different eHTNR.

### **4.3 Adhesive Properties**

The adhesive properties of cWPU on the real leather surface in the account of the different molecular weights of HTNR and different NCO index were tested. Lap shear test and 180 degree peel test were investigated. Also, temperatures of curing adhesive were also studied at room temperature and 70 °C. Moreover, the comparison of the adhesive strength were compared with standard commercial adhesive (non-solvent based and solvent based adhesive).

#### 4.3.1 Leather adherend substrates characterization

To identify the chemical structure of cow leather, FTIR spectroscopy was used to characterize. The FTIR spectra were shown in **Figure 4.57**. The results showed the same structure as non-degreased real cow leather and degreased real cow leather. The analysis result observed that peaks corresponding to -OH stretching and active -NH stretching of amide group on the leather surface in wave range of 3000 – 3600 cm<sup>-1</sup> had reduced in size after cWPU were applied to the surface. The important peaks found at wavenumber of 1650, 1560, 1450 and 1250 cm<sup>-1</sup> were attributed to functional group of -C=O of amide, -NH stretching,  $-CH_2$ - stretching and -C-N-stretching. Another peak found in the range of 600 – 900 cm<sup>-1</sup> was that of -NH wagging of amide group. The results verified that real cow leather surface related to previous work of Mirghani [126] with well-studied the functional group and leather characterization of cow leather. Therefore, from these functional groups, cWPUs had formed hydrogen bonds to the surface, functional groups of the leather, allowing for further hydrogen bonds to form an adhesive bond to substrates.



Figure 4.57 FTIR spectra of real cow leather – before and after degreased.

### 4.3.2 Effects of Molecular weight of HTNR

The adhesive properties of cWPU on the real leather surface in the account of the different molecular weights of HTNR were tested. Lap shear test and 180 degree peel test were investigated. Also, temperatures of curing adhesive were also studied at room temperature and 70  $^{\circ}$ C.

## a) Lap Shear test

The results of lap shear test curves of cWPUs adhesive on real cow leather are shown in **Figure 4.58** and the summary results are listed in **Table 4.30**. Lap shear strength of cWPU with various  $M_n$  of HTNR was tested after curing at two temperature conditions – at room temperature and at 70 °C curing. The lap shear strength values of cWPU from HTNR3000, HTNR2000, and HTNR1000 at room temperature were 0.02, 1.53, and 1.16 N.mm<sup>-2</sup>. In addition, the lap shear strength values of cWPU from HTNR3000, HTNR2000, and HTNR1000 at 70 °C were 0.02, 1.70, and 1.22 N.mm<sup>-2</sup>. Theoretically, the decreasing  $M_n$  of HTNR involved in the enhanced hydrogen bonding of the hard segment and urethane linkage that lead to a higher adhesive strength. According to the results from Kaehin *et al.* [127] who studied the natural rubber based anionic WPU for adhesive on leather application by various molecular weight of HTNR. It was found that adhesive

strength is increased by decreasing molecular weight (from 1000 to 600 g. mole<sup>-1</sup>). However, this work show that the adhesive strength values of cWPU from HTNR1000 is slightly decreased than cWPU from HTNR2000 but a higher than cWPU from HTNR3000. This is due cWPU from HTNR1000 was very brittle lead to low cohesive strength. Data from lap shear test of cWPU from HTNR1000 and HTNR3000 showed adhesive failure occurred within cohesively in the adhesive layer. For cWPU from HTNR2000 showed adhesive failure occurred within cohesively in the adhesive layer and substrate surface failure as shown in **Table 4.29**. These results indicated that this adhesive has a weaker adhesive bond than adherent bond strength.

From the modulus curves, the strength of adhesive from cWPU cured at 70 °C exhibits slightly stronger adhesive materials than when compared to curing at room temperature because at high temperature the physical bonds are accelerated and formed, therefore, they give stronger adhesive values.



Figure 4.58 Force load vs strain curves of cWPU adhesives from different  $M_n$  of HNTR on real cow leather surface from lap shear test.

Codo nomo —	Curing Temperature			
Code name	Room temperature	70 °C		
cWPU7	Cohesive failure	Cohesive failure		
cWPU17	Cohesive and substrate failure	Cohesive and substrate failure		
cWPU18	Cohesive failure	Cohesive failure		

Table 4.29 The rupture behavior of cWPU adhesives on the leather from lap shears strength testing.

# b) 180 degree Peel test

The effect of  $M_n$  of HTNR and the different curing temperature on adhesion properties was investigated by 180 degree peel test as shown in **Figure 4.59** and summarized in **Table 4.30**. It was found that the increasing  $M_n$  of HTNR ( $M_n$  of 1000, 2000 and 3000 g.mole<sup>-1</sup>) lead to decreasing peel strength and the record value of peel strength for cWPU cured at room temperature were 3.95 N 3.86 N, and 1.20N and cWPU cured at 70 °C were 10.4 N, 8.01 N, and 1.59 N, respectively. This is due to increasing  $M_n$  of HTNR as increase soft segment in cWPU structure that relate to decreasing hydrogen bonding in the hard segment [127]. The evidence from this study suggested that cohesive failure was observed. This failure generally occurs in case of the bond to the substrate exceeds the internal strength of the cWPU adhesives. Contrary, adhesive failure can occur in case of lower adhesive forces between the interfacial forces of substrates adherend and the internal strength of the adhesive. In this study, the cohesive forces are from cWPU intra- and inter-chain in the position of –NH and carbonyl hydrogen bonding from urethane linkage density on cWPU backbone while cohesive forces are from hydrogen bonding between a real leather surface (amide group of collagen and amino group) and urethane. Moreover, the electrostatic force between the positive charge of cWPU according to zeta potential results and the electron-rich position carbonyl position on the real cow leather surface, which as seen as a negative charge on the real cow leather, increase the strength between adhesive and adherend [99, 128]. Therefore, the interaction between adherend and adhesive is more than adhesive- adhesive interaction. Moreover, the effect of  $M_n$  of HTNR on the adhesive properties of anionic WPU film with curing temperature at 80 °C was reported by Keanhin *et al.* (2012) [127]. It was found that the peel strength increased in case of lower  $M_n$  of HTNR.

A comparsion between cWPU was cured at room temperature and at 70 °C. It was found that the cWPU cured at 70 °C provide a higher peel strength than the cWPU cured at room temperature. Increasing the curing temperature significantly accelerated the curing process lead to more network structure through chemical bonding. The most obvious finding to emerge from this study is that cationic system of WPU based on HTNR is more suitable to use for adhesive application.



**Figure 4.59** 180 degree peel strength of cWPU adhesives from different  $M_n$  of HNTR.

Curing	Code name	Lap shear strength	<b>T-Peel Force</b>
Temperature		(N.mm <sup>-2</sup> )	(N)
	cWPU7	$0.02 \pm 0.01$	$1.20\pm0.51$
RT	cWPU17	$1.53\pm0.02$	$3.86\pm0.77$
	cWPU18	$1.16\pm0.01$	$3.95\pm0.79$
	cWPU7	$0.02\pm0.00$	$1.59\pm0.07$
70 °C	cWPU17	$1.70\pm0.02$	$8.01\pm0.88$
	cWPU18	$1.22 \pm 0.02$	$10.04 \pm 1.75$

Table 4.30 Summary of adhesive properties of cWPUs base on different  $M_n$  of HTNR.

From the results of adhesive properties testing by lap shear test and 180 degree peel test with different temperature, these cWPUs had high potential in real cow leather adhesive applications. Moreover, the effects of epoxide on the backbone of HTNR was further studied.

## 4.3.3 Effect of epoxide content on leather adhesive application

The adhesive properties of cWPU on the real leather surface in the account of different NCO index were tested. Lap shear test and 180 degree peel test were investigated. Also, temperatures of curing adhesive were also studied at room temperature and 70 °C. Moreover, the comparison of the adhesive strength were compared with standard commercial adhesive (non-solvent based and solvent based adhesive).

## a) Lap shear test

Lap shear results obtained for cWPU/leather assemblies and commercial adhesives/leather assemblies are presented in **Figure 4.60**. Lap shear forces are calculated and listed in **Table 4.31**. In this work, lap shear test are performed after two different drying conditions – at room temperature and at 70 °C. The results obtained after a room temperature drying of eHTNR based cWPU adhesives are shown in **Figure 4.60(a)**. Lap shear force of adhesive testing of cWPU adhesive based on HTNR, eHTNR10, eTHNR20, and eHTNR30 are 1.09, 1.00, 0.25, and 0.75

N/mm<sup>2</sup>, respectively, while lap shear forces form commercial adhesive were 1.25, 0.71, and 0.19 N/mm<sup>2</sup> for commercial A, commercial B, and commercial C, respectively. In this case, it is indicated that adhesive strength of eHTNR20 are lowest strength and HTNR based are highest adhesive strength for synthesized adhesive while commercial A is highest strength in this temperature.

Cala	Lap shear strength (N.mm <sup>-2</sup> )		
Code	70 °C	RT	
cWPU-HTNR	1.06	1.09	
cWPU-eHTNR10	Break in Leather part	1.00	
cWPU-eHTNR20	0.30	0.25	
cWPU-eHTNR30	0.64	0.75	
<b>Commercial A</b>	0.08	1.25	
Commercial B	0.26	0.71	
<b>Commercial C</b>	0.11	0.19	

**Table 4.31** Summary of Lap shear strength results of cWPU consisted of different eHTNR and dry condition compared with commercial adhesives.

The elongation at break is also higher for HTNR based adhesive, in correlation with intrinsic mechanical properties of adhesives (more ductile behavior for HTNR based cWPU). The locus of failure, which is cohesive inside the adhesive layer, is able to explain this correlation with intrinsic mechanical properties.

On the other hand, at temperature of 70 °C, the strength of adhesive are fluctuated as shown in **Figure 4.60(b)**. Lap shear forces of prepared cWPU adhesive from cWPU based on HTNR, eHTNR20, and eHTNR30 are 1.06, 0.30, and 0.64 N/mm<sup>2</sup>, respectively, while lap shear force of commercial A, commercial B, and commercial C were 0.08, 0.26, and 0.11 N/mm<sup>2</sup>, respectively. Theoretically, the strength of the lap-shear test result is dependent on cohesive forces and the adhesive force of the adhesive-adhesive interactions and adhesive-material interactions [128, 129]. In this work, cohesive forces is from cWPU intra- and inter-chain in position of –NH and carbonyl hydrogen bonding from urethane linkage and different epoxide density on cWPU backbones while

adhesive force come from hydrogen bonding between real leather surface (amide group of collagen and amino group) and urethane and epoxide in backbone cWPU. Moreover, electrostatic force between the positive charge of cWPU according to zeta potential results and the electron rich position carbonyl position on the real cow leather surface, which as seen as a negative charge on the real cow leather, increase the strength measured by lap shear testing [99, 128]. In this work, the failure is globally cohesive due to residual layer of a polymer on both sides of leather surface as indicated with optical microscopes.

Surprisingly, eHTNR10 based cWPU was highest strength with very strong adhesion force. Leather is tore in case of cWPU-eHTNR10 adhesive dried at 70 °C, and the failure occurs inside the leather part, indicating that the adherence is higher than the leather cohesion.





Figure 4.60 Force vs Strain curves of eHTNR based cWPU adhesive compared to commercial adhesives with different drying temperature condition -(a) room temperature and (b) 70 °C. (Note: cWPU-eHTNR10\* and # is Break in leather part)

From the Lap shear strength results, it can be described by the reaction mechanism between cWPU based on eHTNR adhesive and reactive amine group on leather surface, presented in **Figure 4.61**. Nucleophilic amine from collagen structure of real cow leather reacted on less hindrance and high electrophilic position on epoxide structure of eHTNR to form covalent bonding. Epoxide structure opened and reacted with the nearby epoxide structure to form new furan ring then [130, 131]. This phenomenon could occur in case of high density and near position of epoxide structure as in case of eHTNR20 and eHTNR30. Therefore, density of epoxide content and position of epoxide on eHTNR backbone of epoxide are the important parameter to open ring-by-ring and form new furan ring. In this work, the optimum epoxide content on eHTNR structure to form covalent bonding with leather is about 10% by showing very strong adhesive strength because low density of epoxide and its position can form covalent bond more than furan ring. On the other hand, in case of eHTNR20 and eHTNR30, adhesive strength is dropped because high density of epoxide structure and properly position formed furan ring more than formed covalent bond. Normally, furan ring is

not effective or very less effective on adhesive strength as well as effects from epoxide structure, therefore, adhesive strength from high density of furan ring is less than adhesive strength from high density of epoxide.

Clearly, adhesion forces from synthesized cWPU adhesive were higher than solvent based in all conditions. It can be claimed that water based adhesive are higher strength and better than solvent based adhesive. These synthesized adhesives exhibit then better adhesive properties than some commercial adhesives<del>.</del>



**Figure 4.61** Possible model of adhesive reaction of leather and cWPU in part of epoxidized natural rubber reaction.

## b) 180 degree peel test

180 degree peel test is also used to perform the peel strength for real cow leather joints of the synthesized polyurethanes. 180 degree peel strength values of joints made with cWPUs based on difference eHTNR are studied after different curing temperature – at room temperature and at 70 °C and the results are in the **Table 4.32**. In condition of room temperature curing, peel force of cWPU with HTNR, eHTNR10, eHTNR20, and eHTNR30 were 2.21, 15.42, 0.81, and 3.61 N, respectively, whilst commercial A, commercial B, and commercial C were 3.18, no adherence, and 2.04 N, respectively. On the other hand, dried at 70 °C, peel force of cWPU with HTNR, eHTNR10, eHTNR20, and eHTNR30 were 3.51, 26.35, 0.89, and 1.68 N, respectively, while commercial A, commercial B, and commercial C were 4.34, no adherence (spontaneous delamination), and 1.30 N, respectively. The result of 180 degree peel strength agreed with the results of lap shear strength can be described by the same phenomenon. In this work, the change of curing temperature from room temperature to 70 °C can be aroused the physical crosslink from the reactive group in the cWPU main chain and the most effective condition from this effect is eHTNR10 based cWPU. The properly position and density of urethane linkage and epoxide on the soft segment backbone is aroused by showing increasing about 2 times because of occurring physical crosslinking and covalent bonding. Moreover, the hypothesis is that at 70 °C the water in the system can be eliminated more surely while at room temperature condition some residual water molecules could remain trapped in the main chain and reduce the hydrogen bonding between urethane linkage interchain and intra-chain. Therefore, the adhesive result of 180 degree peel force from curing temperature at 70 °C is higher than curing at room temperature condition.

Cala	Peel Force (N)		
Code	Cured at RT	Cured at 70 °C	
cWPU-HTNR	2.21	3.51	
cWPU-eHTNR10	15.42	26.35	
cWPU-eHTNR20	0.81	0.89	
cWPU-eHTNR30	3.61	1.68	
Commercial A	3.18	4.34	
Commonoial D	No adherence	No adherence	
Commercial B	(delamination)	(delamination)	
<b>Commercial C</b>	2.04	1.30	

Table 4.32 Peel force by mean force of cWPU based on different eHTNR.

In comparison, synthesized cWPU have higher peel strength than standard commercial adhesive in case of non-solvent and solvent based. The highest peel strength value is cWPU-eHTNR10 adhesive and lowest peel strength value is cWPU-eHTNR20. The surfaces after adhesive peel tests have been analyzed using optical microscope. The images are shown in **Table 4.33**. The failure is also globally cohesive (residual layer of a polymer on both sides) as describe in lap shear test.

Cada	Surface after Peel testing at different temperature curing					
Code	<b>Room Temperature</b>	70 °C				
cWPU- HTNR	The OC					
cWPU- eHTNR10	m. co	Sourm.				
cWPU- eHTNR20	mı CC2	500 L/m				
cWPU- eHTNR30	nu σσ	. e 2				
Commercial A	The Decision of the Decision o					
Commercial B	τιμου	500 µm				

Table 4.33 Optical microscope images of cWPU adhesive after 180 degree peel testing.



The adhesive results of the cWPU indicate their potential in real cow leather adhesive applications. In the effects of molecular weight of HTNR, the adhesive strength is increased by reducing molecular weight of HTNR because of shorter chain of soft segment, higher content of urethane linkage, and higher wettability. To improve the wettability and the adhesive strength, this study modify the structure of HTNR (soft segment) with epoxide structure. The results showed that the adhesive strength is increased as well. However, the optimum content of epoxide on HTNR for the leather adhesive application of cWPU is 10% epoxide on HTNR backbone because the content and position of epoxide can form covalent bond with leather more than furan ring. Moreover, the result clearly showed that synthesized cWPUs give higher adhesive strength than the standard commercial adhesives from both solvent based adhesive and water based adhesive.

### **CHAPTER 5**

# CONCLUSION

The main objective of this research work was an elaboration of novel natural rubber (NR) based cationic waterborne polyurethane (cWPU) and evaluation of their adhesive properties on leather. In this work, natural rubber has been modified to prepare polyols substrates, named hydroxyl telechelic natural rubber (HTNR), for polyurethane preparation to reduce the use of fossil fuel based polyols. HTNR was well-controlled molecular weight in three different (approximately 1000, 2000, and 3000 g.mole<sup>-1</sup>) by the semi-solution process. Firstly, epoxidized NR (ENR) was first prepared by epoxidation reaction. The target molecular weight of HTNR had been controlled *via* epoxide percentage about 1.96, 3.85, and 9.09 for approximately 3000, 2000, and 1000 g.mole<sup>-1</sup>, respectively. ENR was then cleaved by the reaction to obtain carboxyl telechelic NR (CTNR) and followed by the reduction reaction of CTNR to obtain HTNR. The expected molecular weight of HTNR for 1000, 2000, and 3000 g.mole<sup>-1</sup> with well-controlled reaction and reproducibility.

Natural rubber based cWPU adhesives were synthesized by step-growth polymerization with controlled % TSC approximately 20 %. First of all, the most vital parameter for the stability of cWPU system was the amount of generated cationic emulsifier, *N*- methyl diethanolamine (NMDEA) and acetic acid. With fixing molecular weight of HTNR of about 3000 g.mole<sup>-1</sup> and isocyanate index of 100, the cWPU was well dispersion with NMDEA content more than 1.50 mole and the appearance of the cWPU latex was milky-blue with long shelf life time more than 10 months. The particle of cWPU was spherical with the size in the range of 60 nm to 87 nm confirmed by TEM and zeta nanosizer. Particle size was decreased by increasing NMDEA concentration and zeta potential was in the range of +50 and +70 mV. The optimum concentration of NMDEA was 2.25 mole (5.67 %wt). Unfortunately, this prepared cWPUs were very poor mechanical properties.

In order to improve mechanical properties of cWPU, chain extender was first introduced into cWPU system. This work used ethylene glycol (EG) as a chain extender and the result showed that it worked well. The mechanical properties were increased by increasing EG content under the condition of fixing molecular weight of HTNR of about 3000 g. mole<sup>-1</sup>, NMDEA 5.67 % wt, and isocyanate index of 100. The particle sizes rose up from 60 nm to 453 nm by increasing EG from

0 to 3 mole. Also, zeta potential values dropped from +71 mV to +63 mV by increasing EG content. The swelling ratio in THF was dropped and water up take value was up by increasing EG content. From the mechanical properties, these cWPUs films changed from elastic behavior to hard plastic by increasing chain extender amount. Moreover, thermal properties of prepared these cWPUs were in the same range of  $T_g$  by DMTA and DSC within the range of natural rubber mobility of -51°C to -54°C. However, in case of high EG content, the stability of cWPU was dropped.

The other parameter was the effect of molecular weights of HTNR (3000 to 1000 g. mole<sup>-1</sup>) on cWPU properties. In this investigation, the NMDEA 5.67 %wt, the EG content of 1 mole, and isocyanate index of 100 were fixed. This study has shown that the particle size of cWPU jumped up from 76 nm to 591 nm and zeta potential values were slightly down from +71 mV to +67 mV by reducing the molecular weight of HTNR from 3000 to 1000 g.mole<sup>-1</sup>. Water uptake percentage and swelling ratio of cWPU films in THF were dropped in account of reducing the molecular weight. The mechanical properties of cWPUs were changed from elastomeric materials to very hard plastic materials by decreasing molecular weight of HTNR. In case of HTNR molecular weight about 1000 g.mole<sup>-1</sup>, cWPU film was brittle in comparison of higher molecular weight. Also,  $T_g$  values of cWPU were shifted into higher temperature range by reducing the molecular weight of HTNR.

One of the significant findings from this study is the influent of NCO index on mechanical strength of cWPUs. The NCO index was varied in the range from 100 to 150 in the case of with and without EG. The system was fixed with molecular weight of HTNR about 3000 g.mole<sup>-1</sup>, NMDEA 5.67 %wt, with 1 mole of EG and without EG. The results of cWPUs with 1 mole of EG show the stability of cWPU and well- dispersed except in case of NCO index of 150 was agglomerated. By contrast, cWPU in the case of without EG gives a stable dispersion of all cWPU. The stability was dropped by increasing of NCO index. Particle size of these cWPUs were up in range of 59 nm to 193 nm and zeta potential values were dropped from +71 mV to +60 mV. This parameter had strongly effected on physical properties, mechanical properties, and thermal properties. Obviously, the inversion of soft elastic to hard plastic behavior were indicated by increasing NCO index. However, in case of adding chain extender had more mechanical properties than without chain extender.

Finally, the different epoxide percentages on HTNR backbone (0-30 %epoxide) effected on cWPU properties were also studied by fixing starting molecular weight of HTNR about 3000 g.mole<sup>-1</sup>, NMDEA 5.67 %wt, 1 mole of EG, and NCO index of 100. The increase of cWPU particle sizes from 76 nm to 188 nm and decrease of zeta potential values from +71 mV to +50 mV were indicated by increasing epoxide content on eHTNR backbone. The physical properties, mechanical properties, and thermal properties of cWPU films were improved by increasing epoxide structure on HTNR backbone. The cWPU film was inversed from ductile elastomeric behavior to hard plastic behavior by increasing epoxide units on HTNR backbone.

Moreover, the adhesive properties of cWPUs on the real leather surface in the account of the different molecular weights of HTNR and different degree of epoxide content on HTNR were tested. Lap shear test and 180 degree peel test were investigated and compared with commercial adhesives, solvent, and non-solvent based adhesive. Also, temperatures of curing adhesive were also studied at room temperature and 70  $^{\circ}$ C.

With the different molecular weight of HTNR, cWPU adhesives had no significantly different on lap shear results curing temperature. At room temperature results, the adhesive properties from the lap shear test values were 1.09, 1.53, and 1.16 MPa for cWPUs with HTNR molecular weight about 3000, 2000, and 1000 g.mole<sup>-1</sup>, respectively. Likewise, lap shear test at curing temperature of 70 °C were 1.06, 1.70, 1.22 MPa, for cWPUs with HTNR molecular weight about 3000, 2000, and 1000 g.mole<sup>-1</sup>, respectively. Therefore, the best adhesive result balancing of adhesive and cohesive failure were from cWPU based on HTNR molecular weight of 1800 g.mole<sup>-1</sup>. In addition, for peel test results, it was found that peel forces were up by increasing HTNR molecular weight from about 1000 to 3000 g.mole<sup>-1</sup>. The temperature had the effects on peel test by showing 1.20, 3.90, and 4.00 N for cWPUs with HTNR molecular weight about 3000, 2000, and 1000 g.mole<sup>-1</sup>, respectively. Three forms temperature is the effect of cWPUs with HTNR molecular weight about 3000, 2000, and 1000 g.mole<sup>-1</sup>. The temperature had the effects on peel test by showing 1.20, 3.90, and 4.00 N for cWPUs with HTNR molecular weight about 3000, 2000, and 1000 g.mole<sup>-1</sup>, respectively, in case of curing at room temperature. Meanwhile, at curing temperature of 70°C, the peel test of cWPUs with HTNR molecular weight about 3000, 2000, and 1000 g.mole<sup>-1</sup> were 1.60, 8.00, 10.00 N, respectively. These WPUs indicate their potential in real cow leather adhesive applications.

Epoxide content on HTNR backbone had strongly effect on adhesive properties. In this part, curing temperature could be had the effects on adhesive strength and bonding process. For lap shear test, the force of adhesive testing cured at room temperature of cWPU adhesive based on HTNR,

eHTNR10, eHTNR20, and eHTNR30 were 1.09, 1.00, 0.25, and 0.75 N/mm<sup>2</sup>, respectively, while lap shear forces of prepared cWPU adhesive cured at 70°C based on HTNR, eHTNR20, and eHTNR30 were 1.06, 0.30, and 0.64 N/mm<sup>2</sup>, respectively. With 70°C, in case of cWPU base on eHTNR10 were cohesive failure in leather. For peel test results, in condition of room temperature curing, peel force of cWPU with HTNR, eHTNR10, eHTNR20, and eHTNR30 were 2.21, 15.42, 0.81, and 3.61 N, respectively, while curing at 70 °C, peel forces of cWPU with HTNR, eHTNR10, eHTNR20, and eHTNR30 were 3.51, 26.35, 0.89, and 1.68 N, respectively. Therefore, lap shear test and 180 degree peel test of cWPUs indicated their potential in real leather adhesive applications, with best adhesive result coming cWPU from 10% epoxide content on eHTNR (eHTNR10). Moreover, adhesive strength in condition of curing at 70 °C is higher than adhesive strength in condition of curing at room temperature because of chemical bonding occurred during the fabrication process. In comparison to non-solvent based commercial adhesives and solvent based commercial adhesive, the adhesive strengths of these synthesized cWPU adhesive were stronger than standard commercials.

A possibility and extension of this research work is used for adhesive application on negative charge substrates or simple polar substrate such as glass, metal, glass and textile. With the particle size in the nanometer scale and zeta potential showing high positive surface charge, the synthesized cWPUs are appropriated to use for adhesive applications with those prefer adherends. In order to apply these cWPUs for adhesives application on the surface of an electron rich, the cWPUs high density of positive charge on their particle surface to obtain a higher electrostatic force to improve the strength of the adhesion forces. Another reason is that there are high surface energy for these prepared cWPU adhesives. In addition, high surface energy values can be indicated that it is very easy to get good wettability and adhesion with any materials.

In conclusion, novel natural rubber based cWPU adhesives were successfully synthesized and well-studied by step-growth polymerization. These result works had been shown the potential of natural rubber based cWPUs as a green adhesive material from renewable resources suitable in aqueous environments allowing a development for using in leather industry. Moreover, these synthesized adhesives can be extended to apply to other substrates.

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APPENDICES

## APPENDIX A

## Code name and formulation of cWPU

Coloren	nome M of HTNB NCO index			Recipe (mole)			
Code name	$M_n$ of HINK	NCO index	HTNR	NMDEA	TDI	EG	
cWPU1	~3000	100	1	0	1	0	
cWPU2	~3000	100	1	0.75	1.75	0	
cWPU3	~3000	100	1	1.5	2.5	0	
cWPU4	~3000	100	1	1.75	2.75	0	
cWPU5	~3000	100	1	2	3	0	
cWPU6	~3000	100	1	2.25	3.25	0	
cWPU7	~3000	100	1	2.42	4.42	1	
cWPU8	~3000	100	1	2.51	5.01	1.5	
cWPU9	~3000	100	1	2.6	5.6	2	
cWPU10	~3000	100	1	2.77	6.77	3	
cWPU17	~2000	100	1	1.91	3.91	1	
cWPU18	~1000	100	1	1.02	2.02	1	
cWPU19	~3000	125	1	2.42	4.6	0	
cWPU20	~3000	150	1	2.25	4.88	0	
cWPU21	~3000	175	1	2.25	6.5	0	
cWPU22	~3000	125	1	2.25	5.31	1	
cWPU23	~3000	150	1	2.25	6.38	1	
cWPUeHTNR10	~3000	100	1	2.65	4.55	1	
cWPUeHTNR20	~3000	100	1	2.7	4.65	1	
cWPUeHTNR30	~3000	100	1	2.76	4.76	1	

 Table 1A Code name and the formulation relation of the synthesized cWPU

#### **APPENDIX B**





Figure 1B FTIR spectra of different eHTNR with different epoxide content.



Figure 2B<sup>1</sup>H NMR spectra of different eHTNR with different epoxide content.

# **APPENDIX C**





Figure 1C. MALDI-TOF mass spectra of HTNR.



Figure 2C. MALDI-TOF mass spectra of eHTNR10.







Figure 4C. MALDI-TOF mass spectra of eHTNR30.

## APPENDIX D

# PUBLICATIONS

# Synthesis of Novel Cationic Waterborne Polyurethane from Natural Rubber and Its Properties Testing

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**Keywords:** Natural rubber, Cationic waterborne polyurethane, Hydroxyl telechelic natural rubber, N-methyl diethanol amine

**Abstract.** The novel natural rubber based cationic waterborne polyurethanes (cWPUs) with having quaternary amine as an emulsifier were successfully synthesized by additional polymerization. These polyurethanes were synthesized by the reaction of hydroxyl the method of telechelic natural rubber. Molecular weight approximately of hydroxyl telechelic natural rubber (HTNR) for 3000 g.mole<sup>-1</sup>, toluene-2,4-diisocyanate (TDI), and N-methyl diethanol amine (NMDEA) (used as an emulsifier) were prepared for cWPU. The concentrations of NMDEA were examined in range of 0 – 2.0 moles. From the results under the isocyanate index of 100, the study revealed that cWPU with well-distributing had to consist of emulsion concentration more than 1.50 moles. Zetasizer nano range was used to identify the prepared cWPU particle size distribution. The results showed that the particle size of cWPU was decreased from 86.6 to 78 nm with increasing of NMDEA concentration. The smallest particle size was 2 moles with non-acetic acid odor, and very soft film. In addition, cWPU would be well-dispersed more than 4 months. The <sup>1</sup>H NMR spectroscopy and FT-IR confirmed that the cWPU has been successfully synthesized from natural rubber.

#### Introduction

Polyurethane (PU) widely used in all application sectors is one of materials that need to be used as a green material and non-effect to human and environment in the period of reducing global warming cause. Waterborne polyurethane (WPU), generally composed of isocyanate hard segment and polyol soft segment, is one of PU forms. Normally, there are three types of WPU. Those are non-ionic, anionic, and cationic. WPU is now very interesting to be used and replaced of solvent based polyurethane because of its environmentally friendly, non-irritation, and safety for human. It has been widely used in coating, adhesive and painting application because of their excellent adhesion properties and film-formability at low temperature [1, 2]. For many decades, there are many research groups that find novel or new natural based materials and to replace petroleum based solvent applied in industrial and household sectors to reduce polyols from petroleum resource.

Most of materials from nature such as vegetables and oil plants [2-7] are used and being focused to replace polyols by many researchers. For those types of oil, they are low molecular weight polymers that acquire polyurethane foam or low-elastic polyurethane due to obtaining short soft segment in polyurethane.

Natural rubber (NR) is now an interesting choice of natural polymer that can be modified to become a reactive hydroxyl polymer [8]. Natural rubber has the reactive double bond with good elastic properties from cis-1,4-polyisoprene structure [9] which can be broken to be a lower molecular weight and then modified to be hydroxyl group [10]. There are many works attempting to prepare PU from natural rubber reported by our research group [8, 11-13]. In the present, anionic WPU from natural rubber is successfully studied [13], but cationic polyurethane has no details for preparing WPU yet.

The objective of this research is to study the feasibility of the novel natural rubber based cationic waterborne polyurethanes (cWPUs) from HTNR with molecular weight of approximately 3000

g.mole<sup>-1</sup>. Synthesis will be based on traditional addition reaction by introducing NMDEA into the polyurethane emulsion system and neutralizing NMDEA with acetic acid obtaining well-dispersed cWPU particle in water. Hence, this study was carried on the pH of system, emulsion stability, emulsion particle and film formation.

#### Experiment

#### Materials

High ammonia concentrated latex of natural rubber (0.7% ammonia) with dry rubber content (DRC) of approximately 60 % and total solid content (TSC) of approximately 62% was purchased from Yala Latex Industry co., Ltd. (Th ailand). Hydrogen peroxide ( $H_2O_2$ ) and Sodium borohydride (NaHB<sub>4</sub>) were purchased from Ajax Finechem (Unilab®) (Australia). Formic acid (HCOOH) was purchased from BASF-YPC Company Limited (China). Methyl ethyl ketone (MEK) was purchased from Fisher Scientific UK Limited (England). Periodic acid ( $H_5IO_6$ ), 99% N-methyl dimethanol amine (NMDEA), 98% 2,4-Toluene diisocyanates (TDI), and dibutyltindilaurate (DBTL) were purchased from Sigma-Aldrich (Germany), and 95% acetic acid was purchased from Carlo Erba (Italy).

#### **Preparation of HTNR**

The hydroxyl telechelic natural rubbers (HTNR) with molecular weight of approximately 3000 g.mole<sup>-1</sup> were prepared from cis-1,4-polyisoprene via epoxy natural rubber (ENR) and carbonyl telechelic natural rubber (CTNR) according to a methodology described in Saetung et. al [11].

#### **Preparation of cWPU**

cWPU based on natural rubber was prepared by prepolymer mixing process by adjusting the methodology of Lu and Larock [2]. For common condition, HTNR3000, NMDEA, DBTL and MEK were added into the reactor equipped with stirrer set, nitrogen inlet, condenser, and thermal controller. Diisocyanate was drop wised into the mixture at 70 °C with mechanical stirring. The reaction was run on 70 °C for 4 hours. After that, the polymer solution was cooled to room temperature, and then was neutralized by acid followed by dispersion at high speed with deionized water to produce the cationic polyurethane with solid content in water after removing MEK by vacuum evaporation.

Effects of NMDEA on the properties of the polyurethane by various NMDEA concentrations of 0, 0.75, 1.50, 1.75, and 2.00 equivalent moles, respectively were investigated. The molecular weight used of HTNR was approximately 3000 g.mole<sup>-1</sup> and TDI content with the NCO index of 100.

#### **Preparation of film**

The cWPU film was formed by casting into poly(tetrafluoroethylene) molds with the cavity depth of 0.3 mm. After mold casting, emulsion solution was left at room temperature for 7 days then emulsion solution was dried in an oven at 70  $^{\circ}$ C for 24 hours.

#### Stability test

The stability of cWPU was studied by keeping the cWPU in the storage vial at room temperature. The appearance of dispersion was observed.

#### Characterization

Fourier transform infrared (FT-IR) spectra were corrected with a Tensor 207 Fourier Transform Infrared Spectrometer (Bruker Company, Germany) in the range of wave numbers from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> in transmission of ATR mode.

Nuclear magnetic resonance (NMR) spectra were recorded on Oxford 500 MHz Superconducting Magnet (Varian, USA) for <sup>1</sup>H NMR (500 MHz) by diluting sample in CDCl<sub>3</sub>. Chemical shifts were reported in ppm relative to the deuterated solvent resonances.

Particle size and size distribution of synthesized cWPU were characterized by Nano-ZS particle sizer (Malvern Instruments Company, UK).

Table 1 Results of prepared cWPU physical properties with containing different NMDEA content

Moles of				Propertie	es	
NMDEA	TSC (%)	Stability	Appearance	рН	Film appearance	Particle size (nm) (PDI) <sup>b</sup>
0	N/A <sup>a</sup>	Unstable	Solid	N/A	N/A	N/A
0.75	N/A	Unstable	Solid	N/A	N/A	N/A
1.50	22.43	Stable <sup>c</sup>	Milky blue	4.31	Could not form film	86.6(0.220)
1.75	26.82	Stable <sup>c</sup>	Milky blue	4.32	Could not form film	83.8(0.276)
2.00	26.31	Stable <sup>c</sup>	Milky blue	4.34	Very-yellowish soft film	78.0(0.257)

 $\frac{a}{N}$  N/A Not available

<sup>b</sup> Polydispersity index

<sup>c</sup> more than 4 months

#### **Properties of cWPU**

The properties of cWPU based on natural rubber were shown in Table 1. All cWPUs were prepared with total solid content (TSC) in range of 22 - 26 %. The stability of dispersion was clearly observed that the NMDEA content had a significant effect on stability and particle size of dispersion. For instance, the NMEDA content was less than 0.75 moles. The waterborne polyurethane could not be stable and coagulated. On the other hands, the NMDEA content was more than 1.5 moles. The waterborne polyurethanes were well-dispersion, and the particle size of dispersions was the range from 86.6 to 78.0 nm. Moreover, the appearances of dispersion were milky blue and non-acetic acid odor or less. Their shelf-life with well dispersion is more than 4 months.

After drying the waterborne polyurethane films, the appearance of cWPU films with containing different NMDEA content was also studied. The samples showed that the content of NMDEA below 1.75 moles was not able to form film whereas the content of NMDEA 2 mole was able to form film and gave a yellowish and very soft behavior. However, the strength of cWPU film could increase by adding some chemical, chain extender or crosslinker.

#### Structure analysis

The <sup>1</sup>H NMR spectrum of synthesized cWPU was shown in the Fig. 1. The signals of isoprene unit from polyol based on natural rubber were observed at 5.12, 2.07, 1.67, and 1.25 ppm corresponding to 3 (-CH<sub>2</sub>(CH<sub>3</sub>)C=CHCH<sub>2</sub>-), 1 (-CH<sub>2</sub>(CH<sub>3</sub>)C=CHCH<sub>2</sub>-), 2 (-CH<sub>2</sub>(CH<sub>3</sub>)C=CH-), and 9 (-CH<sub>2</sub>(CH<sub>3</sub>)CHO-), respectively. In addition, new signals were also observed at 7.23, 7.03, and 6.97 ppm corresponding to benzene ring protons 11-13 of TDI structure [14, 15]. Moreover, the important signal at 8.14 ppm corresponding to urethane linkage 10 (-C(O)NH-Ph-) was observed. These results revealed that the synthesis of cWPU was successful.

FT-IR spectra of cWPU samples were shown in the Fig. 2. The chemical structures of polyurethane were observed at 3302, 1707, and 1538 cm<sup>-1</sup> assigned to -N-H stretching, -C=O ester stretching, and -N-C=O vibration of polyurethane linkage, respectively [1, 11, 12, 16]. Moreover, the absorption band of cis-1,4 polyisoprene of natural rubber was revealed in the wave numbers of 2970, 1449, 1376, and 836 cm<sup>-1</sup> corresponding to -C-H stretching, -CH<sub>2</sub>- deformation, -CH<sub>3</sub> deformation, and =C-H out of plane deformation, respectively [8, 13]. From the spectra, the region of isocyanate (-NCO) absorption peak at 2270 cm<sup>-1</sup> had disappeared showing that toluene diisocynates had completely reacted in the last process by water. From these results, this study revealed that the cWPU synthesis based on natural rubber was successfully synthesized with this technique.



Figure 2 FT-IR spectra of synthesized cWPU based on natural rubber

#### **Summary**

The novel natural rubber based cationic waterborne polyurethanes were successfully synthesized by simple additional polymerization of HTNR with molecular weight 3000, NMDEA, and TDI. <sup>1</sup>H NMR and FT-IR were confirmed for the structure of polyurethane. In addition, the particle size of the dispersion in range of 1.50 - 2.00 moles was decreased with increasing NMDEA concentration and had well dispersion with shelf-life more than 4 months. The cWPU with NMDEA 2 moles was the smallest particle size, non-acetic acid odor, and very soft film. This study is the first example of cWPU based on natural rubber, thus providing valuable cWPU from a renewable raw material and usage of solvent free.

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# Applied Polymer

# Synthesis and characterization of novel natural rubber based cationic waterborne polyurethane—Effect of emulsifier and diol class chain extender

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**ABSTRACT**: Novel cationic waterborne polyurethanes (cWPU) were synthesized by step-growth polymerization of hydroxyl telechelic natural rubber, molecular weight of 2800 g mol<sup>-1</sup>, toluene-2,4-diisocyanate, *N*-methyl diethanolamine (NMDEA) as an emulsifier. The chemical structure of cWPU was confirmed by <sup>1</sup>H-nuclear magnetic resonance and Fourier transform infrared spectroscopy. The amounts of NMDEA and ethylene glycol under isocyanate (NCO) index of 100 on the properties of cWPU were studied. It was found that cWPU was stable under the concentration of NMDEA more than 1.50 mol and the particle sizes decreased with increasing of NMDEA content. Also, contact angle shows more hydrophilic materials by increasing of NMDEA. Extended cWPU was found in two ranges of nano size. Chain extender has strongly affected cWPU film formation, increasing of mechanical properties, and thermal properties. In addition, stress–strain curve and scanning electron microscopy image shows the change of behavior from soft elastic to ductile plastic by adding ethylene glycol. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *134*, 45715.

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#### INTRODUCTION

Polyurethane is normally composed of isocyanate in part of hard segment and polyol in part of soft segment. In conventional term to stabilize them, most are based on volatile organic solvent, composed of 40%-60%,1 which is very hazardous to environmental and human activity or daily life.<sup>2-5</sup> Up to date, there is new materials type of polyurethane named waterborne polyurethane (WPU) which is nonsolvent system. It is extremely extensively studied to avoid these organic solvents, and now it is important and interesting type developed and improved into industrial sector for replacing these conventional polyurethanes. There are three types of WPU possessing anionic, cationic, and nonionic.<sup>6</sup> The main structures are similar to polyurethane, but for the waterborne there are special emulsifiers. Meaning of cationic and anionic WPU is always composed of internal emulsifier while nonionic emulsifier is composed of external emulsifier. For example, anionic WPU (aWPU) is usually composed of 2,2-dimethylolpropionic acid,<sup>7–10</sup> cationic WPU (cWPU) is usually composed of *N*-methyl diethanolamine (NMDEA),<sup>11–13</sup> and nonionic WPU is mostly used glycol class such as poly(ethylene glycol).<sup>14</sup>

Presently, cWPU is now very interested for our group. Having better advantage, cWPU has been recorded that there were high adhesion to various ionic surface,<sup>12,15,16</sup> especially glass, paper, leather, and also in part of automotive applications. Their other intense applications are widely used in many sectors of industrials such as fabric coating,<sup>17</sup> novel electrolyte,<sup>18</sup> and in special field of gene carrier<sup>19,20</sup> and also DNA transfection.<sup>21</sup>

As basic knowledge, ordinary WPUs are based on polyol from fossil-fuel feedstock petroleum, used commercial chemicals in class of polyether and polyester,<sup>13,17–19,22,23</sup> that is very stress now against environmental friendly. To replace the usage of petroleum-based polyol, cWPU is the intended material to find the new way or new resource for synthesizing base on natural





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Novel cationic waterborne polyurethane (cWPU)

Scheme 1. Preparation of cationic waterborne polyurethane. [Color figure can be viewed at wileyonlinelibrary.com]

and renewable resource materials. There are a few classes of modified plant oil from natural-based cWPU such as soybean oil,<sup>12,24</sup> because they are too limited in main properties resulting from low molecular weight.

Our group interested in natural rubber (NR) for modifying them as polyol based substrate named hydroxyl telechelic natural rubber (HTNR) replacing petroleum-based elastomers,<sup>25</sup> films,<sup>26,27</sup> photo-cured polyurethane,<sup>28</sup> polyurethane foam,<sup>29</sup> as well as WPU.<sup>8,27</sup> Theoretically, there are many preparing telechelic NR methods such as redox method,<sup>30</sup> ozonolysis oxidation method,<sup>31</sup> oxidation at high temperature and pressure method,<sup>32</sup> photochemical method,<sup>33</sup> metathesis reaction,<sup>34</sup> and chemical oxidation reaction.<sup>35–37</sup> As well-controlled method with high selectivity and repeatability, the chemical oxidation reaction was modified to prepare the NR telechelic substrate for this work. By our basic knowledge group, anionic WPU was successfully studied and the effects of emulsifier, molecular weight of HTNR, chain extender, and NCO index were reported.<sup>27</sup> However, cWPU based on HTNR have been never reported in all data base.

Therefore, in this work, novel cWPUs based HTNR with molecular weight about 2800 g mol<sup>-1</sup> were first synthesized. The effect of NMDEA and ethylene glycol (EG) on the structure and properties were investigated. cWPU latex was studied on physical properties, while cWPU films were investigated on physical properties, thermal properties, and mechanical properties.

#### EXPERIMENTAL

#### Materials

Concentrated NR latex with high ammonia (0.7% ammonia) containing dry rubber content of approximately 60% and total solid content (TSC) of approximately 62% is purchased from Yala Latex Industry co., Ltd. (Thailand). 35% Hydrogen peroxide ( $H_2O_2$ ) and 98% sodium borohydride (NaBH<sub>4</sub>) were purchased from Ajax Finechem (Unilab) (Australia). 98% Formic acid (HCOOH) is purchased from BASF-YPC Company Limited (China). Methyl ethyl ketone (MEK) is purchased from Fisher Scientific UK Limited (England). Periodic acid ( $H_5IO_6$ ), 99% NMDEA, 98% 2,4-toluene diisocyanate (TDI), and

dibutyltin dilaurate were purchased from Sigma-Aldrich (Germany). 95% Acetic acid (CH<sub>3</sub>COOH) and 99.5% EG were purchased from Carlo Erba (Italy).

#### Method

HTNR with molecular weight of 2800 g mol<sup>-1</sup> were synthesized by following the method of Saetung *et al.*<sup>27,35,38</sup> and the <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum of HTNR is shown as previous result.<sup>35</sup> Briefly, HTNR was prepared by semisolution method processed via controlling epoxidation percentage of 2.0 in epoxidized NR followed by cleavage reaction to obtain carbonyl telechelic NR. Then, the carbonyl telechelic NR was reduced with NaBH<sub>4</sub>. Summary of this present work, cWPU synthesis, is shown in Scheme 1.

Plain and EG-extended cWPU in this work was synthesized by applying the process of previous researches<sup>8,27</sup> with the recipe as shown in Table I. Briefly, with controlled 20% TSC, HTNR2800, NMDEA, and MEK were mixed in the reactor equipped with stirrer set, nitrogen inlet, condenser, and thermal controller. Under the temperature of 60 °C with stirrer rate of 100 rpm, TDI was slowly dropped into the reaction of mixture. After the stable condition for 4 h, EG was gently dropped into the system for 30 min with stirrer speed of 400 rpm, then the system was cooled and neutralized by acetic acid for 30 min with stirrer speed of 400 rpm, respectively. Finally, MEK solvent was removed out by rotary evaporator to obtain only cWPU in water medium.

#### CHARACTERIZATIONS

#### cWPU Latex

Particle size and size distribution of synthesized cWPU were characterized by Nano-ZS particle sizer (Malvern Instruments Company, UK).

TSC of cWPUs were calculated by differential weight before and after drying. To identify them, cWPU about 1 g was placed in aluminum tray and dried in air oven under the temperature of 100 °C until there is constant weight. The solid content (%TSC) is calculated as average of three samples of each formulation as follows:



								Physic	al properties					
		Recipe (r (NCO/OH =	mole) = 1.00)							Particle siz	ze (nm) (% fc	(pund)	Conta angle	act (°)
	HTNR	NMDEA	TDI	Э	TSC (%)	Stability	Appearance	Hd	Film appearance	First <sup>b</sup>	Second <sup>c</sup>	PDIq	Water	Oil
	1.00	0.00	1.00	0	N/A	Unstable	Solid	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	1.00	0.75	1.75	0	N/A	Unstable	Solid	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	1.00	1.50	2.50	0	22.43	Stable <sup>a</sup>	Milky blue	4.31	could not form film	87.1 (100)	I	0.276	109	35
	1.00	1.75	2.75	0	26.82	Stable <sup>a</sup>	Milky blue	4.32	could not form film	83.8 (100)	I	0.32	102	36
	1.00	2.00	3.00	0	26.31	Stable <sup>a</sup>	Milky blue	4.34	very-yellowish soft film	73.8 (100)	I	0.149	96	37
	1.00	2.25	3.25	0	21.02	Stable <sup>a</sup>	Milky blue	4.37	very-yellowish soft film	59.8 (100)	I	0.14	90	90 8
	1.00	2.25	4.25	1.00	16.67	Stable <sup>a</sup>	Milky blue	3.73	very-yellowish film	76.46(100)	I	0.438	91	35
	1.00	2.25	4.75	1.50	16.34	Stable <sup>a</sup>	Milky blue	3.71	yellowish film	17.24 (10.4)	174.50 (89.6)	0.361	93	35
	1.00	2.25	5.25	2.00	17.43	Stable <sup>a</sup>	Milky blue	3.79	yellowish film	41.51 (24.6)	214.30 (75.4)	0.585	94	0 0
0	1.00	2.25	6.25	3.00	17.14	Stable <sup>a</sup>	Milky blue	3.75	yellowish film	67.60 (8.5)	453.30 (91.5)	0.304	97	30
dis dis ize rsit	months. tribution (p distributior y index fro ible.	ercentage foι η (percentage m nanosizer t	und). found). echnique.											

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Table I. Summary of cWPU Based on Natural Rubber Recipe and their Physical Properties



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$$\%\text{TSC} = \frac{(W_x - W_i)}{W_i} \times 100$$

where  $W_i$  is the weight of the initial weight of cWPU dispersion and  $W_x$  is the weight after drying sample.

The morphology confirmation of synthesized cWPU dispersion was determined by transmission electron microscope (TEM) on a model JEOL JEM-2010 with 160 kV. The samples were diluted by DI water ( $\sim$ 0.05% TSC) over a 200-mesh nickel TEM grid in a dust free condition. After that the dried dispersion film on the TEM was stained with 2% osmium tetraoxide vapor for 1 h prior to test.

The stability of cWPU suspension was observed by keeping the cWPUs in the storage vial at room temperature. The appearance of cWPUs was observed and recorded.

#### cWPU Film

**Structure Confirmation.** Fourier transform infrared (FTIR) spectra were corrected with a Tensor 207 FTIR spectrometer (Bruker Company, Germany) in the range of wave numbers from 4000 to 400 cm<sup>-1</sup> in transmission of attenuated total reflection mode.

NMR spectra were recorded on Fourier transform NMR spectrometer 500 MHz (Unity Inova, Varian, Germany) for <sup>1</sup>H NMR by diluting sample in  $CDCl_3$ . The results were analyzed with flip angle of  $3.150^\circ$ , scan number of 16 scan, and pulse delay time of 1.00 second and nonset relaxation time. NMR chemical shifts were reported in ppm relative to the deuterated solvent resonances.

**Physical Properties.** Hydrophobicity and hydrophilicity were carried out by contact angle using Data physics apparatus (Model: OCA 15EC, input: 55 W, line voltage: 12 V DC, fuses: 6.3 AT) with sessile drop method. Average water contact angel with individual droplet volume of 7  $\mu$ L was determined in three separate measurements with different position for each sample. Average oil contact angle for hydrophilicity measurement using four-stoke motorcycle engine oil with individual droplet volume of 6  $\mu$ L was determined in three separate measurements with different position for each sample.

JEOL JSM-5900 LV SEMs (JEOL Ltd., Tokyo, Japan) were used to examine the morphology. The fracture surface photographs corrected from tensile testing fracture were sputter-coated with a thin layer of gold to prevent electrical charging during the examination. SEM photomicrographs of the fracture surfaces were taken at magnifications of  $\times$ 500.

Swelling properties were characterized by immersing the sample film (6 cm diameter) in tetrahydrofuran (THF) for 24 h in Petri dish. After that, the Petri dish with diameter of each swollen sample was putted on a graph paper to measure and calculate later. The swelling properties were compared and computed the swollen and original specimens.<sup>27,39</sup> The area of cWPU circular film is calculated as follows:

#### $A = \prod r^2$

where r is the radius of the circular film.

The swelling percentage (% S) is calculated as follows:

$$S = \frac{(A_i - A_0)}{A_0} \times 100$$

where  $A_i$  is the area of the immersion treated film and  $A_0$  is the area of initial film.

Water absorption behaviors were assessed with weight each dried sample film  $(1 \text{ cm} \times 1 \text{ cm})$  before and after immersing in distilled water with five replicates for each sample. It was monitored daily day for 7 days to weigh and calculate the percentage exchanging of the sample. The absorption percentage (%A) is calculated as follows:

water adsorption (%) = 
$$\frac{(W_i - W_0)}{W_0} \times 100$$

where  $W_i$  is the weight of the immersion treated film and  $W_0$  is the weight of initial film

**Mechanical Properties.** Tensile properties of cWPU film were prepared following ISO37 with die type 2. The films were characterized by using Instron machine (Model 3365). The apparatus was equipped with 100 N load cell and extensor grip included laser sensor for checking their elongation with cross head speed of 100 mm min<sup>-1</sup>.

**Thermal Properties.** DSC (Selb, Germany) data was collected by NETZSCH DSC 200F3. The process using alumina pan with starting sample weight of about 10 mg was run under nitrogen atmosphere (rate of nitrogen = 100 mL min<sup>-1</sup>) with heating rate of 10 °C min<sup>-1</sup> from -100 to 100 °C. The data was corrected after clearing their thermal history by first time running, and then second heating scan was used to correct glass transition temperature ( $T_{o}$ ) of synthesized WPU.

Thermogravimetric analysis (TGA) (Selb, Germany) analysis was performed on NETZSCH STA 449F3. Weight loss of cWPU film was measured under nitrogen atmosphere with starting weight of about 10 mg. The samples of thermogravimetric analysis were gradually heated from room temperature to 600 °C with heating rate of 10 °C min<sup>-1</sup>.

Dynamic mechanical analyses of the cWPU films were carried out by DMTA (Rheometric Scientific DMTA V) in tensile mode at a frequency of 1 Hz and 0.01% strain with a heating rate of  $3 \,^{\circ}$ C min<sup>-1</sup> by scanning heating temperature of -100 to 150  $^{\circ}$ C. Tensile storage modulus (*E*'), loss modulus (*E*''), and the loss factor (tan  $\delta$ ) as the ratio of loss modulus to storage modulus (*E*''/*E*') are used to indicate the elastic and viscous behavior of a viscoelastic material under deformation.

#### **RESULTS AND DISCUSSION**

#### cWPU Latex

The summary of cWPU properties based on NR in series of emulsifier effect, NMDEA content in range of 0–2.25 mol, was shown in Table I. All cWPUs were prepared with TSC in range of 21%–27%. The stability of dispersion was clearly observed that the NMDEA content had significantly effected on stability and particle size distribution. For instance, the NMEDA content less than 1.50 mol (NMDEA contents of 0–1.00 mol) could not be stable and also coagulated because of emulsifier insufficiency in its system.<sup>6</sup> Notwithstanding, the system of prepared cWPU



# Code name Water contact angle image Oil contact angle image cWPU6 Image Image cWPU10 Image Image

#### Table II. Water and Oil Contact Angle of cWPU Films

was stable with emulsifier content at least 1.50 mol (NMDEA contents of 1.50–2.25 mol).

By the physical appearance, the dispersions of cWPU were milky blue. The systems of emulsion were in acidic with pH in range of 4.31–4.37 by little or nonacetic acid odor. It is indicated that all acetic molecules neutralized tertiary amine position of NMDEA part of chain to obtain the complete cationic charge in cWPU chain. Apart from that, by observing its appearance, shelflife with well dispersion is more than 6 months.

After drying films, the appearance of it with different NMDEA content containing was also studied. The samples showed that the content of NMDEA below 1.75 mol could not be formed film whereas the content of NMDEA 2 and 2.25 mol is able to form film and gave a yellowish and soft behavior. However, the strength of cWPU film could increase by adding some chemical, chain extender, or crosslinker, but they were still stable in the water with well dispersion.<sup>27,40</sup> Therefore, in this work, cWPU containing NMDEA 2.25 mol system is chosen to study the addition of chain extender to improve its all properties in the next step.

To improve the properties, plain novel cWPU was extended that chain and solved the weak point by adding EG as chain extender with concentration of 1.00–3.00 mol. All concluded physical property results of extended cWPU chain were presented in Table II. The samples of cWPU and extended cWPU were similar in part of some results. Extended cWPUs were in range of acidic with pH value of 3.71–3.79 with none or less acetic acid odor with the appearance of very light yellowish milky blue. Because of the long extended cWPU chain affected from EG as chain extender, the medium of extended cWPU system was prepared in aqueous with TSC in range of 16%–18% to decrease the viscosity of the system.

For particle size distribution, cWPUs with NMDEA content more than 1.5 mol were well-dispersed, and the particle sizes of dispersions were in range of 87.1 to 59.8 nm as show in Figure 1. It might be that the Gibb's free energy of water-oil surface of cWPU containing hydrophilic, NMDEA, slightly decreased with increasing of NMDEA content in the cWPU emulsion particle.<sup>41</sup>

Adding EG to the system, it was found that there were two ranges of size—small size range and large size range as presented in Figure 2. It was observed that the small range sizes were increased from 16.71 to 67.60 nm while, large size of cWPUs presented in range of 106.10 to 453.30 nm with increasing of EG content from 1.00 to 3.00, respectively. In the first size distribution, small particle size, the effect of residual short chain EG and NMDEA by reactive OH reacted with free isocyanate in the system which was results of the small size range showed in size distribution display. Meanwhile, the large size distribution is that the extended main-chain cWPU from the plain reaction of NMDEA, HTNR, and TDI prepolymer reacted with EG growing up to long chain cWPU and marking in the large size distribution display.

From both series of cWPU and extended cWPU, they obtained smaller particle size than anionic WPU base on NR that particle of them were in range of micrometer and the smallest particle is presented around 100 nm. While, this work showed the particle size which smaller than other authors presented with smallest particle size of 59.8 nm.<sup>27,38</sup>

In addition, the size distribution of control WPU (WPU3033) was studied by Fan *et al.*<sup>42</sup> The results showed that average particle size of the WPU emulsion was 94.99 nm and its PDI was 0.098. However, it was larger than the cWPU in this work.

Likewise, the film formation after adding chain extender into the main chain showed more strength and could be formed film as well. It is easily removed out from Teflon mold because



**Figure 1.** The result of size distribution by intensity in effect of NMDEA. [Color figure can be viewed at wileyonlinelibrary.com]





**Figure 2.** The result of size distribution by intensity in effect of EG. [Color figure can be viewed at wileyonlinelibrary.com]

it showed the first evidence that its mechanical properties were increased.

These TEM images presented the particles of cWPU base on NR by magnification of 100,000 (a) and 300,000 (b) as shown in the Figure 3. They showed dark point of cWPU phase in TEM images is generally presented with the stained OsO4 on carbon-carbon double bond of HTNR (isoprene unit) because the main part of cWPU is formed by NR more than 70%. Clearly, the PU phase is mostly found in round shape and well dispersed. It is mostly regularly dispersed in water showing the particle size of approximately 20 nm agreed with the value from using zeta nanosizer technique. For this work, the particle sizes of prepared cWPUs were smaller than others because of the nature viscosity of long-chain HTNR is normally higher than natural-resource oils. The spherical size of it is displayed because of shear force between the blade and polymer materials with properly charge in water media during the process of cWPU preparing. Therefore, TEM images can confirm the shape and the distribution of cWPU that can stable in water media by according the results of zeta nanosizer.

From all of view shapes, TEM and zeta nanosizer results, the possible model of cWPU are offered as shape of round. For each well-dispersed particle, it play with the regular shape of round that is stabilized of the cWPU shape by positive  $(N^+)$  charge affected in part of neutralized NMDEA by acetic acid.

The stabilized charge is distributed in the process of synthesizing inserting NMDEA into the chain of PU containing HTNR and TDI as soft segment and hard segment, respectively. The chains of cWPU are rolled in the particle and try to have and get them stable by inserting positive charge out of their particle surfaces. In the particle side, the effect of physical crosslink and hydrogen bonding lead them to have more stable and disperse in water well. Beside, possible model of cWPU behavior in aqueous medium is presented as round shape.

#### cWPU Films

To confirm the structure of cWPU, FTIR is the first method for showing the functional group of synthesized cWPU. FTIR spectra of both cWPU and cWPU added EG samples were shown in the Figure 4. The chemical structures of polyurethane shown as important functional groups were observed at 3302, 1707, 1602, 1538, and 1224 cm<sup>-1</sup>assigned to -N-H stretching, -C=O ester stretching, N-H bending of urethane position, -N-C=O vibration of polyurethane linkage, and C-O acyl stretching of urethane linkage, respectively.<sup>17,29,38,43,44</sup> Moreover, the absorption band of cis-1,4 polyisoprene of NR is revealed in the wave numbers of 836  $\text{cm}^{-1}$  corresponding to =C-H out of plane deformation.<sup>27,35</sup>After adding EG into the active chain of cWPU to obtain the chain extender in the system, FTIR spectrum showed quite familiar spectrum of cWPU without EG, but there is a peak showed in the spectrum. With wavenumber of 1409 cm<sup>-1</sup>, it ascribed to symemetric stretching of glycolate bridge (-O-C=O).45

By all spectra results, the region of isocyanate (-NCO) absorption peak at 2270 cm<sup>-1</sup> had disappeared showing that free active isocyanate had completely reacted in the last process by water. By the FTIR results, this result issued as the basis confirmation that the cWPU synthesis based on NR is successfully synthesized with this technique.

The chemical structure confirmation of prepared cWPU is observed by <sup>1</sup> H NMR spectrum as shown in the Figure 5. For the important peak, the signals of isoprene unit from polyol based on NR were observed at 5.12, 2.07, 1.67, and 1.25 ppm corresponding to **3** ( $-CH_2(CH_3)C=CHCH_2-$ ), **1**( $-CH_2(CH_3)$ **C**=CHCH<sub>2</sub>-), **2**( $-CH_2(CH_3)C=CH-$ ), and **9** ( $-CH_2(CH_3)CHO-$ ), respectively. In addition, new signals were also observed at 7.23, 7.03, and 6.97 ppm corresponding to benzene ring protons **11–13** 



Figure 3. TEM images of synthesized cWPU6 at magnification of (a) ×100,000 (b) ×300,000.



**Figure 4.** FTIR spectra of film of HTNR2800, cWPU6, and cWP10. [Color figure can be viewed at wileyonlinelibrary.com]

of TDI structure.<sup>46,47</sup> Moreover, the important signal at 8.14 ppm corresponding to urethane linkage **10** (-C(O)NH-Ph-) is observed. After adding EG into the system of cWPU emulsion, it is no different point of <sup>1</sup>H NMR signal because the chain extender in this work is also normal hydrocarbon of diol agent and did not change the chemical backbone structure.

Figure 6 showed the effect of EG content on water uptake under NCO index 100 and constant NMDEA 2.25 mol. For instances, all cWPU films immersed into water for 7 days is shown slightly increased with increasing of EG content as well as immersion time. In the day 7, it is found that percentage of water uptake were 7.77%, 12.75%, 13.81%, and 19.28% with EG content of 1.00, 1.50, 2.00, and 3.00 mol, respectively. The results showed that increased percentage of water uptake with EG increasing contents clearly. Therefore, the more EG content, the more hydrophilic hard segment in class of isocyanate because of high possibility of reaction between isocyanate-terminated chain and active short chain hydroxyl group of EG. Like this, it can be assumed that the chain of cWPU has more hydrophilic block in the chain because of EG content effect. However, its results



Figure 5. <sup>1</sup>H NMR spectrum of synthesized cWPU. [Color figure can be viewed at wileyonlinelibrary.com]



**Figure 6.** Water absorption by the cWPU films with varying ethylene glycol contents (cWPU7 = EG 1 mol, cWPU8 = EG 1.50 mol, cWPU9 = EG 2 mol, and cWPU10 = EG 3 mol). [Color figure can be viewed at wileyonlinelibrary.com]

were significantly different in comparison of other polyol based because of nature of hydrocarbon NR in their structure on this our cWPU. For the anionic WPU base on NR with equal percentage of emulsifier amount (5.6%), Saetung *et al.*<sup>27</sup> reported that the water uptake results their cWPU films immerged for 7 days were in range of 17%–45% their work is higher than this work. Primarily, the result prove that cWPU based on NR is more properly in field of adhesive, coating and all material sensitive to water than aWPU. It is assumed that because of the different interaction of intra-/interchain of nature charge of anionic and cationic WPU.

The swelling properties of cWPU in chosen solvent of THF were shown in Table III. Normally, isocyanate hard segment is hardly dissolved in THF, while NR soft segment is easily dissolved in THF. It was observed that cWPU with EG content of 1.00 mol was completely dissolved because of high nonpolar nature of NR and high linear structure content. Meanwhile, cWPU with EG content more than 1.50 mol had the more shape stable because of higher content of isocyanate hard segment in intrachain. They showed that swelling percentage of film was decreased with increasing of EG content. The swelling percentages of cWPU film with EG containing of 1.50, 2.00, and 3.00 mol were 236%, 100%, and 56%, respectively. What the supporting reason of these is the more hard segment promoting physical bonding from intra-/interchain hydrogen bonding led to lower swelling values of cWPU films.<sup>27</sup>

Table II presented summary results of contact angle hydrophobicity and hydrophilicity of prepared cWPU film. For NMDEA effect results, water contact angle and oil contact angle were shown trendy of hydrophilicity increasing by increasing of NMDEA content. As summary in the Table I, the contact angle results of cWPU film with NMDEA contents of 1.50, 1.75, 2.00, and 2.25 mol were 109°, 102°, 96°, and 90° for water contact angle and were 35°, 36°, 37°, and 39° for oil contact angle, respectively. By the effect of neutralized NMDEA content by acetic acid, it made more positive-charge in system leading to more hydrophillicity property in the cWPU. However, water contact angle is quite high degree because of effect of nonpolar NR soft segment, but it still clearly showed the effect of



Code name	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Swelling in THF (%)
cWPU7	$1.14 \pm 0.23$	$1.70 \pm 0.19$	$116.64 \pm 1.38$	N/A
cWPU8	$2.04 \pm 0.07$	$1.79 \pm 0.11$	$117.12 \pm 4.13$	236.11
cWPU9	$8.05 \pm 0.04$	$2.70 \pm 0.02$	$118.89 \pm 0.75$	100.69
cWPU10	$44.66\pm0.58$	$4.73\pm0.59$	$162.62 \pm 5.83$	56.25

Table III. Mechanical Properties and Swelling Percentages of cWPU with Different EG Content

N/A, cannot measure.

NMDEA content with increasing of water-like property. It maybe concern that synthesized cWPU had more polar resulted from more concentrate of positive charge of NMDEA effect.

The contact angle resulted that film of cWPU with EG content of 0, 1.00, 1.50, 2.00, and 3.00 mol were 90°, 91°, 93°, 94°, and 97°, respectively for water drop testing, and were 39°, 35°, 35°, 33°, and 30°, respectively for oil drop testing. The results in range of 1.00–3.00 mol of EG showed the trend of results by increasing of water contact angle with EG increasing content. Furthermore, oil drop contact angle showed the properties as showed in the water drop with increasing of EG content by increasing of hydrophobicity, decreasing oil contact angle. Although, EG was used as chain extender to obtain longer chain of cWPU gathering hard segment part, cWPUs still contained high content ratio of NR part in the system, so oil drop contact angle were not significantly different in degree.

Young's modulus, tensile strength and elongation at break of cWPU films based on HTNR2800 with different amounts of EG varied from 1.00 to 3.00 mol are summarized in Table III. The results exhibit tensile stress–strain behavior inversing from elastomer to tough plastics as shown in the Figure 7. The behaviors are clearly shown that is depending on the EG content that all show two functions of chain extender and diol. Without EG content, it showed very soft film, so there are no data of cWPU6. For the added EG system, EG content of 1.00 to 2.00 mol are observed for elastomeric polymer with modulus increased slightly from 1.14 to 8.05 MPa.

Also, tensile strength and elongation at break increased slightly with value of 1.70 to 2.70 MPa, and 116.64% to 118.89%, respectively. Having more EG content, 3.00 mol, demonstrate tough plastic in the first period of measurement and then run the result as elastomeric polymer with modulus, tensile strength, and elongation at break of 44.66 MPa, 4.73 MPa, and 162.62%, respectively. The modulus of cWPU10 is observed that there was increase five times compared with cWPU9. There are increased mechanical properties due to high physical bonding with hydrogen bonding and entanglement effect. In addition, urethane linkage is developed and contributed in inner particle between the same chain and particle surface of cWPU<sup>40</sup> that lead to increased mechanical properties of prepared cWPU by increasing of EG content. All these behaviors are showed and related with SEM images of cross section film from tensile testing as shown in Figure 8. The effect of these behaviors significantly depends on HTNR based that are used as the main soft segment in this work, so all samples of prepared cWPU showed elastomer behavior. Comparing to anionic WPU from the NR based of Saetung *et al.*<sup>27</sup> with the same condition (about 5.6% emulsifier and 2% chain extender), it was reported that elongation at break was not significantly different. Moreover, tensile strength of the cationic was higher than the anionic for two times, while cWPU had lower Young's modulus about eight times.

In addition, mechanical strength of pure WPU in work of Gao *et al.*<sup>48</sup> showed the value of 3.6 MPa that was less than mechanical strength of this present work. Also, comparing with fully petroleum-based WPU dispersion in work of Fu *et al.*<sup>49</sup> cWPU in this work had more mechanical strength values. Tensile strength of that work was only 0.1 MPa that showed lower mechanical strength than this work about 40 times which showed 4.73 MPa.

Furthermore, morphology of cWPUs were studied and confirmed by SEM technique which used cWPU film specimens from the cross section of tensile testing. The roughs and fracture behaviors were shown in Figure 8.

By the cross-sectional SEM images from tensile testing, it showed the effect of chain extender addition with roughness of cWPU film surface by magnification of  $\times$ 500. The material surfaces exhibited the trend of increasing roughness of surface with increasing of EG content from 1 to 3 mol. It is indicated that the matrix of specimen tearing contributed to higher tensile strength by slightly showing from brittle fraction to ductile fraction while it is tearing. With the EG content of 1.00 mol, it showed quite smooth surface because of its brittle fraction



Figure 7. Stress–strain curves of cWPU films with various EG content. [Color figure can be viewed at wileyonlinelibrary.com]





Figure 8. SEM image of cWPU film resulted from cross section of tensile test (×500).

property related with its mechanical property from tensile results that showed very low strain and stress. In addition, EG content more than 1.50 showed the tear of cWPU film matrix with higher ductile evidence by tearing as sheet-like and also pillar-like (higher rough surface) before it is tear apart. Sheetlike tear is the evidence showed that its matrix is extended and held until it broke. Meanwhile, pillar-like tear of cWPU film is the important part that showed more colonies in surface with adding more EG content in cWPU system. Both of tear evidences would be the important of tear behavior to improve the mechanical properties which affected of chain extender of EG content by showing in Figure 7. They were confirmed by tensile properties that slightly increased with increasing of EG content in range of 1.00 to 2.00 mol, but its tensile properties is suddenly increased with adding EG into the system by 3.00 mol. For the highest content of EG in this work, its property is closely presented to plastic behavior.

For thermal properties, TGA, DSC, and DMTA were used to obtain and carry out of the results of cWPU series and its substrate.

Thermal degradation of cWPU film is showed in the TGA and DTG results as show in Figure 9(a,b), respectively. They provided the calculated composition of each segment by comparing mass decomposition in each step. For HTNR part, its decomposition result showed only one step in temperature 377 °C on

account of pure HTNR. Moreover, their thermal degradation behavior showed that all spectra of cWPU with various content of EG were not significantly different. They were same steps of decomposition by having two main decomposition steps. There are in the range of 205–215 °C for first step decomposition attributed to breaking of urethane linkage as EG, HTNR, isocyanate, and also loss of carbon dioxide from urethane deformation.<sup>27</sup> Closely, some of cracking part decomposed in near range of higher temperature that showing in first temperature. For second decomposition step, mass of sample is changed in the temperature range of 377–382 °C related to the decomposition of HTNR as indicated in pure polyols substrate. It provided the ship of temperature degradation because it had longer chain and more physical hydrogen bonding between those chains.<sup>39</sup> Besides, there are more stable in higher temperature.

In order to analyze mass percentage, the mass change of each step was applied to calculate the percentage content in that referred part after cWPU formation labeled as real content. Contrary, the amount of each composition before the reaction started was labeled as calculated content. For the hard segment calculation from TGA, the first decomposition was used to refer to hard segment decomposition that the mass change prefer to the summation content of TDI, NMDEA, and EG part which are short chain segment, while, soft segment was referred to HTNR part decomposed in the second step of TGA result.





Figure 9. Thermal gravimetric results of cWPU. (a) TGA curve and (b) DTG curve. [Color figure can be viewed at wileyonlinelibrary.com]

The results were shown in Table (I and IV). Indicating the component of soft segment, the result showed calculated content is lower than real content because of the effect of more physical bonding like hydrogen bonding in the system by shifting from the higher temperature resistance of some part of hard segment. On the other hand, hard segment in real content is lower than calculated content because adding EG into the system affected

Table IV. Thermal Properties of Synthesized cWPU



Figure 10. DSC thermograms of HTNR28000 and series of cWPU. [Color figure can be viewed at wileyonlinelibrary.com]

to the more hydrogen bonding. By the effect of these, the content of hard segment in real content is lost in the result of TGA, but their compositions were shifted into the part of soft segment content.

Thermal property from DSC technique is one main point to provide the important data as show in Figure 10. It can be identified as the part of amorphous, crystallize, and also fusion behavior of cWPUs as well as showing in  $T_g$  value which depend on main chain movement of polymer backbone. Normally,  $T_g$  of polymer will be showed in the part of amorphous that is a chain mobility and flexibility with lower  $T_g$  showed in the DSC thermogram. By the work, HTNR28000 obtained very low  $T_g$  in the temperature range of about -54 °C showing amorphous phase. It is strongly affected and constantly showed in all sample which confirmed that HTNR in the cWPU had more efficient in cWPU properties. All cWPU amorphous part showed  $T_g$  values in the quiet same temperature by slightly increasing in range of -54 °C as varying EG.

				Thermal	properties			
		Firstst step			Second step			
		Mass o conte	change/ ent (%)		Mass c conter	hange/ nt (%)	Mass	
Code name	T <sub>max</sub> (°C)	Cal <sup>a</sup>	Real <sup>b</sup>	T <sub>max</sub> (°C)	Cal <sup>a</sup>	Real <sup>b</sup>	residual (%)	$Tan\;\delta^c$
HTNR2800	_	_	_	377.2	100.00	92.90	0.11	N/A
cWPU6	215.2	21.35	10.07	380.6	78.83	79.49	1.45	N/A
cWPU7	210.7	27.97	10.20	379.8	72.89	74.50	2.77	-54
cWPU8	213.2	30.86	10.29	380.1	70.33	74.42	3.39	-53
cWPU9	205.7	33.58	10.39	378.4	67.89	72.50	3.67	-54
cWPU10	205	38.51	10.84	379.9	63.59	70.12	4.57	-55

<sup>a</sup>Cal, percentage content is added into the reaction.

<sup>b</sup>Real, percentage content is found in TGA.

<sup>c</sup>Tan δ from DMTA result.

N/A, cannot measure.





**Figure 11.** DMTA curves of cWPU film. (a) Tan  $\delta$ , (b) storage modulus. [Color figure can be viewed at wileyonlinelibrary.com]

Overall, DSC thermograms of cWPUs are observed the  $T_g$  of poly(ether urethane) linkage that normally were observed in the range 40–70 °C.<sup>50</sup> In this work, the linkage of urethane that had the effect of NR and TDI were displayed in range of 41.6–41.9 °C by slightly increasing with increasing of EG content from 1.00 to 3.00 mol, respectively. However, the urethane linkage  $T_g$  of cWPU without EG as chain extender is not clearly showed in DSC thermogram.

DMTA is an equipment to enter the molecular mobility of polymer sensitively. As show in Figure 11, tan  $\delta$  and storage modulus is presented with a function of temperature for observing the effect of EG content and all properties to defy them.  $T_{g}$ glassy state of polymer, is defined by tan  $\delta$  while the stiffness of prepared materials, extended cWPU, is determined by storage modulus of DMTA. As in Figure 11(a), tan  $\delta$  of cWPU7-10, extended cWPU, is observed in the temperature of -53.98, -52.56, -54.10, and -54.97 °C for cWPU7, cWPU8, cWPU9, and cWPU10, respectively. The results show tan  $\delta$  in the range of elastic properties of main part of NR that normally found in range of about -60 °C. Comparing the results,  $T_g$  from DMTA and from DSC is quite similar trend because it is found only one glassy state with relating temperature. It can be proved that the most content in extended cWPU is NR part and can describe as the reasons of DSC part. Figure 11(b) illustrates the storage modulus by clearly result. The obvious results from

DMTA can describe clearly the effect of EG on storage modulus result because it more sensitive from molecular chain mobility. In the first period of graph, -100 to -60 °C, glass phase or hard plastic behavior is found in all samples by observing that the stiffness is gradually rose up with adding more EG content. It is normally that the effect of chain extender on extended cWPU chain and high crosslink chance and hydrogen bonding from urethane linkage are that the following effect. For second state, all samples show the major relaxation found in temperature range about -60 to -40 °C determined by dramatically decreased in storage modulus. This state is in range of  $T_g$  of prepared cWPU by presenting major effect of HTNR on cWPU. The last phase found in curve is rubbery state or elastomer that it is observed in temperature above -40 °C. This phase is very clear the effect of EG on cWPU by showing highest stiffness materials in cWPU10 and lowest value in cWPU7. These can confirm the properly extended cWPU in the system via the normal reaction in this work.

#### CONCLUSIONS

Novel HTNR based cWPU with NMDEA, and EG as chain extender under NCO index of 100 was successfully synthesized. FTIR and <sup>1</sup>H-NMR truly confirmed the chemical structure of cWPU. The particle size and hydrophobicity of the stabled cWPU were slightly down with increasing of NMDEA content and EG content. The particles of cWPU in the aqueous system are ordinary dispersed with round shape in nano size range by TEM image. In addition, the increasing of EG content led to increased water uptake but decreased swelling in THF properties. Moreover, These added EG cWPUs changed from elastic behavior to hard plastic showing highest Young's modulus, elongation at break, and tensile strength value of  $44.66 \pm 0.58$ MPa,  $4.73 \pm 0.59$  MPa,  $162.62 \pm 5.83\%$ , respectively. However, thermal properties of prepared EG-extended cWPU were in the same range of  $T_g$  by DMTA and DSC with the range of NR mobility of -51 to -54 °C. Therefore, these cWPUs are successfully synthesized in the solvent-free medium and they can access to the advantages as normal PU. Renewable resources and environmental friendly raw materials from NR and their medium are deserved as solvent-based PU.

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Bachelor of Science (Che	mistry) Ubon Ratchathani University	2012

#### **Scholarship Awards during Enrolment**

Science Achievement Scholarship of Thailand (2009 – 2017; Bachelor to Doctoral degree).

Grant of Graduate School, Prince of Songkla University, Thailand.

Grant of Faculty of Science, Prince of Songkla University, Thailand.

The scholarship of an overseas thesis research from the graduate school of Prince of Songkla University, Thailand.

Scholarship from Natural Rubber Innovation Research Institute, Prince of Songkla University, Thailand

#### List of Publications, Proceedings and Communications

- 1. Poster
- Nathapong Sukhawipat. Chemical degradation of Anionic Polyacrylamide (aPAM) in Aqeous solution. The 1<sup>st</sup> International Symposium on Sustainable Agriculture and Agro-Industry. July 3-4, 2014.

#### 2. Talks

- Nathapong SUKHAWIPAT, Nitinart SAETUNG and Anuwat SAETUNG. Synthesis of Novel Cationic Waterborne Polyurethane from Natural Rubber and Its Properties Testing. 2016
   6<sup>th</sup> International Conference on Key Engineering Materials (ICKEM 2016), Hongkong. March 12<sup>th</sup> -14<sup>th</sup>, 2016. (best selected paper for work shop presentation)
- Nathapong SUKHAWIPAT, Nitinart SAETUNG, Jean-Francois PILARD, Sophie BISTAC, Anuwat SAETUNG. First Study the Effects of Molecular Weight of Hydroxyl Telechelic

*Natural Rubber on Cationic Waterborne Polyurethane Properties.* 4<sup>th</sup> International Conference on Plastics, Rubber and Composites (ICPRC2017), Phuket, Thailand, May 19<sup>th</sup> -20<sup>th</sup>, 2017.

Nathapong SUKHAWIPAT, Nitinart SAETUNG, Jean-Francois PILARD, Sophie BISTAC, Anuwat SAETUNG. *Study the effects of NCO index on mechanical properties of natural rubber based cationic waterborne polyurethane – New approach to water-based adhesive applications*. International Polymer Conference of Thailand : PCT-8, Bangkok, June 14<sup>th</sup>-15<sup>th</sup>, 2018

#### 3. Publications

- Nathapong SUKHAWIPAT, Nitinart SAETUNG and Anuwat SAETUNG. Synthesis of Novel Cationic Waterborne Polyurethane from Natural Rubber and Its Properties Testing. Key Engineering Materials, ISSN: 1662-9795, Vol. 705, pp 19-23 (doi:10.4028/www.scientific.net/KEM.705.19)
- Sukhawipat, N.; Saetung, N.; Pilard, J.-F.; Bistac, S.; Saetung, A., Synthesis and characterization of novel natural rubber based cationic waterborne polyurethane—Effect of emulsifier and diol class chain extender. J. Appl. Polym. Sci. 2017, 135, 45715 (1 - 12).

#### 4. Awards

Nathapong SUKHAWIPAT, Nitinart SAETUNG and Anuwat SAETUNG, Wanida RAKSANAK. Natural rubber based cationic waterborne polyurethane adhesive. <u>Rubber</u> <u>Innovation Award 2018</u>.