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ปีการศึกษา 2557

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ALKANOLAMINE COMPLEXES

Miss Wannisa Jitaree

จุฬาลงกรณ์มหาวิทยาลัย
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A Thesis Submitted in Partial Fulfillment of the Requirements
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วรรณิศา จิตต์อารีย์ : การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-แอลคานอลามีน (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ALKANOLAMINE COMPLEXES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.นวลพรรณ จันทรศิริ, 100 หน้า.

งานวิจัยนี้เป็นการสังเคราะห์ตัวเร่งปฏิกิริยาชนิดใหม่ที่ไม่มีกลิ่นเหม็น และช่วยลดปริมาณการเกิดไอระเหยจากสารประกอบอินทรีย์ที่เกิดขึ้นจากกระบวนการเตรียมโฟมพอลิยูรีเทนแบบแข็ง การสังเคราะห์ตัวเร่งปฏิกิริยาจากปฏิกิริยาระหว่างโลหะแอซิเทตกับแอลคานอลามีนเกิดเป็นสารประกอบเชิงซ้อนโลหะ-แอลคานอลามีน เพื่อนำสารประกอบเชิงซ้อนโลหะนี้มาใช้เป็นตัวเร่งปฏิกิริยาสำหรับการเตรียมโฟมพอลิยูรีเทนแบบแข็ง โลหะแอซิเทตที่ใช้ คือ คอปเปอร์แอซิเทตและซิงก์แอซิเทต แอลคานอลามีนที่ใช้ คือ เอทานอลามีนและไดเอทานอลามีน พิสูจน์เอกลักษณ์ของสารประกอบเชิงซ้อนโลหะ-แอลคานอลามีนโดยใช้ยูวี-วิซิเบิลสเปกโทรสโกปี อินฟราเรดสเปกโทรสโกปี และแมสสเปกโทรเมตรี นำสารประกอบเชิงซ้อนโลหะ-แอลคานอลามีนมาใช้เป็นตัวเร่งปฏิกิริยาในการเตรียมโฟมพอลิยูรีเทนแบบแข็ง ศึกษาเวลาที่ใช้ในการเกิดปฏิกิริยาของการเกิดโฟม 4 ช่วง คือ เวลาที่สารผสมเป็นครีม เวลาที่สารผสมเป็นเจล เวลาที่ผิวหน้าของโฟมไม่เกาะติดวัสดุสัมผัส และเวลาที่โฟมหยุดฟู ศึกษาความสมบูรณ์ของการเกิดปฏิกิริยาพอลิเมอไรเซชันโดยใช้อินฟราเรดสเปกโทรสโกปี และคำนวณหาเปอร์เซนต์การเกิดปฏิกิริยาของไอโซไซยาเนต เปรียบเทียบผลการทดลองที่ได้กับไดเมทิลไซโคลเฮกซิลามีน ซึ่งเป็นตัวเร่งปฏิกิริยาที่ใช้ในอุตสาหกรรมการเตรียมโฟมพอลิยูรีเทนแบบแข็ง จากผลการทดลองพบว่า สารประกอบเชิงซ้อนคอปเปอร์-เอทานอลามีน เร่งปฏิกิริยาการเกิดโฟมได้ดีเทียบเท่ากับไดเมทิลไซโคลเฮกซิลามีน โฟมที่เตรียมด้วยสารประกอบเชิงซ้อนคอปเปอร์-เอทานอลามีน มีความหนาแน่นของโฟม และมีความสามารถทนทานต่อแรงอัดเท่ากับ 43 kg/m^3 และ 362 kPa ตามลำดับ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5572099923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: METAL-ALKANOLAMINE / ETHYLENE GLYCOL / RIGID POLYURETHANE FOAM / CATALYST

WANNISA JITAREE: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ALKANOLAMINE COMPLEXES. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 100 pp.

In this research, we developed new catalysts which have no odor and have less amount of volatile organic compound (VOC) in the rigid polyurethane foam preparation process. The catalysts were synthesized from the reaction between metal acetate and alkanolamine to give metal-alkanolamine complexes. These complexes were used as catalysts in the preparation of rigid polyurethane foams. Metal acetates employed were copper acetate and zinc acetate. Alkanolamine employed were ethanolamine and diethanolamine. UV-Vis spectroscopy, FTIR spectroscopy and mass spectrometry were used to characterize the metal-alkanolamine complexes. Rigid polyurethane foams were prepared by using metal-alkanolamine complexes as catalysts. The reaction times of the foam formation, namely cream time, gel time, tack-free time and rise time were studied. The completion of polymerization reaction was studied by using FTIR spectroscopy and isocyanate conversion was calculated. The results were compared with those from dimethylcyclohexylamine, which is a commercial catalyst used in the preparation of rigid polyurethane foam. From the result, the copper-ethanolamine complex rendered comparable catalytic activity to dimethylcyclohexylamine. Density and compressive strength of polyurethane foam catalyzed by copper-ethanolamine complex was 43 kg/m^3 and 362 kPa, respectively.

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Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
Academic Year:	2014		

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Finally, I would like to express my deepest gratitude to my lovely family, especially my mother, my father, my sister and my friends, who give their love, encouragement and care to me and always stand beside me.

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LIST OF ABBREVIATIONS

%	percentage
ε	molar absorptivity
ATR-IR	attenuated total reflectance-infrared
acac	acetylacetonate
CFCs	chlorofluorocarbons
cm	centimeter
cm^{-1}	wavenumber
°C	degree Celsius
DBTDL	dibutyltin dilaurate
DEA	diethanolamine
DMCHA	N,N-dimethylcyclohexylamine
EA	ethanolamine
EG	ethylene glycol
en	ethylenediamine
FTIR	Fourier transform infrared
g	gram
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
kg	kilogram
kV	kilovolt
M	metal
$M(OAc)_2$	metal acetate
m^3	cubic meter
MDI	4,4′-methane diphenyl diisocyanate
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mmol	millimole

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NCO	isocyanate
OH	hydroxyl
OHV	hydroxyl value
pbw	parts by weight
PIR	polyisocyanurate
PMDI	polymeric 4,4′-methane diphenyl diisocyanate
PU	polyurethane
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
ref	reference
sec	second
SEM	scanning electron microscopy
Sn Oct	stannous octoate
t	time
TDI	toluene diisocyanate
TEDA	triethylenediamine
T_{max}	maximum core temperature
UV-Vis	ultraviolet-visible

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CHAPTER I
INTRODUCTION

Rigid polyurethane foam (RPUR foam) is widely used in many industries such as building construction, thermal insulation, transportation, packaging and refrigeration because it was light in weight, low thermal conductivity, good mechanical resistance and strength at low density.

RPUR foam can be prepared by a two-step method. In the first step, all of materials, such as polyol, surfactant, catalyst and blowing agent are mixed in a paper cup until homogeneous. In the second step, isocyanate is added into the mixture. The main three reactions of polyurethane foams leading to polyurethane and polyisocyanurate are (i) gelling reaction, which is the reaction between isocyanate and hydroxyl groups to form urethane functionality, (ii) blowing reaction, which is the reaction between isocyanate groups and blowing agent (water) to release carbon dioxide gas and (iii) trimerization reaction, which is the reaction of three isocyanate groups to form isocyanurate.

A catalyst is an important component for the foaming reaction. The reaction cannot be completed without catalysts because the reaction between isocyanate and hydroxyl groups is slow. Tertiary amine and organometallic compounds, such as dibutyltin dilaurate (DBTDL), N,N-dimethylcyclohexylamine (DMCHA), pentamethyldiethylenetriamine (PMDETA) and dibutyltin mercaptide, are used as catalysts in the industrial manufacturing of polyurethane foam because of their excellent catalytic activity. However, amine catalysts cause odor problem during the preparation of RPUR foam. Therefore, this research developed a new catalyst as metal-alkanolamine complexes which do not have odor for the preparation of RPUR foams.

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Objectives

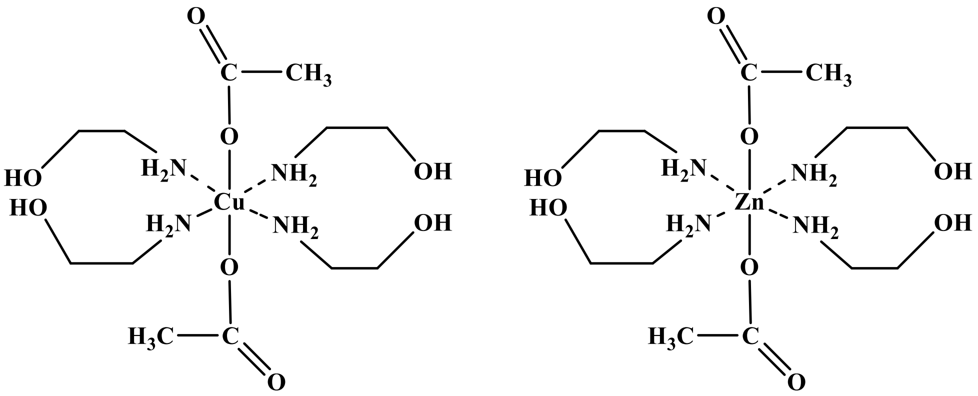
The objective of this research is focused on the preparation of rigid polyurethane foam catalyzed by metal-alkanolamine complexes. It was expected that the synthesized metal-alkanolamine complexes would have no odor while having good solubility and good catalytic activity. Reaction times during RPUR foam preparation, physical and mechanical properties of RPUR foams were investigated.

Scope of the research

The scopes of this research were to prepare RPUR foams using metal-alkanolamine complexes as catalysts. The experiment was divided into 2 steps. The first step was synthesis of metal-alkanolamine complexes from metal acetate and alkanolamine. Metal acetates employed were copper acetate [$Cu(OAc)_2$] and zinc acetate [$Zn(OAc)_2$]. Alkanolamines employed were ethanolamine (EA) and diethanolamine (DEA). The obtained catalysts were copper-ethanolamine complex [$Cu(OAc)_2(EA)_4$], zinc-ethanolamine complex [$Zn(OAc)_2(EA)_4$], copper-diethanolamine complex [$Cu(OAc)_2(DEA)_4$] and zinc-diethanolamine complex [$Zn(OAc)_2(DEA)_4$] (Schemes 1.1). UV-visible spectroscopy, FTIR spectroscopy and mass spectrometry were used to characterize metal-alkanolamine complexes.

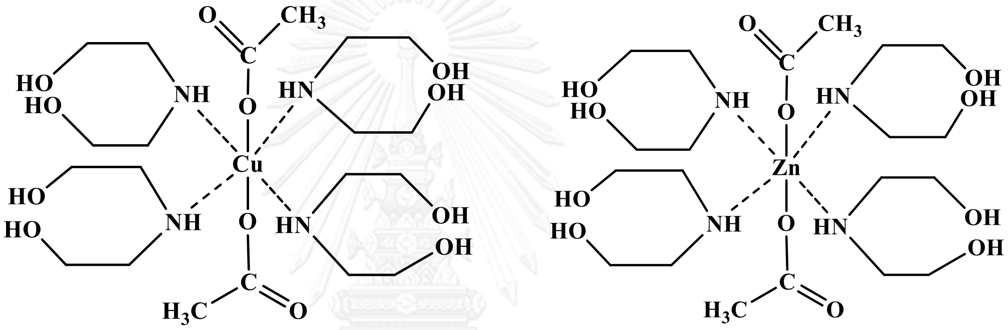
In the second step, RPUR foams were prepared using metal-alkanolamine complexes as catalysts. The reaction times during the foam rising were recorded, namely gel time, cream time, rise time and tack free time. FTIR spectroscopy was used to characterize RPUR foams. Physical and mechanical properties of RPUR foams were investigated using scanning electron microscopy (SEM) and compression testing.

Catalyst types, amount of catalyst and blowing agent were varied. The obtained results in the preparation of RPUR foam catalyzed by metal-alkanolamine complexes were compared with those catalyzed by DMCHA, which is a commercial reference catalyst.



Copper-ethanolamine complex
$[Cu(OAc)_2(EA)_4]$

Zinc-ethanolamine complex
$[Zn(OAc)_2(EA)_4]$



Copper-diethanolamine complex
$[Cu(OAc)_2(DEA)_4]$

Zinc-diethanolamine complex
$[Zn(OAc)_2(DEA)_4]$

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Scheme 1.1 Structures of the metal-alkanolamine complexes

CHAPTER II

THEORY AND LITERATURE REVIEW

Polyurethane foams are prepared using a polyol containing on average of two or more hydroxyl groups (-OH groups) per molecule with an isocyanate compound containing two or more isocyanate groups (-NCO groups) per molecule. Polyols and isocyanate are the main components and other components such as catalyst, surfactant and blowing agent are used. The properties of PU foams are greatly influenced by the types of polyols and isocyanates. The PU foams are divided into three types, rigid, semi-rigid and flexible foams.

Rigid polyurethane (RPUR) foam is one of the most versatile polymers used in many industries such as building engineering applications, insulation to packaging and commercial refrigeration because of their good mechanical resistance, light weight and low thermal conductivity [1, 2].

2.1 Raw materials

The main ingredients to make PU foams are polyols and isocyanate to form urethane linkages. Other materials are added to help processing the foams or to change the properties of foams. The chemical and physical characteristics, morphology and molecular size of these compounds influence the polymerization reaction as well as final properties of rigid polyurethane foams [3].

2.1.1 Isocyanate

Isocyanate used to prepare PU foam must have two or more isocyanate groups per molecule. The most common isocyanate used is aromatic isocyanate such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) in an oligomeric type because the aromatic isocyanates have high reactivity in foaming reactions while the aliphatic isocyanates react slowly with hydroxyl groups (-OH groups) [4, 5]. Variation of the types of isocyanate used affects the properties of PU foams [6].

2.1.1.1 Toluene diisocyanate (TDI)

Toluene diisocyanate (TDI) is an colorless organic compound with the formula $CH_3C_6H_3(NCO)_2$. TDI is produced by phosgenation of diaminotoluene, which is obtained by the reaction of nitrotoluene. Two of the six possible isomers are commercially important; 2,4-TDI and 2,6-TDI in mole ratio of 80:20 or 65:35. Its main use is to produce flexible polyurethane foams [5, 6]. Toluene diisocyanate isomers are shown in Figure 2.1.

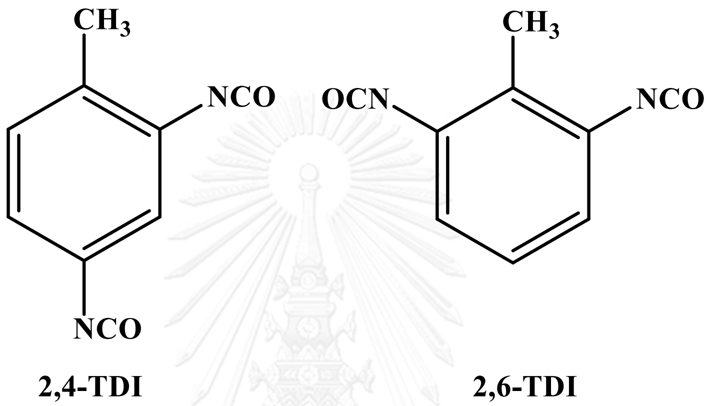

Figure 2.1 Toluene diisocyanate isomers

TDI has high vapor pressure and toxic hazard since it causes skin irritation [4]. Therefore, methylene diphenyl diisocyanate (MDI) is used instead because it has lower volatility than TDI.

2.1.1.2 Methylene diphenyl diisocyanate (MDI)

Methylene diphenyl diisocyanate (MDI) is obtained from the reaction between aniline and formaldehyde in acid-catalyzed reaction [7]. Its functionality is varied between 2.3 to 3.0. Both types of MDI; monomeric MDI (or pure MDI) and polymeric MDI (or PMDI) are obtained as products [6].

Monomeric MDI (or pure MDI) (Figure 2.2) consists almost of 4,4′-isomer and less of 2,4′- isomer and is mainly used for elastomer and coating [6]. Polymeric MDI (Figure 2.3) differently consists of various ratios and form of isomer; 55% of 4,4'-diisocyanate and 2,4'-diisocyanate, 20-25% of triisocyanate and the rest is 2,2′-diisocyanate. Polymeric MDI is liquid with yellow to dark brown color at room temperature. Its viscosity proportionally depends on its polymeric isocyanate percentage and molecular weight. Polymeric MDI possesses higher functionality compared to that of monomeric MDI. This advantage of polymeric MDI is functionality provides itself a preference for forming a cross-linked, rigid, and high aromatic property which is the best suited for polyurethane foam application. Additionally, due to that the variation of polymeric MDI is functionality, composition, and chemical structure, polymeric MDI synthesized polyurethane types and properties are also varied. Besides, MDI synthesized polyurethanes is the fastest in becoming yellow when exposing to light among the commercial isocyanate due to its vulnerability to radical-oxidize process which results in yellow chromophore of a conjugated quinine-imide structure [8].

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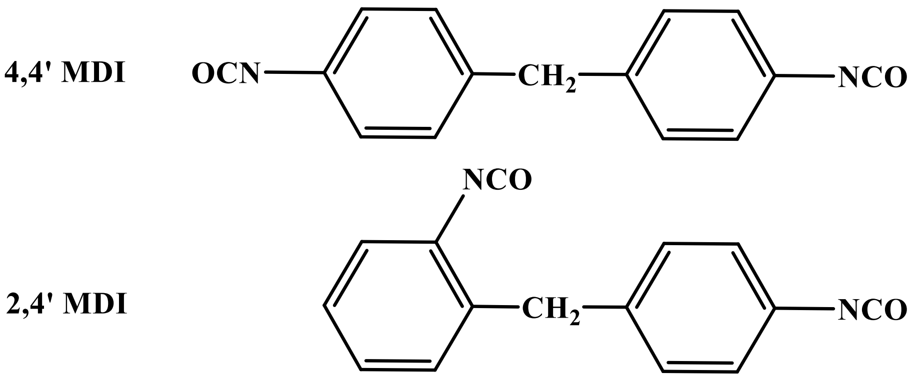
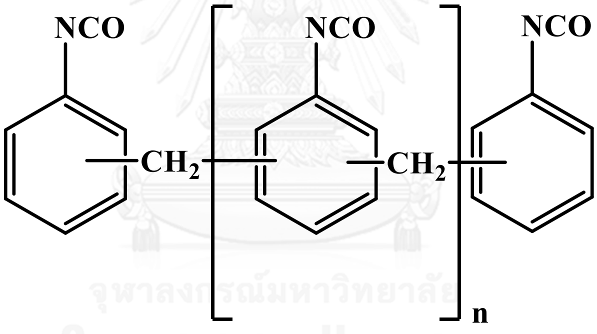


Figure 2.2 Isomeric structures of monomeric MDI



Polymeric MDI

Figure 2.3 Structure of a polymeric MDI

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2.1.2 Polyols

The polyols used for the preparation of RPUR foams are divided into two types, polyether and polyester polyols. Commonly, polyols for rigid foam have functionality 2.5-8.0, molecular weight of 150-1000 g/mol and hydroxyl value 250-1000 mgKOH/g [9]. Polyether polyols give softer, more resilient foams with better hydrolysis resistance than polyester polyols, while the polyester polyols give greater tensile strength and better resistance to oil, oxidation and solvents than polyether polyols [10]. Lower molecular weight and higher functionality initiators such as sorbital, sucrose and glycerol (some polyol characteristics are shown in Table 2.1) are used in the preparation of RPUR foams, while the higher molecular weight and lower functionality polyols are used in the preparation of flexible polyurethane (FPUR) foams. Because of RPUR foams need the higher degree of crosslinking which contributes to the stiffness of polymer. It is essential to utilize various polyols to prepare polyurethane with requisite properties.

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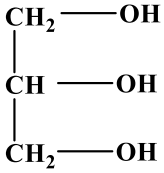
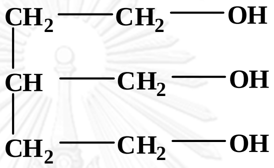
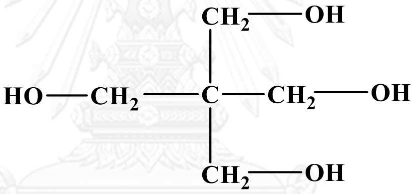
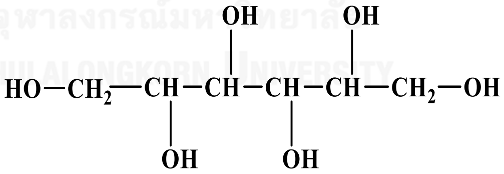
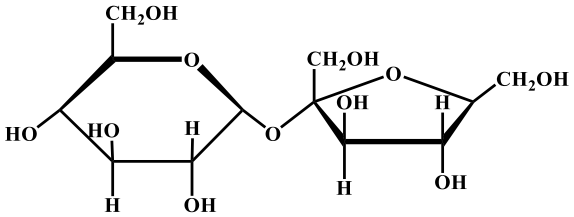
Table 2.1 Functionality of some common polyols [5]

Hydroxylated compound	Chemical structure	Functionaliy
Ethylene glycol (EG)	$HO-CH_2-CH_2-OH$	**2**
Glycerol	 $\begin{array}{l} CH_2-OH \\ \vert \\ CH-OH \\ \vert \\ CH_2-OH \end{array}$	**3**
Trimetylol propane (TMP)	 $\begin{array}{l} CH_2-CH_2-OH \\ \vert \\ CH-CH_2-OH \\ \vert \\ CH_2-CH_2-OH \end{array}$	**3**
Pentaerythritol	 $\begin{array}{c} CH_2-OH \\ \vert \\ HO-CH_2-C-CH_2-OH \\ \vert \\ CH_2-OH \end{array}$	**4**
Sorbitol	 $HO-CH_2-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2-OH$	**6**
Sucrose		**8**

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2.1.2.1 Polyether polyols

Polyether polyols are produced by the ring opening of alkylene oxides. Polyether polyols phase are varied between low viscous liquids to solids depending on their molecular weight and chemical structure. Polyether polyols possess a wide range of functionality, and equivalent weight together with lower viscosity results in easier handling and cost effective production [8]. These properties are their advantages compared to those of polyester polyols. On the other hand, polyether polyols possesses lower resistance to oxidation than that of polyester polyols [6]. 90% of RPUR foam is produced from sucrose-based polyether polyols (Figure 2.4) due to those advantages mentioned above.

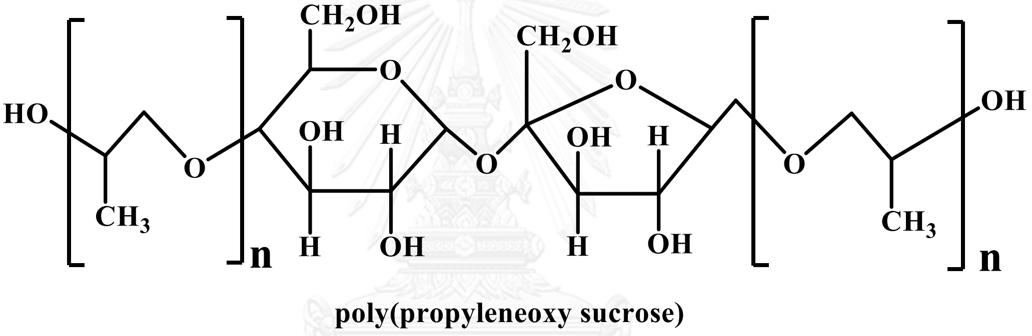

Figure 2.4 Structure of sucrose-based polyether polyol [poly(propyleneoxy sucrose)]

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2.1.2.2 Polyester polyols

Polyester polyols are products of condensation and also step-growth polymerization among diols (and triols) and dicaboxylic acid; adipic acid, sebacic acid and three isomeric phthalic acids. Polyester polyols themselves possess high viscosity and low functionality which leads to difficult-to-handle, low stability, and less cost effective foam product [5]. In addition, development of polyether polyols application is able to provide better dimensional stability with less organic solubility foam product which greatly reduces significance of polyester polyols application. However, those polyester polyols are still needed whenever their superior properties are required.

2.1.3 Surfactants

Silicone surfactants, polydimethylsiloxane (PDMS) backbone and polyethylene oxide-co-propylene oxide (PEO-PPO) are generally used in polyurethane foam production. An example of silicone surfactant is shown in Figure 2.5. They reduce surface tension of liquid mixing components so that polyols-isocynate interface is easy to be emulsified. Silicone surfactants also support a foaming structure at very early stage until polymer network’s cell wall is adequately generated. Importantly, the surfactants significantly stabilize bubbles in a foaming process. The amount of silicone surfactants is in the range of 0.4-2.0% w/w of the additive in a polyol formulation [11].

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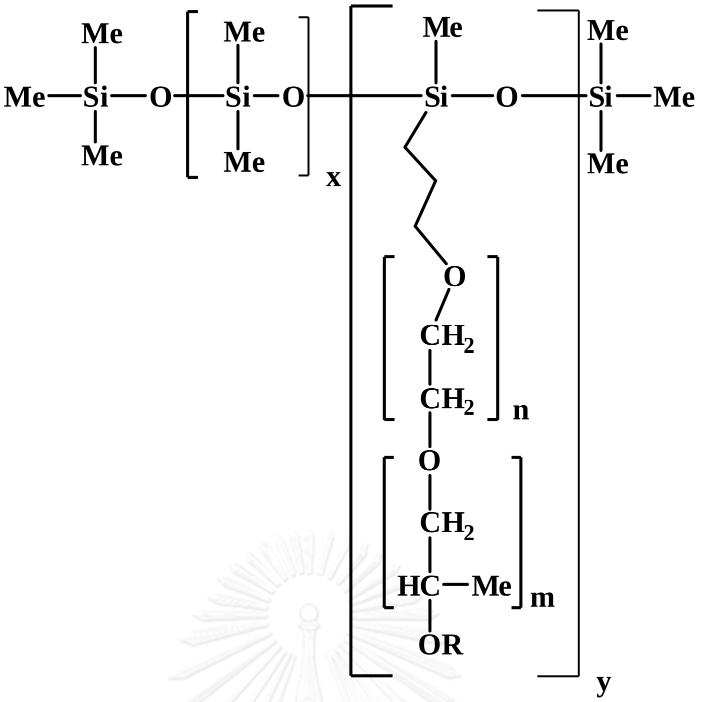

Figure 2.5 An example of silicone surfactant [11]

2.1.4 Blowing agent

Types and contents of blowing agents considerably influence the properties of RPUR foams. Blowing agents for preparation of RPUR foams are divided into two types as physical and chemical blowing agents.

Water is one of chemical blowing ag^{1}ents used for the foaming reaction. Water reacts with isocyanate groups to generate carbon dioxide (CO_2) gas. It has been used since the beginning of the PU foam industry for both rigid and flexible foams. Physical blowing agents are inert liquids and low molecular weight compounds having low boiling points, low toxic hazard, non-flammability and non-reactivity with isocyanate groups [11]. The physical blowing agents used in industry are hydrofluorocarbons (HFCs), chlorofluorocarbons (CFCs), perfluorinated hydrocarbons (PFCs) and hydrochlorofluorocarbons (HCFCs) from which it causes depletion of the ozone layer and thus the use are regulated in many countries. Therefore, water and other type of physical blowing agents such as cyclopentane have replaced such environmentally hazardous blowing agents [12].

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The use of water alone has some disadvantages, e.g. increasing of water amount gives higher reaction exotherm, which is the cause of fire or scorching, system viscosity is high, so the flow ability of foaming systems in the mold becomes worse [6].

Water reacts with isocyanate groups to generate carbon dioxide gas. The amount normally used is 3-5 parts of water per 100 parts of polyol. The reaction between water and isocyanate is exothermic reaction and results to the formation of amine. The blowing agent affects cellular morphology and density of RPUR foams [12].

2.1.5 Catalysts

Catalyst is an important component for RPUR foam preparation. It controls balancing rate of three reactions including (i) the blowing reaction of isocyanate with water (H_2O) to form carbon dioxide gas (CO_2) and polyurea, (ii) the gelling reaction of isocyanate with polyol to form polyurethane and (iii) trimerization of isocyanate. Moreover, types and quantity of the catalysts influences the rate of reaction and the final properties of RPUR foams. Normally, the amount of catalyst used is about 1-4 parts by weight per 100 parts of polyol [13]. The most important catalysts are shown in Table 2.2 and Figure 2.6 [11].

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Table 2.2 Frequently used catalysts in RPUR foams [11]

Catalyst type	**Abbreviation**	**Reaction catalyzed**
Tertiary amines		
Pentamethyldiethylenetriamine	PMDETA	Blowing
Triethylenediamine	TEDA	Gelling
Dimethylcyclohexylamine	DMCHA	Blowing/ Gelling
Alkali metal carboxylates		
Potassium acetate	K Ac	Gelling/ Trimer formation
Potassium octoate	K Oct	Gelling/ Trimer formation
Tin compounds		
Stannous octoate	Sn Oct	Gelling
Dibutyltin dilaurate	DBTDL	Gelling

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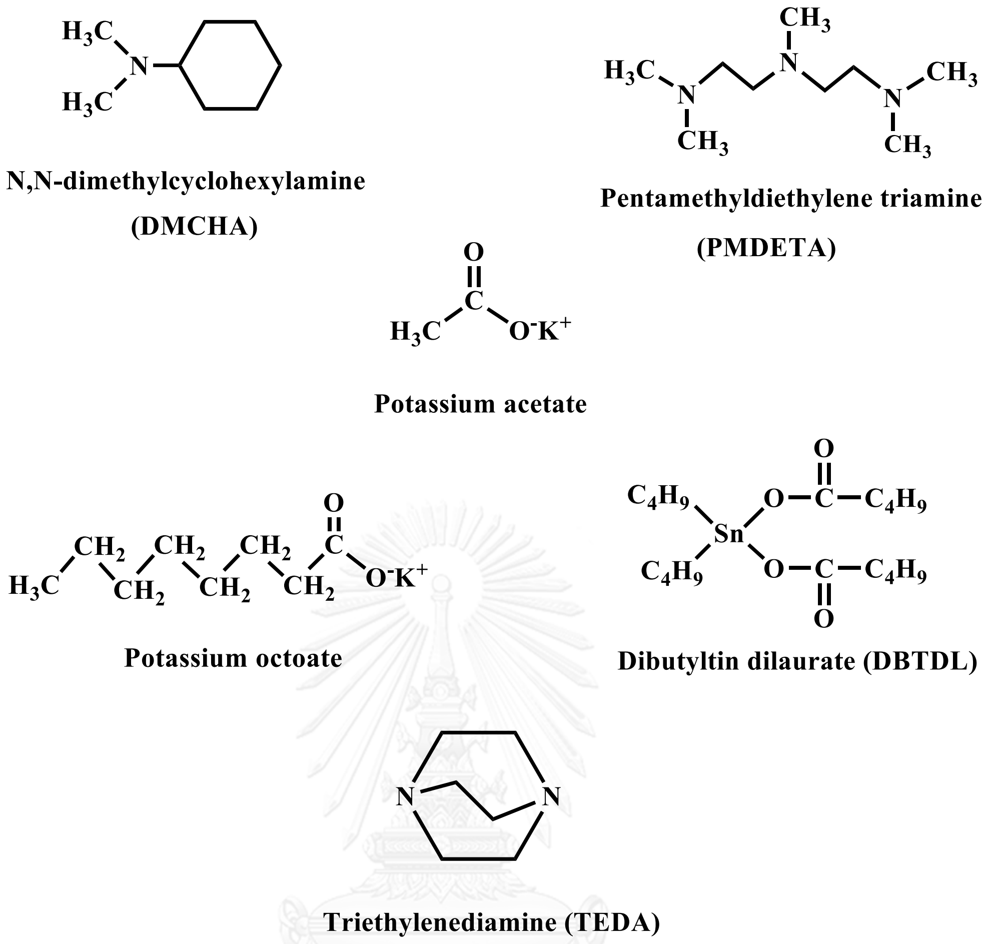

N,N-dimethylcyclohexylamine (DMCHA)

Pentamethyldiethylene triamine (PMDETA)

Potassium acetate

Potassium octoate

Dibutyltin dilaurate (DBTDL)

Triethylenediamine (TEDA)

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Figure 2.6 Commercial catalysts used in RPUR foams

Poor quality of foam is caused by two reasons. First reason, a too strong catalyst promotes excessively the blowing reaction; much of the CO_2 gas will be evolved before sufficient reaction of polyol with isocyanate has occurred. Then, the CO_2 gas will be bubbled out of the formulation, resulting in collapse of the foam. Second reason, a catalyst too strongly promotes the gelling reaction; most of the CO_2 gas will be evolved after a significant degree of polymerization has occurred as a result of high density, broken or poorly defined cells, or other undesirable features.

Commonly, tin complexes are one of the most preferred catalysts that are widely used in this industry. It accelerates mainly the isocyanate-polyol reaction, which is then called “gelling catalyst”. On the other hand, tertiary amine catalysts accelerate mainly the isocyanate-water reaction, which releases CO_2 gas and they are considered as “blowing catalysts”. Furthermore, tertiary amines catalyze both the gelling and blowing reactions but tin catalysts catalyze mainly the isocyanate-polyol reaction [6, 7, 14].

Tertiary amine catalysts have low molecular weight, therefore they have strong odor. Moreover, it releases toxic chemical during foam processing, and residual amine in consumer products is generally undesirable [15].

Tin and tertiary amine catalysts are used in most application, not only to provide the desired balance of blowing and gelling reactions but also to tune these reactions to meet the needs of production equipment [10].

2.2 Catalytic mechanisms

2.2.1 Amine catalysts

Two mechanisms have been proposed for tertiary amine catalysts as follows [16]:

- Baker mechanism

The activation starts by the nitrogen atom of amine using its lone pair of electrons to coordinate to the positive electron charged carbon atom of the isocyanate group. The intermediate then reacts with active hydrogen atom from alcohol to generate a urethane group (Scheme 2.1).

- Farka mechanism [15]

The activation starts by the nitrogen atom of amine coordinating to the proton source (polyols, amine, water). The intermediate then reacts with the isocyanate to generate a urethane group (Scheme 2.2).

Basicity and steric hindrance of nitrogen atom in amine are factors that influence the activity of tertiary amine.

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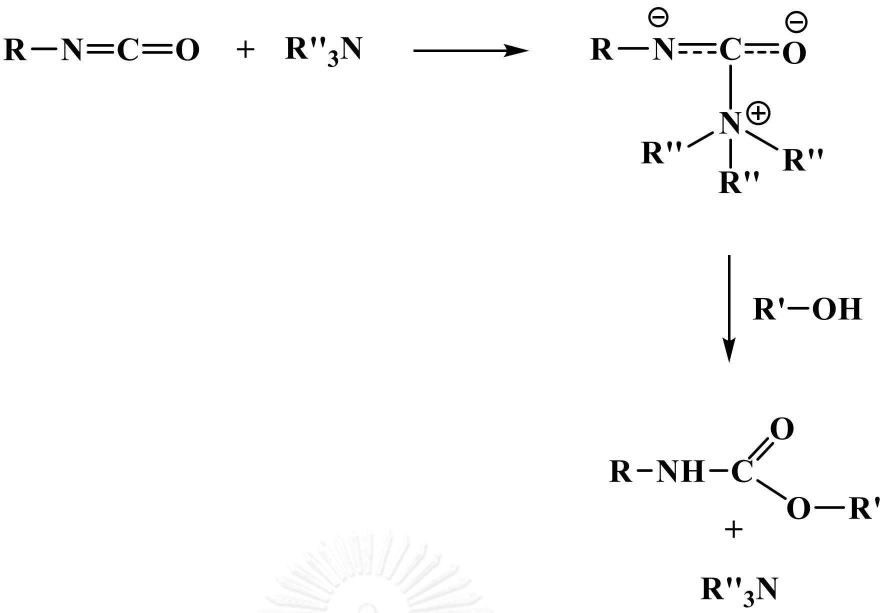
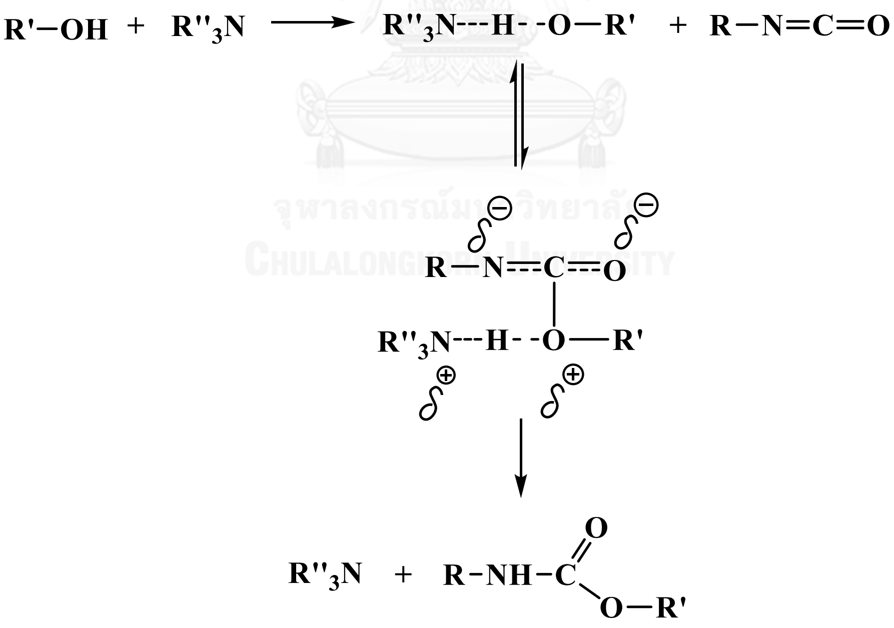


Scheme 2.1 Baker mechanism of amine catalyst



Scheme 2.2 Farka mechanism of amine catalyst

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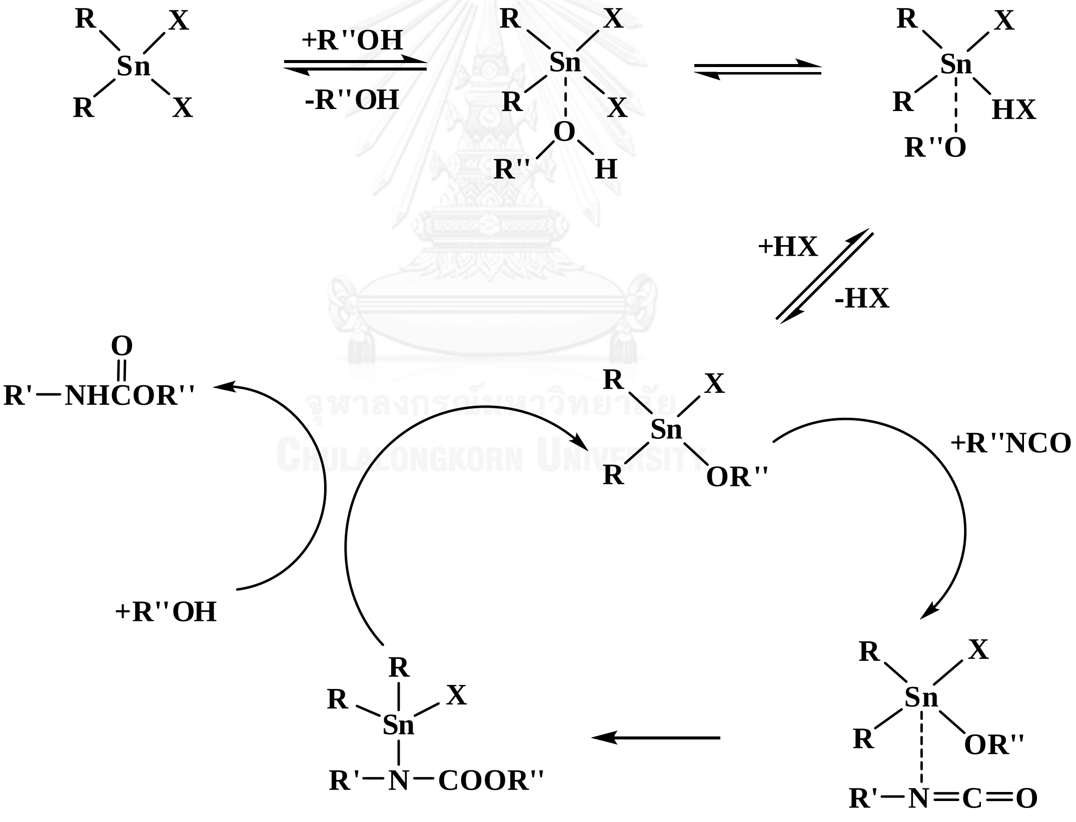
2.2.2 Organometallic catalysts

The proposed catalytic mechanism of tin (IV) catalysts, namely dialkyltin dicarbonate and dialkyltin dialkylthiolate, is shown in Scheme 2.3. The reaction between tin and polyol forms tin alkoxide and then reacts with isocyanate to form a complex. The alkoxide anion transferred onto the coordinate complex affords an N-stannylurethane, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide. Otherwise, tin coordinates to the nitrogen atom of isocyanate activates the electrophilic nature of the carbon. Therefore, hydroxyl group of polyol can attack the isocyanate group easier.



Scheme 2.3 Mechanism of tin (IV) catalyst

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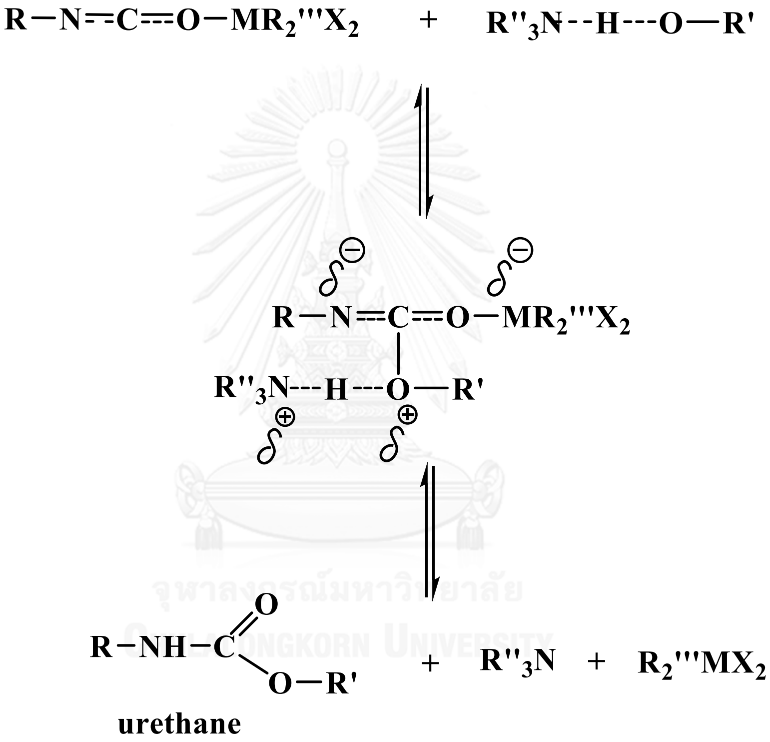
2.2.3 Synergism of metal-amine catalysts

When tin (IV) and amine catalysts are used together, synergism of these two catalysts are observed. The metal coordinates to the oxygen atom of the NCO group to make the carbon more electrophilic. While amine coordinates to the hydrogen atom of the OH group, then it makes the oxygen atom become more nucleophillic. The mechanism of metal-amine synergism is shown in Scheme 2.4.



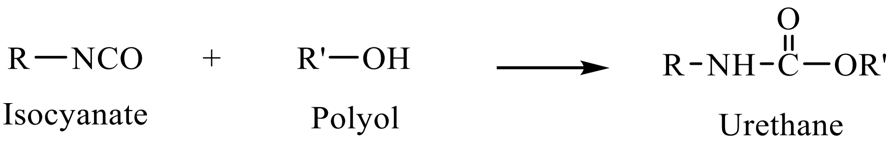
Scheme 2.4 Mechanism of metal-amine synergism

2.3 Basic Chemistry [18]

2.3.1 Primary reaction of isocyanates

2.3.1.1 Reaction with polyol

The reaction between isocyanate with polyol to form a urethane (Equation 2.1).

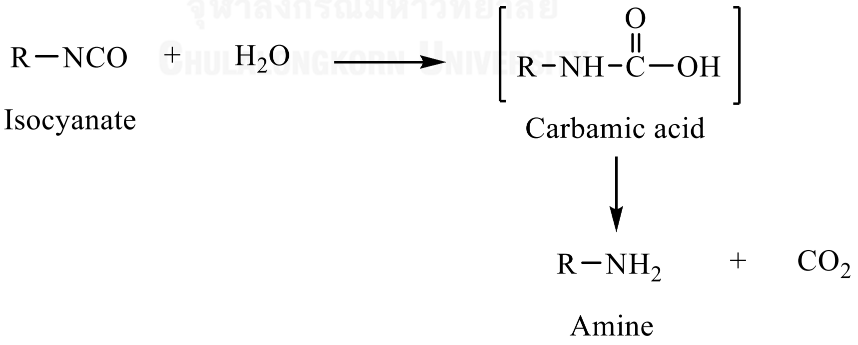


$$\underset{\text{Isocyanate}}{R-NCO} \quad + \quad \underset{\text{Polyol}}{R'-OH} \quad \longrightarrow \quad \underset{\text{Urethane}}{R-NH-\overset{\overset{O}{\|}}{C}-OR'} \qquad [2.1]$$

This reaction is called the "gelling reaction". It must be temperature controlled because it is an exothermic reaction. The chemical structure of isocyanate and polyols affects the rate of polymerization. The catalyst is used to accelerate the reaction rate.

2.3.1.2 Reaction with water

The reaction between isocyanate and water produces unstable carbamic acid, which immediately decomposes into an amine and carbon dioxide. (Equation 2.2). This carbon dioxide gas diffuses into the already present air bubbles. Therefore, this results in a rise of foam [13, 16].



$$\underset{\text{Isocyanate}}{R-NCO} \quad + \quad H_2O \quad \longrightarrow \quad \underset{\text{Carbamic acid}}{\left[R-NH-\overset{\overset{O}{\|}}{C}-OH \right]} \quad \longrightarrow \quad \underset{\text{Amine}}{R-NH_2} \quad + \quad CO_2 \qquad [2.2]$$

This reaction is called a "blowing reaction" because the CO_2 gas produced is used for blowing the foam. The best choice of a catalyst system affects the reaction rate.

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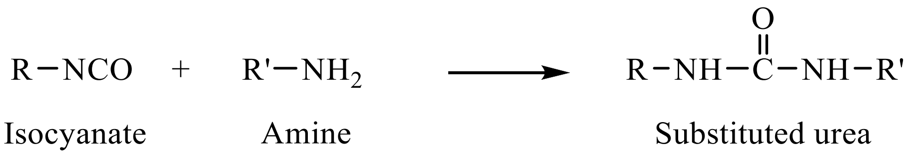
2.3.1.3 Reaction with amines

The reaction between isocyanate and amine to form the urea linkange (Equation 2.3).



$$R{-}NCO \quad + \quad R'{-}NH_2 \longrightarrow R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R' \qquad [2.3]$$

Commonly, the reactions of unhindered isocyanates with primary amines occur about 100-1000 times faster than those with primary alcohols. Therefore, amines are often used as chain-extenders and curing agents in polyurethane manufacture [18].

2.3.2 Secondary reaction of isocyanates

Isocyanate may react, under suitable conditions, with the active hydrogen atoms of urethane and urea linkages from the primary reactions as shown below:

2.3.2.1 Reaction with urethane

The reaction between isocyanate and the hydrogen atom on the nitrogen atom of the urethane linkages to form branched allophanates [6] (Equation 2.4).

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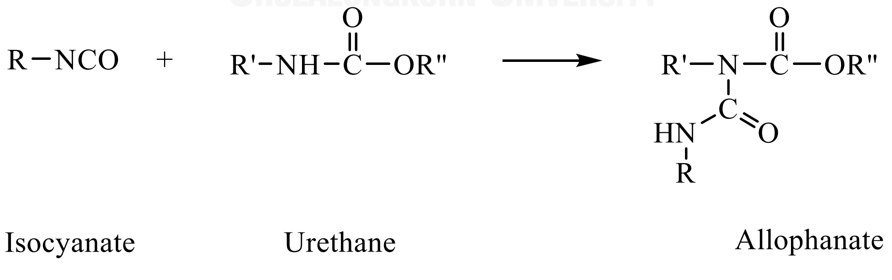
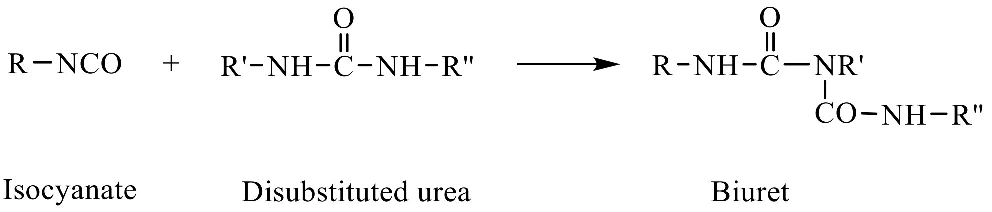


[2.4]

The formation of the allophanate is a high temperature and reversible reaction. The allophanate linkage causes further polymer crosslinking. Furthermore, the typical catalysts used in polyurethane foam formulations do not encourage this reaction. The high internal temperatures of the foam would prefer its immediate decomposition.

2.3.2.2 Reaction with urea

The reaction between isocyanate and hydrogen atom of the disubstituted urea forms branched biuret (Equation 2.5).



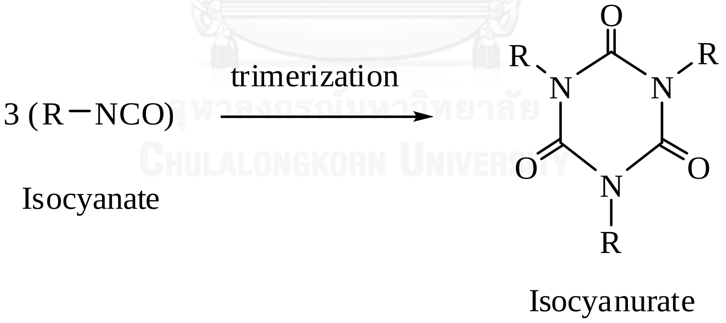
$$R-NCO + R'-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R'' \longrightarrow R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CO-NH-R''}{|}}{N}R'$$

[2.5]

The formation of the allophanates and the biurets in polyurethane is a method of crosslinking the polymer. However, the reaction between isocyanates and urea groups is significantly faster and occur at lower temperatures than that with urethane groups [17].

2.3.2.3 Trimer formation

The trimerization of isocyanate leads to high temperature resistant isocyanurate group [19] (Equation 2.6).



[2.6]

The isocyanate trimer can be formed on heating either aliphatic or aromatic isocyanate. Basic catalysts such as sodium and potassium salts of carboxylic acids used to accelerate this reaction [18].

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2.4 Formulations

The amount of isocyanate needed to react with polyol and other reactive components can be calculated to gain chemically stoichiometric equivalents. This theoretical amount is called “isocyanate index”, which could be adjusted depending on the polyurethane system, properties required, surrounding conditions and scale of production.

$$\text{Isocyanate index} = \frac{\text{actual amount of isocyanate}}{\text{theoretical amount of isocyanate}} \times 100$$

The conventional way of calculating the ratio of the components required for polyurethane manufacture is to calculate the number of part by weight of the isocyanate required to react with 100 parts by weight of polyol and use appropriate amount of hydroxyl additives. The analytical data needed for the calculation are the isocyanate value of the isocyanate and hydroxyl value, residual acid value and water content of the polyol and other reactive additives [4, 18].

Isocyanate value (or isocyanate content) is the weight percentage of reactive -NCO groups:

$$\text{Isocyanate value, \% NCO group} = \frac{42 \times \text{functionality}}{\text{molar mass}} \times 100$$

$$= \frac{4200}{\text{equivalent weight}}$$

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Hydroxyl value (hydroxyl number; OHV)

The hydroxyl value (OHV) or the hydroxyl number of the polyol, is used as a measurement of the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol and is expressed in mg KOH/g of polyol. This may be defined as the weight of KOH in milligrams to the active functions (hydroxyl content) of 1 g of the compound or polymer.

$$\text{Hydroxyl value} = \frac{56.1 \text{ x functionality}}{\text{molar mass}} \text{ x } 1000$$

$$= \frac{56.1}{\text{equivalent weight}} \text{ x } 1000$$

Acid value is also expressed as mgKOH/g of polyol and numerically equal to OHV in isocyanate useage.

Water content; water reacts with two -NCO groups and the equivalent weight of water is thus:

$$\text{Equivalent weight} = \frac{\text{molar mass}}{\text{functionality}} = \frac{18}{2}$$

Isocyanate conversion (α), isocyanate conversion is defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0. Isocyanate conversion can be calculated using ATR-FTIR data:

$$\text{Isocyanate conversion (\%)} = \left[1 - \frac{NCO^{f}}{NCO^{i}}\right] \text{ x } 100$$

NCO^f (Final isocyanate) = the area of isocyanate absorbance peak area at time t

NCO^i (Initial isocyanate) = the area of isocyanate absorbance peak area at time 0

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2.5 Mechanical properties

Compressive properties are the most important mechanical properties for polyurethane foam. Compressive energy absorption characteristic and deformation characteristics of foam mainly depend on density, type of base polymer and the predominance of either open or closed cells.

Closed cell foam deformation involves cell walls bending and bucking, gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rapture as shown in Figure 2.7 [18].

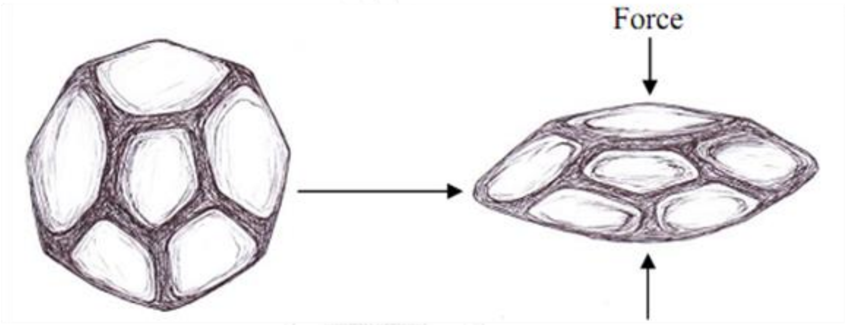

Figure 2.7 Closed cell deformation [18]

Closed cell of rigid polyurethane foams exhibited from very limited to no yielding behavior. Consequently, gas compression and matrix strength play important roles during the mechanical deformation of rigid foams. In addition, cell rupture often occurs during the energy absorption process. The energy absorption characteristics of foam can be represented in term of compression stress-strain curves. Figure 2.8 shows a typical compression stress-train curve of rigid polyurethane foams.

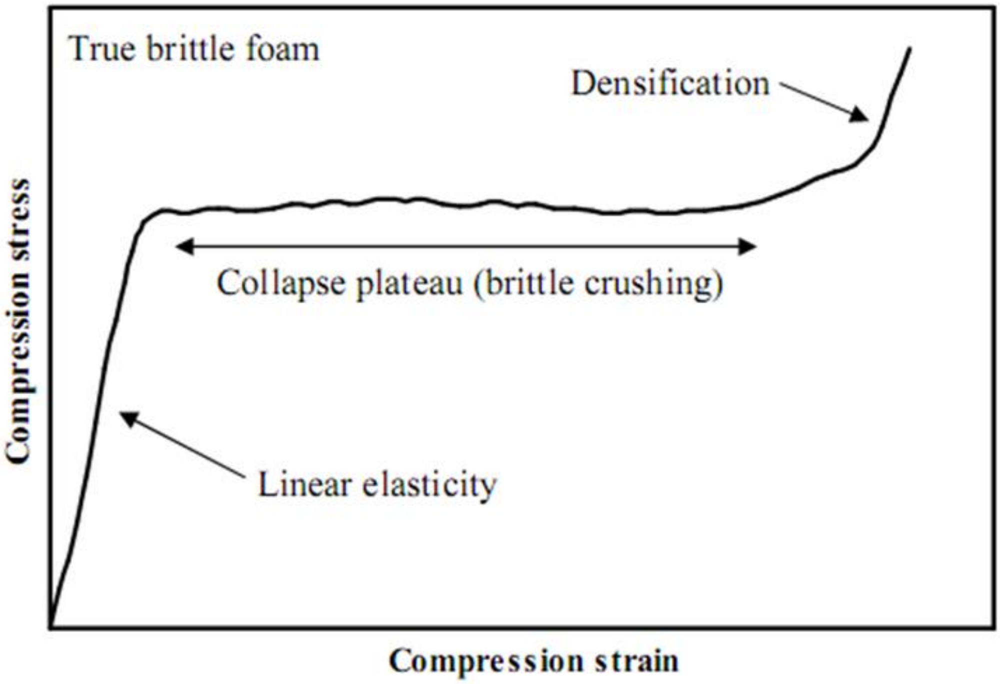

Figure 2.8 Typical compression stress-train curve of rigid polyurethane foams [18]

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For rigid foams, the compression stress-strain curve is divided into three regions; (i) initial linear elasticity, which is controlled by cell wall bending and by cell wall stretching due to the contained gas pressure, (ii) plateau, which is due to collapse of cell wall or in brittle foams and (iii) densification, which occurs as foam density increases.

The compressive strength of rigid cellular polymers is usually reported at some definite deformation (5% or 10%). The compressive strength of rigid polyurethane foam of the foam cell in the direction of foam rise is higher than that in the direction of perpendicular to foam rise [20].

2.6 Literature reviews

A catalyst is an important component in the polyurethane foam industry. The commercial amine catalyst makes the reaction proceed faster but it produces strong amine odor during the manufacturing process. Development of new catalysts with increased catalytic activity and reduces volatile organic compound are interesting research area.

Blank and coworkers [21] studied metal compound catalysts which exhibited increased selectivity for the isocyanate-hydroxyl reaction. They found that zirconium acetyl acetonate was a good catalyst. Zirconium chelates activates the hydroxyl groups and catalyzed the isocyanate-hydroxyl reaction by an insertion mechanism. This reaction is selective and preferred over the isocyanate-water reaction. Moreover, zirconium catalyst is less toxic than dibutyltin dilaurate (DBTDL), which is a commercial catalyst.

The activities of metal-acetyl acetonate [$M(acac)_n$; where M = Mn, Fe, Co, Ni and Cu] and tertiary amine-$M(acac)_n$ catalysts were studied by Inoue and coworkers [22]. The catalytic activity of $M(acac)_n$ was lower than DBTDL because hexamethylene diisocyanate (HDI) was inert in coordination to $M(acac)_n$. When using $M(acac)_n$ together with triethylenediamine (TEDA), TEDA-$Mn(acac)_2$ showed comparable catalytic activity to DBTDL. TEDA-$Mn(acac)_2$ showed good catalytic activity (95% NCO conversion), while other amines exhibited lower catalytic activity (75% NCO conversion).

Sardon and coworkers [23] reported a comparative study of the catalytic activity of tin and zirconium compounds in the polymerization of isophorone diisocyanate based waterborne polyurethanes (WBPU). The results showed that when tin compound was used as a catalyst, the synergistic effect of tin compounds with amines was obtained. Zirconium compound showed a slightly higher catalytic activity than tin compound. In the presence of triethylamine and tin catalyst, the secondary isocyanate group was more reactive than the primary group. For zirconium catalyst, the primary and secondary isocyanate groups showed the same reactivity.

Rothe and coworkers [24] reported that the main sources of volatile organic compound (VOC) were silicone surfactants and amine catalysts. It was found that by using reactive amines, namely dimethylethanolamine and dimethylaminoethoxyethanol (Figure 2.9), the amine emission could be eliminated. The total VOC could be reduced by 50% for TDI- based formulations and by 80% for MDI-based ones. By replacing the standard non-reactive amines by reactive ones, reaction profiles were similar to the reference formulation. The physical foam properties were only slightly affected.

Dimethylaminoethoxyethanol

Dimethylethanolamine

Figure 2.9 Reactive amine catalysts [24]

Ethanolamine (EA) and diethanolamine (DEA) are used in different applications as follows:

Yu and coworkers [25] prepared liquefied wood-based polyurethane (PU) foams by mixing polyethylene glycol liquefied wood of Cryptomeria japonica with 4,4"-diphenylmethane diisocyanate. Glycolysis of foams was conducted by using diethylene glycol, ethylene glycol, and propylene glycol as solvents in the presence of diethanolamine (DEA) as a catalyst. The best condition for glycolysis of liquefied wood-based polyurethane foams was conducted in diethylene glycol with a weight ratio of 0.5/1 at 190 °C.

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Kaushiva and coworkers [26] investigated the influence of concentration of diethanolamine (DEA), a commercially utilized crosslinking agent on the viscoelastic and morphological properties of molded foams. It was found that DEA resided largely in the hard domains and altered their "*para*-crystalline" ordering. These resulted in lower rubbery moduli and lower overall load-bearing properties and the overall numbers of crosslinking points were not increased in the polymer. Thus, the softening occurred because DEA altered the chemical structure of the hard segments, reducing their ability to form the bidentate hydrogen bond which typically increases foam stiffness.

Stirna and coworkers [27] synthesized the polyols from castor oil (CO) with diethanolamine (DEA) and triethanolamine (TEA) for the polymerization of polyurethane and polyurethane foam. Rigid polyurethane foams obtained from CO/DEA and CO/TEA polyols have good compressive and tensile strength properties. Polyurethane foams obtained from CO/TEA polyols showed higher elongation at break and high closed-cell content than those obtained from CO/DEA polyols.

More and coworkers [28] synthesized PVC plasticizer from poly(ethylene terephthalate) and ethanolamine using zinc acetate as a catalyst. It was found that the product obtained completely fused with PVC and the elongation of PVC was increased. Glass transition temperature also decreased with an incorporation of the new plasticizer as compared to virgin PVC.

Humar and coworkers [29] using copper–ethanolamine solutions for impregnating of Norway spruce wood blocks. After impregnation, the specimens were dried at four different temperatures (25, 50, 75 and 103 °C). The results showed that increased temperatures during fixation increased copper leaching. Moreover, ethanolamine did not evaporate from wood.

Kong and coworkers [30] investigated the effect of chain extenders, namely triethanolamine, diethanolamine and glycerol on reaction reactivity, cell structure and mechanical properties of the flame retardant high resilience polyurethane foam. It was found that the foam prepared using diethanolamine showed better process stability and mechanical properties than those prepared from triethanolamine or glycerol.

From the previous work in our research group, Pengjam and coworkers [31] synthesized copper-amine complexes, namely $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$. These metal-amine complexes were prepared from copper acetate [$Cu(OAc)_2$] and aliphatic amines, namely ethylenediamine (en) and triethylenetetramine (trien). The metal-amine complexes were used as the new catalysts in rigid polyurethane (RPUR) foam preparation. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ had very low odor as compared to DMCHA, which is a reference commercial amine catalyst. It was found that $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ showed similar catalytic activity to DMCHA.

To continue our previous work, the scope of this work is the synthesis of metal-alkanolamine complexes as catalysts for RPUR foam. Metal-alkanolamine complexes could be prepared from metal acetates and alkanolamines. Metal acetates employed were copper acetate and zinc acetate. Alkanolamine employed were ethanolamine and diethanolamine. Since both ethanolamine and diethanolamine have high boiling point, the metal-alkanolamine complexes should have very low odor. The obtained results in RPUR foam preparation using the metal-alkanolamine complexes were compared with those of commercial amine catalyst, DMCHA, which is used as a reference catalyst.

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CHAPTER III
EXPERIMENTAL

3.1 Chemicals

3.1.1 Synthesis of metal-alkanolamine complexes

Copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$] and zinc acetate dihydrate, [$Zn(OAc)_2.2H_2O$] were obtained from Aldrich Co. Ltd. Ethanolamine and diethanolamine were obtained from Merck Co. Ltd. Ethylene glycol was obtained from Huntsman Co. Ltd. All chemicals were used without purification.

3.1.2 Preparation of rigid polyurethane foams

The starting materials for preparation of rigid polyurethane foams were supplied by Huntsman (Thailand) Co., Ltd as follows:

- Polymeric MDI (4,4´-methane diphenyl diisocyanate; PMDI, Suprasec® 5005, %NCO = 31.0 wt%, viscosity at 25 °C = 170-270, specific gravity at 25 °C = 1.3, average functionality = 2.7, appearance = medium brown color)
- Polyol (Daltolac® R180, sucrose-based polyether polyol) was supplied by Huntsman (Thailand) Co., Ltd. The specification of polyol are hydroxy value (mgKOH/g) = 440, viscosity at 25 °C = 5500 cP, specific gravity at 25 °C = 1.1, functionality = 4.3)
- Polysiloxane surfactant (Tegostab® B8460)
- N,N-dimethyl cyclohexylamine (DMCHA, a commercial reference catalyst)

Distilled water was used as a chemical blowing agent.

3.2 Synthetic procedures

Metal-alkanolamine complexes were prepared from the reaction between metal acetate [$M(OAc)_2$] and alkanolamine using acetone or ethylene glycol as solvents (Scheme 3.1). In the case of the synthesis using acetone as a solvent, acetone was removed from the metal-alkanolamine complex before using in the preparation of RPUR foam. For the case of the synthesis using ethylene glycol as a solvent, an aqueous solution containing metal-alkanolamine complex was obtained, which can be further used as a catalyst for RPUR foam preparation without purification. The reactivity in foaming reaction of the metal-alkanolamine complexes synthesized in acetone and ethylene glycol were compared. Metal acetates used in this research were copper (II) acetate [$Cu(OAc)_2$] and zinc acetate [$Zn(OAc)_2$]. Alkanolamine used in this research were ethanolamine (EA) and diethanolamine (DEA).

3.2.1 Synthesis of copper and zinc-alkanolamine complexes using acetone as a Solvent

Metal-alkanolamine complexes were synthesized using acetone as a solvent. The complexes obtained from the synthesis using acetone as a solvent were designated as $Cu(OAc)_2(EA)_4$-acetone, $Cu(OAc)_2(DEA)_4$-acetone, $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone. The composition of starting material in synthesis of metal-alkanolamine complexes in acetone are shown in Table 3.1.

$Cu(OAc)_2(EA)_4$-acetone was synthesized using the procedure as follows: ethanolamine (EA) (0.54 ml, 2.25 mmol) was dissolved in acetone (0.85 ml) for 20 minutes at room temperature. Afterwards, $Cu(OAc)_2.H_2O$ (0.45 g, 2.25 mmol) was added into the solution. The solution mixture was stirred continuously for 2 hours at room temperature. After the complex formation was completed, acetone was removed and the copper complex was dried under vacuum. $Cu(OAc)_2(EA)_4$-acetone was obtained as odorless dark blue viscous liquids: IR (cm^{-1}); 3213 (N-H stretching), 2924 (C-H stretching), 1555 (C=O asymmetric stretching), 1397 (C=O symmetric stretching), 1330 (C-N stretching) and 1041 (C-O stretching). UV; λ_{max}(MeOH) = 235 nm. MALDI-TOF m/z of $CuC_{12}H_{34}O_8N_4$ [$Cu(OAc)_2(EA)_4$]$^+$: 425.966; found 444.635 [$^{63}Cu(OAc)_2(EA)_4+H_2O+H$]$^+$ and 261.273 [$^{63}Cu(OAc)_2(EA)+H_2O+H$]$^+$.

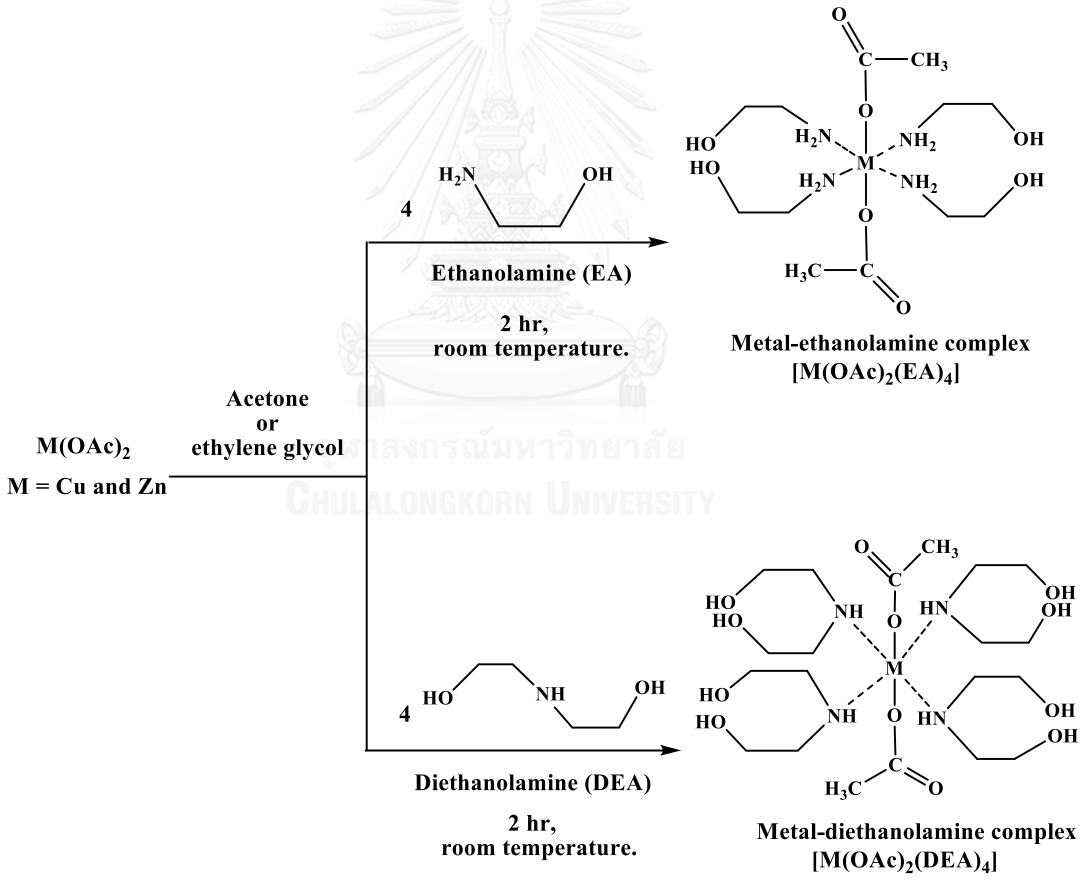
$Cu(OAc)_2(DEA)_4$-acetone, $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone were synthesized using the same procedure as $Cu(OAc)_2(EA)_4$-acetone.

$Cu(OAc)_2(DEA)_4$-acetone: IR (cm^{-1}); 3223 (N-H stretching), 2931 (C-H stretching), 1560 (C=O asymmetric stretching), 1396 (C=O symmetric stretching), 1333 (C-N stretching) and 1065 (C-O stretching). UV; λ_{max}(MeOH) = 259 nm.

MALDI-TOF m/z of $CuC_{20}H_{50}O_{12}N_4$ $[Cu(OAc)_2(DEA)_4]^+$: 602.190; found 521.817 $[^{63}Cu(OAc)_2(DEA)_3+Na+H]^+$ and 440.248 $[^{63}Cu(OAc)(DEA)_3+2H]^+$.

$Zn(OAc)_2(EA)_4$-acetone: IR (cm^{-1}); 3240 (N-H stretching), 2934 (C-H stretching), 1560 (C=O asymmetric stretching), 1397 (C=O symmetric stretching), 1333 (C-N stretching) and 1015 (C-O stretching). MALDI-TOF m/z of $ZnC_{12}H_{34}O_8N_4$ $[Cu(OAc)_2(EA)_4]^+$: 427.829; found 360.285 $[^{64}Zn(OAc)_2(EA)_2+3H_2O+H]^+$, 285.175 $[^{64}Zn(OAc)_2(EA)+H_2O+Na]^+$ and 267.208 $[^{64}Zn(OAc)_2(EA)+Na]^+$.

$Zn(OAc)_2(DEA)_4$-acetone: IR (cm^{-1}); 3270 (N-H stretching), 2941 (C-H stretching), 1555 (C=O asymmetric stretching), 1401 (C=O symmetric stretching), 1370 (C-N stretching) and 1048 (C-O stretching).



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Scheme 3.1 Synthesis of copper- and zinc-alkanolamine complexes using acetone or ethylene glycol as a solvent

Table 3.1 Composition of starting materials in the synthesis of metal- alkanolamine complexes using acetone as a solvent

Metal complexes	Amount of $M(OAc)_2$ (g, mmol)	Amount of alkanolamine (ml, mmol)		Amount of acetone (ml)	Appearance
		EA	DEA		
$Cu(OAc)_2(EA)_4$-acetone	(0.45, 2.25)	(0.54, 2.25)	-	0.85	Dark blue viscous liquid
$Cu(OAc)_2(DEA)_4$-acetone	(0.32, 1.60)	-	(0.62, 1.62)	0.85	Blue viscous liquid
$Zn(OAc)_2(EA)_4$-acetone	(0.47, 2.14)	(0.52, 2.17)	-	0.85	Dark yellow viscous liquid
$Zn(OAc)_2(DEA)_4$-acetone	(0.34, 1.55)	-	(0.60, 1.57)	0.85	Light yellow viscous liquid

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3.2.2 Synthesis of copper and zinc-alkanolamine complexes using ethylene glycol (EG) as a solvent

Metal-alkanolamine complexes were synthesized using ethylene glycol (EG) as a solvent. The complexes obtained from the synthesis in ethylene glycol were designated as $Cu(OAc)_2(EA)_4$-EG, $Cu(OAc)_2(DEA)_4$-EG, $Zn(OAc)_2(EA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG. The compositions of starting materials in the synthesis 60 wt% metal-alkanolamine complex solution in ethylene glycol are shown in Table 3.2.

$Cu(OAc)_2(EA)_4$-EG was synthesized using the procedure as follows: ethanolamine (EA) (0.54 ml, 2.25 mmol) was dissolved in ethylene glycol (EG)

(0.60 ml) and the mixture was stirred for 20 minutes at room temperature. Afterwards, $Cu(OAc)_2.H_2O$ (0.45 g, 2.25 mmol) was added into the solution. The solution mixture was stirred continuously for 2 hours at room temperature to obtain dark blue odorless solution of 60 wt% of $Cu(OAc)_2(EA)_4$ in ethylene glycol: UV; λ_{max}(MeOH) = 235 nm. MALDI-TOF m/z of $CuC_{12}H_{34}O_8N_4$ $[Cu(OAc)_2(EA)_4]^+$: 425.966; found 330.386 $[^{63}Cu(OAc)(EA)_3+Na+2H]^+$ and 261.385 $[^{63}Cu(OAc)_2(EA)+H_2O+H]^+$.

$Cu(OAc)_2(DEA)_4$-EG, $Zn(OAc)_2(EA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG were synthesized using the same procedure as $Cu(OAc)_2(EA)_4$-EG.

$Cu(OAc)_2(DEA)_4$-EG: UV; λ_{max}(MeOH) = 259 nm. MALDI-TOF m/z of $CuC_{20}H_{50}O_{12}N_4$ $[Cu(OAc)_2(DEA)_4]^+$: 602.190; found 521.988 $[^{63}Cu(OAc)_2(DEA)_3+Na+H]^+$.

$Zn(OAc)_2(EA)_4$-EG: MALDI-TOF m/z of $ZnC_{12}H_{34}O_8N_4$ $[Cu(OAc)_2(EA)_4]^+$: 427.829; found 285.299 $[^{64}Zn(OAc)_2(EA)+H_2O+Na]^+$ and 268.221 $[^{64}Zn(OAc)_2(EA)+Na+H]^+$.

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Table 3.2 Composition of starting materials in the synthesis of metal- alkanolamine complexes using ethylene glycol as a solvent

Metal complexes	Amount of $M(OAc)_2$ (g, mmol)	Amount of alkanolamine (ml, mmol)		Amount of ethylene glycol (ml)	Appearance
		EA	DEA		
$Cu(OAc)_2(EA)_4$-EG	(0.45, 2.25)	(0.54, 2.25)	-	0.60	Dark blue Solution
$Cu(OAc)_2(DEA)_4$-EG	(0.32, 1.60)	-	(0.62, 1.62)	0.60	Blue solution
$Zn(OAc)_2(EA)_4$-EG	(0.47, 2.14)	(0.52, 2.17)	-	0.60	Dark yellow Solution
$Zn(OAc)_2(DEA)_4$-EG	(0.34, 1.55)	-	(0.60, 1.57)	0.60	Light yellow solution

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3.3 Preparation of rigid polyurethane (RPUR) foam

The preparation of rigid polyurethane (RPUR) foams via a two-step method is shown in Figure 3.1. In the first step, the polyol, surfactant, catalyst (metal-alkanolamine complexes or DMCHA) and blowing agent (water) were mixed in a paper cup (700 ml) and stirred continuously until a homogeneous mixture was obtained. In the second step, PMDI was added into the mixture and stirred by a mechanical stirrer at 2000 rpm for 20 s. The formulation of rigid polyurethane foams is shown in Table 3.2.

Reaction times for polymerization of RPUR foam understudy were cream time, gel time, rise time and tack free time. Afterwards, the foams were kept for 48 hours at room temperature after which mechanical and physical properties characterizations were carried out.

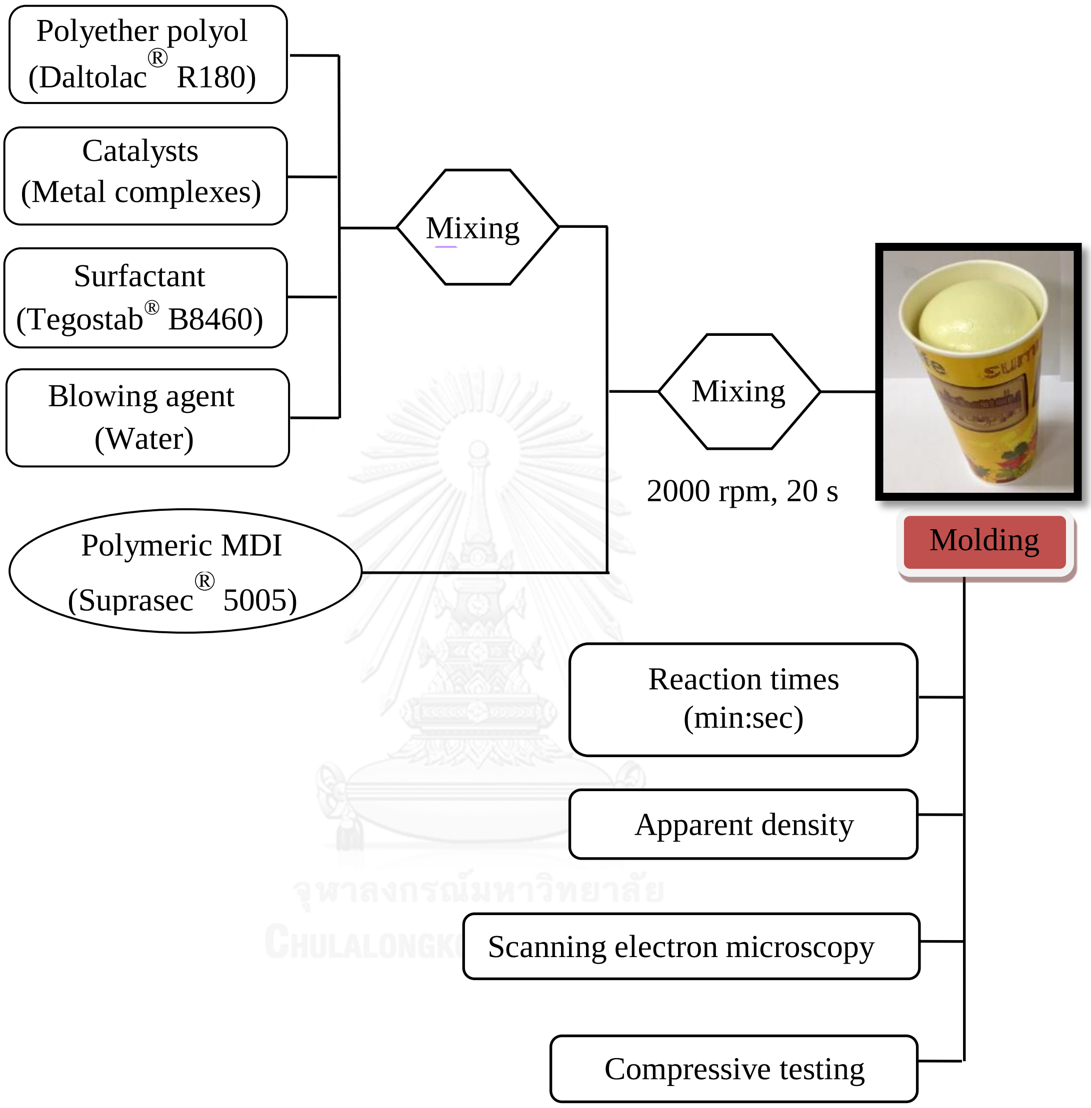

Figure 3.1 Procedure for the preparation of RPUR foam

Table 3.3 Formulation of rigid polyurethane foams at the NCO index of 100 (in parts by weight unit, pbw)

Starting materials	**Formulation (parts by weight, pbw)**	
	1	**2**
Polyether polyol (Daltolac® R180)	100.0	100.00
Catalysts (DMCHA or Metal-alkanolamine complex)	1.67	1.67
Surfactant (Tegotab® B8460)	2.50	2.50
Blowing agent (water)	3.00	4.00
PMDI (Suprasec® 5005)	154.30	169.35

3.4 Rigid polyurethane (RPUR) foam preparations by using plastic bags

Preparation of RPUR foams using a plastic bag (10 cm x 10 cm x 10 cm). The polyol, surfactant, catalyst (metal-alkanolamine complexes or DMCHA) and blowing agent (water) were mixed in a paper cup (700 ml) and stirred continuously until homogeneous. PMDI was then added into the mixture and stirred for 20 seconds at a speed of 2000 rpm by a mechanical stirrer until the mixture was homogeneous. The mixture was poured into plastic bags and allowed to rise independently. The foams kept for 48 hours at room temperature for mechanical and physical properties characterizations were carried out.

The rigid polyurethane foams (RPUR) obtained from different catalysts has the same IR spectra. Therefore, only the IR data of RPUR foam obtained from $Cu(OAc)_2(EA)_4$ is reported as follows: IR (ATR-IR, cm^{-1}); NH-stretching (amine group) 3317 cm^{-1}, Ar-H (phenyl group) at 1593 cm^{-1}, N-H bending (urethane group) at 1508 cm^{-1}, C-N (isocyanate) at 1407 cm^{-1}, C=O stretching (urethane) at 1701 cm^{-1} and C-O (urethane) at 1218 cm^{-1}.

3.5 Instrumentation

3.5.1 Infrared spectroscopy

Fourier transform infrared (FTIR) spectrometer was used to characterize the metal-alkanolamine complexes and rigid polyurethane foam including study about NCO conversion of RPUR foam.

Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Nicolet 6700 FTIR spectrometer using an ATR probe at room temperature over the range 700-4000 cm^{-1} at a resolution of 4 cm^{-1} and a total of 64 interferograms were signal averaged. The ATR crystal was integrated into the beam of and ATR-IR spectrometer (Nicolet 6700) in such a way that IR light was passed through. ATR occurred on the measuring surface which was in contact with the foam sample. The IR bands shown in the Table 3.4 were used for the analysis. The measurement was controlled by the Omnic software.

Table 3.4 Characteristic IR bands of RPUR foam

Functional group	**Vibration mode**	**IR peak (cm^{-1})**
NCO	NCO antisymm. Str.	2180-2310
CO	CO str.(urethane, urea, isocyanurate, allophanate, Biuret, etc.	1620-1760
Isocyanurate	Ring deformation and CH_2-deformation in PMDI	1370-1443
Amide	CN-str. (urethane, urea)	1155-1245
Reference	Non-reaction groups in polyol and isocyanate	935-1050

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3.5.2 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analyses such as highly conjugated organic compounds and transition metal ions. UV-Visible spectra were recorded on ultraviolet and visible spectrophotometer at room temperature. Absorption spectra were obtained on Varian Cary 50 UV-Vis spectrophotometer. At a medium speed the samples were scan over the range 200-800 nm. Methanol was used as a solvent.

3.5.3 Mass spectrometry (MS)

Mass spectrometry (MS) is an analytical technique that produces spectra of the mass (m)-to-charge (z) ratio (m/z) of charge particles. The type of mass spectrometer used was MALDI-TOF mass spectra were determined on Bruker Daltonics MALDI-TOF using 2-cyano-4-hydroxy cinnamic acid (CCA) as the matrix. High resolution mass spectra were determined on Bruker Daltonics Data Analysis 3.3 with an electrospray ion source using methanol as a solvent.

3.5.4 Digital Stopwatch

Digital Stopwatch was measured the reaction times namely, cream time, gel time, tack free time and rise time.

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3.5.5 Thermocouple

Thermocouple is a widely used as a temperatures sensor for measurement. The foaming temperatures were recorded by a dual thermocouple, Digicon DP-71.

3.6 Physical and Mechanical Properties of RPUR Foams

3.6.1 Density

The density of RPUR foams was measured according to ASTM D 1622. A foam specimen having a size of 3.0 cm x 3.0 cm x 3.0 cm. (width x length x thickness) was measured. An average of the values of three samples were reported.

3.6.2 Compressive testing

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise direction were performed using a universal testing machine (Lloyd) according to ASTM D 695. The sample size was 3.0 cm x 3.0 cm x 3.0 cm (width x length x thickness) dimension, the rate of crosshead movement was fixed at 2.54 mm/min and the preload cell used was 0.100 N.

3.6.3 Scanning electron microscopy (SEM)

The cell size and morphology of RPUR foams were measured on a JSM-5800 LV scanning electron microscope (SEM). The foam sample was cut to give a thickness of 1.0 nm and coating with gold before scanning to the rising direction to provide an electrically conductive surface. The foam samples were loaded at accelerating power of 20 kV.

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CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of the metal-alkanolamine complexes

Metal-alkanolamine complexes were synthesized from the reaction between metal acetate and alkanolamine. Metal acetates employed were copper (II) acetate [$Cu(OAc)_2$] and Zinc acetate [$Zn(OAc)_2$]. Alkanolamines employed were ethanolamine (EA) and diethanolamine (DEA). Catalytic activity of the metal-alkanolamine complexes was compared with that of dimethylcyclohexylamine (DMCHA), which is a commercial tertiary amine catalyst.

4.1.1 Synthesis of copper-alkanolamine complexes [$Cu(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$]

The reaction between copper acetate and alkanolamine gave two copper-alkanolamine complexes, $Cu(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$, as shown in Scheme 3.1. The mole ratio of copper acetate to alkanolamine employed was 1:4. Copper-alkanolamine complexes were synthesized using two methods. The first method used acetone as a solvent. After the complex formation was completed, acetone was removed and the copper complex was dried under vacuum. In the second method, the synthesis was done in ethylene glycol (EG). The copper complexes were obtained as solutions in ethylene glycol and could be used in RPUR foam formulation without further purification.

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$Cu(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$ obtained from the synthesis in acetone was designated as $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-acetone, respectively. $Cu(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$ obtained from the synthesis in ethylene glycol was designated as $Cu(OAc)_2(EA)_4$-EG and $Cu(OAc)_2(DEA)_4$-EG, respectively. $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-acetone were obtained as odorless dark blue and light blue viscous liquids, respectively. UV-Visible spectroscopy, IR spectroscopy and mass spectrometry were used to identify the structure of copper-alkanolamine complexes.

4.1.2 Characterization of copper-alkanolamine complexes

4.1.2.1 UV-Visible spectroscopy of copper-alkanolamine complexes

Copper-alkanolamine complexes were dissolved in methanol and UV-Vis spectra were obtained. The spectra are shown in Figures 4.1-4.2. The complexes synthesized in acetone and those synthesized in EG gave the same maximum wavelength. The maximum wavelength (λ_{max}) of $Cu(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$ appeared at 235 and 259 nm, respectively. These peaks shifted from peak of $Cu(OAc)_2$, which appeared at 247 nm. This result confirmed the complex formation.

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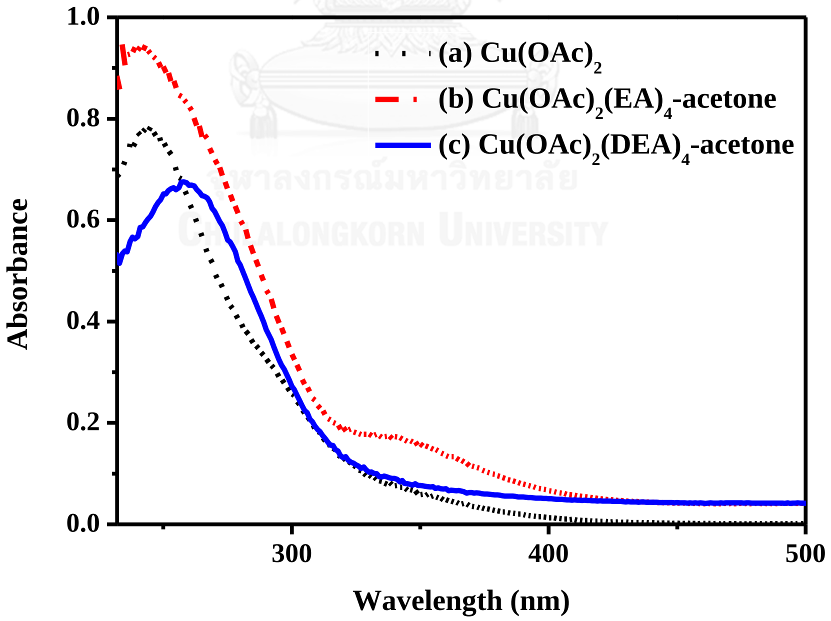

Figure 4.1 UV-Vis spectra of (a) $Cu(OAc)_2$, (b) $Cu(OAc)_2(EA)_4$-acetone and (c) $Cu(OAc)_2(DEA)_4$-acetone

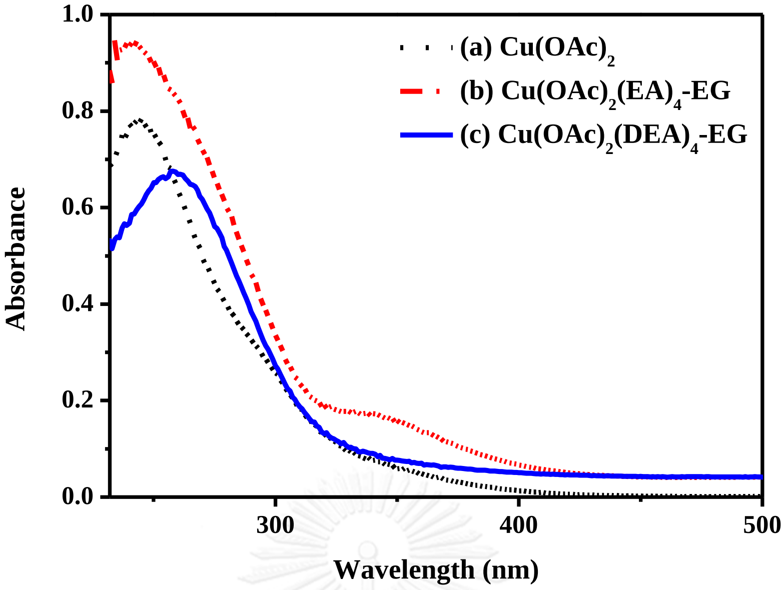

Figure 4.2 UV-Vis spectra of (a) $Cu(OAc)_2$, (b) $Cu(OAc)_2(EA)_4$-EG and (c) $Cu(OAc)_2(DEA)_4$-EG

4.1.2.2 IR spectroscopy of copper-alkanolamine complexes

IR spectra of $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-acetone are shown in Figure 4.3. IR spectra of $Cu(OAc)_2(EA)_4$-EG and $Cu(OAc)_2(DEA)_4$-EG could not be obtained due to the strong absorption of hydroxyl groups in EG. $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-acetone exhibited absorption bands at 3213-3223 cm^{-1} (N-H stretching), 2924-2931cm^{-1} (C-H stretching), 1555-1560 cm^{-1} (C=O asymmetric stretching), 1396-1397cm^{-1} (C=O symmetric stretching), 1330-1333 cm^{-1} (C-N stretching) and 1041-1065 cm^{-1} (C-O stretching). Asymmetric C=O stretching in $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-acetone appeared as absorption bands at 1555 cm^{-1} and 1560 cm^{-1}, respectively. Symmetric C=O stretching in $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-acetone appeared as absorption bands at 1397 cm^{-1} and 1396 cm^{-1}, respectively. These C=O stretching bands were different from those of $Cu(OAc)_2$, which appeared at 1594 cm^{-1} (asymmetric C=O stretching) and 1420 cm^{-1} (symmetric C=O stretching). These IR data confirmed the formation of copper-alkanolamine complexes.

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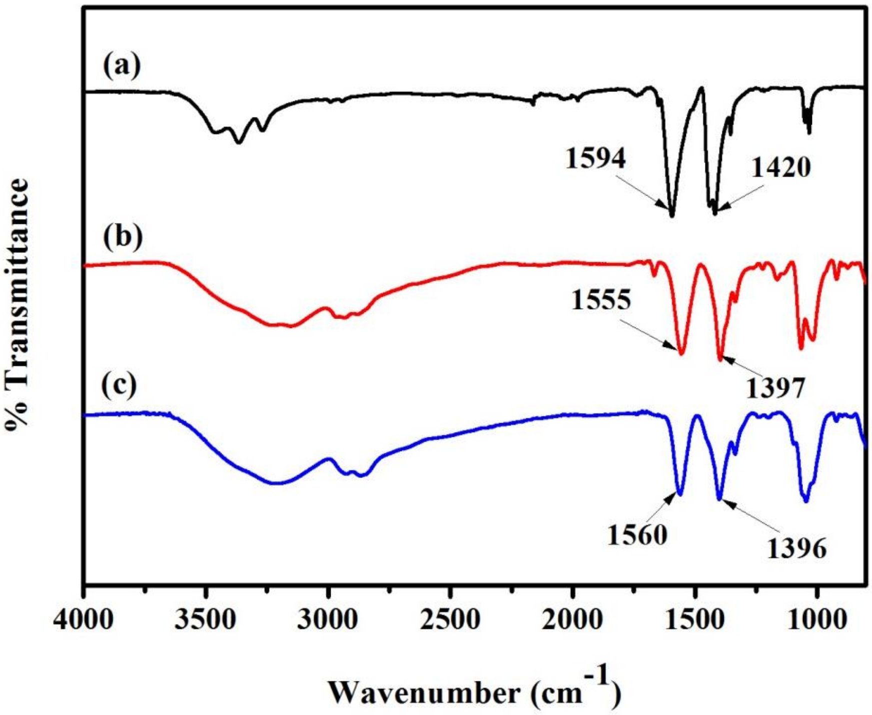

Figure 4.3 IR spectra of (a) $Cu(OAc)_2$, (b) $Cu(OAc)_2(EA)_4$-acetone and (c) $Cu(OAc)_2(DEA)_4$-acetone

4.1.2.3 Mass spectrometry of copper-alkanolamine complexes

MALDI-TOF mass spectra of copper-alkanolamine complexes are shown in Figures 4.4-4.7. The complexes synthesized in acetone and those synthesized in EG exhibited similar mass spectra. For $Cu(OAc)_2(EA)_4$-acetone and $Cu(OAc)_2(EA)_4$-EG (Figures 4.4 and 4.5, respectively), the peak of $[Cu(OAc)_2(EA)_4]^+$ at m/z 425.966 was not observed. $Cu(OAc)_2(EA)_4$-acetone showed two peaks at m/z 444.635 $[^{63}Cu(OAc)_2(EA)_4+H_2O+H]^+$ and m/z 261.273 $[^{63}Cu(OAc)_2(EA)+H_2O+H]^+$ (Figure 4.4). $Cu(OAc)_2(EA)_4$-EG showed two peaks at m/z 330.386 $[^{63}Cu(OAc)(EA)_3+Na+2H]^+$ and m/z 261.385 $[^{63}Cu(OAc)_2(EA)+H_2O+H]^+$ (Figure 4.5). These results confirmed the complex formation.

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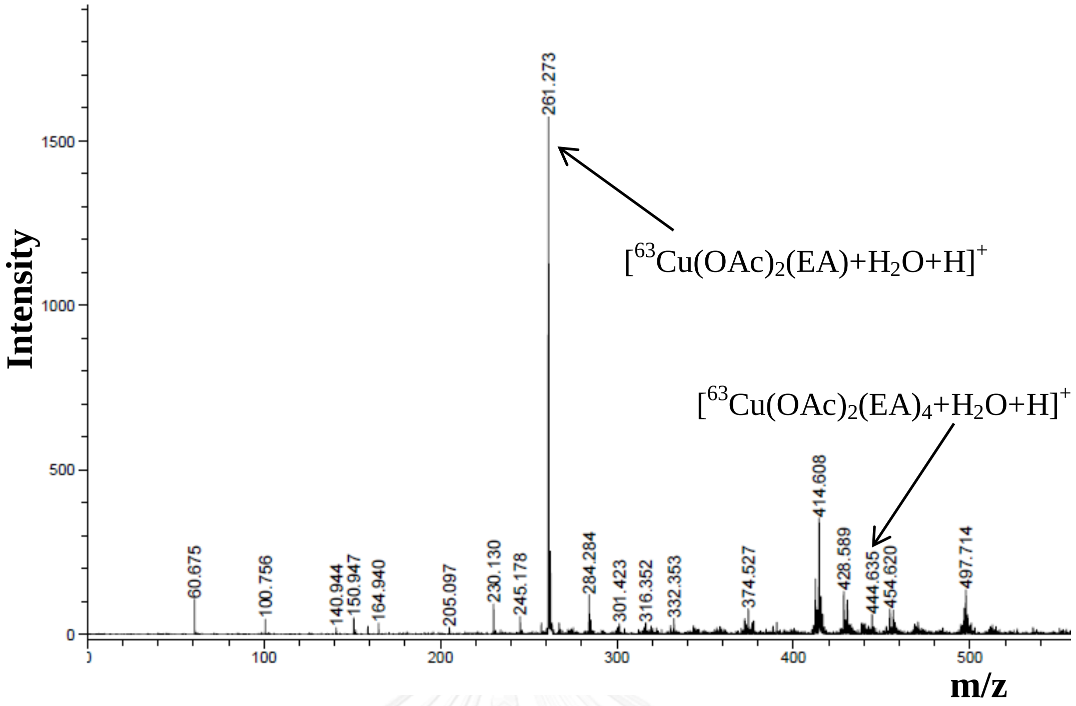

Figure 4.4 Mass spectrum of $Cu(OAc)_2(EA)_4$-acetone

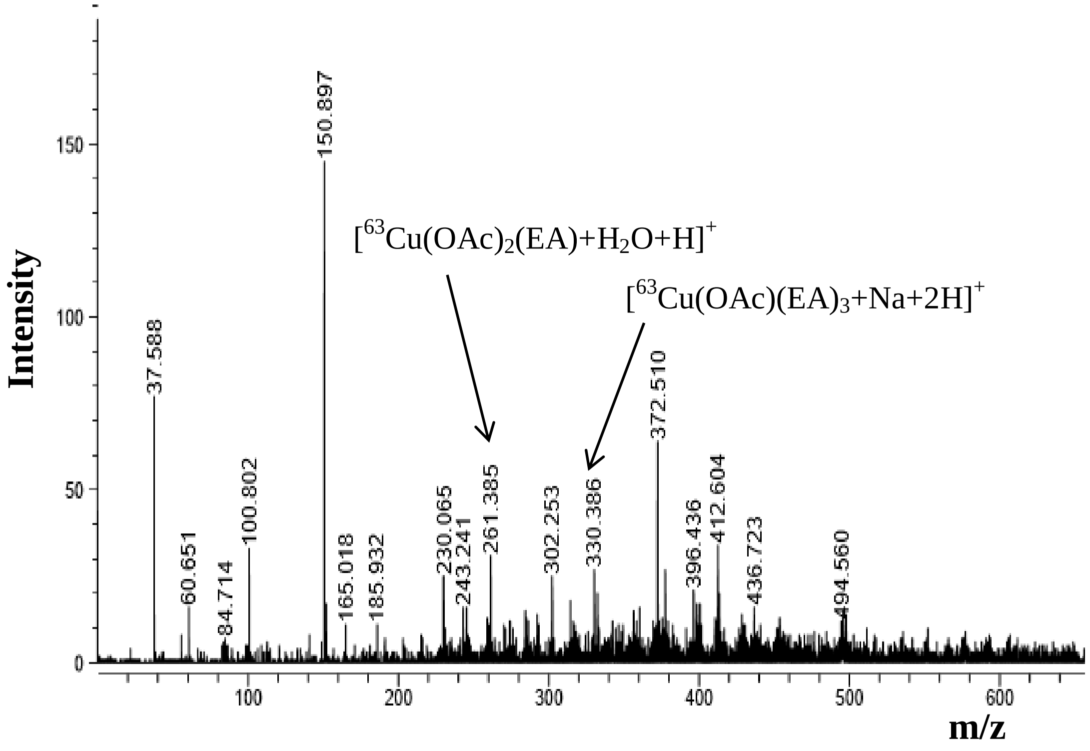

Figure 4.5 Mass spectrum of $Cu(OAc)_2(EA)_4$-EG

Figures 4.6 and 4.7 show mass spectra of $Cu(OAc)_2(DEA)_4$-acetone and $Cu(OAc)_2(DEA)_4$-EG, respectively. m/z of $[Cu(OAc)_2(DEA)_4]^+$ at 602.190 was not observed. $Cu(OAc)_2(DEA)_4$-acetone showed two peaks at m/z 521.817 $[^{63}Cu(OAc)_2(DEA)_3+Na+H]^+$ and m/z 440.248 $[^{63}Cu(OAc)(DEA)_3+2H]^+$. $Cu(OAc)_2(DEA)_4$-EG showed one peak at m/z 521.988 $[^{63}Cu(OAc)_2(DEA)_3+Na+H]^+$.

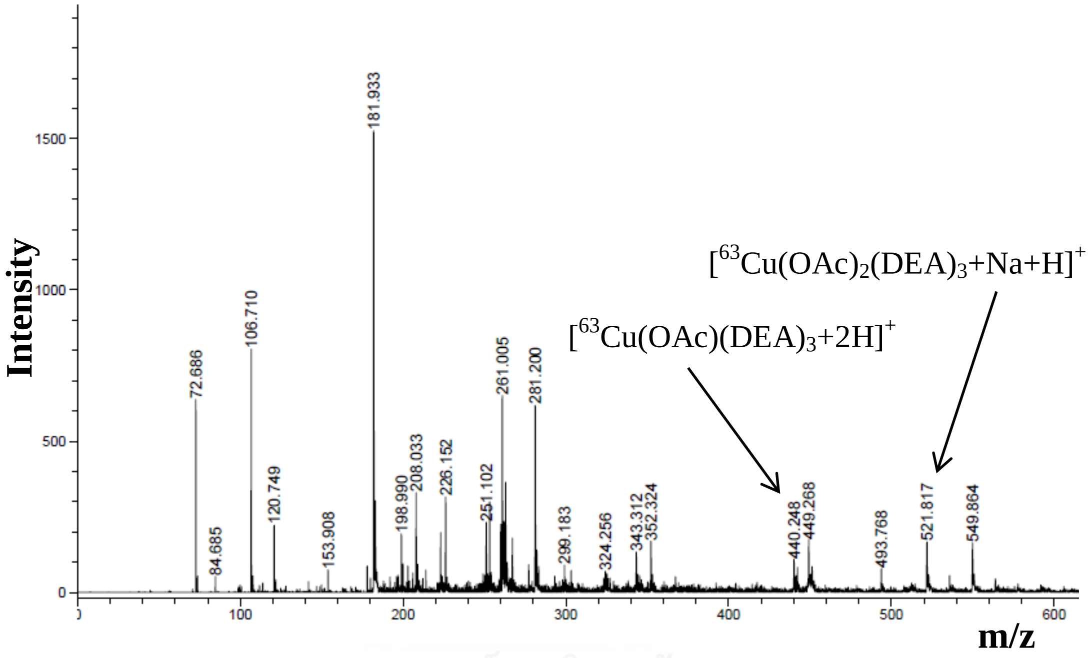

Figure 4.6 Mass spectrum of $Cu(OAc)_2(DEA)_4$-acetone

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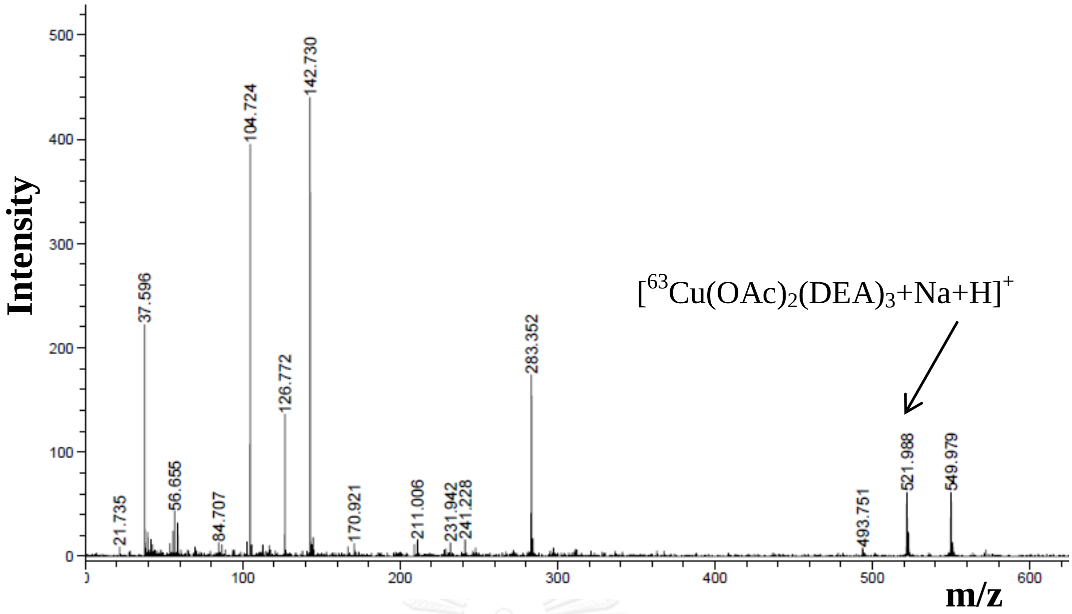

Figure 4.7 Mass spectrum of $Cu(OAc)_2(DEA)_4$-EG

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4.1.3 Synthesis of zinc-alkanolamine complexes

The reaction between zinc acetate and alkanolamine gave two zinc-alkanolamine complexes, $Zn(OAc)_2(EA)_4$ and $Zn(OAc)_2(DEA)_4$, as shown in Scheme 3.1. The mole ratio of zinc acetate to alkanolamine employed was 1:4. Zinc-alkanolamine complexes were synthesized using two methods. The first method used acetone as a solvent. After the complex formation was completed, acetone was removed and the zinc complexes were dried under vacuum. In the second method, the synthesis was done in EG. The zinc complexes were obtained as solutions in ethylene glycol could be used in RPUR foam formulation without further purification.

$Zn(OAc)_2(EA)_4$ and $Zn(OAc)_2(DEA)_4$ obtained from the synthesis in acetone was designated as $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone, respectively. $Zn(OAc)_2(EA)_4$ and $Zn(OAc)_2(DEA)_4$ obtained from the synthesis in ethylene glycol was designated as $Zn(OAc)_2(EA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG, respectively. $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone were obtained as odorless dark yellow and light yellow viscous liquids, respectively. IR spectroscopy and mass spectrometry were used to identify the structure of zinc-alkanolamine complexes. UV-Vis spectra of $Zn(OAc)_2(EA)_4$ and $Zn(OAc)_2(DEA)_4$ could not be obtained since electron configuration of zinc metal is $4s^2$ $3d^{10}$, and therefore zinc complexes do not have UV-Vis absorption.

4.1.4 Characterization of zinc-alkanolamine complexes

4.1.4.1 IR spectroscopy of zinc-alkanolamine complexes

IR spectra of $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone are shown in Figure 4.8. IR spectra of $Zn(OAc)_2(EA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG could not be obtained due to high intensity of hydroxyl bands in EG. $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone exhibited absorption bands at 3240-3270 cm^{-1} (N-H stretching), 2934-2941 cm^{-1} (C-H stretching), 1555-1560 cm^{-1} (C=O asymmetric stretching), 1397-1401 cm^{-1} (C=O symmetric stretching), 1333-1370 cm^{-1} (C-N stretching) and 1015-1048 cm^{-1} (C-O stretching). Asymmetric C=O stretching in $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone appeared as absorption bands at 1560 cm^{-1} and 1555 cm^{-1}, respectively. Symmetric C=O stretching in $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(DEA)_4$-acetone appeared as absorption bands at 1397 cm^{-1} and 1401 cm^{-1}, respectively. These C=O stretching bands were different from those of $Zn(OAc)_2$, which appeared at 1531 cm^{-1} (asymmetric C=O stretching) and 1440 cm^{-1} (symmetric C=O stretching). These IR data confirmed the formation of zinc-alkanolamine complexes.

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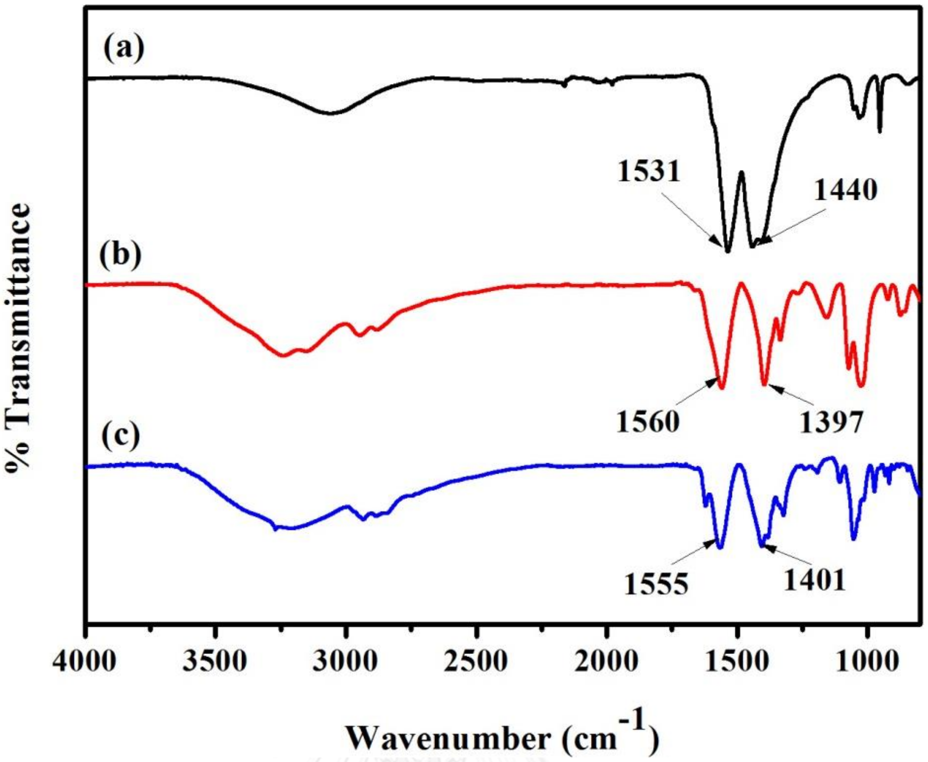

Figure 4.8 IR spectra of (a) $Zn(OAc)_2$, (b) $Zn(OAc)_2(EA)_4$-acetone and (c) $Zn(OAc)_2(DEA)_4$-acetone

4.1.4.2 Mass spectrometry of zinc-alkanolamine complexes

MALDI-TOF mass spectra of $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(EA)_4$-EG are shown in Figures 4.9 and 4.10, respectively. Mass spectra of $Zn(OAc)_2(DEA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG could not be obtained. $Zn(OAc)_2(EA)_4$-acetone and $Zn(OAc)_2(EA)_4$-EG exhibited the similar mass spectra. For $Zn(OAc)_2(EA)_4$-acetone, the peak of $[Zn(OAc)_2(EA)_4]^+$ at m/z 427.829 was not observed. $Zn(OAc)_2(EA)_4$-acetone showed three peaks at m/z 360.285 $[^{64}Zn(OAc)_2(EA)_2+3H_2O+H]^+$, m/z 285.175 $[^{64}Zn(OAc)_2(EA)+H_2O+Na]^+$ and m/z 267.208 $[^{64}Zn(OAc)_2(EA)+Na]^+$. $Zn(OAc)_2(EA)_4$-EG showed two peaks at m/z 285.299 $[^{64}Zn(OAc)_2(EA)+H_2O+Na]^+$ and m/z 268.221 $[^{64}Zn(OAc)_2(EA)+Na+H]^+$. These results confirmed the complex formation.

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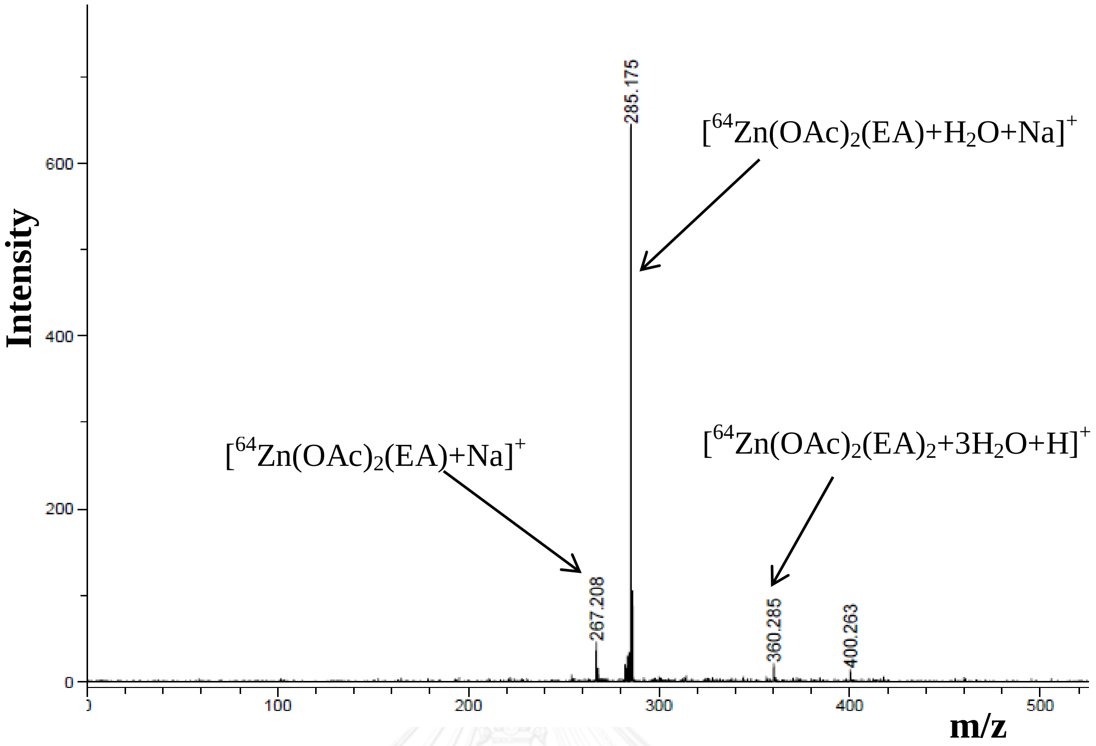

Figure 4.9 Mass spectrum of Zn(OAc)$_2$(EA)$_4$-acetone

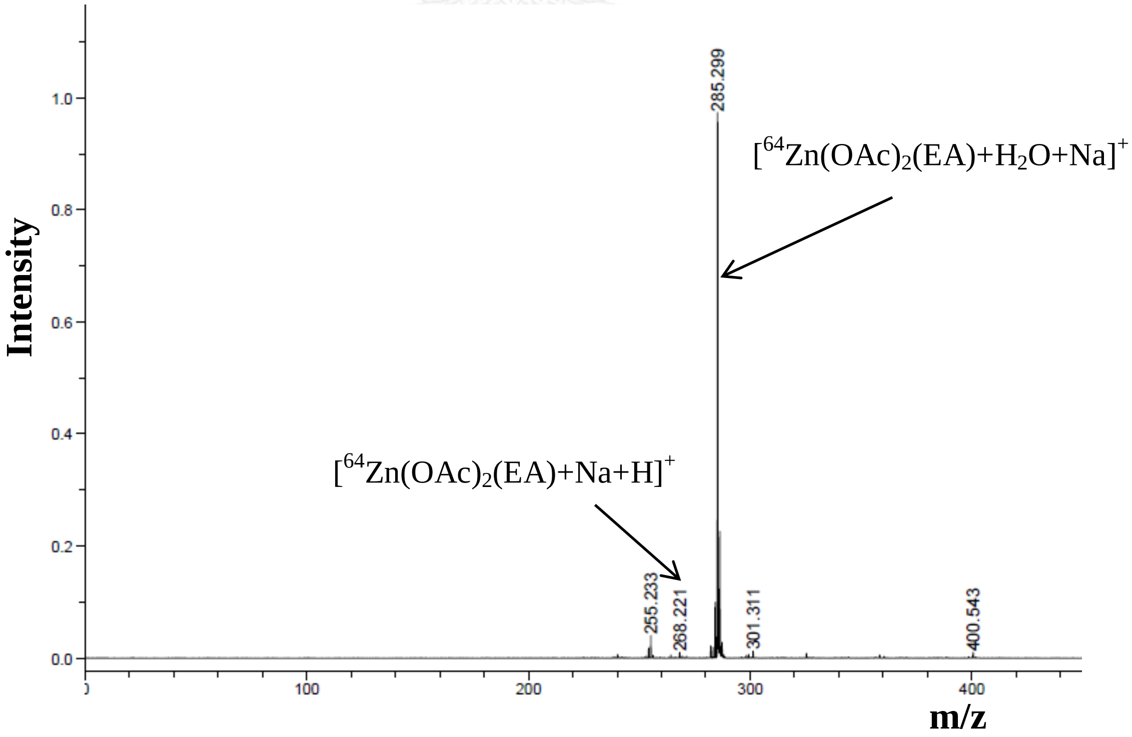

Figure 4.10 Mass spectrum of Zn(OAc)$_2$(EA)$_4$-EG

4.2 Preparation of rigid polyurethane (RPUR) foams

4.2.1 Preparation of RPUR foams catalyzed by metal-alkanolamine complexes

Metal-alkanolamine complexes obtained were $Cu(OAc)_2(EA)_4$-acetone, $Cu(OAc)_2(DEA)_4$-acetone, $Zn(OAc)_2(EA)_4$-acetone, $Zn(OAc)_2(DEA)_4$-acetone, $Cu(OAc)_2(EA)_4$-EG, $Cu(OAc)_2(DEA)_4$-EG, $Zn(OAc)_2(EA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG. These complexes were used as catalysts in the preparation of RPUR foams. Two-step method for preparation of RPUR foams was used. In the first step, polyol, surfactant, catalysts (metal-alkanolamine complexes or DMCHA) and blowing agent (water) were mixed in a paper cup (700 ml) and stirred together by mechanical stirrer at speed 2000 rpm until homogeneous. Then, isocyanate was added into the mixture and stirred at speed 2000 rpm for 20 seconds. Figure 4.11 shows RPUR foams prepared by using a 700 ml paper cup.

During the polymerization of RPUR foams, the reaction times studied were cream time, gel time, rise time and tack free time. The foams were kept 48 hours at room temperature to complete the polymerization reaction. Afterwards, physical and mechanical properties of RPUR foams were studied. Table 3.3 shows the formulation of RPUR foams used in this work.

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Figure 4.11 RPUR foam prepared by using a 700 ml paper cup

RPUR foams prepared by using a plastic bag (10 cm x 10 cm x 10 cm) are shown in Figure 4.12. Homogeneous solution of reactants was prepared in a paper cup before pouring into the plastic bag. RPUR foams prepared in plastic bag showed the similar trend to those prepared in paper cup.

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Figure 4.12 RPUR foam prepared by using a plastic bag

4.2.2 Reaction times [8, 18]

The stages in the foaming process are described by the characteristic reaction times, with the start of mixing is set of zero. These reaction times are referred as cream time, gel time or sting time, rise time and tack free time. The cream time is the time from mixing to initiation of foaming. The gel time is identified as the point when stings of polymer can be withdrawn. The rise time is the time from mixing to full expansion of foaming. The tack free time is the time when the foam surface stops being tacky to the touch. The reaction times of RPUR foams catalyzed by metal-alkanolamine complexes were compared with those catalyzed by a commercial catalyst (DMCHA). As the reference systems, copper acetate, zinc acetate, ethanolamine and diethanolamine were also used as catalysts in the preparation of RPUR foams.

The reaction times of RPUR foam catalyzed by metal-alkanolamine complexes synthesized in acetone are shown in Table 4.1 and those synthesized in EG are shown in Table 4.2 and Figure 4.11. It was found that the metal-alkanolamine complexes synthesized in acetone and those synthesized in EG gave similar reactivity. Since the preparation of metal-alkanolamine complexes in EG was more convenient than the preparation in acetone, further study was done using metal-alkanolamine complexes synthesized in EG.

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Table 4.1 Reaction times of RPUR foams prepared at the NCO index of 100 and catalyzed by metal-alkanolamine complexes synthesized in acetone (catalyst: 1 pbw, H_2O: 4 pbw)

Catalysts	**Cream time (min:sec)**	**Gel time (min:sec)**	**Tack free time (min:sec)**	**Rise time (min:sec)**	**Density (kg/m^3)**	**Height (cm)**
*DMCHA (ref.)	0:28	0:43	3:05	2:20	41.50	14.0
$Cu(OAc)_2$	1:30	3:20	24:15	15:24	56.30	5.5
$Zn(OAc)_2$	3:30	5:30	30:30	14:20	54.60	6.5
EA	2:00	5:30	25:00	10:00	53.00	9.0
DEA	1:30	4:30	30:00	10:00	54.00	9.5
$Cu(OAc)_2(EA)_4$-acetone	0:41	1:22	2:48	3:00	42.43	14.0
$Zn(OAc)_2(EA)_4$-acetone	0:46	1:58	3:30	3:53	34.41	16.0
$Cu(OAc)_2(DEA)_4$-acetone	0:41	1:20	2:35	2:42	48.20	12.5
$Zn(OAc)_2(DEA)_4$-acetone	1:00	1:55	4:15	4:00	35.31	16.0
$Cu(OAc)_2(EA)_4$: $Zn(OAc)_2(EA)_4$-acetone	0:36	1:35	2:50	3:00	33.52	16.5
$Cu(OAc)_2(DEA)_4$: $Zn(OAc)_2(DEA)_4$-acetone	0:52	1:40	3:15	3:20	37.43	14.5

*****DMCHA = 1 pbw : H_2O = 3 pbw

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Table 4.2 Reaction times of RPUR foams prepared at the NCO index of 100 and catalyzed by metal-alkanolamine complexes synthesized in ethylene glycol (EG) (catalyst: 1 pbw, H_2O: 4 pbw)

Catalysts	**Cream time (min:sec)**	**Gel time (min:sec)**	**Tack free time (min:sec)**	**Rise time (min:sec)**	**Density (kg/m^3)**	**Height (cm)**
*DMCHA (ref.)	0:28	0:43	3:05	2:20	41.50	14.0
$Cu(OAc)_2$	1:30	3:20	24:15	15:24	56.30	5.5
$Zn(OAc)_2$	3:30	5:30	30:30	14:20	54.60	6.5
EA	2:00	5:30	25:00	10:00	53.00	9.0
DEA	1:30	4:30	30:00	10:00	54.00	9.5
$Cu(OAc)_2(EA)_4$-EG	0:41	1:21	2:46	2:57	42.54	14.0
$Zn(OAc)_2(EA)_4$-EG	0:45	2:05	3:29	3:53	34.38	16.0
$Cu(OAc)_2(DEA)_4$-EG	0:40	1:20	2:35	2:40	48.13	12.5
$Zn(OAc)_2(DEA)_4$-EG	1:00	1:55	4:10	4:00	35.20	16.0
$Cu(OAc)_2(EA)_4$: $Zn(OAc)_2(EA)_4$-EG	0:36	1:30	2:50	2:57	33.04	16.5
$Cu(OAc)_2(DEA)_4$: $Zn(OAc)_2(DEA)_4$-EG	0:50	1:40	3:15	3:20	37.32	14.5

*****DMCHA = 1 pbw : H_2O = 3 pbw

The reaction times of RPUR foams catalyzed by metal-alkanolamine complexes compared with those catalyzed by DMCHA. Among all metal-alkanolamine complexes, $Cu(OAc)_2(EA)_4$ showed the highest catalytic activity. RPUR foams catalyzed by $Cu(OAc)_2(EA)_4$ gave the similar foam height and foam density to those catalyzed by DMCHA. RPUR foam catalyzed by $Cu(OAc)_2(EA)_4$ had a slightly shorter tack free time than DMCHA, which suggested that $Cu(OAc)_2(EA)_4$ had better catalytic activity in gelling reaction than DMCHA. $Cu(OAc)_2(EA)_4$ and DMCHA gave an equal foam height. Considering the rise time, DMCHA gave a shorter rise time than $Cu(OAc)_2(EA)_4$, which suggested that DMCHA had a better catalytic activity in blowing reaction than $Cu(OAc)_2(EA)_4$.When considering both the tack free time and rise time, $Cu(OAc)_2(EA)_4$ was a good catalyst since the foam continued to rise when the polymerization reaction was almost complete. RPUR foams catalyzed by $Cu(OAc)_2(EA)_4$ gave a stable foam structure that would not collapse. In the reference system, when copper acetate, zinc acetate, ethanolamine and diethanolamine were used as the catalysts, the reactivity in polymerization was poor and RPUR foams had collapsed cell structures as shown in Figure 4.13.

From the reactivity results in Figure 4.14, the preparation of RPUR foams using copper-alkanolamine complexes as a catalyst gave shorter tack free time than zinc-alkanolamine complexes, which indicated that the copper-alkanolamine complexes had a better catalytic activity in gelling reaction than zinc-alkanolamine complexes. The RPUR foams catalyzed by zinc-alkanolamine complexes had the higher foam height than those catalyzed by copper-alkanolamine complexes. This suggested that zinc-alkanolamine complexes had better catalytic activity in blowing reaction than copper-alkanolamine complexes.

The RPUR foams catalyzed by the mixed metal-alkanolamine complexes, namely $Cu(OAc)_2(EA)_4$:$Zn(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$:$Zn(OAc)_2(DEA)_4$, were studied. It was found that the foam catalyzed by the mixed metal-alkanolamine complexes gave reaction times similar to those catalyzed by DMCHA. RPUR foams having low density and large holes at the bottom of the mold were obtained, which resulted in poor morphology of foams as shown in Figure 4.15.

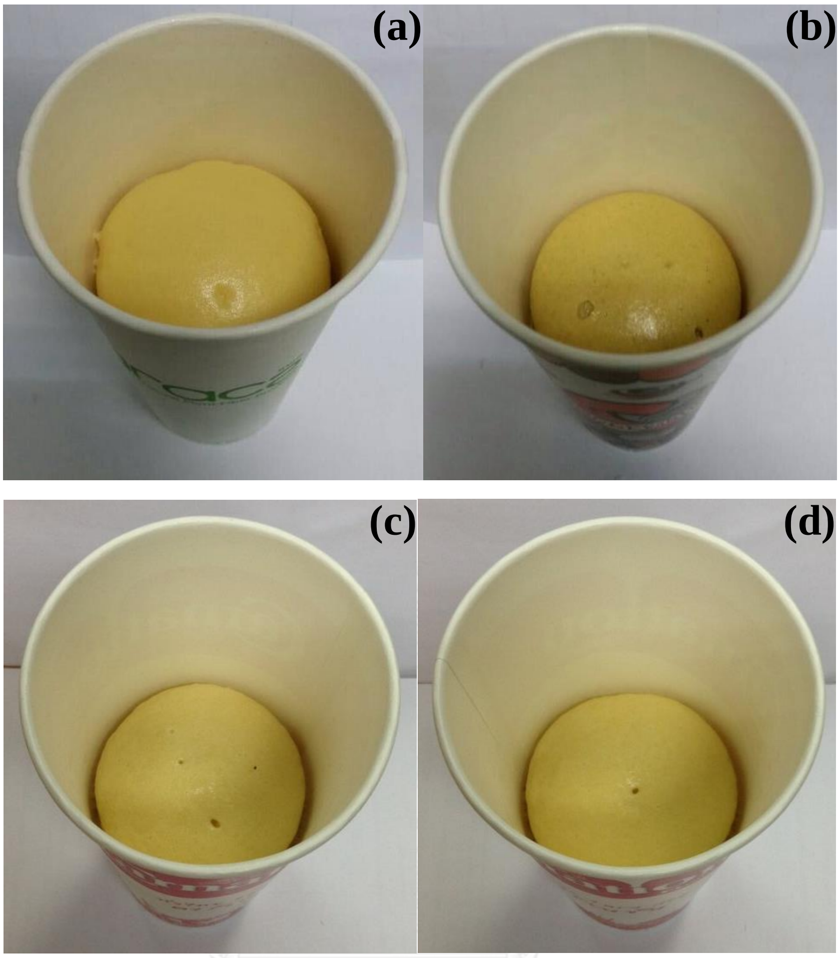

Figure 4.13 Appearances of RPUR foams catalyzed by (a) $Cu(OAc)_2$, (b) $Zn(OAc)_2$, (c) EA and (d) DEA

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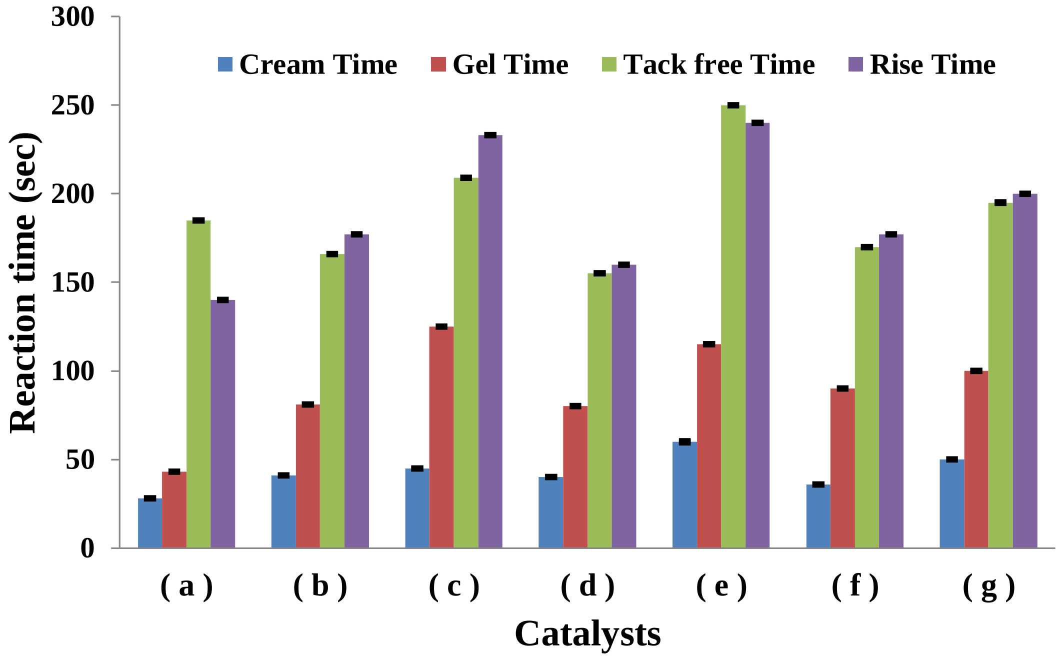

Figure 4.14 Reaction times of RPUR foams catalyzed by (a) DMCHA, (b) $Cu(OAc)_2(EA)_4$-EG, (c) $Zn(OAc)_2(EA)_4$-EG, (d) $Cu(OAc)_2(DEA)_4$-EG, (e) $Zn(OAc)_2(DEA)_4$-EG, (f) $Cu(OAc)_2(EA)_4$:$Zn(OAc)_2(EA)_4$-EG and (g) $Cu(OAc)_2(DEA)_4$:$Zn(OAc)_2(DEA)_4$-EG (catalyst: 1 pbw, H_2O: 4 pbw)

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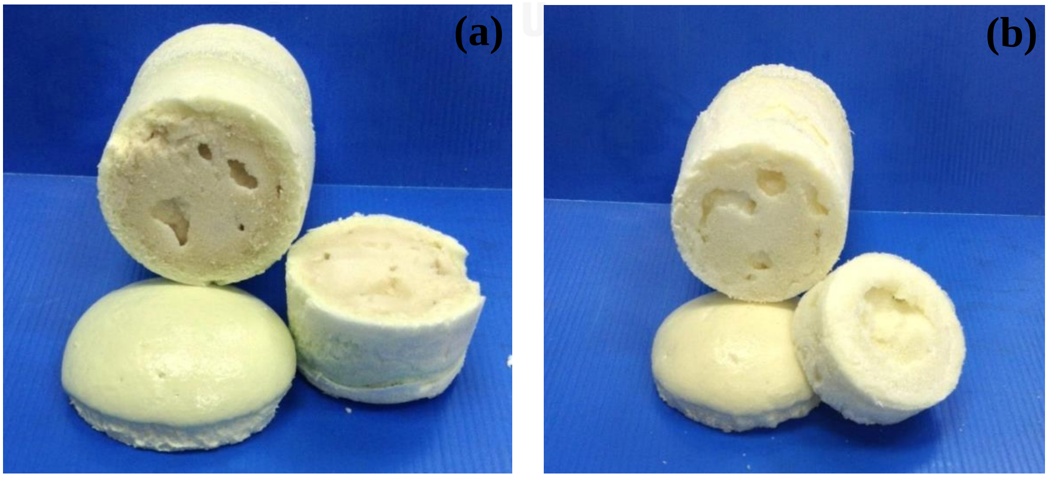

Figure 4.15 RPUR foams catalyzed by (a) $Cu(OAc)_2(EA)_4$:$Zn(OAc)_2(EA)_4$-EG and (b) $Cu(OAc)_2(DEA)_4$:$Zn(OAc)_2(DEA)_4$-EG

Rise profiles of RPUR foams catalyzed by metal-alkanolamine complexes are shown in Figure 4.16. They showed a similar trend to that of DMCHA. The results agreed with the rise time. Copper-alkanolamine complexes gave a shorter rise time than zinc-alkanolamine complexes and DMCHA had a shorter rise time than copper-alkanolamine complexes.

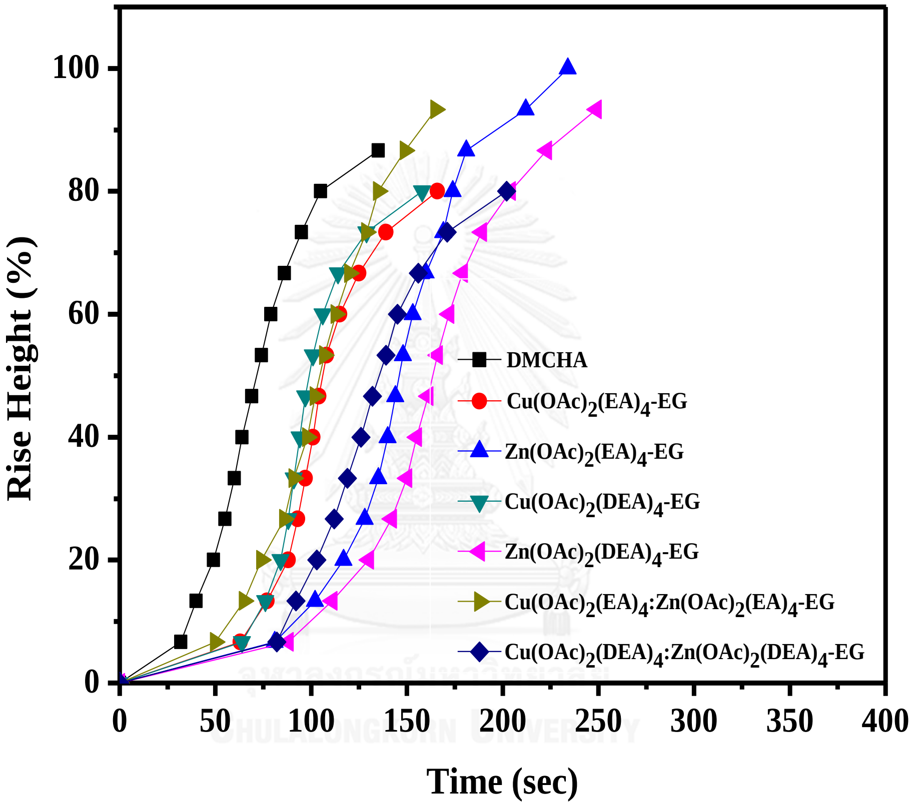

Figure 4.16 Rise profiles of RPUR foams catalyzed by the metal-alkanolamine complexes

4.2.2.1 Effect of catalyst contents on reaction times

The effect of catalyst contents on reaction times of RPUR foam was investigated. Figures 4.17 and 4.18 show the reaction times of metal-alkanolamine complexes and mixed metal-alkanolamine complexes, respectively. The reaction time decreased when the amount of catalyst was increased. For $Cu(OAc)_2(EA)_4$ and $Zn(OAc)_2(EA)_4$, a slight decrease in reaction times was observed. For $Cu(OAc)_2(DEA)_4$ and $Zn(OAc)_2(DEA)_4$, a large decrease in reaction times was observed. Although high catalyst content at 1.5 and 2.0 pbw gave faster reaction times, there are large holes at the bottom of the mold which resulted in poor property of foams. From this reason, the optimum catalyst content for the foam formulation was 1.0 pbw. RPUR foam catalyzed by the mixed metal-alkanolamine complexes showed a similar reaction time to DMCHA, however, there are large holes at the bottom of the mold which resulted in poor property of foams.

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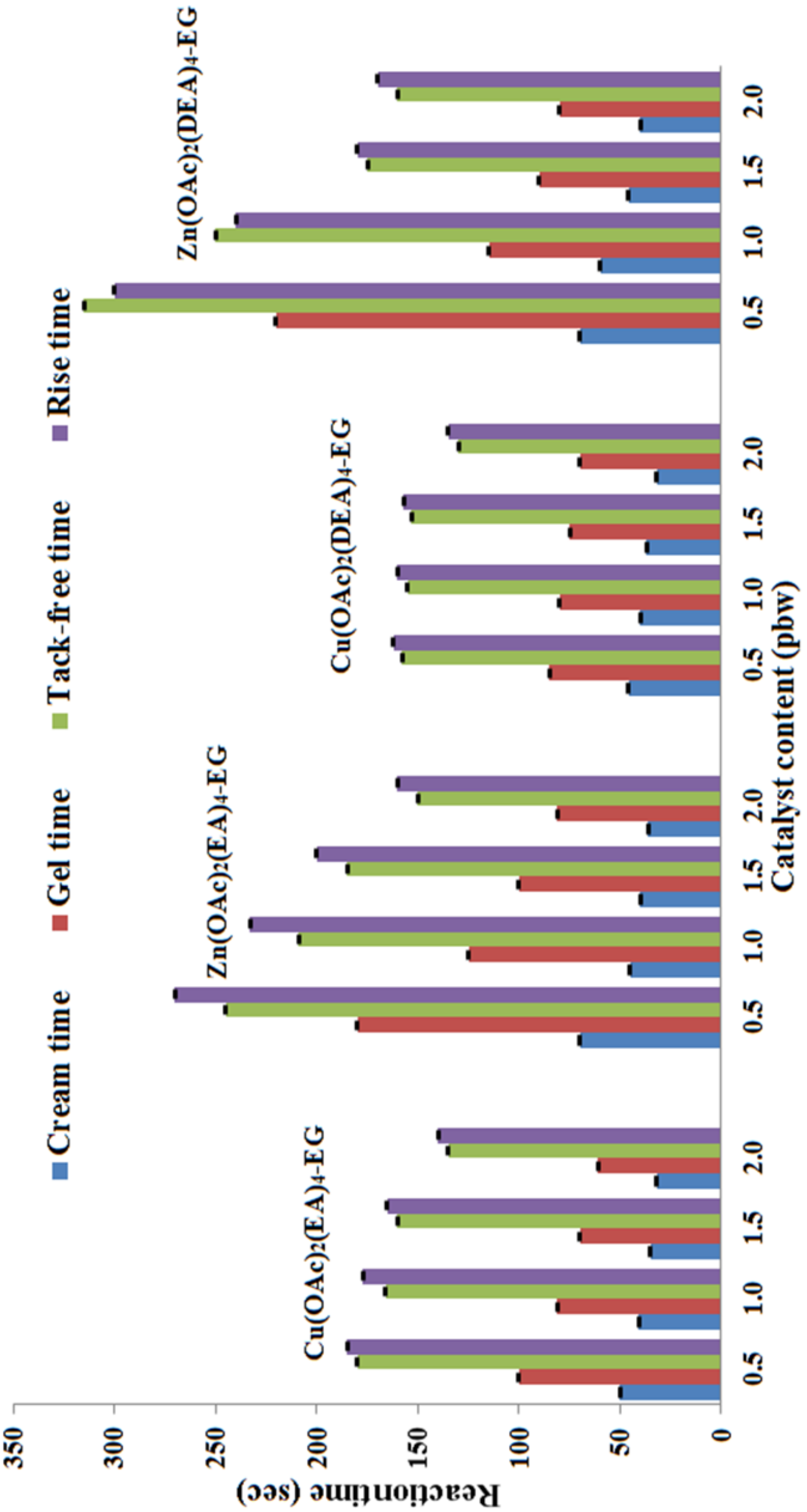

Figure 4.17 The effect of catalyst contents on reaction times of RPUR foams catalyzed by metal-alkanolamine complexes

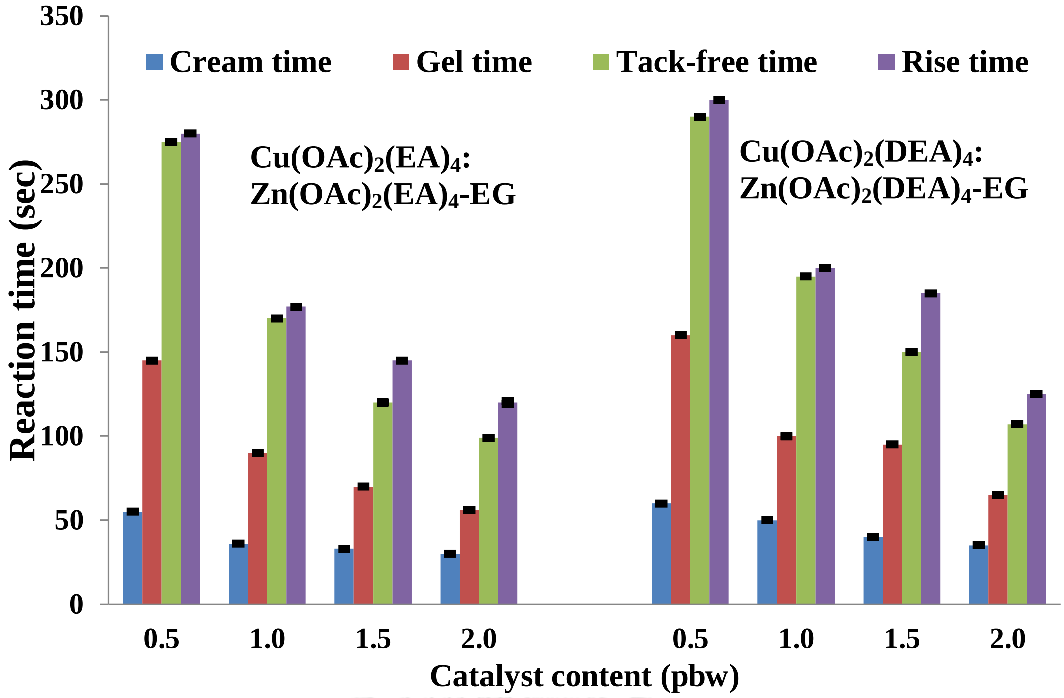

Figure 4.18 The effect of catalyst contents on reaction times of RPUR foams catalyzed by mixed metal-alkanolamine complexes

4.2.3 Apparent density

RPUR foam density was kept at room temperature for 48 hours. Then, the foams were cut into cubic shape with the dimension of 3.0 cm x 3.0 cm x 3.0 cm (Figure 4.19). The foam samples were weighted and their density was calculated.

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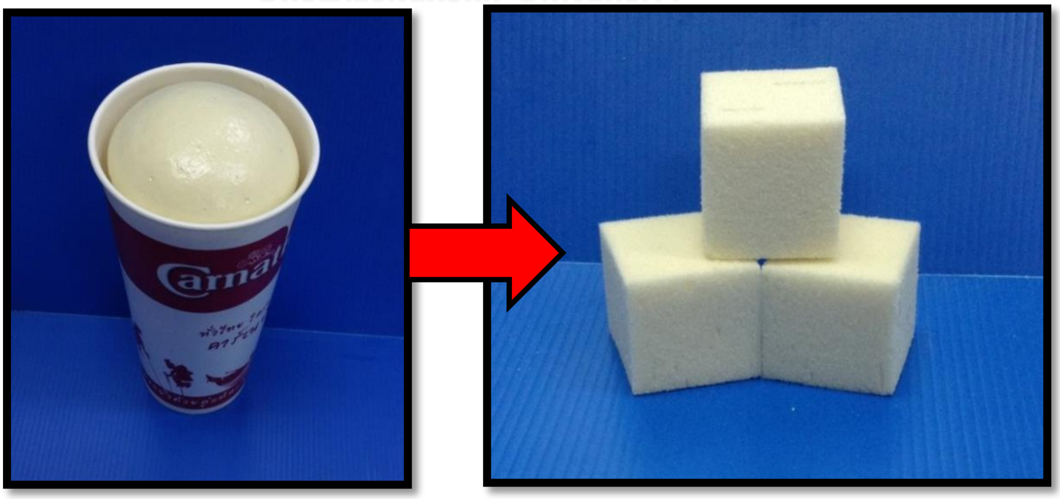

Figure 4.19 RPUR samples for foam density measurements

4.2.3.1 Effect of blowing agent quantity on foam density

The effect of blowing agent quantity on foam density is shown in Figure 4.20. The foam density decreased when the amount of blowing agent (water) was increased because water reacts with isocyanate group to give CO_2 gas. Therefore, the results indicated that the preparation of RPUR foams prepared using 4 pbw of water had the higher foam heights and less foam density than those prepared using 3 pbw of water (Figure 4.21). From these results, the amount of water which was suitable for RPUR foam formulation was 4 pbw.

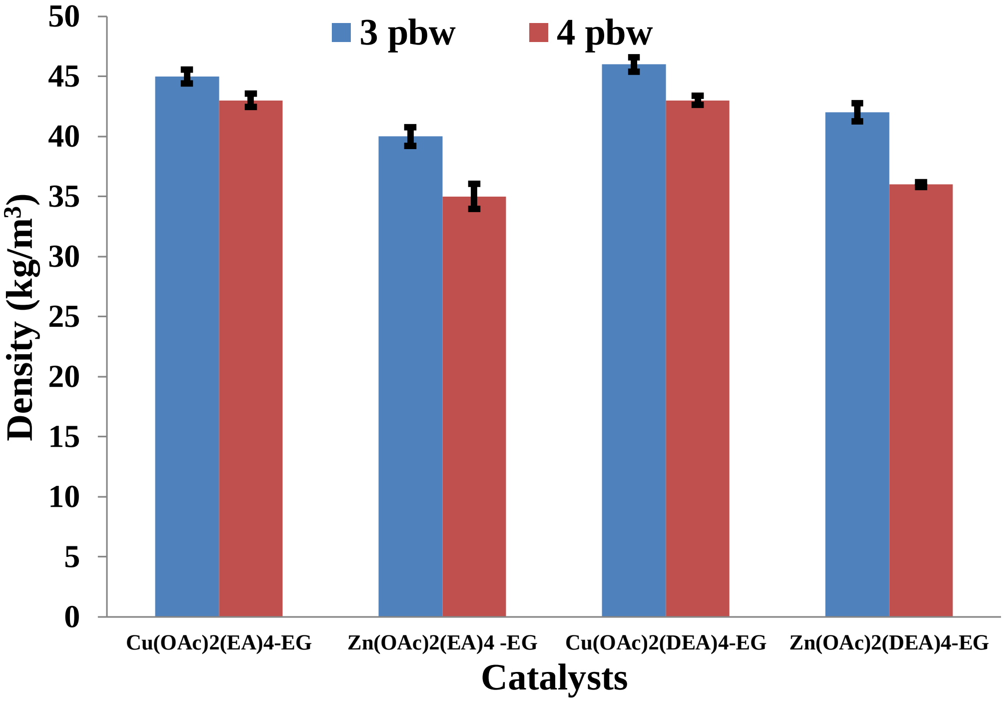

Figure 4.20 Effect of blowing agent quantity on foam density at the NCO index of 100

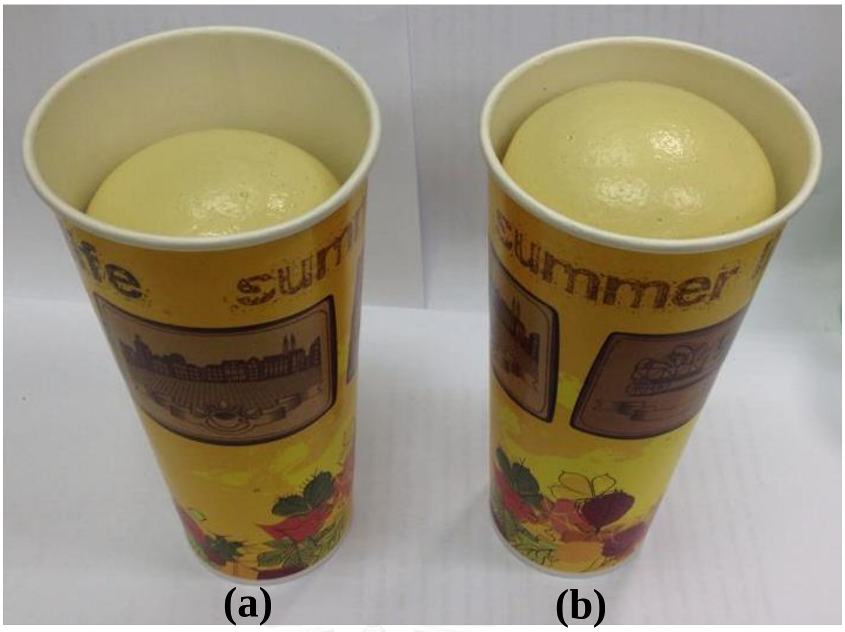

Figure 4.21 Appearance of RPUR foams catalyzed by metal-alkanolamine complexes using different amounts of blowing agent (water) (a) 3 pbw and (b) 4 pbw

4.2.3.2 Effect of catalyst quantity on foam density

Effect of catalyst quantity on foam density is shown in Figure 4.22. The foam density decreased when the amount of catalyst was increased because increasing the amount of catalyst also increased the blowing reaction. RPUR foams catalyzed by amount of catalyst at 2 pbw gave better blowing reaction and lower foam density than those prepared from 1.5, 1 and 0.5 pbw of catalyst (Figure 4.23). From these results, the amount of catalyst which was suitable for RPUR foam formulation was 1 pbw.

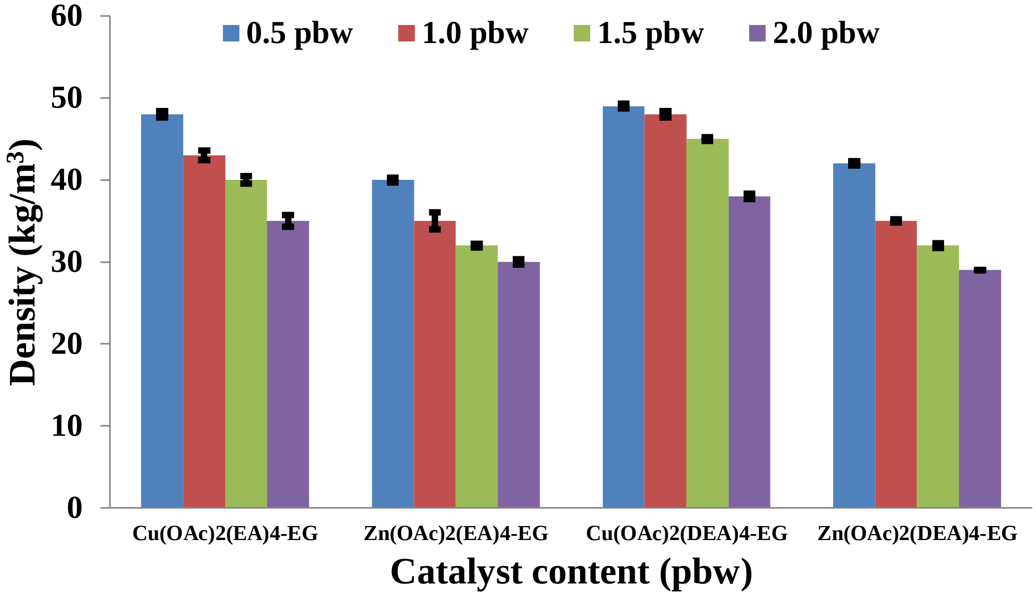

Figure 4.22 Effect of catalyst quantity on foam density

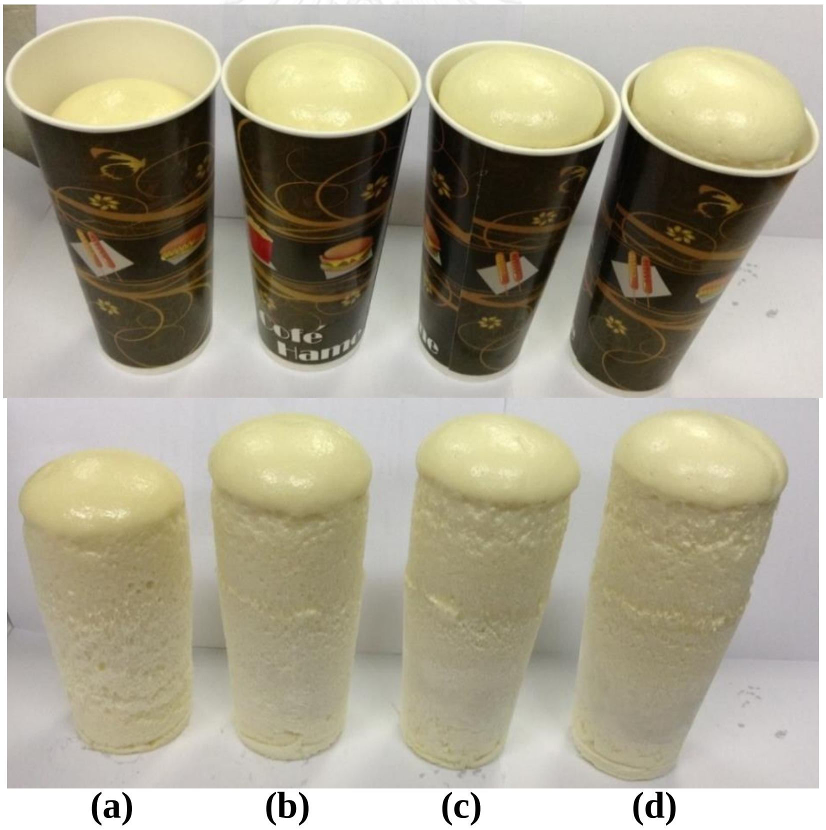

Figure 4.23 Appearance of RPUR foams prepared at different catalyst contents (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 pbw

4.2.4 Foaming Temperature

Figure 4.24 shows the temperature profile of RPUR foams catalyzed by $Cu(OAc)_2(EA)_4$-EG, $Zn(OAc)_2(EA)_4$-EG, $Cu(OAc)_2(DEA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG. The results were compared with RPUR foam catalyzed by DMCHA. It was found that all foams had similar temperature profiles and the polymerization reaction was exothermic, which was due to the released heat from the reactions between isocyanate-polyol and isocyanate-water. The maximum core temperature was in the range 121-133 °C (Table 4.3). $Cu(OAc)_2(EA)_4$-EG gave the highest core temperature, which indicated that it had the highest catalytic activity.

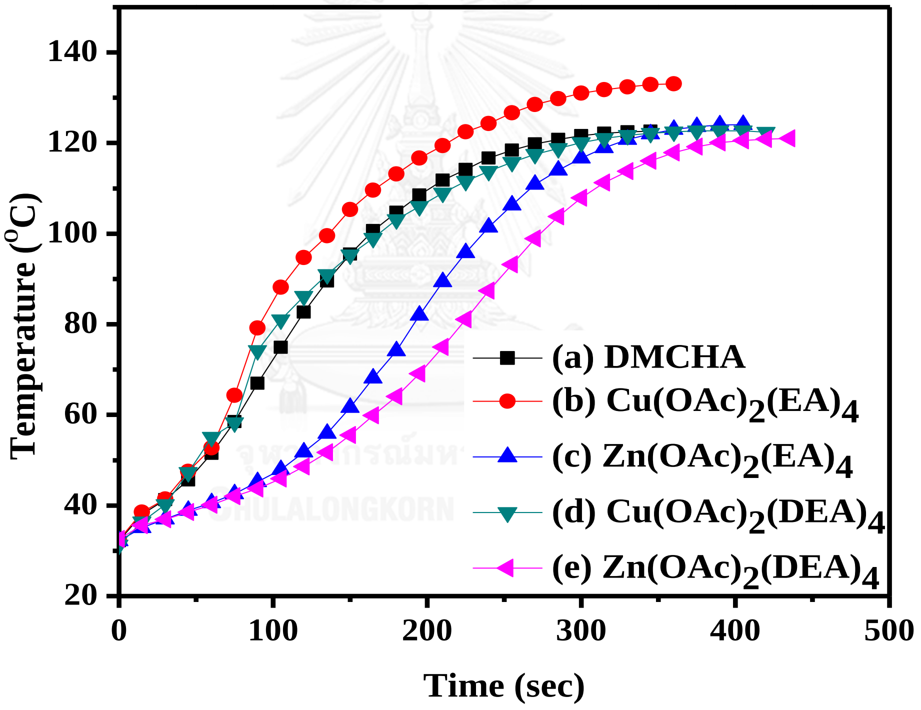

Figure 4.24 Temperature profiles of RPUR foams catalyzed by (a) DMCHA, (b) $Cu(OAc)_2(EA)_4$-EG, (c) $Zn(OAc)_2(EA)_4$-EG, (d) $Cu(OAc)_2(DEA)_4$-EG and (e) $Zn(OAc)_2(DEA)_4$-EG

Table 4.3 The maximum core temperature of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(EA)_4$-EG, $Zn(OAc)_2(EA)_4$-EG, $Cu(OAc)_2(DEA)_4$-EG and $Zn(OAc)_2(DEA)_4$-EG

Catalyst	**Maximum core temperature (°C)**	**Starting times (sec) at T_{max}***
DMCHA (ref.)	122.6	375
$Cu(OAc)_2(EA)_4$-EG	133.1	360
$Zn(OAc)_2(EA)_4$-EG	124.1	435
$Cu(OAc)_2(DEA)_4$-EG	122.7	375
$Zn(OAc)_2DEA)_4$-EG	121.0	445

*T_{max} = The maximum core temperature

4.2.5 Characterization of RPUR foams

IR spectra of starting materials, polyether polyol, polymeric MDI and RPUR foam catalyzed by DMCHA and metal-alkanolamine complexes are shown in Figures 4.25-4.26. IR spectrum of polyether polyol shows broad band at 3426 cm^{-1}, which is due to the stretching vibration of hydroxyl groups (OH group). Polymeric MDI shows high intensity peak of isocyanate (NCO) stretching at 2277 cm^{-1}.

All RPUR foams show similar IR absorptions as follows: NH stretching of urethane and urea at 3397 cm^{-1}, NH bending of urethane and urea at 1522 cm^{-1}, C=O stretching of urethane and urea at 1722 cm^{-1} and peak of C-O of urethane at 1101 cm^{-1}. From IR spectra of RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes, it was found that the peaks of isocyanate groups at 2277 cm^{-1} disappeared because they underwent reaction with polyether polyol and water to form urethane and urea linkages, respectively. These results confirmed that the foaming reaction catalyzed by DMCHA and metal-alkanolamine complexes was completed.

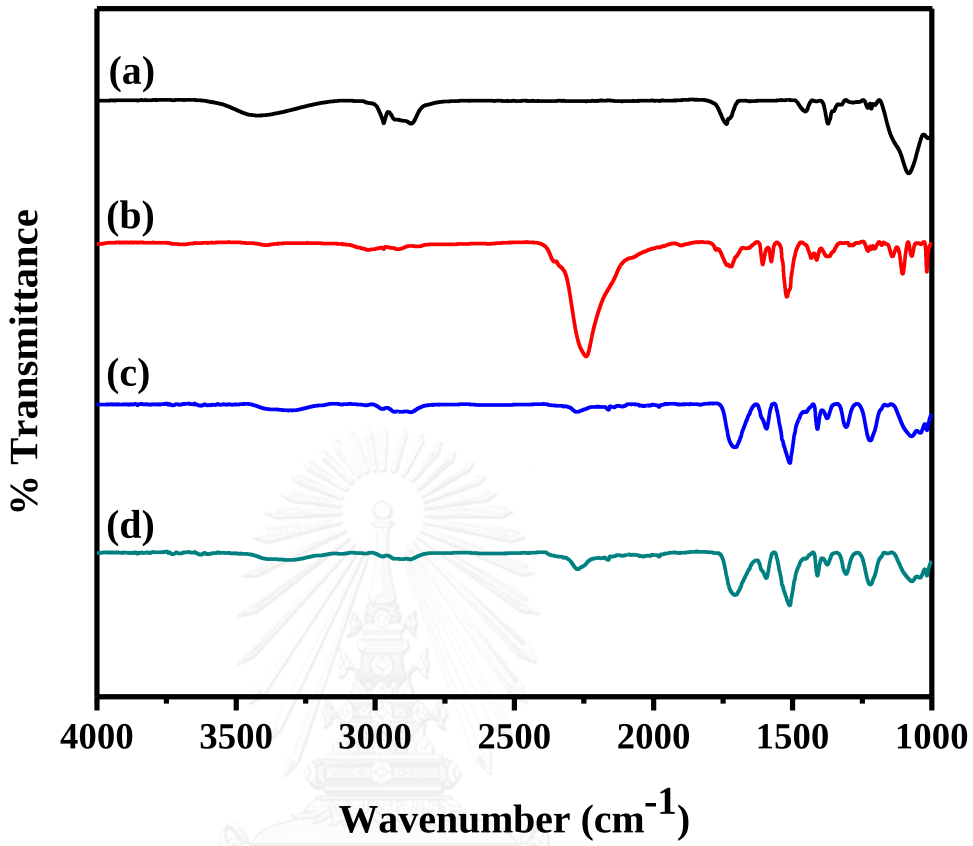

Figure 4.25 IR spectra of (a) polyether polyol, (b) polymeric MDI, RPUR foams catalyzed by (c) DMCHA and (d) $Cu(OAc)_2(EA)_4$-EG

4.2.6 Isocyanate (NCO) conversion of RPUR foams

FTIR spectra of polymeric MDI and RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes (Figure 4.26) were used to calculate the reaction progress of RPUR foam system. The peak area of functional groups used for calculation of % NCO conversion and PIR:PUR ratios are shown in Table 4.4. The calculation results are shown in Table 4.5.

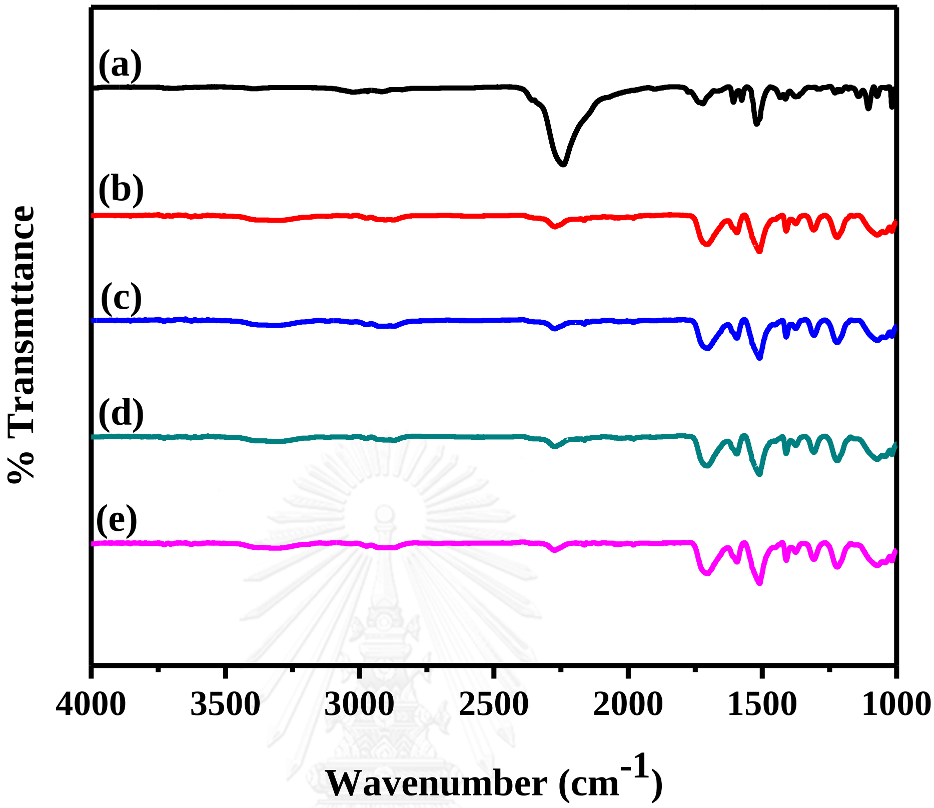

Figure 4.26 IR spectra of (a) polymeric MDI and RPUR foams catalyzed by (b) $Cu(OAc)_2(EA)_4$-EG, (c) $Zn(OAc)_2(EA)_4$-EG, (d) $Cu(OAc)_2(DEA)_4$-EG and (e) $Zn(OAc)_2(DEA)_4$-EG

The NCO conversion was determined from IR spectra and was defined as the ratio between isocyanate peak area at time 0 and isocyanate peak at time t as shown in the following equation:

$$\text{NCO conversion (\%)} = [1 - \frac{NCO^f}{NCO^i}] \times 100$$

NCO^f = the area of isocyanate peak area at time t (Figure 4.26 b-f)

NCO^i = the area of isocyanate peak area at initial time 0 (Figure 4.26 a)

Quantity of free NCO in RPUR foams was normalized by aromatic ring absorption band at 1595 cm^{-1}. Polyisocyanurate: polyurethane (PIR:PUR) ratio was calculated from the peak area of isocyanate group at 1415 and urethane group at 1220 cm^{-1}.

Table 4.4 Wavenumber of the functional groups used in calculation of NCO conversion

Functional groups	Wavenumber (cm^{-1})	Chemical structure
Isocyanate	2277	N=C=O
Phenyl	1595	Ar-H
Isocyanurate	1415	PIR
Urethane	1220	-C-O-

Table 4.5 NCO conversion and PIR:PUR ratio of RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes

Catalysts	NCO conversion (%)	PIR/PUR
DMCHA	99.59	1.8650
$Cu(OAc)_2(EA)_4$-EG	99.51	0.1549
$Zn(OAc)_2(EA)_4$-EG	99.25	0.1805
$Cu(OAc)_2(DEA)_4$-EG	99.07	0.1953
$Zn(OAc)_2DEA)_4$-EG	99.36	0.2043

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From Table 4.5, it was found that all RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes gave quantitative (approximately 99%) of NCO conversion and had the polyurethane:polyisocyanurate (PIR:PUR) ratio less than 0.22. Therefore, the reaction between polyol and isocyanate to give urethane group was the major reaction and trimerization reaction of isocyanate to form isocyanurate group was a minor reaction. It could be concluded that all metal-alkanolamine complexes were good catalysts for preparation of RPUR foams.

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4.3 Compressive properties of RPUR foams

Compressive strength of RPUR foams is an important parameter for their applications. Compression stress-strain curves of RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes in parallel and perpendicular to the foam rising direction are shown in Figures 4.27-4.28.

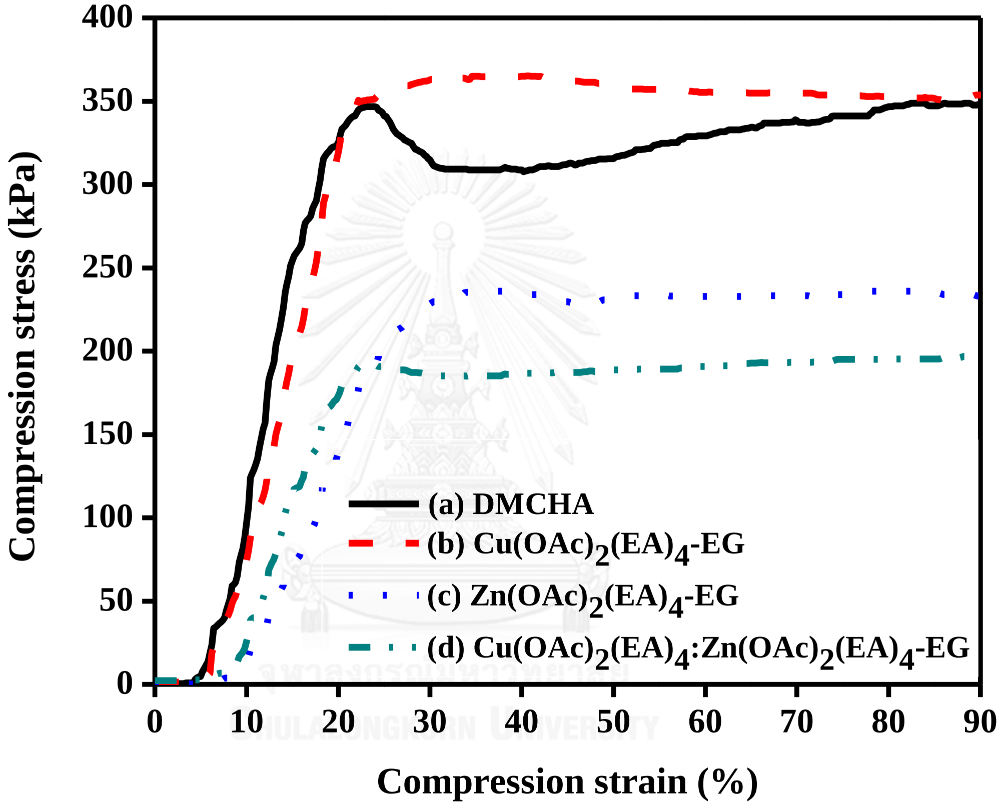

Figure 4.27 Compressive stress-strain curves of RPUR foams in parallel to the foam rising direction

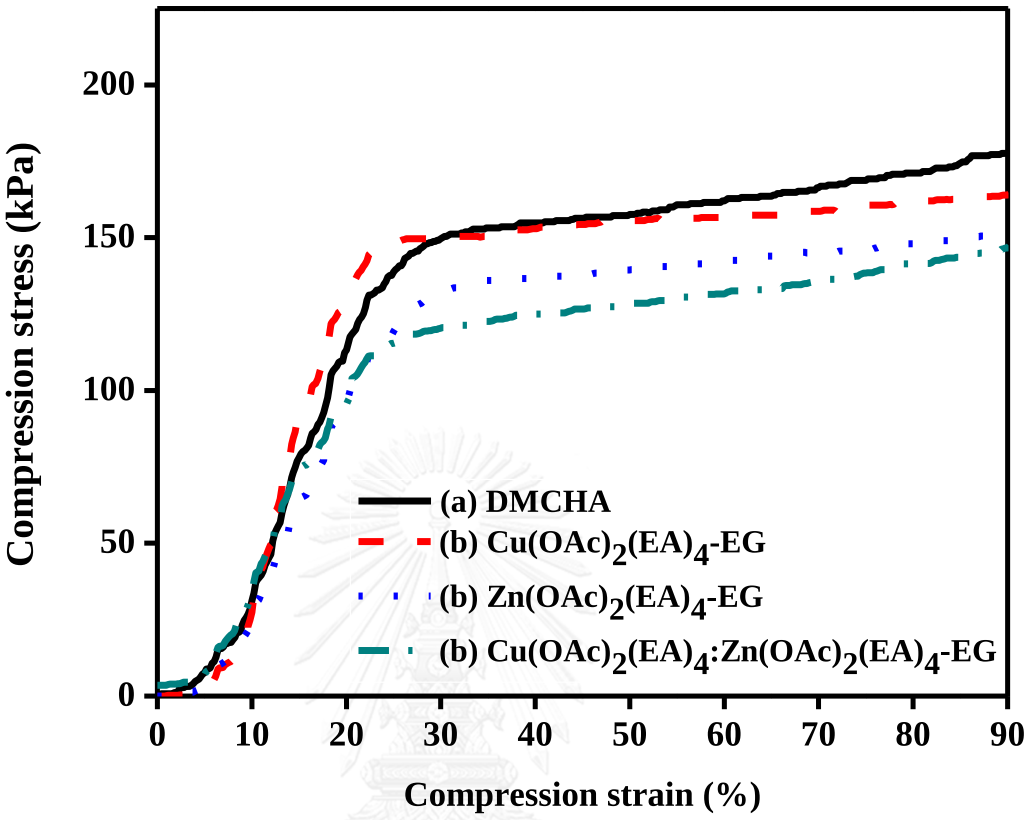

Figure 4.28 Compressive stress-strain curves of RPUR foams in perpendicular to the foam rising direction

From the compressive stress-strain curve, it was found that the compressive strength in parallel to the foam rising direction are higher than that of perpendicular to the foam rising direction. The results indicated that the shape of foam cell is anisotropic and having an ellipsoid shape. RPUR foam catalyzed by Cu(OAc)$_2$(EA)$_4$-EG had the highest compressive strength since the foam had the highest density.

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4.4 RPUR foam morphology

Morphology of RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes in parallel and perpendicular to the foam rising direction is shown in Figures 4.29-4.32. From SEM micrographs, all cell structure of RPUR foams are closed cell. RPUR foam catalyzed by Cu(OAc)$_2$(EA)$_4$-EG had similar cell size with RPUR foam catalyzed by DMCHA and had smaller cell size than RPUR foam catalyzed by Zn(OAc)$_2$(EA)$_4$-EG (Table 4.6).

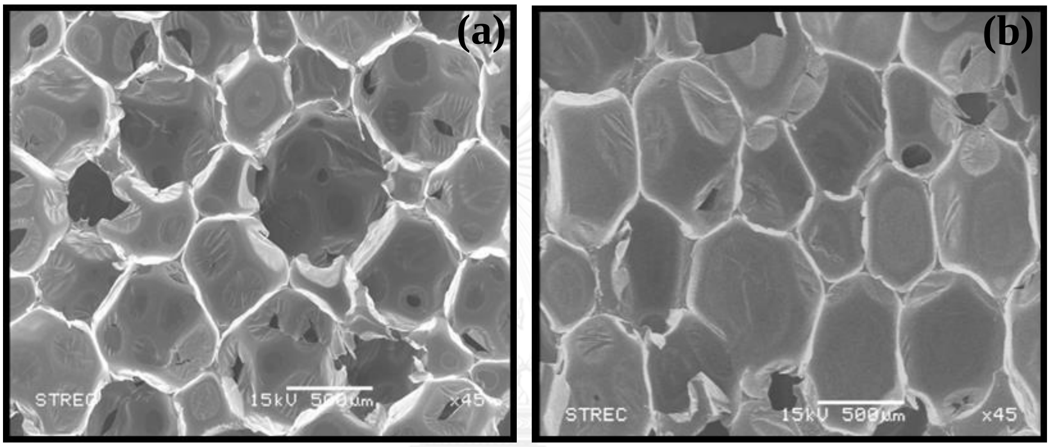

Figure 4.29 SEM micrographs of RPUR foams catalyzed by DMCHA (a) perpendicular and (b) parallel to the foam rising direction (45x)

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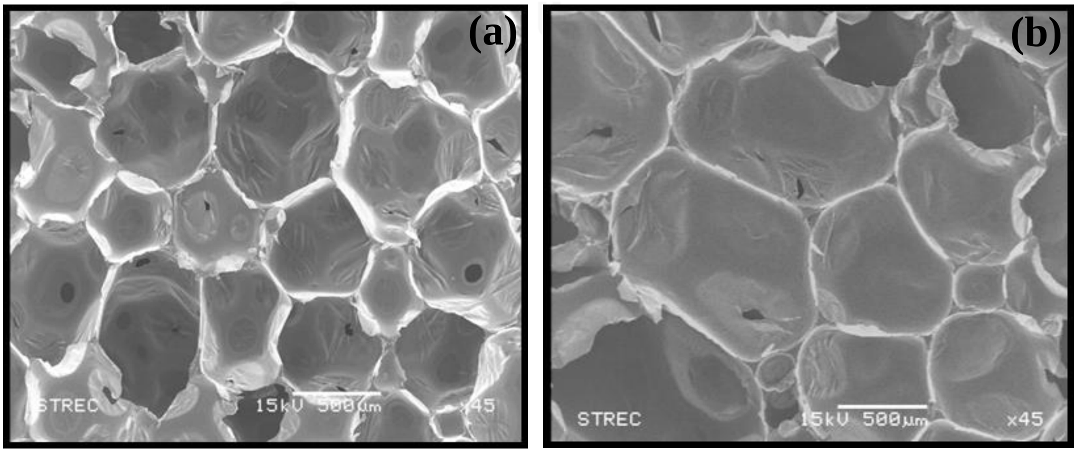

Figure 4.30 SEM micrographs of RPUR foams catalyzed by Cu(OAc)$_2$(EA)$_4$-EG (a) perpendicular and (b) parallel to the foam rising direction (45x)

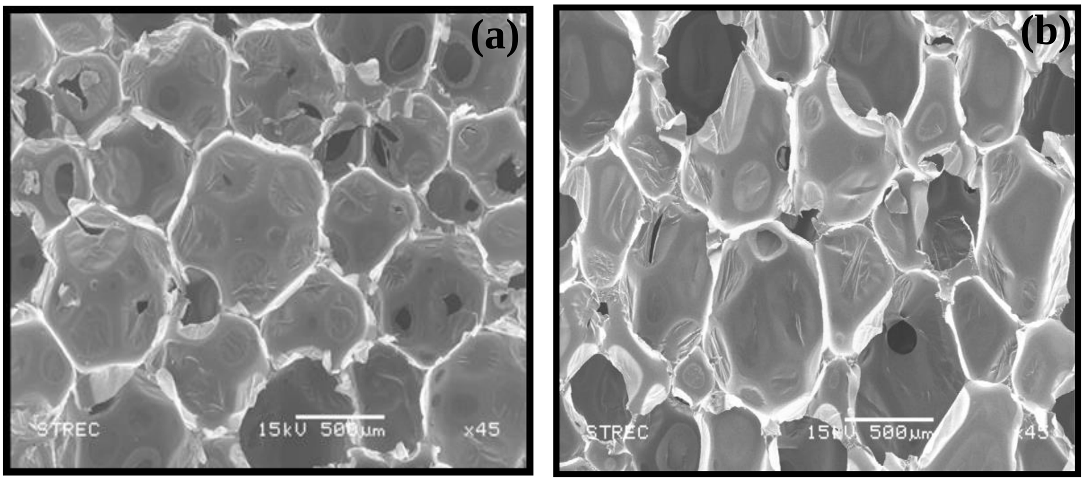

Figure 4.31 SEM micrographs of RPUR foams catalyzed by Zn(OAc)$_2$(EA)$_4$-EG (a) perpendicular and (b) parallel to the foam rising direction (45x)

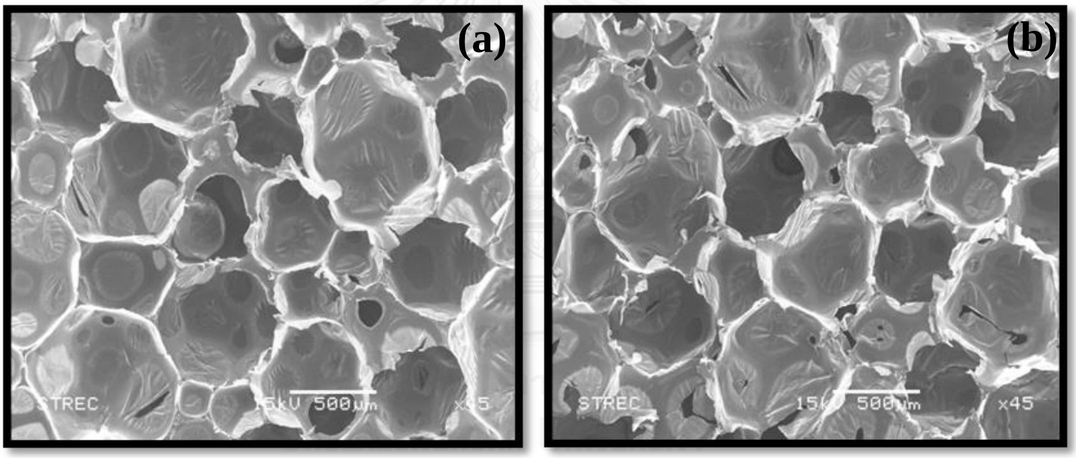

Figure 4.32 SEM micrographs of RPUR foams catalyzed by Cu(OAc)$_2$(EA)$_4$:Zn(OAc)$_2$(EA)$_4$-EG (a) perpendicular and (b) parallel to the foam rising direction (45x)

Table 4.6 Cell size of RPUR foams catalyzed by DMCHA and metal-alkanolamine complexes

Catalysts	**Perpendicular to the foam rising direction**		**Parallel to the foam rising direction**	
	Cell size (μm)	**S.D.**	**Cell size (μm)**	**S.D.**
DMCHA	340	9.82	295	10.15
$Cu(OAc)_2(EA)_4$-EG	352	9.77	300	11.21
$Zn(OAc)_2(EA)_4$-EG	450	18.96	341	22.23
$Cu(OAc)_2(EA)_4$: $Zn(OAc)_2(EA)_4$-EG	520	25.00	422	27.12

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CHAPTER V
CONCLUSIONS

5.1 Conclusions

Metal-alkanolamine and mixed metal-alkanolamine complexes, namely $Cu(OAc)_2(EA)_4$, $Cu(OAc)_2(DEA)_4$, $Zn(OAc)_2(EA)_4$, $Zn(OAc)_2(DEA)_4$, $Cu(OAc)_2(EA)_4$: $Zn(OAc)_2(EA)_4$ and $Cu(OAc)_2(DEA)_4$: $Zn(OAc)_2(DEA)_4$, were prepared as pure metal-alkanolamine complexes and solutions in ethylene glycol. They were used as catalysts for RPUR foam preparation. The pure metal-alkanolamine complexes were obtained as odorless viscous liquid. The metal-alkanolamine complexes in the form of solutions in ethylene glycol were obtained as odorless and low viscosity liquids. Both pure metal-alkanolamine complexes and metal-alkanolamine complex solutions in ethylene glycol could be easily dissolved in the raw materials of RPUR foam formulations. UV-visible spectroscopy, FTIR spectroscopy and mass spectrometry were used to characterize the metal complexes. UV and mass spectra confirmed that the same metal complexes could be synthesized in acetone and ethylene glycol to obtain pure metal-alkanolamine complexes and solutions of metal-alkanolamine complexes in ethylene glycol, respectively.

The catalytic activity of the metal-alkanolamine complexes for RPUR foam preparation has been investigated. From the reaction times, the metal-alkanolamine complexes showed comparable catalytic activity to the commercial catalyst (DMCHA). Thus, these complexes are suitable to be used as a catalyst for RPUR foam formulation. Both complexes synthesized in acetone and ethylene glycol (EG) gave the similar reactivity results. Therefore, the preparation of metal-alkanolamine complexes in EG is more convenient than the preparation in acetone since the solution of metal-alkanolamine complexes in EG can be further used in the preparation of polyurethane foam without purification.

By varying the catalyst contents, it was found that the reaction times and foam density decreased when the amount of catalyst was increased. The optimum amount of catalyst in RPUR foam formulation was 1 pbw. Among all metal-alkanolamine complexes, $Cu(OAc)_2(EA)_4$ showed the highest catalytic activity and gave good appearance of foam

By varying the blowing agent quantity, it could be concluded the foam density decreased when the amount of blowing agent was increased and the optimum amount of blowing agent in RPUR foam was 4 pbw. The amount of blowing agent at 4 pbw released more CO_2 and gave higher foam height than the amount of blowing agent at 3 pbw.

Rise profile of RPUR foaming reaction catalyzed by copper-alkanolamine complexes gave shorter rise time than zinc-alkanolamine complexes and had similar trend to that of DMCHA. Copper-alkanolamine catalysts had better catalytic activity than zinc-alkanolamine catalysts. The polymerization of RPUR foams was exothermic reaction. The maximum core temperature was in the range of 121-133 °C and RPUR foam catalyzed by $Cu(OAc)_2(EA)_4$ had higher core temperature than those prepared from other metal- alkanolamine complexes.

The NCO conversion could be investigated by FTIR spectroscopy. All RPUR foams catalyzed by metal-alkanolamine complexes gave approximately 99% of NCO conversion and had the polyurethane:polyisocyanurate (PIR:PUR) ratio less than 0.22. Therefore, the reaction between polyol and isocyanate to give urethane group was the major reaction and trimerization reaction of isocyanate to form isocyanurate group was a minor reaction. It could be concluded that all metal-alkanolamine complexes were good catalysts for preparation of RPUR foams.

From the compressive stress-strain curve, it was found that the compressive strength in parallel to the foam rising direction are higher than that in perpendicular to the foam rising direction. The results indicated that RPUR foams are anisotropic materials and having ellipsoid cell shape.

From SEM micrographs, the cell structure of RPUR foams are closed cell. RPUR foam catalyzed by $Cu(OAc)_2(EA)_4$ had the similar cell size with that catalyzed by DMCHA and had smaller cell size than that catalyzed by $Zn(OAc)_2(EA)_4$.

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5.2 Suggestion for future work

Since $Cu(OAc)_2(EA)_4$ can be used to catalyze RPUR foam reactions. The suggestion for future work is to use $Cu(OAc)_2(EA)_4$ in the other system such as waterborne polyurethane system.

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APPENDIX

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APPENDICE A

NCO index and NCO conversion calculations

NCO index calculation

Example Calculate the parts by weight (pbw) of PMDI (Suprasec® 5005), molar mass = 365.8, functionality = 2.7 at an isocyanate index of 100 required to react with the following formulation:

Starting materials	**Formulation (part by weight, pbw)**
Daltolac® R180 (OHV = 440 mgKOH/g, functionality = 4.3)	100.0
Catalysts (60%wt in ethylene glycol)	1.0
Surfactant	2.5
Blowing agent (water, MW = 18 g/mole, functionality = 2)	3.0
PMDI (Suprasec® 5005), NCO index of 100	?

Equivalent weight of Daltolac® R180 $= \frac{56.1}{440} \times 1000 = 127.5$

Equivalent weight of water $= \frac{18}{2} = 9.0$

Equivalent weight of ethylene glycol $= \frac{62}{2} = 31.0$

Note: Surfactants and catalysts are neglected in stoichiometric calculations because they do not react with NCO groups.

Number of equivalent in formulation $= \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$

Equivalent in the above formulation:

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Polyol (Daltolac® R180) = $\frac{100}{127.5}$ = 0.784

Water (blowing agent) = $\frac{3.0}{9.0}$ = 0.333

Ethylene glycol (solvent) = $\frac{1.98}{31.0}$ = 0.064

Total equivalent weight = 1.181

For stoichiometric equivalence, PMDI pbw is total equivalent x equivalent weight because PMDI reacts with polyol, water and ethylene glycol.

Thus:

PMDI (pbw) = 1.181 x $\frac{PMDI\ molar\ mass}{functionality}$ = 1.181 x $\frac{365.8}{2.7}$ = 160.0

Note: 160.0 defines the isocyanate quantity at the NCO index of 100

Where;

$$\text{Isocyanate index} = \frac{actual\ amount\ of\ isocyanate}{theoretical\ amount\ of\ isocyanate} \text{ x } 100$$

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Thus:

Isocyanate index = 100;

$$\text{Isocyanate actual} = \frac{160.0}{100} \text{ x } 100 = 160.0 \text{ pbw}$$

Table A1 Isocyanate quantity at different amount of blowing agent in the above formulations (NCO index of 100)

Formulation (pbw)	Blowing agent quantity (pbw)	
	3.0	**4.0**
Polyol (Daltolac® R180)	100	100
Catalysts	1.0	1.0
Surfactant	2.5	2.5
PMDI (Suprasec®5005)	154.30	169.35

<u>NCO conversion calculation</u>

The NCO conversion can be calculated by FTIR method, defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0, as shown in the following equation:

$$\text{Isocyanate conversion (\%)} = \left[1 - \frac{NCO^f}{NCO^i}\right] \text{ x } 100$$

Where;

NCO^f is the area of isocyanate absorbance peak area at time t

NCO^i is the area of isocyanate absorbance peak area at time 0

Quantity of free NCO in RPUR foams were normalized by aromatic ring absorption band at 1595 cm^{-1}

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Table A2 Free NCO absorbance peak area in PMDI (Suprasec® 5005) from ATR-IR

PMDI (Suprasec® 5005) spectra	**NCO absorbance peak area (normalized @ 1.0 Ar-H peak area)**
1	98.02
2	97.96
3	98.10
Average (NCO^i); ATR-IR	98.00

Example Calculate the conversion of isocyanate (α) and PIR:PUR of rigid polyurethane foams catalyzed by $Cu(OAc)_2(EA)_4$ catalyst at the NCO index of 100

<u>Conversion of isocyanate (%)</u>

Data at **Table A2**

Absorbance peak area of initial NCO = 98.0 = NCO^i

The data from **Table A3** at NCO index 100, absorbance peak area of free NCO was normalized by aromatic ring quantity:

Absorbance peak area of final NCO = 0.4813 =NCO^f

Thus, conversion of isocyanate (%) = $\left[1 - \frac{NCO^f}{NCO^i}\right]$ x 100

= $\left[1 - \frac{0.4813}{98.0}\right]$ x 100

% NCO conversion = 99.51

PIR:PUR ratio

Absorbance peak area of PIR (polyisocyanurate) = 0.836

Absorbance peak area of PUR (polyurethane) = 5.397

Thus, PIR:PUR = $\frac{0.836}{5.397}$ = 0.1549

Table A3 NCO conversion of RPUR foam catalyzed by DMCHA at the NCO index of 100 (catalyst = 1 pbw, H_2O = 3 pbw)

Catalyst	**Peak area**					**NCO conversion (%)**	**PIR/ PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
DMCHA	0.865	2.155	1.066	5.715	0.4014	99.59	0.1865

Table A4 NCO conversion of RPUR foams catalyzed by metal-alkanolamine complexes synthesized in EG at the NCO index of 100 (catalyst = 1 pbw, H_2O = 3 pbw)

Catalysts	**Peak area**					**NCO conversion (%)**	**PIR/ PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
$Cu(OAc)_2(EA)_4$-EG	1.442	1.891	0.952	4.629	0.7626	99.22	0.2057
$Zn(OAc)_2(EA)_4$-EG	1.640	2.152	1.051	4.974	0.7621	99.22	0.2113
$Cu(OAc)_2(DEA)_4$-EG	1.778	1.964	0.937	4.592	0.9053	99.08	0.2041
$Zn(OAc)_2(DEA)_4$-EG	2.436	2.518	0.935	4.354	0.9674	99.01	0.2147

Table A5 NCO conversion of RPUR foams catalyzed by metal-alkanolamine complexes synthesized in EG at the NCO index of 100 (catalyst = 1 pbw, H_2O = 4 pbw)

Catalysts	**Peak area**					**NCO conversion (%)**	**PIR/ PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
$Cu(OAc)_2(EA)_4$-EG	0.966	2.007	0.836	5.397	0.4813	99.51	0.1549
$Zn(OAc)_2(EA)_4$-EG	1.442	1.973	0.900	4.986	0.7309	99.25	0.1805
$Cu(OAc)_2(DEA)_4$-EG	1.614	1.769	0.960	4.916	0.9124	99.07	0.1953
$Zn(OAc)_2(DEA)_4$-EG	1.333	2.142	1.022	5.003	0.6223	99.36	0.2043

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Table A6 NCO conversion of RPUR foams catalyzed by metal-alkanolamine complexes synthesized in acetone at the NCO index of 100 (catalyst = 1 pbw, H_2O = 4 pbw)

Catalysts	**Peak area**					**NCO conversion (%)**	**PIR/ PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
$Cu(OAc)_2(EA)_4$-acetone	0.879	1.688	0.739	4.192	0.5207	99.5	0.176
$Zn(OAc)_2(EA)_4$-acetone	1.373	1.509	0.756	4.147	0.9099	99.1	0.182
$Cu(OAc)_2(DEA)_4$-acetone	1.809	1.759	0.772	4.193	1.0284	99.0	0.184
$Zn(OAc)_2(DEA)_4$-acetone	1.983	1.886	0.829	4.689	1.0514	98.9	0.177

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APPENDICE B

Reaction times

Table B1 Formulation, reaction times, physical and mechanical properties of RPUR foams catalyzed by commercial reference catalyst (DMCHA) at the NCO index of 100

Formulations (pbw)	Catalysts at NCO index 100	
	DMCHA (ref.)	
Polyol (Daltolac® R180)	100	
Catalysts	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Suprasec® 5005)	154.30	
Efficiency parameters	**Data**	**S.D.**
Reaction times		
Cream time (min:sec)	0:28	0:03
Gel time (min:sec)	0:43	0:05
Tack free time (min:sec)	3:05	0:04
Rise time (min:sec)	2:20	0:02
Density (kg/m^3)	41.5	0.39
Mechanical properties		
Compressive strength (kPa) ($\perp$)*	337.40	9.40
Compressive strength (kPa) ($\parallel$)*	150.80	2.40

*($\perp$) = (perpendicular to the foam rising direction)
*($\parallel$) = (parallel to the foam rising direction)

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Table B2 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(EA)_4$ at the NCO index of 100 (H_2O = 4 pbw)

$Cu(OAc)_2(EA)_4$	**Catalyst quantity (pbw)**							
	0.5		**1.0**		**1.5**		**2.0**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D**	**Data**	**S.D.**
Reaction times								
Cream time (min:sec)	0:50	0:05	0:41	0:02	0:35	0:01	0:32	0:06
Gel time (min:sec)	1:40	0:03	1:21	0:04	1:10	0:05	1:01	0:05
Tack free time (min:sec)	3:00	0:01	2:46	0:02	2:40	0:03	2:15	0:02
Rise time (min:sec)	3:05	0:02	2:57	0:03	2:45	0:04	2:20	0:01
Density (kg/m^3)	48.32	0.41	42.54	0.58	40.17	0.48	35.41	0.74
Mechanical properties								
Compressive strength (kPa) (⊥)	-	-	362.00	3.25	-	-	-	-
Compressive strength (kPa) (∥)	-	-	153.55	3.94	-	-	-	-

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Table B3 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Zn(OAc)_2(EA)_4$ at the NCO index of 100 (H_2O = 4 pbw)

$Zn(OAc)_2(EA)_4$	**Catalyst quantity (pbw)**							
	0.5		**1.0**		**1.5**		**2.0**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D**	**Data**	**S.D.**
Reaction times								
Cream time (min:sec)	1:10	0:05	0:45	0:03	0:04	0:04	0:36	0:05
Gel time (min:sec)	3:00	0:02	2:05	0:03	1:40	0:02	1:21	0:04
Tack free time (min:sec)	4:05	0:03	3:29	0:02	3:05	0:03	2:30	0:02
Rise time (min:sec)	4:30	0:01	3:53	0:05	3:20	0:03	2:40	0:02
Density (kg/m^3)	40.53	0.31	34.38	1.07	32.71	0.26	30.53	0.35
Mechanical properties								
Compressive strength (kPa) ($\perp$)	-	-	242.88	3.12	-	-	-	-
Compressive strength (kPa) ($\parallel$)	-	-	126.30	2.30	-	-	-	-

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Table B4 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(DEA)_4$ at the NCO index of 100 (H_2O = 4 pbw)

$Cu(OAc)_2(DEA)_4$	**Catalyst quantity (pbw)**							
	0.5		**1.0**		**1.5**		**2.0**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D**	**Data**	**S.D.**
Reaction times								
Cream time (min:sec)	0:46	0:06	0:40	0:01	0:37	0:05	0:32	0:03
Gel time (min:sec)	1:25	0:03	1:20	0:01	1:15	0:03	1:10	0:03
Tack free time (min:sec)	2:38	0:04	2:35	0:02	2:33	0:02	2:10	0:04
Rise time (min:sec)	2:42	0:03	2:40	0:04	2:37	0:02	2:15	0:03
Density (kg/m^3)	48.54	0.33	48.13	0.40	45.35	0.26	38.41	0.34
Mechanical properties								
Compressive strength (kPa) ($\perp$)	-	-	-	-	-	-	-	-
Compressive strength (kPa) ($\parallel$)	-	-	-	-	-	-	-	-

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Table B5 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Zn(OAc)_2(DEA)_4$ at the NCO index of 100 (H_2O = 4 pbw)

$Zn(OAc)_2(DEA)_4$	**Catalyst quantity (pbw)**							
	0.5		**1.0**		**1.5**		**2.0**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D**	**Data**	**S.D.**
Reaction times								
Cream time (min:sec)	1:10	0:05	1:00	0:03	0:46	0:03	0:40	0:03
Gel time (min:sec)	3:40	0:04	1:55	0:03	1:30	0:02	1:20	0:05
Tack free time (min:sec)	5:15	0:05	4:10	0:05	2:55	0:01	2:40	0:02
Rise time (min:sec)	5:00	0:03	4:00	0:04	3:00	0:01	2:55	0:02
Density (kg/m^3)	42.15	0.28	35.20	0.22	32.45	0.30	29.50	0.24
Mechanical properties								
Compressive strength (kPa) (⊥)	-	-	-	-	-	-	-	-
Compressive strength (kPa) (‖)	-	-	-	-	-	-	-	-

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Table B6 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(EA)_4$:$Zn(OAc)_2(EA)_4$ at the NCO index of 100 (H_2O = 4 pbw)

$Cu(OAc)_2(EA)_4$: $Zn(OAc)_2(EA)_4$	**Catalyst quantity (pbw)**							
	0.5		**1.0**		**1.5**		**2.0**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D**	**Data**	**S.D.**
Reaction times								
Cream time (min:sec)	0:55	0:01	0:36	0:02	0:33	0:06	0:30	0:04
Gel time (min:sec)	2:25	0:02	1:30	0:04	1:10	0:07	0:56	0:05
Tack free time (min:sec)	4:35	0:05	2:50	0:05	2:00	0:04	1:39	0:05
Rise time (min:sec)	4:40	0:04	2:57	0:05	2:25	0:03	2:00	0:03
Density (kg/m^3)	41.27	0.19	33.04	0.49	31.95	0.18	29.87	0.46
Mechanical properties								
Compressive strength (kPa) (⊥)	-	-	201.38	8.62	-	-	-	-
Compressive strength (kPa) (∥)	-	-	107.40	5.00	-	-	-	-

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Table B7 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(DEA)_4$:$Zn(OAc)_2(DEA)_4$ at the NCO index of 100 (H_2O = 4 pbw)

$Cu(OAc)_2(DEA)_4$: $Zn(OAc)_2(DEA)_4$	**Catalyst quantity (pbw)**							
	0.5		**1.0**		**1.5**		**2.0**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D**	**Data**	**S.D.**
Reaction times								
Cream time (min:sec)	1:00	0:01	0:50	0:02	0:40	0:02	0:35	0:02
Gel time (min:sec)	2:40	0:05	1:40	0:02	1:35	0:06	1:05	0:02
Tack free time (min:sec)	4:50	0:02	3:15	0:05	2:30	0:03	1:47	0:03
Rise time (min:sec)	5:00	0:06	3:20	0:02	3:05	0:01	2:05	0:02
Density (kg/m^3)	46.57	0.24	37.32	0.15	36.24	0.22	33.38	0.42
Mechanical properties								
Compressive strength (kPa) (⊥)	-	-	-	-	-	-	-	-
Compressive strength (kPa) (‖)	-	-	-	-	-	-	-	-

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