การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนคอปเปอร์-แอมีนที่เตรียมในน้ำ

นางสาวพรสวรรค์ น้อยอาษา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY COPPER-AMINE COMPLEXES PREPARED IN WATER

Miss Phornsawan Noiasa

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
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Field of Study	Chemistry
Thesis Advisor	Associate Professor Nuanphun Chantarasiri, Ph.D.

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พรสวรรค์ น้อยอาษา : การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนคอปเปอร์-แอมีนที่เตรียมในน้ำ (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY COPPER-AMINE COMPLEXES PREPARED IN WATER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.นวลพรรณ จันทรศิริ, 72 หน้า.

งานวิจัยนี้เป็นการพัฒนาตัวเร่งปฏิกิริยาสำหรับเตรียมพอลิยูรีเทนโฟมแบบแข็งเพื่อลดกลิ่นเหม็นเมื่อเทียบกับตัวเร่งปฏิกิริยาที่ใช้ในอุตสาหกรรม คือ ไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA) ซึ่งมีกลิ่นเหม็น โดยตัวเร่งปฏิกิริยาที่สังเคราะห์เป็นสารประกอบเชิงซ้อนคอปเปอร์-แอมีน คือ $Cu(OAc)_2(amine)_2$ และ $Cu(OAc)_2(amine)$ เมื่อ amine คือ เอทิลีนไดแอมีน (en), ไตรเอทิลีนเตตรามีน (trien), เตตระเอทิลีนเพนทามีน (tetraen) และ เพนตะเอทิลีนเฮกซามีน (pentaen) การสังเคราะห์สารประกอบเชิงซ้อนคอปเปอร์-แอมีนใช้วิธีการสังเคราะห์ภายใต้เคมีสีเขียว คือ ใช้น้ำเป็นตัวทำละลาย จะได้เป็นสารละลายของสารประกอบเชิงซ้อนคอปเปอร์-แอมีนที่ละลายในน้ำ ซึ่งสามารถนำสารละลายดังกล่าวไปใช้ในการเตรียมพอลิยูรีเทนโฟมแบบแข็งโดยไม่ต้องทำให้บริสุทธิ์ การพิสูจน์เอกลักษณ์ของสารประกอบเชิงซ้อนคอปเปอร์-แอมีนใช้ยูวี-วิสสิเบิลสเปกโทรสโกปี อินฟราเรดสเปกโตรสโกปี และแมสสเปกโทรเมตรี ศึกษาประสิทธิภาพในการเร่งปฏิกิริยาของสารละลายของสารเชิงซ้อนคอปเปอร์-แอมีนจากเวลาที่ใช้ในการเกิดปฏิกิริยา สมบัติทางกายภาพและสมบัติเชิงกลของพอลิยูรีเทนโฟม เปรียบเทียบกับโฟมที่เร่งปฏิกิริยาด้วยไดเมทิลไซโคลเฮกซิลแอมีน จากผลการทดลองพบว่า สารละลายคอปเปอร์-แอมีนในน้ำสามารถผสมได้เข้ากันกับสารตั้งต้นในการเตรียมพอลิยูรีเทนโฟมได้ดี โดย $Cu(OAc)_2(en)_2$ และ $Cu(OAc)_2(trien)$ มีความว่องไวในการเร่งปฏิกิริยาสูง โฟมที่ได้มีความหนาแน่นที่เหมาะสม มีสมบัติเชิงกายภาพและสมบัติเชิงกลที่ดี ดังนั้น $Cu(OAc)_2(en)_2$ และ $Cu(OAc)_2(trien)$ จึงมีความเหมาะสมสำหรับใช้เป็นตัวเร่งปฏิกิริยาของพอลิยูรีเทนโฟมแบบแข็ง

ภาควิชา เคมี

สาขาวิชา เคมี

ปีการศึกษา 2559

ลายมือชื่อนิสิต ....

ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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KEYWORDS: RIGID POLYURETHANE FOAM / COPPER-AMINE COMPLEX / CATALYST

PHORNSAWAN NOIASA: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY COPPER-AMINE COMPLEXES PREPARED IN WATER. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 72 pp.

In this research, the catalysts for preparation of rigid polyurethane (RPUR) foams were developed in order to reduce odor as compared with dimethylcyclohexylamine (DMCHA), which has strong odor. These synthesized catalysts were copper-amine complexes, namely $Cu(OAc)_2(amine)_2$ and $Cu(OAc)_2(amine)$, where amine = ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pantaethylenehexamine (pentane). The synthesis of copper-amine complexes was done using green chemistry approach, which used water as a solvent. The aqueous solutions of copper-amine complexes in water were obtained. These aqueous solutions could be further used in the preparation of RPUR forms without purification. Characterization of copper-amine complexes was done by using UV-visible spectroscopy, Fourier transform infrared spectroscopy and mass spectrometry. The catalytic activity was studied by investigation of the reaction times. Physical and mechanical properties of RPUR foams were studied. The data were compared with those obtained from DMCHA. The experimental results showed that the aqueous solutions of all copper-amine complexes could be easily dissolved in the starting materials of RPUR foam formulation. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ had high catalytic activity. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ gave the RPUR foams having appropiate density, good physical and mechanical properties. Therefore, $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ were suitable catalysts for preparation of RPUR foams.

Department:	Chemistry	Student's Signature	....
Field of Study:	Chemistry	Advisor's Signature	....
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LIST OF ABBREVIATIONS

3^{O}	tertiary
%	percentage
ε	molar absorptivity
α	isocyanate conversion
λ_{max}	maximum absorption peak
acac	acetylacetonate
ATR-IR	attenuated total reflectance-infrared
ASTM	American Society for Testing and Material
NH_3	ammonia
BDMAEE	bis (2-dimethylaminoethyl) ether
cm	centimeter
cm^{-1}	unit of wavenumber
^{o}C	degree Celsius (centrigrade)
Cd	cadmium
CO_2	carbon dioxide gas
CFCs	chlorofluorocarbons
Co	cobolt
$Cu(OAc)_2$	copper acetate

Cr	chromium
DBTDL	dibutyltin dilaurate
DMCHA	*N*,*N*-dimethylcyclohexylamine
ESI	electrospray ionization
EG	ethylene glycol
en	ethylenediamine
e.g.	example
FTIR	Fourier transform infrared spectrophotometer
FPUR	flexible polyurethane
g	gram
h	hour
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
KOH	potassium hydroxide
kg	kilogram
kV	kilovolt
M	metal
m^3	cubic meter
MDI	4,4'-methane diphenyl diisocyanate

mg	milligram
min	minute
mL	milliliter
mm	millimeter
mmol	millimole
MPa	megapascal
NCO	isocyanate group
OAc	acetate
Pentane	pentaethylenetatramine
Pbw	part by weight
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PUR	polyurethane
Ref	reference
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
sec	second
Sn	tin
SEM	scanning electron microscopy

t	time
T_{max}	maximum core temperature
TEDA	triethylenediamine
TMP	trimethylol propene
tetraen	tetraethylenetriamine
TDI	toluene diisocyanate
TMP	trimetylol propane
trien	triethylenetetramine
UV-vis	ultraviolet visible

CHAPTER I

INTRODUCTION

Polyurethane foams that are widely used are flexible polyurethane foams and rigid polyurethane (RPUR) foams. The cell of flexible polyurethane foam is an open cell. Therefore, this type of foam is used as cushioning for furniture, carpet, bedding and packaging. The cell of RPUR foam is a closed cell which is most suitable for thermal insulation due to their low thermal conductivity, low density, small cell size and high closed cell content. Therefore, RPUR foams can be used as the insulator in the building and the refrigerators [1, 2].

Polyurethane foams are foamed by exothermic reaction between polyfunctional isocyanate and poly functional OH species. Polyurethane foam synthesis involves two main reactions, namely blowing and gelling reactions. Blowing reaction is the reaction of an isocyanate group (-NCO) with water and yields urea and generates carbon dioxide, which gives air bubbles entrapped inside the RPUR foam. Gelling reaction is the reaction between an isocyanate group (-NCO) and a hydroxyl group (-OH) of polyol to form a urethane linkage [3, 4]. However, these two reactions are slow. Therefore, the catalysts are required for preparation of RPUR foams.

Tertiary amines such as *N,N*-dimethylcyclohexylamine (DMCHA) and organotin compounds such as dibutyltin dilaurate (DBTDL) are widely used as commercial catalysts for preparation of RPUR foams [5]. The problems in using amine and organotin catalysts are their strong odor and toxicity, respectively. Several attempts have been made in order to replace them by different catalysts with weak odor and low toxicity, such as zirconium compounds [6] and metal-amine complexes [7].

In our previous researches, copper-amine complexes with good catalytic activity for the preparation of RPUR foams were synthesized. These catalysts were copper-ethylenediamine [$Cu(OAc)_2(en)_2$] and copper-triethylenetetramine [$Cu(OAc)_2(trien)$] complexes. Both $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ are odorless. The preparation of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ can be done by two methods. The first method uses acetone as a solvent, which is then removed to obtain pure copper-amine complexes before further uses in the preparation of RPUR foams [8]. The second method uses ethylene glycol as a solvent [9]. Copper-amine complexes are obtained as solutions in ethylene glycol, which can be used in the preparation of RPUR foams without purification. This is a convenient preparation procedure and copper-amine complex solutions in ethylene glycol have good solubility in the RPUR foam formulation.

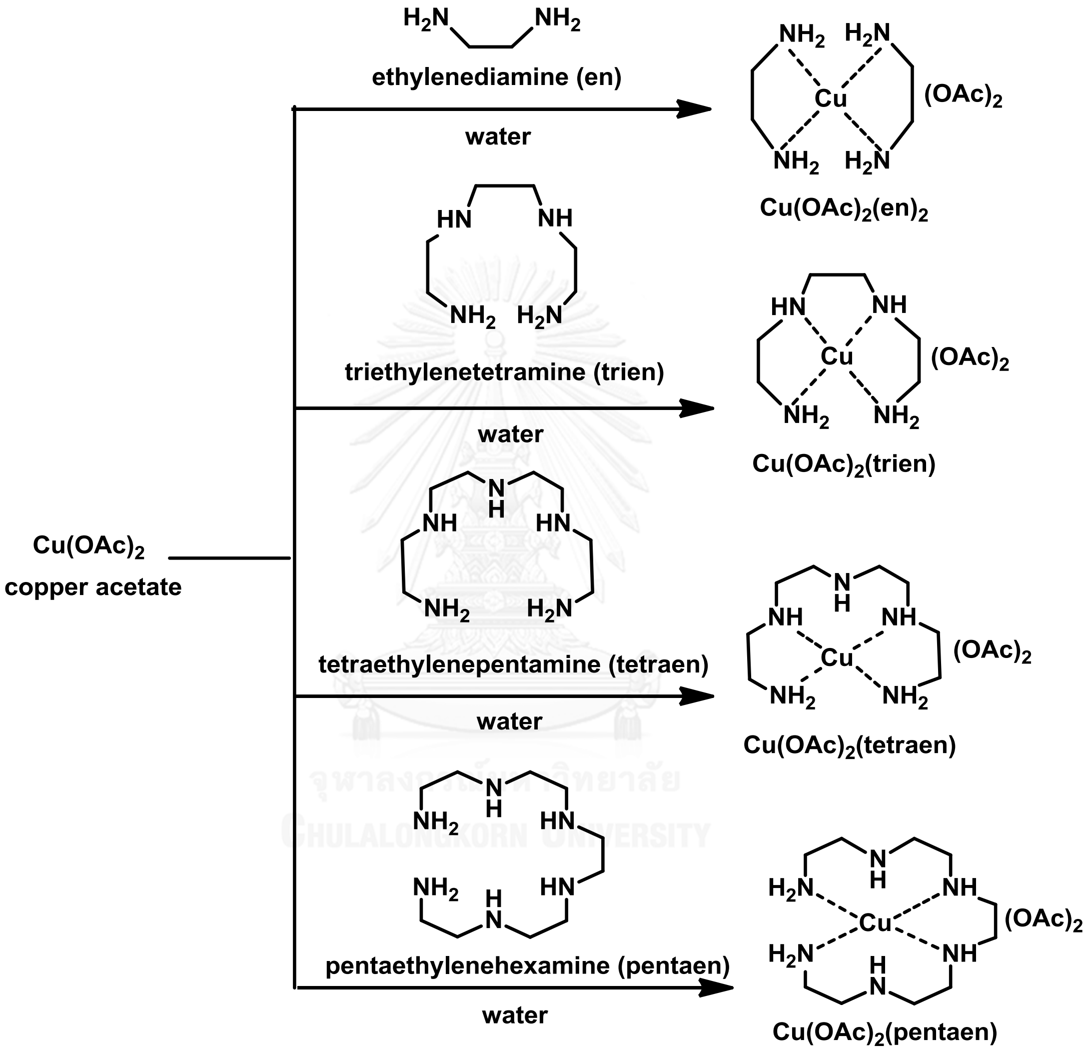
Objective

The objective of this work was to synthesize copper-amine complexes in the form of solution in water or aqueous solution as catalysts, which was done using green chemistry since water was used as a solvent. Copper-amine complexes synthesized were $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$ and $Cu(OAc)_2(pentaen)$ (where OAc = acetate, en = ethhylenediamine, trien = triethylenetetramine, tetraen = tetraethylenepentamine and pentane = pentaethylenehaxamine). The procedure was convenient since the aqueous solutions of copper-amine complexes could be used in RPUR foam preparation without purification. Moreover, the properties of foams catalyzed by copper-amine complexes in aqueous solution were compared to those catalyzed by DMCHA, which is a commercial catalyst.

Scope of the research

The scope of this work can be divided into 2 parts. The first part is the synthesis of copper-amine complexes in the aqueous solution (Scheme 1.1). Characterization of copper-amine complexes was done by using UV-Vis, FTIR spectroscopy, mass spectrometry and elemental analysis.

In the second part, copper-amine complexes prepared in the first step were used as catalysts in preparation of RPUR foam. The preparation of RPUR foam was done using standard cup test method for the investigation of reaction time, free rise density, rise profile and temperature profile. All other properties were investigated on RPUR foams which were prepared in the mold. All properties of RPUR foams were compared with those prepared from DMCHA, which is a commercial catalyst.



Scheme 1.1 Synthesis of copper-amine complexes as aqueous solutions

CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Raw materials

The preparation of RPUR foam consists of five important compounds including polyol, isocyanate, catalyst, surfactant and blowing agent [2, 10].

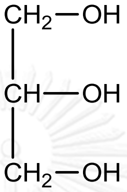
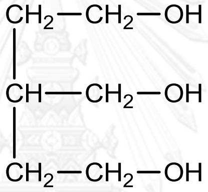
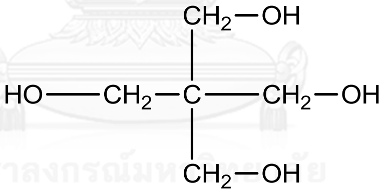
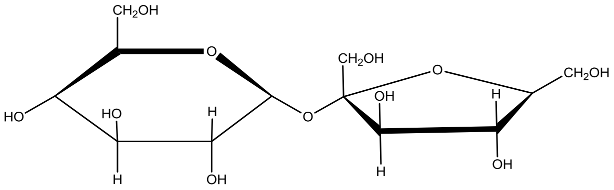
2.1.1 Polyols

The polyols generally used to produce polyurethane foams can be classified into two groups, polyether polyols and polyester polyols. The properties of polyurethane foams depend on the structure, functionality and molecular weight of polyols. The functionality and molecular weight of polyols are normally 2.0-8.0 and 200-800, respectively. The difference between polyether and polyester polyols are polyether polyols give softer and more flexible foam with better hydrolysis resistance than polyester polyols. On the other hand, polyester polyols give the foam with better resistance to oils, oxidation and solvents. The production of rigid polyurethane (RPUR) foam uses higher functionality and lower molecular weight polyols, while lower functionality and higher molecular weight polyols are used in the production of flexible polyurethane (FPUR) foams for increasing chain length of polymer.

2.1.1.1 Polyether polyols

Polyether polyols are the polymeric reaction products of an organic oxide which have low molecular weight polyols. Polyether polyols are manufactured by ring opening reaction of ethylene oxides or propylene oxides. Glycerol, ethylene glycol, sucrose, sorbital and trimethylolpropane are used as the polyfunctional initiators (Table 2.1) [1].

Table 2.1 Functionality of some common polyols

Hydroxylated Compound	Chemical Structure	Functionality
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 propene (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	$HO-CH_2-(CHOH)_4-CH_2-OH$	6
Sucrose		8

2.1.1.1 Polyester polyols

Polyester polyols are produced by polycondensation of a diacid with excess diol such as adipic acid, sebacic acid and phthalic acid. The viscosity of polyester polyols is higher than polyether polyols [3]. Therefore, polyester polyols are usually used in flexible polyurethane foams more than polyether polyols.

2.1.2 Isocyanates

The main isocyanates used for preparation of RPUR foam are diphenylmethane diisocyanate (MDI) and their derivatives, because they have high reactivity in foaming reaction. MDI consists of two forms, namely purified monomeric MDI and polymeric MDI (PMDI). Pure MDI mainly used for elastomers and coatings [11]. The chemical structures of MDI isomer and polymeric MDI are shown in Figures 2.1-2.2.

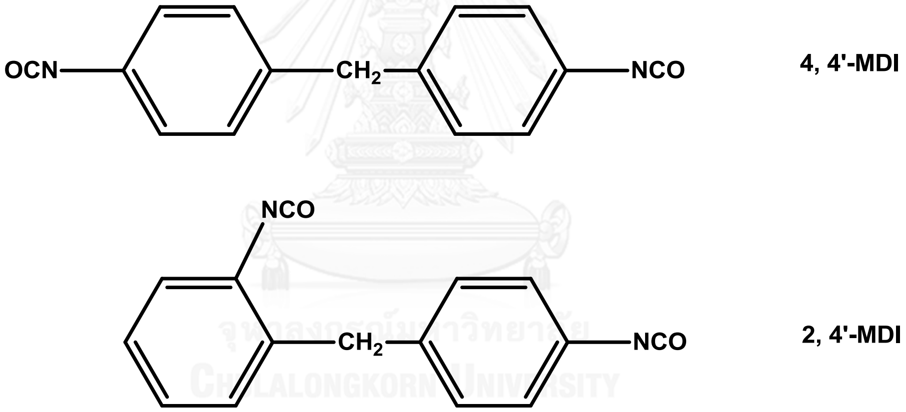


Figure 2.1 Structure of MDI

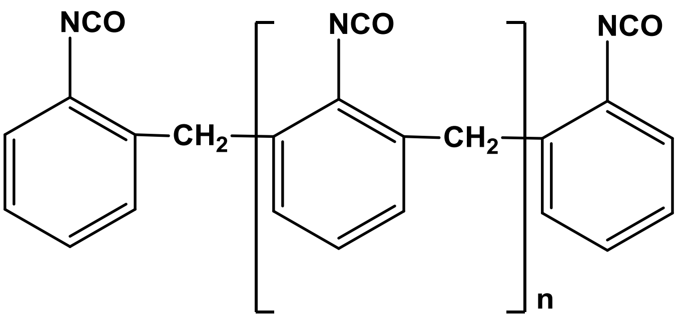


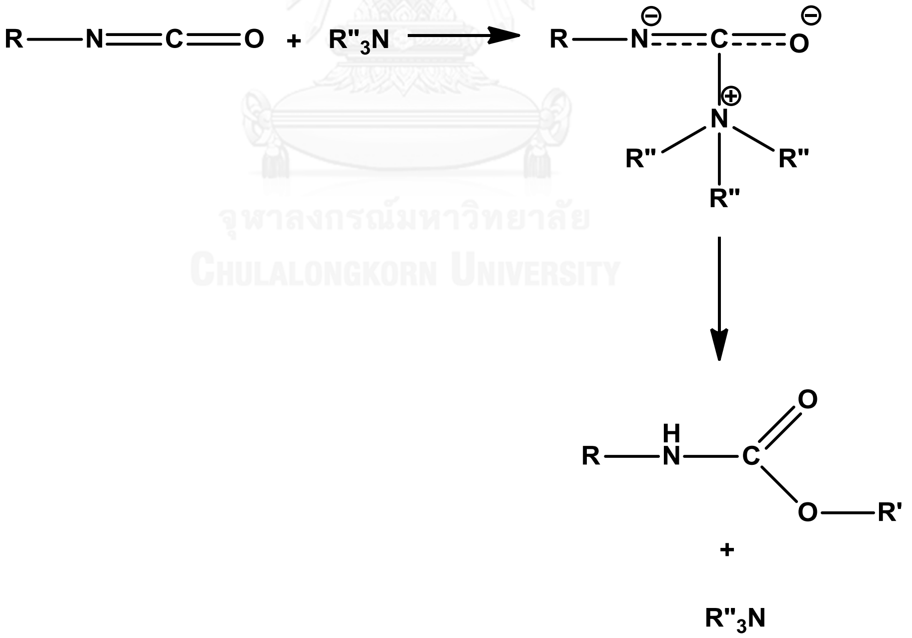
Figure 2.2 Structure of PMDI

2.1.3 Catalysts

Catalysts can balance rate of reactions of isocyanate with polyol and isocyanate with water. The common catalysts used are tertiary amines, organometallic compounds and carboxylic acid salts.

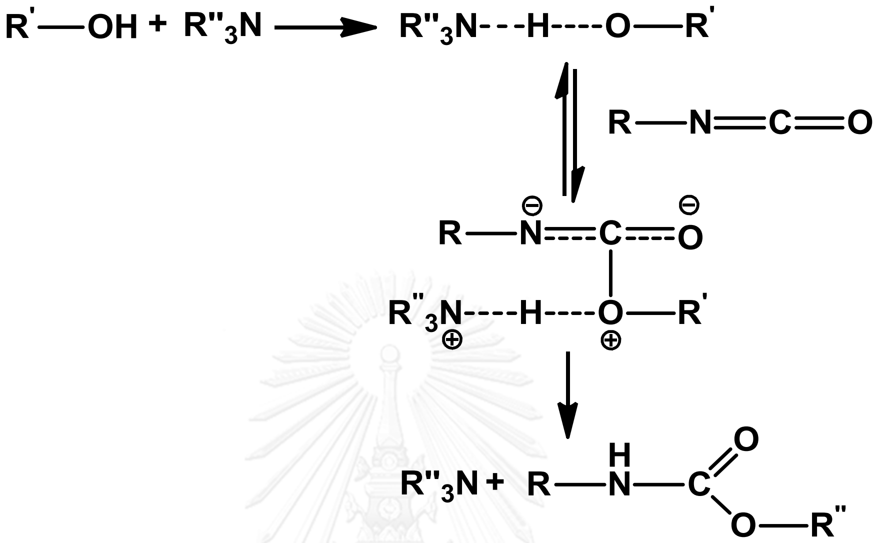
2.1.3.1 Amine catalysts

For tertiary amine catalysts, two mechanisms have been proposed [2]. The first mechanism proposed by Baker is shown in Scheme 2.1. Starting by tertiary amine (3° amine) uses its lone pair of electrons to coordinate to the positive electron charged carbon of the NCO group, which contribute activates the electrophilic nature of the carbon. Therefore, OH group of polyols can attack at isocyanate carbon more easily.



Scheme 2.1 Baker mechanism of 3° amine catalyst

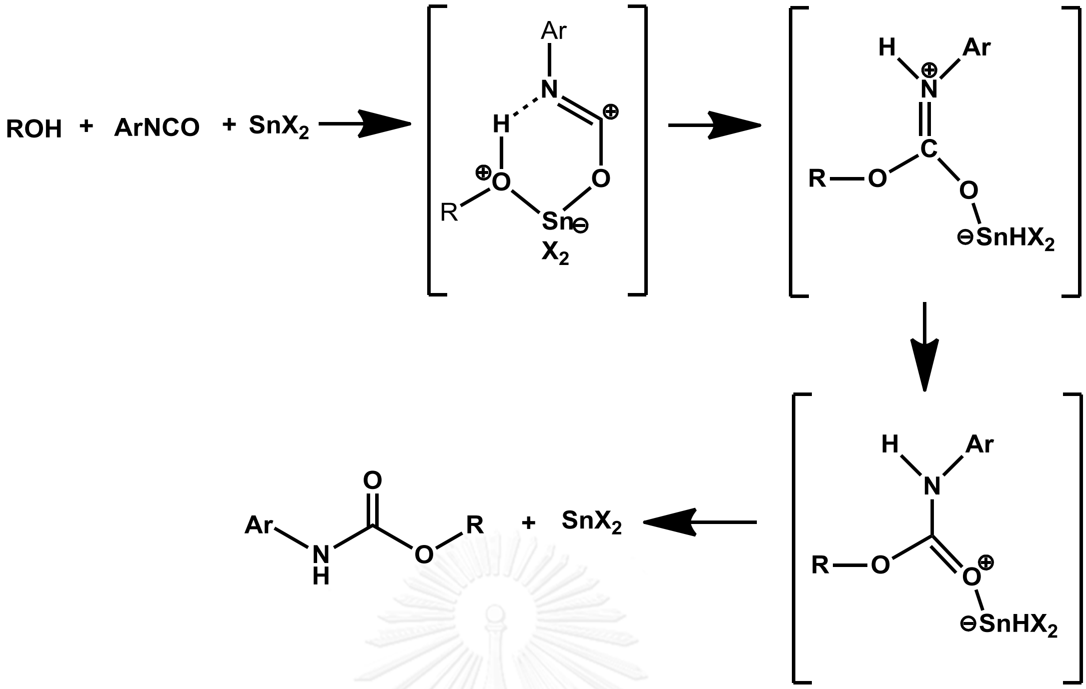
The second mechanism that is proposed by Farka is shown in Scheme 2.2. The activation starts by nitrogen atom of 3° amine coordinates with hydrogen atom of OH group. Then, it forms a transition state to activate urethane formation. This shows that 3° amine can catalyze reaction between OH group and isocayanate more easily.



Scheme 2.2 Farka mechanism of 3° amine catalysts

2.1.3.2 Organotin catalysts

The proposed mechanism of tin (II) salts catalysts is shown in Scheme 2.3. First of all, coordination between OH group and tin (II) salt creates a tin alkoxide, which can react with isocyanate to form a ternary complex. Then, the alkoxide anion is transferred onto the coordinated isocyanate. Next, lone pair electron of tin connected oxygen atom delocalize to coordinate isocyanate, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide.



Scheme 2.3 Mechanism for tin (II) salts

2.1.4 Blowing agents

Blowing agents are used to generate the air bubbles entrapped inside the reactive mixture. The foaming process of PU foam can be carried out with chemical, physical or a mixture of chemical and physical blowing agents. The blowing agent concentrations are 3-5 parts per 100 part of polyol [1].

Chemical blowing agents are a chemical compound or a mixture of chemical compounds producing gas as a result of chemical reactions. One of the common chemical blowing agents is water.

Physical blowing agents are gases or volatile compounds which produce gas as a result of physical processes such as halogenated hydrocarbons (e.g. CFCs, HFCs, methyl chloride, methylene chloride and trichloethylene) and aliphatic hydrocarbons (e.g. butane, pentane and hexane) [1].

Nowadays, the earth's atmosphere is affected by the CFCs, HFCs and methylene dichloride, and they are prohibited in PU industry.

2.1.5 Surfactants

Surfactants or surface-active agent are compounds which can reduce the surface tension of water. The properties of surfactant can help the mixing of all ingredients as homogeneous and control the size of expanding foam by stabilizing the gas bubbles from the producing foam reaction and reducing the stress-concentrations on the cell wall [12]. For the preparation of polyurethane foam, surfactant was used to add in this process. An example is polydimethylsiloxane copolymers or silicone surfactants as shown in Figure 2.1. They are normally added in the amount of 0.4-2.0% w/w in the polyol formulation [1].

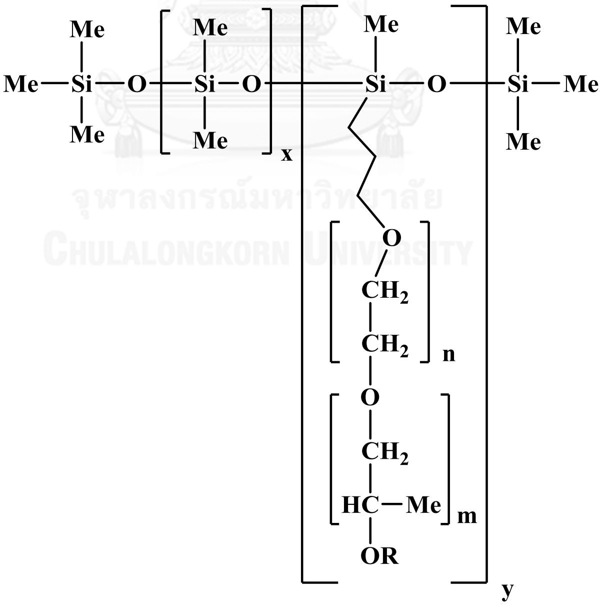


Figure 2.3 Structure of silicone surfactants that used in PUR foams manufacture

2.2 Basic chemistry [3]

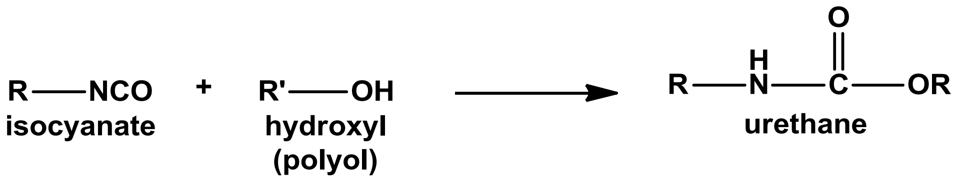
Polyurethane is formed by exothermic polymerization reaction between di- or polyfunctional isocyanate and di- or polyfunctional OH groups. For a simple example, the basic principle of urethane chemistry is explained below in section 2.2.1 using monofunctional reagents.

2.2.1 Primary reactions of isocyanates

The primary reactions of isocyanate groups with hydroxyl groups and water yield urethane, carbon dioxide (CO_2) gas and substituted urea. These reactions strongly influence the physical and mechanical properties of polyurethane foams.

2.2.1.1 Reaction of isocyanate with polyol

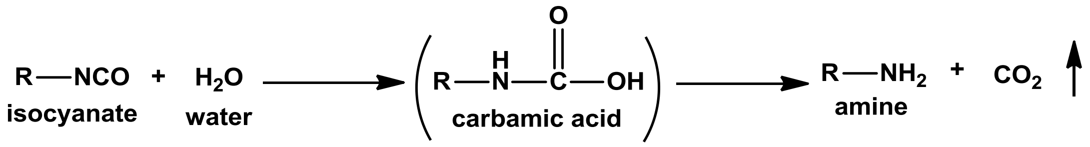
The important reaction in the preparation of polyurethanes is known as gelling reaction, which is the reaction between an isocyanate group and a hydroxyl group of polyol to form a urethane linkage. The rate of polymerization is affected by the chemical structure of both isocyanate and polyol compounds, that comprise the steric hindrance of isocyanate group and the type of the hydroxyl group (primary or secondary). The reaction rate is accelerated by using catalysts.



$$R{-}NCO + R'{-}OH \longrightarrow R{-}NH{-}C(=O){-}OR$$

2.2.1.2 Reaction of isocyanate with water

The reaction between isocayanate with water forms unstable carbamic acid, which decomposes to give amine and CO_2. The obtained CO_2 expands as air bubbles entrapped inside the reactive mixture and generates the cellular structure of PU foams.



$$R{-}NCO + H_2O \longrightarrow \left(R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH \right) \longrightarrow R{-}NH_2 + CO_2\uparrow$$

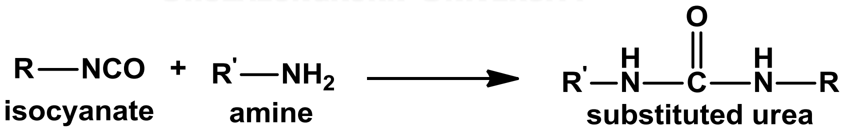
isocyanate, water, carbamic acid, amine

This reaction is known as the “blowing reaction” since CO_2 produced used for expanding PU foams has an effect on density of foams. The rate of reaction is accelerating by suitable choice of catalysts.

2.2.2 Secondary reactions of isocyanates

2.2.2.1 Reaction of isocyanate with amine

The reaction between isocyanate with amine produces the urea linkage. The reaction of isocyanate with primary amine occurs faster than with primary alcohol. Therefore, amine can be used as chain extenders and curing agents for PU manufacture.

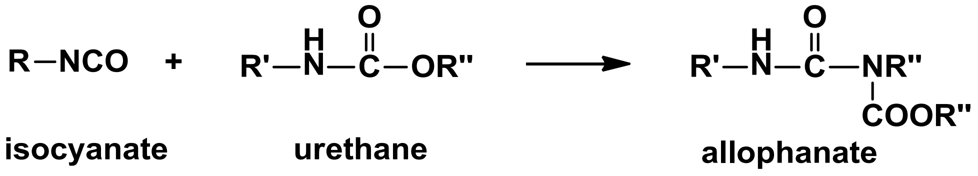


$$R{-}NCO + R'{-}NH_2 \longrightarrow R'{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R$$

isocyanate, amine, substituted urea

2.2.2.2 Reaction of isocyanate with urethane

Isocayanate can react with the nitrogen atom of the urethane group to form branched allophanate.

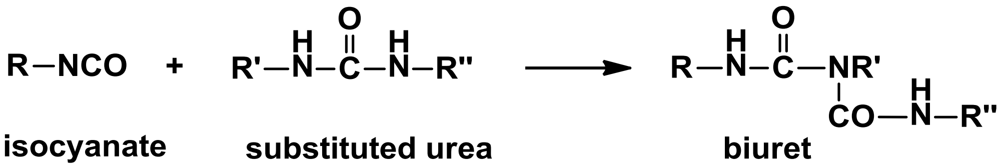


$$R{-}NCO + R'{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OR'' \longrightarrow R'{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{COOR''}{NR''}$$

isocyanate, urethane, allophanate

2.2.2.3 Reaction of isocyanate with urea

The biuret was formed by reaction between isocyanate and substituted urea.



2.3 RPUR Formulations [3, 4]

The amount of isocyanate needed to react with polyol and other reactive ingredients in RPUR formulations can be calculated to obtain chemically stoichiometric equivalents is called isocyanate index. Isocyanate index required depends on the RPUR system, properties required, conditions and scale of production.

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

To calculate the amount of parts by weight (pbw) of the isocyanate needs to react with 100 parts by weight of polyol and other additives, the data required for calculation are isocyanate value, hydroxyl value and equivalent weight.

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

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

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

Hydroxyl value is defined as the milligrams of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound or polymer. It is used as a measurement of the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol.

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

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

Equivalent weight can be calculated from ratio between molar mass and functionallity

$$\textbf{Equivalent weight} = \frac{\textbf{molar mass}}{\textbf{functionality}}$$

2.4 Mechanical properties

One of the most important mechanical properties for RPUR foams is compressive property. This property depend on density, type of foams and type of cell foams including open cell and closed cell structure as shown in Figures 2.4-2.5. For closed cell structure found in RPUR foams, the cell has the thin cell wall. Thus, it helps to increase the durability to the pressure and has a high strength. For open cell structure found in flexible polyurethane foams, the cell surfaces do not have thin cell wall. Therefore, it is flexible when compressed.

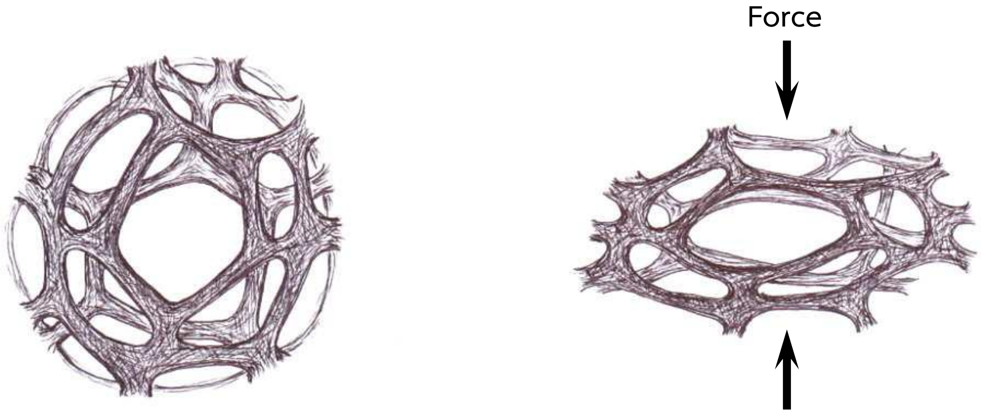


Figure 2.4 Schematic representation of open cell deformation [1]

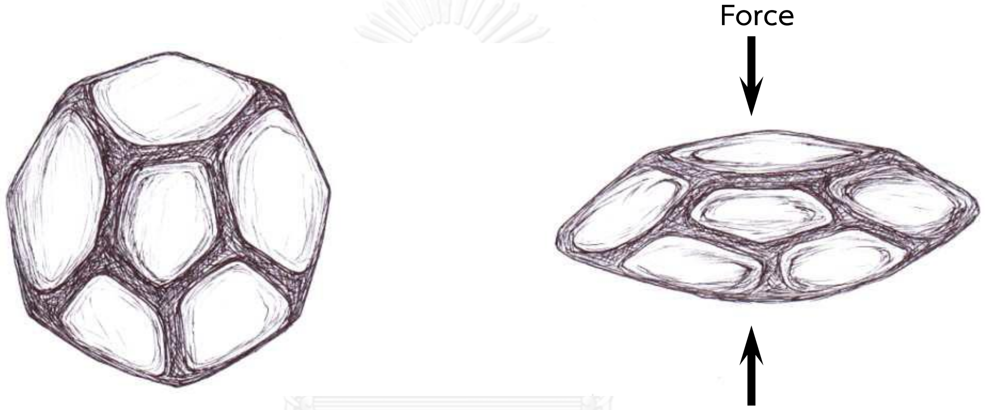
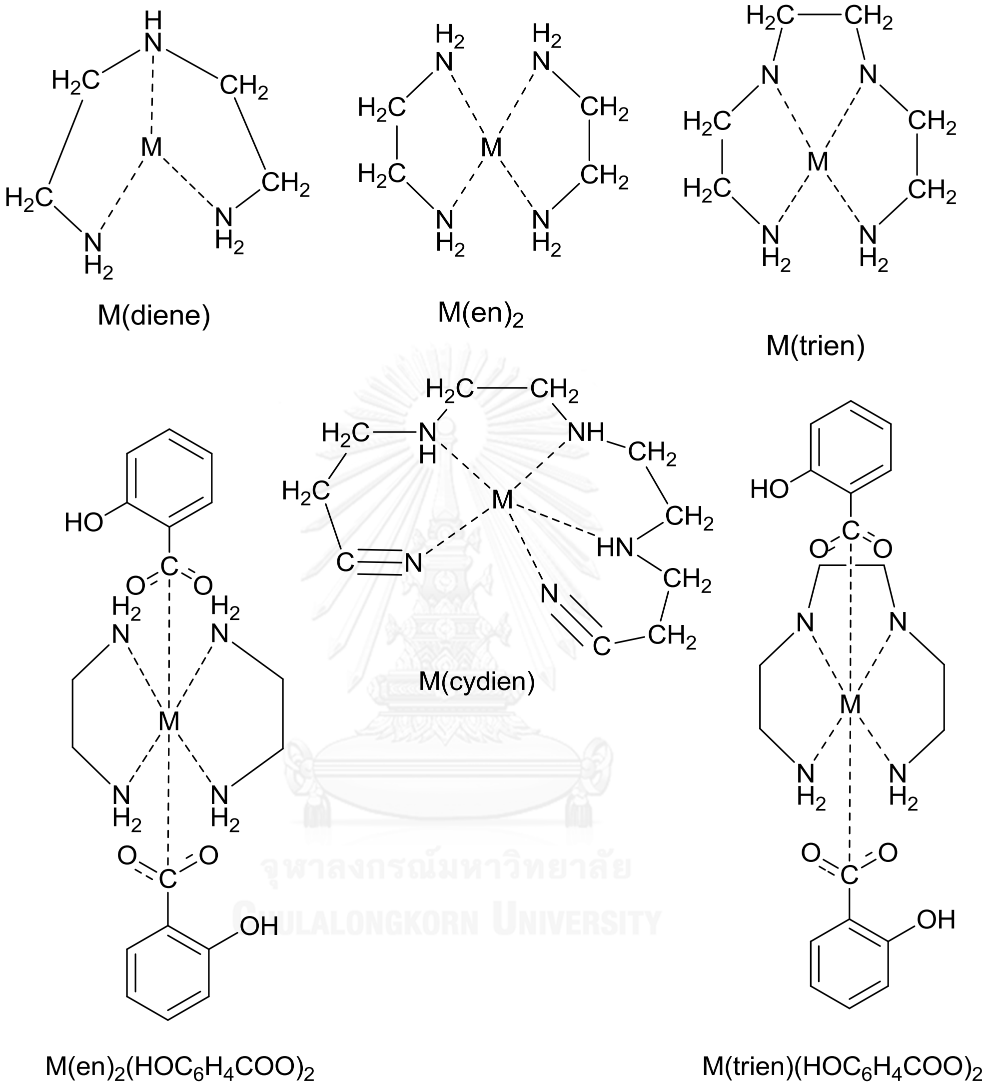


Figure 2.5 Schematic representation of closed cell deformation [1]

2.5 Literature reviews

In the preparation of RPUR foams, catalyst is needed to complete polymerization reaction. There are several researches that study about catalysts used in RPUR foam preparation.

In 1993, Kurnoskin and coworkers [13] studied use of the metal-amine complexes in the synthesis of metal-containing epoxy polymers. Many metal-amine complexes were synthesized from transition metal salts and aliphatic amines (Figure 2.6). These metal-amine complexes served as curing agents in the polymerization reaction to give crosslinked epoxy polymers. It was found that the reaction rate of complex formation depended on both metal ion and ligand and decreased in the following order: Metal : $Cu^{2+} > Co^{2+} > Fe^{3+} > Ni^{2+} > Zn^{2+}$ and ligand : trien ~ cydien > dien > en.



M(diene)

M(en)$_2$

M(trien)

M(cydien)

M(en)$_2$(HOC$_6$H$_4$COO)$_2$

M(trien)(HOC$_6$H$_4$COO)$_2$

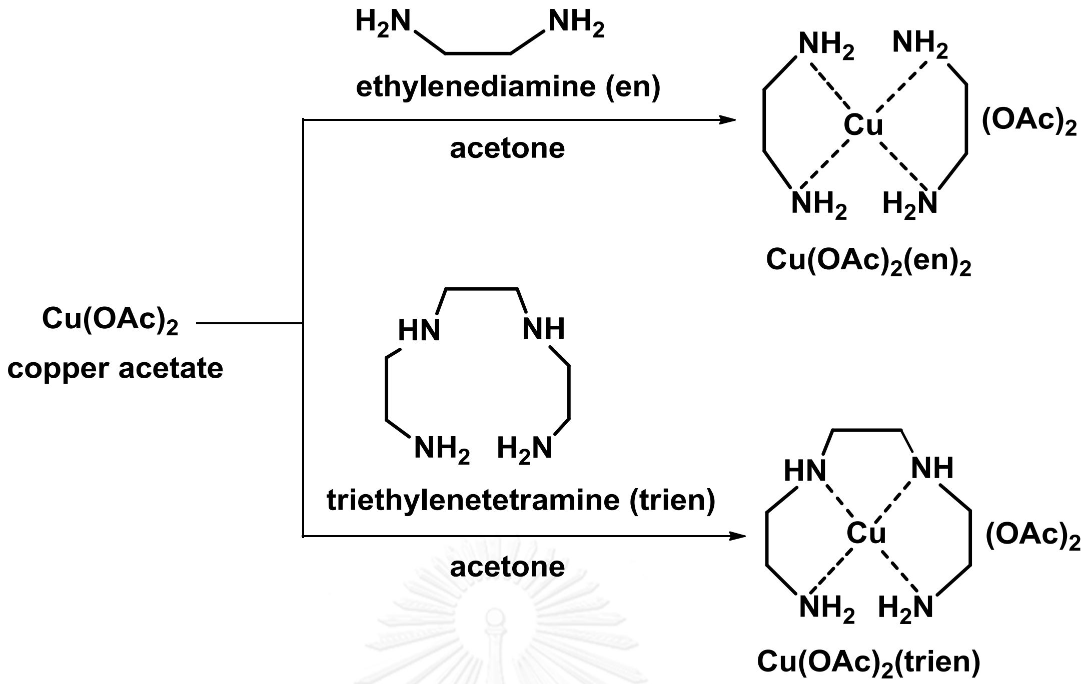
Figure 2.6 Structures of metal complexes

In 2002, Inoue and coworker [14] studied the catalytic activity of new catalyst system which is M(acac)$_n$-amine catalysts. M(acac)$_n$-amine were co-catalysts of metal acetylacetonate [where M = Mn, Cu, Co, Ni and Fe] and tertiary amines, namely triethylenediamine (TEDA), *N,N′,N′*-trimethylaminoethylpiperazine, *N,N,N′,N′*-tetramethylethylenediamine (TE), *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (DT) and bis(2-dimethylaminoethyl) ether (ETS). M(acac)$_n$-amine were used as catalysts for the reaction between hexamethylene diisocyante (HDI) with diethylene glycol (DEG). The catalytic activity of M(acac)$_n$-amine was compared with that of dibutyl dilaurate (DBTDL), which is a commercial catalyst. The order of catalytic activity of M(acac)$_n$-amine was TEDA-Mn(acac)$_2$ > TEDA-Fe(acac)$_3$ > TEDA-Co(acac)$_2$ > TEDA-Ni(acac)$_2$ > TEDA-Cu(acac)$_2$. TEDA-Mn(acac)$_2$ had higher catalytic activity than DT-Mn(acac)$_2$ and TE-Mn(acac)$_2$. However, TEDA-Mn(acac)$_2$ had lower catalytic activity than DBTDL.

In 2009, Sardon and coworkers [2] studied the synthesis of waterborne polyurethane catalyzed by zirconium acetylacetonate/triethylamine and dibutyltin diacetate/ triethylamine systems. Zirconium acetylacetonate had low toxicity than dibutyltin diacetate. It was found that zirconium acetylacetonate/triethylamine was suitable catalyst for preparing waterborne polyurethane.

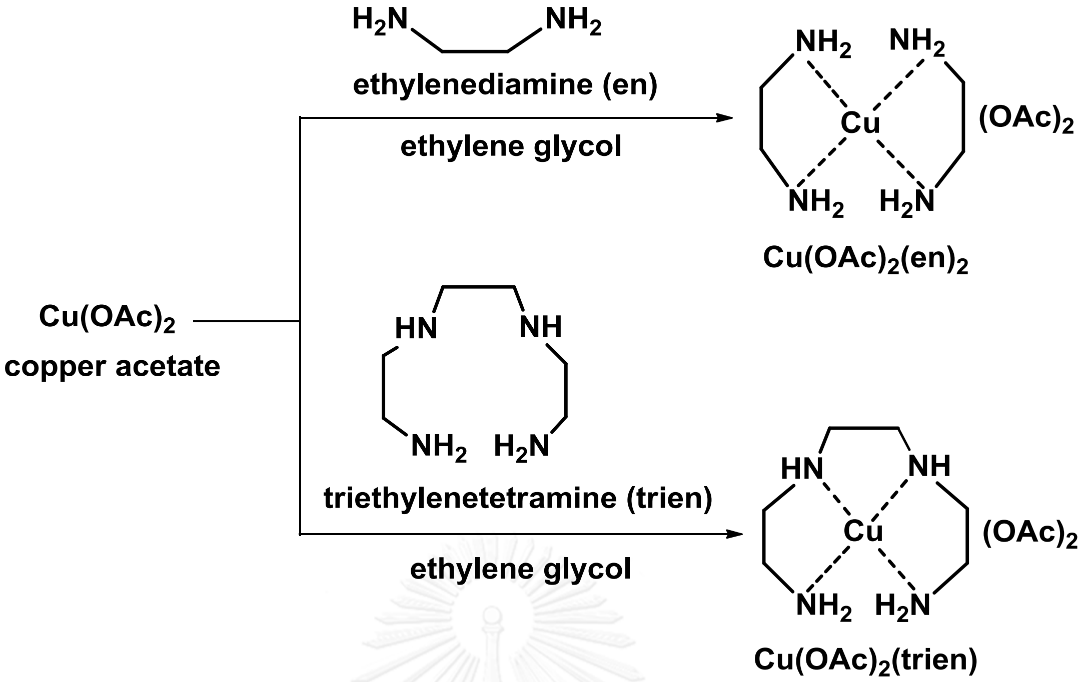
The previous work in our research group focused on using metal-amine as catalysts in the preparation of RPUR foams to instead of *N,N*-dimethylcyclohexylamine (DMCHA), which is a commercial catalyst. DMCHA has disadvantage that it has strong amine odor.

In 2011, Pengjam and coworkers [8] synthesized copper-amine complexes, namely Cu(OAc)$_2$(en)$_2$ and Cu(OAc)$_2$(trien) [OAc = acetate; en = ethylenediamine; trien = triethylenetetramine] (Scheme 2.4). These copper-amine complexes were used as catalysts for preparation of RPUR foams. The synthesis of copper-amine complexes used acetone as a solvent. In the final step, acetone was removed by evaporation and dried under vacuum to obtain copper-amine complexes. It was found that Cu(OAc)$_2$(en)$_2$ and Cu(OAc)$_2$(trien) could be used as catalysts to prepare RPUR foams.



Scheme 2.4 Synthesis of copper-amine complexes using acetone as a solvent

In 2015, Sridaeng and coworkers [9] developed the method for synthesis of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ in the form of solution in ethylene glycol (Scheme 2.5). $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ were prepared using ethylene glycol as a solvent. for preparation of flexible polyurethane foams. The preparation of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ were convenient since the ethylene glycol solutions of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ could be used as catalysts in the preparation of flexible polyurethane foam without purification. It was found that the ethylene glycol solution of $Cu(OAc)_2(en)_2$ was a good catalyst.



Scheme 2.5 Synthesis of copper-amine complexes using ethylene glycol as a solvent

2.5.1 Literature reviews about synthesis of copper complexes as aqueous solutions

The reaction between copper (II) ion (Cu^{2+}) and ammonia (NH_3) could form copper-amine complex, $[Cu(NH_3)_4(H_2O)_2](OH)_2$, in the form of solution in water. The color of $Cu(NH_3)_4(H_2O)_2](OH)_2$ aqueous solution is deep blue [15, 16].

$$Cu(OH)_2 + 4\ NH_3 + 2\ H_2O \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2\ OH^-$$

In 2008, Yaha and coworkers [17], studied stability constant of metal complexes of different metal ions and 4-amino hippuric acid in aqueous solutions. The metal ions investigated were Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+} and La^{3+}. It was found that these metal complexes in aqueous solutions have bidentate ligand. Bonding in these metal complexes occurs through lone pair electrons of the amide nitrogen atom and oxygen atom of the carboxylate ion.

In 2009, Ibrahim and coworkers [18] studied the metal complexes of tris(2-aminoethyl)amine (Tren) and two metal ions, namely Cu (II) and Zn (II) ions in aqueous solution. They found that the structure of metal-Tren complexes were $\{[(Tren)Cu]_2(\mu\text{-}OH)\}^{3+}$ and $\{[(Tren)Zn]_2(\mu\text{-}OH)\}^{3+}$.

The researches described above suggest that Cu (II) ion (Cu^{2+}) and amines, namely ethylenediamine (en) and triethylenetetramine (trien), can form copper-amine complexes in aqueous solution. The aqueous solutions of copper-amine complexes should be suitable catalysts for preparation of RPUR foams.

Therefore, the objective of this this research was to synthesize the copper-amine complexes in the form of solutions in water (or aqueous solutions). The aqueous solution of copper-amine complexes were then used as catalysts in the preparation of RPUR foams. The use aqueous solution of the copper-amine complex for RPUR foams preparation is convenient because no purification of catalysts is required. The aqueous solution of the copper-amine complex contains water, which serves as a blowing reagent in RPUR foam formulation.

CHAPTER III

EXPERIMENTAL

3.1 Raw materials and chemicals

3.1.1 Synthesis of copper-amine complexes as aqueous solutions

Copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$], ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pentaethylenehexamine (pentaen) were obtained from Aldrich and used without further purification.

3.1.2 Preparation of rigid polyurethane (RPUR) foams

Polymeric 4,4´-methylene diphenyl diisocyanate (PMDI, Suprasec® 5005, % NCO = 31.0 wt%, average functionality = 2.7), polyol (Daltolac® 180, sucrose-based polyether polyol, hydroxyl value = 440 mg of KOH/g, functionality = 4.3), polysiloxane surfactant (Tegostab® B8460) and DMCHA were supplied by Huntsman (Thailand) Co. Ltd. and IRPC Public Company Limited. Distilled water was used as a blowing agent.

3.2 Synthetic procedures

The copper-amine complexes were synthesized in the form of solution in water or aqueous solution to obtain odorless and have had good solubility in water. The procedure was modified from the method reported in the literature [8]. The solution of copper-amine complexes can be used as catalysts in the preparation of RPUR foams without purification.

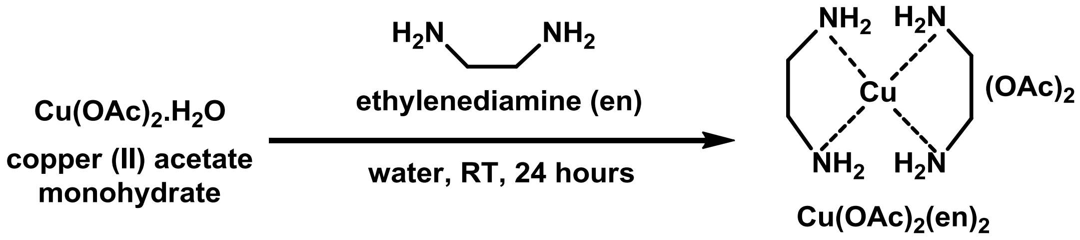
3.2.1 Synthesis of copper-amine complexes in aqueous solutions

The aqueous solutions of copper-amine complexes, namely copper-ethylenediamine [$Cu(OAc)_2(en)_2$], copper-triethylenetetramine [$Cu(OAc)_2(trien)$], copper-tetraethylenepentamine [$Cu(OAc)_2(tetraen)$] and copper-pentaethylenehaxamine [$Cu(OAc)_2(pentaen)$] were prepared by using various mole ratios between copper (II) acetate and amines (Table 3.1). The obtained aqueous solutions contained 25 wt% of copper-amine complexes in water.

Table 3.1 Composition of strating meterials in the synthesis of copper-amine complexes in water solution (25 wt% solution)

Copper-amine complexes	Mole ratios of $Cu(OAc)_2.H_2O$: amine	$Cu(OAc)_2.H_2O$ (g)	Amine (ml)				Appearance
			en	trien	tetraen	pen-taen	
$Cu(OAc)_2(en)_2$	1 : 2	0.624	0.42	-	-	-	purple solution
$Cu(OAc)_2(trien)$	1 : 1	0.577	-	0.43	-	-	blue solution
$Cu(OAc)_2$-(tetraen)	1 : 1	0.513	-	-	0.49	-	blue solution
$Cu(OAc)_2$-(pentaen)	1 : 1	0.462	-	-	-	0.57	blue solution

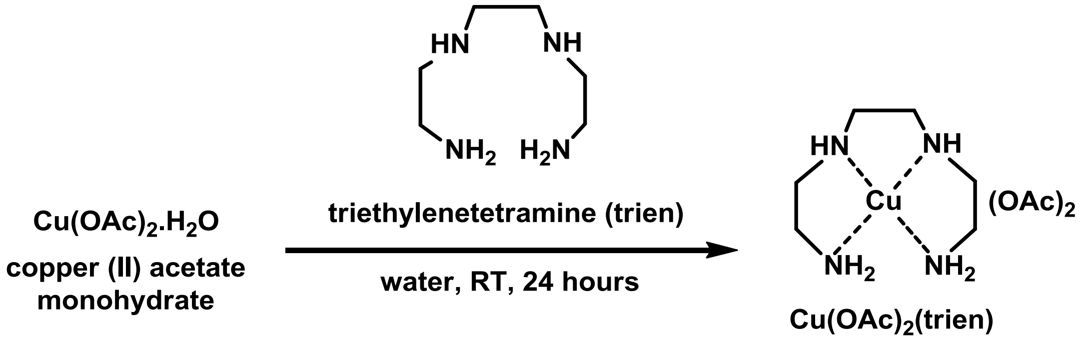
3.2.1.1 Synthesis of copper-ethylenediamine complex [Cu(OAc)$_2$(en)$_2$]



Scheme 3.1 Synthesis of copper-ethylenediamine complex [Cu(OAc)$_2$(en)$_2$]

The mole ratio of copper (II) acetate monohydrate to ethylenediamine was 1 : 2. The solution of 25 wt% Cu(OAc)$_2$(en)$_2$ in water was prepared by using the following procedure : A solution of Cu(OAc)$_2$.H$_2$O (0.624 g, 3.12 mmol) in water (3 ml) was stirred at room temperature. After that, ethylenediamine (0.42 ml, 6.28 mmol) was added to the Cu(OAc)$_2$.H$_2$O solution and the reaction mixture was stirred at room temperature for 24 hours. The aqueous solution of 25 wt% Cu(OAc)$_2$(en)$_2$ in water was obtained as an odorless purple solution.

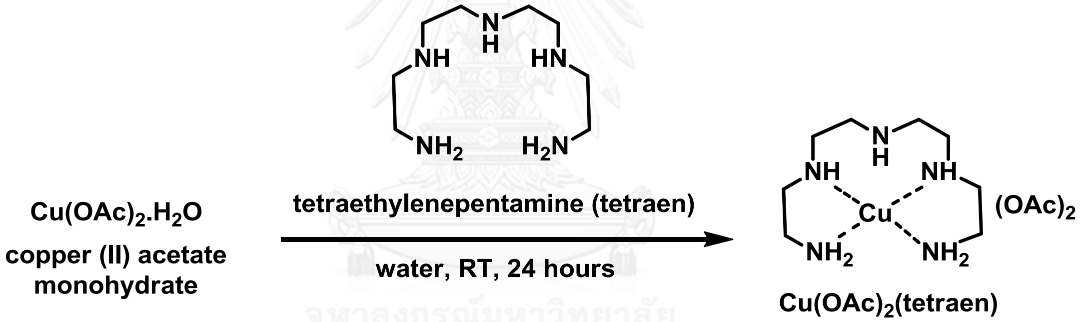
3.2.1.2 Synthesis of copper-triethylenetetramine complex [Cu(OAc)$_2$(trien)]



Scheme 3.2 Synthesis of copper-triethylenetetramine complex [Cu(OAc)$_2$(trien)]

The mole ratio of copper (II) acetate monohydrate to triethylenetetramine was 1 : 1. The solution of 25 %wt $Cu(OAc)_2$(trien) in water was prepared by using the following procedure : A solution of $Cu(OAc)_2.H_2O$ (0.577 g, 2.89 mmol) in water (3 ml) was stirred at room temperature. After that, triethylenetetramine (0.43 ml, 2.89 mmol) was added to the $Cu(OAc)_2.H_2O$ solution and the reaction mixture was stirred at room temperature for 24 hours. The aqueous solution of 25 wt% $Cu(OAc)_2$(trien) in water was obtained as an odorless blue solution.

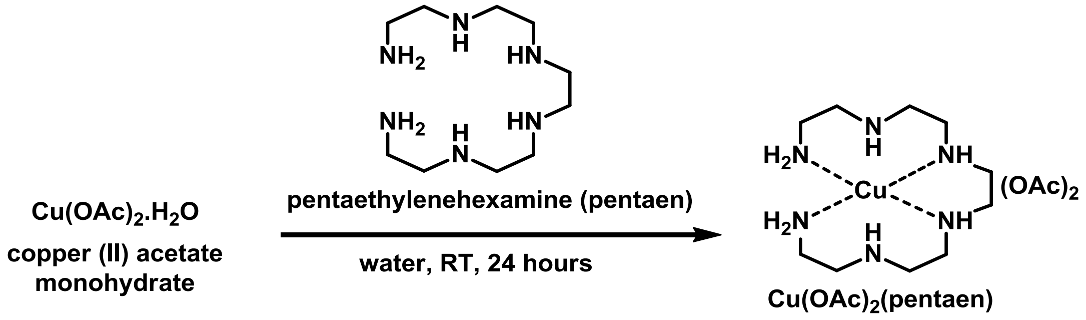
3.2.1.3 Synthesis of copper-tetraethylenepentamine complex [$Cu(OAc)_2$(tetraen)]



Scheme 3.3 Synthesis of copper-tetraethylenepentamine complex [$Cu(OAc)_2$(tetraen)]

The mole ratio of copper (II) acetate monohydrate to tetraethylenepentamine was 1 : 1. The solution of 25 %wt $Cu(OAc)_2$(tetraen) in water was prepared by using the following procedure : A solution of $Cu(OAc)_2.H_2O$ (0.513 g, 2.57 mmol) in water (3 ml) was stirred at room temperature. After that, tetraethylenepentamine (0.49 ml, 2.57 mmol) was added to the $Cu(OAc)_2.H_2O$ solution and the reaction mixture was stirred at room temperature for 24 hours. The aqueous solution of 25 wt% $Cu(OAc)_2$(tetraen) in water was obtained as an odorless blue solution.

3.2.1.4 Synthesis of copper-pentaethylenehexamine complex [$Cu(OAc)_2$(pentaen)]



Scheme 3.4 Synthesis of copper-pentaethylenehexamine complex [$Cu(OAc)_2$(pentaen)]

The mole ratio of copper (II) acetate monohydrate to pentaethylenehexamine was 1 : 1. The solution of 25 %wt $Cu(OAc)_2$(pentaen) in water was prepared by using the following procedure : A solution of $Cu(OAc)_2.H_2O$ (0.462 g, 2.31 mmol) in water (3 ml) was stirred at room temperature. After that, pentaethylenehexamine (0.57 ml, 2.32 mmol) was added to the $Cu(OAc)_2.H_2O$ solution and the reaction mixture was stirred at room temperature for 24 hours. The aqueous solution of 25 wt% $Cu(OAc)_2$(pentaen) in water was obtained as an odorless blue solution.

3.3 Rigid polyurethane (RPUR) foam preparation

The preparation of RPUR foam was done both in cup-test and molded methods. RPUR foam prepared by cup-test method was used for the investigation of the reaction time, free rise density, rise profile, temperature profile, NCO conversion and morphology. RPUR foam prepared by molded method was used for the investigation of compression properties.

The reaction times of foaming reactions investigated were cream time (which is the time while CO_2 is occurred until the starting foam expansion), gel time (which is the time while polymerization of the reactants occurs or the time that RPUR foam starts to harden), tack free time (which is the time when polymerization is completed or it can be determined at the point on the surface of RPUR foam that is not sticky) and free rise time (which is the time while CO_2 is not generated or the time when RPUR foam reaches its maximum height).

3.3.1 Preparation of RPUR foams by cup test method

The steps of rigid polyurethane foams preparation were made according to the process is illustrated in Figure 3.1 and the formulation is shown in Table 3.2. First of all, polyol, catalysts (DMCHA or copper-amine complexes as aqueous solution), surfactant and blowing agent (distilled water) were mixed in a paper cup (700 ml) by hand mixing and mechanical stirrer at 2000 rpm for 40 seconds. Then, PMDI was added into the cup and the mixture was mixed again by mechanical stirrer at 2000 rpm for 18 seconds. RPUR foam was then allowed to rise freely at room temperature. The reaction times of foaming reactions were measured. After that, the foams were kept for 48 hours at room temperature in order to accomplish all of the reactions before measuring free rise density, physical and mechanical properties.

3.3.2 Preparation of RPUR foams by molded method

The preparation of RPUR foams by molded method used the same mixing step as cup test method, except the amount of all staring materials were increased to 4-5 folds. After all starting materials were mixed in a paper cup, the mixture was poured into a 10 × 10 × 10 cm plastic bag (Figure 3.2) and allowed to rise freely at room temperature. Then, the foam density was measured and these foams were used for investigation of the mechanical properties.

Table 3.2 RPUR foam formulations at different NCO indexes

Formulation	**Weight (pbw)**[a]	
	NCO index 100	**NCO index 130**
Polyol (Daltolac® R180)	100.0	100.0
Surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (water)	3.0[b,c]	3.0[b,c]
Catalyst (DMCHA or aqueous solutions of copper-amine complexes)	1.0[d]	1.0[d]
PMDI (Suprasec®5005)	151.3	196.7

[a] Parts by weight (pbw) is 1 g in 100 g of polyol.

[b] Water was added to the polyol blend for RPUR foam catalyzed by DMCHA.

[c] Calculated from the weight of water in aqueous solution of copper-amine complexes.

[d] Calculated from the weight of copper-amine complexes in aqueous solution of copper-amine complexes.

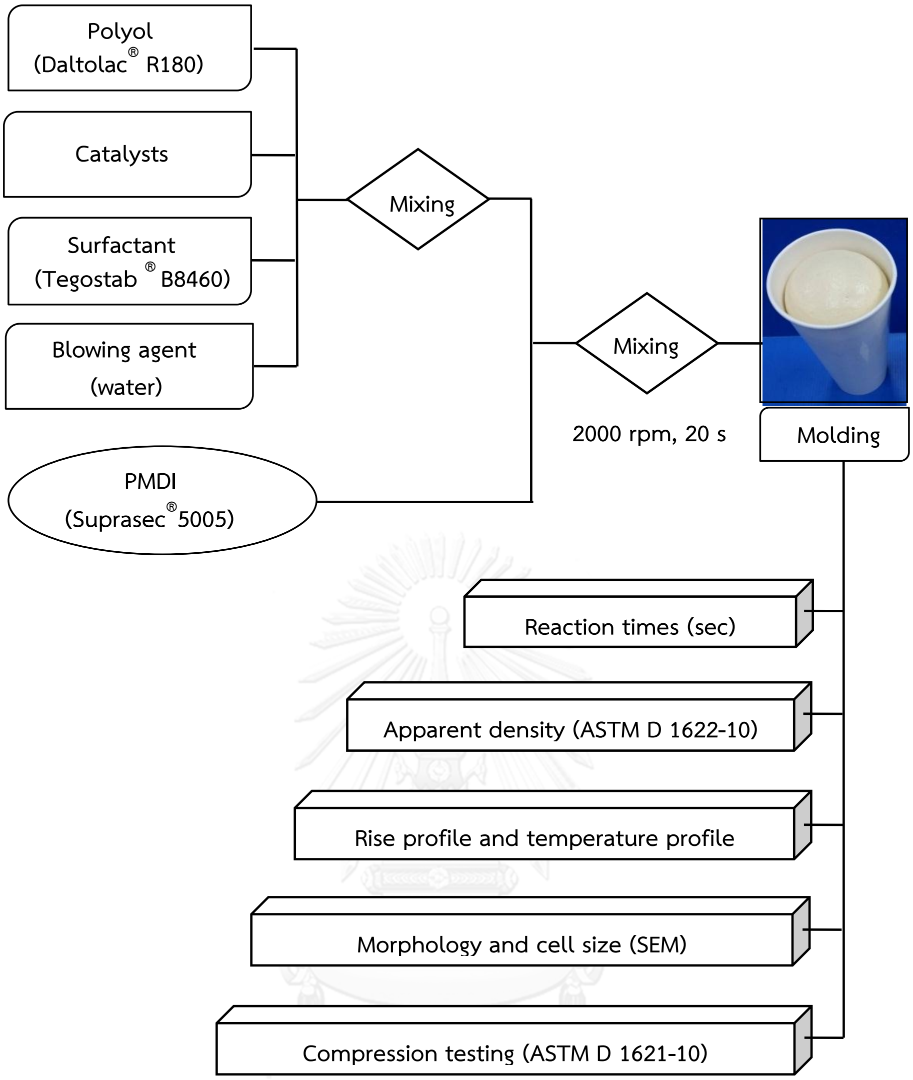


Figure 3.1 Process for the preparation of RPUR foams

Figure 3.2 Plastic bag used in molded method

3.4 Characterization of copper-amine complexes

3.4.1 Ultraviolet-visible spectroscopy

UV-Vis spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer at room temperature. Absorption spectra were obtained and the samples were scan over range 200-800 nm at a medium speed. The solvent used was water. Molar absorptivity (ε) was calculated using the following equation :

$$\varepsilon = A/bc$$

(where A= absorbance, b = length of light path through the sample in mm, c = sample concentration in moles/liter)

3.4.2 Infrared spectroscopy

Copper-amine complexes in aqueous solution were characterized by using Spectrum One PerkinElmer Fourier transform infrared (FTIR) spectrometer.

3.4.3 Mass spectrometry (MS)

Electrospray ionization (ESI) mass spectrometry was used to confirm the complex formations by their mass-to-charge ratio. This method depends on the fact that every compound has a unique fragmentation pattern in the mass spectrum. The sample is ionized, then sample ions are separated based on their different masses and relative abundance. Water is a solvent used for sample preparation.

3.5 Characterization of RPUR foams

3.5.1 Reaction times

The reaction times namely, cream time, gel time tack free time and rise time were investigated by using a digital stopwatch in accordance with ASTM D7487-13 [19].

3.5.2 Free rise density

The free rise density of RPUR foams was measured in accordance with ASTM D 1622-09 [20]. The size of specimen was 3.0 cm x 3.0 cm x 3.0 cm (width x length x thickness) and the average values of three samples was reported.

3.5.3 Foaming temperature

A thermocouple Digicon DP-71 was used to detect the foaming temperatures of RPUR foams. These temperature data is presented by temperature profiles.

3.5.4 Infrared spectroscopy

The infrared spectroscopy was used to characterize the functional groups and study about NCO conversion of RPUR foams by using a Nicolet 6700 FTIR spectrometer over the range 800-4000 cm^{-1}. The main peaks given in Table 3.3 were used for the analysis.

Table 3. 3 Characteristic of main peaks of RPUR foams

Functional groups	Vibration mode	Peak (cm^{-1})
NCO	NCO antisymmetric Stretching	2180-2310
CO	C=O (urethane, urea, isocyanurate, allophanate, Biuret, etc.	1620-1760
Amide	C-N stretching (urethane, urea)	1155-1245
Free NCO in RPUR foams	phenyl group	1595

3.5.5 Scanning electron microscope (SEM)

The cell size and morphology of RPUR foams were measured on a JSM-6480 LV scanning electron microscope (SEM). RPUR foams were cut in both parallel and perpendicular to the foaming direction for SEM analysis. The foam sample was coated with gold before scanning in order to provide an electrically conductive surface. The specimens were done at accelerating voltage of 15 kV.

3.5.6 Compressive testing

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise direction were carried out by using universal testing machine (Lloyd/LRX) according to ASTM D 695 [21]. The specimen size of samples was 5.0 x 5.0 x 5.0 cm (length x width x thickness) dimension, the rate of crosshead movement was fixed at 50 mm/min and the preload cell used was 0.100 N.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of copper-amine complexes in aqueous solutions

Reactions between $Cu(OAc)_2$ and amine in water gave aqueous solutions of copper-amine complexes at the concentration of 25wt% of copper-amine complexes in water (Scheme 4.1). The appearances of copper-amine complex aqueous solutions are shown in Figure 4.1. It was found that $Cu(OAc)_2(en)_2$ 25wt% in water was obtained as blue-violet solution. $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) 25wt% in water were obtained as blue solutions. All of copper-amine complexes were odorless and had good solubility in water which were used in the preparation of RPUR foams without purification.

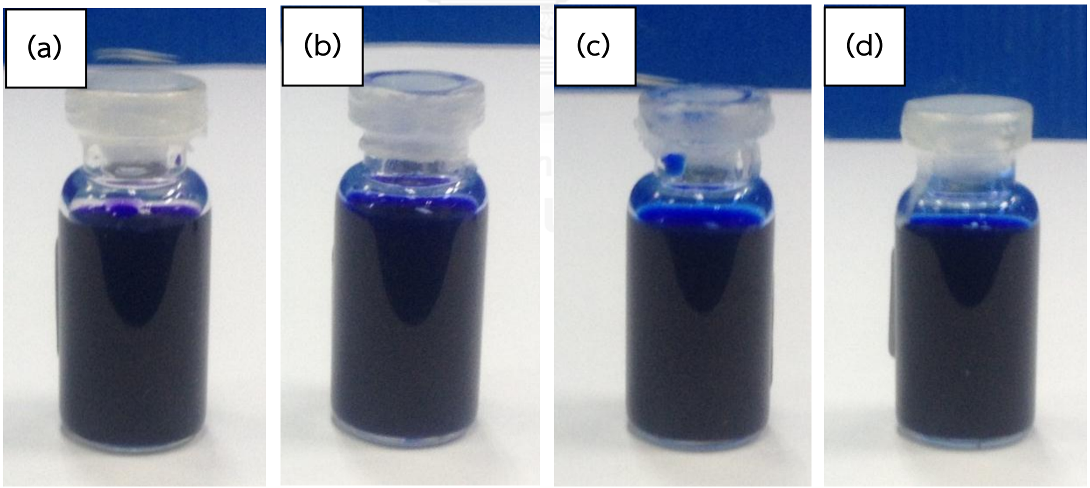
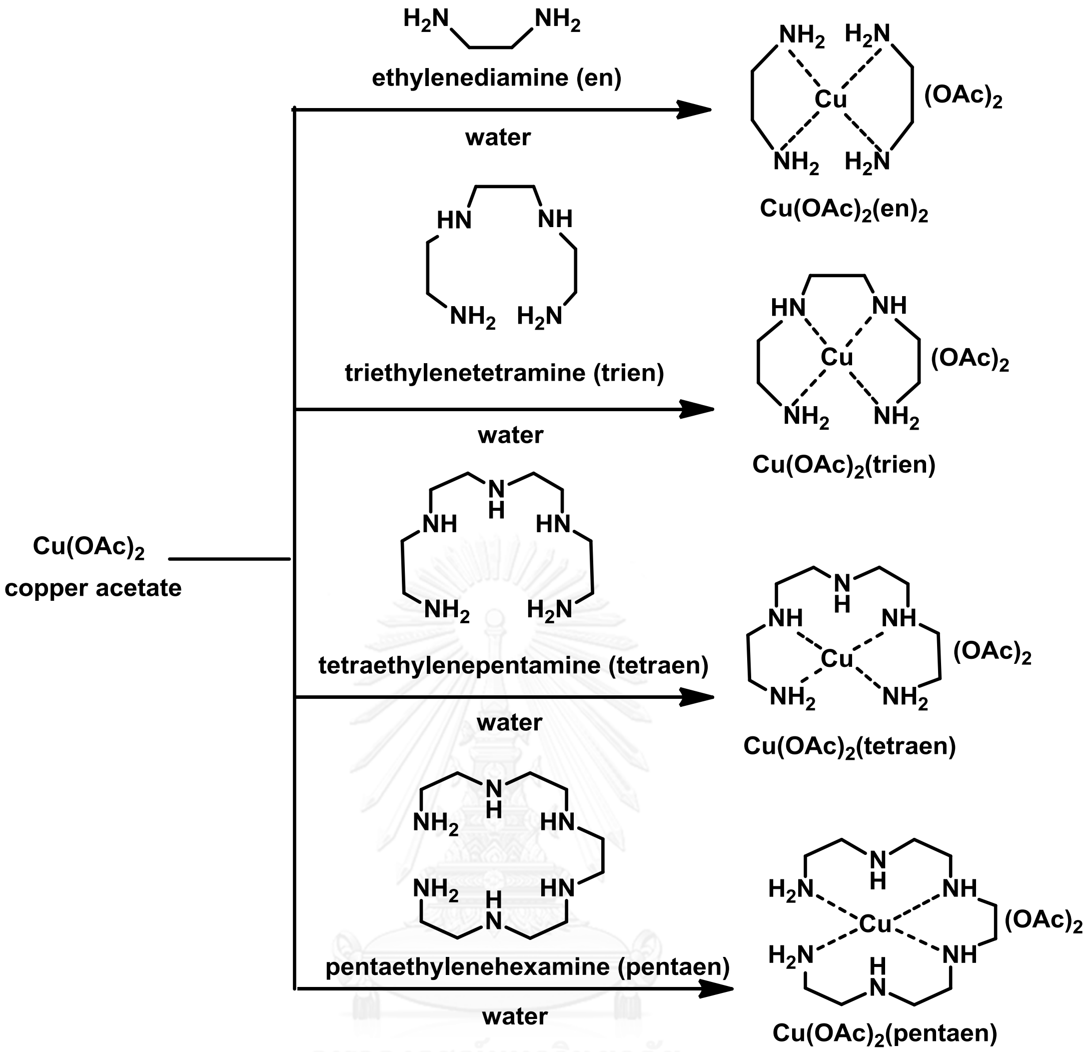


Figure 4.1 Copper-amine complexes 25wt% in water (a) $Cu(OAc)_2(en)_2$, (b) $Cu(OAc)_2$(trien), (c) $Cu(OAc)_2$(tetraen) and (d) $Cu(OAc)_2$(pentaen)



Scheme 4.1 Synthesis of copper-amine complexes [$Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen)] in water (aqueous solutions)

4.2 Characterization of copper-amine complexes as aqueous solutions

4.2.1 UV-visible spectroscopy of copper-amine complexes

UV-vis spectra of copper-amine complexes were obtained from their aqueous solutions as shown in Figure 4.2. $Cu(OAc)_2$ does not dissolve in water, therefore, UV-vis spectrum of $Cu(OAc)_2$ was obtained from its methanolic solution. The absorption of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) showed the maximum wavelength (λ_{max}) at 229, 258, 267 and 266 nm, respectively and molar absorptivity (ε) of 6,559, 4,365, 1,615 and 1,546, respectively). These λ_{max} shifted from that of $Cu(OAc)_2$, which appeared at 245 nm. These results suggested that the copper-amine complexes in water were formed.

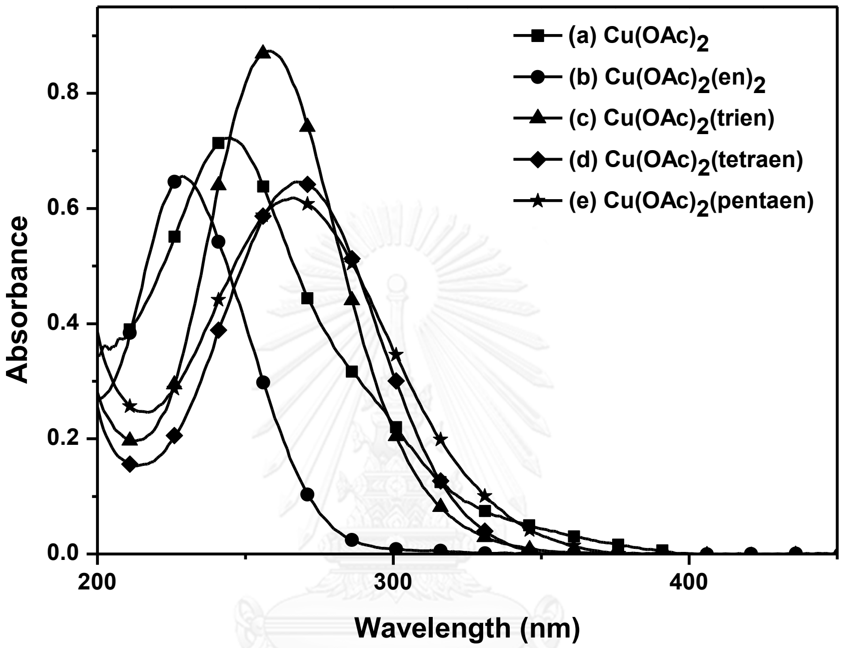


Figure 4.2 UV spactra of (a) $Cu(OAc)_2$, (b) $Cu(OAc)_2(en)_2$, (c) $Cu(OAc)_2$(trien), (d) $Cu(OAc)_2$(tetraen) and (d) $Cu(OAc)_2$(pentaen)

4.2.2 IR spectroscopy of copper-amine complexes

IR spectra were obtained from aqueous solutions of copper-amine complexes.

IR spectrum of $Cu(OAc)_2$ in water is shown in Figure 4.3(a). It exhibited absorption band at 3400 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in water), 1643 cm^{-1} (C=O asymmetric stretching) and 1416 cm^{-1} (C=O symmetric stretching).

IR spectrum of $Cu(OAc)_2(en)_2$ in water is shown in Figure 4.3(b). It exhibited absorption band at 3271 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in water), 1555 cm^{-1} (C=O asymmetric stretching), 1409 cm^{-1} (C=O symmetric stretching), at 1344 cm^{-1} (C-N stretching) and at 1045 cm^{-1} (C-O stretching).

IR spectrum of $Cu(OAc)_2$(trien) in water is shown in Figure 4.3(c). It exhibited absorption band at 3237 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in water), 1549 cm^{-1} (C=O asymmetric stretching), 1402 cm^{-1} (C=O symmetric stretching), at 1342 cm^{-1} (C-N stretching) and at 1026 cm^{-1} (C-O stretching).

IR spectrum of $Cu(OAc)_2$(tetraen) in water is shown in Figure 4.3(d). It exhibited absorption band at 3233 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in water), 1550 cm^{-1} (C=O asymmetric stretching), 1403 cm^{-1} (C=O symmetric stretching), at 1343 cm^{-1} (C-N stretching) and at 1017 cm^{-1} (C-O stretching).

IR spectrum of $Cu(OAc)_2$(pentaen) in water is shown in Figure 4.3(e). It exhibited absorption band at 3232 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in water), 1551 cm^{-1} (C=O asymmetric stretching), 1401 cm^{-1} (C=O symmetric stretching), at 1341 cm^{-1} (C-N stretching) and at 1012 cm^{-1} (C-O stretching).

The C=O stretching of carbonyl group in copper-amine complexes in water appeared as absorption band at 1555 cm^{-1}, 1549 cm^{-1}, 1550 cm^{-1} and 1551 cm^{-1} (asymmetric C=O), respectively and 1409 cm^{-1}, 1402 cm^{-1}, 1403 cm^{-1} and 1401 cm^{-1} (symmetric C=O), respectively, which were different from the typical $Cu(OAc)_2$ peaks. It was found that the IR peaks of copper-amine complexes shifted from those of $Cu(OAc)_2$ to lower energy because of the influence of amine coordination, which indicated that the metal-amine complexes were formed.

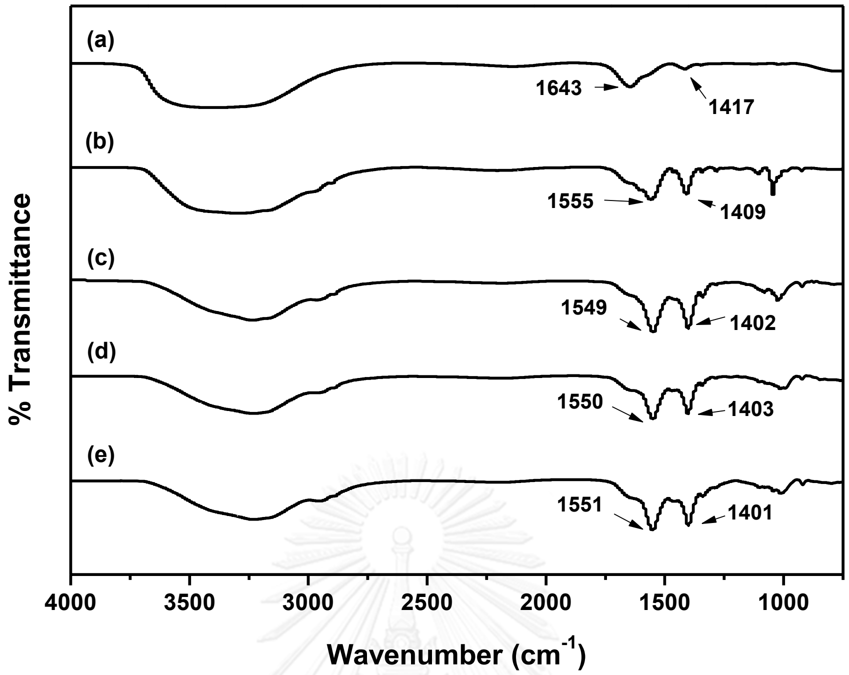


Figure 4.3 IR spactra of (a) $Cu(OAc)_2$, (b) $Cu(OAc)_2(en)_2$, (c) $Cu(OAc)_2$(trien), (d) $Cu(OAc)_2$(tetraen) and (e) $Cu(OAc)_2$(pentaen) aqueous solutions

4.2.3 Positive ESI mass spectrometry of copper-amine complexes

Positive ESI mass spectra were obtained from aqueous solutions of metal-amine complexes Mass spectra peak corresponded to the molecular weight of copper-amine complexes, which could be used to identify the copper-amine complexes structures and confirmed the complex formation. The molecular ion peaks of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) are shown in Figures 4.4, 4.5, 4.6 and 4.7 respectively. The data of molecular ion peaks corresponding and *m/z* ratio are shown in Table 4.1. The data showed the molecular ion of $[Cu(OAc)_2(en)_2+H]^+$ at *m/z* 303.06 . $Cu(OAc)_2(en)_2$ with loss of the ethylenediamine (en) unit to give $[Cu(OAc)_2(en)+H]^+$, which appeared at *m/z* 242.13. The molecular ions of $[Cu(OAc)_2(trien)+H]^+$, $[Cu(OAc)_2(tetraen)+H]^+$ and $[Cu(OAc)_2(pentaen)+H]^+$ appeared at *m/z* 329.16, 371.95 and 415.13, respectively.

Table 4.1 Molecular ion peak corresponding and *m/z* ratio of copper-amines complexes

Molecular ion peak	*m/z* (Calculated)	*m/z* (Found)
$[Cu(OAc)_2(en)_2+H^+]^+$	302.83	303.06
$[Cu(OAc)_2(trien)+H^+]^+$	328.87	329.16
$[Cu(OAc)_2(tetraen)+H^+]^+$	371.93	371.95
$[Cu(OAc)_2(pentaen)+H^+]^+$	415.01	415.13

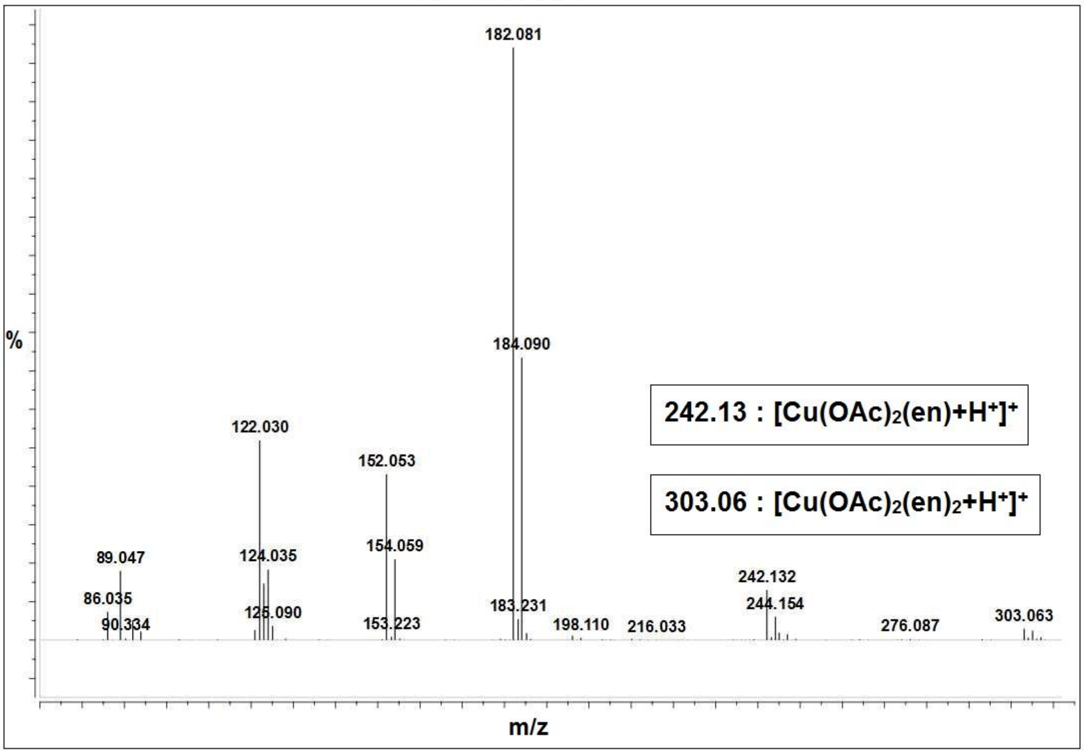


Figure 4.4 Positive ESI mass spectrum of $Cu(OAc)_2(en)_2$ aqueous solution

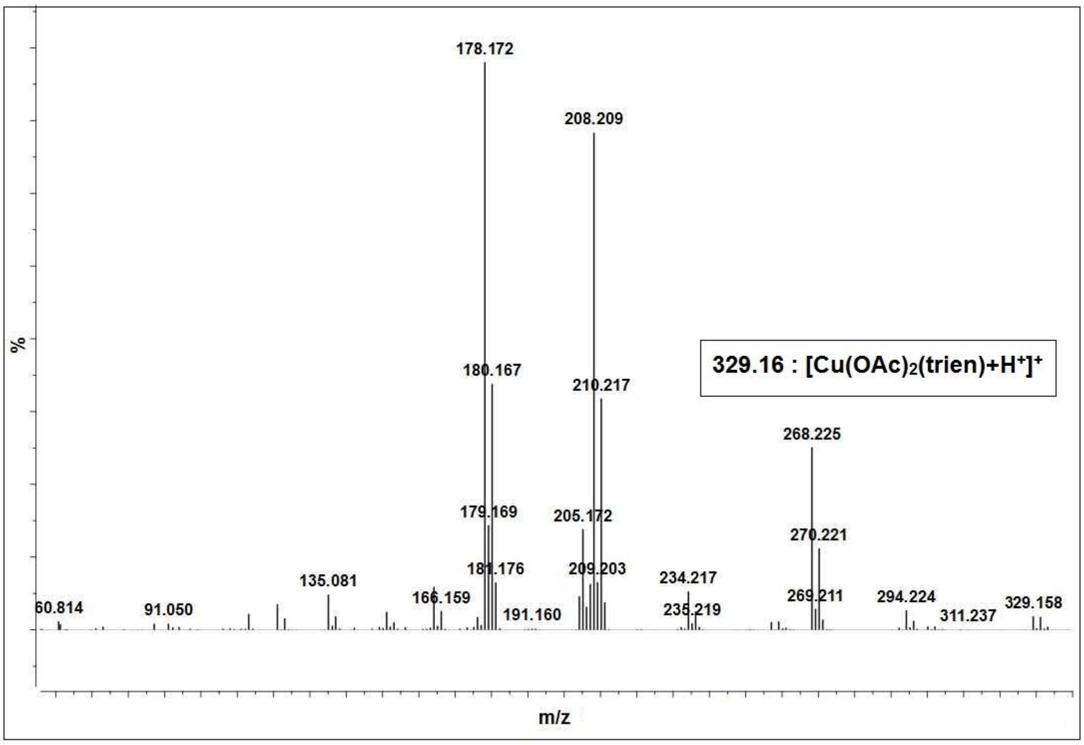


Figure 4.5 Positive ESI mass spectrum of $Cu(OAc)_2$(trien) aqueous solution

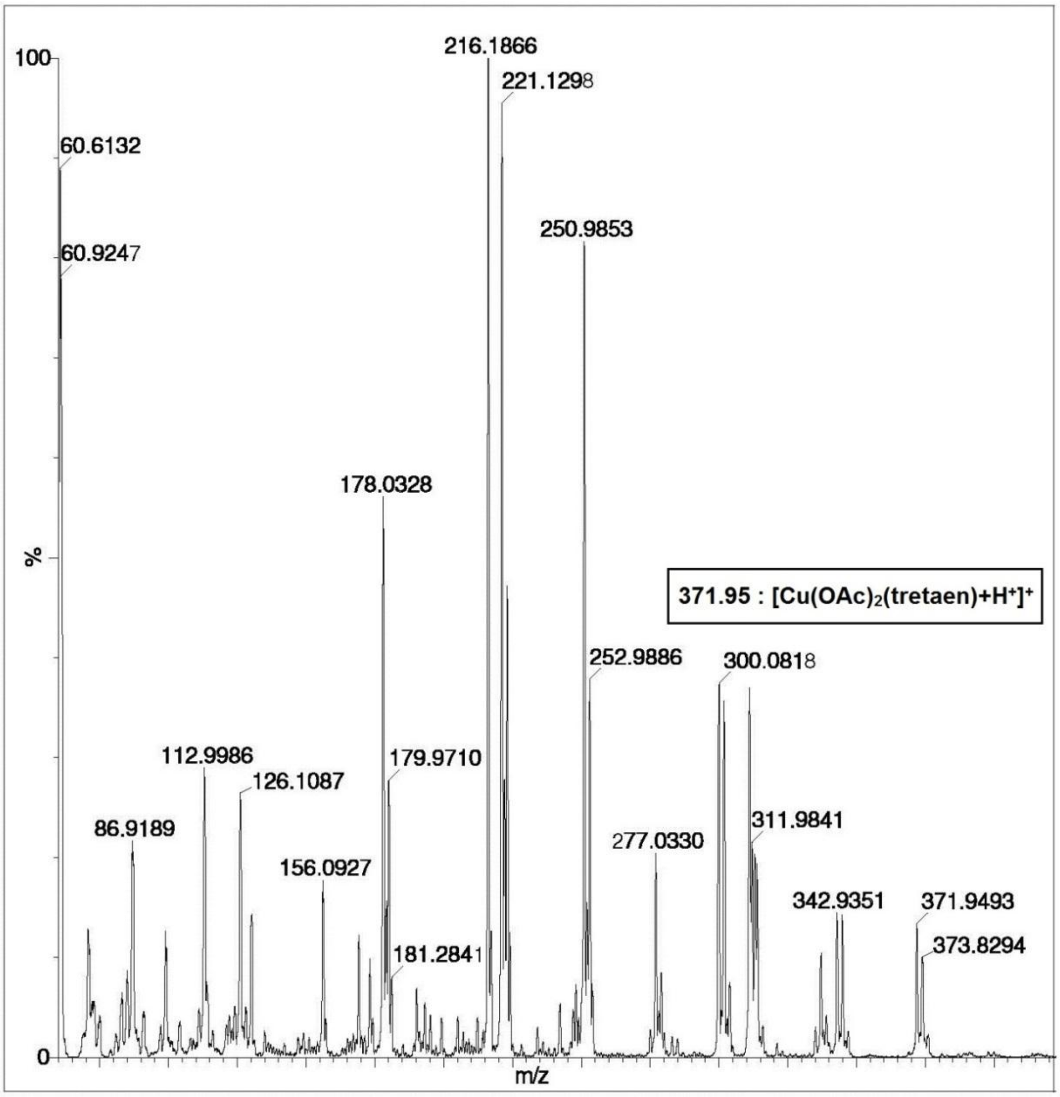


Figure 4.6 Positive ESI mass spectrum of Cu(OAc)$_2$(tetraen) aqueous solution

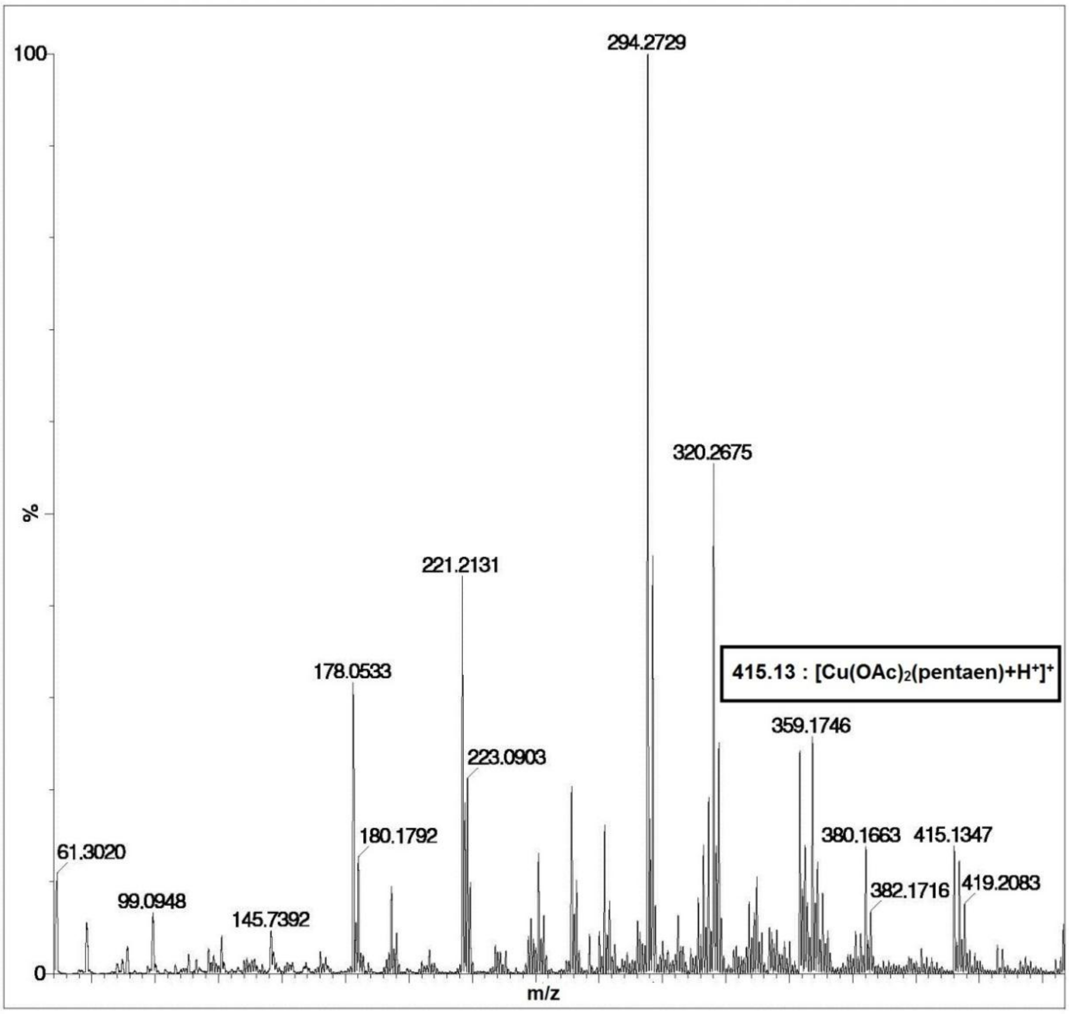


Figure 4.7 Positive ESI mass spectrum of $Cu(OAc)_2$(pentaen) aqueous solution

From all previous results, the characterization of the copper-amine complexes by UV-visible spectroscopy, IR spectroscopy and positive ESI mass spectrometry confirmed the formation of copper-amine complexes.

4.3 Preparation of rigid polyurethane (RPUR) foams

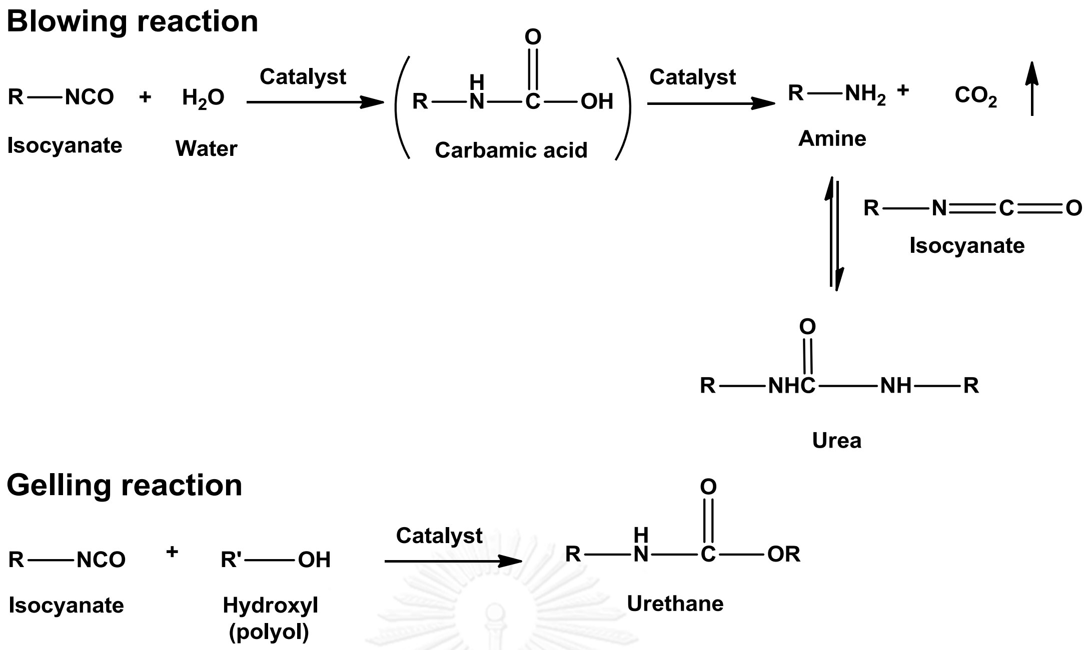
The amines in copper-amine complexes, namely $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) had different structures. Therefore, it is interesting to study the catalytic activity of these copper-amine complexes in the preparation of RPUR foams.

4.3.1 Preparation of RPUR foams by cup test and molded method

The preparation of RPUR foams was done both in cup-test and molded methods. RPUR foams obtained from cup test method were used for the investigation of reaction times, density, NCO conversion, rise profiles, temperature profiles and morphology of foams. RPUR foams obtained from molded method were used for the investigation of compressive properties. All properties of RPUR foams catalyzed by copper-amine complexes were compared with those catalyzed by DMCHA, which is used commercially.

4.3.1.1 Reaction times and density of RPUR foams

The catalytic activity of the blowing and gelling reactions (Scheme 4.2) in the preparation of RPUR foams was determined by reaction times, namely cream time (the time while RPUR foam starts to expand), gel time (the time while RPUR foam starts to harden), tack-free time (the time while polymerization is completed and surface of RPUR foam is not sticky) and rise time (the time while CO_2 generation stops and RPUR foam reaches its maximum height). Moreover, gel time and tack free time are the time when foam flows into and outside of the mold, respectively. Therefore, the target of this research was to increase gel time, while tack free time should be decreased when compared with RPUR foams catalyzed by DMCHA.



Scheme 4.2 Blowing and gelling reactions of RPUR foam

The density of RPUR foams was measured in accordance with ASTM D 1622-09 [20]. The foam was cut into the size of 3.0 x 3.0 x 3.0 cm (length x width x thickness) (Figure 4.8). The cubic shape was measured to obtain the volume. The weight divided by volume is equals to density. The height of RPUR foam prepared in a cup was measured as shown in Figure 4.9.

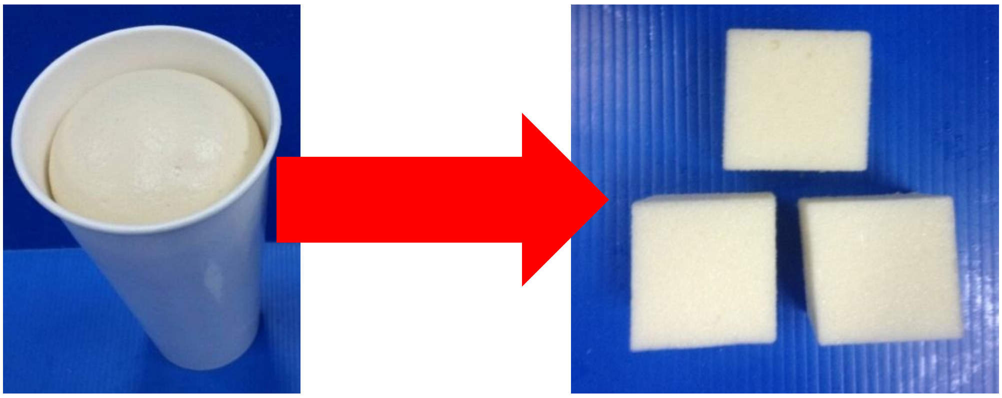


Figure 4.8 RPUR foam samples for foam density measurement

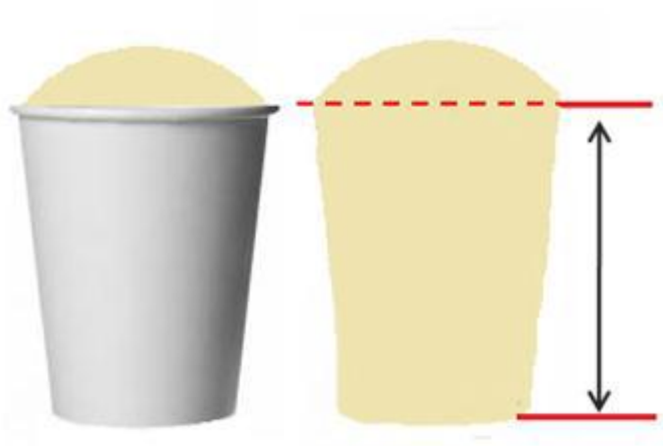


Figure 4. 9 Measurement of RPUR foam height [22]

The reaction times, density and height of RPUR foams catalyzed by DMCHA and copper-amine complexes are shown in Table 4.2 and Figure 4.10. Firstly, investigation of gel time indicated that RPUR foams prepared from all synthesized copper-amine complexes gave longer gel time (44-77 sec) than DMCHA (32 sec). This suggested possible uses of these copper-amine complex catalysts in industry because there are longer period of time for flowing the liquid mixture of starting materials into a mold before the foam hardening occurs.

Secondly, all observed tack free time from the reaction catalyzed by all copper-amine complexes (69-121 sec) were found to be shorter than DMCHA (172 sec). As a result, the copper amine catalyst gained a benefit in terms of the shorter time for preparing RPUR forms in industry.

Lastly, rise time of RPUR foams catalyzed by $Cu(OAC)_2(en)_2$ (93 sec) were shorter than DMCHA (124 sec), while those prepared from $Cu(OAc)_2$(trien) (127 sec) had similar rise time to that prepared from DMCHA. The rise time of $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) (140-154 sec) were longer than that of DMCHA. These results indicates that $Cu(OAC)_2(en)_2$ has the best catalytic activity in blowing reaction.

According to the results from Table 4.2, RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) gave low density foams (37.52 and 39.18 kg/m^3, respectively) as compared with DMCHA (37.05 kg/m^3). This confirmed the achievement to prepare the low density foams using catalysts in aqueous media. Moreover, RPUR foams prepared from Cu(OAc)$_2$(tetraen) and Cu(OAc)$_2$(pentaen) had higher density (40.41 and 41.33 kg/m^3, respectively) than DMCHA. This is because these two copper complexes had slow catalytic reactivity in blowing reaction. CO_2 could not be completely generated for foams expansion before the polymerization is completed. The obtained RPUR foams had low height, therefore density of the foams were high.

From external appearance of above RPUR foams prepared from Cu(OAc)$_2$(tetraen) and Cu(OAc)$_2$(pentaen) at the NCO index of 100 and 130 (Figure 4.11), the height and the width of RPUR foams are small. Therefore, RPUR foams were prepared at the NCO index of 130 to increase the dimension of foam. It was found that RPUR prepared at the NCO indexes of 100 and 130 had similar height the width. However, RPUR foams were prepared at the NCO index of 130 had higher density more than those prepared at the NCO index of 100. Therefore, Cu(OAc)$_2$(tetraen) and Cu(OAc)$_2$(pentaen) are not suitable catalysts for RPUR foam preparation.

Table 4.2 Reaction times, density and height of RPUR foams prepared by cup test method.

Catalyst Types	Cream time (sec)	Gel time (sec)	Tack free time (sec)	Rise time (sec)	Free rise density (kg/m^3)	Foam height (%)
DMCHA (ref.) (NCO index 100)	25	32	172	124	37.05	90
$Cu(OAc)_2(en)_2$ (NCO index 100)	33	44	69	93	37.52	95
$Cu(OAc)_2$(trien) (NCO index 100)	36	66	95	127	39.18	89
$Cu(OAc)_2$(tetraen) (NCO index 100)	38	67	112	140	40.41	86
$Cu(OAc)_2$(pentaen) (NCO index 100)	39	77	121	154	41.33	83
$Cu(OAc)_2$(tetraen) (NCO index 130)	38	71	112	153	44.11	91
$Cu(OAc)_2$(pentaen) (NCO index 130)	39	75	127	166	43.88	90

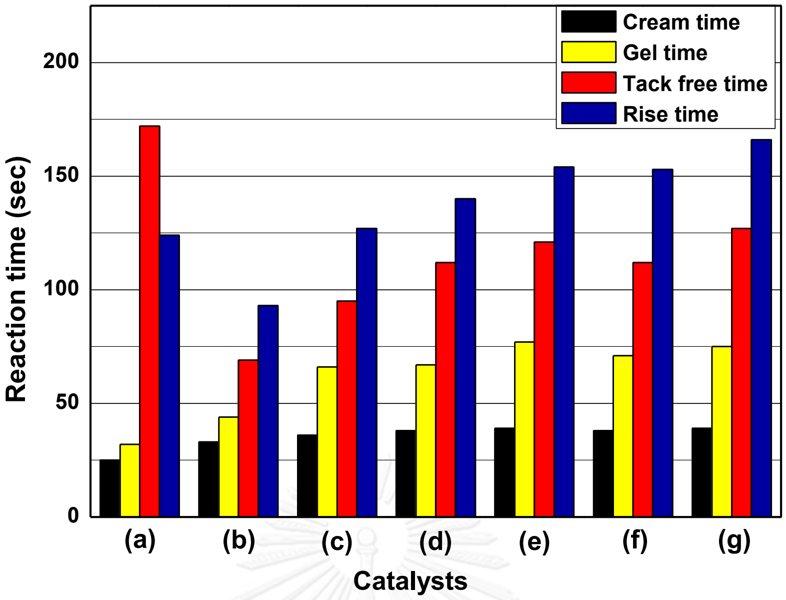


Figure 4.10 Reaction time of RPUR foams catalyzed by (a) DMCHA (NCO index 100), (b) $Cu(OAc)_2(en)_2$ (NCO index 100), (c) $Cu(OAc)_2$(trien) (NCO index 100), (d) $Cu(OAc)_2$(tetraen) (NCO index 100), (e) $Cu(OAc)_2$(pentaen) (NCO index 100), (f) $Cu(OAc)_2$(tetraen) (NCO index 130) and (f) $Cu(OAc)_2$(pentaen) (NCO index 130)

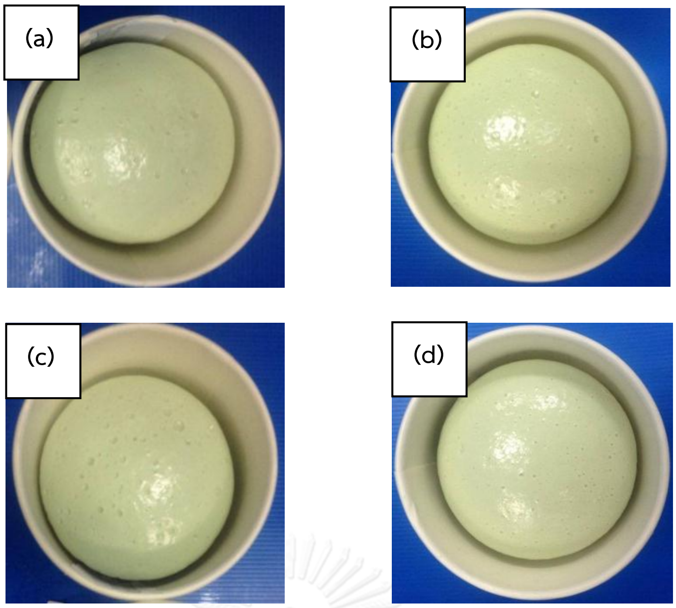
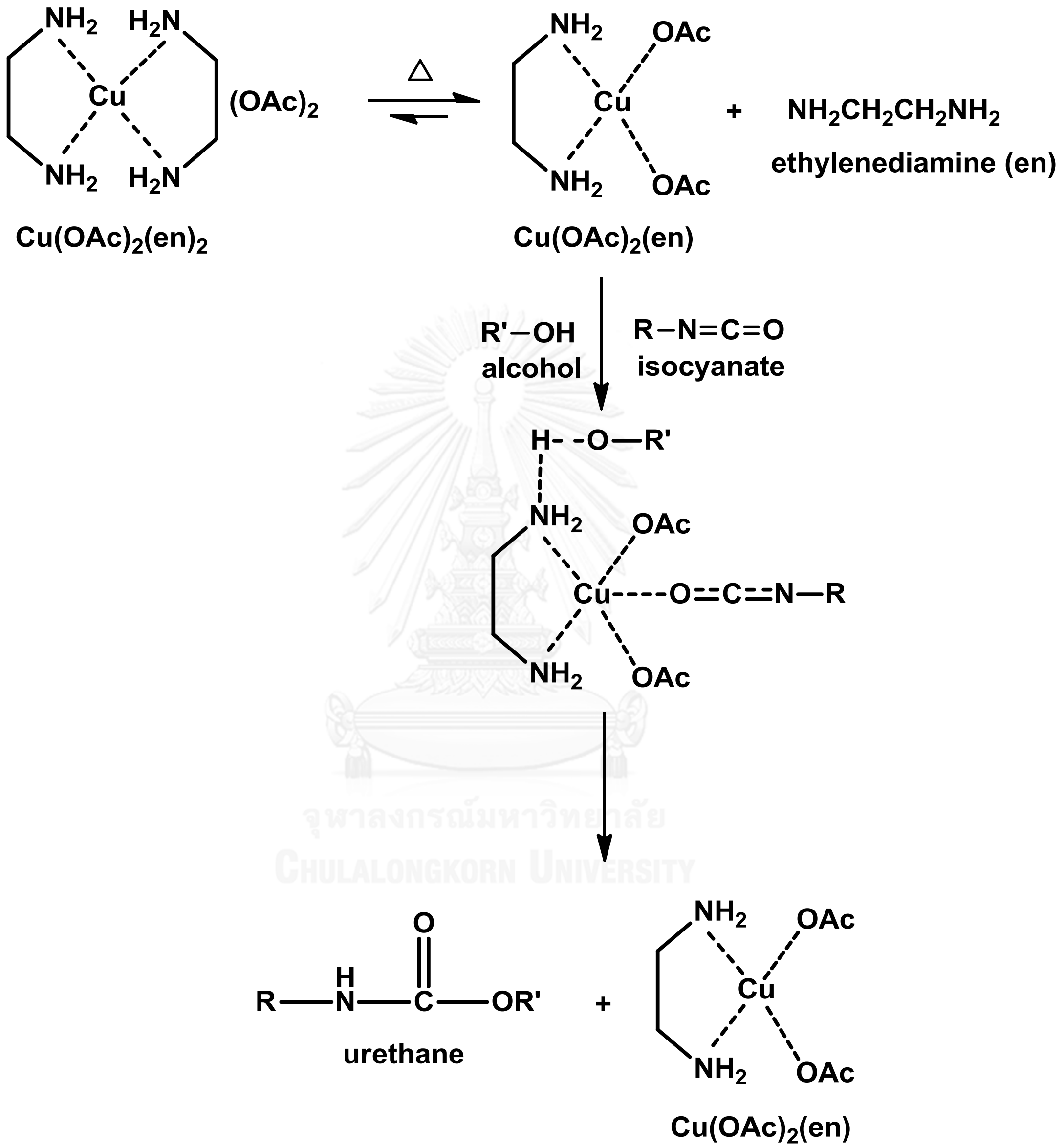


Figure 4.11 External appearance of RPUR foams catalyzed by $Cu(OAc)_2$(tetraen) (a) (NCO index 100), (b) (NCO index 130) and $Cu(OAc)_2$(pentaen) (c) (NCO index 100), (d) (NCO index 130)

From all previous results, the obtained experimental data indicated that the order of catalytic activity of copper-amine complexes was $Cu(OAc)_2(en)_2$ > $Cu(OAc)_2$(trien) > $Cu(OAc)_2$(tetraen) > $Cu(OAc)_2$(pentaen) due to catalytic mechanism of copper-amine complexes. They contain copper atom and amine groups in their structures. The catalytic mechanism of gelling reaction between isocyanate and hydroxyl groups is proposed as shown in Scheme 4.3 [9]. The polymerization reactions of RPUR foams are exothermic reaction. The heat causes $Cu(OAc)_2(en)_2$ to dissociate into $Cu(OAc)_2$(en) that could be observed from ESI-MS. Copper atom in $Cu(OAc)_2$(en) can act as a Lewis acid and coordinate to oxygen atom of the NCO group, causing the NCO carbon to be more electrophilic. Nitrogen atom in $Cu(OAc)_2$(en) interacts with the proton of the hydroxyl group and causes the hydroxyl oxygen to be more nucleophilic, reacting with the isocyanate group to give a urethane linkage. The catalytic mechanism of $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) is proposed to be similar to that of $Cu(OAc)_2(en)_2$. They showed less catalytic activity than Cu(OAc)$_2$(en)$_2$ due to the steric effect of the amines, namely trien, tetraen and pentaen, which was larger than ethylenediamine.



Scheme 4.3 Proposed polymerization mechanism catalyzed by Cu(OAc)$_2$(en)$_2$

4.3.1.2 Rise profiles

Rise profiles data are the relationship between the height of foam in cup test method after mixing with the rise time (Figure 4.12). It was found that DMCHA had higher reactivity in blowing reaction at the beginning of reaction than copper-amine complexes, while $Cu(OAc)_2(en)_2$ exhibited a very quick rise curve in the latter stage. The reactivity in blowing reaction of $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) were lower than that of $Cu(OAc)_2(en)_2$.

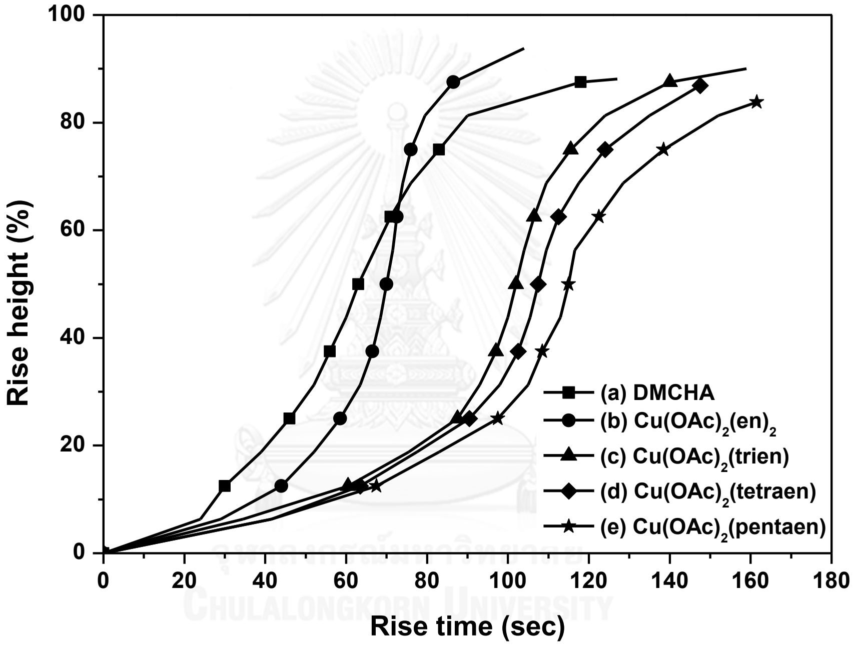


Figure 4.12 Rise profiles of RPUR foams catalyzed by (a) DMCHA (ref.), (b) $Cu(OAc)_2(en)_2$, (c) $Cu(OAc)_2$(trien), (d) $Cu(OAc)_2$(tetraen) and (e) $Cu(OAc)_2$(pentaen)

4.3.1.3 Temperature profiles

The data of temperature profiles were recorded from the core temperature of RPUR foams in cup test method versus the time. Temperature profiles of RPUR foams catalyzed by aqueous solutions of copper-amine complexes were investigated and compared with the foam catalyzed by DMCHA as shown in

Figure 4.13. It was found that the polymerization reaction was exothermic reaction and the all RPUR foams had the same temperature profile. The maximum core temperature was in the range 126.1-132.6 °C (Table 4.3) that was appropriate for polymerization reaction of RPUR foams because the foam did not burn at this maximum temperature.

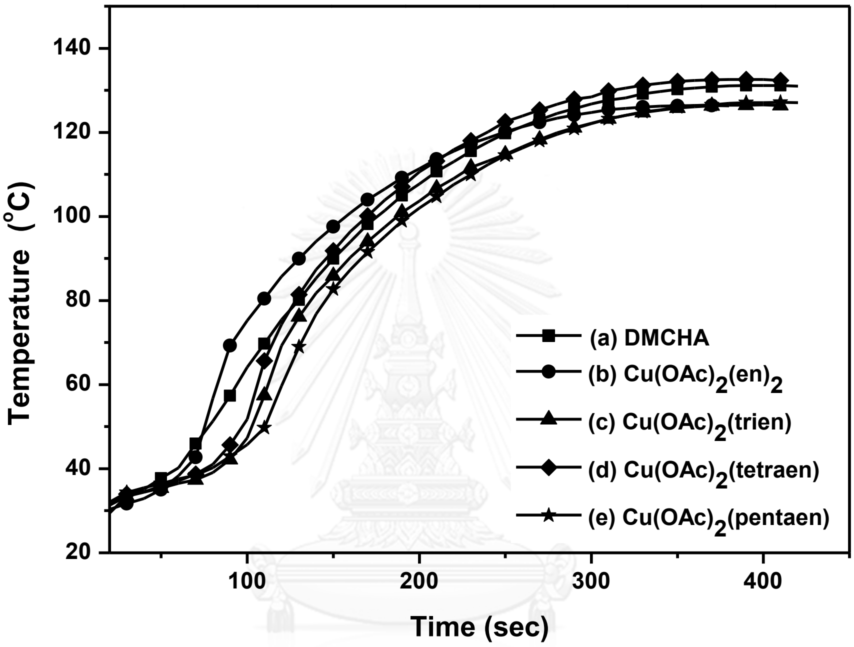


Figure 4.13 Temperature profiles of RPUR foams catalyzed by (a) DMCHA (ref.), (b) $Cu(OAc)_2(en)_2$, (c) $Cu(OAc)_2$(trien), (d) $Cu(OAc)_2$(tetraen) and (e) $Cu(OAc)_2$(pentaen)

Table 4.3 The maximum core temperature of RPUR foams catalyzed by DMCHA (ref.), copper-amine complexes aqueous solutions

Catalysts	**Maximum core temperature (°C)**	**Starting times (sec) at T_{max}**
DMCHA (ref.)	131.2	410
$Cu(OAc)_2(en)_2$	126.4	370
$Cu(OAc)_2$(trien)	126.5	400
$Cu(OAc)_2$(tetraen)	132.6	390
$Cu(OAc)_2$(pentaen)	127.2	410

4.3.2 Characterization of rigid polyurethane (RPUR) foams

To study and investigate the polymerization reaction of RPUR foams by using ATR-FTIR spectroscopy. IR spectra of PMDI, polyol, RPUR foams catalyzed by copper-amine complexes aqueous solutions and DMCHA are illustrated in Figure 4.14 for comparison. Polyol showed a broad band at 3409 cm^{-1} which indicated stretching vibration of hydroxyl groups. PMDI showed high intensity of free NCO absorption band at 2277 cm^{-1}. Besides, the absorption bands at 3318-3332, 1705-1710 and 1075 cm^{-1} were the stretching vibrations of amine group (N-H), carbonyl group (C=O) of urethane and urea and C-O of urethane, respectively, while the absorption band at 1520 cm^{-1}could be attributed to N-H bending vibration and C-N stretching vibration of urethane and urea groups, respectively. The band at 1219-1222 cm^{-1} was associated with the characteristic stretching vibration of C-N-H bond of urethane and urea.

IR spectra of all RPUR foams indicated that the reactions of isocyanate with hydroxyl groups and water were completed by disappearance of isocyanate peak at 2277 cm^{-1}.

Among all catalysts, the order of catalytic activity in gelling reaction was DMCHA.> $Cu(OAc)_2(en)_2$ > $Cu(OAc)_2$(trien) > $Cu(OAc)_2$(tetraen) > $Cu(OAc)_2$(pentaen). When higher NCO index of 130 was used in the foam formulation, it was found that high intensity of free NCO absorption band at 2277 cm^{-1} could be observed in RPUR foams. Therefore, preparation of RPUR foams at the NCO index of 130 catalyzed by $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) were not suitable for RPUR foam preparation.

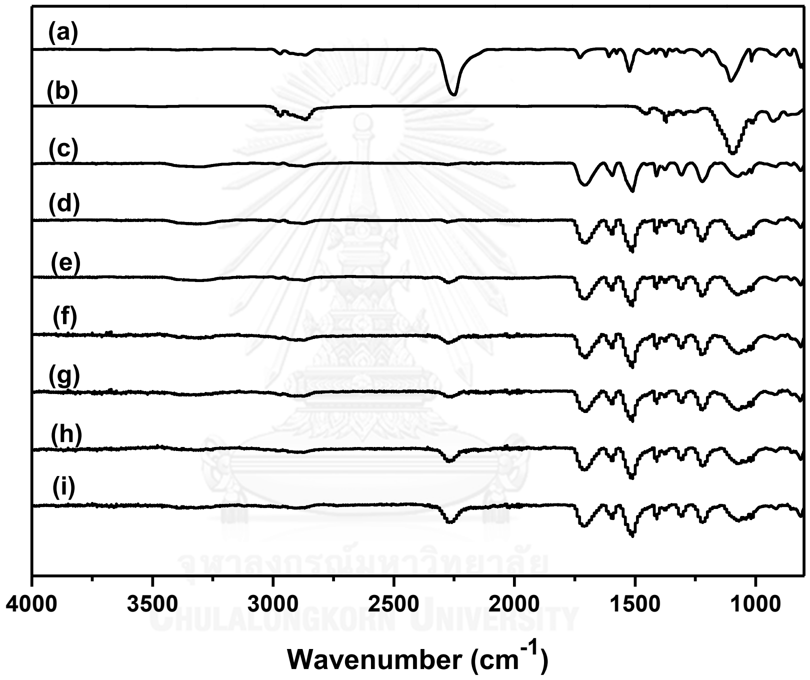


Figure 4.14 IR spactra of (a) PMDI (starting material), (b) polyol (starting material), RPUR foams catalyzed by (c) DMCHA (ref.; NCO index 100), (d) $Cu(OAc)_2(en)_2$ (NCO index 100), (e) $Cu(OAc)_2$(trien) (NCO index 100), (f) $Cu(OAc)_2$(tetraen) (NCO index 100), (g) $Cu(OAc)_2$(pentaen) (NCO index 100), (h) $Cu(OAc)_2$(tetraen) (NCO index 130) and (i) $Cu(OAc)_2$(pentaen) (NCO index 130)

4.3.3 NCO conversion of RPUR foams

In 2001, Modesti and co-worker studied NCO conversion defining as the ratio between isocyanate peak area at time 0 and isocyanate peak area at time t as shown in following equation :

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

where;

NCO^{f} = the peak area of isocyanate at time t [Figure 4.14 (c-i)]

NCO^{i} = the peak area of isocyanate at time 0 [Figure 4.14 (b)]

The peak area of free NCO in RPUR foams were normalized by aromatic ring (Ar-H) absorption band at 1595 cm^{-1}.

Polyisocyanurate : polyurethane (PIR/PUR) ratio was calculated from the peak area of isocyanurate and urethane at 1415 and 1220 cm^{-1}, respectively (Table 4.4).

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

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

From the result of NCO conversion of RPUR foams catalyzed by DMCHA and copper-amine complexes are shown in Table 4.5, it was found that all catalysts at isocyanate index 100 gave approximately more than 99% of NCO conversion which showed that the polymerization reactions were completed. The PIR/PUR ratio of all catalysts at isocyanate index 100 was low. On the other hand, the catalysts at isocyanate index 130 gave less than 99% of NCO conversion with slightly higher PIR/PUR ratio.

Table 4.5 NCO conversion of RPUR foams catalyzed by DMCHA and copper-amine complexes

Catalyst Types	**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**		
DMCHA (ref.) (NCO index 100)	0.242	2.269	1.027	5.591	0.1067	99.9	0.18
$Cu(OAc)_2(en)_2$ (NCO index 100)	0.262	2.596	1.172	6.163	0.1009	99.9	0.19
$Cu(OAc)_2$(trien) (NCO index 100)	1.515	2.369	0.987	5.577	0.6395	99.3	0.18
$Cu(OAc)_2$(tetraen) (NCO index 100)	2.240	2.505	1.108	5.754	0.8942	99.1	0.19
$Cu(OAc)_2$(pentaen) (NCO index 100)	2.109	2.354	0.967	5.236	0.8959	99.1	0.18
$Cu(OAc)_2$(tetraen) (NCO index 130)	4.460	2.360	1.115	4.914	1.8898	98.1	0.23
$Cu(OAc)_2$(pentaen) (NCO index 130)	6.586	2.545	1.135	4.654	2.5878	97.4	0.24

4.3.4 Morphology of RPUR foams

Foam morphology catalyzed by copper-amine complexes in parallel and perpendicular direction of foam rising was investigated and compared with the foam catalyzed by DMCHA (Figures 4.15-4.19). It was found that RPUR foams had mainly closed cell foam structure. The cell shape of foams showed spherical shape and ellipsoidal shape as shown in (a) top view and (b) side view, respectively. These results indicated that the foams were anisotropic materials and the compressive strength data also confirmed this result. The average cell size of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) are shown in Tables 4.6 and 4.7. The average cell size of RPUR foam were determined by the image analysis according to Figure 4.20 (a), which the spherical cell was measured from cell-w and cell-h of spherical shape and Figure 4.20 (b), which the ellipsoidal cell was measured from cell-w and cell-h.

From the top view and side view, it was found that cell size of RPUR foams catalyzed by all $Cu(OAc)_2(en)_2$ was smaller than RPUR foam catalyzed by DMCHA. Therefore, Therefore, RPUR foams catalyzed by all copper-amine complexes should have less compressive strength than RPUR foam catalyzed by DMCHA. This is because the large cell size of RPUR foam gave less compressive strength.

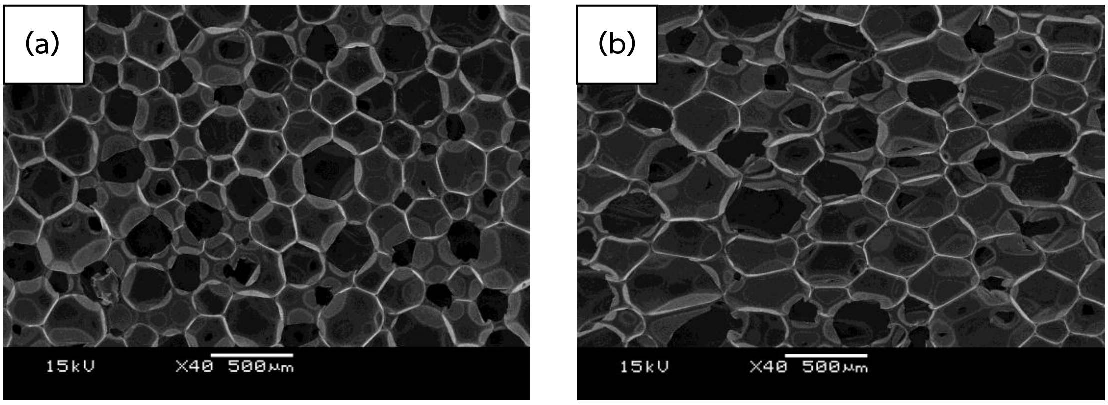


Figure 4.15 SEM of RPUR foam catalyzed by DMCHA (a) top view, (b) side view (40x)

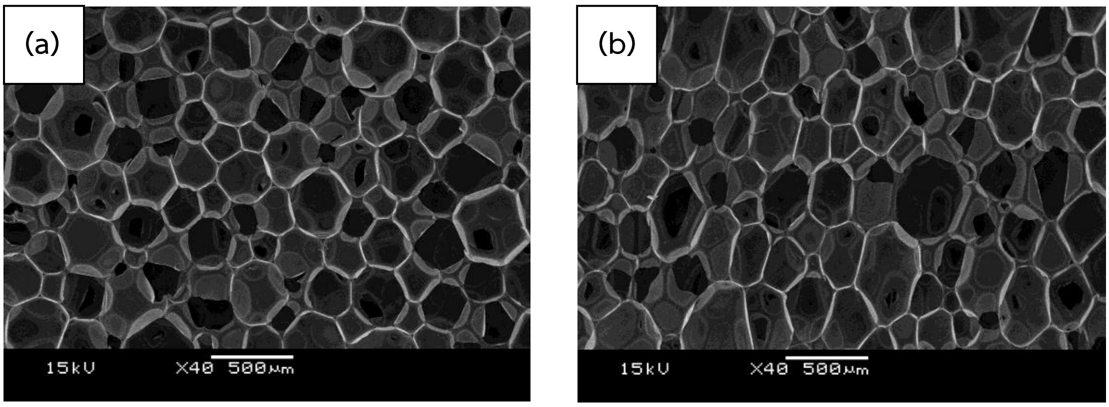


Figure 4.16 SEM of RPUR foam catalyzed by $Cu(OAc)_2(en)_2$ (a) top view, (b) side view (40x)

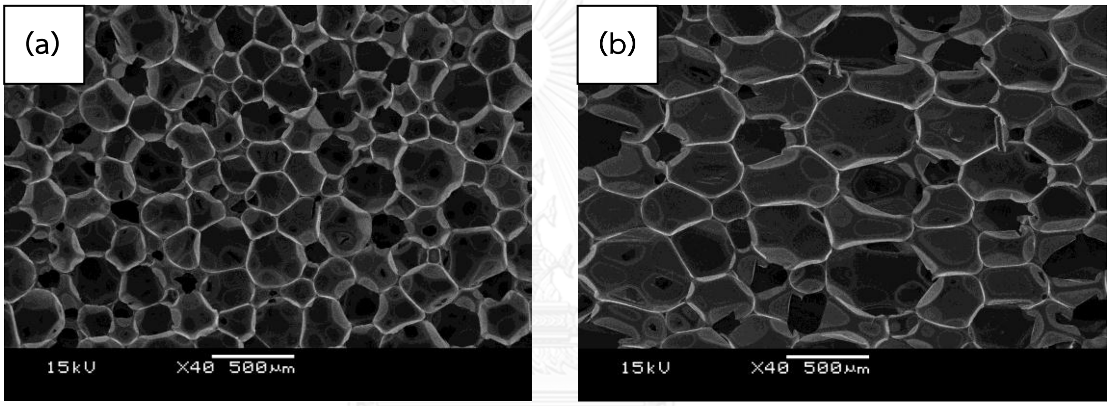


Figure 4.17 SEM of RPUR foam catalyzed by $Cu(OAc)_2$(trien) (a) top view, (b) side view (40x)

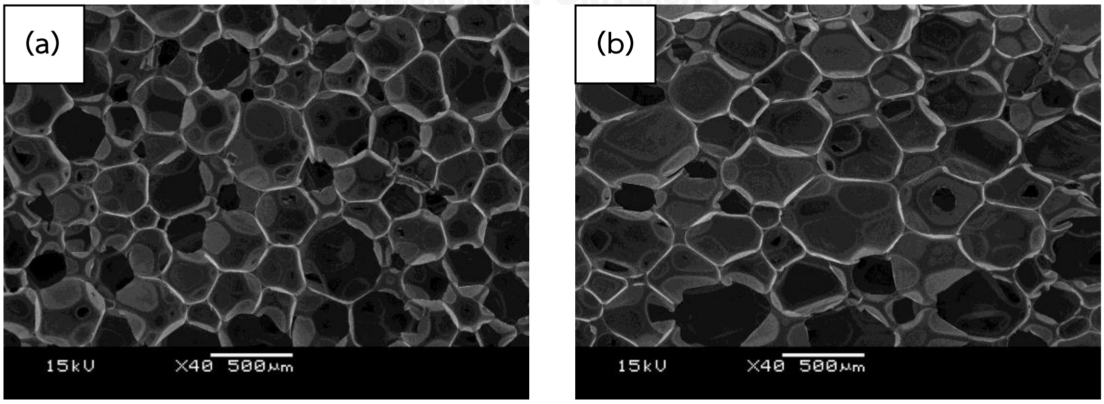


Figure 4.18 SEM of RPUR foam catalyzed by $Cu(OAc)_2$(tetraen) (a) top view, (b) side view (40x)

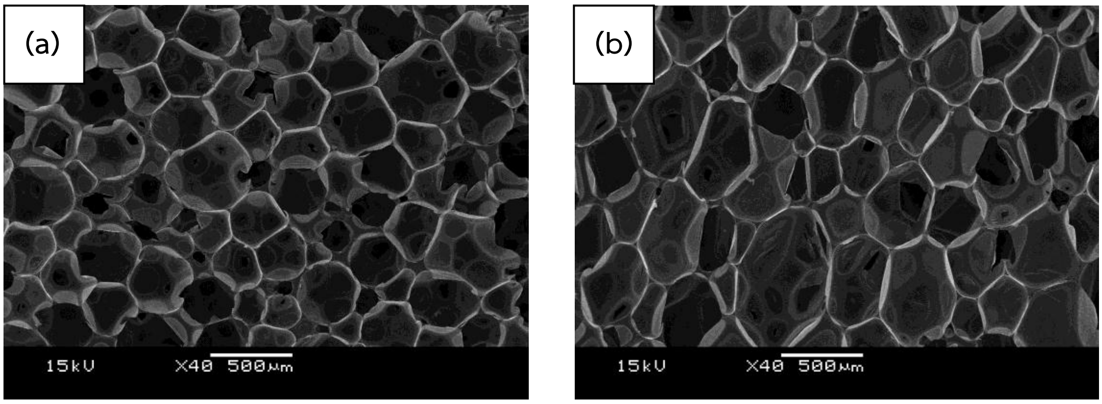


Figure 4.19 SEM of RPUR foam catalyzed by $Cu(OAc)_2(pentaen)$ (a) top view, (b) side view (40x)

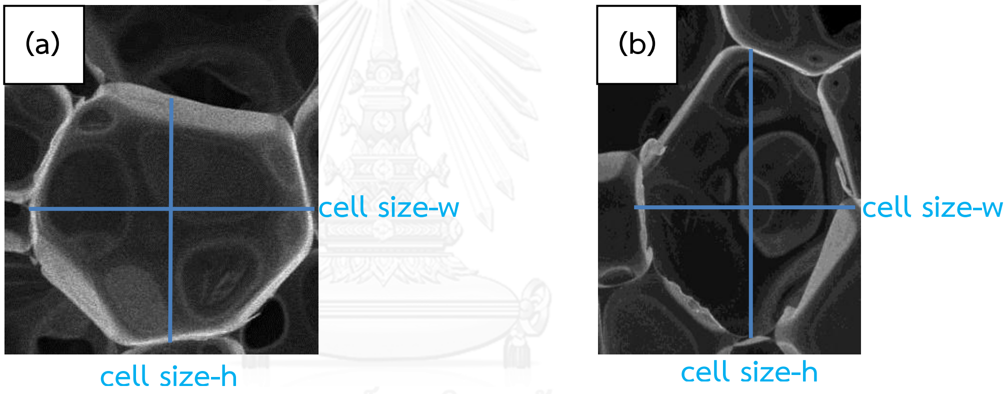


Figure 4.20 Measurement of cell size of RPUR foam

Table 4.6 The cell size (top view) of RPUR foams catalyzed by DMCHA and copper-amine complexes

Catalyst Types	Top view	
	Cell size-w (µm)	Cell size-h (µm)
DMCHA (ref.)	287 ± 38.08	288 ± 39.87
$Cu(OAc)_2(en)_2$	296 ± 45.90	306 ± 43.37
$Cu(OAc)_2(trien)$	296 ± 42.35	293 ± 41.86
$Cu(OAc)_2(tetraen)$	359 ± 47.68	365 ± 50.32
$Cu(OAc)_2(pentaen)$	369 ± 46.92	367 ± 48.14

Table 4.7 The cell size (side view) of RPUR foams catalyzed by DMCHA and copper-amine complexes

Catalyst Types	Side view	
	Cell size-w (μm)	Cell size-h (μm)
DMCHA (ref.)	285 ± 33.96	371 ± 52.63
$Cu(OAc)_2(en)_2$	277 ± 44.67	424 ± 67.22
$Cu(OAc)_2$(trien)	320 ± 56.99	489 ± 74.54
$Cu(OAc)_2$(tetraen)	359 ± 44.22	482 ± 67.54
$Cu(OAc)_2$(pentaen)	375 ± 50.50	516 ± 64.08

4.3.5 Mechanical properties of FPUR foams (molded method)

The compression stress-strain curves of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) are demonstrated in Figures 4.21-4.22, which show the compressive strength in perpendicular and parallel to the foam rising direction. From the results, the perpendicular compressive strength of RPUR foams was higher than that of parallel compression direction. Moreover, the compressive strength of RPUR foam catalyzed by $Cu(OAc)_2$(pentane) had the highest compressive strength (245.7 kPa).

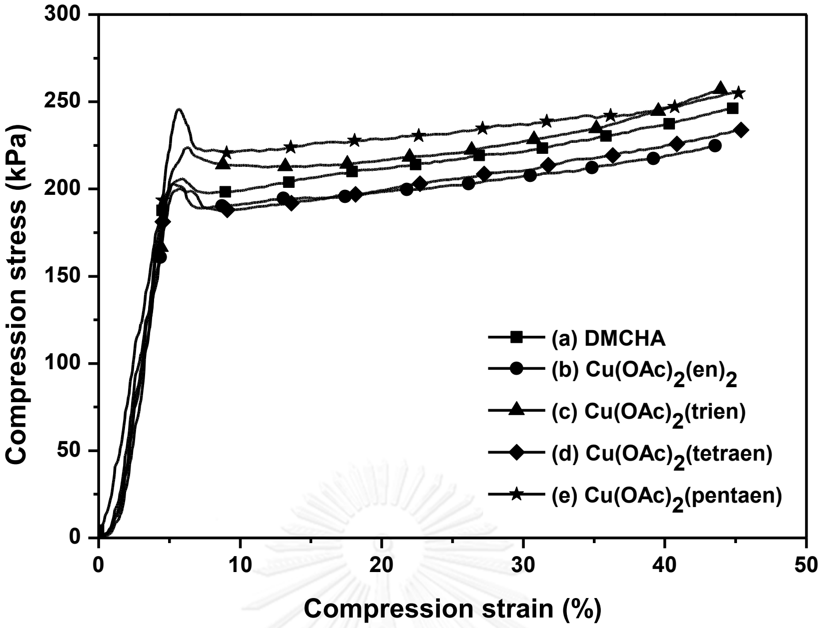


Figure 4.21 Compression stress-strain curves of RPUR foams in perpendicular to the foam rising direction

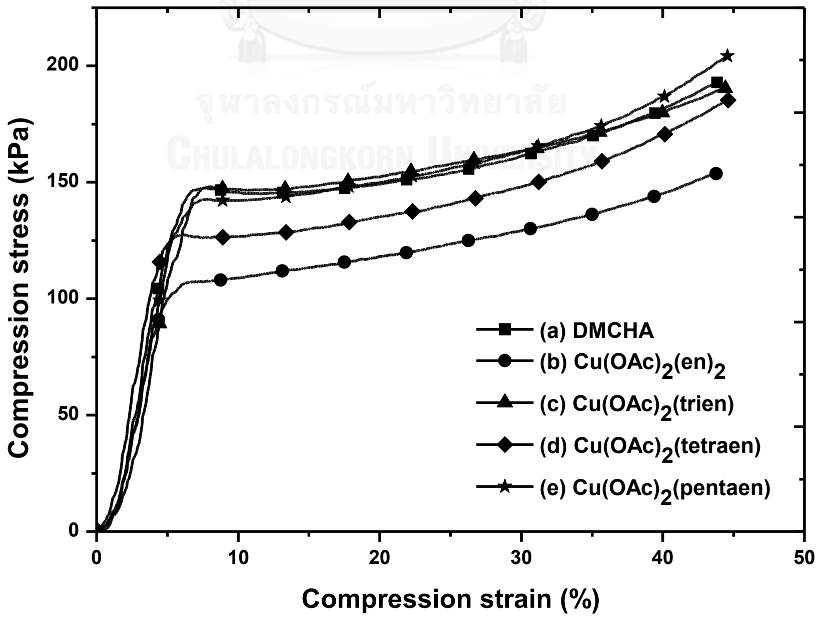


Figure 4.22 Compression stress-strain curves of RPUR foams in parallel to the foam rising direction.

Table 4.8 Comparison of compressive strength of RPUR foams between parallel and perpendicular direction of foam rising

Catalysts	Compressive strength (kPa) in parallel	Compressive strength (kPa) in perpendicular
DMCHA (ref.)	205.9	147.6
$Cu(OAc)_2(en)_2$	200.2	107.6
$Cu(OAc)_2$(trien)	223.8	148.2
$Cu(OAc)_2$(tetraen)	201.9	126.4
$Cu(OAc)_2$(prntaen)	245.7	142.6

CHAPTER V

CONCLUSION

5.1 Conclusion

Copper-amine complexes, namely $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$ and $Cu(OAc)_2(pentaen)$ could be synthesized in aqueous solution and could be used as catalyst for preparation of RPUR foam without purification. The copper-amine complexes aqueous solutions were obtained as odorless solution with low viscosity and could be easily dissolved in the raw materials of RPUR foam formulations. UV-visible spectroscopy, IR spectroscopy and mass spectrometry confirmed the complex formation.

$Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ gave comparable catalytic activity and density to that obtained from commercial catalyst (DMCHA). Moreover, RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ gave low density foams as compared with DMCHA.

Rise profile of RPUR foaming reaction catalyzed by $Cu(OAc)_2(en)_2$ had longer reaction time in beginning of reaction and had very fast reaction in the later state when compared with DMCHA. $Cu(OAc)_2(trien)$ and DMCHA gave similar rise time.

The reaction of RPUR foams is exothermic and the maximum core temperature during foaming reaction was in the range of 126.1-132.6 °C. This was appropriate for polymerization of FPUR foam since the foam did not burn at this temperature range. The NCO conversion was approximately more than 99% at the NCO index of 100.

Morphology of RPUR foams indicated that all RPUR foams had closed cell. The shape of foam cells in the top view (perpendicular to the foam rising direction) was spherical. The shape of foam cells in the side view (parallel to the foam rising direction) was ellipsoidal.

RPUR foams catalyzed by all copper-amine complexes have less compressive strength than RPUR foam catalyzed by DMCHA. Because the large cell size of RPUR foam gave less compressive strength.

In summary, the best catalysts that could be used instead of commercial catalyst (DMCHA) are $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ aqueous solutions.

5.2 Suggestion for future work

The suggestion for future work is to use $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ aqueous solutions as catalysts for preparation of the other types of foams such as flexible and semi-rigid polyurethane foams.

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APPENDIX

APPENDIX A

NCO index and NCO conversion calculations

NCO index calculation

For example Calculate the parts by weight (pbw) of PMDI (Suprasec®5005), molar mass = 365.8, functionality = 2.7 at an isocyanate index of 100 and 130 required to react with the following formulation:

Formulation	Weight (pbw)	
	NCO index 100	NCO index 130
Polyol (Daltolac® R180, OHV=440 mgKOH/g, functionality = 4.3)	100.0	100.0
Surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (water, H_2O, Mw = 18 g/mole, functionality = 2)	3.0	3.0
Catalyst (DMCHA or aqueous solutions of copper-amine complexes)	1.0	1.0
PMDI (Suprasec®5005)	?	?

$$\text{Equivalent weight of polyol} = \frac{56.1}{440} \times 1000 = 127.5$$

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

$$\text{Equivalent weight in formation} = \frac{\text{parts by weight (pbw)}}{\text{equivalent weight}}$$

Equivalent weight in the above formulation:

$$\text{polyol} = \frac{100}{127.5} = 0.784$$

$$\text{water} = \frac{3.0}{9.0} = 0.333$$

$$\text{Total equivalent weight} = 1.117$$

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

$$\text{PMDI (pbw)} = 1.117 \times \frac{\text{PMDI molarmass}}{\text{functionality}} = 1.117 \times \frac{365.8}{2.7} = 151.3$$

where;

$$\text{Isocyanate index} = \frac{\text{actualamount of isocyanate}}{\text{theoreticalamount of isocyanate}} \times 100$$

Therefore:

at isocyanate index = 100

$$\text{Isocyanate actual} = \frac{151.3}{100} \times 100 = 151.3 \text{ pbw}$$

at isocyanate index = 130

$$\text{Isocyanate actual} = \frac{151.3}{100} \times 130 = 196.7 \text{ pbw}$$

Table A1 Isocyanate quantity at different NCO indexes

Formulation	Weight (pbw)	
	NCO index 100	NCO index 130
Polyol (Daltolac® R180, OHV=440 mgKOH/g, functionality = 4.3)	100.0	100.0
Surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (water, H_2O, Mw = 18 g/mole, functionality = 2)	3.0	3.0
Catalyst (DMCHA or aqueous solutions of copper-amine complexes)	1.0	1.0
PMDI (Suprasec® 5005)	151.3	196.7

NCO conversion calculation

NCO conversion defining as the ratio between isocyanate peak area at time 0 and isocyanate peak area at time t as shown in following equation :

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

where;

NCO^f = the peak area of isocyanate at time t

NCO^i = the peak area of isocyanate at time 0

The peak area of free NCO in RPUR foams were normalized by aromatic ring (Ar-H) absorption band at 1595 cm^{-1}.

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

PMDI (Suprasec®5005) spectra	**NCO absorbance peak area normalized @ 1.0 Ar-H peak area**
1	98.02
2	97.95
3	98.11
Average (NCO^i)	98.0

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

The example calculate the conversion of isocyanate (α) of RPUR foams catalyzed by DMCHA at NCO index 100

NCO^i = 98.0

NCO^f = 0.1067

$\alpha = [1 - (0.1067/98.0)] \times 100 = 99.9$

APPENDIX B

external appearance of RPUR foams

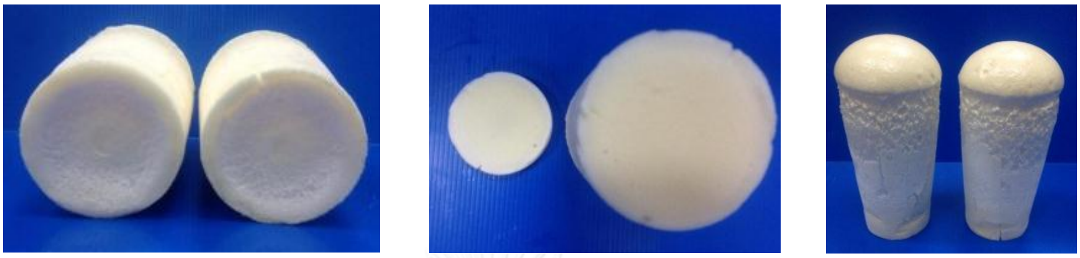

Figure B1 External appearance of RPUR foams catalyzed by DMCHA

Figure B2 External appearance of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$

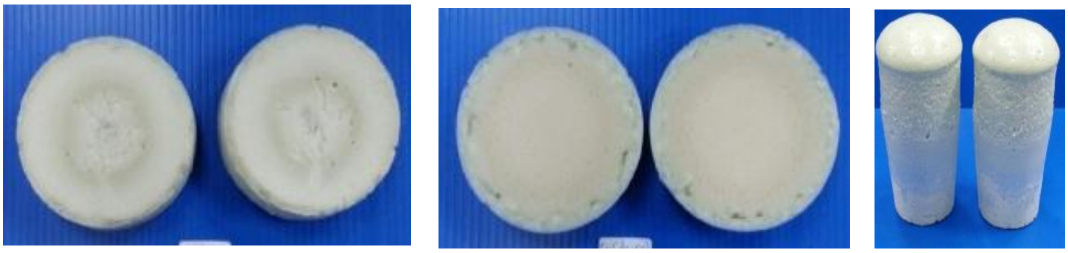

Figure B3 External appearance of RPUR foams catalyzed by $Cu(OAc)_2$(trien)

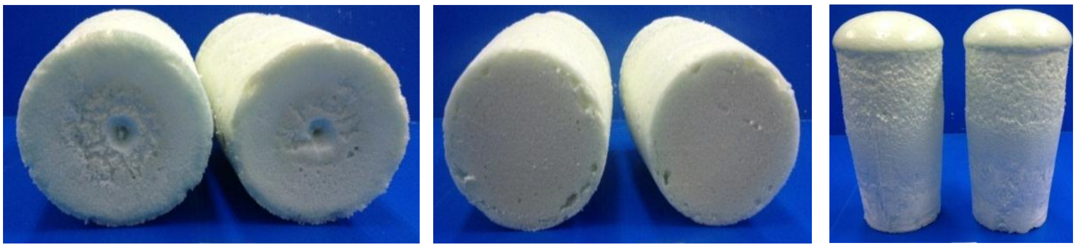

Figure B4 External appearance of RPUR foams catalyzed by $Cu(OAc)_2$(tetraen)

Figure B5 External appearance of RPUR foams catalyzed by $Cu(OAc)_2$(pentaen)

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