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Development of Biodegradable Polyurethane Foam: the Effect of Chain Extenders on Properties and Biodegradation

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งานวิจัยนี้เป็นการศึกษาเกี่ยวกับการสังเคราะห์โพลิยูรีเทนโฟมที่สามารถย่อยสลายได้ทางชีวะภาพ ซึ่งโพลิยูรีเทนโฟมสามารถเตรียมได้จากปฏิกิริยาพอลิเมอร์ไรเซชั่นแบบเติมระหว่างสารประเภทพอลิออลกับสารประเภทไดไอโซไซยาเนต โดยปกติแล้วคุณสมบัติของโพลิยูรีเทนโฟมจะขึ้นกับสารตั้งต้นที่เลือกมาใช้ ดังนั้นในงานวิจัยนี้ไม่เพียงแต่ศึกษาการปรับปรุงคุณสมบัติของโพลิยูรีเทนโฟมจากความแตกต่างความยาวของสารต่อสายโซ่ แต่ยังศึกษาการย่อยสลายของโพลิยูรีเทนโฟมได้ในธรรมชาติหลังจากการใช้งาน ในการทดลองจึงมีการปรับเปลี่ยนชนิดของสารต่อสายโซ่และสัดส่วนของโพลิออล พอลิคาโพรแลคโตน (PCL) มีคุณสมบัติไม่ชอบน้ำ ถูกใช้เป็นสายโซ่หลักของส่วนอ่อน เนื่องจากพอลิคาโพรแลคโตนมีความเป็นผลึกสูง ในขณะที่พอลิโพรพีลีนไกลคอล (PPG) มีคุณสมบัติชอบน้ำ สามารถเพิ่มอัตราการย่อยสลายได้ และในงานวิจัยนี้จะมุ่งเน้นการศึกษาการใช้สารต่อสายโซ่ในการปรับปรุงคุณสมบัติซึ่งเป็นส่วนแข็ง ได้แก่ เอททีลีนไกลคอล (EG) หนึ่งสี่บิวเทนไดออล (BDO) และ หนึ่งหกเฮกเซนไดออล (HDO) สำหรับผลการวิเคราะห์โครงสร้างด้วยอินฟราเรดสเปคโตรสโคปีพบว่าเกิดพันธะยูรีเทน และฟังก์ชันนอลอื่นในสายโซ่พอลิเมอร์ และไม่พบพีคของไอโซไซยาเนต จึงยืนยันได้ว่าปฏิกิริยาเกิดได้อย่างสมบูรณ์ จากการเพิ่มปริมาณของพอลิโพรพีลีนไกลคอล (PPG) มากขึ้นพบว่า การวิเคราะห์ค่าความแข็งกด และค่ามอดูลัสของยัง การวิเคราะห์ค่าอุณหภูมิคล้ายแก้วของโฟมด้วยดิฟเฟอร์เรนเชียลสแกนนิ่งแคลอรีมิเตอร์ รวมถึงค่าความหนาแน่นของโฟมที่ได้จะมีค่าลดลง แต่ค่าการดูดซับน้ำจะเพิ่มขึ้น และเมื่อความยาวของสารต่อสายโซ่ที่เพิ่มขึ้นจะพบว่า การวิเคราะห์ค่าความแข็งกด ค่ามอดูลัสของยัง และค่าการดูดซับน้ำลดลง ในขณะที่การวิเคราะห์ค่าอุณหภูมิคล้ายแก้วของโฟม และค่าความหนาแน่นของโฟมที่ได้จะเพิ่มมากขึ้น นอกจากนี้ลักษณะของโฟมหลังจากการย่อยสลายทางชีวภาพถูกยืนยันด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (SEM) พบว่าขนาดของรูพรุนเพิ่มมากขึ้น และมีลักษณะที่ไม่สม่ำเสมอเมื่อเพิ่มปริมาณของพอลิโพรพีลีนไกลคอล (PPG) มากขึ้น และสังเคราะห์โฟมด้วยสารต่อสายโซ่หนึ่งหกเฮกเซนไดออล (HDO)

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
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MUTITAPORN PIMDEED: Development of Biodegradable Polyurethane Foam: the Effect of Chain Extenders on Properties and Biodegradation. ADVISOR: PROF. PIYASAN PRASERTHDAM, D.Eng., CO-ADVISOR: NOPPAWAN MOTONG, Ph.D., 72 pp.

This research studied a synthesis of biodegradable polyurethane foam which is usually synthesized by polyaddition polymerization of difunctional isocyanates, polyols and chain extenders. Recently, the properties of PU foam are primarily depended on varying raw material. In this study, there not only synthesized biodegradable polyurethane foams with different chain extender length to improve their properties but also investigated the accelerative degradation after disposed it into environment. The chain extender structure and content ratio of polyols were varied. Hydrophobic material, Polycaprolactone (PCL) is one of widely used as a main building block of soft segment due to its crystallinity. While polypropylene glycol (PPG) as a hydrophilic material, it can enhance the hydrolytic degradation. This work is focus on the use of cheap accessible diols as the chain extender, ethylene glycol (EG), 1,4 butanediol (BDO) and 1,6 hexanediol (HDO). The urethane linkage and other functional group in PU foam was found by the FTIR spectra. With increasing of PPG content, the compressive strength and young's modulus, density, as well as the glass transition temperature (Tg) by DSC of all PU foam become to lower. The longer chain of chain extender showed the results that the compressive strength and young's modulus and water absorption become lower. While the Tg and density become higher. Moreover, the morphologies of cell foam after degradation was confirmed by using SEM, it was showed that the cell size increased and irregular pore characteristic when increasing PPG content up to 10% and synthesizing with HDO chain extenders.

Department:	Chemical Engineering	Student's Signature ....
Field of Study:	Chemical Engineering	Advisor's Signature ....
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CHAPTER I

INTRODUCTIONS

Polyurethanes are a special class of synthetic materials that are widely used in many modern industries of fiber, elastomer, adhesive and coating. And polyurethane foam (PUF) are used as structural, cushioning, insulating, electrical, floating and packaging materials. These polymers made by polyaddition polymerizations of difunctional isocyanates as a hard segment and multifunctional alcohols (polyols) as a soft segment. Urethane linkage –NH–(C=O)–O– that characterized from polyurethane foams is shown in the model reaction **equation 1.1** [1, 2]. As the rule, polyurethanes foam properties and applications are primarily dependent on raw materials and can be modified by variety of additives, such as crosslink-agents, the low molecular weight chain extenders, catalyst, surfactant, blowing agent and reinforcement [3-5].

$$\text{R–NCO} + \text{R'–OH} \longrightarrow \text{R–NH–(C=O)–O–R'} \qquad (1.1)$$

It is know that polymer foam cannot be naturally decomposed, so it caused various pollution to the environment and lifetime of polymer foam was so long up to 280 years before it to decompose [6]. Therefore, biodegradable polymer foam has been necessary developed for friendly environment. Biodegradation of polyurethanes has been studied so far, and principal factors influencing the biodegradability have been proposed [7, 8]. Excellent mechanical properties of biodegradable polyurethane foam can be obtained by introduction of a chain extender to increase the hard segment length. However, for environmental friendly purpose, the suitable chain extender should also accelerate hard segment degradation. From the industry point of view, the biodegradable polyurethane foam that biodegradable time can be controlled is preferred.

On the utilization of tunable properties for the manufacture of biodegradable polyurethane foam, this work is focus on the use of easily and cheap accessible diols as the chain extender for commercial biodegradable polyurethane foam synthesis. Two types of diisocyanate are also chosen, Hexamethylene diisocyanate (HDI) and Methylenediphenyl diisocyanate (MDI). HDI is the well-known and widely used for biodegradable PU foam synthesis [7], while MDI is the in house product from our collaborate Industry (Inac (Thailand) Co., LTD.) [3, 9].

According to most biodegradable polyurethane, Poly(caprolactone)(PCL) is one of the most frequency used building blocks for soft segments of degradable polyurethane [3]. However, the rate of degradation of PCL is rather slow due to its crystallinity and hydrophobicity [10, 11]. It is demonstrated that combined PCL with some hydrophilic materials as the soft segment enhance the hydrolytic degradation. Poly(ethylene glycol) (PEG) based polyurethanes were weak and tacky. On the other hand, combined PEG with PCL shown remarkably improved properties. PEG enhances degradation, while PCL provides well mechanical properties [10, 11]. In this study, inexpensive polypropylene glycol (PPG) is chosen as the hydrophilic materials because it has good attractive properties in common with PEG. The molar ratios between hydrophilic (PPG) and hydrophobic (PCL) components will be 0:100, 30:70, 40:60, 50:50, 60:40, 70:30, respectively.

The aims of this research are to synthesis biodegradable polyurethane foam and to investigate the qualities in term of mechanical behavior of these new materials. The effects of molar ratios between hydrophilic and hydrophobic components in soft segments will also be investigated.

1.1 Objectives

The objectives of this work are as follow:

1.1.1 To synthesis biodegradable polyurethane foam with different chain extenders that are ethylene glycol (EG), 1,4-butandiols (BDO) and 1,6-Hexandiols (HDO).

1.1.2 To study the effect of chain extenders on the physical, mechanical thermal and biodegradability properties of polyurethane foam.

1.2 Research scope

The scopes in this work are to synthesis polyurethane foam with different chain extenders two types of polyols as a soft segment and two types of isocyanate. To compare the influence of the use of cheap and accessible diols as the chain extender for commercial biodegradable polyurethane foam on the mechanical and degradability properties. The scopes are reported as follows.

1.2.1 Biodegradable polyurethane foams will be synthesized with commercial material: as followed that: polypropylene glycol (PPG) and polycaprolactone (PCL) as polyols and ethylene glycol (EG), 1,4-butandiols (BDO) and 1,6-Hexandiols (HDO) as chain extender.

1.2.2 The molar ratio of polyols that are polypropylene glycol (PPG) and polycaprolactone (PCL) will be experimented with 0:100 and 10:90, respectively.

1.2.3 The effect of different chain extenders, EG, BDO and HDO, will be studied to compare on the physical, mechanical thermal and biodegradability properties of polyurethane foam. The differences of diisocyanate structure, aliphatic (HDI) and aromatic (MDI), were also compared.

1.2.4 Biodegradation system will be investigated by soil burial method according to previous report.

1.3 Benefit

1.3.1 To understand the structure of polyurethane foam derived from the several commercial materials synthesis with same condition and procedure.

1.3.2 Improvable properties of polyurethane foam can be managed by usable new material or adapted ratio of materials.

1.3.3 The appropriate condition bring about biodegradable polyurethane foam with desired properties.

1.4 Research Methodology

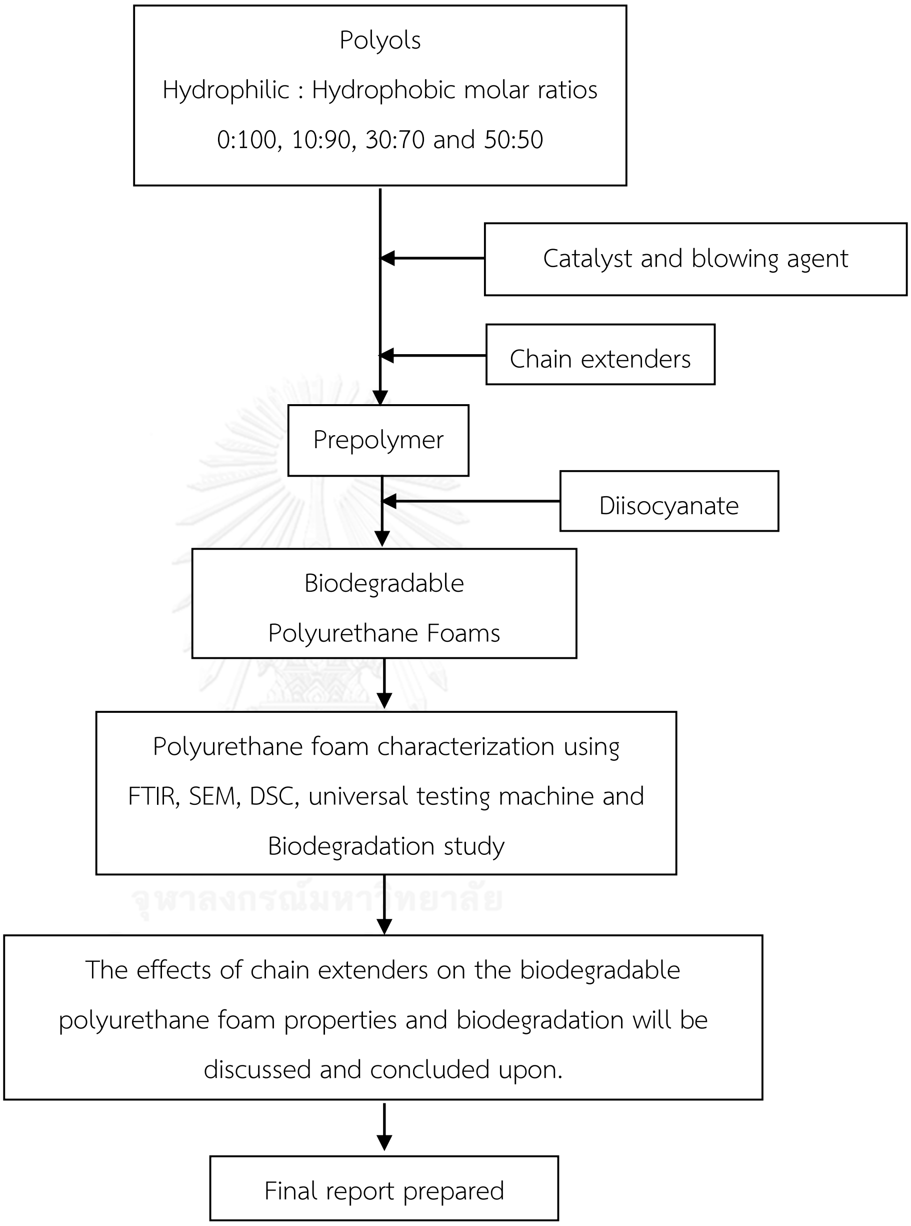


Figure 1.1 Flow diagram research methodology

1.5 Research plant

Details	2013		2014												2015					
	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6
Literature review	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨					
Plane project		▨	▨	▨	▨	▨							▨	▨	▨					
Propose proposal																▨				
Synthesis of PU foams			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			
Characterization of PU foams								▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
Test biodegradation																	▨	▨	▨	
Result and discussion																		▨	▨	
Conclusion																		▨	▨	
Defense																				▨

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Biodegradable Polyurethane Foams

Polyurethane Foams that usually referred to as PUF are called plastic foams, cellular plastics, or polymeric foams [2]. This cellular plastic is wildly used in the modern industries or automotive industries. It has been various utilized in wide range applications such as cushioning, insulation for roof or refrigerator, structure in furniture, electrical, floating and packaging materials [1, 12]. These PUF are synthesized with polyaddition polymerization reaction. The PUF structures have consisted of two sections. The biodegradable soft segments as a polyols provide elastomer, and the hard segment as diisocyanate and chain extender provide mechanical properties. The classified polyurethane foams with polyols component and elastic modulus are shown in **table 2.1** [2]. However, the resulting of PUF properties can be adjusted by different raw commercial material such as isocyanate, polyols and chain extender.

Table 2.1 Classification of Urethane Foams [2].

Polyol	Rigid Foam	Semirigid Foam	Flexible Foam
OH No. (mg KOH/g)	350-560	100-200	5.6-70
OH Equivalent (56,110/OH No.)	160-100	560-280	10,000-800
Functionality	3.0-8.0	3.0-3.5	2.0-3.1
Elastic Modulus at 23°C			
MPa	>700	700-70	<70
lb/in^2	>100,000	100,000-10,000	<10,000

The most of currently biodegradable polymer have two major application, the first is as biomedical polymers and the other is as ecological polymers that keep the clean earth environments [13]. Generally, the most of polyurethane foams in modern industrial can not be degraded after disposal because of raw material that was used, results in negative effect on environments. Although, the degradation of PU foam can be improved with suitable soft segment. Polyether-based PU foam, such as glycerine, polyethylene glycol (PEG) and polypropylene glycol (PPG), have hydroxyl reaction group which it provide the greater foam properties [14, 15]. Polyether-based PU foam are better resilience and resistant to hydrolysis than polyester-based foams [2, 16, 17]. While biodegradable polyester-based, comprise of polycaprolactone (PCL), polylactic acid (PLA) [13-15, 18] and diethylene glycol (DEG) [16] has been provided to be biodegradable foam which the degradation process are occurred with ester bond in their polymer backbone [19].

Jianhua W. and co-workers [18] studied different polymer chains, such as polyethylene glycol (PEG), polycaprolactone (PCL), polylactic acid (PLA) and polytetramethylene oxide (PTMG), with different molecular structure and molar ratio of polyols on degradable polyurethane foams (PUF). A series of PU foam sample with mixed PEG/PCL and PLA/PCL as soft segment was synthesized. The PU foam sample was characterized by tensile and compressive testing, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The results revealed that Tg and storage modulus (E) decrease by different polymer chain sequence: PLA>PCL>PEG>PTMG. For the degradation of polymer in soil, the degradation rate increase with increasing content of PEG chain.

2.2 Raw Materials

Polyurethane mainly included three raw material reactants: polyol, diisocyanate, and chain extender. The final properties of the polyurethane are dependent on the chemical and physical nature of these raw materials.

2.2.1 Polyols

The polyols for urethane foams are liquid oligomers or polymeric compounds with at least two hydroxyl groups which are usually a polyether (with a repeating structure of -R-O-R'-) or a polyester (with repeating structure of -R-COO-R'-) [20]. Polyols can react with isocyanate during the foaming process to form flexible PU foam as showed in **figure 2.1**. At room temperature, polyols can be liquid or wax-like phase. Generally, in the synthesis of foam, product properties depend on their molecular weight and functionality of each polyols as showed in **table 2.2** [21]. The flexible of foams can be increased with increasing polymer chain length and having functionality of hydroxyl from two to three. Therefore, polyols is one of all raw material that can affect to properties of foam product and various application in many field.

Table 2.2 The foam product properties with polyols types.

Properties	Flexible foam	Rigid foam
Molecular Weight (g/mol)	1000-6500	150-1000
Functionality	2.0-3.0	2.5-8.0
Hydroxyl value (mgKOH/g)	28-160	250-1000

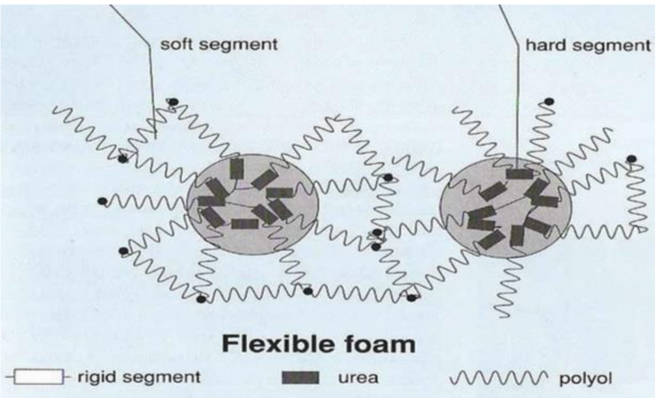


Figure 2.1 Morphology of TPU and Flexible polyurethane foam [22]

2.2.1.1 Polycaprolactone (PCL)

PCL is used mainly in thermoplastic polyurethane and well known as a biodegradable aliphatic polyester with low melting point at around 60°C and a glass transition temperature about -60°C. PCL is high hydrophobicity, high degree of crystallization and a long hydrolytic bulk degradation times up to 2~4 years which it is proper to be a disposable application or medical field [23]. PCL is one of biodegradable polyols that can be degraded by microorganisms which it produces enzymes. Ikada Y. and Tsuji H. [13] showed the results that PCL can enzymatically degraded in earth environments, but non-enzymatically in the body. Moreover, especially polyesters, it can be degraded by taking places through hydrolysis and then molecular chain was fragmented. PCL is a non-toxic aliphatic polyester with compatibility, permeability and capacity of blending with various polymers [24]. In the majority of PCL polyols is often used in the manufacture of resins for surface coatings, adhesives for shoes and synthetic leather, fabrics and especially polyurethane industrial [25]. These chemical structure of polycaprolactone (PCL) polyols was shown in **figure 2.2.**

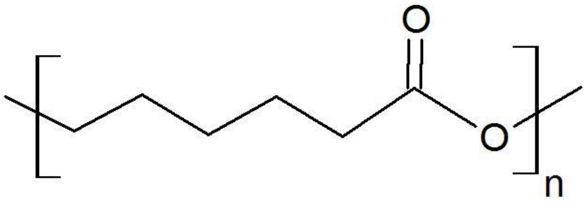
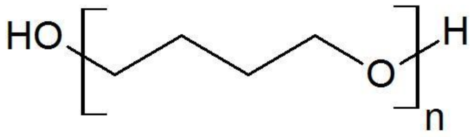


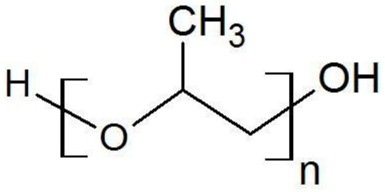
Figure 2.2 The structure of polycaprolactone (PCL)

2.2.1.2 Polypropylene glycol (PPG)

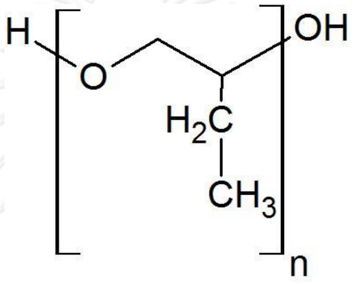
PPG is a small organic with a hydroxyl group in the end of chain and ether bond in all repeating unit that is a polyether polyols. It was mainly used to produce for flexible polyurethane foams, surfactant and wetting agent. Like the closely related compound with polyethylene glycol (PEG), but PPG is less toxic than PEG. PPG is a hydrophilic polymer which solubility in water will lessen with increasing molecular weight. The hydrophilic PPG segment can enhance the degradation. It is readily biodegraded in water or soil [26]. The chemical structure of common polyether polyols was shown in **figure 2.3.**



Polytetramethylene etherglycol (PTMEG)



Polypropylene glycol (PPG)



Polybutylene oxide glycol (PBO)

Figure 2.3 The chemical structure of common polyether polyols.

2.2.2 Isocyanate

Isocyanate is commercially used in the polyurethane industrials, have one or more the functional group with R-NCO formulation. Diisocyanate that has two isocyanate groups was divided into two types that consist of aromatic such as toluene diisocyanate (TDI) as well as methylene diphenyl diisocyanate (MDI) and aliphatic isocyanate such as hexamethylene diisocyanate (HDI). For aromatic isocyanate have been widely used for preparation based-foam because aliphatic is slowly react with hydroxyl groups [2]. Diisocyanate can react with alcohol group at end-chain polyols or chain extender to form urethane linkage. The strong intermolecular interactions of urethane linkage, the forming reaction between isocyanate and chain extender are more rigid than polyols that was called hard segment [20].

2.2.2.1 Methylene diphenyl diisocyanate (MDI)

MDI that is a reactive liquid material that widely used in a markets application such as automotive, furniture, construction, appliances, insulation, and recreation. Reactions of MDI functionality (R-NCO) with polyol (-OH) functional materials produce polyurethane compounds. Their chemical structures are shown in figure 2.4. MDI is available for three types that are: Polymeric MDI (PMDI), Monomeric MDI (MMDI) and Modified MDI. Polymeric MDI is used for rigid and semi-rigid polyurethane foams that is insulation for construction or refrigeration industries. It consist of a mixture of 4, 4’-isomer MDI and other 2, 4’- and 2, 2’-isomers MDI. As for MMDI is used in a multitude of thermoplastic and cast elastomer applications. The reaction of MDI depends on temperature, at above 50°C, the reaction is gradually fast and can be violent, while at below 50°C, the reaction is slow.

Kwon O.J. and co-worker [27] varied NCO/OH molecular ratio and isocyanate type that are TDI, MDI and HDI. The results showed that TDI and MDI aromatic isocyanate gave the higher modulus and compressive than HDI aliphatic isocayanate due to aromatic group of hard segment. On the other hand, HDI aliphatic isocayanate was the highest the absorbency for organic solvent.

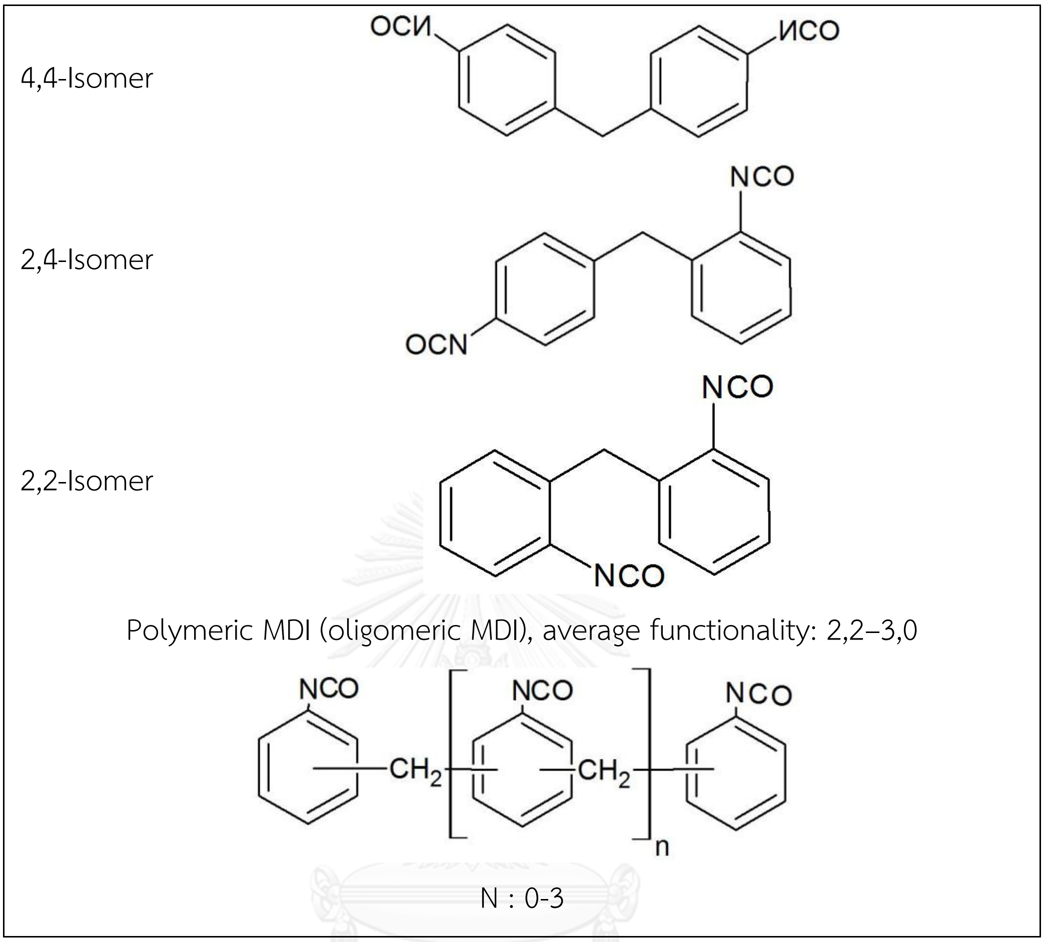
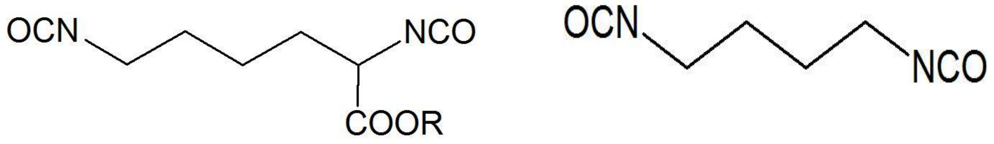


Figure 2.4 Chemical structure of MDI [2]

2.2.2.2 Hexamethylene diisocyanate (HDI).

Hexamethylene diisocyanate (HDI) in figure 2.5 that is an organic compound that have been used in biodegradable polyurethane formulations [28]. HDI has two isocyanate groups (R-NCO) of equal reactivity. It is an aliphatic diisocyanate that has been used in special applications, such as enamel coatings and degradation from ultraviolet light [29]. The glass transition temperature (Tg) of HDI-based PU foam are around -50°C [18]. HDI is the most widely investigated diisocyanate in formulating biodegradable polyurethanes. HDI can degraded in to the soil and water, it will reacted very quickly with water or moisture in soil to form carbon dioxide (CO_2) and urea [1, 12, 14]. HDI is symmetrical molecular structure leads to strong intermolecular attractions through hydrogen bonding resulting in elastomers with high tensile strength that is over 60 MPa and elongation of 580% [28].



Ethyl or Methyl 2,6-diisocyanatohexanoate (R=Ethyl, Methyl)

1,4-Diisocyanatobutane

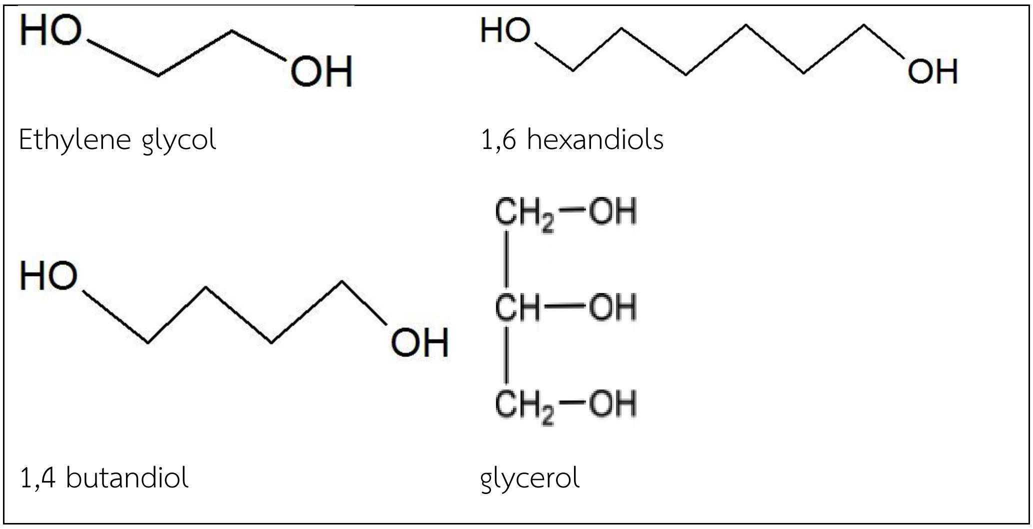
1,6-Diisocyanatohexane

2,2,4-Trimethylhexamethylenediisocyanate

Figure 2.5 Diisocyanates used in biodegradable polyurethane formulations [28]

2.2.3 Chain extender

Chain extenders are low molecular weight diols or triols and amines terminated compound. The reaction between polyols and diisocyanate produces a soft gum rubber with poor mechanical strength. The chain extender was added to improve properties due to the fact that play an important role for producing foams of high flexibility by extended sequence in the polymer chain from alternating chain extenders and diisocyanates. These extended sequences, or hard segments, act both as filler particles and physical crosslink sites to increase mechanical strength [22]. There is common Chain extenders for the synthesis polyurethanes that showed in **figure 2.6.**



Ethylene glycol

1,6 hexandiols

1,4 butandiol

glycerol

Figure 2.6 Chain extenders commonly used for the synthesis of polyurethane foam

2.2.4 Catalyst

Catalyst play a very important role in PU foam production to the reaction between isocyanate and polyols. Catalyst mainly effect on the final PU foam properties. A typical catalyst can be classified into two categories: a tertiary amine, include gelling catalysts, such as tetramethyl butanediamine (TMBDA) and blowing catalysts, such as bis-(2-dimethylaminoethyl)ether and N-ethylmorpholine. For an organo-metallic, compounds, consist of mercury, lead, tin (dibutyltin dilaurate), bismuth (bismuth octanoate) and zinc, especially tin compounds, the important one being stannous octoate. Catalyst mixtures are generally necessary to control the balance of the polymerization and the gas generation reactions that both are exothermic reactions. For flexible urethane foam preparation, two kinds of reactions take place. Tin catalyst promote for the polymerization or gelling reaction, between isocyanate and polyols to form polyurethane. While, amine catalyst promote for the blowing reaction, the isocyanate reacts with water to form polyurea and carbon dioxide. The greater of gelling reaction is major importance production to be a close cell foams and shrinkage. On the other hand, the greater of blowing reaction that too much gas was generated by the reaction will burst thought the weak cell wall and produce an open cell before the polymer is strong enough to contain it. So, internal foam will splits or collapse [21, 22].

2.2.5 Blowing agent

Gas generation is an essential part of plastic foam formation. In preparing polyurethane foams, two kinds of gas generation methods are used: chemical gas generation and physical gas generation, as well as combinations thereof. Chemical blowing agents are chemical compounds that react with isocyanate groups to generate carbon dioxide gas. A typical chemical blowing agent is water that produce CO_2 gas by reaction with an isocyanate. This reaction is exothermic and results in the formation of active urea sites which form crosslinks via hydrogen bonding. And Physical blowing agents, Such as C_5-hydrocarbons, azeotropes with or without halogen and liquefied CO_2, are liquids phase that having low boiling points and non-reactivity to isocyanate groups [2, 21].

2.3 Properties of polyurethane foams

Polyurethane foam has two types, flexible polyurethane foam and rigid polyurethane foam. It is the most adaptable material and well-known to use in wildly range of application from baby toys to airplane wings, and can be adjusted for other application. PUF can be separated into two categories that are as follow:

2.3.1 Flexible polyurethane foam

Flexible polyurethane foam (FPUF) is created by multipolyol that can produce urethane linkage: –NH–(C=O)–O– [2]and urea linkage: –NH–(C=O)–NH– [21] with reaction of isocyanate (R-NCO) [16] FPUF has a broad range of load-bearing capacity and resiliency is the most significant proper mechanical properties used in comfortable cushioning, structure furniture, packaging and wrapping apparel.

2.3.2 Rigid polyurethane foam

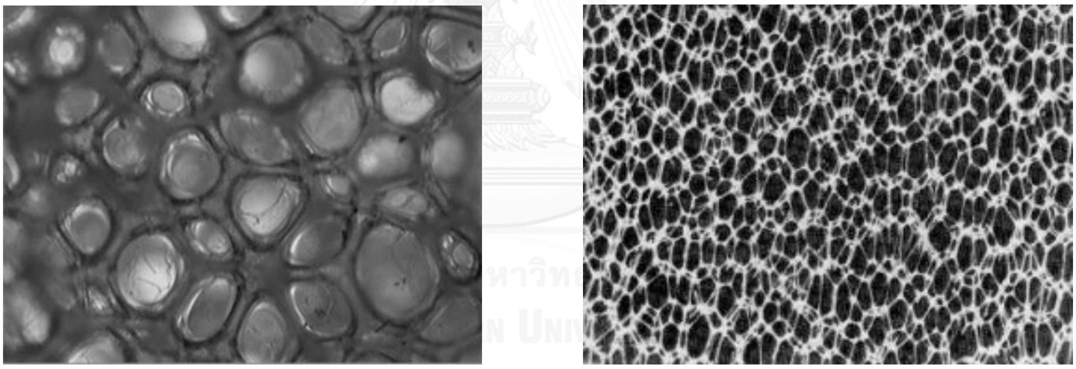
Rigid polyurethane foams consist of a highly crosslinking percent with a closed cells foam structure. It is applied in many kind of material as steel, wood, thermosetting resins, foam and factory-made thermal insulation such as refrigerators, freezers, refrigerated trucks, refrigerated containers, building construction, chemical and petro-chemical plants [2]. These foam are prepared at ambient temperatures without heating. The density of foams that used for thermal insulation normally ranges between 30 kg/m^3 and 45 kg/m^3. For special applications such as extreme mechanical loads, the density of the rigid polyurethane foam (PUR/PIR) can be increased to 3000 kg/m^3 [30]. Moreover, rigid polyurethane foams are resistant to petroleum, oils and other nonpolar solvents [2].

2.3.3 Closed Cell foams

The gas bubble is dispersed with separated bubble phase in the polymer matrix. Gas bubble can be transported by high pressure diffusion pass cell wall of the PUF that bring about to be closed cell of PUFs which occur during the polymer matrix expansion [21]. Kim S. and Kim B. [31] had described that the urethane linkage is produced by reaction between isocyanate and polyols discharge the heat of reaction. After that, the gas bubble is formed and trapped into closed cell of PUF. The most of low thermal conductivity of PUF is ability of with small closed cell structure. So, the closes cell foams effect to application categories, especially for insulation foams because number of cell foam or cell size is necessary to this application properties. The close cell foam shown in **figure 2.7 (a).**

2.3.4 Open Cell foams

The open cell foams have voids gas in their wall that incorporation of solid and gas phase was proceeded. So, the gas can able to flow thought the polymer matrix with some driving force. It was formed in the atmosphere condition. However, in open cell foam, the gases do not exist due to more holes in the cell foam structure which it is released to the air during foam expansion. The morphologies of cells foam do not always have completely closed cell or open cells. Then, foams combine with two types of structure cells, however, characteristic of cells foam depend on raw material that is used in the synthesis [21]. The main physical difference between the two types of cells that is open cell and closed cell as showed in **figure 2.7 (b).**



a) Closed gas structural element b) Open gas structural element

Figure 2.7 Schematic representation of the gas structural element [22, 27]

2.4 Biodegradation

The degradation of biodegradable polymer is a specific type of polymer which chemical bonding was break down into result in natural byproducts gases (CO_2, N_2 or CH_4), water, biomass, and inorganic salts by biological activity (biotic degradation) and mainly microorganism enzymatic action [32]. The biodegradable polymer are found both from natural and synthetic material and largely consist of ester, amide, and ether functional groups. The biodegradation occur for two step, at first, the fragmentation of the high molecular weight polymers was took place to become low molecular weight mass by either abiotic reactions such as oxidation, photo-degradation or hydrolysis or biotic reactions such as degradations by microorganisms. Second, the bio assimilation of the polymer was fragmented by microorganisms and mineralization which an organic substance becomes impregnated by inorganic substances. Which the microorganism have more important to biodegradation. A few research reported that Polyurethane-degrading microorganisms consisted of *Fusarium solani, Curvularia senegalensis, Aureobasidium pullulans and Cladosporidium* sp. were also isolated and *C. senegalensis* can produced the esterase enzyme. Also, *P. chlororaphis* was found to produce a lipase enzyme that responsible for the polyurethane degradation [33]. Moreover, *Actinomyces calcoaceticus* is primary as a terrestrial or aquatic bacteria (soil bacteria) [34]. As for the previous mentioned bacteria type revealed that the soils was plentiful capability for using biodegradation. The biodegradation depends not only on the chemical structure of raw material but also the environment condition [35]. However, the biodegradability will decreases with increasing that parameter such as hydrophobicity, molecular weights and the crystallinity or the size of crystalline domains [32].

Biodegradation of the biodegradable polymer was detected by recording weight loss, molecular weights change, thermal stability change and mechanical properties. The biodegradation testing of plastics can carried out according to standard testing methods such as ISO (International Organization for Standardization), ASTM (American Society for the Testing of Materials), JIS (Japanese Industrial Standards) and DIN (Deutsches Institut für Normung or German Institute for Standardization) [36]. Recently, main detail for all standard tesing is similar, but some detail such as method testing, composition and properties are different.

Lili L., Margaret F. and Kristie J.B. [37] showed that the biodegradabilities of fabrics samples with three levels of characterization and a polyester fabric samples in controlled laboratory condition were investigated according to ASTM D5988-03 methods in natural soils for 3 mounts. The carbon dioxide produced and the weight losses were measured after biodegradation. In soil testing, the polyester fabric showed a slight degradation when compared with fabrics that remained intact under both laboratory conditions. While, the cotton fabric with softener had an accelerated degradation rate, and the cotton fabric with resin showed a relatively slow degradation rate.

In this work, the biodegradation of biodegradable PU foam with varying type of chain extenders were investigated with soil burial methods as followed by **table 2.3** and soil preparing according to ASTM D5988-03 standard method: Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting.

Table 2.3 soil burial methods.

Author	Specimen (mm^3)	Depth (cm)	Temperature (°C)	Moistures	Duration (days)	References
Jianhua W., et al.	40x10x4	15-20	-	-	90-120	[18]
Urgun-Demirtas M., et al.	10.2x3.5x1.8	10	Room temp.	-	75	[3]
Zhang H., et al.	50x50x10	10	25-35	30%	365	[38]
Gouda M.K., et al.	10x10*	-	30	60%	60	[39]
Obasi H.C., et al.	-	10	Room temp.	-	90	[40]

*Polymer film

CHAPTER III

EXPERIMENTAL

3.1 Chemical

The chemical used in this research are shown in **table 3.1**.

Table 3.1 Detail of chemical in this experiment.

Number	Chemical	Trade name	Company
1	1,6-Diisocyanatohexane (HDI)	Hexamethylene diisocyanate	S.M. chemical supplies Co., Ltd.
2	Polymeric 4,4’-Methylenediphenyl Diisocyanate (MDI)	Suprasec 6564	Inoac (Thailand) Co., Ltd.
3	Polypropylene Glycol (PPG)	Polypropylene Glycol	S.M. chemical supplies Co., Ltd.
4	Polycaprolactone (PCL)	Polycaprolactone	S.M. chemical supplies Co., Ltd.
5	Ethylene glycol (EG)	Ethylene Glycol	-
6	1,4-Butanediol (BDO)	1,4-Butanediol	-
7	1,6-Hexanediol (HDO)	1,6-Hexanediol	-
8	Dibutyltin dilaurate (DBTDL)	Dibutyltin dilaurate	S.M. chemical supplies Co., Ltd.
9	Distilled water	Distilled water	-

3.2 Instruments

Table 3.2 shows the instruments that were used in this research.

Table 3.2 Instrument for this experiment.

Number	Instruments	Scales
1	Cup test	6 oz.
2	thermometer	0-100 °C
3	weighing apparatus	-
4	Timer	-
5	Drill equipment	0-10,000 rpm
6	Droplet	-
7	Hot plate	-
8	Micropipette	200 µm
9	Plastic zip	-

3.3 Biodegradable polyurethane foam polymerization

3.3.1 Biodegradable polyurethane foam synthesis

1) Biodegradable polyurethane foam (PUF) was synthesized by mixed all ingredients in plastics cup by drill equipment. Firstly, Pre-mix the hydrophilic and hydrophobic polyols components, PPG and PCL at the molar ratios 0:100, 10:90, 30:70 and 50:50. The nomenclature and the compositions of the ingredients of the PU foam samples Made from different reactant as shown in **table 3.3.**

2) Then chain extender, catalyst and blowing agent were added into previous ingredients.and mixed together for approximately 1 min with speed 2000 rpm. Lastly, isocyanate was added into the mixture, vigorously stirred for 10 s.

3) After that the mixture was released to rise up freely in plastic cups at room temperature.

Table 3.3 The nomenclature and the compositions of the ingredients of the PU foam samples Made from different reactant.

PU foam sample[a]	PPG (g)	PCL (g)	Chain extender (g)	DBTDL (g)	Water (g)	Isocyanate (g)	-NCO/-OH molar ratio
HEG0	0	95	5	1	1	30.79	1
HEG10	9.5	85.5	5	1	1	30.79	1
HEG30	28.5	66.5	5	1	1	30.79	1
HBDO0	0	95	5	1	1	26.57	1
HBDO10	9.5	85.5	5	1	1	26.57	1
HBDO30	28.5	66.5	5	1	1	26.57	1
HHDO0	0	95	5	1	1	24.36	1
HHDO10	9.5	85.5	5	1	1	24.36	1
HHDO30	28.5	66.5	5	1	1	24.36	1
MEG0	0	95	5	1	1	68.65	1
MEG10	9.5	85.5	5	1	1	68.65	1
MEG30	28.5	66.5	5	1	1	68.65	1
MBDO0	0	95	5	1	1	59.24	1
MBDO10	9.5	85.5	5	1	1	59.24	1
MBDO30	28.5	66.5	5	1	1	59.24	1
MHDO0	0	95	5	1	1	54.30	1
MHDO10	9.5	85.5	5	1	1	54.30	1
MHDO30	28.5	66.5	5	1	1	54.30	1

[a] Sample code (X-YYY-Z): X is kind of diisocyanate (H is HDI and M is MDI), YYY are three kind of chain extenders and Z is percent PPG content (0, 10 and 30). For example, HEG10 means the sample that was prepared using HDI as diisocyanate, EG as a chain extenders and 10% of PPG content.

4) The synthesis of polyurethane foam was varied including with variation of three different types of chain extender, Ethylene glycol (EG), 1,4-Butanediol (BDO) and 1,6-Hexanediol (HDO).

5) Polyurethane foam was cured for 24 hours at room temperature.

6) Obtained polyurethane foam was cut into proper size for any characterization.

7) Polyurethane foams was characterized by Fourier Transform Infrared Spectroscopy (FTIR) to confirm the molecular structure evidence of urethane linkage. The foams density was also detected according to ASTM D 3874.

8) The morphology of cell structure such as number of open cell and closed cell foam showed that characteristic of foam and thermal properties or the amount of heat required in each sample and glass transition temperature (Tg) was detected by SEM and DSC, respectively. The density and water absorbency was also measured according to ASTM D 3874 and ASTM F726, respectively.

9) The mechanical properties was studied with using a universal testing machine for compressive strength of foam according to ASTM D 3874.

10) The appropriate polyurethane foam was selected for biodegradation study based on properties result. Biodegradation study was evaluated with soil burial method which bacteria are operable [5], recording the weight loss of the polyurethane foam were reported to investigate degradation.

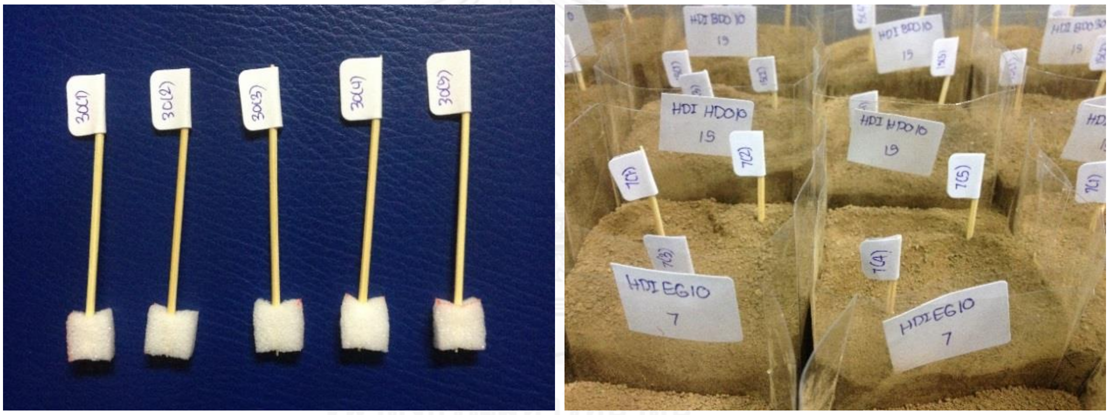
3.3.2 Biodegradation of Biodegradable polyurethane foam

3.3.2.1 Soil burial experiments

The soil in experiments was prepared with simulate condition control, 50-55% relative humidity and pH that have had range from 6.0 to 8.0 in laboratory closed-containers with accelerative temperature. The soil burial method was operated as described in the previous literature reviews [4, 18, 23, 40, 41].

1. First, the obtained soil was sieved to keep the particle size less than 2-mm according to ASTM D 5988. The soil preparing was weighted and added in each plastic bags about 268 g. The Equilibrium Relative Humidity (ERH) that is an equilibrium humidity in close system was controlled by saturated salt solution (NaCl solution) in closed-container.

2. Polyurethane foam samples were buried for 30 days in plastic bag. Specimen samples were cut into 1x1x0.5 cm^3 for five replicate of each foam conditions [42]. After that the obtained PU foams were placed in plastic bag as shown in **figure 3.1**.



(a) (b)

Figure 3.1 The preparing of polyurethane foam (a) before (b) after biodegradation in first day with soil burial.

3. Then, add the water into the soil and saturated salt solution into bottom of container for control the humidity. Lastly, the from the UV light bulb for 50 watts was used to increase the temperature in order to accelerative degradation rates, as shown in **figure 3.2**.


(a) (b)

Figure 3.2 The sample foam (a) after adding the samples and (b) during biodegradation process.

At the end of a period of time, five replicate of each foam was picked up and washed the soil off with distilled water and dry at 70°C overnight [40]. The weight loss can be calculated by **equation 2.1** [38, 43].

$$\text{Weight loss (\%)} = \frac{W_o - W_s}{W_o} \times 100 \qquad (2.1)$$

Where W_O is the weight of polyurethane foam before soil treated and W_S is the weight of polyurethane foam after soil treated. The weight loss values was averages with five samples [44].

3.3.2.2 The soil characteristic and properties [45]

The soil of Kamphaeng Saen Series: Ks was chosen for using in this soil burial experiment. Because the characteristic of this soil is a fine-silty, mixed and semi-active, it is plentiful organic matter. Moreover, the Kamphaeng Saen soil is a loose and sable soil which the water can be well permeated into deep soil. The soil pH values are from the weak acidity range to being neutral (pH 6.0-7.0). The overall properties of Kamphaeng Saen soil are shown in **table 3.4.**

Table 3.4 The overall properties of Kamphaeng Saen soil series.

Depth (cm)	**pH in water (1:1)**	**organic matter**	**Phosphorus (mg/kg)**	**Potassium (mg/kg)**	**Exchange capacity and cations**
0-20	7.3	low	825	495	low
20-36	7.3	low	295	429	low
36-69	7.6	low	495	418	low
69-93	7.6	low	470	264	low

3.4 Characterization Instruments

3.4.1 Fourier transforms infrared (FTIR) spectroscopy [7]

In **figure 3.3**, FTIR spectroscopy was used for characterize the molecular level of functional groups in polymer chain. The functional groups of polyurethane foams, such as hydroxyl group, amine group and carbonyl group was investigated. FTIR spectroscopy is simple to carry out process, fast and precise for produced result. It demands a very small sample amount. The reflectance and transmission are important methods that was used to detect sample functional. FTIR spectroscopy were recorded with Nicolet 6700 FTIR spectrometer that the sample was scanned from 4000 to 400 cm^{-1} wavenumber range.

Figure 3.3 Fourier transforms infrared spectroscopy (FTIR) [46]

3.4.2 Differential scanning calorimetry (DSC) [7]

In **figure 3.4**, Differential scanning calorimetry (DSC) is a technique to quantitative thermal analysis which is usually fast, sensitive and computerized, and using a very small sample. All samples were heated twice. In the first scan, samples were heated and then cooled to remove all impurities and ordered the structure. In the second scan, samples were heated from -100°C to 250°C with the heating rate 20°C/min. The glass transition temperature (Tg) were measured and reported.

Figure 3.4 Differential scanning calorimetry (DSC) [47]

3.4.3 Universal Testing Machine

The compressive strength of PUF can be characterized by using universal testing machine shown in **figure 3.5**. According to ASTM D 3574, Samples were cut into 1 cm by 1 cm by 1 cm thick for compressive testing. The crosshead speed was used at 10 mm/min and recorded value at 50% deformation with load 30 kN [27].

Figure 3.5 Universal Testing Machine [48]

3.4.4 Scanning Electron Microscopy (SEM)

SEM as shown in **figure 3.6** is an electron microscope type that analyze continues to be the best method for estimate structure of sample, especially to identify characteristic surface. SEM helps to characterize for morphology of cell foam, pore size and pore size distribution of PU foam. It is a useful tool to produce three-dimensional images.

Figure 3.6 Scanning Electron Microscopy (SEM) [49]

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The structure of polyurethane foam

From **figure 4.1** and **figure 4.2** shows FTIR spectrum of polyurethane foam different chain extenders and various PPG content, it confirms urethane linkage and other functional group in polyurethane foam with the reaction between NCO group from isocyanate and OH group from polyols. FTIR spectrum scanned from 4000 to 400 cm^{-1} wavenumber range. A band of carbonyl (hydrogen bond C=O stretching in urethane) at 1723-1725 cm^{-1}, 1530-1535 cm^{-1} (-NH bending in urethane) and 1220, 1157, 1097 cm^{-1} (C-O-C band in PPG) were detected. The peak of CH_2 stretching at 2933 cm^{-1} and CH stretching at 2863 cm^{-1} related the chain hydrocarbon length of polyols, the FTIR spectrum showed that there is no difference with chain extender length in wave number position, as shown in **figure 4.1**. Although it can be observed

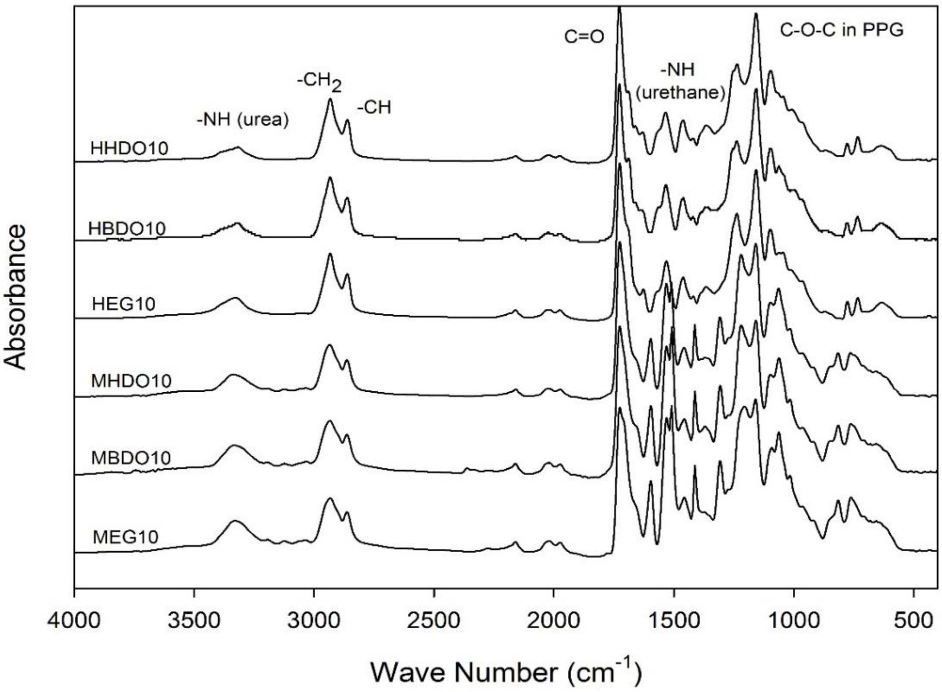


Figure 4.1 FTIR spectroscopy of polyurethane foam with different chain extenders.

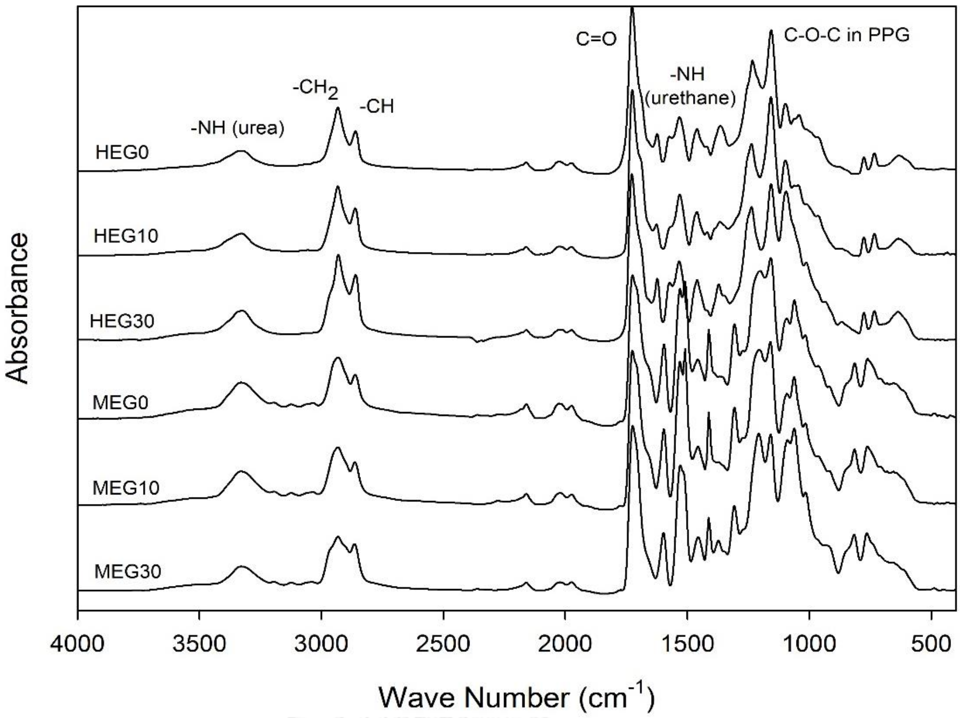


Figure 4.2 FTIR spectroscopy of Polyurethane foam with various PPG content.

high absorbance in y-axis when the high content of PPG was used because the molecular vibration was occurred more when increasing the aliphatic length of polymer, as shown in **figure 4.2**. The reaction between isocyanate and water, both urethane and urea can be generated. The -NH stretching vibration in urea was detected at 3300-3400 cm^{-1}. And the peak of NCO group of isocyanate at 2200-2300 cm^{-1} was still appeared.

The strength of hydrogen bonding was perceived from –NH peak position which it trend to shift to lower frequency due to chain length of ethylene glycol (EG) which is shorter than others (BDO and HDO). So, because of a hard segment, the vibration of the bond between molecules of polymer chain would be less presented.

The band located at 1509 cm^{-1} is –NH deformation band of isocyanurate, it was formed with reaction between isocyanate and urethane groups [50]. The peak of

C-O-C ester bending in PPG chain signal at 1220, 1157 and 1097 cm^{-1}, especially at 1097 cm^{-1} wavenumber would be occurred at high absorbance level when PPG content was increase. Because of the higher molecular vibration in their chain was occurred with the increasing of polymer aliphatic length. The main characteristic urethane bands are summarized in **table 4.1.**

Table 4.1 Main characteristic urethane bands.

Bands (cm^{-1})	Attributions
3320	-NH Stretching vibrations
2933	-CH Stretching vibrations
2863	$O\text{-}CH_2$ Stretching vibrations
2200-2300	-NCO Stretching vibrations
1725	C=O Stretching vibrations
1532	-NH bending in urethane
1220, 1157 and 1097	C-O-C ester bending

4.2 Thermal analysis of polyurethane foams

4.2.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which it could provide the information on the glass transition temperature (Tg) with scan rate 20 °C/min and the first scan. Because the first scan showed that there was no clearly the peak of Tg so in the second scan was no observed definitely. The DSC curve of polyurethane foams as a function of different chain extender and PPG content was reported in **figure 4.3**, **figure 4.4** and **figure 4.5** which T_gs results are summarized in **table 4.2**. The melting point results in an endothermic peak in the DSC curve which the loss of endothermic peaks indicated that the PU foam are no crystalline regions [51]. The glass transition temperature (Tg) of these PU foam decreased from -54 to -58 °C and -20 to -32 °C of PU foam with HDI isocyanate and MDI isocyanate, respectively. It can observed that the aromatic bond in MDI chain affecting the decrease of Tg. As the result shown that the obtained PU foam from aliphatic chain HDI isocyanate have lower Tg than MDI isocyanate. The high content of PPG affecting the slightly decrease of Tg because of the degree of branching leads to more chain ends and large amount of free volume.

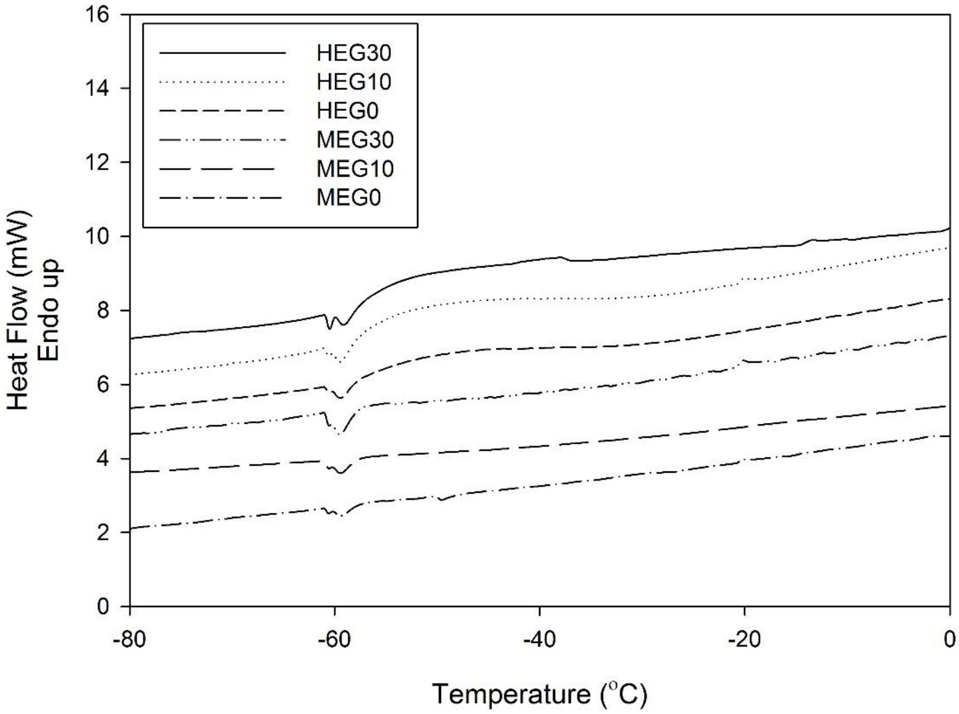


Figure 4.3 DSC curves of polyurethane foams obtained on the first scans: PUF with chain extender (EG) scan rate 20 °C/min and the temperature ranges from -100 to 150 °C.

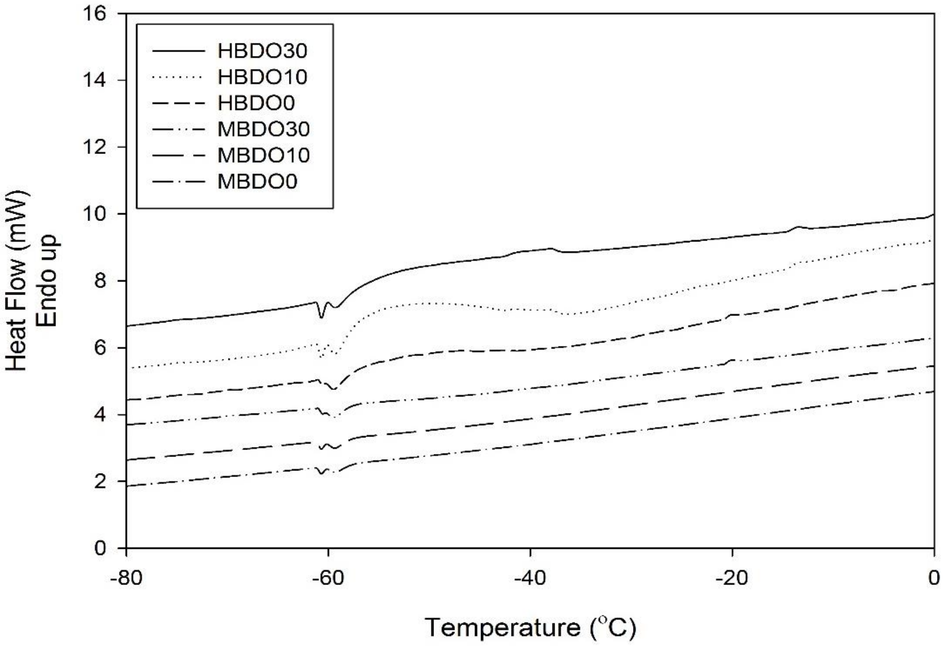


Figure 4.4 DSC curves of polyurethane foams obtained on the first scans: PUF with chain extender (BDO) scan rate 20 °C/min and the temperature ranges from -100 to 150 °C.

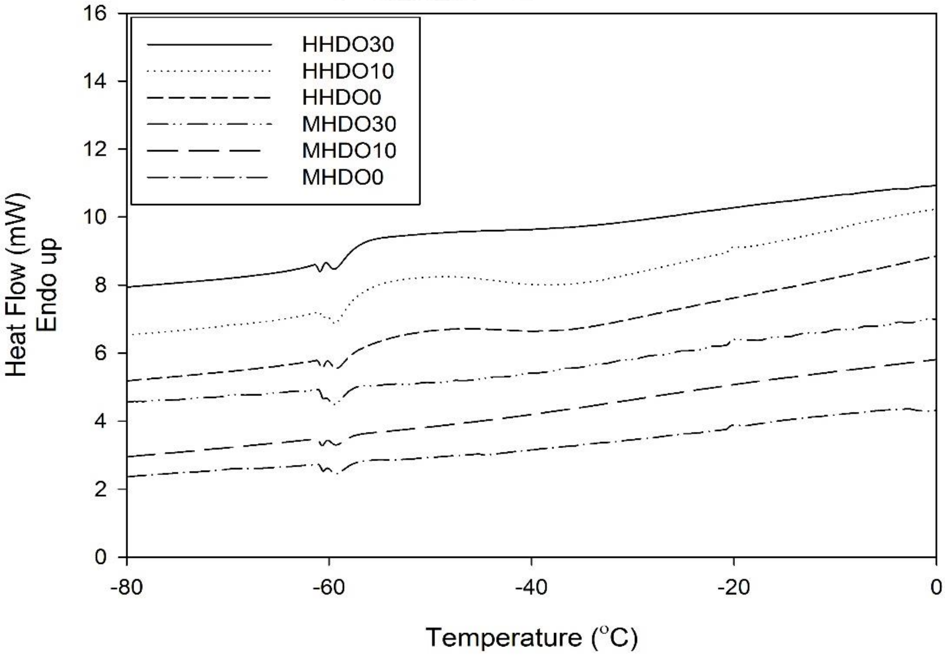


Figure 4.5 DSC curves of polyurethane foams obtained on the first scans: PUF with chain extender (HDO) scan rate 20 °C/min and the temperature ranges from -100 to 150 °C.

Table 4.2 The glass transition temperature (Tg) of synthesized polyurethane foams.

PU foam sample	Tg (C)	PU foam sample	Tg (C)
HEG0	-54.42	MEG0	-20.70
HEG10	-56.26	MEG10	-27.64
HEG30	-57.04	MEG30	-20.86
HBDO0	-55.80	MBDO0	-23.95
HBDO10	-56.18	MBDO10	-31.97
HBDO30	-56.99	MBDO30	-32.71
HHDO0	-56.24	MHDO0	-20.95
HHDO10	-57.52	MHDO10	-27.28
HHDO30	-58.03	MHDO30	-31.66

In addition, the Tg can be changed by polymer chain length. For long chain polymer, it will contribute to increased flexibility of these foams. It is recommended that the larger mobility of polyurethane belong to two mechanisms. First, the phase separation of hard and soft segments can lead to more flexibility of soft segments and larger molecular mobility of polyols chains. And the second mechanism, for all polymer, the tendency of vibration and mobility in the macromolecular main chain structure are higher when the main polymer chain change [52]. So, the Tg would be changed by the effect of different type of chain extenders length in foams. The longest chain of chain extender is HDO revealed that the Tg were shifted to low range temperature, whereas EG that is the shortest chain extender showed the high Tg. It can be seen that the Tg decrease with increasing hydrocarbon chain length of chain extenders in PU foam because hydrocarbon chain is flexible properties. The results showed that, the PU that synthesized from HDI isocyanate, HEG0 had the highest Tg at -54.42 °C and HHDO30 had the lowest Tg at -58.03 °C. While, the PU that synthesized from MDI isocyanate, MEG0 had the highest Tg at -20.70 °C but MBDO30 had the lowest Tg at -32.71 °C.

4.3 Mechanical properties–Universal Testing Machine

In this study, Polyurethane foam was synthesized to investigate the mechanical properties with varying the chain extender length, molar ratio of polyols (PPG content) as well as diisocyanate structure. The mechanical properties of PU foam depended on the previous mention that are important for the compressive strength and the Young's modulus. Due to chain extenders is a short chain and low molecular weight polymer, it resemble a hard segment. But, the chain extender can improve to be more flexible properties due to adding hydrocarbon chain into hard segment. On the other hand, the PPG have had long hydrocarbon chain and hydrophilic property that effect to the lower mechanical properties of PU foam. This trends to decrease the compressive strength and the Young's modulus. The compressive stress–strain curves of polyurethane foams samples as a function of polyols molar ratio (PPG content) and chain extenders length were showed in **figure 4.6** and **figure 4.7.** The stress–strain curves showed the typical behavior of plastic foams characteristic that related to elastic deformation of cells, a plastic yield and a densification part [53]. The Young's modulus would be calculated by the slope of the tangential line of stress–strain curve or defined by **equation 4.1**.

$$E = \frac{\sigma}{\varepsilon} = \frac{F/A}{\Delta L/L} \cdot \qquad (4.1)$$

Where, E is The Young's modulus (kPa)

F is the force exerted on an object under tension (N);

A is the initial cross-sectional area through PU foam which the force is applied (mm^2);

ΔL is the amount by which the length of the object changes (mm);

L is the initial length of the PU foam (mm).

The compressive strength and the Young's modulus of PU foam decreased with increasing PPG content to PCL which PPG can be added up to 30%. It was evident that PCL chains gave a good performance of PU foam than PPG chains. PCL chains showed structural order, moderate polarity and tightly monomer [18]. Because of the PPG degree of branching and hydrophilicity leads to the decreasing of PU foam strength.

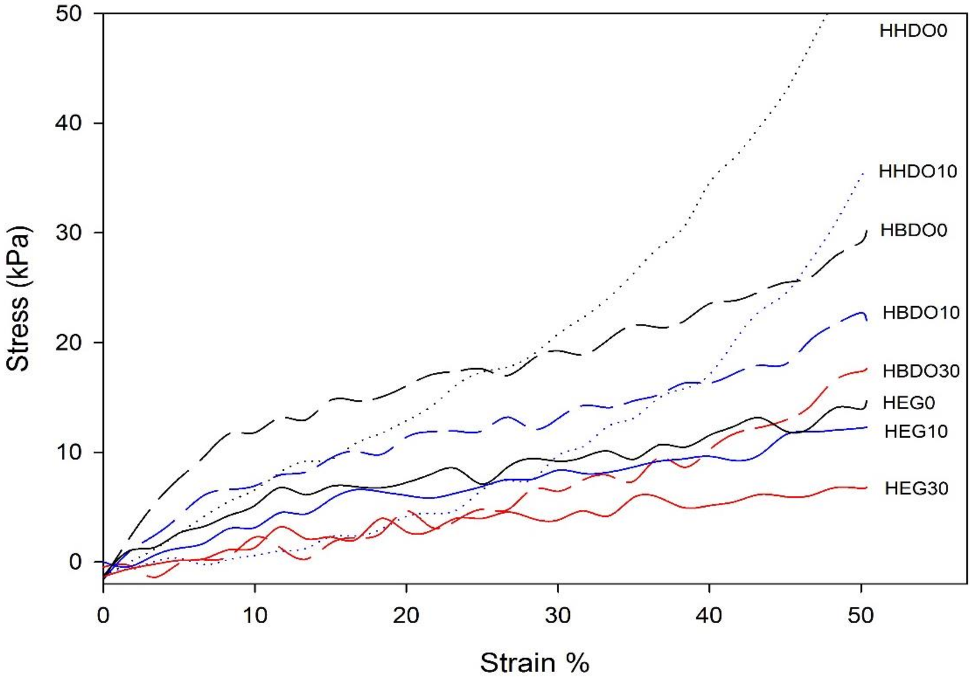


Figure 4.6 Compressive stress–strain curves of polyurethane foams synthesized using HDI isocyanate with three different of chain extenders: EG, BDO and HDO.

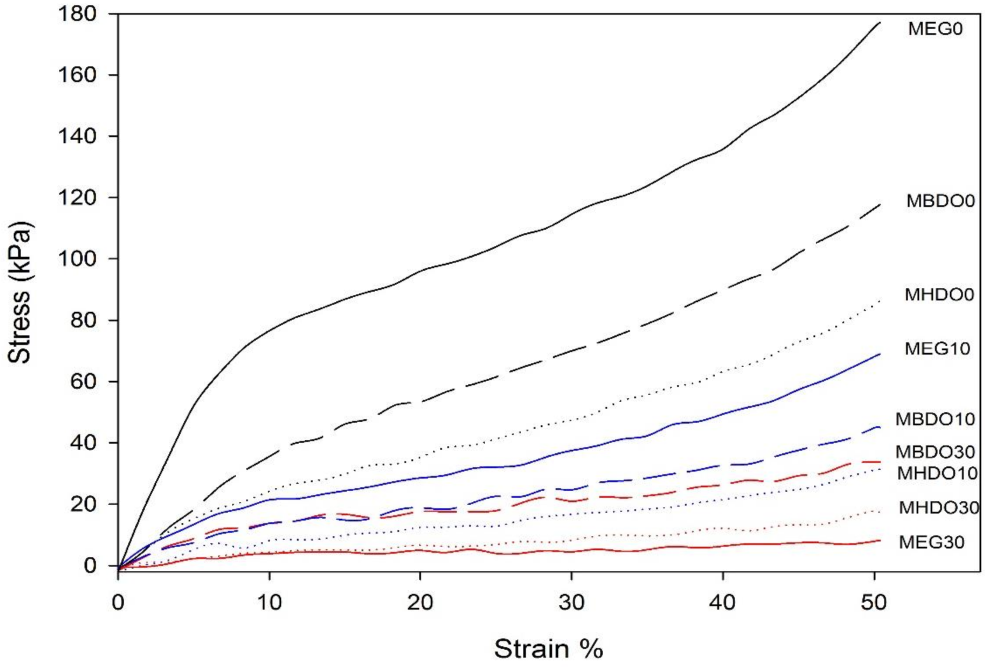
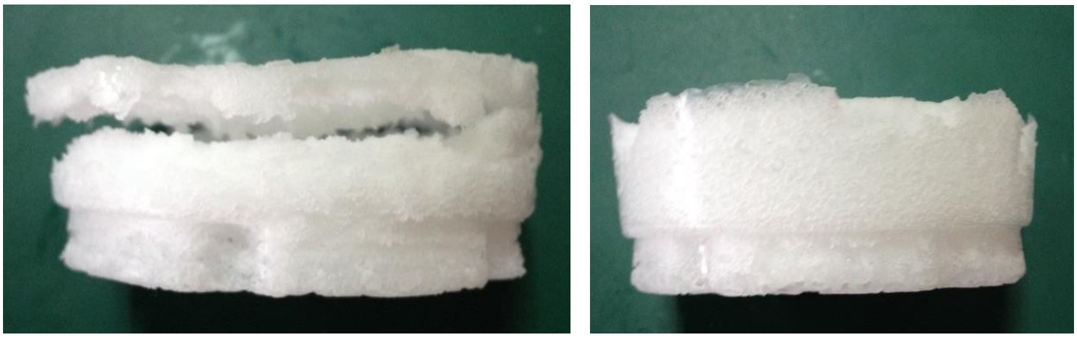


Figure 4.7 Compressive stress–strain curves of polyurethane foams synthesized using MDI isocyanate with three different of chain extenders: EG, BDO and HDO.

As for, a varying chain extenders length, the compressive strength and the Young's modulus of PU foam decreased when the hydrocarbon chain more lengthen (more flexible chains). Therefore, the results of PU foam with HDO chain extender should be the lower compressive strength and the Young's modulus than EG chain extender. Although in the case of the PU foam from HDI isocyanate the result was occurred in conversely. Due to the slow reaction of PPG compared to PCL with HDO chain extenders, the urethane reaction was not complete while the blowing reaction continuously occurred results in the agglomeration of bubble and internal surface collapse. Therefore, the cell wall was broken and collapsed obviously at 30% and 50% of PPG content as shown in **figure 4.8.** That is the reason why PU foam with HDO chain extender by HDI isocyanate was high the compressive strength and the Young's modulus.



(a) (b)

Figure 4.8 The PU foam with HDO chain extenders and PPG content: (a) 30% and (b) 50%.

The molecular structure of polyurethane foam is known to compose both soft-segment and hard segment that is a polyols and isocyanate, respectively. The reaction between polyols and isocyanate will produced the urethane linkage (NHC=OO) that it belongs to hard segment, was showed in **figure 4.9**. In this study, the different isocyanate structure, aromatic and aliphatic, was studied. The results revealed that the compressive strength and the Young's modulus of PU foam from HDI isocyanate showed the lower range than PU foam from MDI isocyanate. Due to the fact that HDI isocyanate have only aliphatic chain groups, while MDI isocyanate have the aromatic chain groups. This can also be discussed by the high reactivity of aromatic bond. The reactivity of the cumulated double bond in aromatic isocyanate group (N=C=O) can be contributed to mobility of the positive charge in the carbon atom. The electron deficiency on the carbon explains the reactivity of isocyanates towards nucleophilic attack. From the structure 1 in **figure 4.10**, the C=N bond is the position that take place the most reaction. In the case of the negative charge on the nitrogen will be distributed throughout the benzene ring easily because of the susceptible double bond, as shown with structure 3 in **figure 4.10**. The Resonance structures of an aromatic isocyanate makes it clear to understand that aromatic isocyanates are more reactive than aliphatic isocyanates [22], followed in **figure 4.10**.

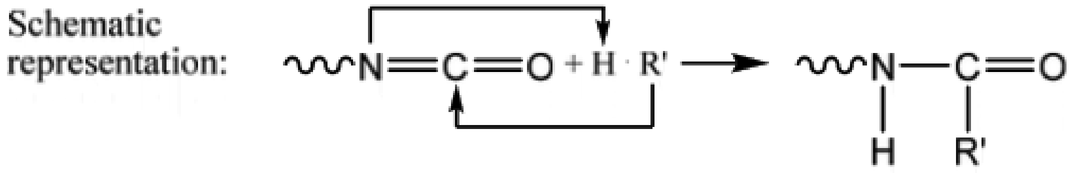


Figure 4.9 Reaction of isocyanates and compounds containing ‘active’ hydrogen atoms [22]

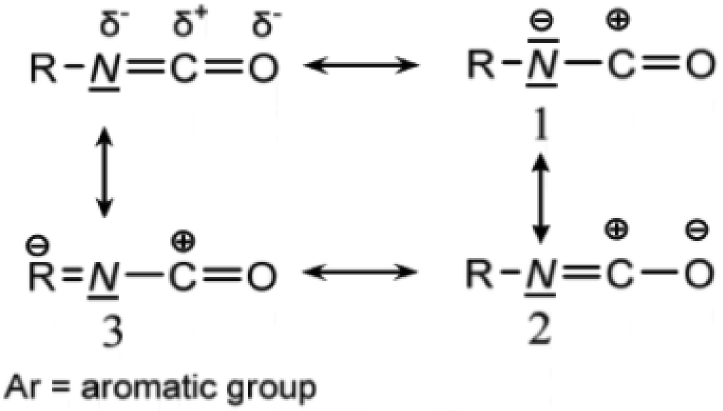


Figure 4.10 Resonance structure of the isocyanate group [22]

In the case of HDI isocyanate, the PU foam containing 0% of PPG with HDO chain extenders (HHDO0) demonstrated the highest value of the compressive strength and the Young’s modulus (56.91 and 113.83 kPa, respectively). While the PU foam containing 30% of PPG with EG chain extenders (HEG30) shown distinctly low value (8.53 and 17.07 kPa, respectively). In the case of MDI isocyanate, the PU foam containing 0% of PPG with EG chain extenders (MEG0) demonstrated the highest value of the compressive strength and the Young’s modulus (176.97 and 353.94 kPa, respectively). While the PU foam containing 30% of PPG with EG chain extenders (MEG30) shown distinctly low value (9.31 and 18.62 kPa, respectively). For all results of the Compressive Strength and Young's modulus of PU foam was calculated by equation 4.1 that was mentioned in previous paragraph, as summarized in **table 4.3.**

Table 4.3 Compressive Strength and Young's modulus result from stress–strain data.

PU foam sample	Compressive Strength (kPa)	Young's modulus (E)
HEG0	15.13 ±1.56	30.25 ±3.13
HEG10	13.10 ±2.16	29.72 ±4.33
HEG30	8.53 ±0.65	17.07 ±1.30
HBDO0	30.24 ±1.80	60.47 ±3.60
HBDO10	23.41 ±1.21	46.81 ±2.42
HBDO30	17.92 ±0.47	35.85 ±0.95
HHDO0	56.91 ±5.74	113.83 ±11.48
HHDO10	35.59 ±5.81	71.16 ±11.62
HHDO30	-	-
MEG0	176.97 ±8.58	353.94 ±17.16
MEG10	69.15 ±15.98	138.29 ±31.96
MEG30	9.31 ±1.19	18.62 ±2.39
MBDO0	117.75 ±9.18	235.50 ±18.37
MBDO10	45.41 ±3.15	90.82 ±6.29
MBDO30	34.34 ±3.08	68.69 ±6.17
MHDO0	86.42 ±10.12	172.85 ±20.24
MHDO10	31.55 ±4.73	63.09 ±9.46
MHDO30	18.16 ±0.69	36.32 ±1.39

4.4 Morphology of polyurethane foam

4.4.1 The apparent density and water absorbency

In general, the PU foams are utilized in many applications. The density and porosity are important factor for foam characteristic. Because the porosity is difficult to estimate, then in this research the apparent density was used as an indirect measurement of the porosity. The results of the apparent density is conversed with the porosity in constant volume. **Figure 4.11** showed the apparent density of polyurethane foam from different isocyanate and chain extenders with various PPG/PCL mixing ratio. In the case of PU synthesized from HDI, the apparent density of the PU foam was decreased with the increasing of PPG content. On the other hand, the PU from MDI isocyanate revealed the increasing of density with the increasing of PPG content. Theoretically, the apparent density would be decreased with the increase of PPG content to PCL. Due to the slow reaction of PPG compared to PCL, there would be sufficient time for the generation of more carbon dioxide gas in the blowing reaction [1]. Although at more than 30% PPG, the urethane reaction was not completed while the blowing reaction continuously occurred resulting in the agglomeration of bubble and internal surface collapse. Therefore, the cell wall was obviously broken at 50% of PPG content in all samples. At the PU foam containing 30% of PPG with EG chain extenders and MDI isocyanate (MDIEG30) the density was increased. It was due to a thick cell wall accompanied by a big porosity was appeared. Moreover, it was found that the density of the foams depended on the mass of expanded polymer [50]. On the other hand, the PU foam with HDI isocyanate has wide range of density than the PU foam with MDI isocyanate, because of low reactivity of HDI isocyanate, it was difficult to react with other functionality. Therefore, the properties of foam would be depended on other factors such as chain extender length or PPG content.

From the result with different chain extender length, it revealed that the density of PU foam with MDI isocyanate series shown the similarity trends. However, the density of PU foam with HDI isocyanate series increased from 66 to 142 kg/m^3 with the increasing the molecular weight of chain extenders or extended chain. The reason is that the foaming ability could be limited by higher the molecular weight of chain. The mobility of HDO molecules was diminished by the viscosity, which was increased by the increase of molecular weight [12, 27]. It was found that the PU foam had the highest density at HHDO0 condition compared to HEG0. Due to HDO chain has longer backbone chain than BDO and EG. As the results, they were difficult to rise up but easy to shrink. It caused that the PU foam from HDO could not rise up to be the foam, and then it collapsed.

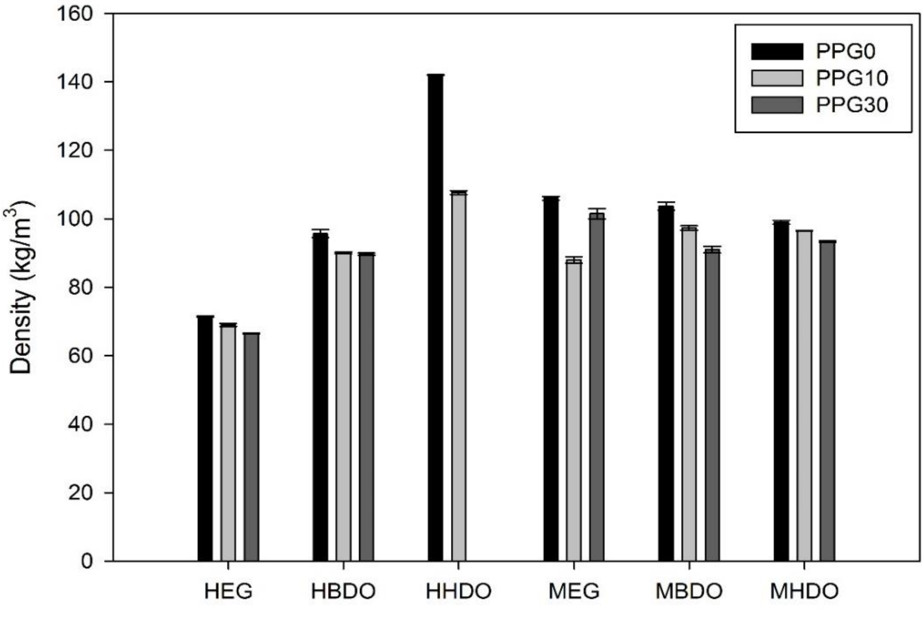


Figure 4.11 The apparent density of polyurethane foam as a function of HDI and MDI isocyanate with various PPG/PCL mixing ratio.

Figure 4.12 showed the distilled water absorption (g/g) of polyurethane foams. The water absorption test was conducted according to ASTM F726. The samples were immersed in distilled water for 24 hr and then weighted the wet weight. The tendency of the water absorption was inversely occurred with the apparent density. The results showed the higher water content in polyurethane foam with the increasing of PPG. It can demonstrated that the hydrophilicity of PPG has an effect on water absorption. Moreover, the isocyanate structure that were used as raw material for synthesis also affected the properties of PU foam. After immersion for 24 hr, the water absorptions of HDI-based polyurethane and MDI-based polyurethane are in the range of 3-10 and 3-6, respectively. The MDI isocyanate have the aromatic chain group which is a hydrophobic, while aliphatic HDI isocyanate that is a long hydrocarbon chain like a hydrophilic. This is the reason why the water absorption with HDI isocyanate was higher than MDI isocyanate [27]. Different chain extender structure is directly affected to the water absorption. The general 'diols' have already two –OH group, when the polar of –OH group in diols chain become less proportion with increasing the length of hydrocarbon chain. The molecule in chain becomes more like a hydrocarbon, which it is a non-polar. Therefore, the solubility of the diols decreases analogously. Thus, the HDO chain extender that is longest of hydrocarbon chain in this series has the lowest ability of the water absorbency.

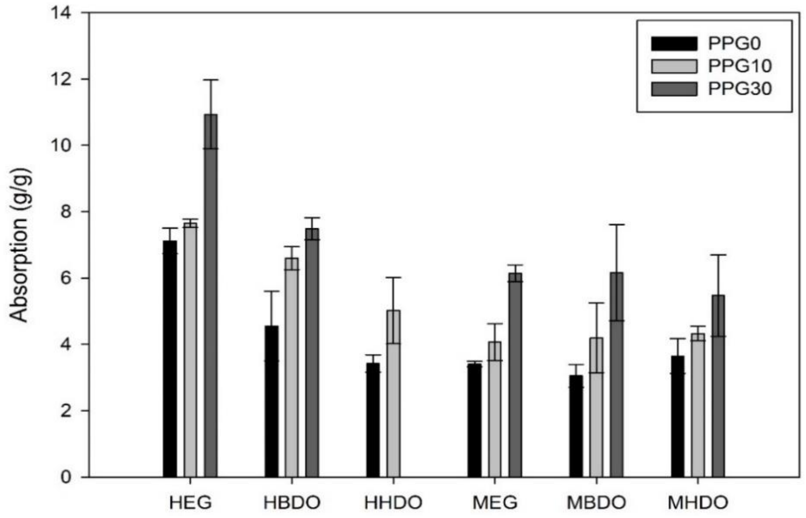


Figure 4.12 The water absorption test of polyurethane foam from HDI and MDI isocyanate with various PPG/PCL mixing ratio.

The cell size of foam in **figure 4.13**, is one of all other important factor for indicated the water absorption. When the cell size was larger, the water can penetrate into cell foam more readily. Thus, the water absorption would definitely increase. However, even if the cells size of 0% PPG PU foam was large but the water absorption depended on intrinsic polymer structure. Hydrophilic PPG has long chain end of linear aliphatic while hydrophobic PCL is a crystallinity. This is a reason why the water absorbency was increased by increasing the amount of PPG. The density, the water absorbency and the cell size of foam were summarized in **table 4.4.**

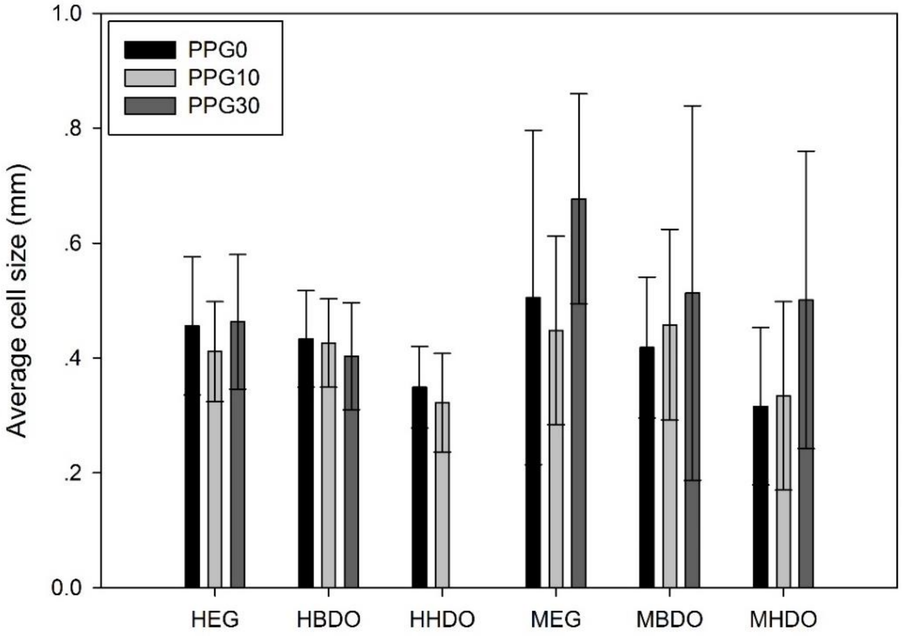


Figure 4.13 The cell size of PU foam as a function of HDI and MDI isocyanate with various PPG/PCL mixing ratio.

Table 4.4 The apparent density, the water absorptions and foam cell size of polyurethane foam.

PU foam samples	Density (kg/m^3)	Water absorption (g/g)	Cell size of foam (mm)
HEG0	71.50 ±2.12	7.12 ±0.39	0.4560 ±0.12
HEG10	69.00 ±4.24	7.65 ±0.13	0.4110 ±0.09
HEG30	66.50 ±0.71	10.93 ±1.04	0.4630 ±0.12
HBDO0	95.67 ±11.6	4.55 ±1.05	0.4330 ±0.08
HBDO10	90.00 ±2.65	6.60 ±0.35	0.4260 ±0.08
HBDO30	89.67 ±3.22	7.49 ±0.33	0.4030 ±0.09
HHDO0	142.00 ±1.00	3.42 ±0.26	0.3490 ±0.07
HHDO10	107.67 ±5.77	5.02 ±1.00	0.3220 ±0.09
HHDO30	-	-	-
MEG0	106.00 ±56.57	3.41 ±0.08	0.5050 ±0.29
MEG10	88.00 ±9.89	4.07 ±0.55	0.4480 ±0.16
MEG30	101.50 ±14.80	6.14 ±0.25	0.6770 ±0.18
MBDO0	103.67 ±11.50	3.05 ±0.34	0.4183 ±0.12
MBDO10	97.33 ±6.50	4.19 ±1.05	0.4580 ±0.17
MBDO30	91.00 ±9.85	6.16 ±1.45	0.5130 ±0.33
MHDO0	99.00 ±5.66	3.65 ±0.52	0.3160 ±0.14
MHDO10	96.5 ±0.71	4.32 ±0.21	0.3340 ±0.16
MHDO30	93.33 ±2.08	5.47 ±1.22	0.5010 ±0.26

4.4.2 Morphology of polyurethane foam

From **figure 4.14** and **4.15** showed the SEM images of PU foam with different chain extenders, various PPG/PCL molar ratio and different isocyanate structure. This image confirmed that had agreed with the density and water absorption in previous discussion. In the **figure 4.14**, the SEM image series of synthesized PU foam with HDI isocyanate based were presented. It was showed that the majority of PU foam structure presented closed-cells at 0% PPG content. While the cellular structure of 30% PPG contents in PU foam exhibited in the chiefly opened-cells foam and average pore size was increased. The cell wall was broken results in the disordered and increasing of water absorption. In consequence, the number of open-cells acts as very an important factor.

The average cell size of PU foam slightly decreased with increasing molecular weight or extended chain and viscosity. This is probably due to the HDO degree of branching which have longer backbone chain leads to more chain ends and low reactivity. This cause the slow reaction of PU foam and then the more carbon dioxide gas was generated. The results showed in the small amount of bubbles in polymer bulk. The properties of different chain extenders structure were summarized in **table 4.5**.

Figure 4.15 shows SEM images of polyurethane foams with different types of isocyanate represent the different characteristic morphology of foam. Polyurethane foam synthesized from MDI showed the closed cells and larger average pore size. Because of the high reactivity of aromatic in isocyanate chain which there are susceptible to react with hydroxyl groups (-OH group). Therefore, the larger bubble were occurred in bulk foam polymer with more carbon dioxide gas generation. Moreover, the sticky reactant prepolymer gave difficult to blend it all together and aromatic bond isocyanate also reacted to form urethane linkage easily and fast. The urethane linkage was sudden created with complete mixture part, while incomplete others was showed the stiff properties from intrinsic isocyanate.

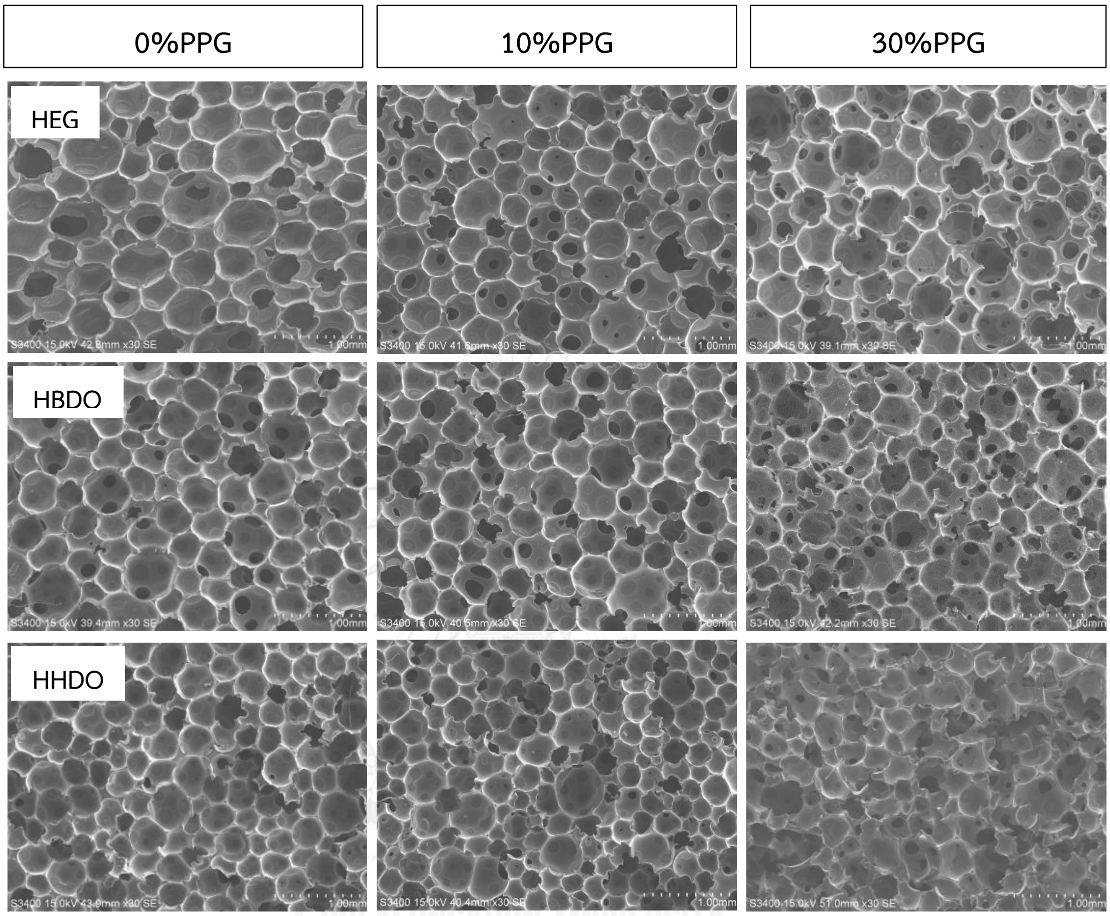


Figure 4.14 Scanning electron microscope (SEM) images (x30) of polyurethane foam in various PPG/PCL content and different chain extenders with HDI isocyanate.

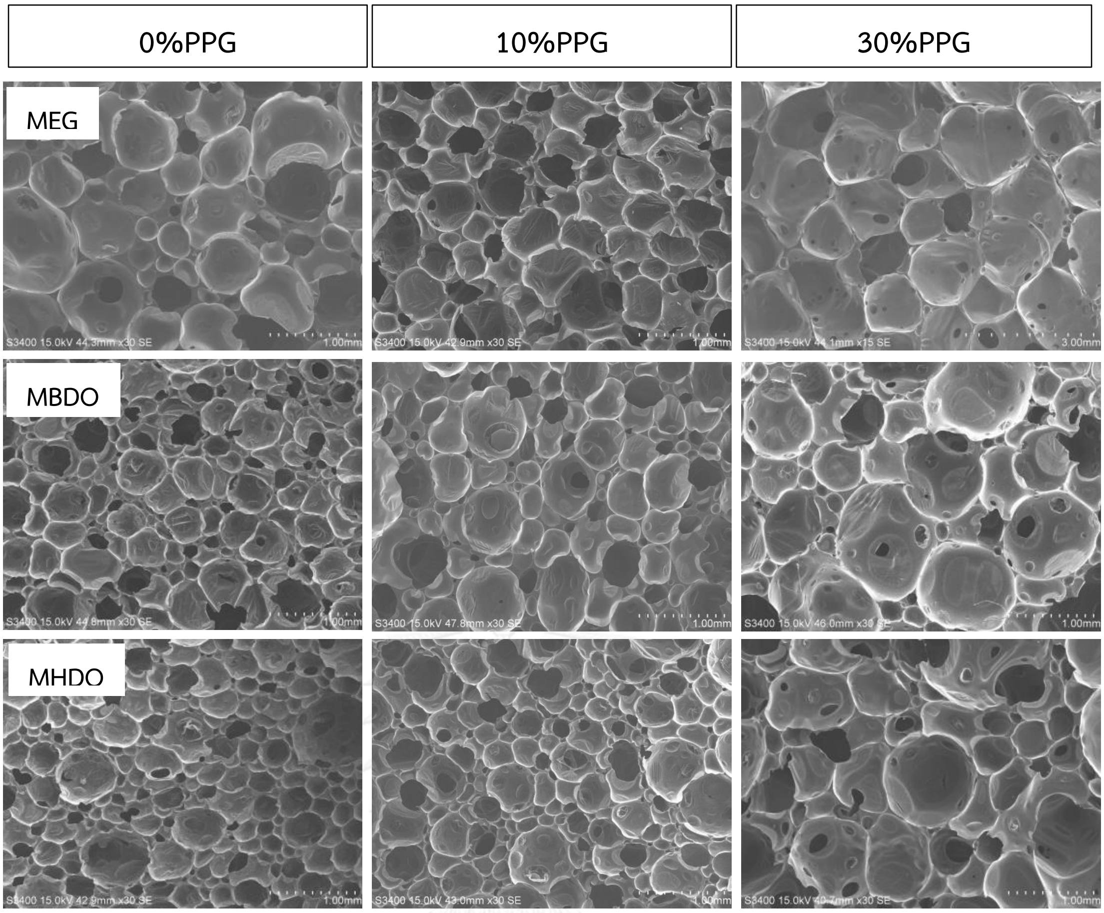


Figure 4.15 Scanning electron microscope (SEM) images (x30) of polyurethane foam in various PPG/PCL content and different chain extenders with MDI isocyanate.

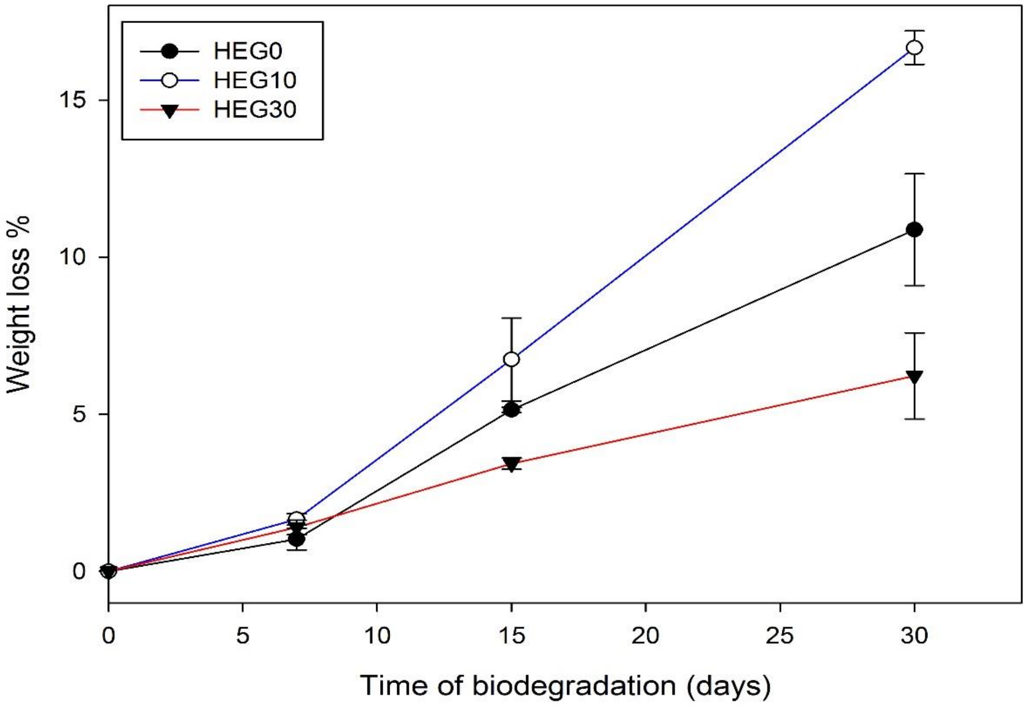
Table 4.5 The properties of different chain extenders structure

Properties	Ethylene glycol (EG)	1, 4 butanediol (BDO)	1, 6 hexanediol (HDO)
Chemical formula	$C_2H_6O_2$	$C_4H_{10}O_2$	$C_6H_{14}O_2$
Molecular weight (g/mole)	62.07	90.12	118.17
Boiling point (°C)	197.3	235	260
Melting point (°C)	-12.9	20.1	42
Density (g/cm^3)	1.11	1.0171	1.116
Solubility in water	Miscible	Miscible	Miscible

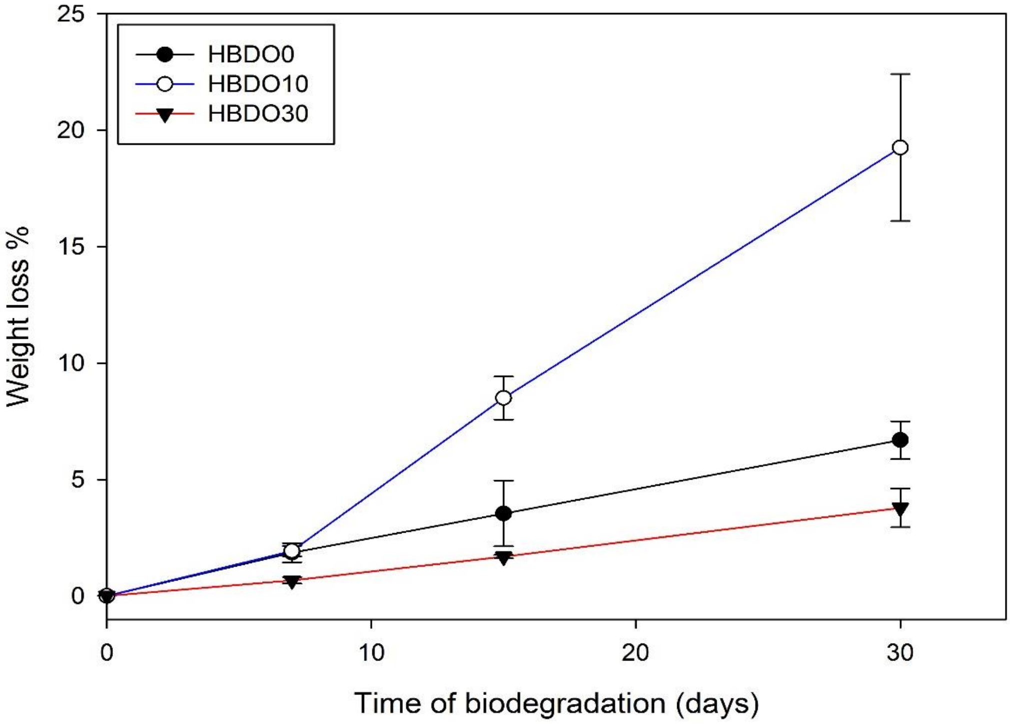
4.5 Biodegradation

The biodegradation testing of all PU foam series for 30 days with accelerative condition in the soil was showed the result of weight loss in **figure 4.16 (a), (b), (c)** and **figure 4.17 (a), (b), (c)**. The results of weight loss was summarized in **table 4.6**. The degradation rate depend on PPG/PCL molar ratio, chain length and different isocyanate structure in PU foam. It can observed that the weight loss of PU foam increase with the increasing of PPG content because it is hydrophilic material result in the higher water absorption of PU foam. Because of the ester groups in PCL chain and urethane linkage is an active position for enzyme that was produced by naturally microorganism. The ester bond was also a dominant factor on the hydrolytic process in PU foam [19] due to enzyme only interacted with ester bond in PCL soft segments and urethane linkage in these polymers structures [15]. Hydrolysis by enzyme is a reaction involving the cracking of a bond in a molecules with the addition of water, showing in **figure 4.18**. The PCL reactant can be degraded with ester bond but it is a hydrophobic properties that caused to drop degradation rates. Consequently, the hydrophilic PPG addition was important to induce the water into cell foams in order to increase the hydrolytic process. Then the average percent of weight loss of PU foam would be increased. Theoretically, the degradation rate of PU foam related to the high content of hydrophilicity of PPG as described above. Although, PU foam with 30%PPG shown the lower degradability because of their thick wall and high density.

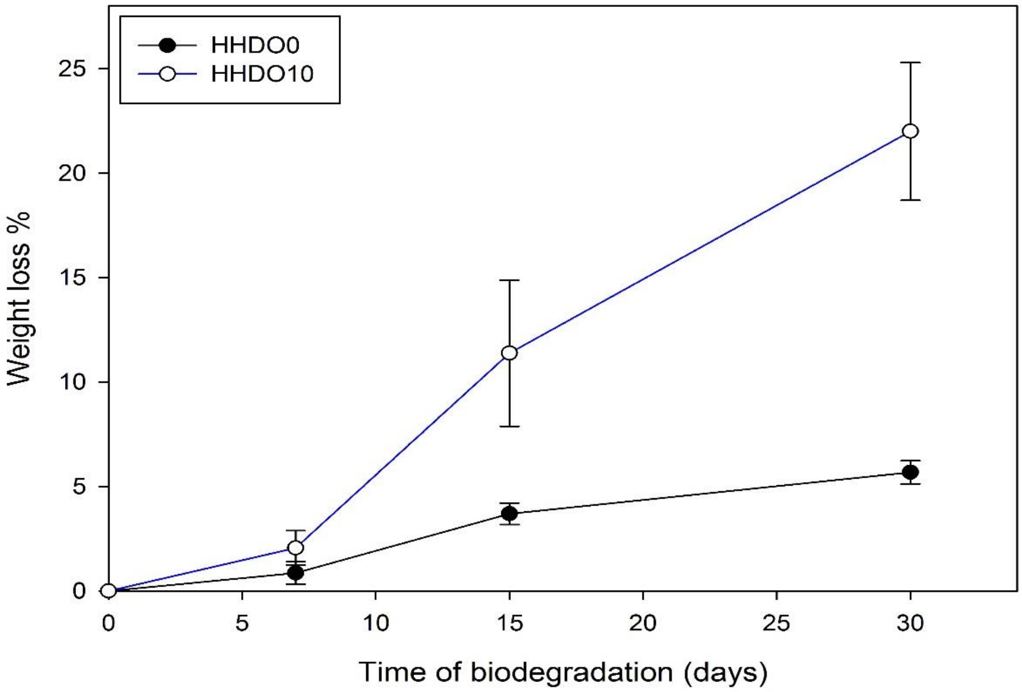
The degradation rates of PU foam were also related to the isocyanate structures. The PU foam synthesized from aliphatic HDI obviously had the higher weight loss than that synthesized from aromatic MDI. It is due to the strong and stable double bond the aromatic structure leads to good mechanical properties and low degradation rate of the samples.



(a) EG chain extenders

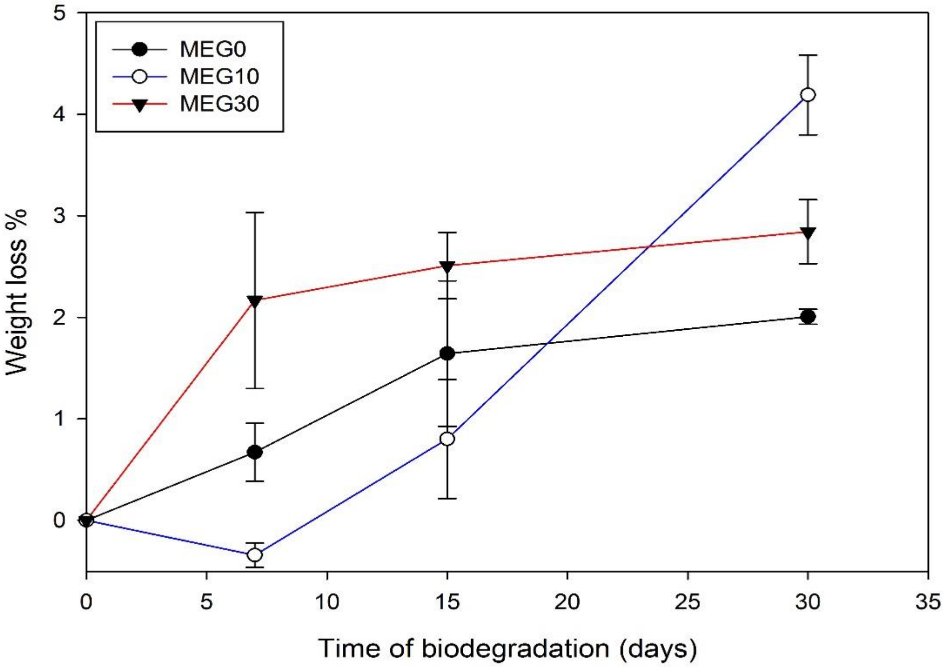


(b) BDO chain extenders

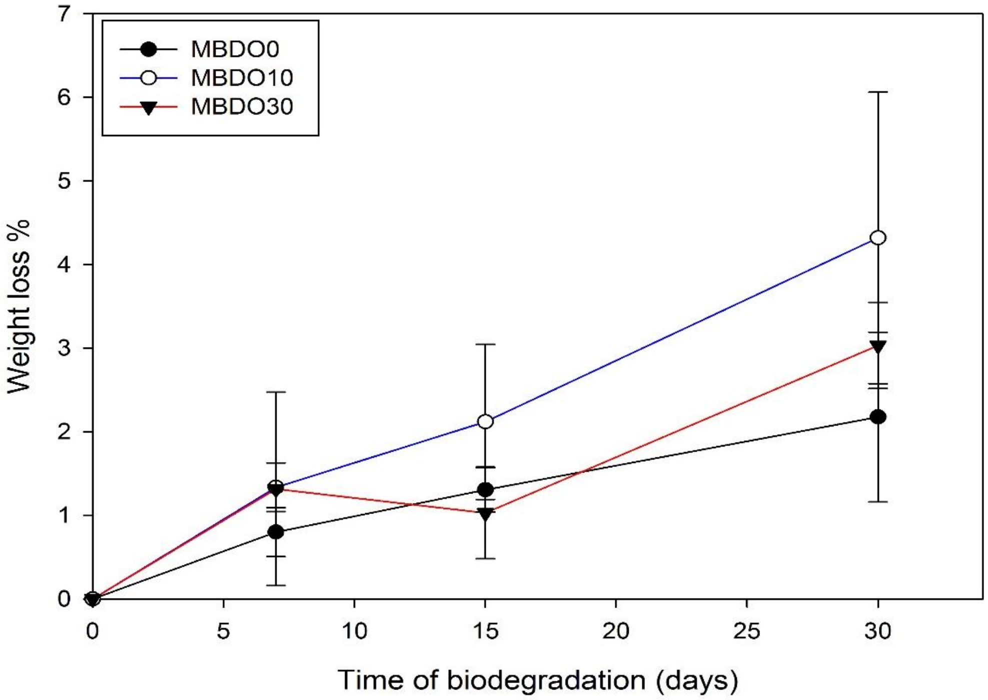


(c) HDO chain extenders

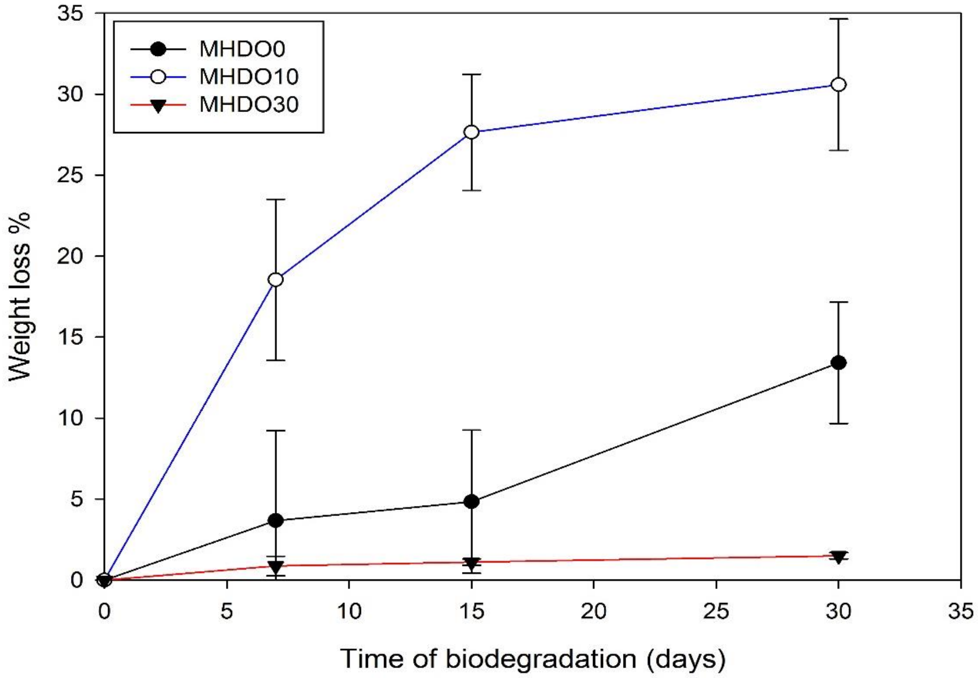
Figure 4.16 Percent weight loss of biodegradable polyurethane foam with HDI-based and different chain extenders after 30 days in soil: (a) EG, (b) BDO and (c) HDO.



(a) EG chain extenders



(b) BDO chain extenders



(c) HDO chain extenders

Figure 4.17 Percent weight loss of biodegradable polyurethane foam with MDI-based and different chain extenders after 30 days in soil: (a) EG, (b) BDO and (c) HDO.

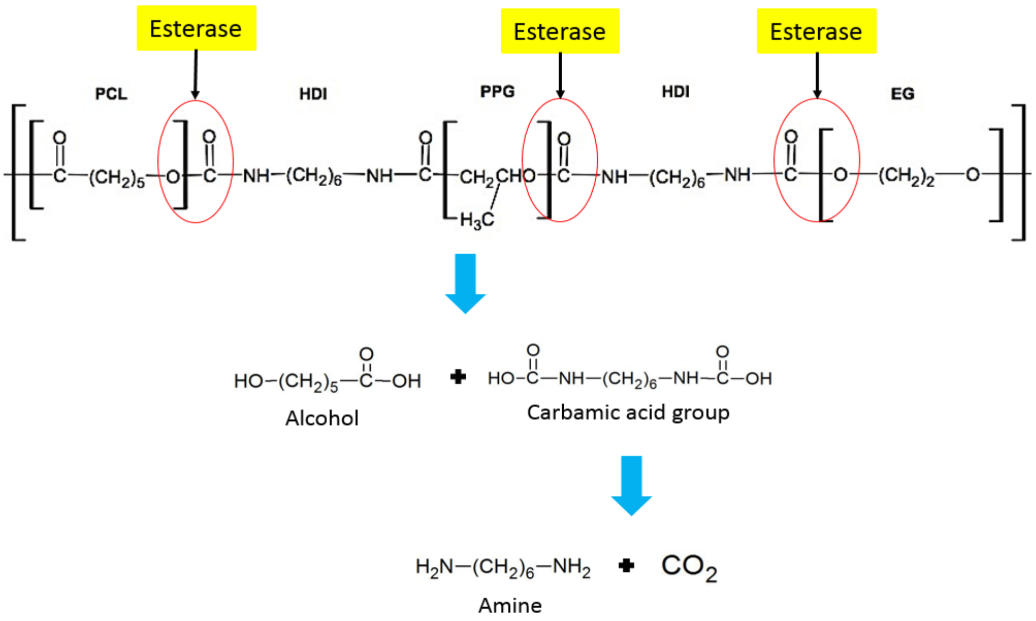


Figure 4.18 Reaction of degradation of ester bond by esterase enzyme.

As for the results of degradation with different chain extenders structure showed that the PU foam with HDO can be well degraded by the enzymatic from microbial soils. The average weight loss increased with the increasing chain length of the chain extender. The ester bond in a polymer chain was cracked into amine acid and carbon dioxide. Amine acid is biologically important organic compound and normal to exist in the earth's atmosphere. This phenomenon can be described by the phase separation domains. The flexible properties of these foam were depended on a portion of that consisted of the hard and soft segment such as the urethane linkage as a hard segment domain and the amorphous polyols as a soft segment domain. The phase separation happened with the mainly non-polar, low-melting soft segment that were incompatible with the polar, high melting hard segments. Because the hard segment which give stiff and immobile chain properties to the polymer foam are formed from isocyanate and chain extenders, while the soft segment which are mobility chain and presented by coiled formation. Therefore, the hard segments are covalently obligated to the soft segments, when the hard segment length increases, the repulsion in each molecule do each other between hard and soft segments. Thus, the driving force for phase separation further increase [54, 55].

Table 4.6 Percent weight loss of biodegradable polyurethane foam with MDI and HDI-based and different chain extenders after 30 days in soil.

Sample	% average weight loss		
	Day7	Day15	Day30
HEG0	1.03 ±0.34	5.14 ±0.08	10.87 ±1.77
HEG10	1.66 ±0.18	6.74 ±1.32	16.66 ±0.53
HEG30	1.40 ±0.23	3.43 ±0.18	6.22 ±1.37
HBDO0	1.86 ±0.41	3.54 ±1.41	6.69 ±0.81
HBDO10	1.93 ±0.23	8.50 ±0.92	19.25 ±3.16
HBDO30	0.67 ±0.14	1.69 ±0.07	3.78 ±0.83
HHDO0	0.86 ±0.53	3.69 ±0.52	5.68 ±0.56
HHDO10	2.06 ±0.82	11.38 ±3.49	22.00 ±3.29
HHDO30	-	-	-
MEG0	0.67 ±0.29	1.64 ±0.72	2.01 ±0.07
MEG10	-0.34 ±0.12	0.80 ±0.59	4.19 ±0.39
MEG30	2.17 ±0.87	2.51 ±0.33	2.84 ±0.32
MBDO0	0.80 ±0.29	1.30 ±0.26	2.18 ±1.02
MBDO10	1.34 ±0.29	2.12 ±0.93	4.32 ±1.74
MBDO30	1.32 ±1.16	1.03 ±0.55	3.03 ±0.51
MHDO0	3.67 ±5.56	4.84 ±4.41	13.4 ±3.75
MHDO10	18.54 ±4.98	27.64 ±3.58	30.58 ±4.06
MHDO30	0.87 ±0.61	1.11 ±0.20	1.50 ±0.19

Figure 4.19 and **figure 4.20** are the results of SEM images of all polyurethane foam surfaces after biodegradation test by soil burial for 30 days. The first column was the surface of the PU foam before biodegradation that showed spherical and regular cell foam. And the second column were that the PU foam after 30 days biodegradability showed not uniform and ruinous cell foam. It appears that the biodegradability of the PU foam was showed more porosity that caused by enzyme from the soil microorganism.

A few research reported that Polyurethane-degrading microorganisms consisted of *Fusarium solani, Curvularia senegalensis, Aure-obasidium pullulans and Cladosporidium* sp. were also isolated and *C. senegalensis* can produced the esterase enzyme. Also, *P. chlororaphis* was found to produce a lipase enzyme that responsible for the polyurethane degradation [33]. Moreover, *Actinomyces calcoaceticus* is primary as a terrestrial or aquatic bacteria (soil bacteria) [34]. As for the bacteria type revealed that the soils was plentiful capability for using biodegradation.

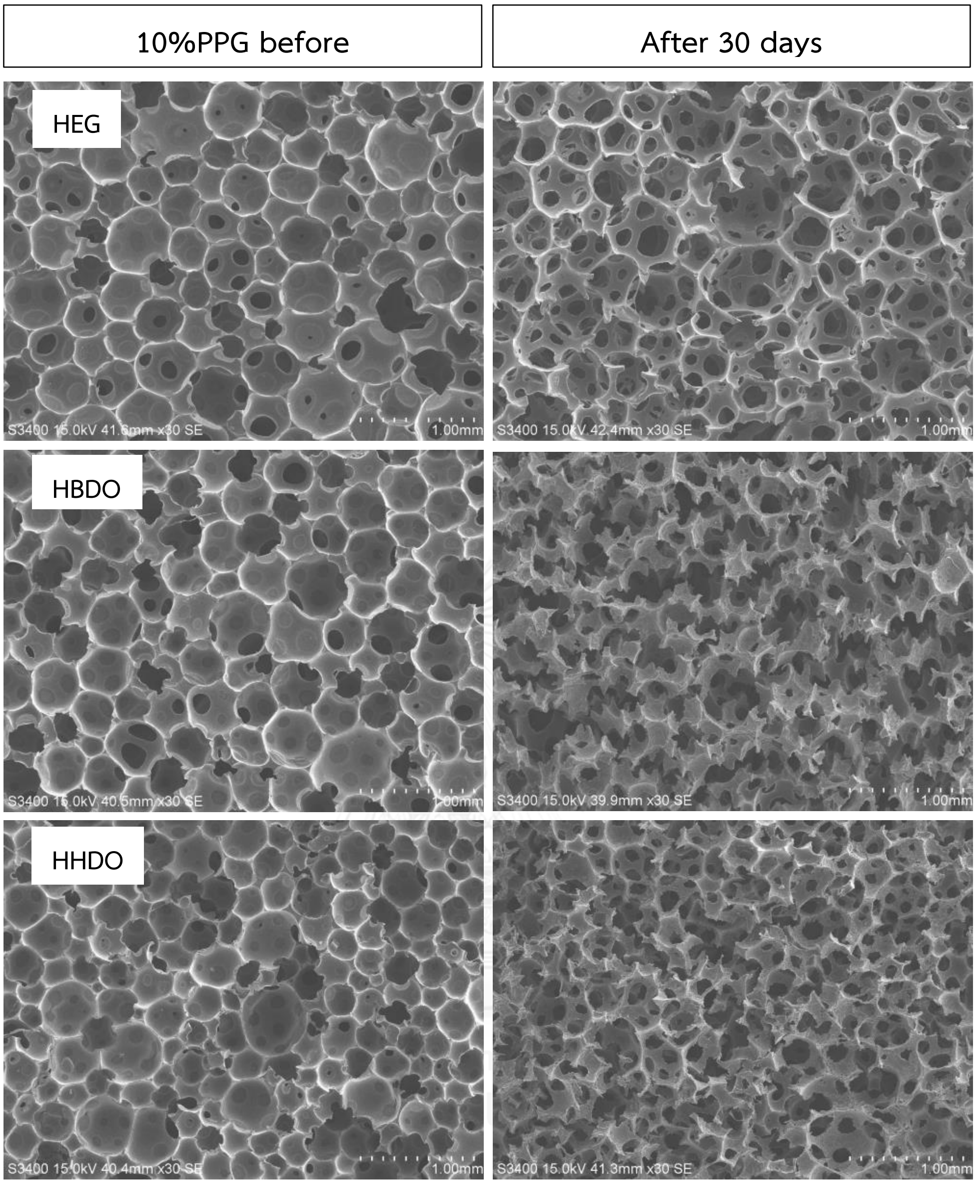


Figure 4.19 SEM images of biodegradable polyurethane foam with HDI isocyanate at 10% PPG molar ratio for 30 days in soil burials experiment.

From the SEM image after 30 days, it was found that the cell sizes were change from small cell pore to the large gap among the decayed cell wall. Because esterase enzyme that was released by soil microorganisms acted as the biocatalyst [56], so it was accelerated to crack the ester bond. The SEM image confirmed the deformational surface of degradable PU foam by enzyme. It can observed that the weight loss of PU foam with HDI-based more than the weight loss of PU foam with

MDI-based significantly. The described of the reason have already mentioned in previous section. This results of statistical significance was confirmed by critical P-value that was showed in **Appendix A**.

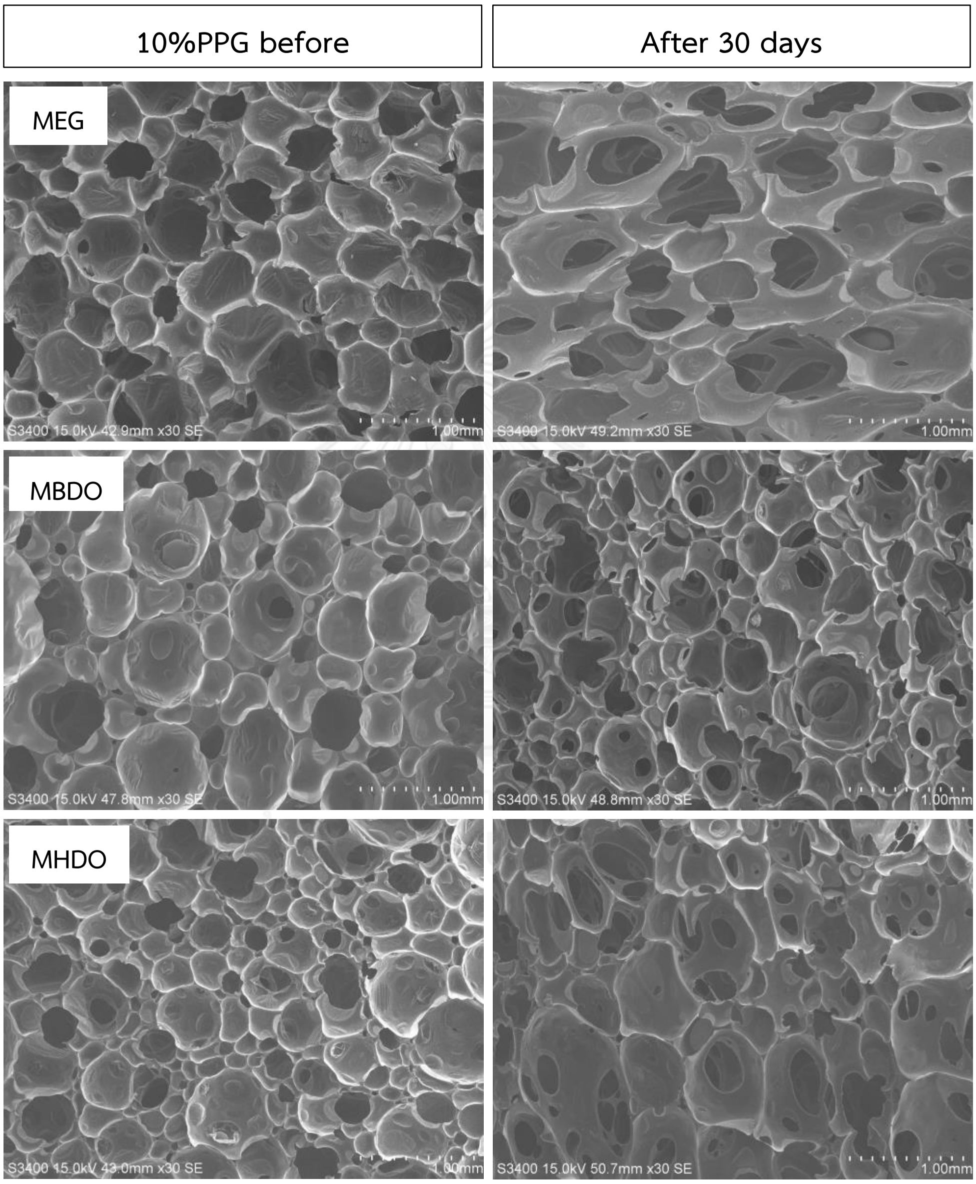


Figure 4.20 SEM images of biodegradable polyurethane foam with MDI isocyanate at 10% PPG molar ratio for 30 days in soil burials experiment.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 conclusions

In the study, the synthesis of polyurethane foam for commercial application such as packaging or cushioning that would be able to biodegrade in the environment condition and improved the mechanical properties with different chain extenders, ethylene glycol (EG), 1,4-butandiols (BDO) and 1,6-Hexandiols (HDO), and PPG/PCL molar ratio. Which the properties could be characterized by FTIR, DSC, SEM, compressive testing, density, water absorption and biodegradation with the soil burial in laboratory condition.

In conclusion, we have successfully prepared biodegradable polyurethane foam with hydrophobic polycaprolactone (PCL) and hydrophilic polypropylene glycol (PPG) as a soft segment. Aliphatic HDI isocyanate and different chain extenders as a hard segment were used in one-step synthesis. Depending on the amount of PPG in the polymers, a variety of polyurethanes foam with different mechanical property and biodegradability could be achieved. The effect of chemical properties was occurred to foam properties more than physicals properties. Moreover, the biodegradability rate depended on these three factor that were varied which the increasing of PPG content was the most affected to biodegradability rate than chain extender length and isocyanate structures.

The FT-IR analysis, the urethane linkage and other functional group peak occur in the PU foam chain. Also, the peak of NCO group at 2200-2300 cm^{-1} was still appeared. The differences of PPG/PCL molar ratio, chain extenders length and isocyanate structure that affected to the physical and mechanical properties were explained. The glass transition temperature (Tg) that were analyzed by DSC, it showed that the Tg trended to lower values when increasing PPG content, longer chain extenders and using HDI aliphatic isocyanate structure due to the mobility of PU polymer chain networks. The compressive strength and young's modulus were decreased with increasing PPG content to PCL and long chain extender with the exception of PU foam from HDI isocyanate due to the cause of phase separation in the foaming reaction. An increase in the water absorption was caused by the hydrophilic PPG which it was minor the polyester polyol properties and decreasing with MDI aromatic isocyanate because their properties like as a hydrophobic material. However, the results of the density decreased when the porosity of PU foam increased depending on the PPG content of polyol mixture, it conversed with the water absorption resulting. It was confirmed by SEM images. Moreover, the higher of PPG content up to 10% lead higher the weight loss of PU foam biodegradability when observed in the soil at laboratory scales.

5.2 recommendations

1. To study and describe the effect of processing condition such as the effect of melting temperature or the effect of varying chain extender content to properties of prepolymer.

2. Use the silicone oil as a surfactant to improve the distributional porosity size of foam for higher strength.

3. To change chain extends structure such as the functional group or functionality. For example, glycerol which has three hydroxyl maybe leads to better mechanical properties.

REFERENCES

[1] Yang, S.-R., Kwon, O.-J., Dae-Hyun, K., and Park, J.-S. Characterization of the Polyurethane Foam Using Alginic Acid as a Polyol. Fibers and Polymers 8(3) (2007): 257-262.

[2] Ashida, K. Polyurethane and Related Foams: chemistry and technology. New York: Taylor & Francis Group, 2007.

[3] Urgun-Demirtas, M., Singh, D., and Pagilla, K. Laboratory investigation of biodegradability of a polyurethane foam under anaerobic conditions. Polymer Degradation and Stability 92(8) (2007): 1599-1610.

[4] Nakajima-Kambe, T., Onuma, F., Akutsu, Y., and Nakahara, T. Determination of the Polyester Polyurethane Breakdown Products and Distribution of the Polyurethane Degrading Enzyme of Comamonas acidovorans Strain TB-35. Journal of Fermentation and Bioengineering 83(5) (1997): 456-460.

[5] Subramanian, M. Polymer Testing: New Instrument Methods. New York: Momentum Press, 2012.

[6] Assink, R.A., Celina, M.C., and Elliott, J.M. Thermal Aging of the Polyurethane Foam for the H1259 Storage Container. California Sandia National Laboratories, 2006.

[7] Tatai, L., et al. Thermoplastic biodegradable polyurethanes: the effect of chain extender structure on properties and in-vitro degradation. Biomaterials 28(36) (2007): 5407-17.

[8] Maafi, E.M., Tighzert, L., and Malek, F. Synthesis and characterization of new polyurethanes: influence of monomer composition. Polymer Bulletin 66(3) (2010): 391-406.

[9] Hatakeyema, H., Tanamachi, N., Matsumura, H., Hirose, S., and Hatakeyama, T. Bio-based polyurethane composite foams with inorganic fillers studied by thermogravimetry. Thermochimica Acta 431(1-2) (2005): 155-160.

[10] Guan, J., Fujimoto, K.L., Sacks, M.S., and Wagner, W.R. Preparation and characterization of highly porous, biodegradable polyurethane scaffolds for soft tissue applications. Biomaterials 26(18) (2005): 3961-71.

[11] da Silva, G.R., da Silva-Cunha, A., Behar-Cohen, F., Ayres, E., and Oréfice, R.L. Biodegradation of polyurethanes and nanocomposites to non-cytotoxic degradation products. Polymer Degradation and Stability 95(4) (2010): 491-499.

[12] Kwon, O.-J., Oh, S.-T., Lee, S.-D., Lee, N.-R., Shin, C.-H., and Park, J.-S. Hydrophilic and Flexible Polyurethane Foams Using Sodium Alginate as Polyol- Effects of PEG Molecular Weight and Cross-linking Agent Content on Water Absorbency. Fibers and Polymers 8(4) (2007): 347-355.

[13] Ikada, Y. and Tsuji, H. Biodegradable polyesters for medical and ecological applications. Macromol. Rapid Commun. 21(3) (2000): 117-132.

[14] Lee, J.-M., et al. Preparation and characterization of polyurethane foam using a PLA/PEG polyol mixture. Fibers and Polymers 15(7) (2014): 1349-1356.

[15] Jiang, X., et al. Synthesis and degradation of nontoxic biodegradable waterborne polyurethanes elastomer with poly(ε-caprolactone) and poly(ethylene glycol) as soft segment. European Polymer Journal 43(5) (2007): 1838-1846.

[16] Eaves, D. Handbook of Polymer Foams. UK: Rapra Technology Limited, 2004.

[17] Russell, J.R., et al. Biodegradation of polyester polyurethane by endophytic fungi. Appl Environ Microbiol 77(17) (2011): 6076-84.

[18] Wang, J.H., Liang, S., Tian, C.R., Zhao, X.L., and Lin, X.Y. Study on Degradable Polyurethane Foams with Mixed PEG/PCL and PLA/PCL Soft Segments. Advanced Materials Research 518-523 (2012): 821-827.

[19] Tonmali, W. The Effect of NCO/OH Ratio on Properties and Biocompatibility of Polyurethane. Master Degree, Chulalongkorn University, 2013.

[20] Patrick, V., Hans, J.G., Gaétan, L., and Robert, G. Biomedical applications of polyurethanes. USA: EUREKAH.COM, 2001.

[21] Pentrakoon, D. and Ellis, J.W. An Introduction to Plastic Faoms. Thailand: Chulalongkorn University Press, 2005.

[22] Efstathiou, K. Synthesis and characterization of a Polyurethane Prepolymer for the development of a novel Acrylate-based polymer foam. (2001).

[23] Shih, T.-Y. Synthesis and Properties of Biodegradable Segmented Poly-ε-caprolactone. Journal of Medical and Biological Engineering 34(3) (2014): 238.

[24] Tjong, S.C., Xu, Y., and Meng, Y.Z. Compatibility and degradation of blends of poly(caprolactone)– poly(ethylene glycol) block copolymer and polypropylene. Polymer 40 (1999): 3703–3710.

[25] Abdel-Motaal, F.F., El-Sayed, M.A., El-Zayat, S.A., and Ito, S.-i. Biodegradation of poly (ε-caprolactone) (PCL) film and foam plastic by Pseudozyma japonica sp. nov., a novel cutinolytic ustilaginomycetous yeast species. 3 Biotech 4(5) (2013): 507-512.

[26] IPCS Chemical Safety Information from Intergovernmental Organizations 2015. Available from: www.inchem.org

[27] Kwon, O.-J., Yang, S.-R., Kim, D.-H., and Park, J.-S. Characterization of polyurethane foam prepared by using starch as polyol. Journal of Applied Polymer Science 103(3) (2007): 1544-1553.

[28] Gunatillake, P., Mayadunne, R., and Adhikari, R. Recent developments in biodegradable synthetic polymers. Biotechnology Annual Review 12 (2006): 301-347.

[29] Abadin, H. and Spoo, W. Toxicological Profile for Hexamethylene Diisocyanate. Georgia: U.S. Department of Health and Human Services, 1998.

[30] Asscociations, F.o.E.R.P.F. Thermal insulation materials made of rigid polyurethane foam (PUR/PIR). (2006).

[31] Kim, S.H. and Kim, B.K. Effect of Isocyanate Index on the Properties of Rigid Polyurethane Foams Blown by HFC 365mfc. Macromolecular Research 16(5) (2008): 467-472.

[32] Avérous, L. and Pollet, E. Environmental Silicate Nano-Biocomposites. Green Energy and Technology (2012): 13-39.

[33] Gu, J.-G. and Gu, J.-D. Methods Currently Used in Testing Microbiological Degradation and Deterioration of a Wide Range of Polymeric Materials with

Various Degree of Degradability: A Review. Journal of Polymers and the Environment 13(1) (2005): 65-74.

[34] J.R., C., J.R., C., L., T., L., S., and W.S., W.W. Biodegradation of a Colloidal Ester-based Polyurethane by Soil Fungi. International Biodeterioration & Biodegradation 33 (1994): 103-113.

[35] Vroman, I. and Tighzert, L. Biodegradable Polymers. Materials 2(2) (2009): 307-344.

[36] Jaewsrithong, S. An Investigation on The Biodegradation of Poly(lactic acid) and Poly(butylene succinate). Master Degree, Chulalongkorn University, 2013.

[37] Li, L., Frey, M., and Browning, K.J. Biodegradability Study on Cotton and Polyester Fabrics. Journal of Engineered Fibers and Fabrics 5(4) (2010): 42-53.

[38] Zhang, H., Pang, H., Zhang, L., Chen, X., and Liao, B. Biodegradability of Polyurethane Foam from Liquefied Wood Based Polyols. Journal of Polymers and the Environment 21(2) (2012): 329-334.

[39] Gouda, M.K., Swellam, A.E., and Omar, S.H. Biodegradation of Synthetic Polyesters (BTA and PCL) with Natural Flora in Soil Burial and Pure Cultures under Ambient Temperature. Journal of Environmental and Earth Sciences 4(3) (2012): 325-333.

[40] Obasi, H.C., Igwe, I.O., and Madufor, I.C. Effect of Soil Burial on Tensile Properties of Polypropylene/Plasticized Cassava Starch Blends. Advances in Materials Science and Engineering 2013 (2013): 1-5.

[41] Obasi, H.C., Onuoha, F.N., Eze, I.O., Nwanonenyi, S.C., Arukalam, I.O., and Uzoma, P.C. Effect of Soil Burial on Properties of Polypropylene(PP)/Plasticized Potato Starch (PPS) Blends. The International Journal Of Engineering And Science (IJES) 2(8) (2013): 14-18.

[42] Ryszkowska, J.L., AuguŚcik, M., Sheikh, A., and Boccaccini, A.R. Biodegradable polyurethane composite scaffolds containing Bioglass® for bone tissue engineering. Composites Science and Technology 70(13) (2010): 1894-1908.

[43] Ge, J., Shi, X., Cai, M., Wu, R., and Wang, M. A Novel Biodegradable Antimicrobial PU Foam from Wattle Tannin. Journal of Applied Polymer Science 90 (2003): 2756–2763.

[44] Dong, W., Zou, B., Yan, Y., Ma, P., and Chen, M. Effect of chain-extenders on the properties and hydrolytic degradation behavior of the poly(lactide)/poly(butylene adipate-co-terephthalate) blends. Int J Mol Sci 14(10) (2013): 20189-203.

[45] Department, L.D. The soil series 2015. Available from: http://www.ldd.go.th/thaisoils_museum/pf_desc/central/Ks.htm

[46] Molecular Materials research center: Beckman Institute California Institute of Technology. Nicolet 6700 FTIR 2015. Available from: http://mmrc.caltech.edu/FTIR/FTIR.html

[47] Direct Industry. Calorimeter DSC/differential scanning 2015. Available from: http://www.directindustry.com/prod/netzsch-geratebau-gmbh/calorimeters-dsc-differential-scanning-39926-363407.html

[48] Direct Industry. Hydraulic universal testing machine 2015. Available from: http://www.directindustry.com/prod/mts-systems-china-co-ltd/hydraulic-universal-testing-machines-54100-1158075.html

[49] SEM/e-beam writing system. (2015).

[50] Ribeiro da Silva, V., Mosiewicki, M.A., Yoshida, M.I., Coelho da Silva, M., Stefani, P.M., and Marcovich, N.E. Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis and physical chemical characterization. Polymer Testing 32(2) (2013): 438-445.

[51] Rivera-Armenta, J.L., Heinze, T., and Mendoza-Martínez, A.M. New polyurethane foams modified with cellulose derivatives. European Polymer Journal 40(12) (2004): 2803-2812.

[52] Semsarzadeh, M.-A., Sadeghi, M., and Barikani, M. Effect of Chain Extender Length on Gas Permeation Properties of Polyurethane Membranes. Iranian Polymer Journal 17(6) (2008): 431-440.

[53] Alfani, R., Iannace, S., and Nicolais, L. Synthesis and Characterization of Starch-Based Polyurethane Foams. Journal of Applied Polymer Science 68 (1998): 739-745.

[54] NEFF, R., ADEDEJI, A., MACOSKO, C.W., and RYAN, A.J. Urea Hard Segment Morphology in Flexible Polyurethane Foam. Journal of Polymer Science Part B 36 (1998): 573-581.

[55] J., B. and H.G., K. Structure of the hard segments in polyurethane elastomers. Polymer : the international journal for the science and technology of polymers. (1960).

[56] A., T. Reactions catalysted by enzyme. in *Applied biocatalyst*. 2005, Britisth Library cataloguing: Taylor & Fransis e-Library.

APPENDIX

APPENDIX A

DATA OF ANOVA ANLYSIS

ASSUMPTIONS

1. $H_0 = \mu_1 = \mu_2 = \mu_3 = \mu_i$

2. $P^* = 0.05$

CASE 1. $P > 0.05$ ⇨ Accept

2. $P < 0.05$ ⇨ Deny

Table A.1 The significant (P) value of ANOVA analysis

Times (days)	Sample of HDI	P	Sample of MDI	P
DAY-7	HEG0-HHDO10	0.005	MEG0-MHDO30	0.000
DAY-15	HEG0-HHDO10	0.000	MEG0-MHDO30	0.000
DAY-30	HEG0-HHDO10	0.000	MEG0-MHDO30	0.000
	HEG0-HEG30	0.005	MEG0-MEG30	0.000
	HBDO0-HBDO30	0.000	MBDO0-MBDO30	0.756
	HHDO0-HHDO30	0.001	MHDO0-MHDO30	0.000
	HEG10/HBDO10/ HHDO10	0.122	All PU foam except MHDO0 and MHDO10	0.569
	HEG0/HEG30/HBDO0/ HBDO30/HHDO0	0.013	MHDO0/MHDO10	0.006

HDI ISOCYANATE

At Days-7 for all sample with HDI isocyanate

One-way ANOVA: HEG0, HEG10, HEG30, HBDO0, HBDO10, HBDO30, HHDO0, HHDO10

```
Source  DF     SS     MS     F      P
Factor   7  5.840  0.834  4.73  0.005
Error   16  2.822  0.176
Total   23  8.662
S = 0.4199   R-Sq = 67.42%   R-Sq(adj) = 53.17%
```

At Days-15 for all sample with HDI isocyanate

One-way ANOVA: HEG0, HEG10, HEG30, HBDO0, HBDO10, HBDO30, HHDO0, HHDO10

```
Source  DF      SS     MS      F      P
Factor   7  213.49  30.50  14.26  0.000
Error   16   34.23   2.14
Total   23  247.73
S = 1.463   R-Sq = 86.18%   R-Sq(adj) = 80.14%
```

At Days-30 for all sample with HDI isocyanate

One-way ANOVA: HEG0, HEG10, HEG30, HBDO0, HBDO10, HBDO30, HHDO0, HHDO10

```
Source  DF       SS      MS      F      P
Factor   7  1031.55  147.36  29.77  0.000
Error   16    79.20    4.95
Total   23  1110.76
S = 2.225   R-Sq = 92.87%   R-Sq(adj) = 89.75%
```

At Days-30 for the sample with EG chain extenders

One-way ANOVA: HEG0, HEG10, HEG30

```
Source  DF      SS     MS      F      P
Factor   2  170.19  85.09  14.91  0.005
Error    6   34.23   5.71
Total    8  204.42
S = 2.389   R-Sq = 83.25%   R-Sq(adj) = 77.67%
```

At Days-30 for the sample with BDO chain extenders

One-way ANOVA: HBDO0, HBDO10, HBDO30

```
Source  DF      SS      MS      F      P
Factor   2  405.37  202.69  53.78  0.000
Error    6   22.61    3.77
Total    8  427.99
S = 1.941   R-Sq = 94.72%   R-Sq(adj) = 92.96%
```

At Days-30 for the sample with HDO chain extenders

One-way ANOVA: HHDO0, HHDO10

```
Source  DF      SS      MS      F      P
Factor   1  399.80  399.80  71.53  0.001
Error    4   22.36    5.59
Total    5  422.16
S = 2.364   R-Sq = 94.70%   R-Sq(adj) = 93.38%
```

At Days-30 for the sample with 10% of PPG contents

One-way ANOVA: HEG10, HBDO10, HHDO10

```
Source  DF     SS     MS     F      P
Factor   2  42.80  21.40  3.04  0.122
Error    6  42.20   7.03
Total    8  84.99
S = 2.652   R-Sq = 50.35%   R-Sq(adj) = 33.80%
```

At Days-30 for the sample with 0% and 30% of PPG contents

One-way ANOVA: HEG0, HEG30, HBDO0, HBDO30, HHDO0

```
Source  DF      SS     MS     F      P
Factor   4   82.11  20.53  5.55  0.013
Error   10   37.01   3.70
Total   14  119.11
S = 1.924   R-Sq = 68.93%   R-Sq(adj) = 56.50%
```

MDI ISOCYANATE

At Days-7 for all sample with MDI isocyanate

One-way ANOVA: MEG0, MEG10, MEG30, MBDO0, MBDO10, MBDO30, MHDO0, MHDO10, MHDO30

```
Source  DF       SS      MS      F      P
Factor   8  1800.64  225.08  58.63  0.000
Error   18    69.10    3.84
Total   26  1869.74
S = 1.959   R-Sq = 96.30%   R-Sq(adj) = 94.66%
```

At Days-15 for all sample with MDI isocyanate

One-way ANOVA: MEG0, MEG10, MEG30, MBDO0, MBDO10, MBDO30, MHDO0, MHDO10, MHDO30

```
Source  DF      SS      MS      F      P
Factor   8  821.00  102.63  15.83  0.000
Error   18  116.69    6.48
Total   26  937.69
S = 2.546   R-Sq = 87.56%   R-Sq(adj) = 82.03%
```

At Days-30 for all sample with MDI isocyanate

One-way ANOVA: MEG0, MEG10, MEG30, MBDO0, MBDO10, MBDO30, MHDO0, MHDO10, MHDO30

```
Source  DF       SS      MS      F      P
Factor   8  2099.83  262.48  28.16  0.000
Error   18   167.80    9.32
Total   26  2267.64
S = 3.053   R-Sq = 92.60%   R-Sq(adj) = 89.31%
```

At Days-30 for the sample with EG chain extenders

One-way ANOVA: MEG0, MEG10, MEG30

```
Source  DF      SS      MS      F      P
Factor   2  7.2810  3.6405  41.99  0.000
Error    6  0.5202  0.0867
Total    8  7.8011
S = 0.2944   R-Sq = 93.33%   R-Sq(adj) = 91.11%
```

At Days-30 for the sample with BDO chain extenders

One-way ANOVA: MBDO0, MBDO10, MBDO30

```
Source  DF     SS    MS     F      P
Factor   2   10.4   5.2  0.29  0.756
Error    6  106.1  17.7
Total    8  116.5
S = 4.206   R-Sq = 8.90%   R-Sq(adj) = 0.00%
```

At Days-30 for the sample with HDO chain extenders

One-way ANOVA: MHDO0, MHDO10, MHDO30

```
Source  DF      SS     MS      F      P
Factor   2  1282.3  641.2  62.92  0.000
Error    6    61.1   10.2
Total    8  1343.5
S = 3.192   R-Sq = 95.45%   R-Sq(adj) = 93.93%
```

At Days-30 for the sample with excepting MHDO0 and MHDO10

One-way ANOVA: MEG0, MEG10, MEG30, MBDO0, MBDO10, MBDO30, MHDO30

```
Source  DF      SS    MS     F      P
Factor   6   37.74  6.29  0.82  0.569
Error   14  106.74  7.62
Total   20  144.48
S = 2.761   R-Sq = 26.12%   R-Sq(adj) = 0.00%
```

At Days-30 for the sample between MHDO0 and MHDO10

One-way ANOVA: MHDO0, MHDO10

```
Source  DF     SS     MS      F      P
Factor   1  442.0  442.0  28.95  0.006
Error    4   61.1   15.3
Total    5  503.0
S = 3.907   R-Sq = 87.86%   R-Sq(adj) = 84.83%
```

APPENDIX B
COMPRESSIVE STRENGTH CALCULATIONS

The compressive strength and the young's modulus was calculated by this **equation 4.1**.

$$\mathrm{E} = \frac{\sigma}{\varepsilon} = \frac{\mathrm{F/A}}{\Delta \mathrm{L/L}} \qquad (4.1)$$

Where, E is The Young's modulus (kPa)

F is the force exerted on an object under tension (N);

A is the initial cross-sectional area through PU foam which the force is applied (mm^2);

ΔL is the amount by which the length of the object changes (mm);

L is the initial length of the PU foam (mm).

For example of HEG0

Load was -1.524 N/mm^2 (1 N/mm^2 =1 MPa)

The compressive strength 50% was -5 mm

The surface area (A) is 100 mm^2

The compressive strength: σ = F/A

= (1.524 N)/ (100 mm^2)

= 0.01524 MPa = 15.24 kPa

The Young's modulus:

From $$\mathrm{E} = \frac{\sigma}{\varepsilon} = \frac{(-1.524\ \mathrm{N})/100\ \mathrm{mm}^2}{-5\ \mathrm{mm}/10\mathrm{mm}}$$

E = 0.03048 MPa = 30.48 kPa

APPENDIX C
ISOCYANATE CALCULATION

The amount of isocyanate that was used in the synthesis of PU foam was calculation as following with **equations C.1**.

$$R_{\text{-NCO/-OH}}=\frac{\dfrac{\text{HDI (g)}\times 2}{168.02}}{\dfrac{\text{PCL(g)}\times 2}{2000}+\dfrac{\text{PPG(g)}\times 2}{2000}+\dfrac{\text{CE(g)}\times 2}{M_{CE}}+\dfrac{\text{Water(g)}\times 2}{18}} \qquad \text{(C.1)}$$

For example of HEG0:

The amount of PCL = 95 g The amount of PPG = 0 g

The amount of EG chain extender = 5 g The amount of Water = 1 g

Molecular weight of EG = 62.07 g/mol

$R_{\text{-NCO/-OH}}$ = 1.0

From this equation

$$R_{\text{-NCO/-OH}}=\frac{\dfrac{\text{HDI (g)}\times 2}{168.02}}{\dfrac{\text{PCL(g)}\times 2}{2000}+\dfrac{\text{PPG(g)}\times 2}{2000}+\dfrac{\text{CE(g)}\times 2}{M_{CE}}+\dfrac{\text{Water(g)}\times 2}{18}}$$

$$1.0=\frac{\dfrac{\text{HDI (g)}\times 2}{168}}{\dfrac{0\times 2}{2000}+\dfrac{95\times 2}{2000}+\dfrac{5\times 2}{62.07}+\dfrac{1\times 2}{18}}$$

HDI = 30.80 g

VITA

Miss Mutitaporn Pimdeed was born in 22nd August, 1990 in Khonkaen, Thailand. I finished high school from Kaennakhon Witthayalai School, khonkaen in 2008 and received bachelor’s degree in Chemical Engineering from the Department of Chemical Engineering, Faculty of Engineering, Khonkaen University, Khonkaen, Thailand in 2013.