การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยตัวเร่งปฏิกิริยาแบบหน่วงที่เตรียมจากสารประกอบเชิงซ้อนคอปเปอร์-แอมีนและกรดคาร์บอกซิลิก

นางสาวกชพรรณ นิมะบุตร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2558

PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY DELAYED ACTION CATALYST DERIVED FROM COPPER-AMINE COMPLEXES AND CARBOXYLIC ACID

Miss Koatchapan Nimaboot

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2015

Thesis Title	PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY DELAYED ACTION CATALYST DERIVED FROM COPPER-AMINE COMPLEXES AND CARBOXYLIC ACID
By	Miss Koatchapan Nimaboot
Field of Study	Petrochemistry and Polymer Science
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กชพรรณ นิมะบุตร : การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยตัวเร่งปฏิกิริยาแบบหน่วงที่เตรียมจากสารประกอบเชิงซ้อนคอปเปอร์-แอมีนและกรดคาร์บอกซิลิก (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY DELAYED ACTION CATALYST DERIVED FROM COPPER-AMINE COMPLEXES AND CARBOXYLIC ACID) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.นวลพรรณ จันทรศิริ, 103 หน้า.

งานวิจัยนี้เป็นการเตรียมโฟมพอลิยูรีเทนแบบแข็งโดยใช้ระบบตัวเร่งปฏิกิริยาแบบหน่วงที่สังเคราะห์จากปฏิกิริยาระหว่างสารประกอบเชิงซ้อนคอปเปอร์-แอมีนและกรดคาร์บอกซิลิกโดยใช้เอทิลีนไกลคอลเป็นตัวทำละลาย เกิดเป็นเกลือของสารประกอบเชิงซ้อนคอปเปอร์-แอมีนและกรดคาร์บอกซิลิก สารประกอบเชิงซ้อนคอปเปอร์-แอมีนที่ใช้ คือ $Cu(OAc)_2(en)_2$ และ $Cu(OAc)_2(trien)$ เมื่อ en = เอทิลีนไดเอมีน และ trien =ไตรเอทิลีนเตตระมีน กรดคาร์บอกซิลิกที่ใช้มี 2 ชนิด คือ กรดซาลิไซลิก (Sal) และกรดแอซิติก (Ac) เกลือของสารประกอบเชิงซ้อนคอปเปอร์-แอมีนและกรดคาร์บอกซิลิกที่ศึกษา คือ $Cu(OAc)_2(en)_2$/Sal, $Cu(OAc)_2(trien)$/Sal และ $Cu(OAc)_2(en)_2$/Ac การพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาใช้เทคนิคยูวี-วิสสิเบิลสเปกโทรสโกปี และอินฟราเรดสเปกโตรสโคปี ศึกษาประสิทธิภาพในการเร่งปฏิกิริยาจากเวลาในการเกิดพอลิเมอไรเซชัน ศึกษาสมบัติทางกายภาพและสมบัติเชิงกลของโฟมพอลิยูรีเทน จากผลการทดลองพบว่า การใช้ตัวเร่งปฏิกิริยาเป็นสารประกอบเชิงซ้อนคอปเปอร์-แอมีนอย่างเดียวทำให้เวลาที่ผิวหน้าของโฟมไม่เกาะติดวัสดุสัมผัสเร็ว แต่เกิดปัญหา คือ เวลาที่ของผสมเกิดการแข็งตัวเร็วเกินไป ส่งผลให้การขึ้นรูปชิ้นงานทำได้ยาก การแก้ไขปัญหาดังกล่าวทำได้โดยใช้เกลือของสารประกอบเชิงซ้อนคอปเปอร์-แอมีนและกรดคาร์บอกซิลิกเป็นตัวเร่งปฏิกิริยา ทำให้เวลาที่ของผสมเป็นเจลช้าลง แต่เวลาที่ผิวหน้าของโฟมไม่เกาะติดวัสดุสัมผัสไม่ช้าเกินไป ตัวเร่งปฏิกิริยา $Cu(OAc)_2(en)_2$/Sal และ $Cu(OAc)_2(trien)$/Sal ที่อัตราส่วนโมลระหว่างสารประกอบเชิงซ้อนคอปเปอร์แอมีน:กรดซาลิไซลิก เท่ากับ 1:1 และ 1:0.5 ตามลำดับ สามารถทำให้ปฏิกิริยาในช่วงเริ่มต้นช้าลงคือ เวลาที่สารผสมเป็นเจลช้าลงอยู่ที่ประมาณ 60 วินาทีซึ่งเป็นเวลาที่เหมาะสมและทำให้มีระยะเวลาเพียงพอในการเทสารผสมลงในแม่พิมพ์ ทำให้การขึ้นรูปโฟมมีความสะดวกมากขึ้น แต่ไม่ทำให้เวลาในการเกิดปฏิกิริยาเป็นพอลิยูรีเทนอย่างสมบูรณ์ช้าลงไปมากเมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาทางการค้า (DMCHA)

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
ปีการศึกษา 2558 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5671902723 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: DELAYED ACTION CATALYST / COPPER-AMINE COMPLEX / CARBOXYLIC ACID

KOATCHAPAN NIMABOOT: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY DELAYED ACTION CATALYST DERIVED FROM COPPER-AMINE COMPLEXES AND CARBOXYLIC ACID. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 103 pp.

In this research, a delayed action catalyst system is used in the preparation of rigid polyurethane foams. The delayed action catalysts were synthesized from reaction between copper-amine complexes and carboxylic acids in ethylene glycol as a solvent to give the salts of copper-amine complex and carboxylic acid. Copper-amine complexes used in this study were $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ (where en = ethylenediamine and trien = triethylenetetramine). Carboxylic acids used were salicylic acid (Sal) and acetic acid (Ac). Copper-amine complex/carboxylic acid salts, namely $Cu(OAc)_2(en)_2$/Sal, $Cu(OAc)_2(en)_2$/Ac and $Cu(OAc)_2(trien)$/Sal were studied. UV-Visible spectroscopy and IR spectroscopy were used to characterize the structure of copper-amine complex/salicylic acid salts. The reaction times in the foam formation, physical and mechanical properties of foams are studied. When only copper-amine complex was used as a catalyst, the foam formation was fast. However, there was a problem with the fast gel time which resulted in difficulty in the foam processing. This problem could be solved by using copper-amine complexes/carboxylic acid salts as catalysts, which gave longer gel time while the tack free time was not too long. $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(trien)$/Sal at the mole ratios of 1:1 and 1:0.5, respectively were suitable catalysts, which had gel time about 60 seconds while tack free time was not too slow when compared with commercial catalyst (DMCHA). The gel time of 60 sec was long enough for pouring the mixture of foam formulation into a mold.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature	....
		Advisor's Signature	....
Academic Year:	2015		

ACKNOWLEDGEMENTS

I would like to express my deep gratitude to my advisor, Associate Professor Dr. Nuanphun Chantarasiri for guidance, supervision and helpful suggestion throughout the course of this research. In addition I would like to thank my committee members, Assistant Professor Dr. Warinthorn Chavasiri, Assistant Professor Dr. Anawat Ajavakom and Dr. Duangruthai Sridaeng, whose comments have been especially valuable.

Definitely, this research cannot be completed without kindness and helpful of many organizations. Firstly, I would like to thank Huntsman (Thailand) Co., Ltd. for supplying the chemical used in this research. Special thanks are due to Program of Petrochemistry and Polymer Science, Chulalongkorn University; Department of chemistry, Faculty of Science, Chulalongkorn University and Scientific and Technological Research Equipment Center, Chulalongkorn University.

I sincerely thank my friends and all members of Supramolecular Chemistry Research Unit for their encouragement, suggestion and generous helps. Finally, I own deep gratitude to my family, especially my father and mother for their love and encouragement.

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%	percentage
ε	molar absorptivity
α	isocyanate conversion
λ_{max}	maximum absorption peak
Ac	acetic acid
ATR-IR	attenuated total reflectance-infrared
ASTM	American Society for Testing and Material
BDMAEE	bis (2-dimethylaminoethyl) ether
cm	centimeter
cm^{-1}	unit of wavenumber
^{o}C	degree Celsius (centrigrade)
CO_2	carbondioxide gas
CFCs	chlorofluorocarbons
$Cu(OAc)_2$	copper acetate
DBU	1,8-diazabicyclo [5.4.0] undec-7-ene
DBTDL	dibutyltin dilaurate
DMCHA	N,N-dimethylcyclohexylamine
EG	ethylene glycol
en	ethylenediamine
FTIR	fourier transform infrared spectrophotometer
FPUR	flexible polyurethane
g	gram
h	hour
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
KAc	potassium acetate
kg	kilogram
kV	kilovolt
KOct	potassium octoate

KOH	potassium hydroxide
lb/in^2	pound per square inch
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
OHV	hydroxyl value
pbw	part by weight
PFCs	perfluorinated hydrocarbons
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PMDETA	pentamethyldiethylene triamine
PUR	polyurethane
ref	reference
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
s	second
Sn	tin
Sal	salicylic acid
SEM	scanning electron microscope
SnOct	stannous octate
t	time
T_{max}	maximum core temperature
TEDA	triethylenediamine
TDI	toluene diisocyanate

TMP	Trimetylol propane
TMR-2	2-hydroxypropyl trimethyl ammonium salt
TMNAEP	l-methyl-4-(2-dimethylaminoethyl) piperazine
trien	triethylenetetramine
UV	ultraviolet

CHAPTER I
INTRODUCTION

Polyurethanes (PUR) are organic polymers that contain the urethane group in the structure. They are typically made by the addition polymerization between isocyanate (–NCO) and hydroxyl (–OH) groups. PUR can be classified into three major classes: flexible foams, semi-rigid foams and rigid foams [1]. All kinds of PUR foam are prepared by the proper choice of polyol and polyisocyanate in respect to chemical structure, equivalent weight, and functionality.

Rigid polyurethane foams (RPUR foams) are used as thermal insulation materials such as refrigerators, refrigerated containers, building, and construction. RPUR foams can be used as thermal insulation materials because of their high compressive-strength properties, light weight and low thermal conductivity [2].

The essential starting materials used for preparation of RPUR foams are polyisocyanate, polyol, blowing agent, catalyst, and surfactant [3, 4]. RPUR foams can be prepared by two steps of mixing. In the first mixing step, raw materials, namely polyol, catalyst, surfactant and blowing agent are mixed until homogeneous liquid is obtained. In the second mixing step, isocyanate is added to the mixture of polyol, catalyst, surfactant and blowing agent. There are two main reactions that lead to the formation of RPUR foam, namely gelling and blowing reactions. Gelling reaction is the reaction between isocyanate (–NCO) and hydroxyl (–OH) groups in polyol, which results in urethane formation. Blowing reaction is the reaction between isocyanate groups and hydroxyl groups in blowing agent (distilled water) which releases carbon dioxide gas. Minor reactions also occur, for example, the reaction of three isocyanate groups to produce isocyanurate group.

However, the gelling and blowing reactions cannot be completed without catalysts because the reaction between isocyanate with hydroxyl group is slow [5, 6]. Examples of commercial catalysts are dibutyltin dilaurate (DBTDL) and *N,N*-dimethylcyclohexylamine (DMCHA). These commercial catalysts have excellent catalytic activity. However, tin compound is highly toxic and amine has strong smell [7]. In some applications, polyurethanes are produced as large objects. Our research group reported the synthesis of copper-amine complexes that can be used as catalysts in the preparation of RPUR foams. These copper-amine complexes have very weak odor as compared to DMCHA. However, these copper-amine complexes have high catalytic activity, the polymerization reaction occurs very fast and the viscosity of the liquid starting materials in RPUR foam formulation increases rapidly [8]. Thus, the liquid starting materials cannot flow and reach each corner of large mold very well. If a lower activity catalyst is used, the reaction proceeds slowly and this problem can be solved. Therefore, the objective of this research was to develop new catalysts synthesized from reaction between copper-amine complexes and carboxylic acids to form copper-amine complex/carboxylic acid salts. The synthesis of copper-amine complex/carboxylic acid salts was done in ethylene glycol to obtain solutions of copper-amine complex/carboxylic acid salts in ethylene glycol, which could be used as catalysts without purification. It was expected that copper-amine complex/carboxylic acid salts would perform as delayed action catalyst, which had slow gel time but tack free time is not too slow. In comparison to copper-amine complexes and DMCHA, copper-amine complex/carboxylic acid salts should have longer gel time, while tack free time was not too slow.

Objectives of the research

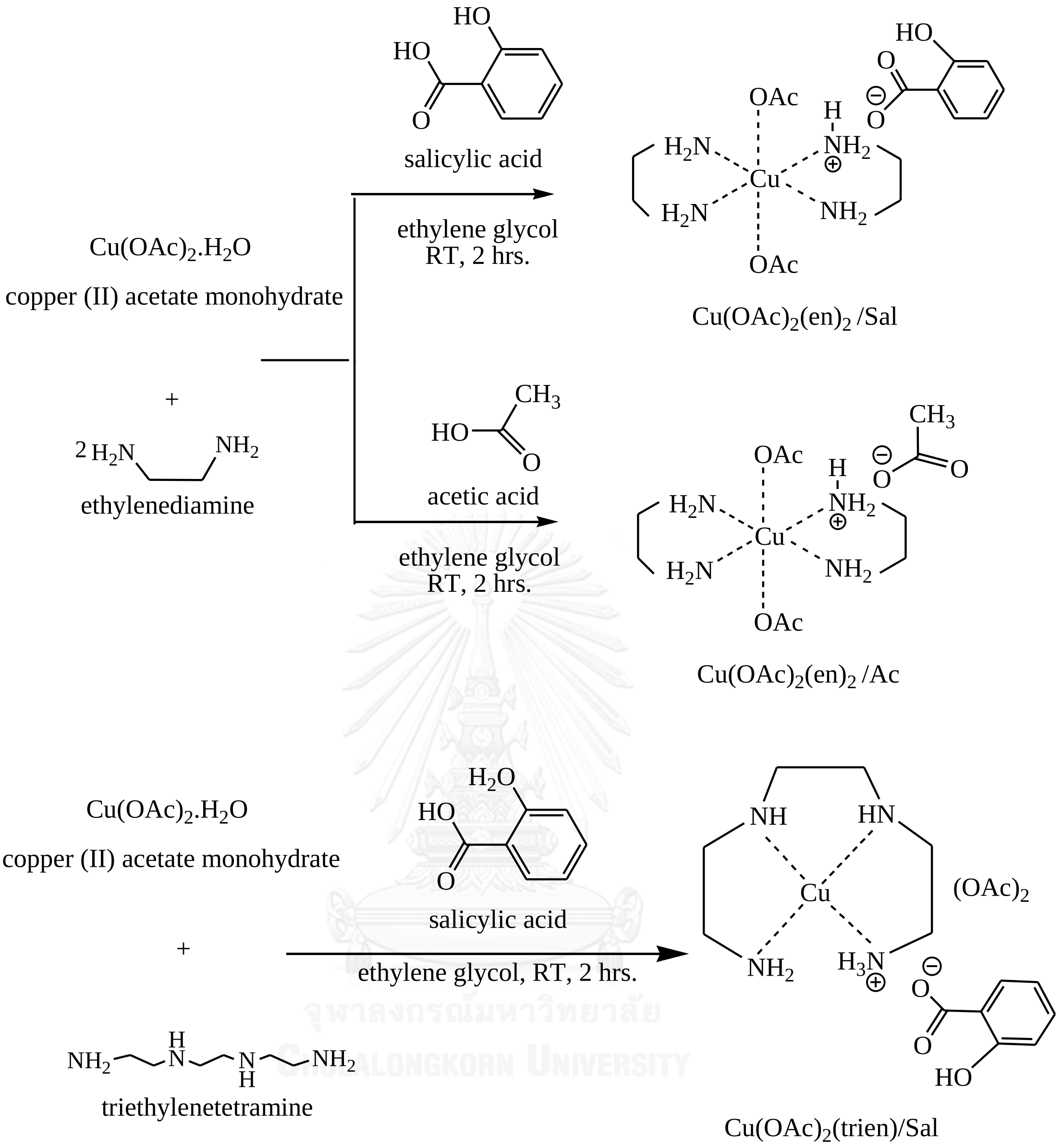
The target of this research was to prepare rigid polyurethane foams catalyzed by copper-amine complex/carboxylic acid salts, namely $Cu(OAc)_2(en)_2$/Sal, $Cu(OAc)_2(en)_2$/Ac and $Cu(OAc)_2$(trien)/Sal (where OAc = acetate, en = ethylenediamine, trien = triethylenetetramine, Sal = salicylic acid, Ac = acetic acid). These salts were prepared from the reaction between copper-amine complexes and carboxylic acids by using ethylene glycol as a solvent. Copper complexes used were $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien). Carboxylic acids used were salicylic acid and acetic acid. It was expected that the synthesized copper-amine complex/carboxylic acid salts showed effective delay in the gel time, while tack free time was not too slow as compared with copper complexes and DMCHA. The expected gel time of 60 sec was long enough for pouring the mixture of foam formulation into a mold.

Scope of the research

The scopes of this research were to prepare RPUR foams using copper-amine complex/carboxylic acid salts as catalysts. Copper-amine complex/carboxylic acid salts were prepared in the form of solutions in ethylene glycol (Scheme 1.1). The experiment was divided into 2 parts. In the first part, copper-amine complex/carboxylic acid salts were synthesized by reaction between copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$], aliphatic amines [ethylenediamine (en) and triethylenetetramine (trien)] and carboxylic acids [salicylic acid (Sal) and acetic acid (Ac)]. The mole ratios between copper-amine complex and carboxylic acid were varied. UV-visible spectroscopy and FTIR spectroscopy were used to characterize copper-amine complex/carboxylic acid salts.

In the second part, RPUR foams were prepared using the solution of copper-amine complex/carboxylic acid salts in ethylene glycol as catalysts. The foams were prepared in cup test method and plastic mold. RPUR foams prepared by the cup test method were used for the investigation of reaction times, foaming temperature, free rise density, height of foams and NCO conversion. The molded foams were used for the investigation of mechanical properties and morphology.

Catalytic efficiency of the copper-amine complex/carboxylic acid salts was compared with that of *N*,*N*-dimethylcyclohexylamine (DMCHA), which is a commercial catalyst.



Scheme 1.1 Synthesis of copper-amine complex/carboxylic acid salts

CHAPTER II

THEORY AND LITERATURE REVIEWS

Polyurethane foam (PUR foam) is a polymer made by addition polymerization between two or more isocyanate (-NCO) groups and polyol molecules containing two or more hydroxyl (-OH) groups. In addition, blowing agents, surfactants and catalysts are used. Polyurethane formation is an exothermic reaction. Polyurethane foams can be manufactured in an extremely wide range of grades, which depends on the structure of starting materials in foam formulation. PUR foams can be classified into three types, namely flexible, semi-rigid and rigid foams.

Rigid polyurethane (RPUR) foams have high compressive-strength properties, light weight and low thermal conductivity. They are used in many constructions for insulation, such as boards for walls and roofs, commercial refrigeration and building engineering applications [4, 9].

Table 2.1 Classification of polyurethane foams based on polyol starting materials [1]

Polyol	**Rigid Foams**	**Semi-rigid Foams**	**Flexible Foams**
OH No.	350–560	100–200	5.6–70
OH Equivalent No.	160–100	560-280	10,000–800
Functionality	3.0–8.0	3.0–3.5	2.0–3.1
Elastic Modulus at 23˚C			
MPa	> 700	700–70	< 70
lb/in^2	> 100,000	100,000–10,000	< 10,000

2.1 Raw materials

Rigid polyurethane (RPUR) foams are formed by reacting di- or polyisocyanates with polyols to give urethane linkages. The physical and chemical character, structure and molecular size of these compounds influence the polymerization reaction, as well as final physical properties of rigid polyurethane foams [10]. In addition, catalysts, surfactants, blowing agents and fillers are used to control and modify the reaction process and performance characteristics of RPUR foam.

2.1.1 Methylene diphenyl diisocyanate (MDI)

Several aromatic and aliphatic isocyanates are available. Diphenylmethane diisocyanate (MDI) and their derivatives is one of the mostly used isocyanate for RPUR foam preparation because of its high reactivity in foaming reaction. MDI is available in two forms, purified monomeric MDI and polymeric MDI (PMDI). Pure MDI consists substantially 4,4′-diphenylmethanediisocyanate or 4,4′-MDI and small amount of 2,4′-MDI. Pure MDI is a white to pale yellow solid of melting point about 38 ˚C and mainly used for elastomers and coatings [1]. Polymeric MDI contains both 4,4′-MDI and 2,4′-MDI. Grade of polymeric MDI depends on ratios of two isomers. Polymeric MDI is a liquid form having dark brown color and has low vapor pressure. The chemical structures of MDI isomer and polymeric MDI are demonstrated in Figures 2.1-2.2.

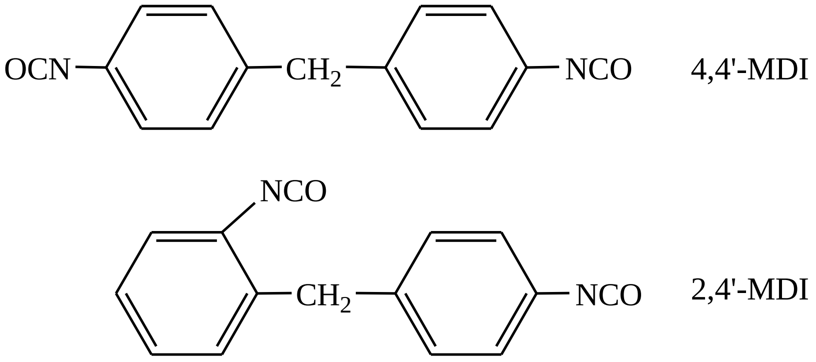
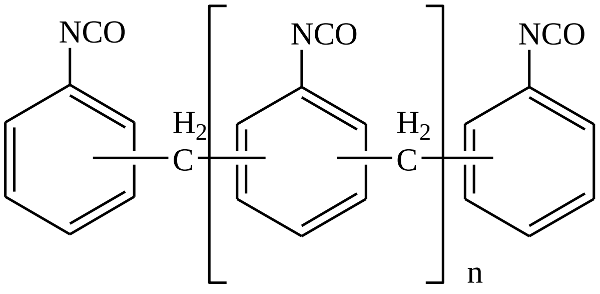


Figure 2.1 Isomeric structures of monomeric MDI



n :0-3

Polymeric MDI

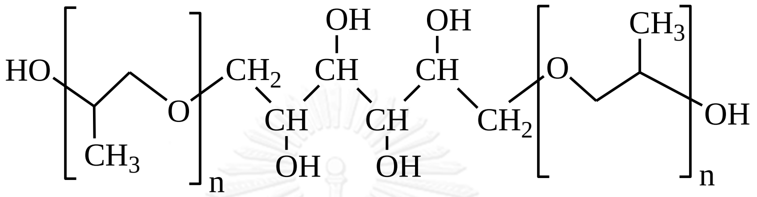
Figure 2.2 Structure of polymeric MDI (PMDI)

2.1.2 Polyols

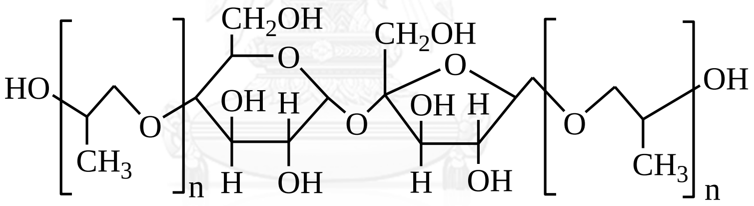
Polyol compounds have hydroxyl groups that react with isocyanates to give polyurethane groups. The polyols used in producing PUR foams are classified in two types, namely polyether polyols and polyester polyols. The structures of polyol play a large part in determining the properties of final PUR foams. The molecular weight and functionality of the polyol are the main factor. The structure of the polyol chains is important. Generally, polyols used for RPUR foam preparation have molecular weight in the range of 150 to 1600, functionality of 3 to 8 and hydroxyl value of 250 to 1000 mgKOH/g [11]. RPUR foams need the higher functionality and lower molecular weight polyols, in order to get the higher degree of crosslinking, which contributes to the stiffness of polymer.

About 90% of polyols used in PUR foam manufacture are polyether polyols due to their low cost and ease of handling (low viscosity). Examples polyether polyols are shown in Figure 2.3. These are produced by the ring opening of alkylene oxides using a polyfuctional as initiator. The polyfunctional initiator compounds are ethylene glycol, glycerol, pentaerythritol, trimethylolpropane, sorbitol and sucrose (Table 2.2). Polyether polyol for producing rigid polyurethane foams has a lower equivalent weight than those used to make flexible foams. The properties of polyether polyols vary with the choice of functionality and equivalent weight. The molecular weight of polyether polyols used for making rigid polyurethane foams is approximately 500 g/mol in order to reduce the distance between crosslinks.

Polyester polyols are made by condensation reactions between diols (and triol) and dicarboxylic acid such as adipic acid, sebacic acid and phthalic acids. Polyester polyols are used to produce both flexible and rigid PUR foams. Polyester polyols are more expensive, more viscous and therefore not easy to handle as compared with polyether polyol [6]. However, these polyester polyols give polyurethane foams with good mechanical properties and tolerance for organic solvents. Therefore, they are only used in applications that need their superior properties.



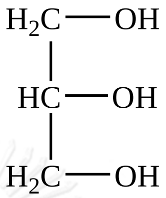
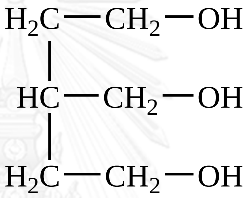
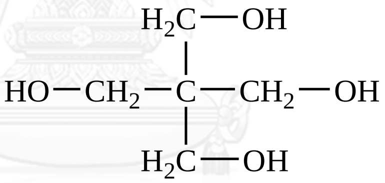
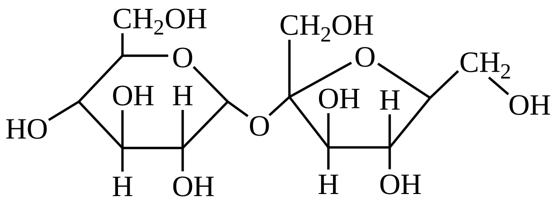
Poly (propyleneoxy) sorbitol



Poly (propyleneoxy) sucrose

Figure 2.3 Structures of polyether polyol based on sorbitol and sucrose

Table 2.2 Polyfunctional initiator compounds used for preparing commercial polyols

Hydroxylated Compound	Chemical Structure	Functionality
Ethylene glycol (EG)	$HO-CH_2-CH_2-OH$	2
Glycerol	 $\begin{array}{l} H_2C-OH \\ \quad \vert \\ HC-OH \\ \quad \vert \\ H_2C-OH \end{array}$	3
Trimetylol propane (TMP)	 $\begin{array}{l} H_2C-CH_2-OH \\ \quad \vert \\ HC-CH_2-OH \\ \quad \vert \\ H_2C-CH_2-OH \end{array}$	3
Pentaerythritol	 $\begin{array}{c} H_2C-OH \\ \vert \\ HO-CH_2-C-CH_2-OH \\ \vert \\ H_2C-OH \end{array}$	4
Sorbitol	$HO-CH_2-(CHOH)_4-CH_2-OH$	6
Sucrose		8

2.1.3 Surfactants

Surface-active materials are essential ingredients for the preparation of PUR foams. The surfactants most widely used in the PUR foam manufacturing are polydimethylsiloxane-polyether copolymers or silicone surfactants [12]. They help in mixing incompatible components in the foam formulation and control the size of the foam cells by stabilizing the gas bubbles formed during nucleation and stabilize the rising foam by reducing stress-concentrations in the thinning cell-walls [13]. An example of silicone surfactant is shown in Figure 2.4.

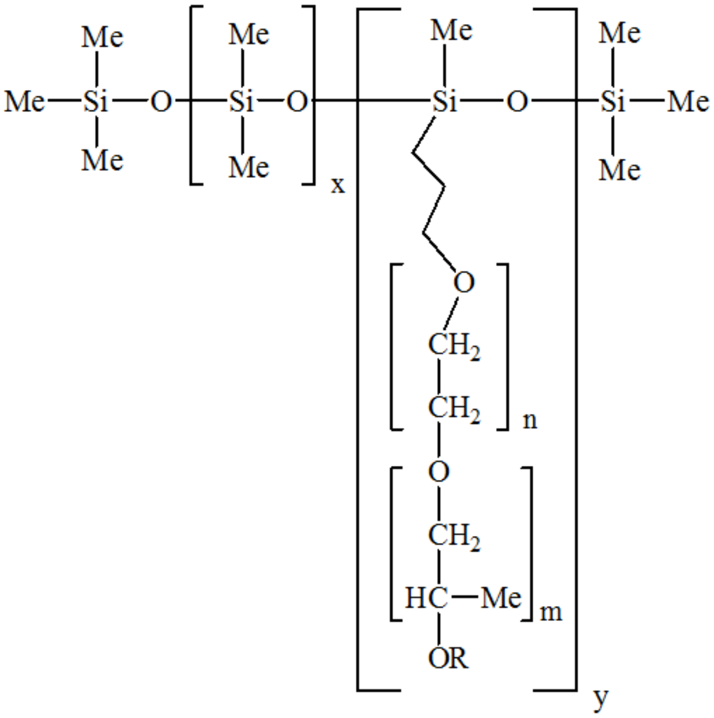


Figure 2.4 An example of silicone surfactant used in the preparation of PUR foams [12]

2.1.4 Blowing agents

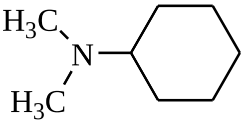
A blowing agent is a substance which creates gas bubbles in the polymerizing reaction mixture to create foam. Blowing agents may be considered in two types, namely physical and chemical blowing agents. Chemical blowing agents are chemical compounds that react with isocyanate groups to generate gas. Water is one of the most widely used the chemical blowing agent, which can react with isocyanate to generate CO_2 gas bubbles and give cellular structure of foams. The amount of water normally used is 3-5 parts of water per 100 parts of polyol. Physical blowing agents are gases that do not react chemically in the foaming process. They are inert liquids that have low boiling points and can be evaporated by the heat from exothermic foamimg reaction. Examples of physical blowing agents are chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and perfluorinated hydrocarbons (PFCs) [1, 12].

2.1.5 Catalysts

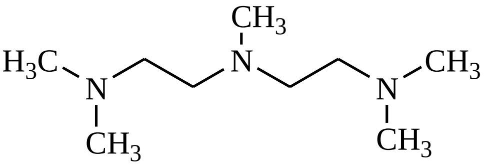
A number of catalysts used for the reaction of isocyanates with water and with polyols include a range of chemical structures, namely aliphatic and aromatic tertiary amines, quaternary ammonium salts, alkali metal carboxylates and organotin compounds (Table 2.3 and Figure 2.5). Their catalytic activity is dependent on their basicity, with steric hindrance on the active site playing a secondary role [14]. In polyurethane foam preparation, catalyst is an important component for controlling the reaction kinetics of three kinds of reaction, which are (a) the blowing reaction of isocyanate with water (H_2O) to form carbondioxide gas (CO_2) and polyurea, (b) the gelling reaction of isocyanate with polyol to form polyurethane and (c) trimerization of isocyanate. Normally, the amount of catalyst is used about 1-4 parts by weight per 100 parts of polyol [2].

Table 2.3 Commercial catalysts used for preparing RPUR foams [15]

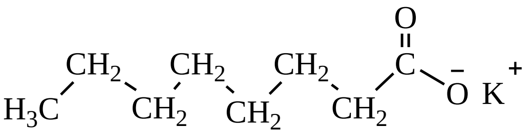
Catalyst Type	Abbreviation	Reaction Catalyzed
Tertiary amines		
Pentamethyldiethylene triamine	PMDETA	Blowing
Triethylenediamine	TEDA	Gelling
Dimethylcyclohexylamine	DMCHA	Blowing/gelling
Quaternary ammonium salts		
2-hydroxypropyl trimethyl ammonium salt	TMR-2	Delayed action/trimer formation
Alkali metal carboxilates		
Potassium acetate	KAc	Gelling/Trimer formation
Potassium octoate	KOct	Gelling/Trimer formation
Tin complexes		
Stannous octate	SnOct	Gelling
Dibutyltin dilaurate	DBTCL	Gelling



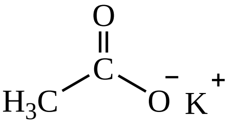
N,N-dimethylcyclohexylamine
(DMCHA)



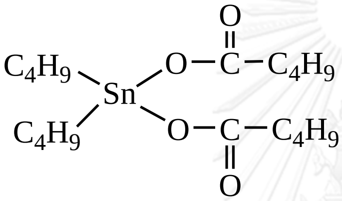
Pentamethyldiethylene triamine
(PMDETA)



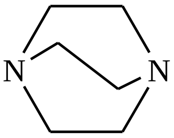
Potassium octoate



Potassiumacetate



Dibutyltin dilaurate (DBTDL)



Triethylenediamine (TEDA)

Figure 2.5 Structures of commercial catalysts used for preparing RPUR foams

In the fact that when the catalyst too strongly promotes the blowing reaction; much of the CO_2 gas will be evolved before sufficient reaction of isocyanate with polyol has occurred. Then, the CO_2 gas will bubble out of the formulation, resulting in collapse of the foam. If a catalyst too strongly promotes the gelling reaction, most CO_2 gas will be generated after a significant degree of polymerization has occurred. This result shows the characteristic of poor quality foam are high density, broken or poorly defined cells or other undesirable features.

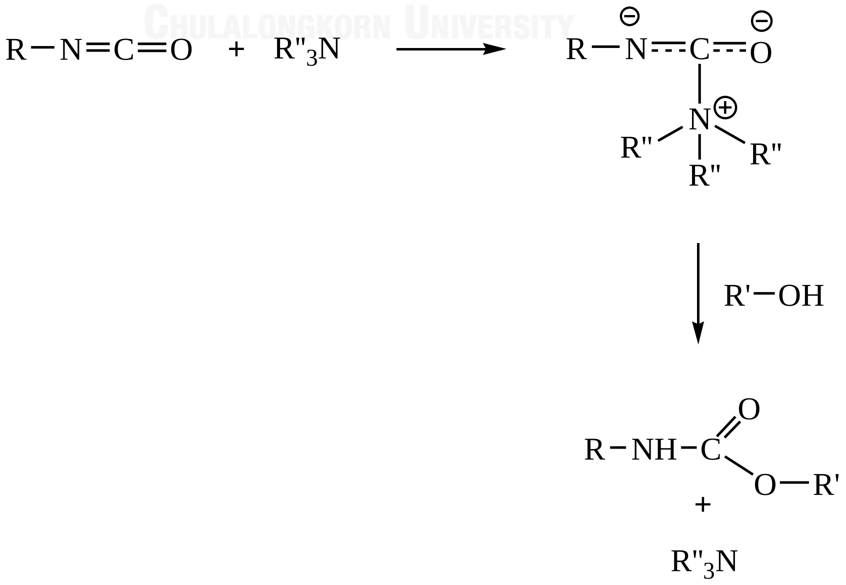
Generally, tin catalysts accelerate mainly isocyanate-polyol reaction and they are considered as “gelling catalysts”. On the other hand, tertiary amine catalysts accelerate mainly the isocyanate-water reaction, which generates CO_2 and they are considered as “blowing catalysts”. Some tertiary amine can catalyze both the blowing and gelling reactions.

Delayed action catalyst is required for the complexity and large molds. Typical delayed action catalysts are tertiary amines blocked with an organic acid, and can be thermally activated. Reaction between organic acids and tertiary amines as a reversible reaction to generate ammonium salts, which exhibit little or no catalytic activity when compared to the initial amine. During the exothermic urethane formation, the amine catalyst is decomposed gradually and foaming to give active amine. For examples, systems with catalytic delayed action are tertiary amines such as triethylenediamine (TEDA) and bis (2-dimethylaminoethyl) ether (BDMAEE) that react with carboxylic acids such as formic or cyanoacetic acid.

2.2 Catalytic mechanisms

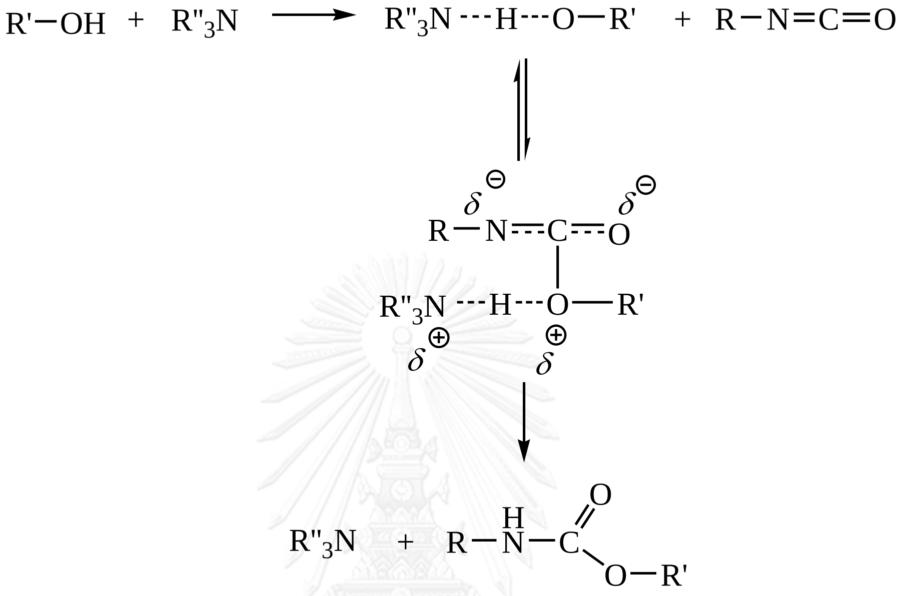
2.2.1 Amine catalysts

For tertiary amine catalyst, two mechanisms have been proposed [3]. The first mechanism is proposed by Baker (Scheme 2.1). The activation starts by the tertiary nitrogen of amine using its lone pair of electrons to coordinate with the positive electron charged carbon of the isocyanate group, and then complex intermediate is formed. This intermediate then reacts with active hydrogen from an alcohol to produce a urethane group.



Scheme 2.1 Baker mechanism of amine catalysts

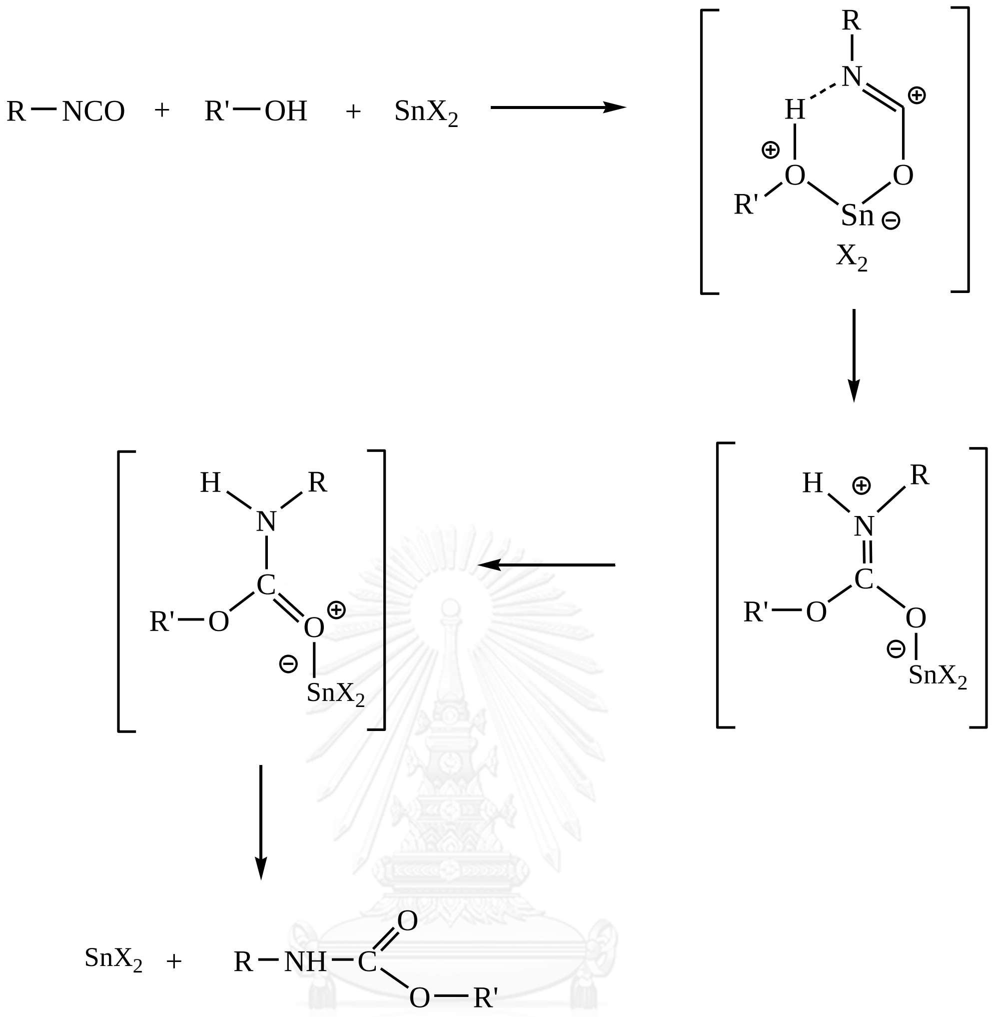
The second mechanism is proposed by Farka (Scheme 2.2). The activation starts by the tertiary nitrogen of amine coordinate to polyol, water or amine to form a complex intermediate. The intermediate then reacts with the isocyanate to produce a urethane group.



Scheme 2.2 Farka mechanism of amine catalysts

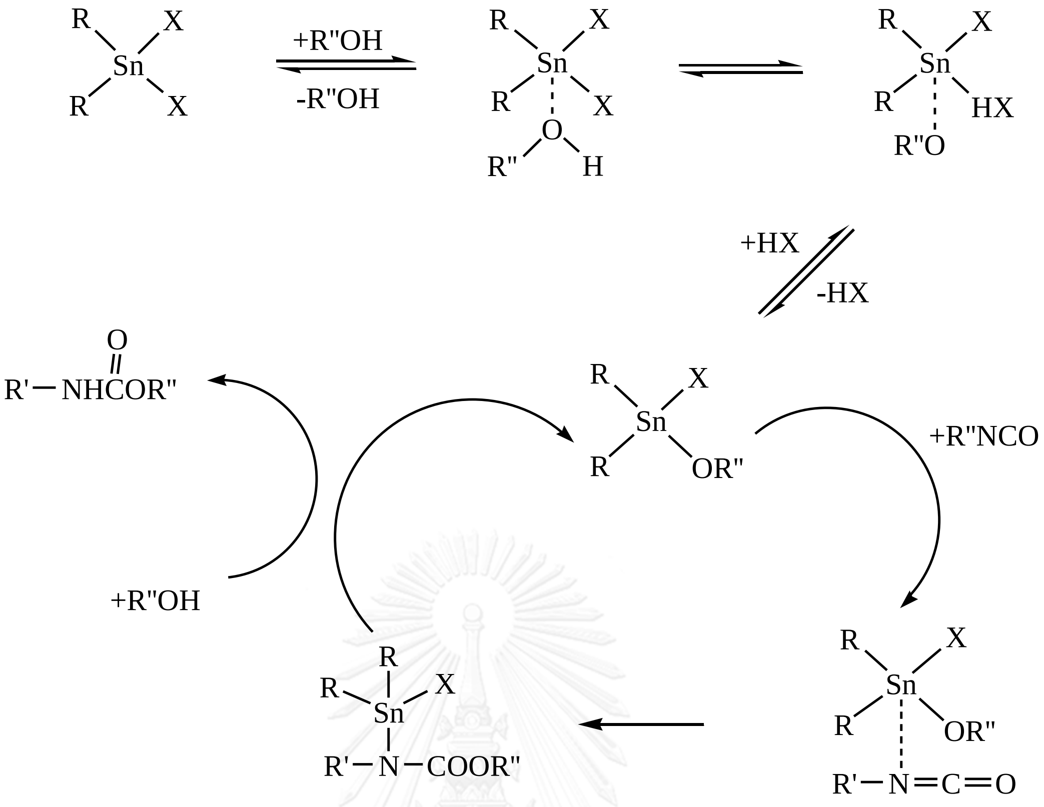
2.2.2 Organotin catalysts

Catalytic mechanism of tin II salt is shown Scheme 2.3. Isocyanate, polyol and tin catalyst form a ternary complex, which then gives the urethane product.



Scheme 2.3 Mechanism of tin (II) salt catalyst

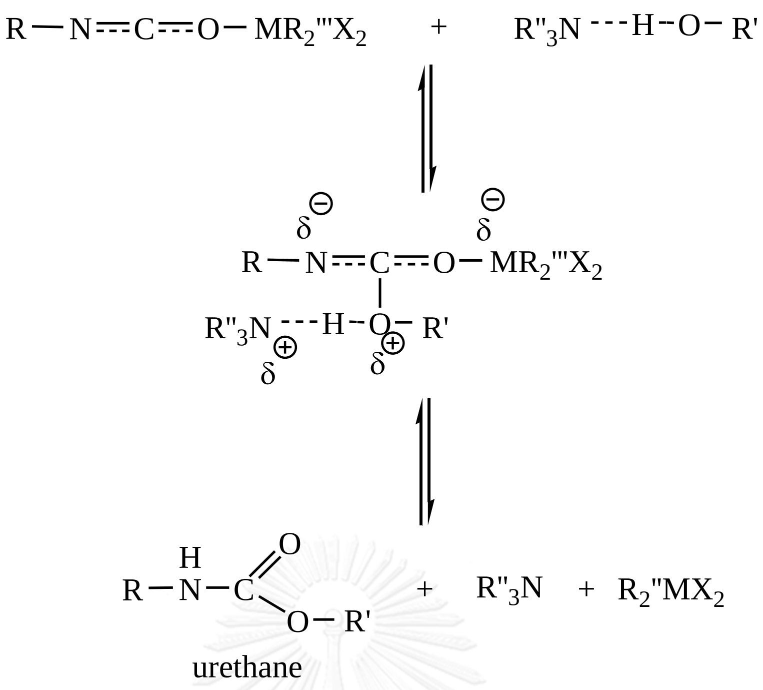
Catalytic mechanisms for tin IV catalysts, such as dialkyltin dicarbonates and dialkyltin dialkylthiolates, is the reaction of the tin with a polyol forming a tin alkoxide, which can then react with the isocyanate to form a complex (Scheme 2.4). Transfer of the alkoxide anion onto the coordinated isocyanate affords an *N*-stannylurethane, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide.



Scheme 2.4 Mechanism of tin (IV) salt catalyst

2.2.3 Synergism of metal-amine catalysts

When both tin compound and amines are used as catalysts, a synergy between metal and amine catalysts is also observed (Scheme 2.5). The metal coordinate to the oxygen of the isocyanate group to activate the electrophilic nature of carbon. While amine coordinate to the hydrogen of OH group and forms a transition state to activate urethane formation reaction.



Scheme 2.5 Mechanism of metal-amine synergism

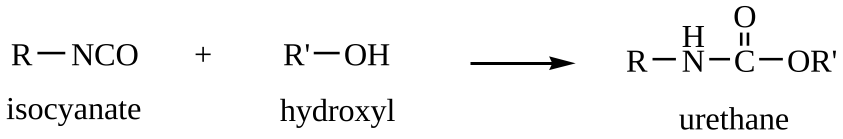
2.3 Basic chemistry

All polyurethanes are based on the exothermic reaction between di- or polyfunctional isocyanates and di- or polyfunctional hydroxyl species. For simplicity, the basic principle of urethane chemistry is described below using monofunctional reagents.

2.3.1 Primary reaction of isocyanates

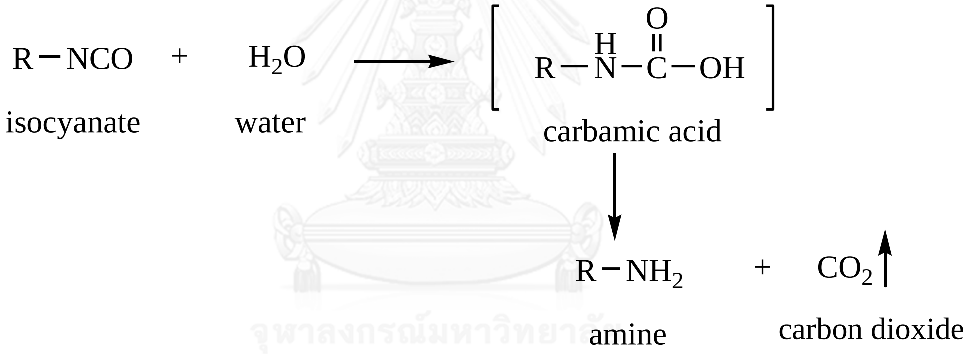
2.3.1.1 Reaction of isocyanate with polyol

The most important reaction in the produce of polyurethanes is the reaction between isocyanate and hydroxyl groups to give polyurethane. This reaction is known as the “gelling reaction” and the reaction is exothermic. The rate of polymerization is affected by chemical structure of the isocyanate and polyols and the catalyst is used to accelerate the reaction rate.



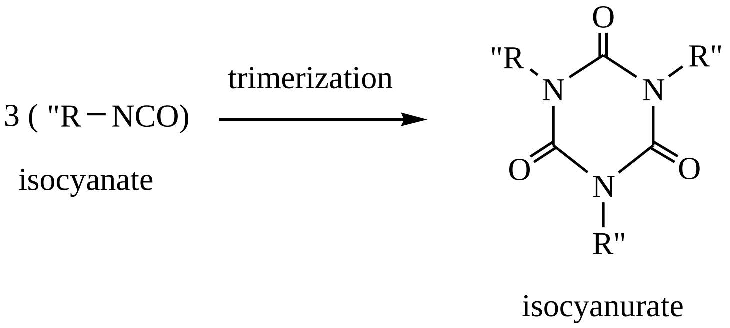
2.3.1.2 Reaction of isocyanate with water

The reaction of isocyanate with water produces an unstable carbamic acid, which immediately decomposes into an amine and carbon dioxide. This carbon dioxide gas diffuses into the already present air bubbles, and this result in a rise of foam due to the increase in the bubble size. This reaction is known as the “blowing reaction” because the CO_2 gas produced is used for blowing the foam and this reaction has an effect to foam density. The reaction rate is accelerating by suitable choice of catalyst system [3].



2.3.2 Secondary reactions of isocyanate

Isocyanate can undergo different secondary reactions. An example is the isocyanurate formation. Isocyanate trimer can be formed on heating either aliphatic or aromatic isocyanates. The reaction is accelerated by basic catalysts such as sodium and potassium salts of carboxylic acids [16].



2.4 Formulations

The amount of isocyanate needed to react with polyol and other reactive components can be calculated to obtain chemically stoichiometric equivalents. This theoretical amount may be adjusted up or down dependent on the PUR system, properties required, ambient conditions and scale of production. The adjusted amount of isocyanate used is referred to as the "isocyanate index".

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

The conventional way of calculating the ratio of the components required for PUR manufacture is to calculate the number of parts by weight (pbw) of the isocyanate needed to react with 100 parts by weight of polyol and use proportionate amount of additives. The analytical data require 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 [5, 16].

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 (hydroxyl number; OHV)

The hydroxyl value (OHV) sometime called 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. The hydroxyl value is also defined as the number of milligrams of potassium hydroxide equivalent 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 usage.

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

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

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

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

where;

NCO^{f} =the area of isocyanate absorbance peak area at time t
(final isocyanate)

NCO^{i} = the area of isocyanate absorbance peak area at time 0
(initial isocyanate)

2.5 Mechanical properties

Compressive property is one of the most important mechanical properties for PUR foams. Compressive energy absorption characteristics and deformation characteristics of foam depend mainly on density, type of base polymer and the predominance of either open or closed cells. Open-cell foams are usually flexible. However, open cell foam relies on cell walls bending and bucking, which is essentially a reversible process. The cell become more compacted during compression, the escape of air through and out of the foam will become increasingly more difficult. The entrapped air will therefore offer some resistance to foam deformation during the final stages of compression (Figure 2.6).

In case closed cell foam, air flow is not a consideration with closed cell foams. Deformation involves cell wall bending and bucking, gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rapture (Figure 2.7) [16].

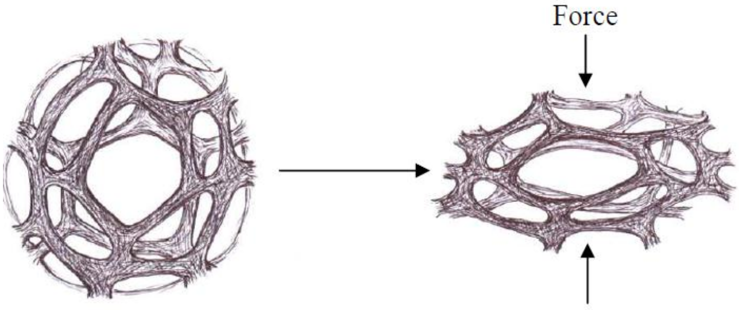


Figure 2.6 Open cell deformation

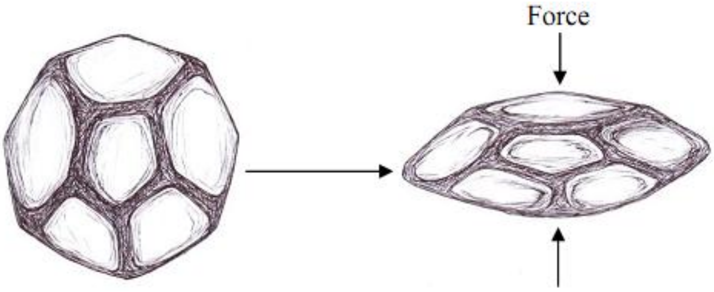


Figure 2.7 Closed cell deformation

Closed cell RPUR foams exhibit 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 RPUR foam can be represented in term of compression stress-strain curve (Figure 2.8).

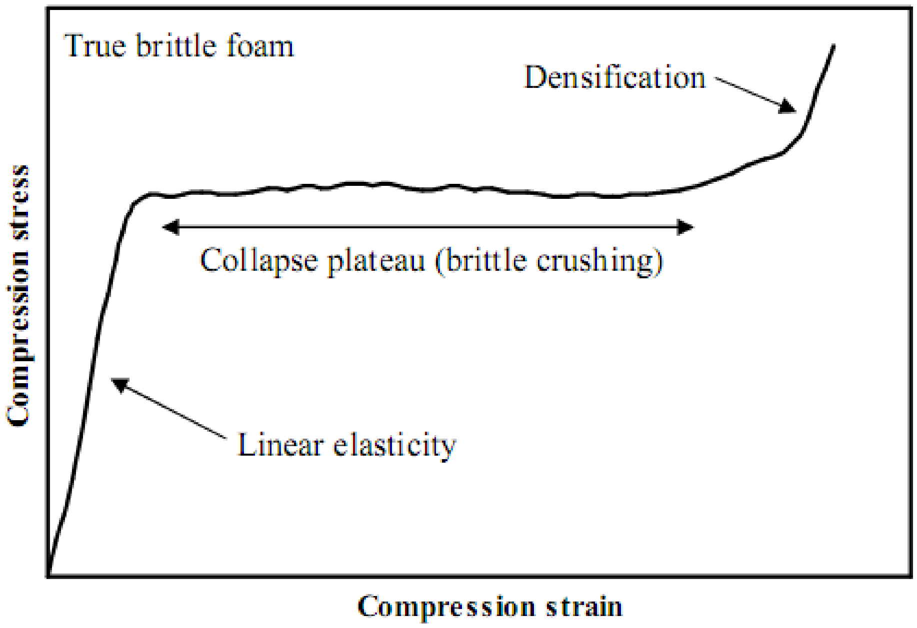


Figure 2.8 Typical compression stress-strain curve for RPUR foam

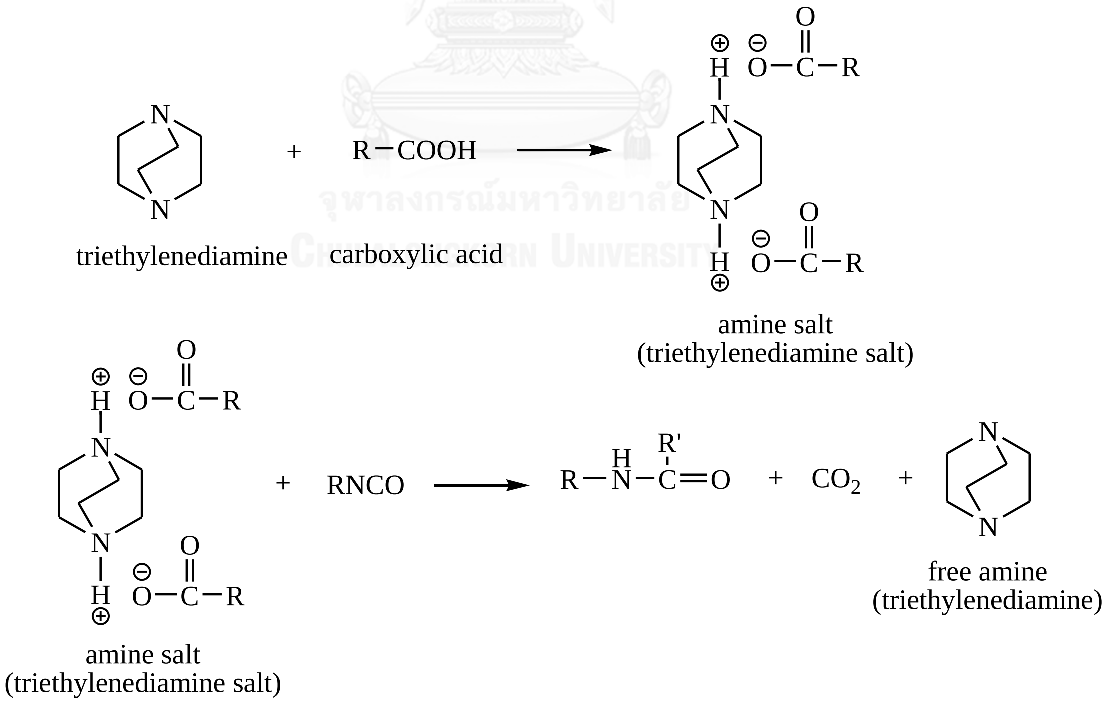
For rigid foams, elements of true brittle crushing are superimposed on the elastic/plastic response. The erratic nature of the collapse plateau corresponds to intermittent rupturing of individual cells. This is due to cell rupture in rigid foams, resilience is dramatically affected. Foams can generally withstand only single impacts, for example the liners used inside riding.

The compressive strength of RPUR foam is usually reported at some definite deformation (5 or 10%). The compressive strength of the foam cell in the direction of foam rise is higher than that in the direction of perpendicular to foam rise [17].

2.6 Literature reviews

Controlled reaction in the initiation period of polyurethane polymerization is important in industry. The catalyst used in his process is known as delayed action catalyst or latent catalyst. Delayed action catalysts are commonly obtained from the reaction between tertiary amines and carboxylic acids to form amine salts or ammonium salts (Scheme 2.6). The amine salts exhibit less catalytic activity than the free amines. This is because nitrogen atom of amine salt is less nucleophilic, which results in the delayed action of initiation time in foaming reaction.

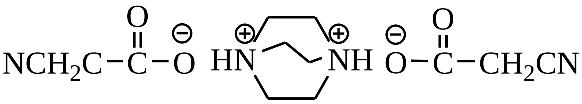
After a period of time, during the exothermic urethane formation, the amine salt is thermally dissociated to give free amine and carboxylic acid. Carboxylic acid reacts with isocyanates to form amide and CO_2. The free amine has better catalytic activity than amine salt, as a result, catalytic activity is slow in initiation time and fast in the latter stage. This initial delay is controlled by the type and amount of carboxylic acid added to the amine.



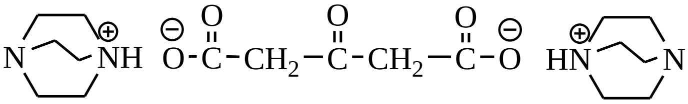
Scheme 2.6 Reaction between triethylenediamine with carboxylic acid to give triethylenediamine salt

Fondots [18] found that the reaction between triethylenediamine (TEDA) with organic acids formed amine salts which was good catalysts for flexible slab and molded foam. When these salts were blended with other amines, it was observed that they could be used to provide an effective delay in the creaming reaction, which corresponded to the delay in rise or cure times. These catalysts could solve some of the major problems involved in pouring starting materials in foam formulation into large and complicated molds.

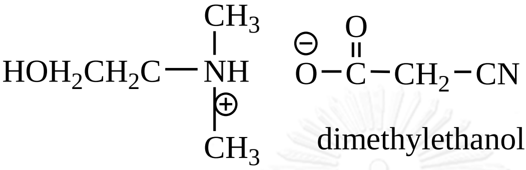
Bechara and coworkers [19] studied salts of triethylenediamine (TEDA) which decompose thermally to release the catalytically effective tertiary amine for polyurethane coatings and epoxy resins. By using reaction between triethylenediamine and acid to form salt of triethylenediamine, for example, triethylenediamine bis cyanoacetate salt (Figure 2.9). The data indicated that triethylenediamine bis-cyanoacetate salt was an effective delayed acting catalyst, which can be activated by elevated temperature and provide the reliable and practical performance associated with a free triethylenediamine catalyst.



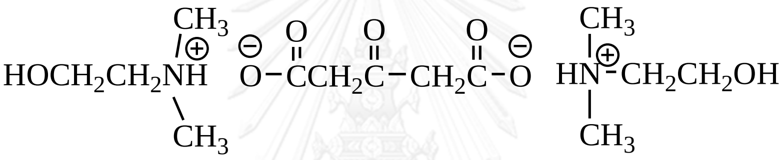
triethylenediamine bis cyanoacetate



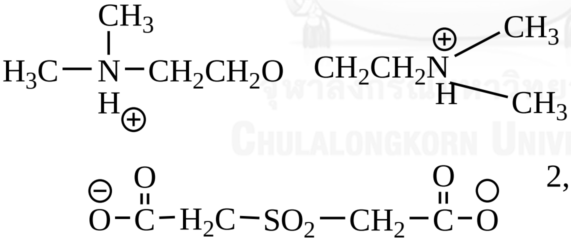
bis triethylenediamine acetone dicarboxylate



dimethylethanolamine cyanaacetate

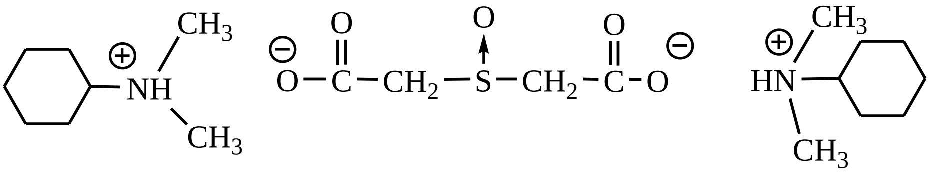


bis dimethylethanolamine acetone dicarboxylate

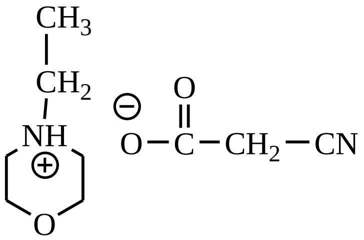


2,2' oxybis-(dimethylethylamino)-
sulfonyl diacetate

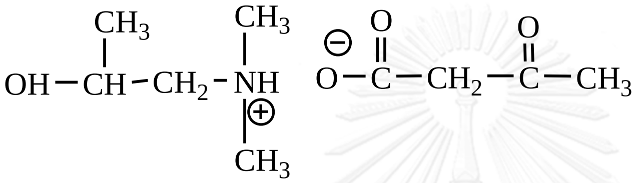
Figure 2.9 Structures of triethylenediamine/carboxylic acid salts



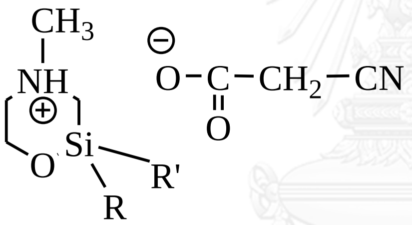
bis(dimethyl cyclohexylamine)
thionyl diacetate



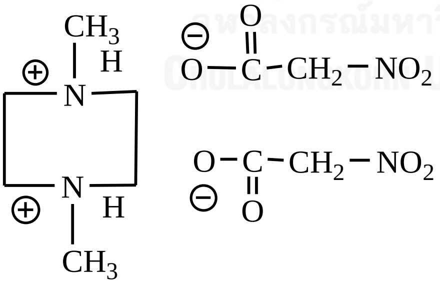
N-ethyl morpholine cyanoacetate



N,N Dimethyl isopropanol
amine aceto-acetate



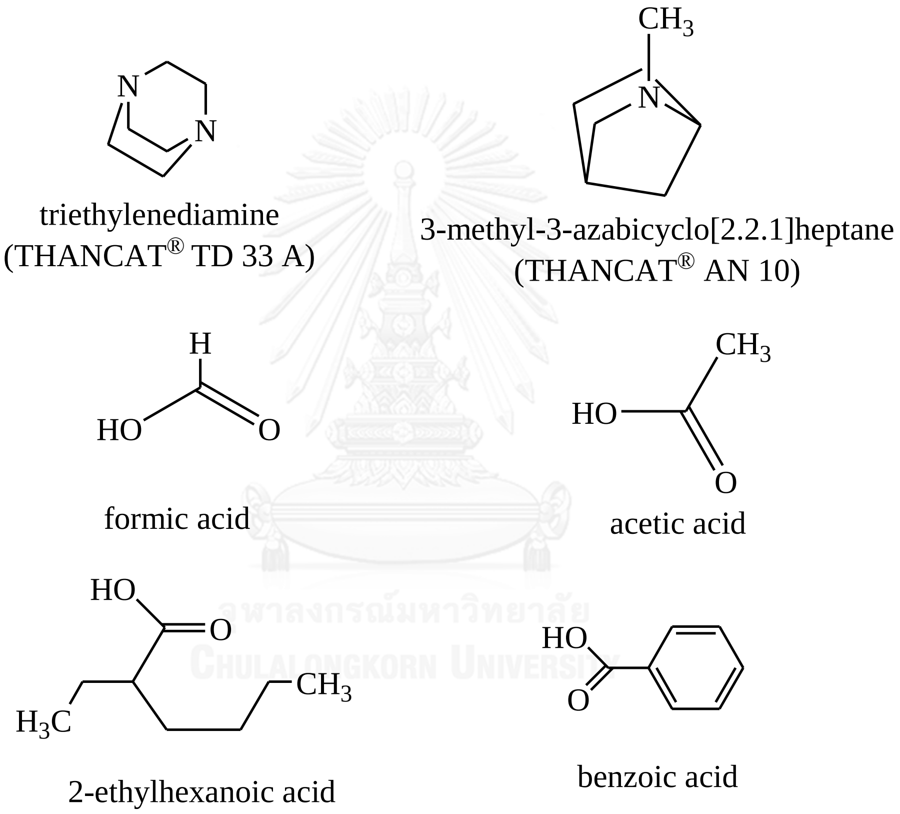
N-methyl silyl morpholino cyano-
acetate



N,N dimethylpiperazine bis nitro-
acetate

Figure 2.9 Structures of triethylenediamine/carboxylic acid salts (continuted)

Diblitz and coworkers [20] studied influence of acids on the delayed-action characteristics of amine catalysts for rigid foam. The catalysts employed were 3-methyl-3-azabicyclo [2.2.1] heptane (THANCAT® AN 10) and triethylenediamine (THANCAT® TD 33 A). These catalysts were reacted with several carboxylic acids, namely formic acid, acetic acid, 2-ethylhexanoic acid and benzoic acid to form amine salts (Figure 2.10). This investigation reported a very effective delay in the gel time was caused by addition of acid. By using benzoic acid, blocking was the most effective. THANCAT® AN 10 was much more sensitive to the addition of acid than THANCAT® TD 33 A. The most striking result was the delay for the combination of THANCAT® AN 10/benzoic acid compared to the unblocked system. In addition, the correlation between parameters like acid strength, steric hindrance and the delaying effect could not be found.



triethylenediamine
(THANCAT® TD 33 A)

3-methyl-3-azabicyclo[2.2.1]heptane
(THANCAT® AN 10)

formic acid

acetic acid

2-ethylhexanoic acid

benzoic acid

Figure 2.10 Structures of amine catalysts and acids.

Casati and coworkers [21] investigated the delayed action characteristic of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) by using three acids, namely phenol, 2-ethyl hexanoic acid and formic acid for preparing rigid polyurethane foam. The results indicated that DBU blocked with phenol had the fastest initiation time and exhibited the highest reactivity. DBU blocked with 2-ethyl hexanoic acid showed a longer initiation time and DBU blocked with formic acid had the longest initiation time.

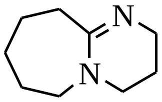


Figure 2.11 Structure of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

Arai and coworkers [22] investigated polyurethane foaming catalysts having an effective delay property. The results indicated that the addition of l-methyl-4-(2-dimethylaminoethyl) piperazine (TMNAEP) (Figure 2.12) to the carboxylic acid gave the salt of TMNAEP, which exhibited a very effective delay property. The initial activity of the catalysts having the delay property could be effectively suppressed by increasing the amount of the carboxylic acid used in the preparation of the catalyst having the delay property. The catalytic activity was enhanced markedly when the polyurethane foam forming reaction proceeded and the reaction temperature was raised.

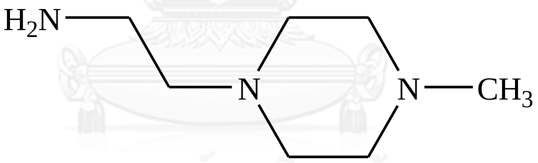
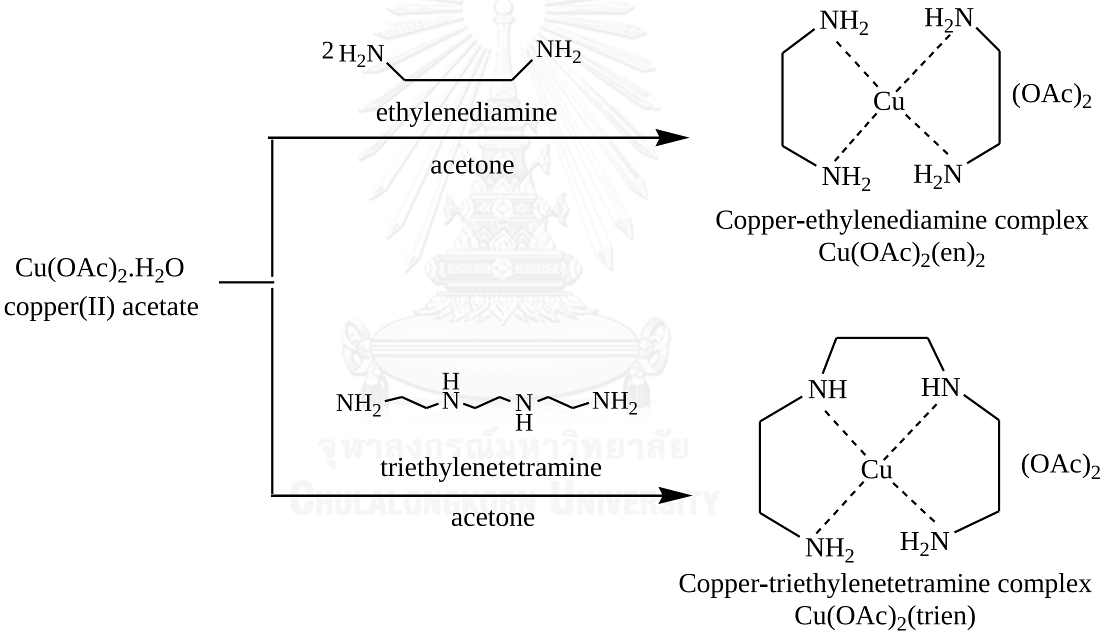


Figure 2.12 Structure of 1-Methyl-4-(2-aminoethyl) piperazine (TMNAEP)

Frisch and Engen [23] studied a bismuth/zinc carboxylate in conjunction with mercaptans as a room temperature curing delayed-action catalyst system for C.A.S.E. (coating, adhesive, sealant and elastomers) applications. It was found that use of the mercaptans in conjunction with the bismuth/zinc carboxylate resulted in a much greater induction period than the use of the bismuth/zinc carboxylate alone. In addition, increasing the concentration of mercaptan in the presence of bismuth/zinc carboxylate resulted in a corresponding delay in the onset of gelation. Incorporation of a standard chain extender, e.g., 1,4-butanediol, also greatly reduced the induction time. Thioglycerol was chosen as the co-catalyst because it has a long induction time and lower odor than mercaptans.

From the previous work in our research group, Pengjam [8] synthesized copper-amine complexes, namely copper-ethylenediamine complex [$Cu(OAc)_2(en)_2$] and copper-triethylenediamine complex [$Cu(OAc)_2(trien)$]. These copper-amime complexes were prepared from copper acetate [$Cu(OAc)_2$] and aliphatic amines, namely ethylenediamine (en) and triethylenetetramine (trien) (Scheme 2.7). The copper-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. The result found that $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ showed similar catalytic activity to DMCHA.



Scheme 2.7 Synthesis of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$

Sridaeng and coworkers [24] prepared flexible polyurethane (FPUR) foams using copper-amine complex solutions in ethylene glycol (EG), namely, $Cu(OAc)_2(en)_2$-EG and $Cu(OAc)_2(trien)$-EG (en = ethylenediamine; trien = triethylenetetramine). These copper-amine complex solutions in ethylene glycol (EG) were obtained as odorless solution and could be used as catalysts for the preparation of FPUR foam. $Cu(OAc)_2(en)_2$-EG and $Cu(OAc)_2$(trien)-EG also have good solubility in FPUR foam formulation.

Consequently, in this research, we were interested to synthesize the salts of copper-amine complex and carboxylic acids. These salts would be prepared in the form of solutions in ethylene glycol and could be used as delayed action catalysts in the preparation of rigid polyurethane foam without purification. The solutions of copper-amine complex/carboxylic acid salts in ethylene glycol were expected to be odorless and had good solubility in other ingredients in the foam formulation.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Synthesis of Copper-amine complex/carboxylic acid salts

Copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$], ethylenediamine (en), salicylic acid (Sal) and ethylene glycol were obtained from Fluka and Aldrich. triethylenetetramine (trien) was obtained from TCI. Acetic acid glacial (Ac) was obtained from BDH Chemicals.

3.1.2 Preparation of rigid polyurethane foams (RPUR foams)

Sucrose-based polyether polyol (Daltolac®, hydroxyl value (OHV) = 440 mgKOH/g and functionality = 4.3), polymeric MDI (4,4'-methane diphenyl diisocyanate; PMDI, Suprasec®-5005, %NCO = 31.0 wt % and average functionality = 2.7), polysiloxane surfactant (Tegostab® B8460) and *N*,*N*-dimethylcyclohexylamine (DMCHA; commercial reference catalyst) were supplied from Huntsman (Thailand) Co., Ltd. Distilled water was used as a chemical blowing agent. Copper-amine complexes and copper-amine complex/carboxylic acid salts were prepared and used as catalysts.

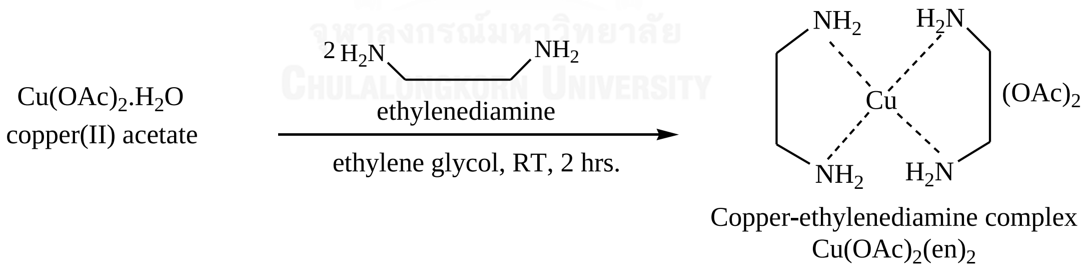
3.2 Synthetic procedures

Copper-amine complexes and copper-amine complex/carboxylic acid salts were synthesized in the form of solutions in ethylene glycol which can be used without purification. RPUR foams were prepared by using solutions of copper-amine complexes and copper-amine complex/carboxylic acid salts as catalysts.

3.2.1 Synthesis of copper-amine complexes as solutions in ethylene glycol

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

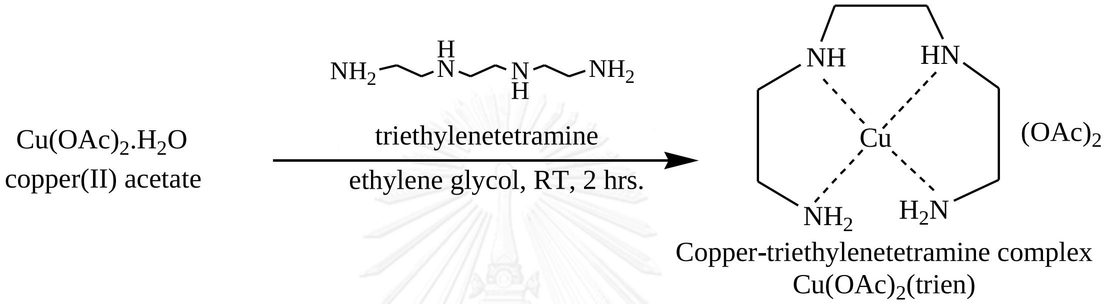
$Cu(OAc)_2(en)_2$ was prepared according to the method reported in the literature [8]. The mole ratio of copper (II) acetate monohydrate to ethylenediamine was 1:2. A solution of 60% wt of $Cu(OAc)_2(en)_2$ in ethylene glycol was prepared using the following procedure: a solution of ethylenediamine (0.42 ml, 6.28 mmol) in ethylene glycol (0.6 ml) was stirred at room temperature for 15 minutes. After that, copper (II) acetate monohydrate (0.624 g, 3.12 mmol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. $Cu(OAc)_2(en)_2$ was obtained as an odorless purple solution: IR (cm^{-1}); 3284 (N-H stretching in copper-amine complex and O-H stretching in ethylene glycol), 2949 (C-H stretching), 1553 (C=O asymmetric stretching), 1403 (C=O symmetric stretching), 1331 (C-N stretching), 1036 (C-O stretching). UV; λ_{max} (MeOH) = 233 nm, molar absorptivity (ε) = 3,606.



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

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

$Cu(OAc)_2(trien)$ was prepared according to the method reported in the literature [8]. The preparation of $Cu(OAc)_2(trien)$ was done as follows: a solution of triethylenetetramine (0.43 ml, 2.89 mmol) was dissolved in ethylene glycol (0.6 ml) at room temperature for 15 minutes. Copper (II) acetate monohydrate (0.578 g, 2.89 mmol) was added to the triethylenetetramine solution. After the reaction mixture was stirred continuously at room temperature for 2 hours, the solution was obtained as an odorless blue solution: IR (cm^{-1}); 3239 (N-H stretching in copper-amine complex and O-H stretching in ethylene glycol), 2929 (C-H stretching), 1562 (C=O asymmetric stretching), 1400 (C=O symmetric stretching), 1335 (C-N stretching), 1042 (C-O stretching). UV; λ_{max} (MeOH) = 259 nm, molar absorptivity (ε) = 1,095.



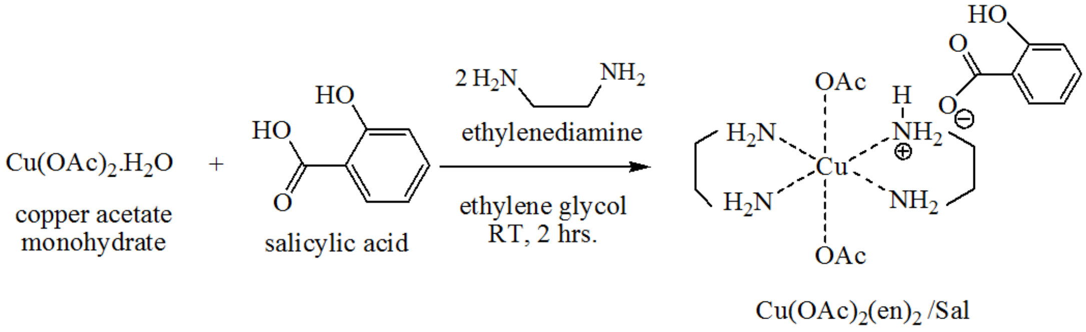
Scheme 3.2 Synthesis of copper-triethylenetetramine complex [$Cu(OAc)_2(trien)$]

3.2.2 Synthesis of copper-amine complex/carboxylic acid salts as solutions in ethylene glycol

3.2.2.1 Copper-ethylenediamine complex/salicylic acid salt [$Cu(OAc)_2(en)_2$/Sal]

The preparation of $Cu(OAc)_2(en)_2$/Sal was done at the mole ratio of $Cu(OAc)_2(en)_2$:Sal = 1:1 was done as follows: a solution of ethylenediamine (0.42 ml, 6.28 mmol) in ethylene glycol (0.6 ml) was stirred at room temperature for 15 minutes. Copper (II) acetate monohydrate (0.624 g, 3.12 mmol) was added to the ethylenediamine solution and the solution was stirred continuously for 10 minute. After that, salicylic acid (0.431 g, 3.12 mmol) was added and the reaction mixture was stirred at room temperature for 2 hours. $Cu(OAc)_2(en)_2$/Sal was obtained as an odorless purple solution: IR (cm^{-1}); 3261 (N-H stretching in copper-amine complex and O-H stretching in ethylene glycol), 2946 (C-H stretching), 1707 C=O stretching), 1593 (Ar-H stretching), 1564 (C=O asymmetric stretching in copper acetate), 1456-

1483 (C-H bending), 1384, (C=O symmetric stretching in copper acetate), 1330 (C-N stretching), 1230 (C-O stretching) and 767 (C-H bending in aromatic ring). UV; λ_{max} (MeOH) = 203 nm, molar absorptivity (ε) = 43,872. The solutions of $Cu(OAc)_2(en)_2$/Sal were synthesized by using various mole ratios between $Cu(OAc)_2(en)_2$ and salicylic acid. The mole ratios of $Cu(OAc)_2(en)_2$:salicylic acid used were 1:0.5, 1:1 and 1:1.5.

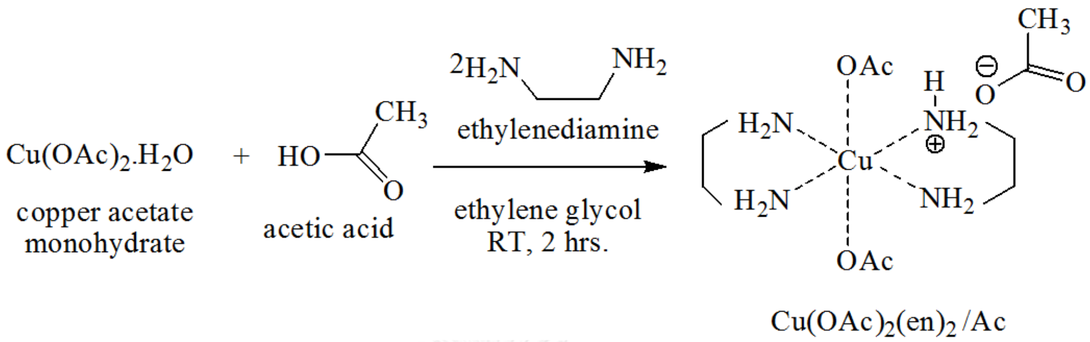


Scheme 3.3 Synthesis of copper-ethylenediamine complex/salicylic acid salt [$Cu(OAc)_2(en)_2$/Sal]

3.2.2.2 Copper- ethylenediamine complex/acetic acid salt [$Cu(OAc)_2(en)_2$/Ac]

The preparation of $Cu(OAc)_2(en)_2$/Ac was done at the mole ratio of $Cu(OAc)_2(en)_2$:Ac = 1:1.5 was done as follows: a solution of ethylenediamine (0.42 ml, 6.28 mmol) in ethylene glycol (0.6 ml) was stirred at room temperature for 15 minutes. Copper (II) acetate monohydrate (0.624 g, 3.12 mmol) was added to the ethylenediamine solution and the solution was stirred continuously for 10 minute. After that, acetic acid (0.27 ml, 4.72 mmol) was added and the reaction mixture was stirred at room temperature for 2 hours. $Cu(OAc)_2(en)_2$/Ac was obtained as an odorless purple solution: IR (cm^{-1}); 3257 (N-H stretching in copper-amine complex and O-H stretching in ethylene glycol), 2943 (C-H stretching), 1704 (C=O stretching), 1556 (C=O asymmetric stretching in copper acetate), 1399 (C=O symmetric stretching in copper acetate), 1334 (C-N stretching) 1039 (C-O stretching). UV; λ_{max} (MeOH) = 234 nm, molar absorptivity (ε) = 3,482. The solutions of

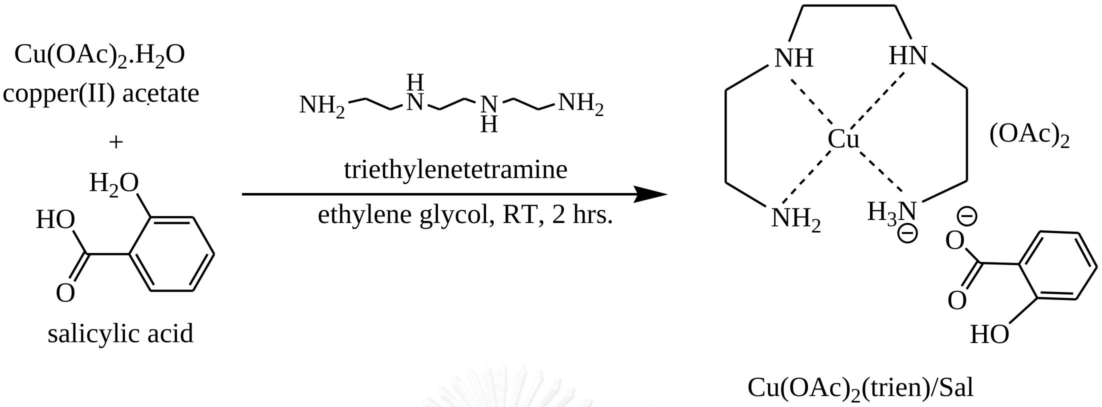
$Cu(OAc)_2(en)_2$/Ac were synthesized by using various mole ratios between $Cu(OAc)_2(en)_2$ and acetic acid. The mole ratios of $Cu(OAc)_2(en)_2$:acetic acid used were 1:0.5, 1:1, 1:1.5 and 1:2.



Scheme 3.4 Synthesis of copper-ethylenediamine complex/acetic acid salt [$Cu(OAc)_2(en)_2$/Ac]

3.2.2.3 Copper- triethylenetetramine complex/salicylic acid salt [$Cu(OAc)_2$(trien)/Sal]

The preparation of $Cu(OAc)_2$(trien)/Sal was done at the mole ratio of $Cu(OAc)_2$(trien):Sal = 1:0.5 done as follows: a solution of triethylenetetramine (0.43 ml, 2.89 mmol) in ethylene glycol (0.6 ml) was stirred at room temperature for 15 minutes. Copper (II) acetate monohydrate (0.578 g, 2.89 mmol) was added to the triethylenetetramine solution and the solution was stirred continuously for 10 minute. After that, salicylic acid (0.20 g, 1.45 mmol) was added and the reaction mixture was stirred at room temperature for 2 hours. $Cu(OAc)_2$(trien)/Sal was obtained as an odorless blue solution: IR (cm^{-1}); 3250 (N-H stretching in copper-amine complex and O-H stretching in ethylene glycol), 2936 (C-H stretching), 1706 (C=O stretching), 1590 (Ar-H stretching) 1567 (asymmetric C=O, acetate), 1456-1486 (C-H bending), 1570 (C=O asymmetric stretching in copper acetate), 1385 (C=O symmetric stretching in copper acetate), 1338 (C-N stretching), 1041 (C-O stretching) and 762 (C-H bending in aromatic ring). UV; λ_{max} (MeOH) = 204 nm, molar absorptivity (ε) = 10,204. The solutions of $Cu(OAc)_2$(trien)/Sal were synthesized by using various mole ratios between $Cu(OAc)_2$(trien):salicylic acid. The mole ratios of $Cu(OAc)_2(en)_2$: salicylic acid used were 1:0.25, 1:0.5, 1:0.75 and 1:1.



Scheme 3.5 Synthesis of copper-triethylenetetramine complex/salicylic acid salt [$Cu(OAc)_2$(trien)/Sal]

The solutions of copper-amine complex/carboxylic acid salts, namely $Cu(OAc)_2(en)_2$/Sal , $Cu(OAc)_2(en)_2$/Ac and $Cu(OAc)_2$(trien)/Sal were synthesized by using various mole ratios between copper-amine complex:carboxylic acid. The variation in an amount of carboxylic acid was employed as shown in Table 3.1.

Table 3.1 Composition of chemicals in the synthesis of copper-amine complexes and copper-amine complex/ carboxylic acid salts in ethylene glycol (60 wt% solution)

Copper-amine complexes and copper-amine complex/ carboxylic acid salts	**Mole ratios of copper-amine complex:carboxylic acid**	**$Cu(OAc)_2$ (g)**	**Salicylic acid (g)**	**Acetic acid (ml)**	**Amine (ml)**	**Color of solution**
$Cu(OAc)_2(en)_2$	-	0.624	-	-	0.42	Purple
$Cu(OAc)_2$(trien)	-	0.578	-	-	0.43	Blue
$Cu(OAc)_2(en)_2$/Sal	1:0.5	0.624	0.216	-	0.42	Purple
$Cu(OAc)_2(en)_2$/Sal	1:1	0.624	0.432	-	0.42	Purple
$Cu(OAc)_2(en)_2$/Sal	1:1.5	0.624	0.648	-	0.42	Purple
$Cu(OAc)_2(en)_2$/Ac	1:0.5	0.624	-	0.09	0.42	Purple
$Cu(OAc)_2(en)_2$/Ac	1:1	0.624	-	0.18	0.42	Purple
$Cu(OAc)_2(en)_2$/Ac	1:1.5	0.624	-	0.27	0.42	Purple
$Cu(OAc)_2(en)_2$/Ac	1:2	0.624	-	0.36	0.42	Purple
$Cu(OAc)_2$(trien)/Sal	1:0.25	0.578	0.100	-	0.43	Blue
$Cu(OAc)_2$(trien)/Sal	1:0.5	0.578	0.200	-	0.43	Blue
$Cu(OAc)_2$(trien)/Sal	1:0.75	0.578	0.299	-	0.43	Blue
$Cu(OAc)_2$(trien)/Sal	1:1	0.578	0.399	-	0.43	Blue

en = ethylenediamine, trien = triethylenetetramine, Sal = salicylic acid, Ac = acetic acid

3.3 Rigid polyurethane (RPUR) foam preparations

3.3.1 Preparation of rigid polyurethane (RPUR) foams by cup test method

RPUR foam samples were made according to the formulation presented in Table 3.2. In the experiment, each batch of foam was based on 100 grams of polyol and NCO index employed was 100. The foams were prepared in two steps of mixing. In the first mixing step, polyol, catalysts (copper amine complex/carboxylic acid salts or DMCHA), surfactant and blowing agent (distilled water) were mixed in a 700 ml plastic cup by mechanical stirrer at 2000 rpm for 20 seconds. In the second mixing step, PMDI was added into the mixed polyol from first mixing then the mixture were mixed in homogeneous mixture by mechanical stirrer at 2000 rpm for 20 seconds at room temperature. At the end of the mixing sequence, the polymerization times, cream time (the time when first bubbles are formed and the foam started to rise), gel time (the time when the foam mixture started to gel), tack free time (the time at which the outer skin of the foam loses its stickiness) and rise time (the period of time until the foam stopped rising) were investigated. Besides, the temperature and rise profiles versus time were recorded and compared to those catalyzed with *N*,*N*-dimethylcyclohexylamine (DMCHA), which is used commercially. Finally, the foams were kept at room temperature for 48 hours and then physical and mechanical characterization were done.

3.3.2 Preparation of rigid polyurethane foam in a plastic mold

After all of the starting materials were mixed in a plastic cup as described in 3.3.1, the homogeneous liquid was poured into a plastic mold, which was a 10 ×10× 10 cm (length×width×height) plastic bag and allowed to rise freely. Density and appearance of RPUR foams prepared by using plastic bag were the same as those prepared in plastic cup. The RPUR foams were kept at room temperature for 48 hours. The foam density was measured. These foams were used for investigation of the mechanical properties and morphology.

RPUR foams obtained from different catalysts have the same IR spectra. All RPUR foam had similar IR absorption as follows : NH stretching of urethane and urea at 3326 cm^{-1}, C=O stretching of urethane and urea at 1705 cm^{-1}, C-O of urethane at 1076 cm^{-1}, while the band at 1511 cm^{-1} could be attributed to NH-bending vibration and C-N stretching vibration of urethane and urea groups. The band at 1222 cm^{-1} was associated with the characteristic stretching vibration of C-N-H bond of urethane and urea.

Table 3.2 RPUR foam formulation prepared at the NCO index of 100 (in parts by weight unit, pbw)

Chemicals	**Weight (pbw)**
Polyether polyol (Daltolac® R180)	100.0
Catalyst (copper-amine complex/carboxylic acid salts or DMCHA)	1.0
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5
Blowing agent (H_2O)	3.0
Polymeric MDI (PMDI, Suprasec®5005)	154.3, 151.3

*pbw: parts by weight or 1 gram in 100 grams of polyol

Table 3.3 RPUR foam formulation prepared at the NCO index of 100 (in gram unit which was used in the preparation by cup test method)

Chemicals	**Weight (g)**
Polyether polyol (Daltolac® R180,)	10.0
Catalyst (copper-amine complex/carboxylic acid salts or DMCHA)	0.1
Silicone surfactant (polysiloxane, Tegostab® B8460)	0.25
Blowing agent (H_2O)	0.3
Polymeric MDI (PMDI, Suprasec®5005)	15.43, 15.13

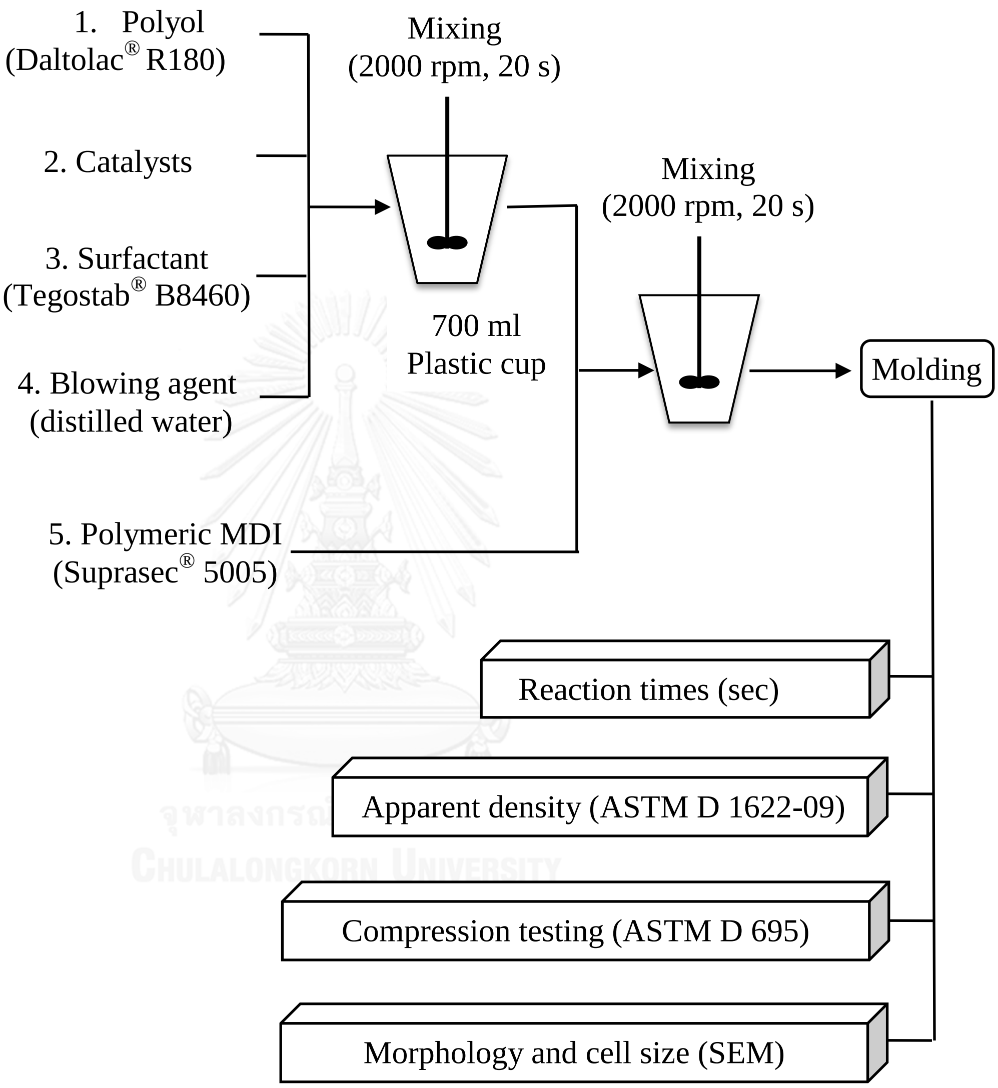


Figure 3.1 Process of preparation of rigid polyurethane foams

3.4 Characterizations

3.4.1 Infrared spectroscopy

Copper-amine complexes, copper-amine complex/carboxylic acid salts and polyurethane foams were characterized at room temperature by using a Nicolet 6700 at a resolution of 4 cm^{-1} and a total of 64 interferograms were signal averaged. It is important that the samples are pressed, reproducibly and with a constant pressure, against the IR-transmitting ATR crystal. The ATR crystal is integrated into the beam of an ATR-IR spectrometer in such a way that IR light is passed through the crystal by means of total reflection. ATR occurs on the measuring surface that is in contact with the foam sample. The IR bands given in Table 3.4 are used for the analysis. The measurement was controlled by Omnic software.

Table 3.4 Characteristic IR bands of RPUR foam [25]

Functional group	**Vibration mode**	**IR 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
Reference	Non-reaction groups in polyol and isocyanate	935-1050

3.4.2 Ultraviolet-visible spectroscopy

UV-Vis spectra were recorded as absorption spectra and were obtained on Varian Cary 50 UV-Vis spectrophotometer. The samples were scan over range 200-500 nm at a medium speed. Methanol (analytical grade) is a solvent using in this characterization.

3.4.3 Reaction times

The reaction times namely, cream time, gel time tack free time and rise time were investigated by using a digital stopwatch.

3.4.4 Temperature

The foaming temperatures were recorded by Digicon DP-71 dual thermocouple.

3.5 Physical and Mechanical properties of RPUR foams

3.5.1 Density

Free rise density of foams was measured according to ASTM D 1622-09, the size of specimen was 3.0 x 3.0 x 3.0 cm (length×width×thickness) and the average values of three samples were reported.

3.5.2 Compressive testing

The compressive testing of foams in parallel and perpendicular to the foam rising direction was performed using universal testing machine (Lloyd) according to ASTM D 695. The sample size was 3.0 x 3.0 x 3.0 cm (length×width×thickness). The average values of three samples were reported.

3.5.3 Scanning electron microscopy (SEM)

The morphology and cell size of RPUR foams were measured on a JSM-6480 LV scanning electron microscope (SEM). Rectangular specimens 1.0 mm thick were cut from surface in both parallel and perpendicular to the foaming direction by coating with gold before scanning in order to provide an electrically conductive surface. The specimens were done at accelerating of 15 kV.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of copper-amine complexes

Copper-amine complexes were synthesized from the reaction between copper(II) acetate monohydrate [$Cu(OAc)_2.H_2O$] and amines (as previously shown in Schemes 3.1 and 3.2). Amines used in this study were ethylenediamine (en) and triethylenetetramine (trien). Ethylene glycol was used as a solvent. Copper-amine complexes [$Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$] were prepared as 60% wt solution in ethylene glycol. Copper-amine complexes solutions were obtained as odorless liquids and could be dissolved in other starting materials used in foam formulation.

4.1.1 Synthesis of copper-ethylenediamine complex/carboxylic acid salts [$Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac]

Copper-ethylenediamine complex/carboxylic acid salts were prepared from reaction between copper (II) acetate monohydrate, ethylenediamine and carboxylic acid as previously shown in Schemes 3.3 and 3.4. Carboxylic acids used were salicylic acid (Sal) and acetic acid (Ac). Ethylene glycol was used as a solvent. The reaction between copper-ethylenediamine complex and carboxylic acids gave the salts of copper-ethylenediamine complex and carboxylic acid, namely $Cu(OAc)_2(en)_2$/Sal, and $Cu(OAc)_2(en)_2$/Ac. $Cu(OAc)_2(en)_2$/Sal, and $Cu(OAc)_2(en)_2$/Ac were obtained as solutions in ethylene glycol which can be further used in foam formulation without purification. The solutions of $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac were synthesized by using various mole ratios between $Cu(OAc)_2(en)_2$ and carboxylic acid. The mole ratios of $Cu(OAc)_2(en)_2$: salicylic acid used were 1:0.5, 1:1 and 1:1.5. The mole ratios of $Cu(OAc)_2(en)_2$: acetic acid used were 1:0.5, 1:1, 1:1.5 and 1:2. Both $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac were obtained as odorless viscous purple liquid and could be easily dissolved in other starting materials used in foam formulation. UV-Visible spectroscopy and IR spectroscopy were used to identify the structure of copper-ethylenediamine complex/carboxylic acid salts.

4.1.2 Characterization of copper-ethylenediamine complex/carboxylic acid salts [$Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac]

4.1.2.1 UV-visible spectroscopy of copper-ethylenediamine complex/carboxylic acid salts [$Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac]

The solutions of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac in ethylene glycol were dissolved in methanol and UV-visible spectra were obtained (Figure 4.1). The maximum absorption peak (λ_{max}) of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac appeared at 233, 203 and 234 nm, respectively. It was found that the λ_{max} of $Cu(OAc)_2(en)_2$/Sal shifted from that of $Cu(OAc)_2(en)_2$, which indicated that $Cu(OAc)_2(en)_2$/Sal was a salt of $Cu(OAc)_2(en)_2$ and salicylic acid. However, the λ_{max} of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(en)_2$/Ac were the same, which indicated that $Cu(OAc)_2(en)_2$ and acetic acid did not form a salt.

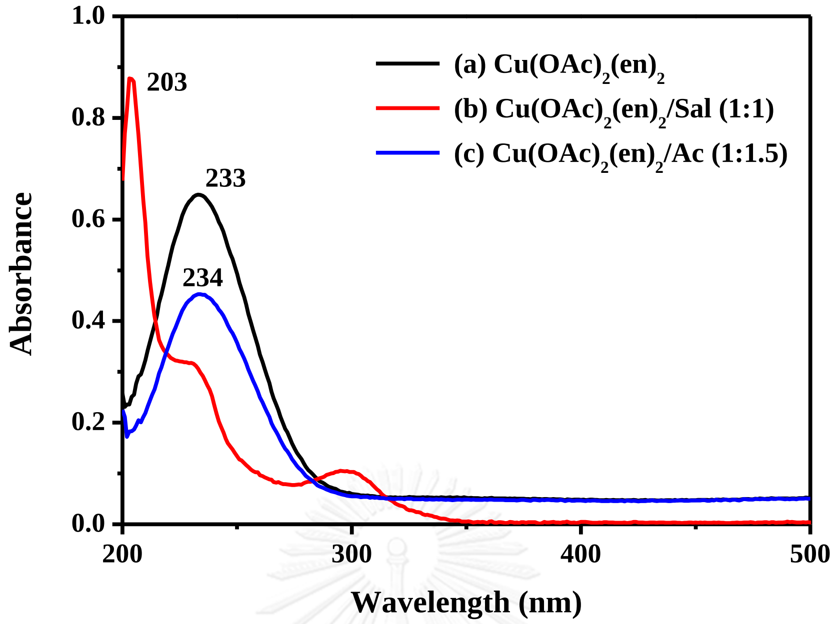


Figure 4.1 UV spectra of (a) $Cu(OAc)_2(en)_2$; (b) $Cu(OAc)_2(en)_2$/Sal (mole ratio 1:1) and (c) $Cu(OAc)_2(en)_2$/Ac (mole ratio 1:1.5)

4.1.2.2 IR spectroscopy of copper-ethylenediamine complex/carboxylic acid salts [$Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac]

The IR spectra of copper-ethylenediamine complex and carboxylic acids are shown in Figure 4.2. IR spectrum of $Cu(OAc)_2(en)_2$ solution in ethylene glycol is shown in Figure 4.2(a). It exhibited absorption band at 3284 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in ethylene glycol), at 2949 cm^{-1} (C-H stretching), at 1553 cm^{-1} (C=O asymmetric stretching), at 1403 cm^{-1} (C=O symmetric stretching), at 1331 cm^{-1} (C-N stretching) and at 1036 cm^{-1} (C-O stretching). The C=O stretching of carbonyl group in $Cu(OAc)_2(en)_2$ appeared as absorption band at 1553 cm^{-1} (asymmetric C=O), and 1403 cm^{-1} (symmetric C=O), respectively, which were different from the typical $Cu(OAc)_2$ peaks normally appears as absorption band around at 1596 cm^{-1} (asymmetric C=O) and 1443 cm^{-1} (symmetric

C=O) [8]. It was found that the IR peaks of $Cu(OAc)_2(en)_2$ shifted from those of $Cu(OAc)_2$, which indicated that the complex was formed.

IR spectrum of $Cu(OAc)_2(en)_2$/Sal (mole ratio 1:1) is shown in Figure 4.2(b). It exhibited absorption band at 3261 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in ethylene glycol), at 2946 cm^{-1} (C-H stretching), at 1707 cm^{-1} (C=O stretching in salicylic acid), at 1564 cm^{-1} (C=O asymmetric stretching in copper acetate), 1384 cm^{-1} (C=O symmetric stretching in copper acetate), at 1593 cm^{-1} (Ar-H stretching), at 1456-1483cm^{-1} (C-H bending), at 1330 cm^{-1} (C-N stretching), at 1230 cm^{-1} (C-O stretching), and at 767 cm^{-1} (C-H bending in aromatic ring). The C=O stretching of carbonyl group in $Cu(OAc)_2(en)_2$/Sal appeared as absorption band at 1564 cm^{-1} (asymmetric C=O), and 1384 cm^{-1} (symmetric C=O), respectively, which were different from the typical $Cu(OAc)_2(en)_2$ peaks normally appears as absorption band around at 1553 cm^{-1} (asymmetric C=O) and 1403 cm^{-1} (symmetric C=O). This indicated that the copper-ethylenediamine complex/salicylic acid salt was formed.

IR spectrum of $Cu(OAc)_2(en)_2$/Ac (mole ratio 1:1.5) is shown in Figure 4.2(c). It exhibited absorption band at 3257 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in ethylene glycol), at 2943 cm^{-1} (C-H stretching), at 1704 cm^{-1} (C=O stretching in acetic acid), at 1556 cm^{-1} (C=O asymmetric stretching in copper acetate), 1399 cm^{-1} (C=O symmetric stretching in copper acetate), at 1334 cm^{-1} (C-N stretching) and at 1039 cm^{-1} (C-O stretching). The C=O stretching of carbonyl group in $Cu(OAc)_2(en)_2$/Ac appeared as absorption band at 1556 cm^{-1} (asymmetric C=O), and 1399 cm^{-1} (symmetric C=O), respectively, which were the same as the typical $Cu(OAc)_2(en)_2$ peaks normally appears as absorption band around at 1553 cm^{-1} (asymmetric C=O) and 1403 cm^{-1} (symmetric C=O). This indicated that the copper-ethylenediamine complex/acetic acid salt was not formed.

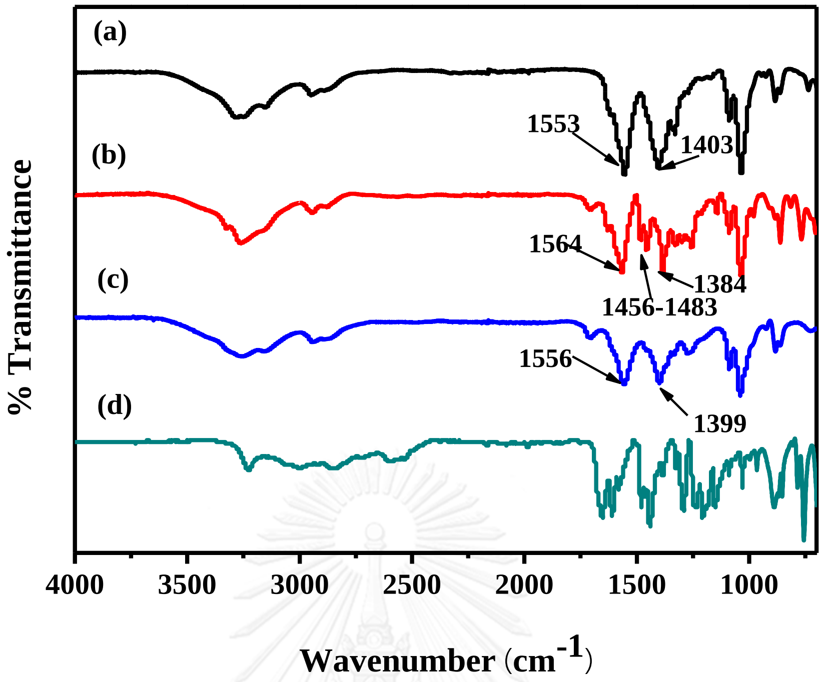


Figure 4.2 IR spectra of (a) $Cu(OAc)_2(en)_2$; (b) $Cu(OAc)_2(en)_2$/Sal (mole ratio 1:1); (c) $Cu(OAc)_2(en)_2$/Ac (mole ratio 1:1.5) and (d) Salicylic acid

4.1.3 Synthesis of copper-triethylenetetramine complex/salicylic acid salt [$Cu(OAc)_2$(trien)/Sal]

Copper-triethylenetetramine complex/salicylic acid salt was prepared from reaction between copper (II) acetate monohydrate, triethylenetetramine and salicylic acid as previously shown in Scheme 3.5. Ethylene glycol was used as a solvent. The reactions between copper-triethylenetetramine complexes and salicylic acid gave the salts of copper-triethylenetetramine complex and salicylic acid, namely $Cu(OAc)_2$(trien)/Sal. $Cu(OAc)_2$(trien)/Sal was obtained as solution in ethylene glycol which can be further used in foam formulation without purification. The solution of $Cu(OAc)_2$(trien)/Sal was synthesized by using various mole ratios between $Cu(OAc)_2$(trien):salicylic acid. The mole ratios of $Cu(OAc)_2$(trien):salicylic acid used were 1:0.25, 1:0.5, 1:0.75 and 1:1. $Cu(OAc)_2$(trien)/Sal was obtained as odorless viscous blue liquid and could be easily dissolved in other starting materials used in foam formulation. UV-Visible spectroscopy and IR spectroscopy were used to identify the structure of copper-triethylenetetramine complex/salicylic acid salt**.**

4.1.4 Characterization of copper-triethylenetetramine complex/salicylic acid salt [Cu(OAc)$_2$(trien)/Sal]

4.1.4.1 UV-visible spectroscopy of copper-triethylenetetramine complex/salicylic acid salt [Cu(OAc)$_2$(trien)/Sal]

The solution of Cu(OAc)$_2$(trien) and Cu(OAc)$_2$(trien)/sal in ethylene glycol were dissolved in methanol and UV-visible spectra were obtained (Figure 4.3). The maximum absorption peak (λ_{max}) of Cu(OAc)$_2$(trien) and Cu(OAc)$_2$(trien)/sal appeared at 259 and 204 nm, respectively. It was found that the λ_{max} of Cu(OAc)$_2$(trien)/Sal shifted from that of Cu(OAc)$_2$(trien), which indicated that Cu(OAc)$_2$(trien)/Sal was a salt of Cu(OAc)$_2$(trien) and salicylic acid.

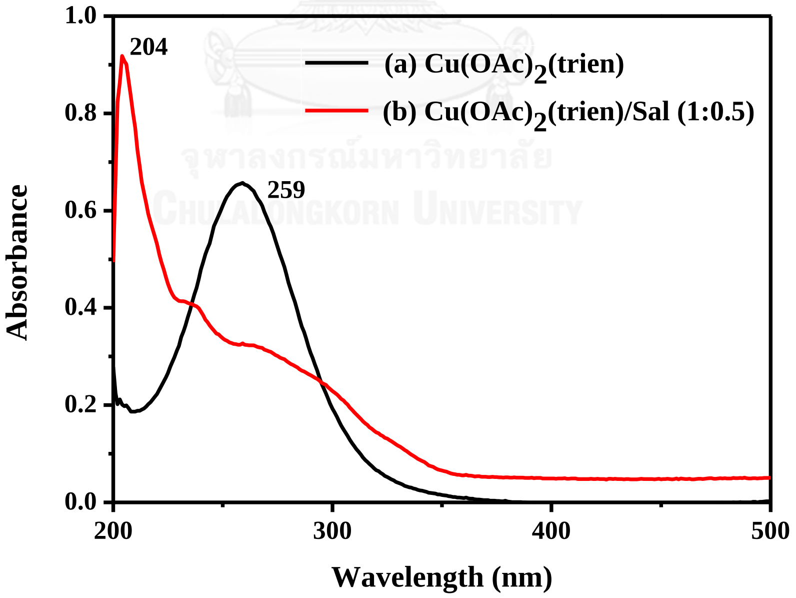


Figure 4.3 UV spectra of (a) Cu(OAc)$_2$(trien) and (b) Cu(OAc)$_2$(trien) /Sal (mole ratio 1:0.5)

4.1.4.2 IR spectroscopy of copper-triethylenetetramine complex/salicylic acid salt [$Cu(OAc)_2$(trien)/Sal]

The IR spectra of copper-triethylenetetramine complex and salicylic acid are shown in Figure 4.4. The IR spectrum of $Cu(OAc)_2$(trien) solution in ethylene glycol is shown in Figure 4.4(a). It exhibited absorption band at 3239 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in ethylene glycol), at 2929 cm^{-1} (C-H stretching), at 1562 cm^{-1} (C=O asymmetric stretching), at 1400 cm^{-1} (C=O symmetric stretching), at 1335 cm^{-1} (C-N stretching) and at 1042 cm^{-1} (C-O stretching). The C=O stretching of carbonyl group in $Cu(OAc)_2(trien)_2$ appeared as absorption band at 1562 cm^{-1} (asymmetric C=O), and 1400 cm^{-1} (symmetric C=O), respectively, which were different from the typical $Cu(OAc)_2$ peaks normally appears as absorption band around at 1596 cm^{-1} (asymmetric C=O) and 1443 cm^{-1} (symmetric C=O). It was found that the IR peaks of $Cu(OAc)_2$(trien) shifted from those of $Cu(OAc)_2$, which indicated that the complex was formed.

IR spectrum of $Cu(OAc)_2$(trien)/Sal (mole ratio 1:0.5) is shown in Figure 4.4(b). It exhibited absorption band at 3250 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl groups in ethylene glycol), at 2936 cm^{-1} (C-H stretching), at 1706 cm^{-1} (C=O stretching in salicylic acid), at 1567 cm^{-1} (C=O asymmetric stretching in copper acetate), 1385 cm^{-1} (C=O symmetric stretching in copper acetate), at 1590 cm^{-1} (Ar-H stretching), at 1456-1486 cm^{-1} (C-H bending), at 1338 cm^{-1} (C-N stretching), at 1041 cm^{-1} (C-O stretching), and at 762 cm^{-1} (C-H bending in aromatic ring). The C=O stretching of carbonyl group in $Cu(OAc)_2$(trien)/Sal appeared as absorption band at 1567 cm^{-1} (asymmetric C=O), and 1385 cm^{-1} (symmetric C=O), respectively, which were different from the typical $Cu(OAc)_2$(trien) peaks normally appears as adsorption band around at 1562 cm^{-1} (asymmetric C=O) and 1400 cm^{-1} (symmetric C=O). This indicated that the copper-triethylenetetramine complex/salicylic acid salt was formed.

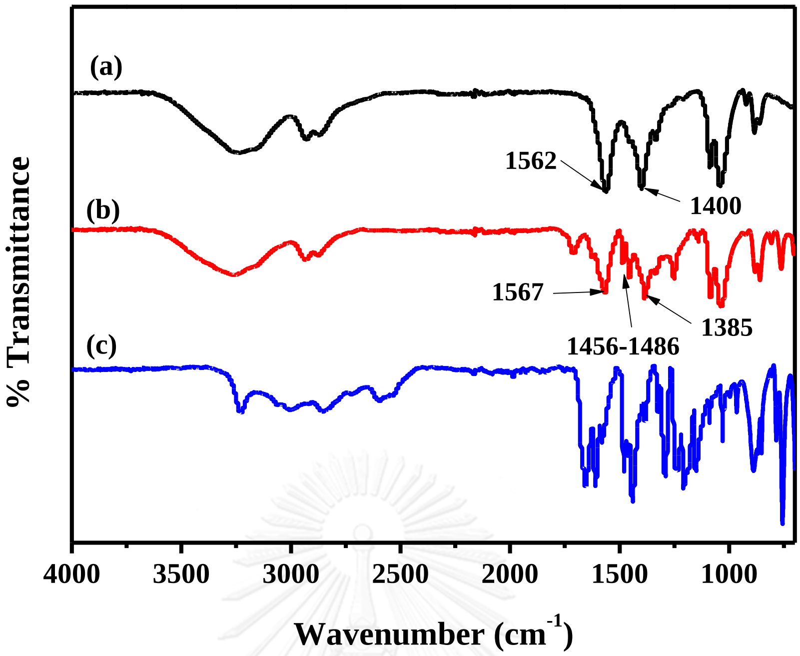


Figure 4.4 IR spectra of (a) $Cu(OAc)_2(trien)$; (b) $Cu(OAc)_2(trien)$/Sal (mole ratio 1:0.5) and (c) Salicylic acid

4.2 Preparation rigid polyurethane foams catalyzed by copper-amine complex/carboxylic acid salts

4.2.1 Preparation of rigid polyurethane (RPUR) foams by cup test method

Rigid polyurethane foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(en)_2$/Sal, $Cu(OAc)_2(en)_2$/Ac, $Cu(OAc)_2(trien)$ and $Cu(OAc)_2(trien)$/Sal were prepared by mechanical mixing technique in two steps method of the mixing. In the first mixing step, polyol, catalysts (copper-amine complex/carboxylic acid salts or DMCHA), surfactant and blowing agent (distilled water) were mixed in a 700 ml plastic cup by mechanical stirrer at 2000 rpm for 20 seconds. In the second mixing step, PMDI was added into the mixed polyol from first mixing then the mixture were mixed in homogeneous mixture by mechanical stirrer (2000 rpm) for 20 seconds at room temperature. At the end of the mixing sequence, the polymerization times, cream time (the time when first bubbles are formed and the foam started to rise), gel time (the time when the foam mixture started to gel), tack free time (the time at which the outer skin of the foam loses its stickiness) and rise time (the period of time until the foam stopped rising) were investigated. Besides, the temperature and rise profiles versus time were recorded and compared to those catalyzed with DMCHA, which is used commercially. Finally, the foams were kept at room temperature for 48 hours before the measurement of free rise density and the investigation of NCO conversion by infrared spectroscopy. The RPUR foam formulation is shown Table 4.1.

Figure 4.5 RPUR foams prepared by using a 700 ml plastic cup and catalyzed by $Cu(OAc)_2(en)_2$/Sal at the mole ratio of 1:1

Table 4.1 RPUR foam formulation at the NCO index of 100 (in parts by weight unit)

Chemicals	pbw
Polyether polyol (Daltolac® R180)	100.0
Catalyst (copper-amine complex/carboxylic acid salts or DMCHA)	1.0
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5
Blowing agent (H_2O)	3.0
Polymeric MDI (PMDI, Suprasec®5005)	154.3, 151.3

*pbw : parts by weight or 1 gram in 100 grams of polyol

4.2.2 Preparation of rigid polyurethane foam in a plastic mold

After all of the starting materials were mixed in a plastic cup as described in 4.2.1, the homogeneous liquid was poured into a plastic mold, which was a plastic bag, and allowed to rise freely. Density and appearance of of RPUR foams prepared by using plastic bag were the same as those prepared in plastic cup. Appearance of RPUR foam prepared in a plastic bag is illustrated in Figure 4.6. The results showed that RPUR foams could be prepared in the larger mold and would not collapse. The RPUR foams were kept at room temperature for 48 hours. The foam density was measured. These foams were used for investigation of the mechanical properties and morphology.

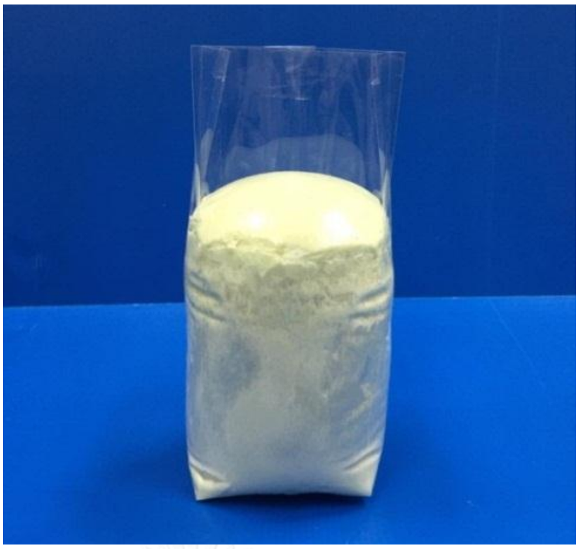


Figure 4.6 RPUR foam prepared by using a plastic bag and catalyzed by $Cu(OAc)_2(en)_2$/Sal at the mole ratio of 1:1

4.2.3 Reaction times, density and height of RPUR foams

By using cup test method in the preparation of RPUR foams, the reaction times, density and height of RPUR foams catalyzed by DMCHA and copper-amine complex/carboxylic acid salts are shown in Table 4.2. The reaction times, namely cream time, gel time, tack free and rise time were measured. The density of RPUR foam was measured in accordance with ASTM D 1622-09. The foam prepared in a cup was cut into the size of 3.0 x 3.0 x 3.0 cm (length×width×thickness) (Figure 4.7). The length, width and height of the cubic shape were 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 4.8. The reaction times, density and height of RPUR foams catalyzed by copper-amine complex/carboxylic acid salts were compared with those obtained from commercial catalyst (DMCHA).

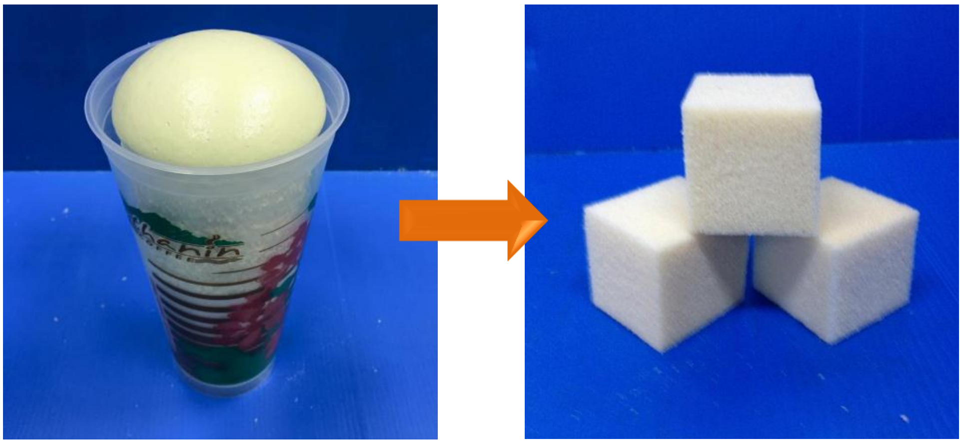


Figure 4.7 RPUR samples for foam density measurement

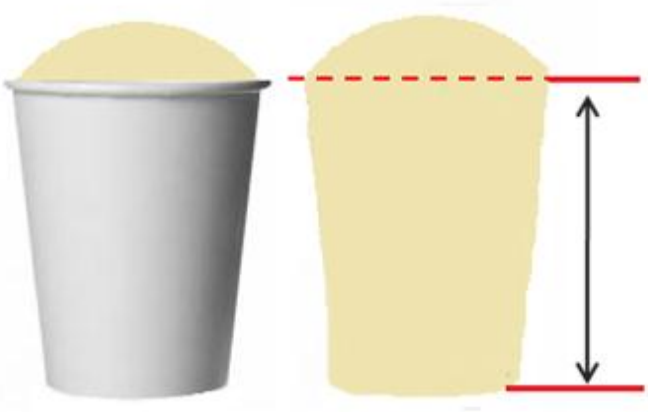


Figure 4.8 Measurement of RPUR foam height

Table 4.2 Reaction times of RPUR foams prepared at the NCO index of 100 and catalyzed by DMCHA, copper-amine complex and copper-amine complex/carboxylic acid salts

Catalysts Types	**Cream time (sec)**	**Gel time (sec)**	**Tack free time (sec)**	**Rise time (sec)**	**Density (kg/m^3)**	**Height (cm)**
*DMCHA (ref.)	15	25	178	128	37.4	14.6
$Cu(OAc)_2(en)_2$	30	35	78	103	36.4	15.5
$Cu(OAc)_2(trien)$	33	45	102	137	38.3	14.5
$Cu(OAc)_2(en)_2$/Sal (1:0.5)	32	45	106	138	37.7	15.0
$Cu(OAc)_2(en)_2$/Sal (1:1)	34	60	129	160	38.2	14.3
$Cu(OAc)_2(en)_2$/Sal (1:1.5)	35	73	148	173	38.2	14.3
$Cu(OAc)_2(trien)$/Sal (1:0.25)	34	55	125	171	39.5	14.0
$Cu(OAc)_2(trien)$/Sal (1:0.5)	35	64	137	178	40.8	13.5
$Cu(OAc)_2(trien)$/Sal (1:0.75)	36	76	179	195	39.9	13.5
$Cu(OAc)_2(trien)$/Sal (1:1)	36	102	202	218	42.2	12.6
$Cu(OAc)_2(en)_2$/Ac (1:0.5)	34	43	83	112	35.3	15.8
$Cu(OAc)_2(en)_2$/Ac (1:1)	36	48	89	113	34.8	15.8
$Cu(OAc)_2(en)_2$/Ac (1:1.5)	36	55	93	120	35.5	15.7

Table 4.2 Reaction times of RPUR foams prepared at the NCO index of 100 and catalyzed by DMCHA, copper-amine complex and copper-amine complex/carboxylic acid salts (continuted)

Catalysts Types	**Cream time (sec)**	**Gel time (sec)**	**Tack free time (sec)**	**Rise time (sec)**	**Density (kg/m^3)**	**Height (cm)**
$Cu(OAc)_2(en)_2$/Ac (1:2)	36	55	97	125	33.7	16.4

4.2.3.1 Effect of carboxylic acid content on reaction time

The effect of carboxylic acid content on reaction time of RPUR foams were investigated as shown in Figures 4.9-4.11. The target of this study was to increase gel time, while tack free time was not too slow when compared with DMCHA. The gel time of 60 sec was long enough for pouring the mixture of foam formulation into a mold. From the catalytic activity results in Table 4.2, DMCHA gave the shortest gel time (25 seconds) and tack free time was longer than rise time. When using copper-amine complexes [$Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien)] as catalysts, the gel times were 35 and 45 seconds, respectively and these catalysts gave shorter tack free time than DMCHA. Both $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) had the problem about the formation of holes at the bottom of the sample.

In the case of copper-ethylenediamine complex/salicylic acid salt [$Cu(OAc)_2(en)_2$/Sal], variation of mole ratio between $Cu(OAc)_2(en)_2$:salicylic acid at 1:0.5, 1:1 and 1:1.5 indicated that an increase in the amount of salicylic acid increased the reaction time. It was found that $Cu(OAc)_2(en)_2$/Sal (1:1) was the most suitable catalyst. $Cu(OAc)_2(en)_2$/Sal (1:1) gave the gel time at 60 seconds and the foam had good dimension stability. The holes at the bottom of the sample was not found. When the amount of salicylic acid was increased, $Cu(OAc)_2(en)_2$/Sal (1:1.5) gave RPUR foam having dark brown color, rough surface and having small holes at the bottom of the sample. In comparison between $Cu(OAc)_2(en)_2$/Sal (1:1) and $Cu(OAc)_2(en)_2$, the reaction time increased, density of foam increased and height of foams decreased.

For copper-ethylenediamine complex/acetic acid salt [$Cu(OAc)_2(en)_2$/Ac], variation of mole ratio between $Cu(OAc)_2(en)_2$:acetic acid at 1:0.5, 1:1, 1:1.5 and 1:2 gave slight delay in the reaction time. The obtained RPUR foams had dark brown color, rough surface and having small holes at the bottom of the sample.

For copper-triethylenetetramine complex/salicylic acid salt [$Cu(OAc)_2$(trien)/Sal], variation of mole ratio between $Cu(OAc)_2$(trien):salicylic acid at 1:0.25, 1:0.5, 1:0.75 and 1:1 indicated that an increase in the amount of salicylic acid increased the reaction time. $Cu(OAc)_2$(trien)/Sal (1:0.5) was the optimum catalyst, which had gel time at 64 seconds. The holes at the bottom of the sample was not found. When using the mole ratio of salicylic acid was greater than 0.5, the tack free time was too long and therefore not suitable for application.

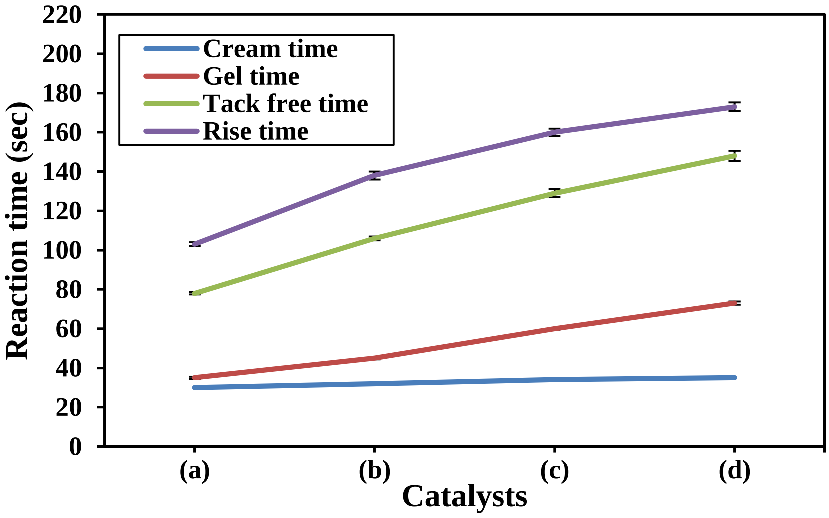


Figure 4.9 Reaction times of RPUR foams catalyzed (a) $Cu(OAc)_2(en)_2$; (b) $Cu(OAc)_2(en)_2$/Sal (1:0.5); (c) $Cu(OAc)_2(en)_2$/Sal (1:1); (d) $Cu(OAc)_2(en)_2$/Sal (1:1.5)

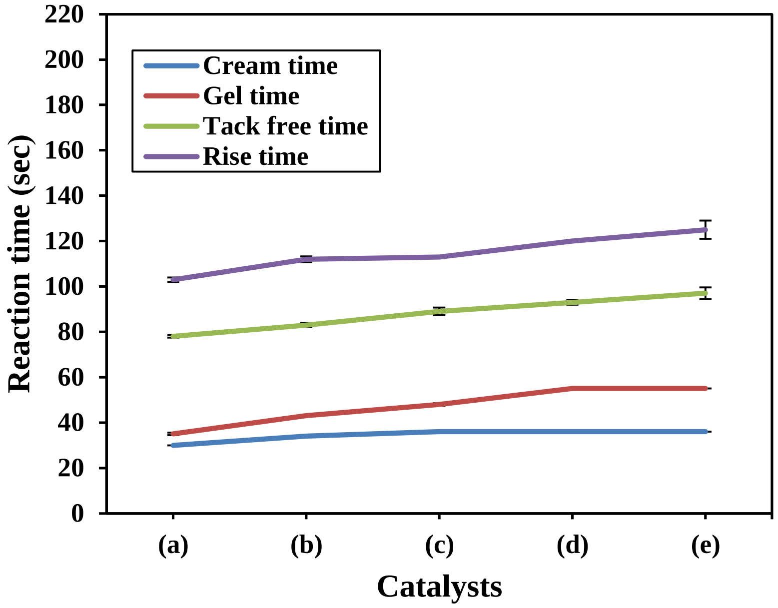


Figure 4.10 Reaction times of RPUR foams catalyzed (a) $Cu(OAc)_2(en)_2$; (b) $Cu(OAc)_2(en)_2/Ac$ (1:0.5); (c) $Cu(OAc)_2(en)_2/Ac$ (1:1); (d) $Cu(OAc)_2(en)_2/Ac$ (1:1.5); (e) $Cu(OAc)_2(en)_2/Ac$ (1:2)

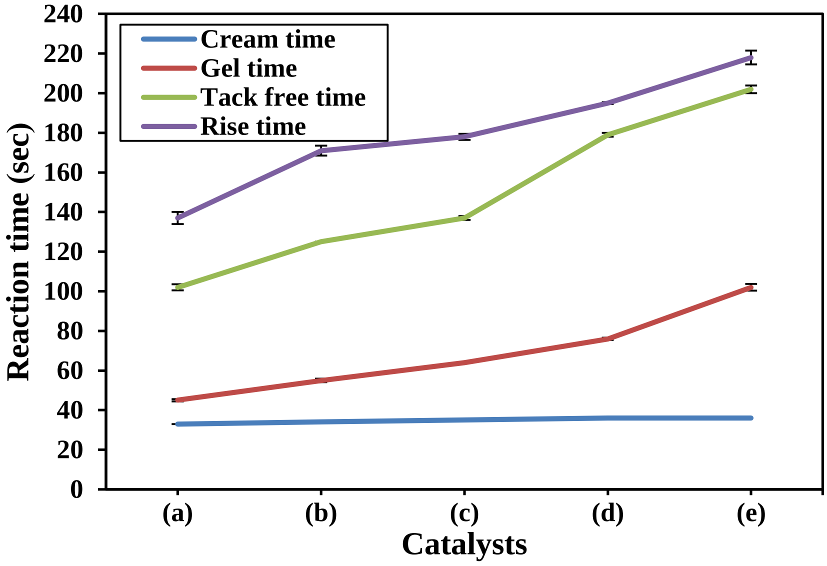


Figure 4.11 Reaction times of RPUR foams catalyzed (a) $Cu(OAc)_2(trien)$; (b) $Cu(OAc)_2(trien)/Sal$ (1:0.25); (c) $Cu(OAc)_2(trien)/Sal$ (1:0.5); (d) $Cu(OAc)_2(trien)/Sal$ (1:0.75); (e) $Cu(OAc)_2(trien)/Sal$ (1:1)

From the results described above, $Cu(OAc)_2(en)_2$/Sal (1:1) and $Cu(OAc)_2$(trien)/Sal (1:0.5) were optimum catalysts for RPUR foam formulation, which gave gel time about 60 seconds and gave shorter tack free time than DMCHA.

4.2.4 Rise profiles

Rise profiles of RPUR foams were recorded from the height of foam in cup test method after mixing in the final step versus the time as shown in Figures 4.12-4.14. Rise time is the time when the foam stopped rising which is the time when CO_2 generation stops (blowing reaction is completed). Tack free time is the time when polymerization reaction is completed. Rise height (%) at the initial of reaction corresponds to cream time and maximum rise high (%) corresponds to rise time in Table 4.2. $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac had longer cream time at the initial of reaction than $Cu(OAc)_2(en)_2$ and exhibited a very quick rise curve in the latter stage. $Cu(OAc)_2$(trien)/Sal showed longer initial cream time than $Cu(OAc)_2$(trien). DMCHA showed faster cream time than $Cu(OAc)_2(en)_2$/Sal and $Cu(OAc)_2(en)_2$/Ac and $Cu(OAc)_2$(trien)/Sal.

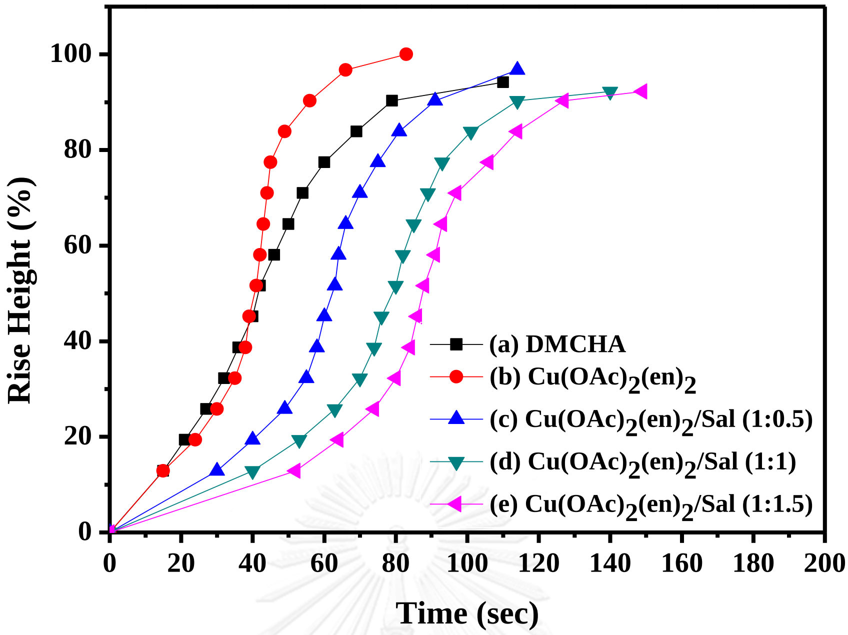


Figure 4.12 Rise profiles of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal at different mole ratios

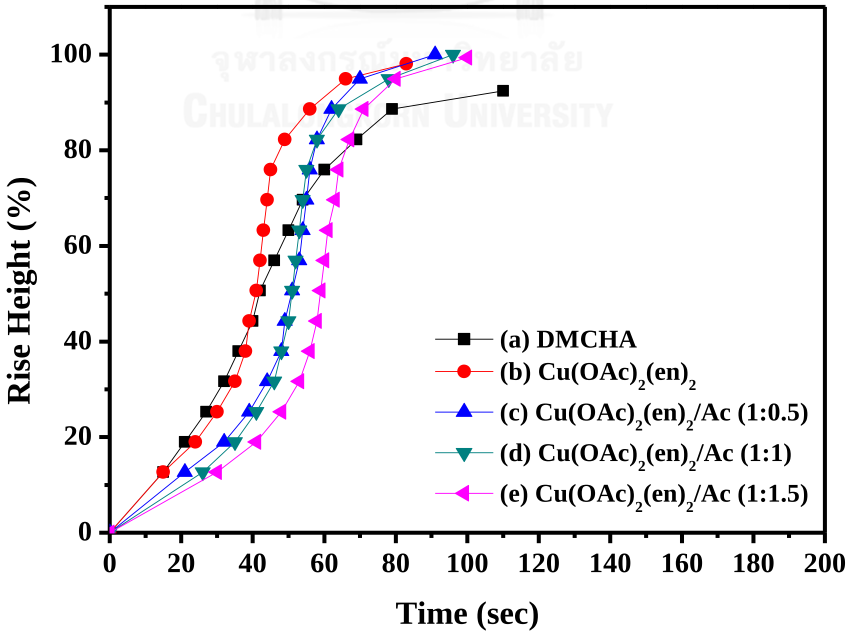


Figure 4.13 Rise profiles of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Ac at different mole ratios

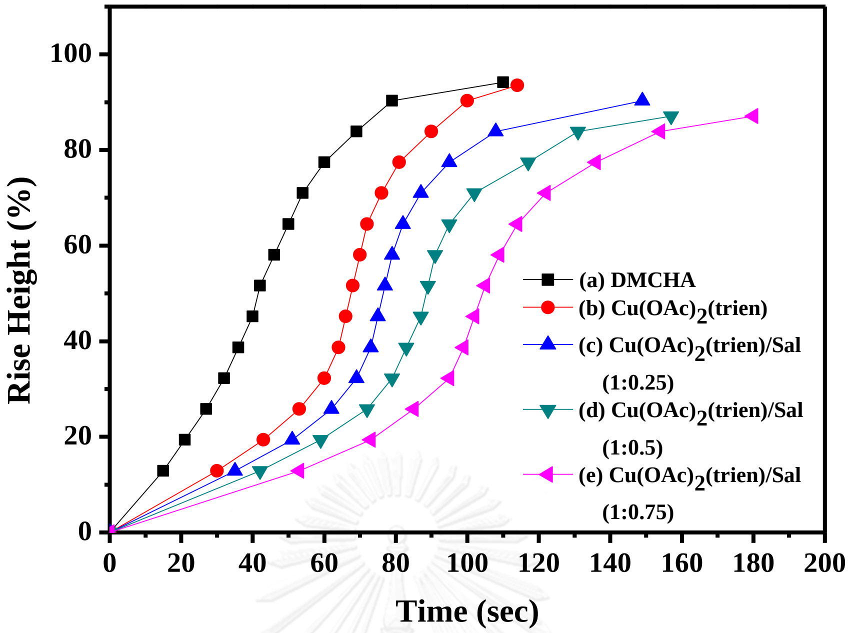


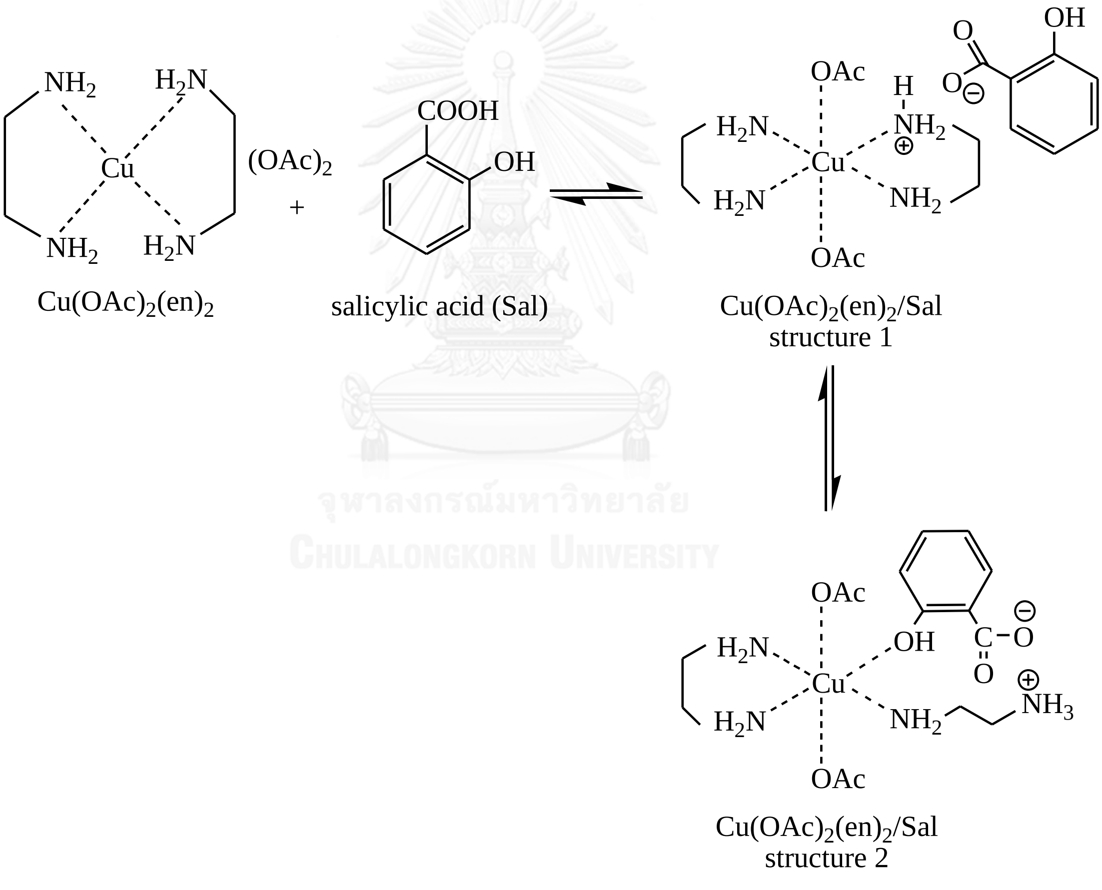
Figure 4.14 Rise profiles of RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ at different mole ratios

4.2.5 Proposed mechanism of copper-amine complex/carboxylic acid salt formation

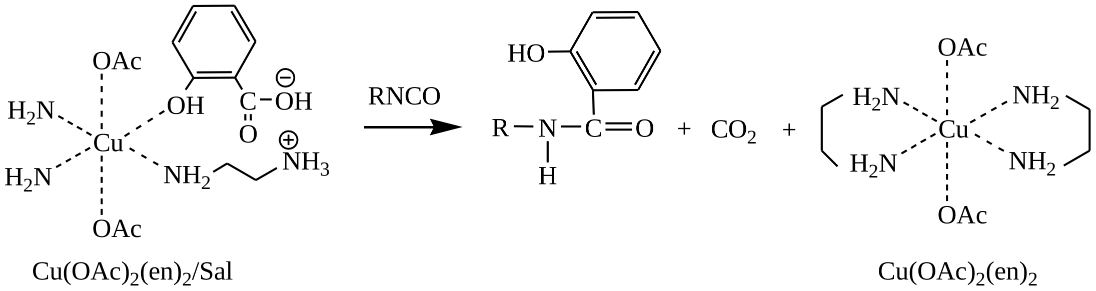
The obtained experimental data indicated that copper-amine complex/salicylic acid salts, namely $Cu(OAc)_2(en)_2/Sal$ and $Cu(OAc)_2(trien)/Sal$ were delayed action catalysts. The catalytic mechanism of namely $Cu(OAc)_2(en)_2/Sal$ is proposed in two steps as follows: In the first step, a nitrogen atom in $Cu(OAc)_2(en)_2$ was protonated by salicylic acid to give amine salt ($Cu(OAc)_2(en)_2/Sal$ structure 1, Scheme 4.1). $Cu(OAc)_2(en)_2/Sal$ structure 1 could change to $Cu(OAc)_2(en)_2/Sal$ structure 2, where $–O^-$ of Sal coordinated with copper atom. This was because $–NH_3^+$ in $Cu(OAc)_2(en)_2/Sal$ might not coordinate very well with copper atom.

This resulted in longer initial cream time because nitrogen atom of $–NH_3^+$ in $Cu(OAc)_2(en)_2/Sal$ was less nucleophilic than $–NH_2$ in $Cu(OAc)_2(en)_2$. In the second step, the exothermic polymerization reaction increased the temperature and $Cu(OAc)_2(en)_2/Sal$ was thermally dissociated to give $Cu(OAc)_2(en)_2$ and salicylic acid, which could undergo a reaction with isocyanate to give amide and carbon dioxide (Scheme 4.2). Since $–NH_2$ in $Cu(OAc)_2(en)_2$ had better catalytic activity than $–NH_3^+$ in $Cu(OAc)_2(en)_2$/Sal, the catalytic activity was fast in the latter stage. Therefore, $Cu(OAc)_2(en)_2$/Sal was a delayed action catalyst.

The catalytic mechanism of $Cu(OAc)_2$(trien)/Sal was proposed to be similar to that of $Cu(OAc)_2(en)_2$/Sal. When acetic was used instead of salicylic acid, $Cu(OAc)_2(en)_2$/Ac did not show a delayed action mechanism. This might be because $Cu(OAc)_2(en)_2$/Ac did not form $–NH_3^+$ group. Since $Cu(OAc)_2(en)_2$/Sal could change the form between structure 1 and structure 2, the $–NH_3^+Cu(OAc)_2(en)_2$/Sal should have better stability than that in $Cu(OAc)_2(en)_2$/Ac.



Scheme 4.1 Reaction between copper-ethylenediamine complex with salicylic acid to give $Cu(OAc)_2(en)_2$/Sal



Scheme 4.2 Dissociation of copper-ethylenediamine complex/salicylic acid salt [$Cu(OAc)_2(en)_2$/Sal] to give $Cu(OAc)_2(en)_2$

4.2.6 Foaming Temperature

The temperature profiles of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(en)_2$/Sal(1:1), $Cu(OAc)_2(en)_2$/Ac (1:1.5), $Cu(OAc)_2$(trien) and $Cu(OAc)_2$(trien)/Sal (1:1) at NCO index 100 were investigated as shown in Figures 4.15-4.16. It was found that the all foams were the same temperature profile and the polymerization reaction was exothermic. The maximum core temperature was in the range 126.4-131.9 °C (Table 4.3).

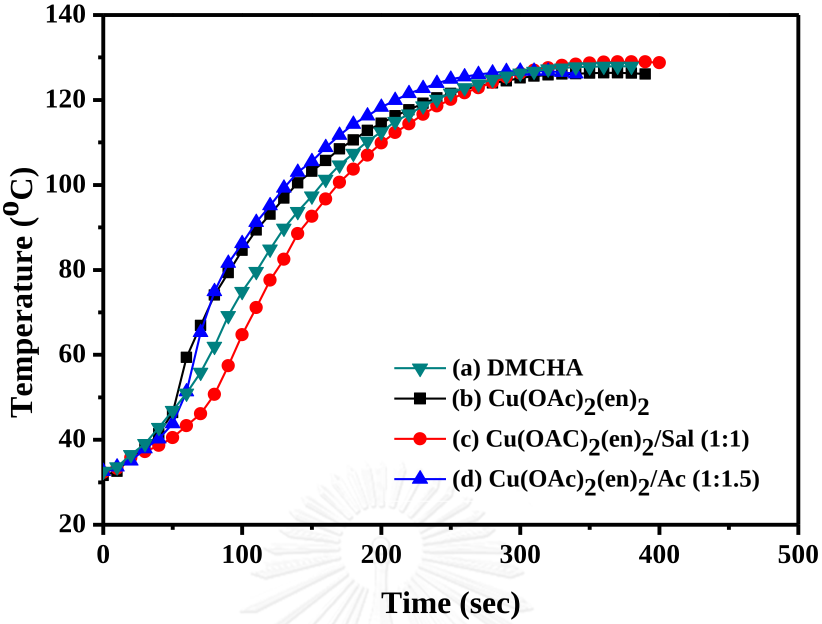


Figure 4.15 Temperature profile of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2(en)_2$/Sal (1:1); (d) $Cu(OAc)_2(en)_2$/Ac (1:1.5)

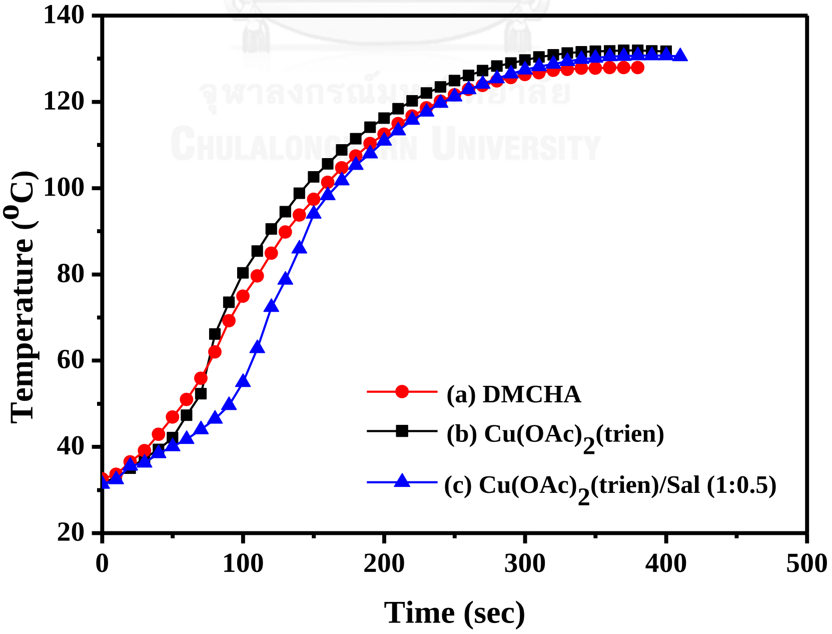


Figure 4.16 Temperature profile of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(OAc)_2$(trien); (c) $Cu(OAc)_2$(trien)/Sal (1:1)

Table 4.3 The maximum core temperature of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(en)_2$/Sal (1:1), $Cu(OAc)_2(en)_2$/Ac (1:1.5), $Cu(OAc)_2$(trien) and $Cu(OAc)_2$(trien)/Sal (1:0.5)

Catalysts	**Maximum core temperature (°C)**	**Starting times (sec) at T_{max}**
DMCHA	127.9	360
$Cu(OAc)_2(en)_2$	126.4	360
$Cu(OAc)_2(en)_2$/Sal (1:1)	129.0	370
$Cu(OAc)_2(en)_2$/Ac (1:1.5)	126.8	300
$Cu(OAc)_2$(trien)	131.9	370
$Cu(OAc)_2$(trien)/Sal (1:0.5)	130.7	380

4.2.7 Characterization of RPUR foams

ATR-FTIR spectroscopy was used to investigate the polymerization of RPUR foam system. IR spectra of starting materials, polyether polyol, polymeric MDI, and RPUR foams catalyzed by copper-amine complexes/carboxylic acid salts are shown in Figure 4.32. Polyether polyol showed the broad band at 3409 cm^{-1} (stretching vibration of hydroxyl groups). Polymeric MDI showed high intensity of NCO absorption band at 2277 cm^{-1}. All RPUR foams had similar IR absorption as follows : NH stretching of urethane and urea at 3326 cm^{-1}, C=O stretching of urethane and urea at 1705 cm^{-1}, C-O of urethane at 1076 cm^{-1}, while the band at 1511 cm^{-1} could be attributed to NH-bending vibration and C-N stretching vibration of urethane and urea groups. The band at 1222 cm^{-1} was associated with the characteristic stretching vibration of C-N-H bond of urethane and urea [26].

From IR spectra of RPUR foams catalyzed by DMCHA and copper amine complex/carboxylic acid salts, the peak of isocyanate groups at 2277 cm^{-1} was not found. This indicated that the reactions of isocyanate with hydroxyl groups and water were completed.

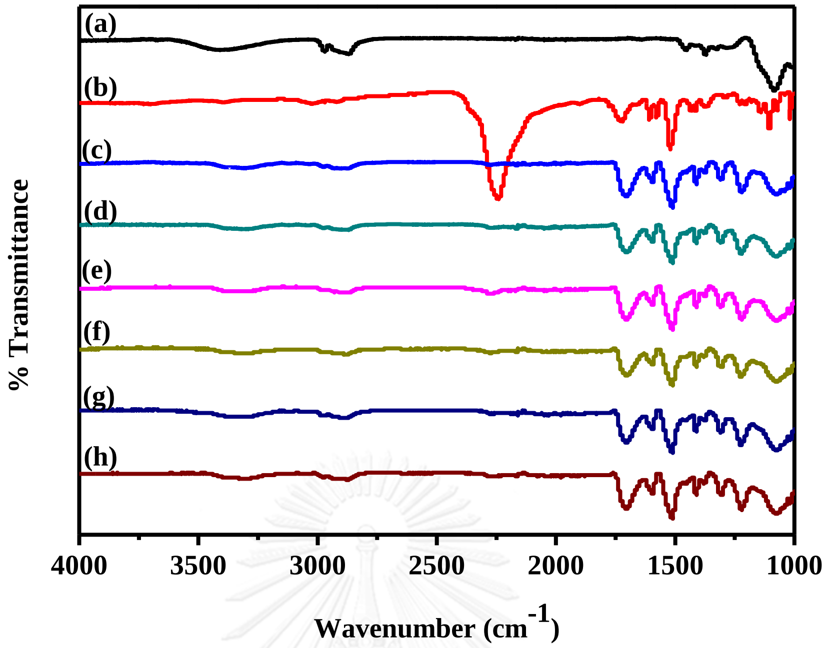


Figure 4.17 IR spectra of starting materials (a) polyether polyol; (b) polymeric MDI, RPUR foams catalyzed by (c) DMCHA; (d) $Cu(OAc)_2(en)_2$; (e) $Cu(OAc)_2(en)_2$/Sal (1:1); (f) $Cu(OAc)_2(en)_2$/Ac (1:1.5); (g) $Cu(OAc)_2$(trien); (h) $Cu(OAc)_2$(trien)/Sal (1:0.5)

4.2.8 Isocyanate (NCO) conversion of RPUR foams

The NCO conversion of RPUR foams catalyzed by DMCHA and copper-amine complex/carboxylic acid salts is shown in Table 4.5. The NCO conversion was defined as the ratio between isocyanate peak area at time 0 and isocyanate peak area at time t as shown in following equation.

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

where;

NCO^{f} = the area of isocyanate absorbance peak area at time t (Figures 4.17 c-h)

NCO^i = the area of isocyanate absorbance peak area at initial time 0 (Figure 4.17 b)

Quantity of free NCO in RPUR foams were normalized by aromatic ring absorption band at 1595 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
Urethane	1220	-C-O-

Table 4.5 NCO conversion of RPUR foams catalyzed by DMCHA and copper-amine complex/carboxylic acid salts

Catalysts Types	Peak Area		NCO conversion (%)
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	
DMCHA	0.316	1.809	99.82
Cu(OAc)$_2$(en)$_2$	0.344	1.537	99.77
Cu(OAc)$_2$(en)$_2$/Sal(1:0.5)	0.506	1.674	99.69
Cu(OAc)$_2$(en)$_2$/Sal (1:1)	0.524	1.703	99.69
Cu(OAc)$_2$(en)$_2$/Sal (1:1.5)	0.574	1.673	99.65
Cu(OAc)$_2$(en)$_2$/Ac (1:0.5)	0.388	1.154	99.66
Cu(OAc)$_2$(en)$_2$/Ac (1:1)	0.527	1.399	99.62
Cu(OAc)$_2$(en)$_2$/Ac (1:1.5)	0.440	1.408	99.68
Cu(OAc)$_2$(en)$_2$/Ac (1:2)	0.583	1.630	99.64
Cu(OAc)$_2$(trien)	0.422	1.739	99.75
Cu(OAc)$_2$(trien)/Sal (1:0.25)	0.549	1.670	99.66
Cu(OAc)$_2$(trien)/Sal (1:0.5)	0.541	1.826	99.70
Cu(OAc)$_2$(trien)/Sal (1:0.75)	0.484	1.531	99.68
Cu(OAc)$_2$(trien)/Sal (1:1)	0.523	1.330	99.60

4.3 Compressive properties of RPUR foams

The compression stress-strain curves of RPUR foams catalyzed by copper complex/carboxylic acid salts are shown in Figures 4.18-4.19. RPUR foams catalyzed by Cu(OAc)$_2$(en)$_2$, Cu(OAc)$_2$(trien), Cu(OAc)$_2$(en)$_2$/Sal (1:1), Cu(OAc)$_2$(en)$_2$/Ac (1:1.5) and Cu(OAc)$_2$(trien) (1:0.5) were tested in compression according to ASTM D 695 and compared to the foam prepared by DMCHA . From the result of compressive properties, the parallel compressive strength of foams was higher than that of perpendicular compression direction. Because of this, the foam cells were elongated in the direction of the rise. All foams were anisotropic materials, which the compressive properties depend on direction of measurement. Generally, a high compressive strength in one direction occurred at the expense of the compressive strength in the other directions which were could be explained by the foam cell model as shown in Figure 4.21. From the compressive strength, It was found that RPUR foam catalyzed by $Cu(OAc)_2$(trien)/Sal (1:0.5) had highest compressive strength (292.2 kPa) in parallel direction.

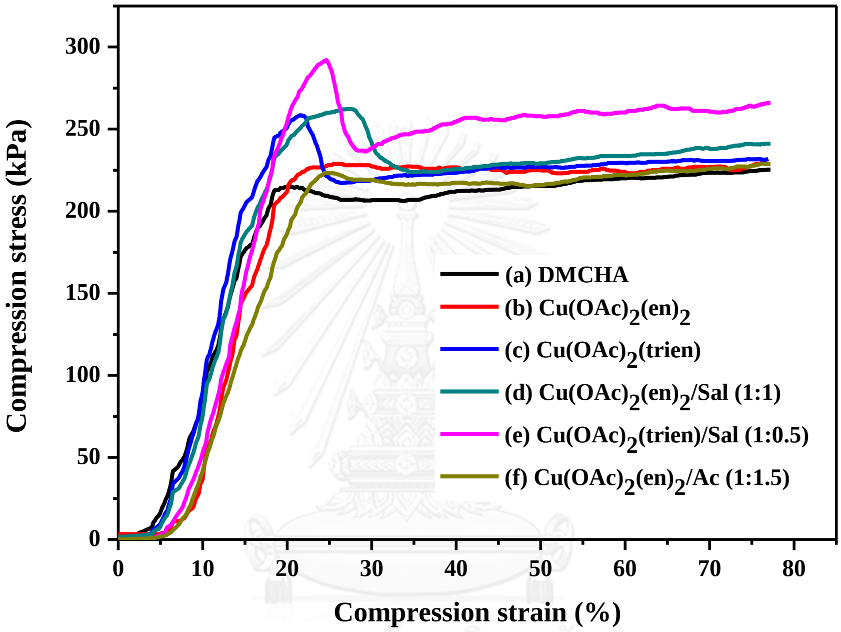


Figure 4.18 Compression stress-strain curves of RPUR foams in parallel to the foam rising direction.

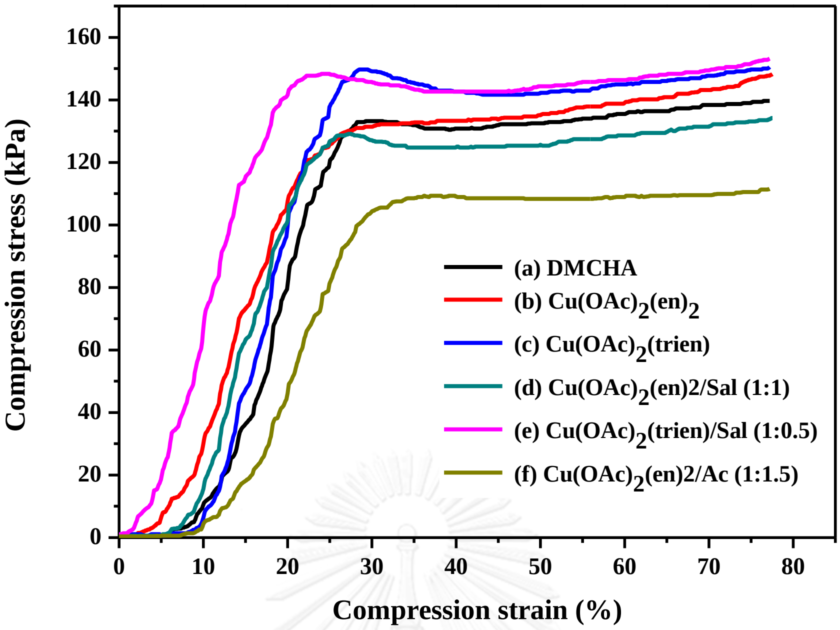


Figure 4.19 Compression stress-strain curves of RPUR foams in perpendicular to the foam rising direction.

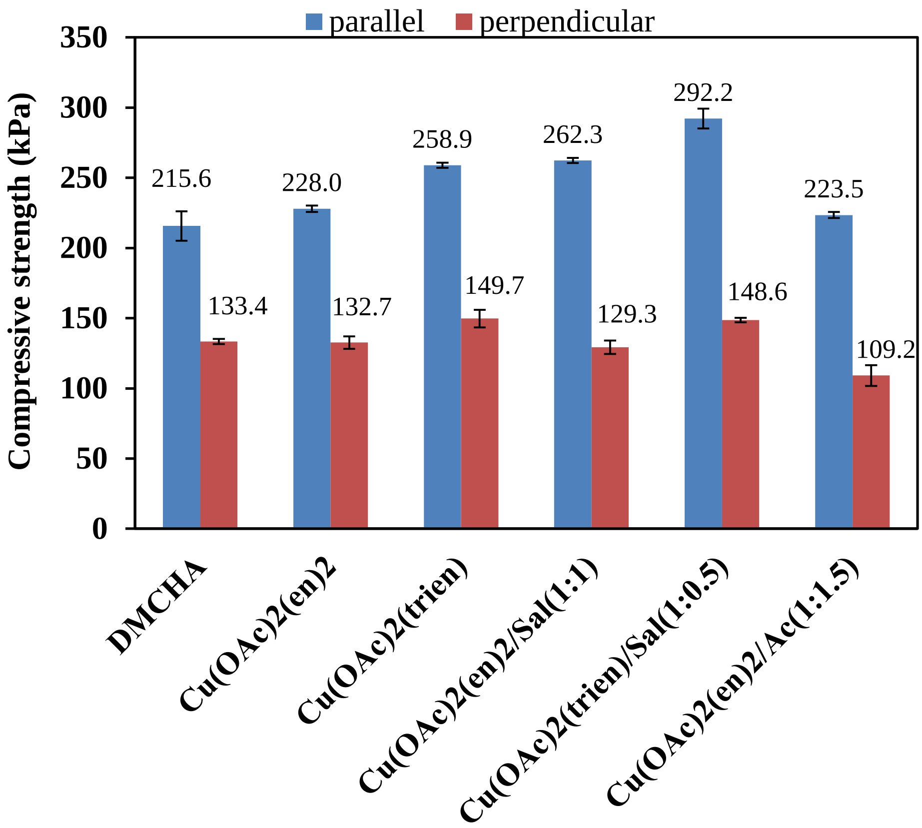
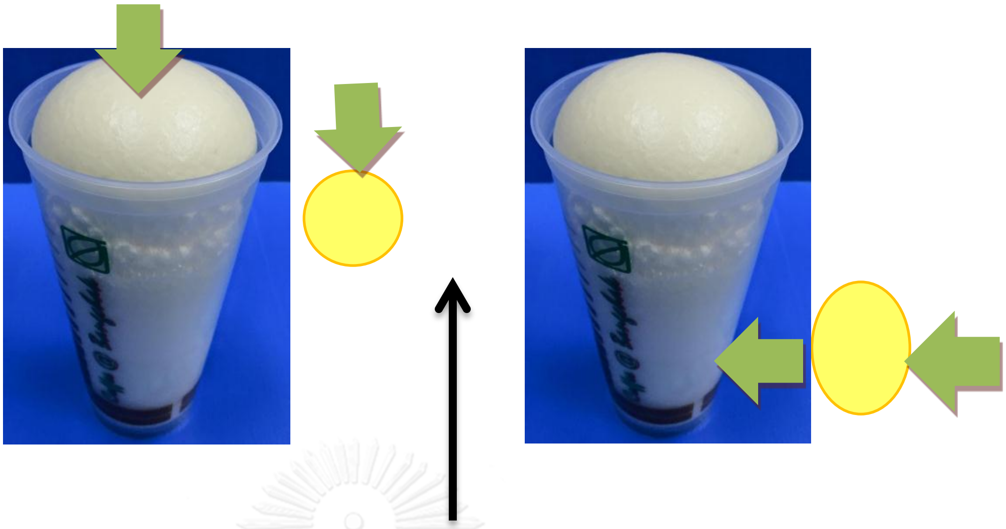


Figure 4.20 Compressive strength of RPUR foams

Table 4.6 Compression stress-strain curves of RPUR foams

Catalysts	**Compressive strength (kPa) in parallel**	**Compressive strength (kPa) in perpendicular**
DMCHA	215.6 ± 10.44	133.4 ± 1.75
$Cu(OAc)_2(en)_2$	228.0 ± 2.34	132.7 ± 4.45
$Cu(OAc)_2(trien)$	258.9 ± 1.85	149.7 ± 6.20
$Cu(OAc)_2(en)_2/Sal$ (1:1)	262.3 ± 1.78	129.3 ± 4.70
$Cu(OAc)_2(trien)/Sal$ (1:0.5)	292.2 ± 7.05	148.6 ± 1.64
$Cu(OAc)_2(en)_2/Ac$ (1:1.5)	223.5 ± 2.11	109.2 ± 7.40

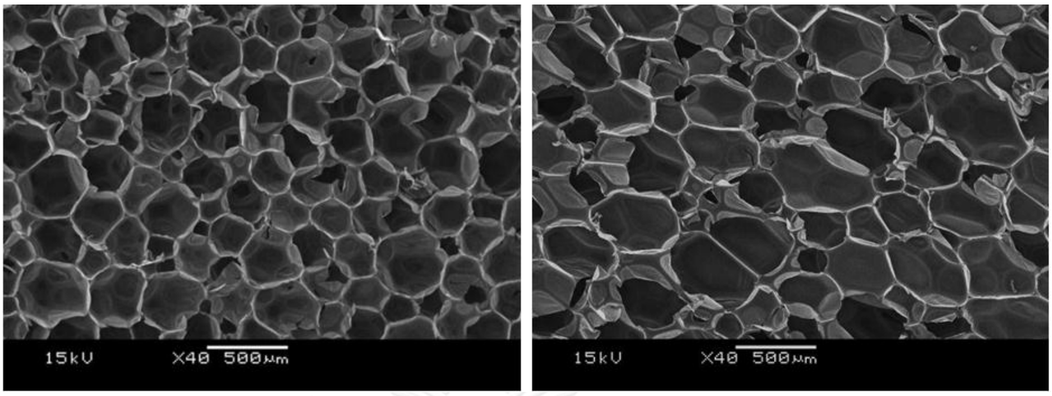


(a) (b)

Figure 4.21 (a) spherical cells, equal properties in all directions; (b) ellipsoid cells, which properties depend on direction

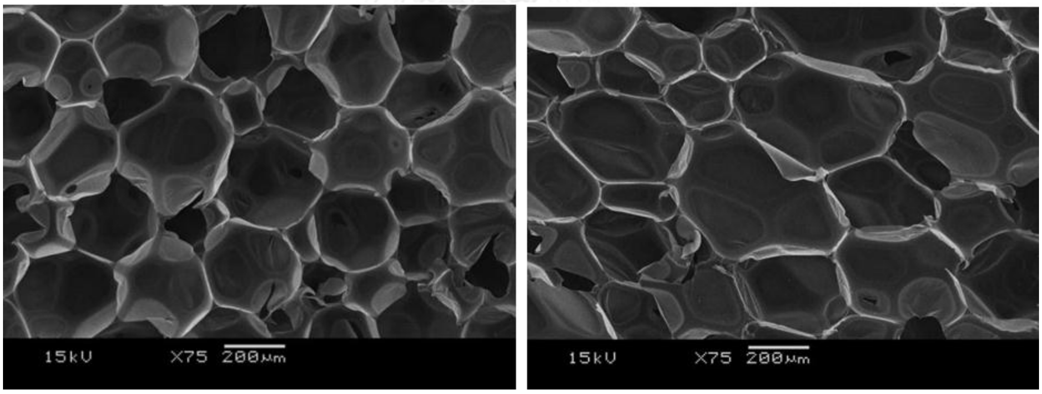
4.4 RPUR foams morphology

Morphology of RPUR foam catalyzed by DMCHA, $Cu(OAc_2en)_2$, $Cu(OAc)_2(en)_2$/Sal (1:1), $Cu(OAc)_2(trien)$ and $Cu(OAc)_2(trien)$/Sal (1:0.5) in parallel and perpendicular direction of foam rising are shown in Figures 4.22-4.31. It was found that all RPUR foams had closed cell. The foam cells in the top view were spherical shape and the side view is an elliptical shape. This indicated that the foams were anisotropic materials. The average cell size of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(en)_2$/Sal (1:1), $Cu(OAc)_2(trien)$ and $Cu(OAc)_2(trien)$/Sal (1:0.5) are shown in Tables 4.7-4.8. In the case of spherical shape, the cell size was measured from cell size$_1$ and cell size$_2$ (Figure 4.32a). In the case of elliptical shape, the size of cell was measured from short length (cell size$_1$) and long length (cell size$_2$) (Figure 4.32b). RPUR foam catalyzed by $Cu(OAc)_2(trien)$/Sal (1:0.5) had smaller cell size than RPUR foam catalyzed by DMCHA. This result indicated that the small cell size gave more strength to the RPUR foam.



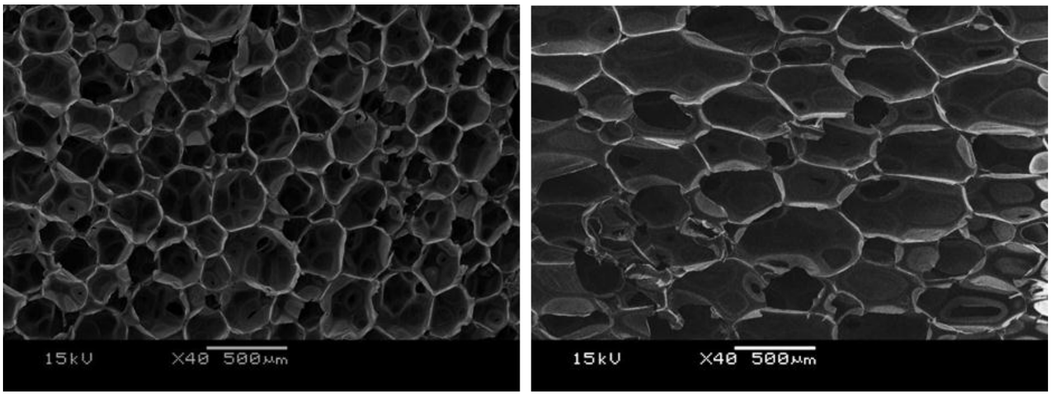
(a) (b)

Figure 4.22 SEM of RPUR foams catalyzed by DMCHA (a) top view; (b) side view (40x)



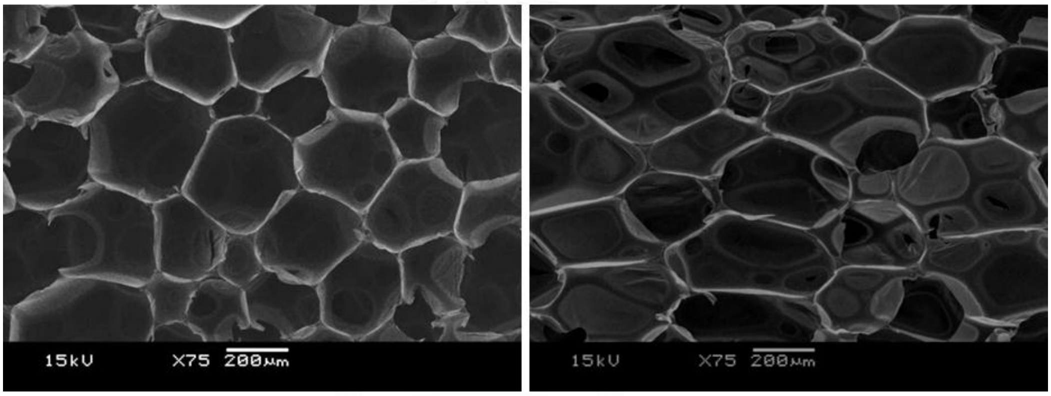
(a) (b)

Figure 4.23 SEM of RPUR foams catalyzed by DMCHA (a) top view; (b) side view (75x)



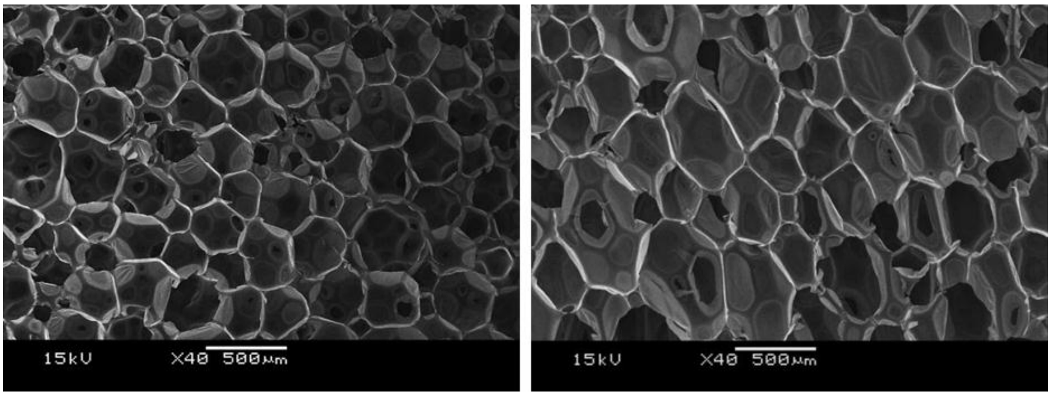
(a) (b)

Figure 4.24 SEM of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ (a) top view; (b) side view (40x)



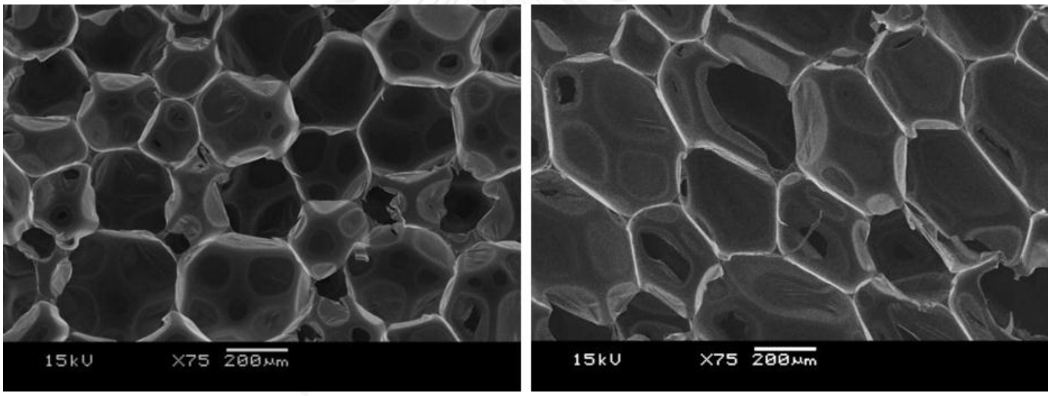
(a) (b)

Figure 4.25 SEM of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ (a) top view; (b) side view (75x)



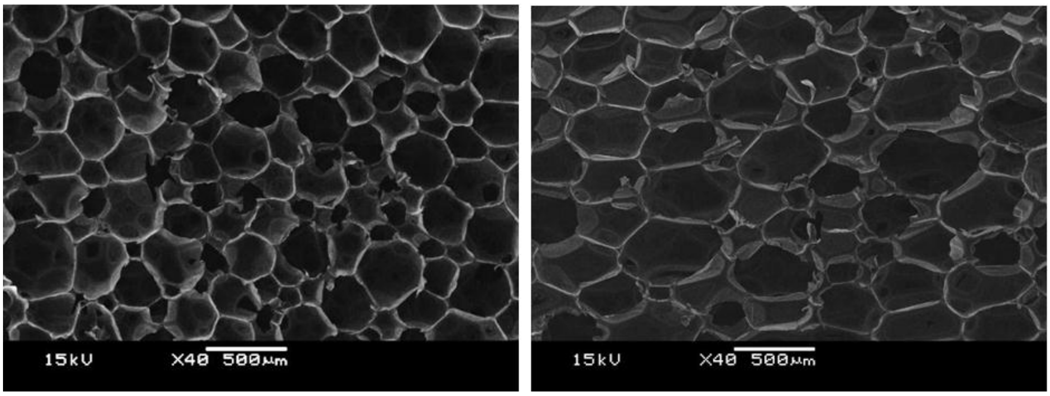
(a) (b)

Figure 4.26 SEM of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:1) (a) top view; (b) side view (40x)



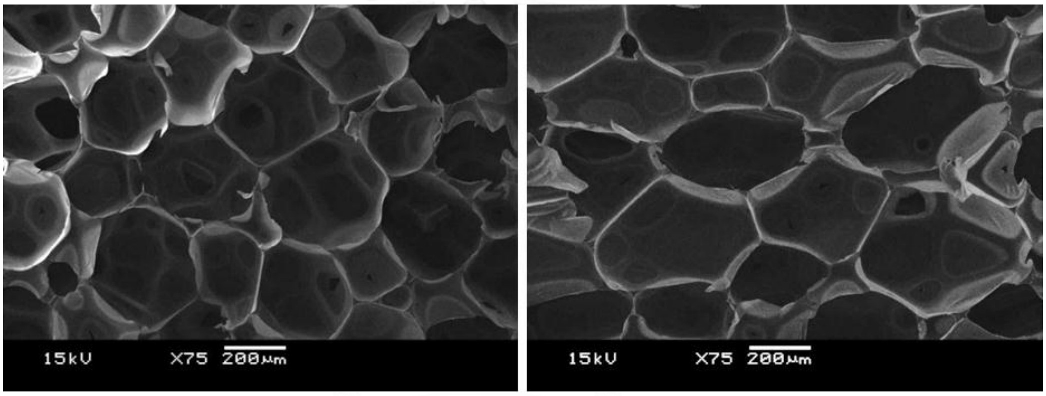
(a) (b)

Figure 4.27 SEM of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:1) (a) top view; (b) side view (75x)



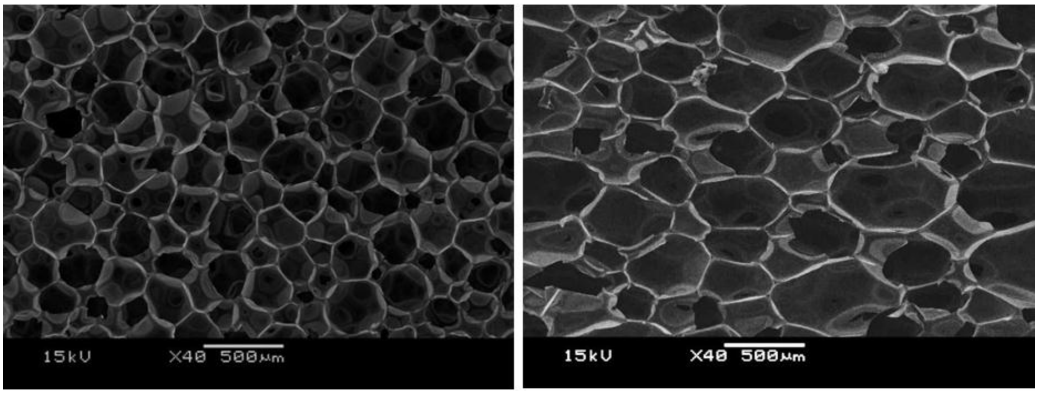
(a) (b)

Figure 4.28 SEM of RPUR foams catalyzed by $Cu(OAc)_2(trien)$ (a) top view; (b) side view (40x)



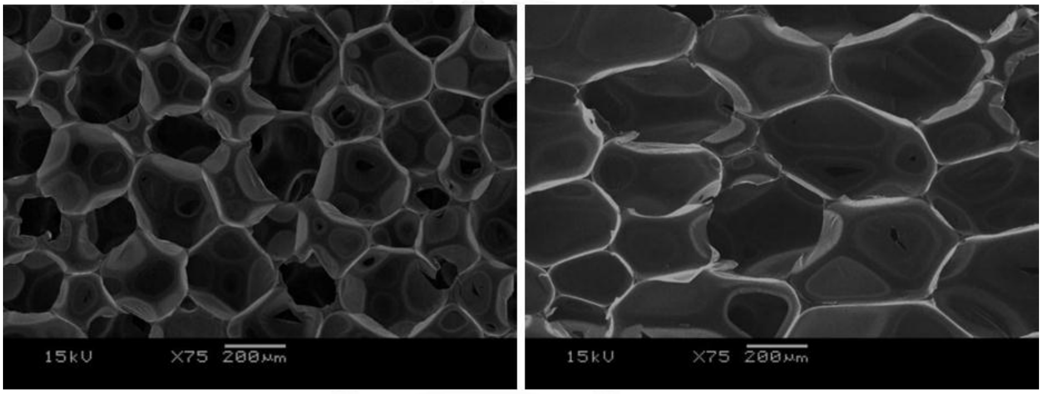
(a) (b)

Figure 4.29 SEM of RPUR foams catalyzed by $Cu(OAc)_2(trien)$ (a) top view; (b) side view (75x)



(a) (b)

Figure 4.30 SEM of RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:0.5) (a) top view; (b) side view (40x)



(a) (b)

Figure 4.31 SEM of RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:0.5) (a) top view; (b) side view (75x)

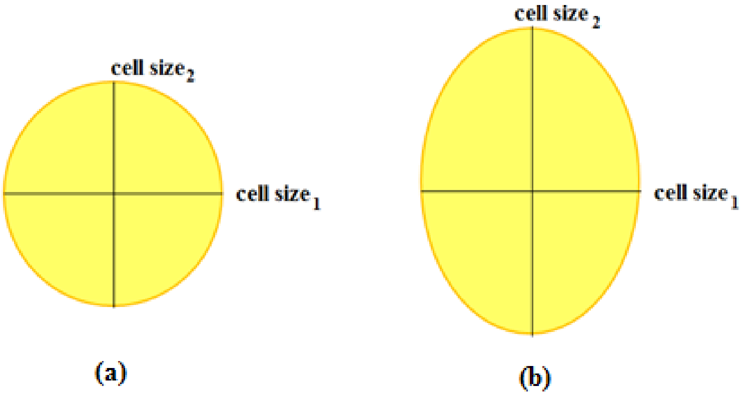


Figure 4.32 Measurement of cell size

Table 4.7 The cell size (top view) of RPUR foams catalyzed by DMCHA and copper-amine complex/carboxylic acid salts

Catalysts	Top view	
	Cell size$_1$ (μm)	Cell size$_2$ (μm)
*DMCHA (ref.)	296 ± 38.31	290 ± 35.39
Cu(OAc)$_2$(en)$_2$	279 ± 39.12	272 ± 39.42
Cu(OAc)$_2$(trien)	266 ± 43.71	262 ± 37.93
Cu(OAc)$_2$(en)$_2$/Sal (1:1)	263 ± 35.93	259 ± 31.07
Cu(OAc)$_2$(trien)/Sal (1:0.5)	236 ± 35.98	231 ± 36.56

Table 4.8 The cell size (side view) of RPUR foams catalyzed by DMCHA and copper-amine complex/carboxylic acid salts

Catalysts	Side view	
	Cell size$_1$ (μm)	Cell size$_2$ (μm)
*DMCHA (ref.)	294 ± 38.66	415 ± 41.36
Cu(OAc)$_2$(en)$_2$	278 ± 39.05	419 ± 46.94
Cu(OAc)$_2$(trien)	264 ± 34.50	400 ± 43.33
Cu(OAc)$_2$(en)$_2$/Sal (1:1)	264 ± 22.45	423 ± 36.06
Cu(OAc)$_2$(trien)/Sal (1:0.5)	235 ± 28.64	403 ± 44.05

Appearances of RPUR foams obtained from cup test were investigated. The foam was cut across the top and the base (2 cm from the bottom of a cup) of the sample (Figures 4.33a and 4.33b, respectively). The foam was also cut along the side of the sample (Figure 4.33c). Morphology of RPUR foams are shown in Figures 4.34-4.47.

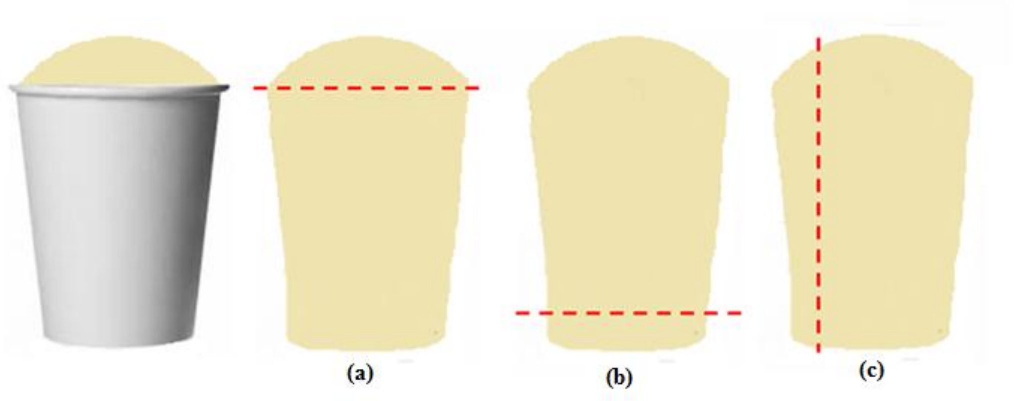


Figure 4.33 Cutting line for RPUR foams

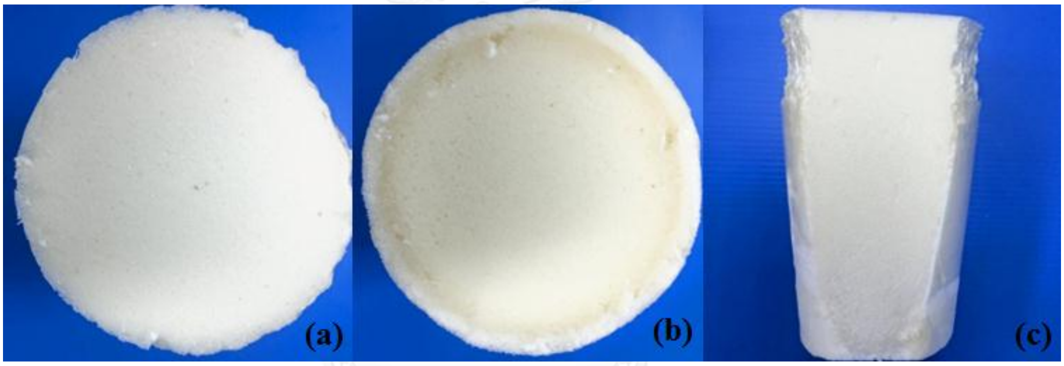


Figure 4.34 RPUR foams catalyzed by DMCHA (a) top; (b) bottom; (c) side of the foam sample

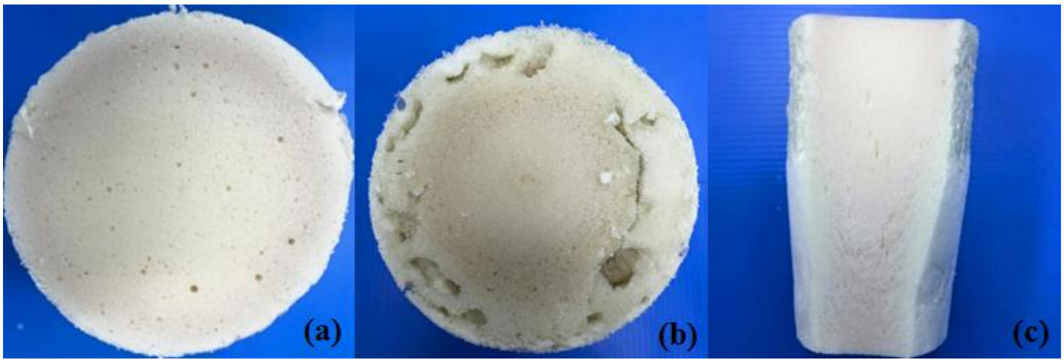


Figure 4.35 RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ (a) top; (b) bottom; (c) side of the foam sample

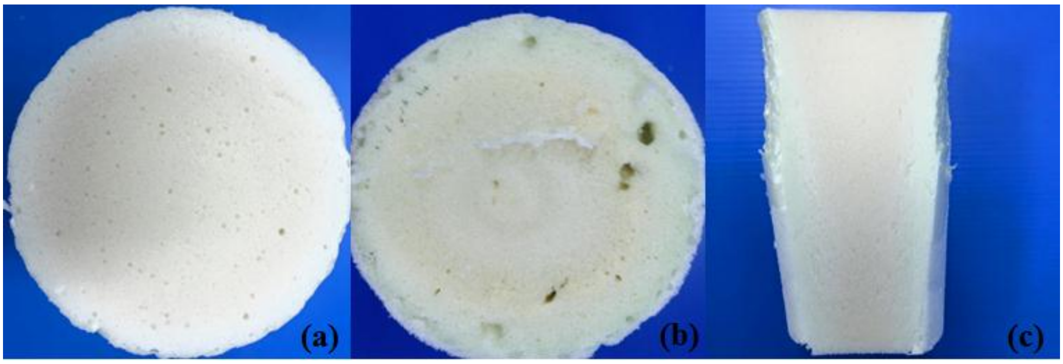


Figure 4.36 RPUR foams catalyzed by $Cu(OAc)_2(trien)$ (a) top; (b) bottom; (c) side of the foam sample

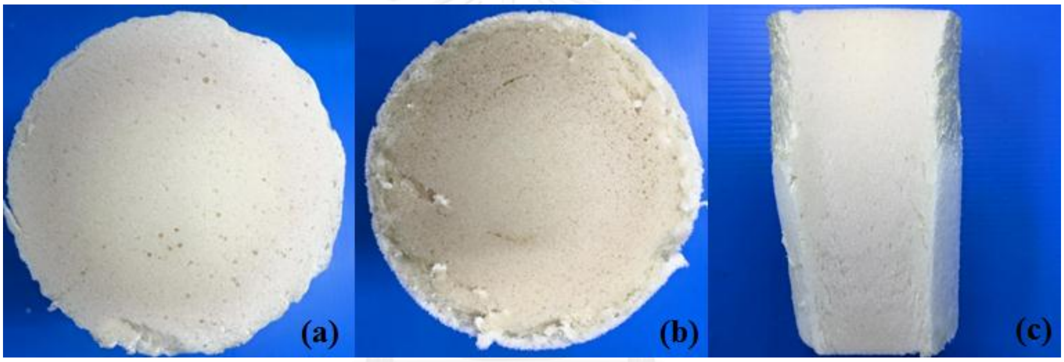


Figure 4.37 RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:0.5) (a) top; (b) bottom; (c) side of the foam sample

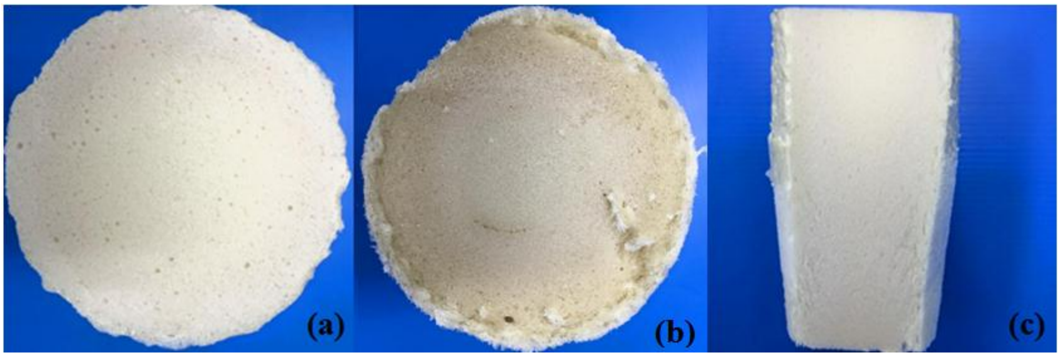


Figure 4.38 RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:1) (a) top; (b) bottom; (c) side of the foam sample

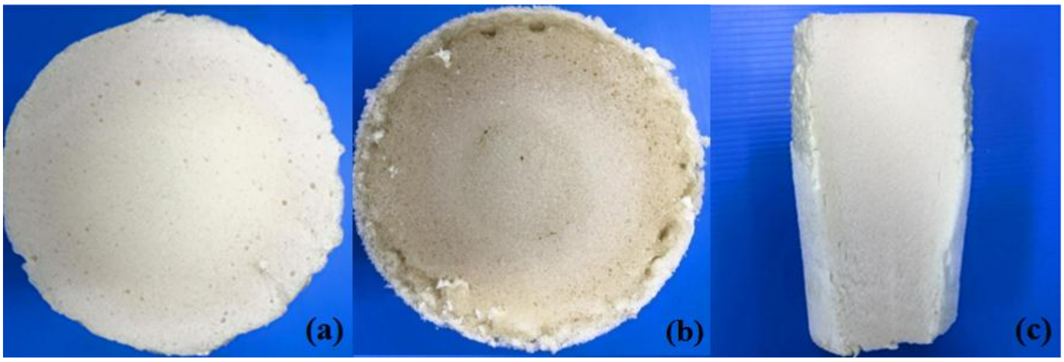


Figure 4.39 RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:1.5) (a) top; (b) bottom; (c) side of the foam sample

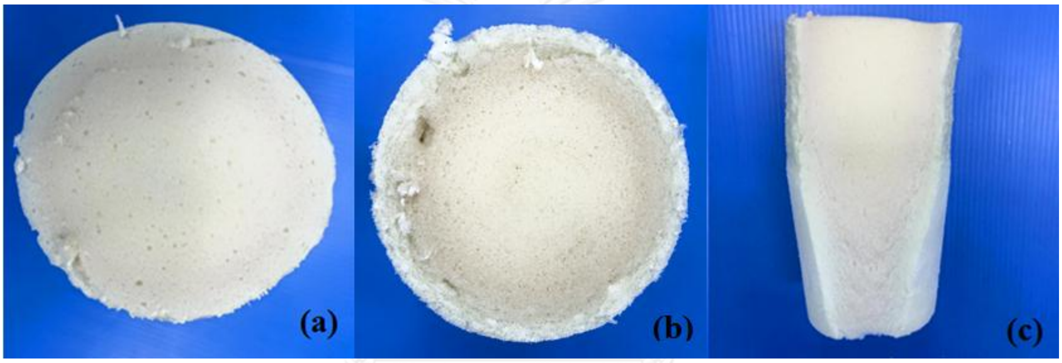


Figure 4.40 RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Ac (1:0.5) (a) top; (b) bottom; (c) side of the foam sample

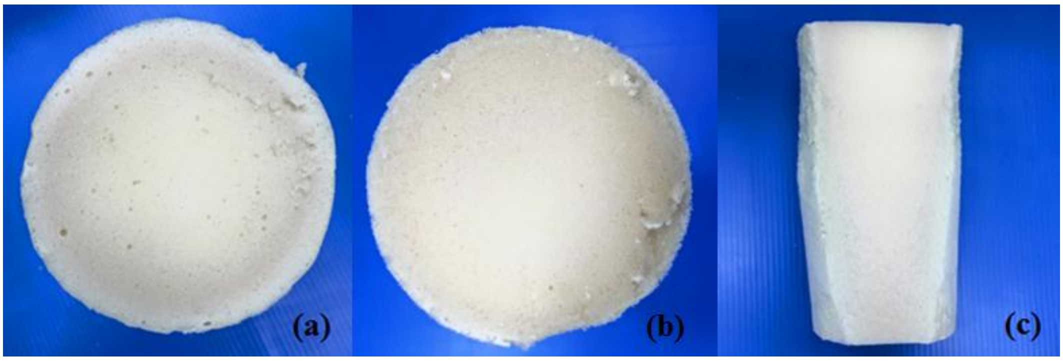


Figure 4.41 RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Ac (1:1) (a) top; (b) bottom; (c) side of the foam sample

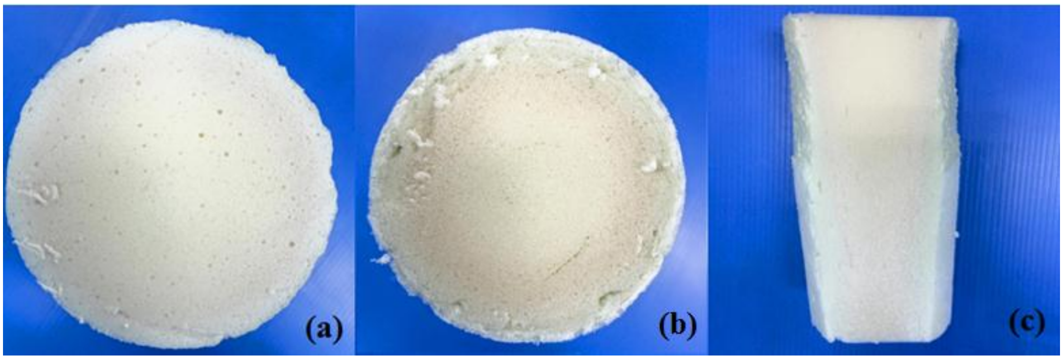


Figure 4.42 RPUR foams catalyzed by $Cu(OAc)_2(en)_2/Ac$ (1:1.5) (a) top; (b) bottom; (c) side of the foam sample

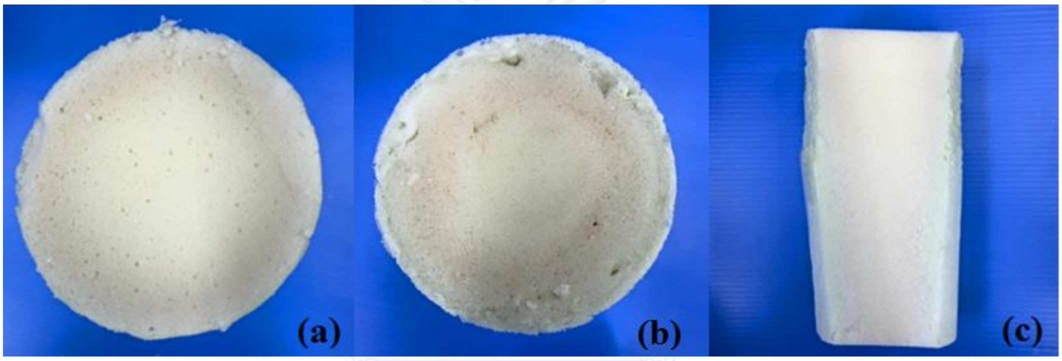


Figure 4.43 RPUR foams catalyzed by $Cu(OAc)_2(en)_2/Ac$ (1:2) (a) top; (b) bottom; (c) side of the foam sample

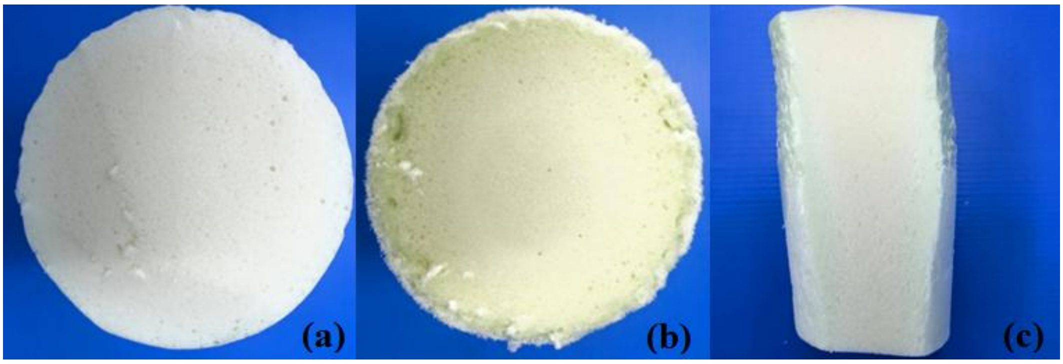


Figure 4.44 RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:0.25) (a) top; (b) bottom; (c) side of the foam sample

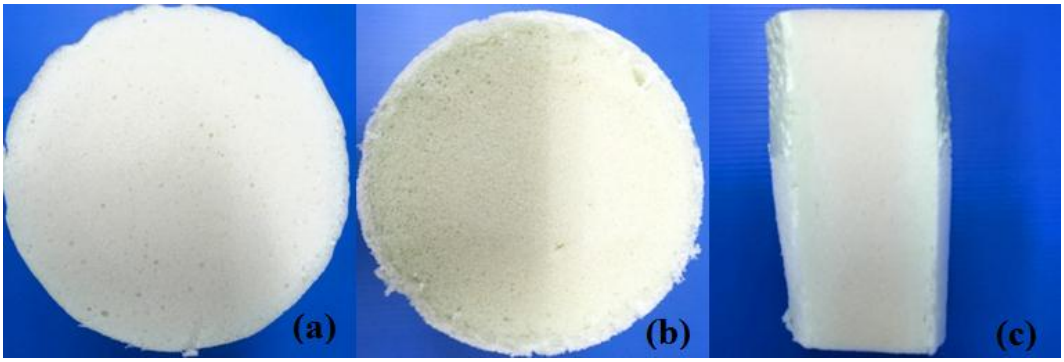


Figure 4.45 RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:0.5) (a) top; (b) bottom; (c) side of the foam sample

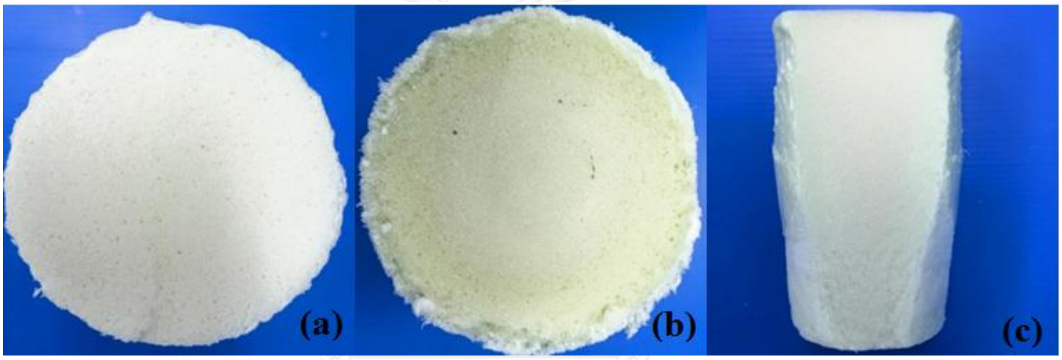


Figure 4.46 RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:0.75) (a) top; (b) bottom; (c) side of the foam sample

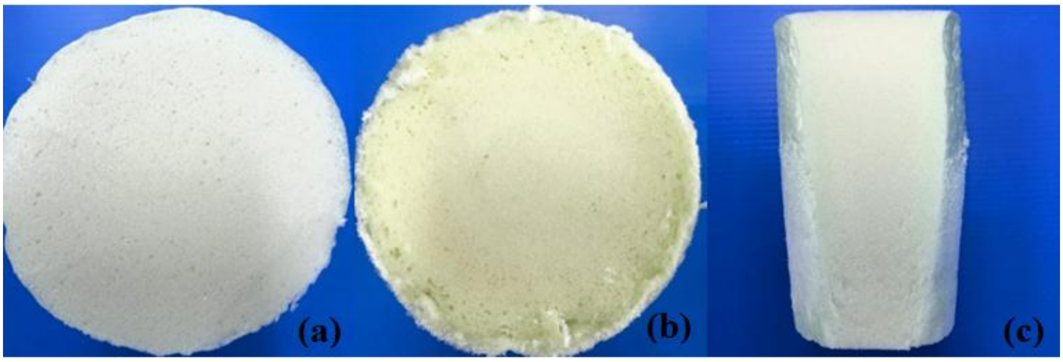


Figure 4.47 RPUR foams catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:1) (a) top; (b) bottom; (c) side of the foam sample

CHAPTER V

CONCLUSION

5.1 Conclusion

The solutions of copper-amine complexes and copper-amine complex/carboxylic acid salts, namely $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(en)_2/Sal$, $Cu(OAc)_2(en)_2/Ac$ and $Cu(OAc)_2(trien)/Sal$ in ethylene glycol were used as catalysts for rigid polyurethane foam preparation. The solution of copper-amine complexes and copper-amine complex/carboxylic acid salts were obtained as odorless viscous liquid and could be easily dissolved in other starting materials used in foam formulation. UV-Visible spectroscopy and IR spectroscopy were used to characterize the structure of copper-amine complex/carboxylic acid salts**.**

The target of this study was to increase gel time, while tack free time was not too slow when compared with commercial catalyst (DMCHA). The gel time of 60 sec was long enough for pouring the mixture of foam formulation into a mold. From the reaction times, copper-amine complex/carboxylic acid salts, namely $Cu(OAc)_2(en)_2/Sal$, $Cu(OAc)_2(en)_2/Ac$ and $Cu(OAc)_2(trien)/Sal$ showed comparable catalytic activity to DMCHA. $Cu(OAc)_2(en)_2/Sal$ and $Cu(OAc)_2(trien)/Sal$ at the mole ratio of 1:1 and 1:0.5 respectively are suitable delayed action catalysts, which had gel time at 60 and 64 seconds, respectively. It was found that an increase in the amount of salicylic acid increased the reaction time. In the case of $Cu(OAc)_2(en)_2/Ac$ showed slight delay in the reaction time.

Rise profile of RPUR foaming reaction catalyzed by $Cu(OAc)_2(en)_2/Sal$ and $Cu(OAc)_2(en)_2/Ac$ had longer cream time at the initial of reaction than $Cu(OAc)_2(en)_2$ and exhibited a very quick rise curve in the latter stage. $Cu(OAc)_2(trien)/Sal$ showed longer initial cream time than $Cu(OAc)_2(trien)$. DMCHA showed faster cream time than $Cu(OAc)_2(en)_2/Sal$ and $Cu(OAc)_2(en)_2/Ac$ and $Cu(OAc)_2(trien)/Sal$.

The polymerization reaction is exothermic and the maximum core temperature during foaming reaction was in the range 126.4-131.9 °C. NCO conversion was investigated by ATR-FTIR spectroscopy. It was found that all RPUR foams had the

NCO conversion higher than 99%. The data from the reaction times and NCO conversion indicate that copper-amine complex/carboxylic acid salts have good catalytic reactivity in both gelling and blowing reactions.

From the result of compressive properties, compressive strength of foams in the parallel direction to the foam rising direction was higher than that in the perpendicular direction. This was because the foam cells were elongated in the foam rising direction. It was found that RPUR foam catalyzed by $Cu(OAc)_2(trien)/Sal$ (1:0.5) had highest compressive strength of 292.2 kPa in parallel direction.

Morphology of RPUR foams obtained by SEM indicated that all RPUR foams had closed cell. The foam cells in the top view (perpendicular to the foam rising direction) were spherical shape and the side view (parallel to the foam rising direction) is an elliptical shape. This indicated that the foams were anisotropic materials.

5.2 Suggestion for future work

$Cu(OAc)_2(en)_2/Sal$ and $Cu(OAc)_2(trien)/Sal$ are effective delayed action catalysts for preparing rigid polyurethane foams. The suggestion for future work is use $Cu(OAc)_2(en)_2/Sal$ and $Cu(OAc)_2(trien)/Sal$ as catalysts for the other foam systems such as flexible and semi-rigid polyurethane foams.

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APPENDICES

APPENDIX 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:

Chemicals	**Part by weight (pbw)**
Daltolac® R180 (OHV=440 mgKOH/g, functionality = 4.3)	100.0
Catalysts	1.0
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5
Blowing agent (H_2O, Mw = 18 g/mole, functionality = 2)	3.0
Polymeric MDI (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 weight in the above formulation:

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

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

Ethylene glycol (solvent) $= \dfrac{0.67}{31.0} = 0.022$

Total equivalent weight $= 1.139$

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

Thus:

$$\text{PMDI (pbw)} = 1.139 \times \frac{\text{PMDI molar mass}}{\text{functionality}} = 1.139 \times \frac{365.8}{2.7} = 154.3$$

Note: 154.3 defines the isocyanate quantity at 100 index

where;

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

Thus:

#Isocyanate index = 100;

$$\text{Isocyanate actual} = \frac{154.3}{100} \times 100 = 154.3 \text{ pbw}$$

Table A1 Isocyanate quantity at the NCO index 100

Chemicals	**Part by weight (pbw)**
Daltolac® R180 (OHV=440 mgKOH/g, functionality = 4.3)	100.0
Catalysts	1.0
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5
Blowing agent (H_2O, Mw = 18 g/mole, functionality = 2)	3.0
Polymeric MDI (PMDI, Suprasec®5005), NCO index of 100	154.3

NCO conversion calculation

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, following equation:

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

where;

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

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

Quantity of free NCO in RPUR foams were normalized by aromatic ring 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}); ATR-IR	98.0

Example Calculate the conversion of isocyanate (α) of rigid polyurethane foams catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:1) catalyst at NCO index 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 = 0.524 = NCO^{f}

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

$$= \left[1-\frac{0.3077}{98.0}\right]\times 100$$

% NCO conversion = 99.69

Table A3 NCO conversion of RPUR foam catalyzed by $Cu(OAc)_2(en)_2$/Sal (1:1) at the NCO index 100

Catalyst	**Peak Area**			**NCO Conversion (%)**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**NCO^f (Ar-H=1.0)**	
$Cu(OAc)_2(en)_2$/Sal (1:1)	0.524	1.703	0.3077	99.69

Table A4 NCO conversion of RPUR foam catalyzed by different catalysts at the NCO index 100

Catalyst	**Peak Area**			**NCO Conversion (%)**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**NCO^{f} (Ar-H=1.0)**	
DMCHA	0.316	1.809	0.1747	99.82
$Cu(OAc)_2(en)_2$	0.344	1.537	0.2238	99.77
$Cu(OAc)_2(en)_2$/Sal(1:0.5)	0.506	1.674	0.3023	99.69
$Cu(OAc)_2(en)_2$/Sal (1:1)	0.524	1.703	0.3077	99.69
$Cu(OAc)_2(en)_2$/Sal (1:1.5)	0.574	1.673	0.3431	99.65
$Cu(OAc)_2(en)_2$/Ac (1:0.5)	0.388	1.154	0.3362	99.66
$Cu(OAc)_2(en)_2$/Ac (1:1)	0.527	1.399	0.3767	99.62
$Cu(OAc)_2(en)_2$/Ac (1:1.5)	0.440	1.408	0.3125	99.68
$Cu(OAc)_2(en)_2$/Ac (1:2)	0.583	1.630	0.3577	99.64
$Cu(OAc)_2$(trien)	0.422	1.739	0.2427	99.75
$Cu(OAc)_2$(trien)/Sal (1:0.25)	0.549	1.670	0.3287	99.66
$Cu(OAc)_2$(trien)/Sal (1:0.5)	0.541	1.826	0.2963	99.70
$Cu(OAc)_2$(trien)/Sal (1:0.75)	0.484	1.581	0.3061	99.69
$Cu(OAc)_2$(trien)/Sal (1:1)	0.523	1.330	0.3932	99.60

APPENDIX B
Reaction times

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

Formulations (pbw)	**Catalyst at NCO index 100**	
	DMCHA (ref.)	
Polyol (Daltolac® R180)	100.0	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Suprasec®5005)	151.3	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	15	0.00
Gel time	25	0.00
Tack free time	178	2.00
Rise time	128	1.15
Density (kg/m^3)	37.4	0.62
Mechanical properties		
Compressive strength (kPa) in parallel	215.6	10.44
Compressive strength (kPa) in perpendicular	133.4	1.75

Table B2 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ at the NCO index 100

Formulations (pbw)	**Catalyst at NCO index 100**	
	$Cu(OAc)_2(en)_2$	
Polyol (Daltolac® R180)	100.0	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Suprasec®5005)	154.3	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	30	0.00
Gel time	35	0.58
Tack free time	78	0.58
Rise time	103	1.00
Density (kg/m^3)	36.4	0.64
Mechanical properties		
Compressive strength (kPa) in parallel	228.0	2.34
Compressive strength (kPa) in perpendicular	132.7	4.45

Table B3 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(trien)$ at the NCO index 100

Formulations (pbw)	**Catalyst at NCO index 100**	
	$Cu(OAc)_2(trien)$	
Polyol (Daltolac® R180)	100.0	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Suprasec®5005)	154.3	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	33	0.00
Gel time	45	0.58
Tack free time	102	1.53
Rise time	137	3.06
Density (kg/m^3)	38.3	0.43
Mechanical properties		
Compressive strength (kPa) in parallel	258.9	1.85
Compressive strength (kPa) in perpendicular	149.7	6.20

Table B4 Formulations of RPUR foams catalyzed by $Cu(OAc)_2(en)_2/Sal$, $Cu(OAc)_2(en)_2/Ac$ and $Cu(OAc)_2(trien)/Sal$ at the NCO index 100

Formulations (pbw)	**Catalysts**										
	$Cu(OAc)_2(en)_2/Sal$			**$Cu(OAc)_2(en)_2/Ac$**				**$Cu(OAc)_2(trien)/Sal$**			
	1:0.5	**1:1**	**1:1.5**	**1:0.5**	**1:1**	**1:1.5**	**1:2**	**1:0.25**	**1:0.5**	**1:0.75**	**1:1**
Polyol (Daltolac® R180)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Catalyst	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Surfactant	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Blowing agent	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
PMDI (Suprasec® 5005)	154.3	154.3	154.3	154.3	154.3	154.3	154.3	154.3	154.3	154.3	154.3

Table B5 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Sal at the NCO index 100

$Cu(OAc)_2(en)_2$/Sal	**The mole ratios of $Cu(OAc)_2(en)_2$: salicylic acid**					
	1:0.5		**1:1**		**1:1.5**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times (sec)						
Cream time	32	0.00	34	0.00	35	0.00
Gel time	45	0.58	60	0.52	73	0.84
Tack free time	106	1.00	129	2.00	148	2.61
Rise time	138	2.00	160	1.90	173	2.17
Density (kg/m^3)	37.7	0.72	38.2	0.63	38.2	0.53
Mechanical properties						
Compressive strength (kPa) in parallel	-	-	262.3	1.78	-	-
Compressive strength (kPa) in perpendicular	-	-	129.3	4.70	-	-

Table B6 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$/Ac at the NCO index 100

$Cu(OAc)_2(en)_2$/Ac	**The mole ratios of $Cu(OAc)_2(en)_2$: acetic acid**							
	1:0.5		**1:1**		**1:1.5**		**1:2**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times (sec)								
Cream time	34	0.00	36	0.00	36	0.00	36	0.00
Gel time	43	0.00	48	0.58	55	0.00	55	0.00
Tack free time	83	0.96	89	1.73	93	1.00	97	2.65
Rise time	112	1.29	113	0.58	120	0.58	125	4.00
Density (kg/m^3)	35.30	0.52	34.70	0.50	35.49	0.36	33.62	0.47
Mechanical properties								
Compressive strength (kPa) in parallel	-	-	-	-	223.5	2.11	-	-
Compressive strength (kPa) in perpendicular	-	-	-	-	109.2	7.40	-	-

Table B7 Reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(OAc)_2$(trien)/Sal at the NCO index 100

$Cu(OAc)_2$(trien)/ Sal	**The mole ratios of $Cu(OAc)_2$(trien): salicylic acid**							
	1:0.25		**1:0.5**		**1:0.75**		**1:1**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times (sec)								
Cream time	34	0.00	35	0.00	36	0.00	36	0.00
Gel time	55	0.82	64	0.00	76	0.50	102	1.67
Tack free time	125	0.00	137	1.00	179	0.96	202	1.92
Rise time	171	2.52	178	1.53	195	0.50	218	3.49
Density (kg/m^3)	39.5	0.44	40.8	0.50	39.9	0.55	42.2	1.07
Mechanical properties								
Compressive strength (kPa) in parallel	-	-	292.2	7.05	-	-	-	-
Compressive strength (kPa) in perpendicular	-	-	148.6	1.64	-	-	-	-

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