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PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ALKANOLAMINE COMPLEXES

Mr. Nuttapong Jongjitsatitmun

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A Thesis Submitted in Partial Fulfillment of the Requirements
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งานวิจัยนี้เป็นการสังเคราะห์ตัวเร่งปฏิกิริยาสำหรับใช้ในการเตรียมโฟมพอลิยูรีเทนแบบแข็งเพื่อลดกลิ่นเหม็นเมื่อเทียบกับตัวเร่งปฏิกิริยาที่ใช้ในอุตสาหกรรม คือ ไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA) โดยตัวเร่งปฏิกิริยาที่ศึกษาเป็นสารประกอบเชิงซ้อนโลหะ-แอลคานอลามีนในตัวทำละลายเอทิลีนไกลคอล ได้แก่ $Cu(OAc)_2(EA)_2$ และ $Zn(OAc)_2(EA)_2$ เมื่อ OAc คือ acetate และ EA คือ ethanolamine ซึ่งสารประกอบเชิงซ้อนที่สังเคราะห์ได้สามารถนำมาใช้เป็นตัวเร่งปฏิกิริยาในการเตรียมโฟมพอลิยูรีเทนแบบแข็งได้โดยไม่ต้องทำให้บริสุทธิ์ พิสูจน์เอกลักษณ์ของสารประกอบเชิงซ้อนโลหะ-แอลคานอลามีนโดยใช้ยูวี-วิซิเบิลสเปกโทรสโกปี อินฟราเรดสเปกโทรสโกปี และแมสสเปกโทรเมตรี ศึกษาสมบัติทางกายภาพและสมบัติเชิงกลของโฟมพอลิยูรีเทนแบบแข็งที่ได้ และศึกษาเวลาที่ใช้ในการเกิดปฏิกิริยาของการเกิดโฟม เปรียบเทียบกับโฟมที่เร่งปฏิกิริยาด้วยไดเมทิลไซโคลเฮกซิลแอมีน จากผลการทดลองพบว่า สารประกอบเชิงซ้อน 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) และ 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) ที่สังเคราะห์ได้มีลักษณะเป็นสารผสมเนื้อเดียว โฟมพอลิยูรีเทนแบบแข็งที่เตรียมได้จากสารประกอบเชิงซ้อนนั้นมีเวลาที่สารผสมเป็นเจล เวลาที่ผิวหน้าของโฟมไม่เกาะติดวัสดุสัมผัสและเวลาที่โฟมหยุดฟู นานกว่าโฟมที่ได้จากไดเมทิลไซโคลเฮกซิลแอมีน ดังนั้น $Cu(OAc)_2(EA)_2$ และ $Zn(OAc)_2(EA)_2$ เหมาะสำหรับโฟมพอลิยูรีเทนแบบแข็งที่ต้องการเวลาที่สารผสมเป็นเจลนาน

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NUTTAPONG JONGJITSATITMUN: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ALKANOLAMINE COMPLEXES. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 81 pp.

In this research, the catalysts for preparation of rigid polyurethane (RPUR) foams were developed in order to reduce odor as compared with commercial catalyst as dimethyl-cyclohexylamime (DMCHA). The investigated catalysts were metal-alkanolamine complexes in ethylene glycol solution, namely $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$, where OAc = acetate and EA = ethanolamine. These complexes were further used as catalysts in the preparation of rigid polyurethane foams without purification. Characterization of metal-alkanolamine complexes were done using UV-visible spectroscopy, FTIR spectroscopy and mass spectrometry. Physical and mechanical properties of RPUR foams were studied. The reaction times of the foam formation were studied. The data were compared with those obtained from DMCHA. The experimental results showed that 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) were obtained as homogeneous solutions. RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) gave longer gel time, tack free time and rise time as compare with DMCHA. Therefore, $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ are suitable for RPUR foam applications which require longer gel time.

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LIST OF ABBREVIATIONS

3^{O}	tertiary
%	percentage
ε	molar absorptivity
α	isocyanate conversion
λ_{max}	maximum absorption peak
acac	acetylacetonate
ATR-IR	attenuated total reflectance-infrared
ASTM	American Society for Testing and Material
NH_3	ammonia
BDMAEE	bis (2-dimethylaminoethyl) ether
cm	centimeter
cm^{-1}	unit of wavenumber
^{o}C	degree Celsius (centrigrade)
Cd	cadmium
CO_2	carbon dioxide gas
CFCs	chlorofluorocarbons
Co	cobolt
$Cu(OAc)_2$	copper acetate
Cr	chromium
DBTDL	dibutyltin dilaurate
DMCHA	*N,N*-dimethylcyclohexylamine
ESI	electrospray ionization
EG	ethylene glycol
en	ethylenediamine
e.g.	example
FTIR	Fourier transform infrared spectrophotometer
FPUR	flexible polyurethane

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g	gram
h	hour
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
KOH	potassium hydroxide
kg	kilogram
kV	kilovolt
M	metal
m^3	cubic meter
MDI	4,4'-methane diphenyl diisocyanate
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mmol	millimole
MPa	megapascal
NCO	isocyanate group
OAc	acetate
Pentane	pentaethylenetatramine
Pbw	part by weight
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PUR	polyurethane
Ref	reference
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
sec	second
Sn	tin
SEM	scanning electron microscopy

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t	time
Tmax	maximum core temperature
TEDA	triethylenediamine
TMP	trimethylol propene
tetraen	tetraethylenetriamine
TDI	toluene diisocyanate
TMP	trimetylol propane
trien	triethylenetetramine
UV-vis	ultraviolet visible
$Zn(OAc)_2$	zinc acetate

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CHAPTER I
INTRODUCTION

Polyurethanes are widely used in broad range of products as rigid (RPUR) and flexible polyurethane foams. Flexible polyurethane foams are used as packaging, automotive interiors and cushioning for furniture, since these foams are light and comfortable. RPUR foams are used as insulation in refrigerators and building construction, since these foams have low thermal conductivity and good mechanical properties [1, 2].

Polyurethane foams are produced by the exothermic reaction between diisocyanates or polyisocyanates with polyfunctional OH species or polyols. There are two main reactions involve in the foam formation, namely blowing and gelling reactions. Blowing reaction is the reaction between isocyanate group (-NCO) with blowing agent (water) to release carbon dioxide gas and gives foam structure. Gelling reaction is the reaction between isocyanate group (-NCO) and hydroxyl group (-OH) of polyol to form urethane group and give polyurethane [3].

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The catalysts are important for preparation of RPUR foams. The reactions cannot be completed without catalysts since blowing and gelling reactions are slow. Tertiary amine and organometallic compounds are widely used as commercial catalysts in the industrial manufacturing of polyurethane foam, for examples N,N-dimethylcyclohexylamine (DMCHA) and dibutyltin dilaurate (DBTDL) [4]. Although, these catalysts have excellent catalytic activity, but amine catalysts are strong odor and organometallic catalysts are toxic. Several attempts have been made new types of catalyst in order to reduce odor, such as zirconium compounds [5] and metal-amine complexes [6].

In our previous researches, metal-alkanolamine complexes were used as catalysts for preparation of RPUR foams [7]. These catalysts were copper-ethanolamine [$Cu(OAc)_2(EA)$] and zinc-ethanolamine [$Zn(OAc)_2(EA)$] complexes. $Cu(OAc)_2(EA)$ and $Zn(OAc)_2(EA)$ were prepared from the reaction between metal acetates and ethanolamine using acetone as a solvent. Pure $Cu(OAc)_2(EA)$ and $Zn(OAc)_2(EA)$ were isolated as odorless viscous liquids. These complexes showed good catalytic activity in the preparation of RPUR foams, however, their preparation required long time since acetone had to be completely removed before further uses in the preparation of RPUR foams.

Therefore, this research aimed to synthesize copper-ethanolamine and zinc-ethanolamine complexes in the form of solution in ethylene glycol. The amount of starting materials (metal acetates and ethanolamine) and ethylene glycol was adjusted to obtain the homogeneous solution of copper-ethanolamine and zinc-ethanolamine complexes in ethylene glycol. This gave a convenient for the preparation of copper-ethanolamine and zinc-ethanolamine complexes solutions in ethylene glycol, which could be further used as catalysts in the preparation of RPUR foams without purification.

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Objective

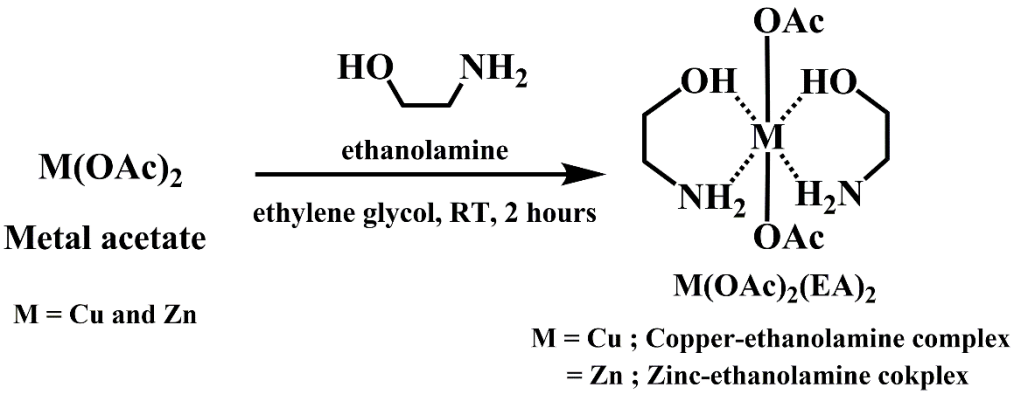
The objective of this research was to synthesize metal-alkanolamine complexes in the form of solution in ethylene glycol as catalysts and use for preparation of RPUR foams. Metal-alkanolamine complexes synthesized were $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ (where OAc = acetate, EA = ethanolamine). It was expected that the synthesized metal-alkanolamine complexes in ethylene glycol were odorless homogeneous solutions while having good solubility in RPUR foam formulation and good catalytic activity. The procedure was convenient since the

metal-alkanolamine complexes in ethylene glycol could be used in RPUR foam preparation without purification. Reaction times during RPUR foam preparation, physical and mechanical properties of RPUR foams catalyzed by metal-alkanolamine complexes in ethylene glycol were investigated and compared to that catalyzed by DMCHA, which is a commercial catalyst.

Scope of the research

The scope of this work consists of two parts. In the first part, the metal-alkanolamine complexes, namely $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$, were synthesized from the reaction between metal acetates and ethanolamine using ethylene glycol as a solvent (Scheme 1.1). Various mole ratios between metal acetate and alkanolamine and different concentrations of metal complexes in ethylene glycol were employed to obtain homogeneous solution. The prepared metal-alkanolamine complex solutions in ethylene glycol were characterized by UV-visible spectroscopy, FTIR spectroscopy and mass spectrometry.

In the second part, metal-alkanolamine complex solutions in ethylene glycol were used as catalysts in the preparation of RPUR foams. The reaction times, free rise density, rise profile, temperature profile, foam morphology and compressive strength were investigated. The free rise density and compressive strength of RPUR foams prepared by matal-alkanolamine complexes were measured according to ASTM D 1622-09 [8] and ASTM D 695 [9], respectively. All properties of RPUR foams prepared by metal-alkanolamine complexes were compared with that catalyzed by DMCHA, which is a reference commercial catalyst.



Scheme 1.1 Synthesis of metal-alkanolamine complex solutions in ethylene glycol

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CHAPTER II
THEORY AND LITERATURE REVIEW

Polyurethane foams are prepared from reaction between a polyol with an isocyanate compound. Polyols and isocyanates are the main components and other components such as surfactant, catalyst, blowing agent and other additives are to regulate the properties of foams. The PU foams that were widely used are flexible polyurethane foams and rigid polyurethane foams.

Rigid polyurethane (RPUR) foams are one of the most versatile polymers used in many applications [1]. The changes in RPUR foam properties are mainly due to the differences in functionality of polyols, functionality of polyols and other additives which decides flexibility or rigidity of the foam [3].

2.1 Raw materials

Rigid polyurethane foams are prepared by five important compounds are polyol, surfactant, catalyst, blowing agent and isocyanate.

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2.1.1 Polyols

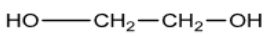
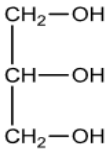
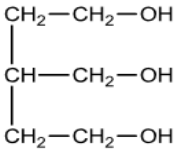
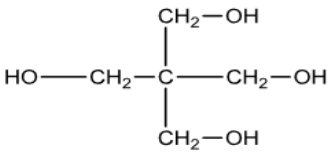
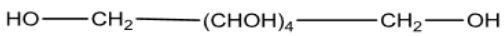
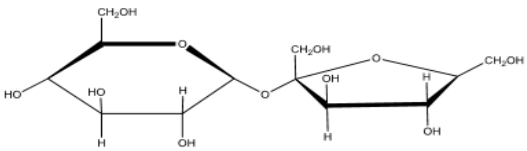
The polyols generally used in manufacture of polyurethane foams are divided into two groups, polyether polyols and polyester polyols. The structure, functionality and molecular weight of polyol influences the properties of polyurethane foams. Commonly, the functionality, molecular weight and hydroxyl value of polyols are 2.0-8.0, 200-800 and 250-1,000 mgKOH/g, respectively. The difference between two groups of polyols are polyether polyols give softer and resilient foam with better hydrolysis resistance than polyester polyols, while polyester polyols give the foam with better

resistance to oils, oxidation and solvents. Lower molecular weight and higher functionality polyols are used in the preparation of rigid polyurethane (RPUR) foams, while higher molecular weight and lower functionality polyols are used in the preparation of flexible polyurethane (FPUR) foams to increasing chain length of polymer for better resilience properties.

2.1.1.1 Polyether polyols

Polyether polyols are the products of polymeric reaction between an organic oxide and low molecular weight polyols. They are produced by the ring opening reaction of alkylene oxides and polyfunctional initiators. An examples common polyols were used as initiators shown in Table 2.1 [2].

Table 2.1 Functionality of some common polyols

Hydroxylated Compound	Chemical Structure	Functionality
Ethylene glycol(EG)		2
Glycerol		3
Trimetylol propene (TMP)		3
Pentaerythritol		4
Sorbitol		6
Sucrose		8

2.1.1.2 Polyester polyols

Polyester polyols are the products of polycondensation between an excess diol and diacid such as adipic acid, sebacic acid and phthalic acid. Polyester polyols have high viscosity and low functionality than polyether polyols [4]. Therefore, polyester polyols are suitable for preparation of flexible polyurethane foams more than polyether polyols.

2.1.2 Surfactants

Surfactants, also called surface-active agent are materials that lower the surface tension between two liquids or between a liquid and a solid. The dynamics of surfactant is of great importance to mixing of all ingredients as homogeneous and control the size of expanding foam, where bubbles are rapidly generated and need to be stabilized. The commercial application of silicone surfactants are used as additives for prepared polyurethane foams. They are typically added in the range of 0.4-2.0% w/w in the polyol formulation [1, 10]. An example of silicone surfactant is shown in Figure 2.1.

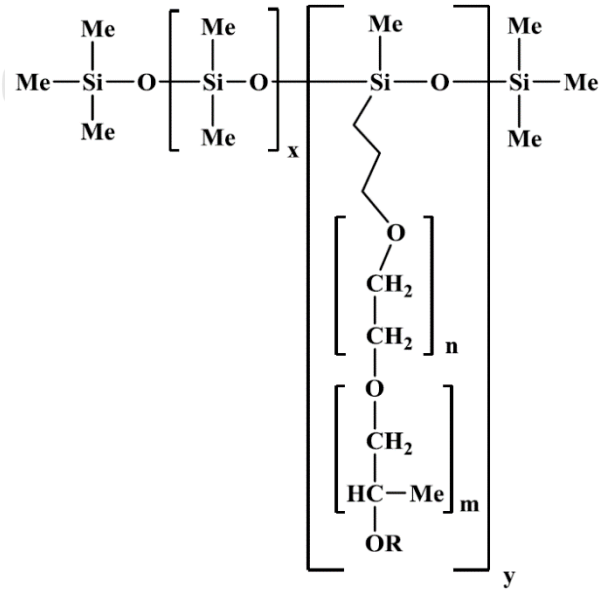


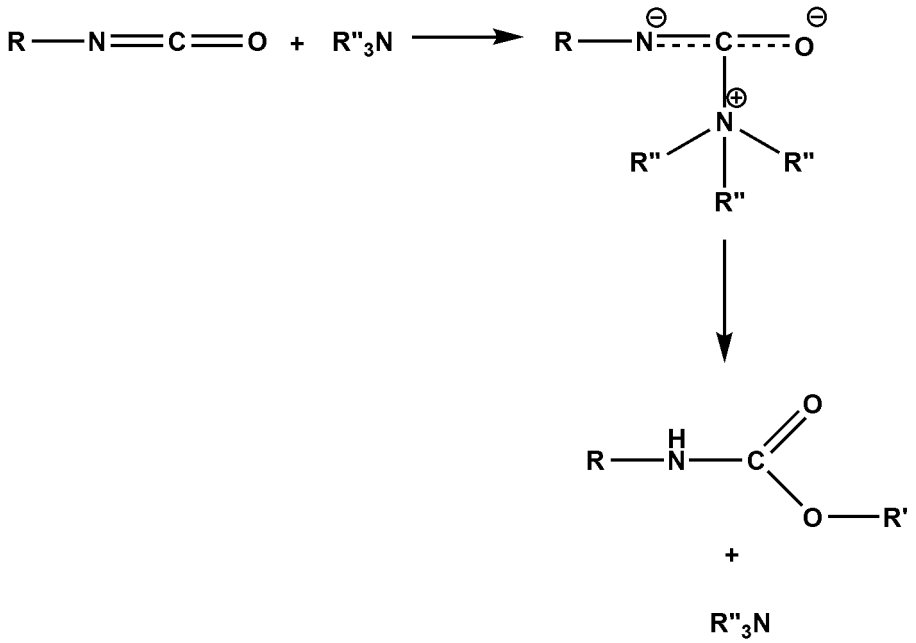
Figure 2.1 Structure of silicone surfactants that used in PUR foams manufacture

2.1.3 Catalysts

The catalyst can balance rate of reactions between isocyanate with polyol and isocyanate with water. The common catalyst for prepared polyurethane foams are tertiary amine and organometallic compounds.

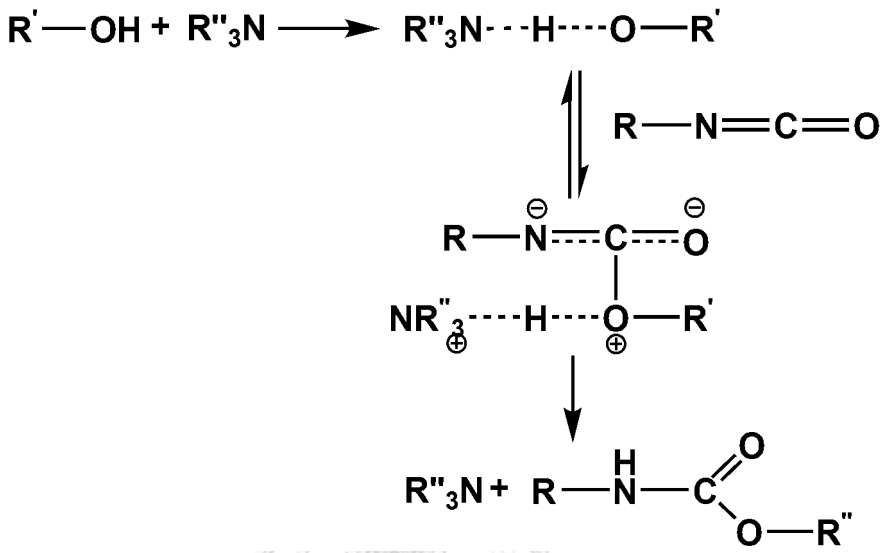
2.1.3.1 Amine catalysts

Tertiary amines are mainly used as catalysts for preparation of polyurethane foam. Two mechanisms have been proposed for tertiary amine catalysis. The first mechanism was proposed by Baker (Scheme 2.1). Tertiary amines using its lone pair of electrons to coordinate to the carbonyl carbon of the NCO group, that formed activates the electrophilic nature of the carbon. The polyols can reacts with isocyanate to generate a urethane group [3].



Scheme 2.1 Baker mechanism of 3o amine catalyst

The second mechanism was proposed by Farka (Scheme 2.2). The nitrogen atom of 3° amine interacts with proton source (polyols, amine, water). Then, it forms the intermediate and reacts with the isocyanate to generate a urethane group



Scheme 2.2 Farka mechanism of 3° amine catalysts

2.1.3.2 Organotin catalysts

The mechanism of tin (II) salts catalysts is shown in Scheme 2.3. The hydroxyl groups are coordinated with tin (II) salt to formed tin alkoxide, then tin alkoxide can react with isocyanate to form a ternary complex. After that, the alkoxide anion is transferred onto the coordinated isocyanate. The lone pair electron of tin delocalize to coordinate isocyanate, which then generated the urethane group and the original tin alkoxide.

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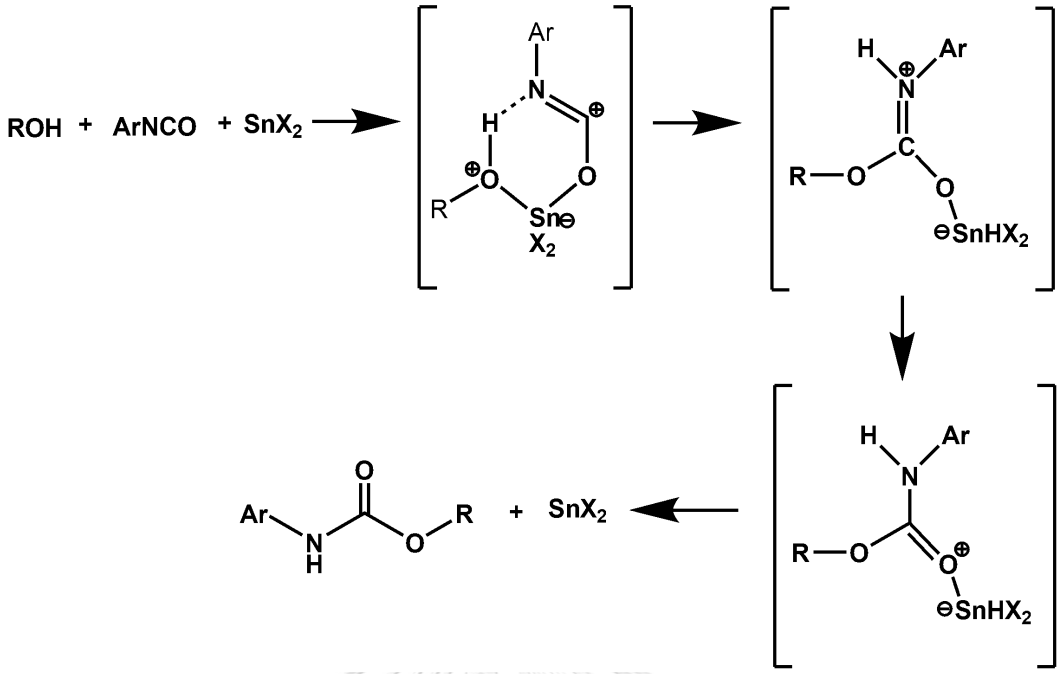

Scheme 2.3 Mechanism for tin (II) salts

2.1.4 Blowing agents

Blowing agents are used to prepared of RPUR foams had two types as physical and chemical blowing agents. Typical concentrations of blowing agents are 3-5 parts of water per 100 parts of polyol [2].

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Physical blowing agents are volatile compounds which generate gas by physical processes such as chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and cyclopentane [1].

Chemical blowing agents are a chemical compound which produce gas by chemical reactions such as water.

2.1.5 Isocyanates

Isocyanate used for preparation of polyurethane foams must have two or more isocyanate groups per molecule such as methylene diphenyl diisocyanate (MDI) and their derivatives [11]. The aromatic isocyanates have high reactivity in foaming reaction than aliphatic isocyanates. Examples of isocyanates are MDI isomer and polymeric MDI as shown in Figures 2.2-2.3.

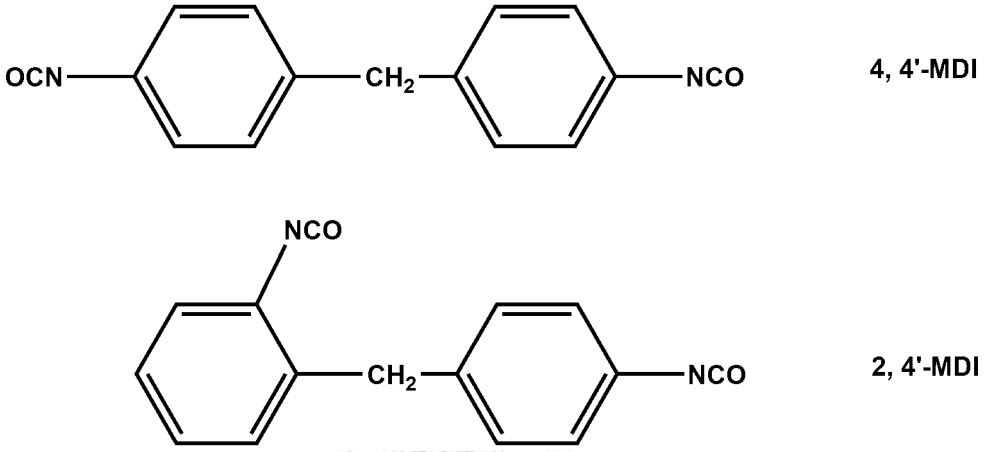


Figure 2.2 Structure of MDI

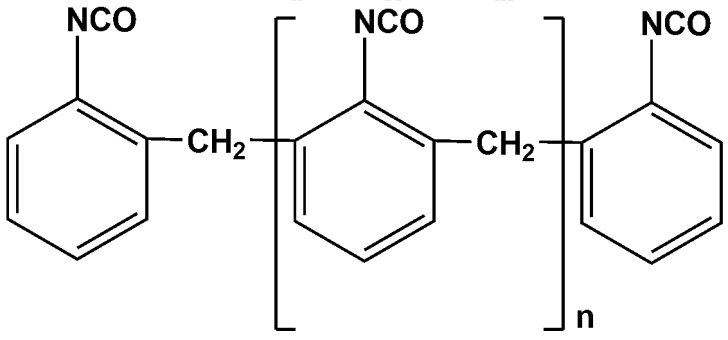


Figure 2.3 Structure of PMDI

2.2 Basic chemistry [4]

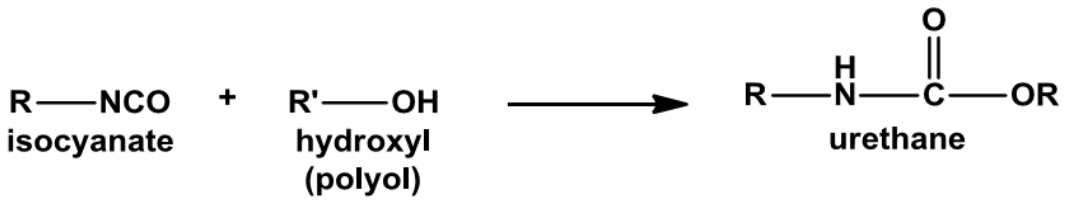
Polyurethane is formed by exothermic reaction between polyfunctional isocyanate and polyfunctional hydroxyl groups. For simplicity, the basic principle of urethane chemistry is explained below in section 2.2.1.

2.2.1 Primary reactions of isocyanates

The primary reactions of isocyanate groups with OH group of polyol and water are generated urethane and carbon dioxide (CO_2) gas, strongly influence the physical and mechanical properties of polyurethane foams.

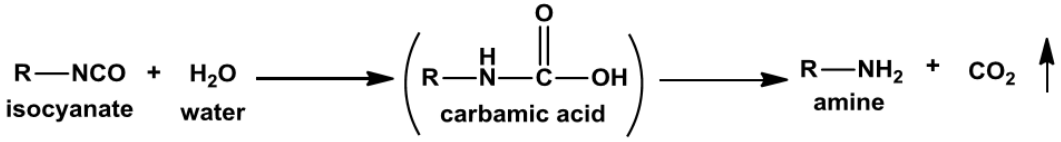
2.2.1.1 Reaction of isocyanate with polyol

The reaction between an isocyanate with polyols generated polyurethane. This important reaction is known as gelling reaction, that formed urethane linkage between hydroxyl group and isocyanate group.



2.2.1.2 Reaction of isocyanate with water

The reaction between isocyanate with water produces unstable carbamic acid, which decomposes to give CO_2 and amine. The obtained CO_2 diffuses into the already present air bubbles entrapped inside the reactive mixture, which is generate the cellular of polyurethane foams.



This reaction is called the “blowing reaction” since the CO_2 produced used for blowing the foam. The rate of reaction must have accelerated by suitable choice of catalysts.

2.2.2 Secondary reactions of isocyanates

Isocyanate in polyurethane foam formulation will react with amine and hydrogen atoms of urethane occurred from the primary reactions as shown below:

2.2.2.1 Reaction of isocyanate with amine

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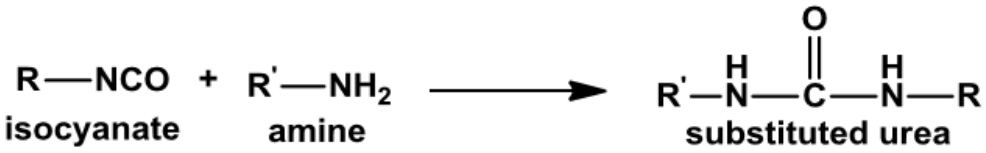
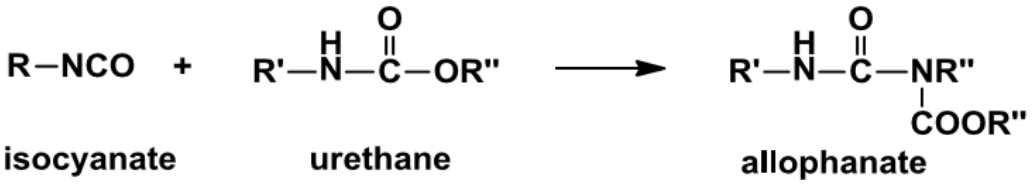
The reaction between isocyanate with amine generates the urea linkage. Since the reaction of isocyanate with primary amine occurs faster than with primary alcohol. Thus, amine is used as chain extenders and curing agents for polyurethane manufacture.



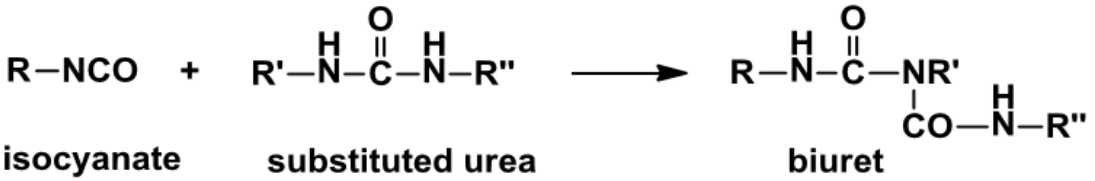
2.2.2.2 Reaction of isocyanate with urethane

The reaction between isocyanate and the nitrogen atom of the urethane group to form branched allophanates. The allophanate formation is a high temperature and reversible reaction.



2.2.2.3 Reaction of isocyanate with urea

The reaction between isocyanate and the hydrogen atom of the substituted urea to form branched biuret structure.



2.3 RPUR Formulations [12, 13]

The amount of isocyanate needed to react with polyols and other reactive ingredients in RPUR formulations could be calculated to obtain chemically stoichiometric equivalents. This theoretical amount is called “isocyanate index”, which could be adjusted depending on the foam formulation, properties required, scale of production and ambient conditions.

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

The conventional way of calculating the ratio of the components required polyurethane manufacture is to calculate the amount of parts by weight (pbw) of the isocyanate required to react with 100 parts by weight of polyol and use appropriate amount of additives, The data needed for calculation are isocyanate value, hydroxyl value, equivalent weight and water content of other reactive additives.

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

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

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

The hydroxyl value is expressed in milligrams of potassium hydroxide to the active functions (hydroxyl content) of 1 g of the compound or polymer (mgKOH/g polyol), is used as a measurement of the isocyanate amount to reactive hydroxyl groups per unit weight of the polyols.

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

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

Equivalent weight can be calculated by ratio of molar mass per functionality

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

2.4 Mechanical properties

Compressive properties are the most important mechanical properties for RPUR foams. Compressive energy absorption characteristic and deformation characteristics of foam mainly depend on density, chain length and functionality of raw materials and type of cell foams structure viz open cell and closed cell as shown in Figures 2.4-2.5.

In simple terms, open cell structure do not have thin cell wall on the cell surfaces. This properties are suitable for flexible polyurethane foams. For closed cell structure, those have thin cell wall on the cell surfaces, it important for rigid polyurethane foams since closed cell structure helps to increase the pressure durability and has a high strength.

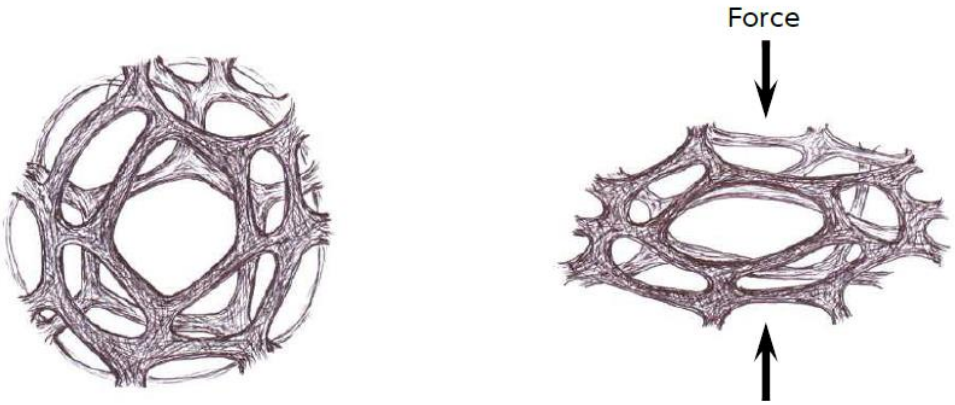

Figure 2.4 Schematic representation of open cell deformation [2]

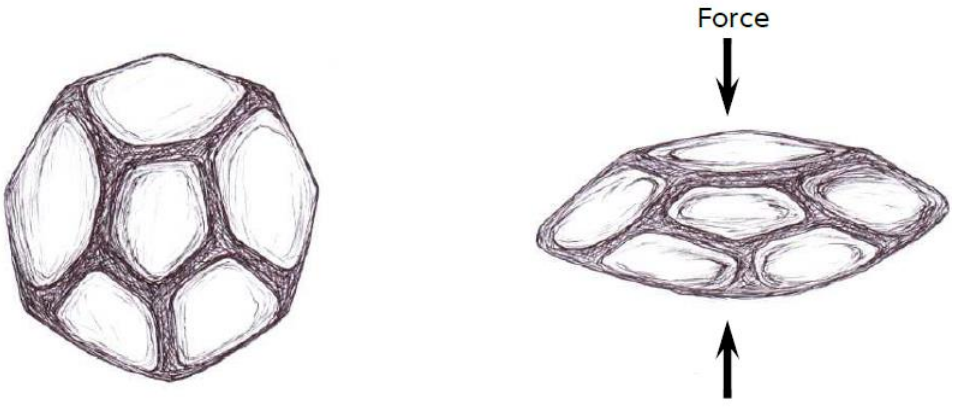

Figure 2.5 Schematic representation of closed cell deformation [2]

2.5 Literature reviews

A catalyst is an important component in for preparation of polyurethane foams in order to complete polymerization reaction. The commercial amine catalyst such as DMCHA can increase the reaction process, however those have strong odor during the manufacturing process. There are several researches that developed of new catalysts used in RPUR foam preparation.

In 2006, Lonkin and coworker [14] studied use of the divalent tin and germanium complexes in the synthesis of the P^O chelating phosphine to the stabilization of divalent tin and germanium compounds. It was found that the divalent tin complexes, namely Sn[-O-C(CF_3)$_2$$CH_2P^tBu_2$] and Sn[-O-C($CF_3$)$_2$$CH_2$P(S)$^tBu_2$] were found to be efficient catalysts for the formation of polyurethanes. The synthesis of Sn[-O-C(CF_3)$_2$$CH_2P^tBu_2$] and Sn[-O-C($CF_3$)$_2$$CH_2$P(S)$^tBu_2$] is shown in Figure 2.6.

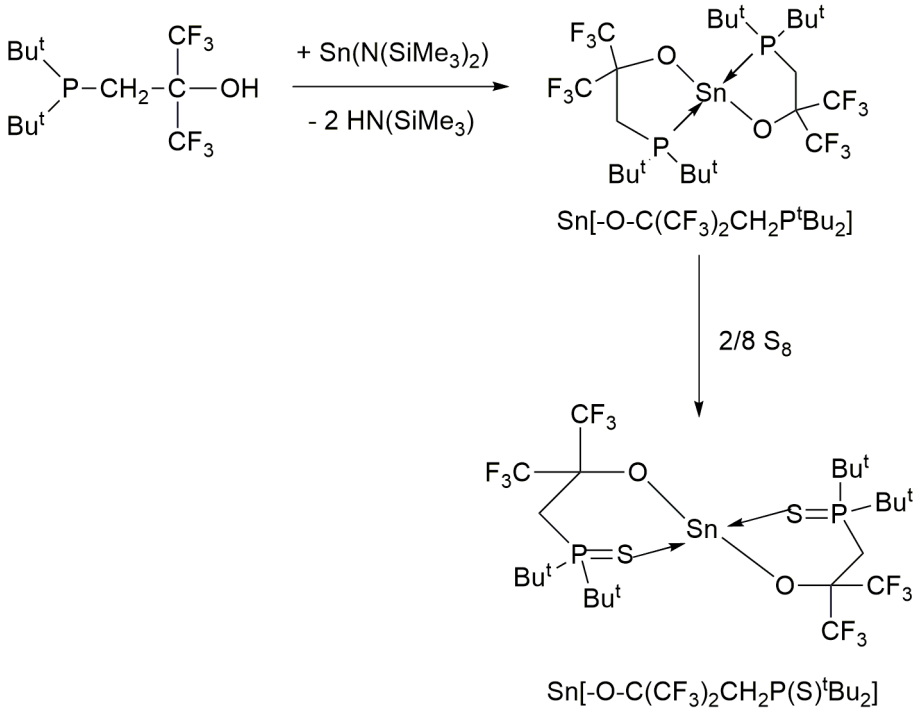

Figure 2.6 Synthesis of Sn[-O-C(CF_3)$_2$$CH_2P^tBu_2$] and Sn[-O-C($CF_3$)$_2$$CH_2$P(S)$^tBu_2$]

In 2009, Sardon and coworker [5] studied the synthesis of waterborne polyurethane catalyzed by cocatalyst of zirconium acetyl acetonate / triethylamine compared and cocatalyst of dibutyltin diacetate / triethylamine. It was found that zirconium acetyl acetonate / triethylamine showed good catalytic activity. Zirconium acetyl acetonate had lower toxicity than dibutyltin diacetate and therefore zirconium acetyl acetonate could be used in place of dibutyltin diacetate.

The previous work in our research group focused on using metal-amine complexes as catalysts for preparation of RPUR foams instead of *N,N*-dimethyl-cyclohexylamine (DMCHA), which is a commercial catalyst with strong odor. The advantage of using metal-amine complexes is they have weak odor.

In 2012, Pengjam and coworker [15] developed catalysts for preparation of RPUR foams. The catalysts were synthesized are copper-amine complexes, namely $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) [OAc = acetate; en = ethylenediamine; trien = triethylenetetramine], using acetone as a solvent (Scheme 2.4). These copper-amine complexes were used as catalysts for preparation of RPUR foams. Acetone must be removed by evaporation and dried under vacuum to obtain pure copper-amine complexes before their further used in the preparation of RPUR foams. It was found that $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) could be used as catalysts to prepare RPUR foams and had comparable catalytic activity as DMCHA.

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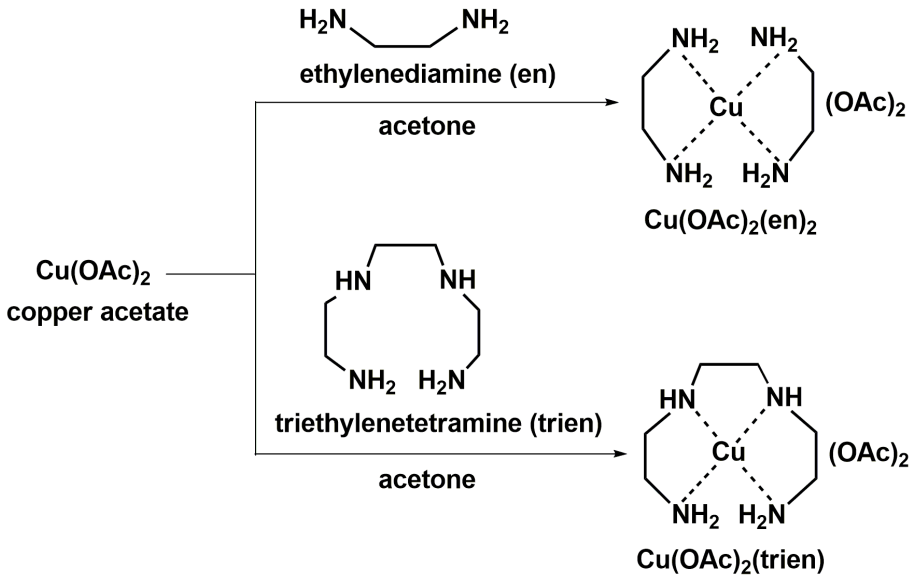
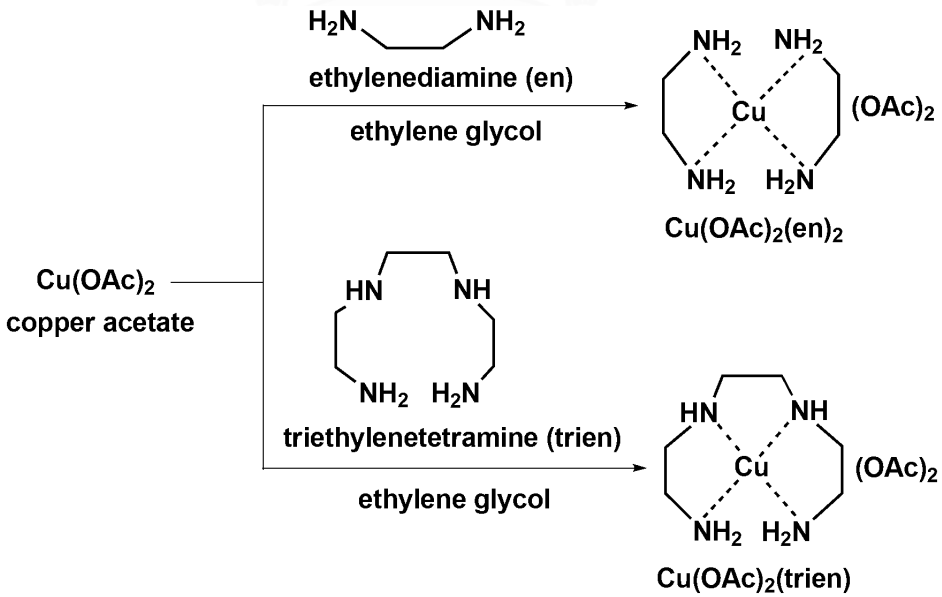


Scheme 2.4 Synthesis of copper-amine complexes using acetone as a solvent

In 2015, Sridaeng and coworkers [16] developed the method for preparation of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) in the form of solution in ethylene glycol (Scheme 2.5). The solution of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) in ethylene glycol could be used as catalysts for the preparation of flexible polyurethane foams without purification. It was found that $Cu(OAc)_2(en)_2$ in ethylene glycol showed good catalytic activity.

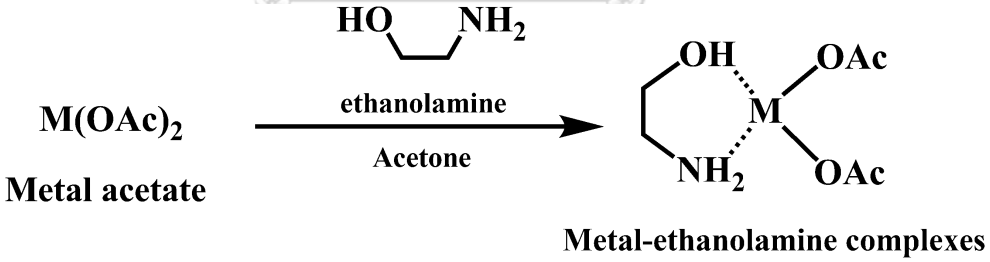


Scheme 2.5 Synthesis of copper-amine complexes using ethylene glycol as a solvent

2.5.1 Literature reviews about synthesis of metal-alkanolamine complexes

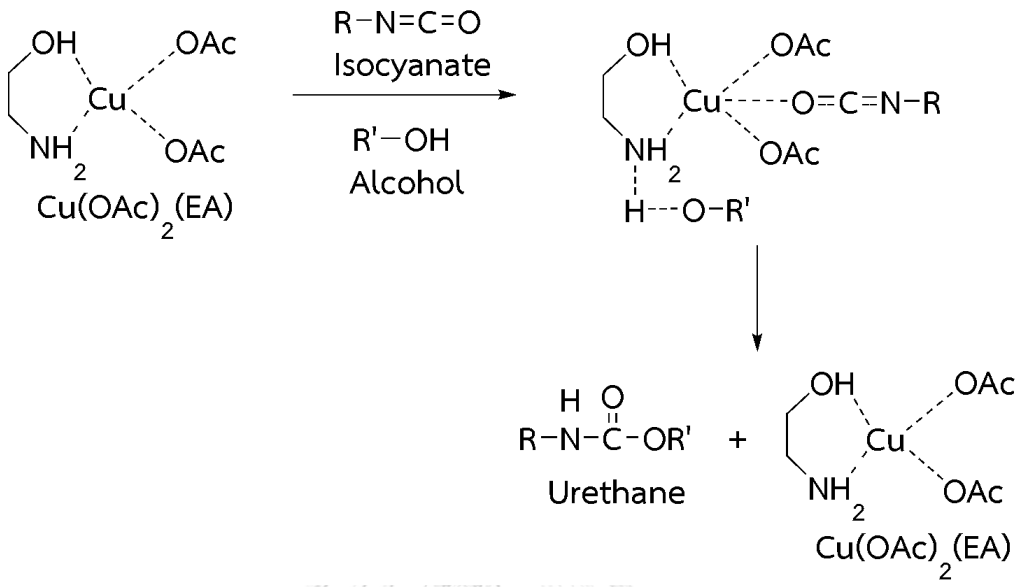
In 1971, Jensen and coworker [17] studied the synthesis of copper-ethanolamine complexes, namely copper nitrate-ethanolamine and copper chloride-ethanolamine. It was found that these complexes were successfully synthesized and their structures were confirmed by elemental analysis and UV-Vis spectroscopy.

In 2016, Sridaeng and coworkers [7] developed the catalysts for preparation of RPUR. The catalysts synthesized were metal-alkanolamine complexes, namely $Cu(OAc)_2(EA)$ and $Zn(OAc)_2(EA)$ [EA = ethanolamine], using acetone as a solvent (Scheme 2.6). In the final step, acetone was removed to obtain pure of metal-alkanolamine complexes. These complexes were used for the preparation of RPUR foams. Comparing with RPUR foam prepared by DMCHA catalyst, it was found that RPUR foams prepared from $Cu(OAc)_2(EA)$ and $Zn(OAc)_2(EA)$ had longer gel time than DMCHA. Thus, RPUR foams prepared by using metal-alkanolamine complexes as catalysts had the advantage that there are longer time available in the foam molding process.



Scheme 2.6 Synthesis of copper-ethanolamine complexes using acetone as a solvent

Scheme 2.7 shows catalytic mechanism of $Cu(OAc)_2(EA)$, copper-ethanolamine coordinates with isocyanate group and hydroxyl group to obtained intermediate complex. Finally, urethane group is generated and original $Cu(OAc)_2(EA)$ was obtained.



Scheme 2.7 catalytic mechanism of copper-ethanolamine complexes

Therefore, the objective of this this research was to synthesize of metal-alkanolamine complexes by using ethylene glycol as a solvent. The solution of metal-alkanolamine complexes in ethylene glycol could be used as catalysts in the preparation of RPUR foams without purification. This gave a convenient way to synthesize metal-alkanolamine complexes.

CHAPTER III
EXPERIMENTAL

3.1 Raw material and chemicals

3.1.1 Synthesis of metal-alkanolamine complexes in ethylene glycol

Copper (II) acetate monohydrate [$Cu(OAc)_2 \cdot H_2O$], Zinc (II) acetate dihydrate [$Zn(OAc)_2 \cdot 2H_2O$], ethanolamine (EA) and ethylene glycol (EG) were obtained from Aldrich and used without further purification.

3.1.2 Preparation of rigid polyurethane (RPUR) foams

Polyol (Polymaxx® 4221, sucrose-based polyether polyol, hydroxyl value = 440 mg of KOH/g, functionality = 4.3, viscosity at 25 °C = 5500 cP), polysiloxane surfactant (Tegostab® B8460), Polymeric 4,4´-methylene diphenyl diisocyanate (PMDI, Raycore® B9001, % NCO = 31.0 wt%, average functionality = 2.7) and N,N-dimethyl cyclohexylamine (DMCHA, a commercial reference catalyst) were supplied by IRPC Public Company Limited. Distilled water was used as a chemical blowing agent.

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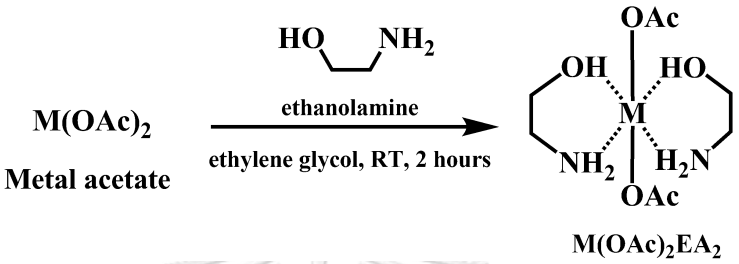
3.2 Synthetic procedures

The metal-alkanolamine complexes were synthesized from metal acetate [$M(OAc)_2$] and alkanolamine using ethylene glycol as solvent [7]. The solution of metal-alkanolamine complexes can be further used as a catalysts to prepare RPUR foams without purification.

3.2.1 Synthesis of metal-alkanolamine complexes in ethylene glycol

The solution of metal-alkanolamine complexes, copper-ethanolamine [$Cu(OAc)_2(EA)_2$] and zinc-ethanolamine [$Zn(OAc)_2(EA)_2$], were prepared in different concentrations and various mole ratios between metal acetate and alkanolamine (Table 3.1).



Scheme 3.1 Synthesis of metal-alkanolamine complexes [$M(OAc)_2(EA)_2$]

Metal-alkanolamine complexes were prepared by using ethylene glycol as a solvent. The solution of 74 wt% $Cu(OAc)_2(EA)_2$ (1:1) was synthesized using the procedure as follows: ethanolamine (EA) (0.139 ml, 2.30 mmol) was dissolved in ethylene glycol (EG) (0.360 ml) and stirred at room temperature for 20 minutes. After that, $Cu(OAc)_2{\cdot}H_2O$ (0.46g, 2.30 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 2 hours. The solution of 74 wt% $Cu(OAc)_2EA_2$ (1:1) was obtained as an odorless viscous dark blue solution with solid.

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The other solutions of metal-alkanolamine complexes were synthesized using the same procedure as 74 wt% $Cu(OAc)_2EA_2$ (1:1).

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

Metal complexes	Concentra-tions of complexes (wt%)	Mole ratios of $M(OAc)_2$: EA	Reactant			Appearances
			$M(OAc)_2$ (g)	EA (ml)	EG (ml)	
$Cu(OAc)_2(EA)_2$	74	1 : 1	0.460	0.140	0.400	Viscous Dark blue solution with solid
		1 : 2	0.460	0.280	0.260	Viscous Dark blue solution with solid
		1 : 3	0.460	0.420	0.120	Dark blue turbid solution
	62	1 : 1	0.380	0.120	0.500	Viscous Dark blue solution with solid
		1 : 2	0.383	0.234	0.383	Viscous Dark blue solution with solid
		1 : 3	0.383	0.351	0.266	Dark blue turbid solution
		1 : 4	0.383	0.468	0.149	Dark blue turbid solution
	56	1 : 4	0.306	0.376	0.200	Dark blue turbid solution

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Table 3.1 (Continued)

Metal complexes	Concentrations of complexes (wt%)	Mole ratios of $M(OAc)_2$: EA	Reactant			Appearances
			$M(OAc)_2$ (g)	EA (ml)	EG (ml)	
$Cu(OAc)_2(EA)_2$	49	1 : 1	0.306	0.094	0.600	Dark blue turbid solution
		1 : 2	0.306	0.188	0.506	Dark blue turbid solution
		1 : 3	0.306	0.282	0.412	Dark blue turbid solution
		1 : 4	0.306	0.376	0.318	Dark blue turbid solution
	43	1 : 0	0.430	-	0.570	insoluble
		1 : 4	0.268	0.328	0.404	Dark blue solution
	30	1 : 1	0.230	0.070	0.700	Dark blue turbid solution
	20	1 : 1	0.153	0.047	0.800	Dark blue turbid solution

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Table 3.1 (Continued)

Metal complexes	Concentrations of complexes (wt%)	Mole ratios of $M(OAc)_2$: EA	Reactant			Appearances
			$M(OAc)_2$ (g)	EA (ml)	EG (ml)	
$Zn(OAc)_2(EA)_2$	48	1 : 0	0.480	-	0.520	insoluble
		1 : 1	0.313	0.087	0.600	Light yellow solution
		1 : 2	0.313	0.174	0.513	Light yellow solution
		1 : 3	0.313	0.261	0.426	Light yellow solution
		1 : 4	0.313	0.348	0.339	Light yellow solution

3.3 Rigid polyurethane (RPUR) foam preparation

The preparation of RPUR foam was done in two methods; cup test and molded. The RPUR foam from cup-test method was used for investigation of reaction times, free rise density, rise profile, temperature profile, NCO conversion and morphology. The RPUR foam from molded method was used for investigation of compression properties.

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The reaction times for polymerization of RPUR foam investigated were cream time (which is time while polyol and isocyanate mixture begins to change from the liquid state to a creamy and starts to expansion subsequently), gel time (which is the time while polymerization occurs and the foam start to stiffen), free rise time (which is the time while the foam reach to its maximum height), tack free time (which is the time while the outer skin of the foam loses its stickiness or polymerization is completed).

3.3.1 Preparation of RPUR foams by cup test method

The preparation of RPUR foams via a two-step method is shown in Figure 3.1 and the formulation of rigid polyurethane foams is shown in Table 3.2. In the first step, polyol, surfactant, catalysts (DMCHA or metal-alkanolamine complexes in ethylene glycol), blowing agent (distilled water) were mixed in a paper cup (700 ml) by hand mixing for 15 seconds to obtain homogeneous mixture. In the second step, PMDI was added into the mixture and mixed by mechanical stirrer at 2,000 rpm for 15 seconds. During the foaming process cream time, gel time, free rise time and tack free time were measured. After that, the foams were kept for 48 hours at room temperature in order to accomplish all of the polymerization reactions. The RPUR foams were cut and measuring free rise density, physical and mechanical properties after leaving at room temperature for 48 hours.

3.3.2 Preparation of RPUR foams by molded method

The preparation of the molded method used the same first step as cup test method, except the amount of all starting materials were increased to 4-5 folds. In second step PMDI was added into the mixture and mixed by mechanical stirrer at 2000 rpm for 15 seconds, the mixture was poured into a 10 × 10 × 10 cm plastic bag (Figure 3.2) and allowed to rise independently at room temperature. The density of RPUR foams was measured and these foams were used for investigation of mechanical properties after leaving at room temperature for 48 hours.

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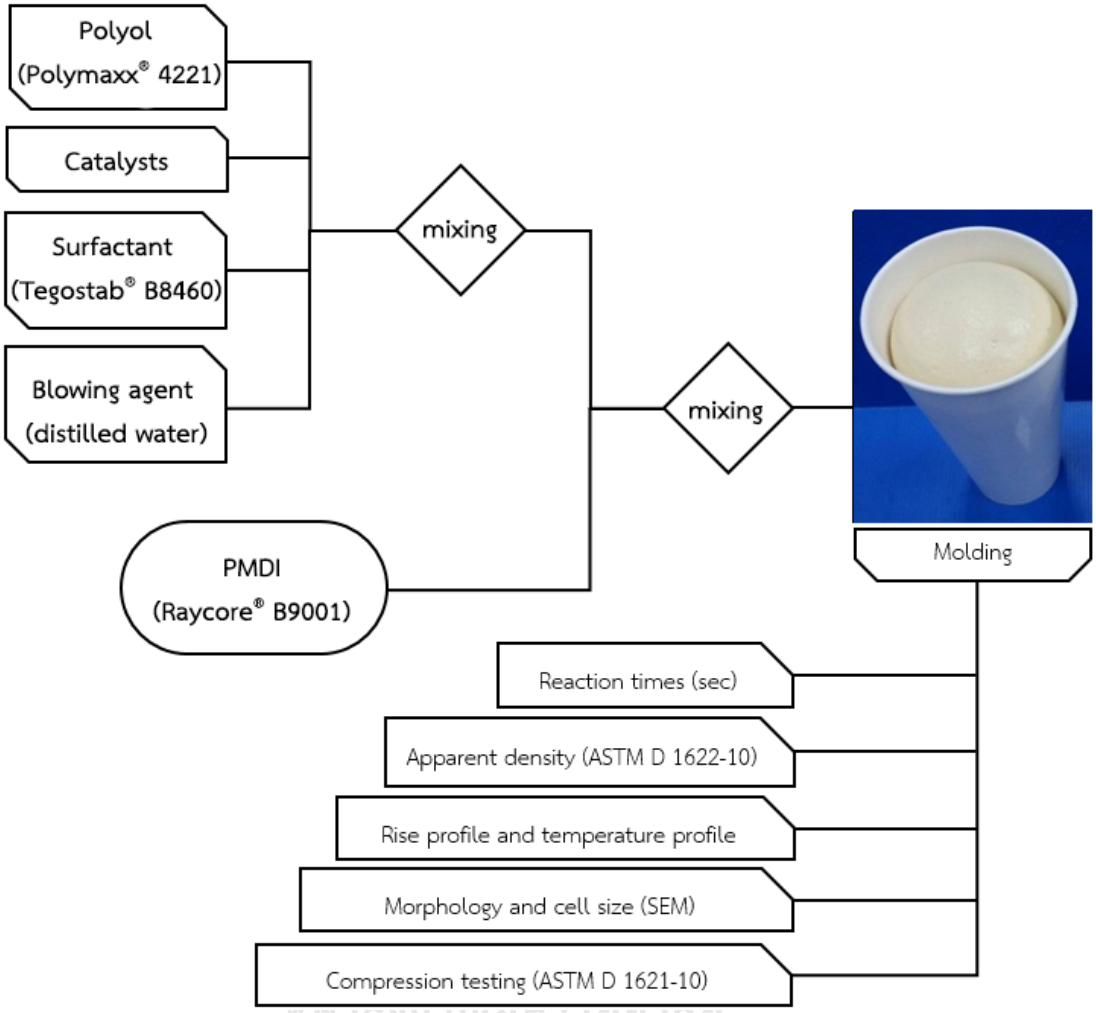

Figure 3.1 Procedure for the preparation of RPUR foams

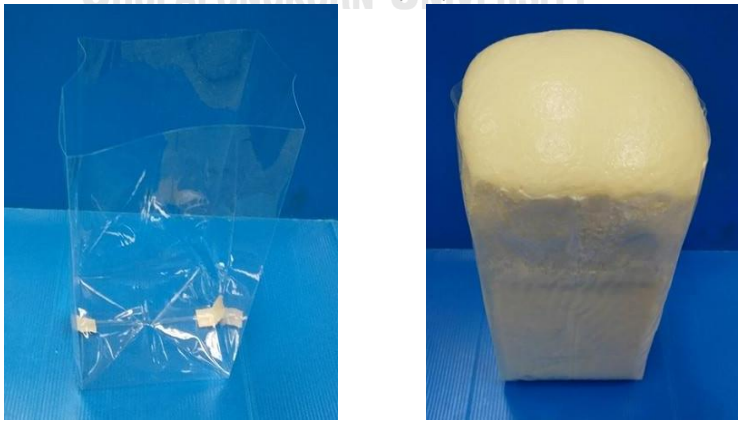

Figure 3.2 Plastic bag for used in molded method

Table 3.2 Formulation of rigid polyurethane foams at the NCO index of 105 (in parts by weight unit, pbw)

Starting materials	Formulation (parts by weights, pbw)[a]	
	1	2
Polyol (Polymaxx® 4221)	100.0	100.0
Surfactant (Tegostab® B8460)	2.5	2.5
Catalysts (DMCHA or metal-alkanolamine complexes in ethylene glycol)	1.0[b]	1.0[b]
Blowing agent (distilled water)	3.0	4.0
PMDI (Raycore® B9001)	164.9	180.7

[a]Parts by weight (pbw) is amount of reactant (g) in 100 g of polyol

[b]Calculated from the weight of metal-alkanolamine complexes in solution of metal-alkanolamine complexes in ethylene glycol

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3.4 Characterization of metal-alkanolamine complexes

3.4.1 Mass spectrometry (MS)

Electrospray ionization (ESI) mass spectrometry was used to confirm the complex formations by their unique mass (mass-to-charge ratio). This method depends on the fact of every compound has a unique fragmentation pattern in the mass spectrum. The sample is vaporized and ionized, then sample ions are separated based on their different masses and relative abundance. Ethylene glycol is a solvent used for sample preparation. The type of mass spectrometer used was MALDI-TOF mass spectra were determined on micrOTOF-Q II 10335.

3.4.2 Infrared spectroscopy

Metal-alkanolamine complexes in ethylene glycol were characterized by using Spectrum One PerkinElmer Fourier transform infrared (FTIR) spectrometer. 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 measurement surface that is in contact with the sample.

3.4.3 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy was routinely used in the quantitative different analyses such as highly conjugated organic compounds and transition metal ions. UV-Vis spectra were obtained on Varian Cary 50 UV-Vis spectrophotometer at room temperature. Absorption spectra were obtained and the samples were scan over range 200-800 nm. The solvent used was ethylene glycol.

3.5 Characterization of RPUR foams

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3.5.1 Kinetic of foaming

The kinetic of RPUR foaming was studied through the reaction times namely, cream time, gel time, free rise time and tack free time by using a digital stopwatch in accordance with ASTM D7487-13 [18].

3.5.2 Density

The density of RPUR foams was measured in accordance with ASTM D 1622-09 [8].A foam specimen having a size of 3.0 cm x 3.0 cm x 3.0 cm (width x length x thickness) and the average values of three samples were reported.

3.5.3 Infrared spectroscopy

The infrared spectroscopy was used to characterize the functional groups and study about NCO conversion of RPUR foams by using a Nicolet 6700 FTIR spectrometer over the range 800-4000 cm^{-1} at the resolution of 16 cm^{-1}. The IR bands given in the Table 3.3 were used for the analysis.

Table 3.3 Characteristic of main peaks of RPUR foams

Functional groups	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
Free NCO in RPUR foams	phenyl group	1595

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3.5.4 Foaming temperature

The measurement of foaming temperature used as a thermocouple, Digicon DP-71 was used to detect the foaming temperatures of RPUR foams. These foaming temperature is represented by temperature profiles.

3.5.5 Compressive testing

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise direction were performed using universal testing machine (Lloyd/LRX) according to ASTM D 695 [9].The sample sized was 5.0 cm x 5.0 cm x 5.0 cm (length x width x thickness) dimension, the rate of crosshead movement was fixed at 50 mm/min and the preload cell used was 0.100 N.

3.5.6 Scanning electron microscope (SEM)

The cell size and morphology of RPUR foams were measured on a JSM-6480 LV scanning electron microscope (SEM). The thickness of RPUR foams sample was prepared for SEM analysis in both parallel and perpendicular by coating with gold before scanning in order to provide an electrically conductive surface. The foam samples were done at accelerating power of 15 kV.

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CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of metal-alkanolamine complexes in ethylene glycol

Metal-alkanolamine complexes were synthesized from the reaction between metal acetate [$M(OAc_2$] and alkanolamine using ethylene glycol as a solvent. Metal-alkanolamine complexes employed in this research were $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$. Catalytic activity of the metal-alkanolamine complexes was compared with the commercial catalyst, dimethyl-cyclohexylamine (DMCHA).

4.1.1 Synthesis of copper-ethanolamine complexes [$Cu(OAc)_2(EA)_2$]

The reaction between copper (II) acetate monohydrate [$Cu(OAc)_2{\cdot}H_2O$] and ethanolamine (EA) in ethylene glycol gave copper-ethanolamine complexes [$Cu(OAc)_2(EA)_2$]. Copper-ethanolamine complex solutions in ethylene glycol were prepared at various mole ratios of $Cu(OAc)_2$:EA, namely 1:1, 1:2, 1:3, 1:4. Different concentration of copper-ethanolamine complex solutions in ethylene glycol (in wt%) was also investigated.

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The appearances of copper-ethanolamine complex solutions in ethylene glycol are shown in Figures 4.1 – 4.4. All copper-ethanolamine complex solutions in ethylene glycol were obtained as odorless dark blue solutions. They were used as catalysts in RPUR foam preparation without further purification.

It was found that 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) was the most homogeneous solution and $Cu(OAc)_2(EA)_2$ was completely soluble in ethylene glycol. Other copper-ethanolamine complex solutions in ethylene glycol had precipitates, which probably were unreacted $Cu(OAc)_2$ or $Cu(OAc)_2(EA)_2$. Therefore, suitable mole ratio of

$Cu(OAc)_2$:EA and amount of ethylene glycol were required to obtain homogeneous solution of copper-ethanolamine complex in ethylene glycol. It is important that copper-ethanolamine complex must be completely soluble in ethylene glycol since the catalyst must be homogeneous with other starting materials in the foam formulation.

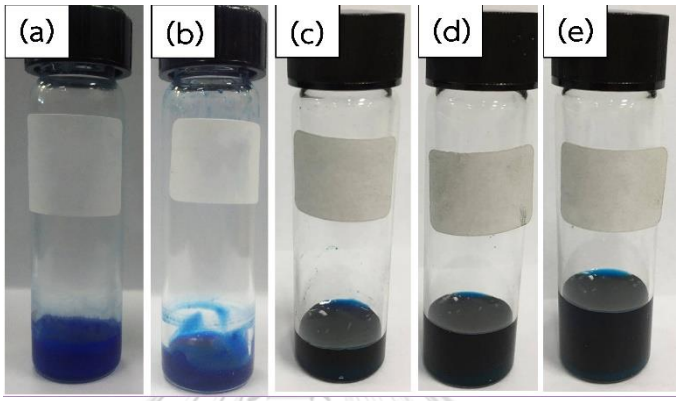

Figure 4.1 $Cu(OAc)_2(EA)_2$ (1:1) complexes in ethylene glycol (a) 74 wt%, (b) 62 wt%, (c) 49 wt%, (d) 30 wt%, (e) 20 wt%

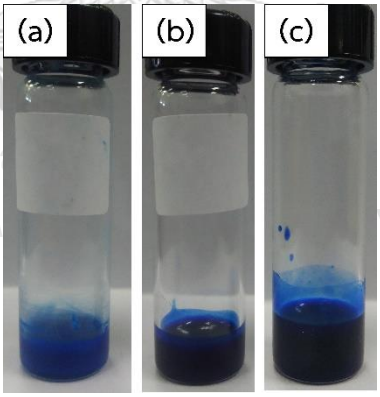

Figure 4.2 $Cu(OAc)_2(EA)_2$ (1:2) complexes in ethylene glycol (a) 74 wt%, (b) 62 wt%, (c) 49 wt%

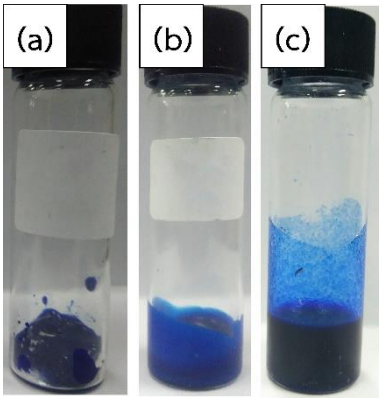

Figure 4.3 $Cu(OAc)_2(EA)_2$ (1:3) complexes in ethylene glycol (a) 74 wt%, (b) 62 wt%, (c) 49 wt%

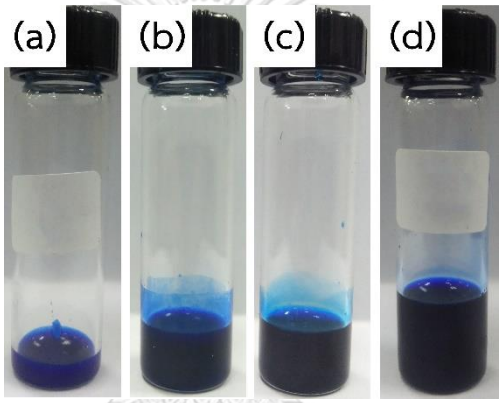

Figure 4.4 $Cu(OAc)_2(EA)_2$ (1:4) complexes in ethylene glycol (a) 62 wt%, (b) 56 wt%, (c) 49 wt%, (d) 43 wt%

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4.1.2 Synthesis of zinc-ethanolamine complexes $[Zn(OAc)_2(EA)_2]$

The reaction between zinc (II) acetate dihydrate $[Zn(OAc)_2{\cdot}2H_2O]$ and ethanolamine (EA) in ethylene glycol gave zinc-ethanolamine complexes $[Zn(OAc)_2(EA)_2]$. The appearances of $Zn(OAc)_2(EA)_2$ solutions in ethylene glycol are shown in Figure 4.5. It was found that these complexes were obtained as light yellow solutions. Since $Zn(OAc)_2$ did not dissolve in ethylene glycol, the homogeneous solution indicated the formation of $Zn(OAc)_2(EA)_2$. All $Zn(OAc)_2(EA)_2$ solutions in ethylene glycol were odorless and complete soluble in ethylene glycol. These $Zn(OAc)_2(EA)_2$ solutions in ethylene glycol were used in the preparation of RPUR foams without purification.

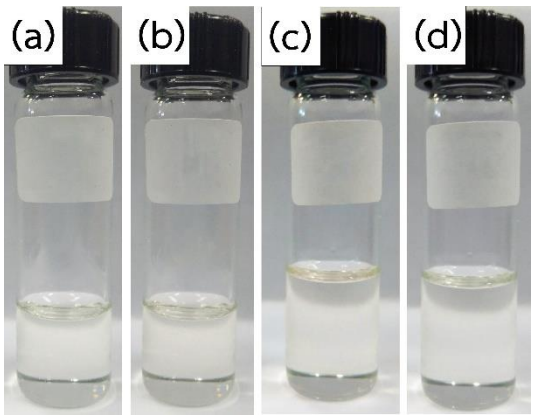

Figure 4.5 Zinc-ethanolamine complexes 48 wt% in ethylene glycol (a) $Zn(OAc)_2(EA)_2$ (1:1), (b) $Zn(OAc)_2(EA)_2$ (1:2), (c) $Zn(OAc)_2(EA)_2$ (1:3), (d) $Zn(OAc)_2(EA)_2$ (1:4)

4.2 Characterization of metal-alkanolamine complexes in ethylene glycol

4.2.1 UV-Visible spectroscopy of metal-alkanolamine complexes

UV-visible spectroscopy was used to identify the complex formation of copper-ethanolamine and zinc-ethanolamine complexes. UV-visible spectra of copper-ethanolamine and zinc-ethanolamine complexes were compared with those of copper acetate and zinc acetate to observe the shift of the maximum wavelength (λ_{max}) of the metal complex.

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4.2.1.1 UV-Visible spectroscopy of copper-ethanolamine complex

UV-visible spectra of copper-ethanolamine complex is shown in Figure 4.6. The absorption of $Cu(OAc)_2$ and $Cu(OAc)_2(EA)_2$ showed the maximum wavelength (λ_{max}) at 245 and 267 nm, respectively. The λ_{max} of $Cu(OAc)_2(EA)_2$ shifted from that of $Cu(OAc)_2$, which suggested the complex formation.

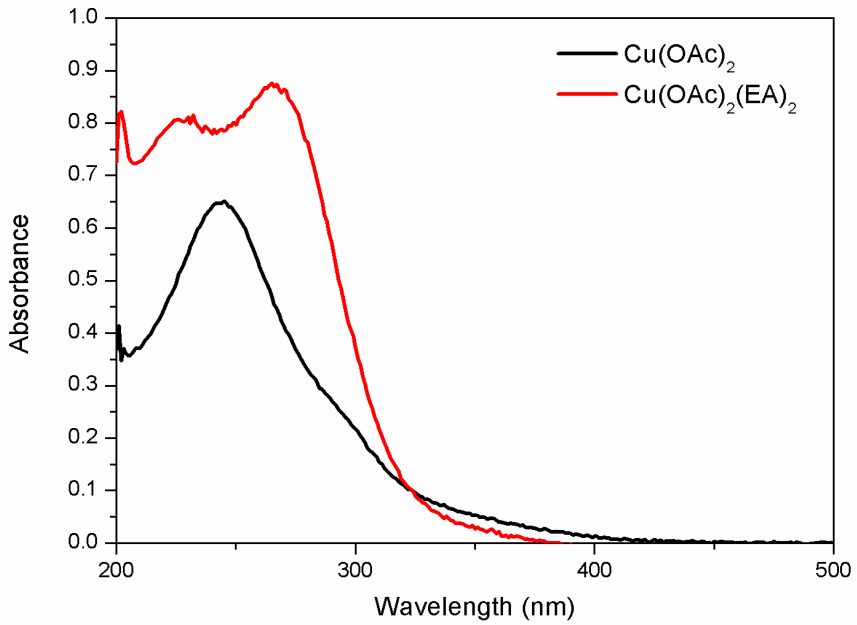

Figure 4.6 UV spectra of (a) $Cu(OAc)_2$ and (b) $Cu(OAc)_2(EA)_2$

4.2.1.2 UV-Visible spectroscopy of zinc-ethanolamine complex

UV-visible spectra of zinc-ethanolamine complex is shown in Figure 4.7. The absorption of $Zn(OAc)_2$ and $Zn(OAc)_2(EA)_2$ showed the maximum wavelength (λ_{max}) at 206 and 202 nm, respectively. The λ_{max} of $Zn(OAc)_2(EA)_2$ shifted from that of $Zn(OAc)_2$, which suggested the complex formation.

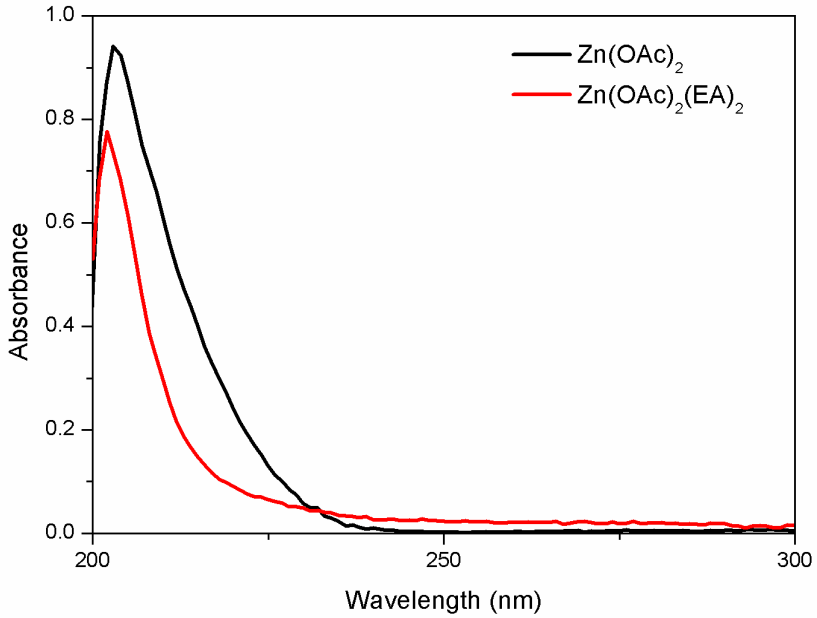

Figure 4.7 UV spectra of (a) $Zn(OAc)_2$ and (b) $Zn(OAc)_2(EA)_2$

4.2.2 IR spectroscopy of metal-alkanolamine complexes

IR spectra of copper-ethanolamine complex in ethylene glycol and zinc-ethanolamine complex in ethylene glycol were obtained. Since Copper acetate and zinc acetate were not soluble in ethylene glycol, their IR spectra were obtained from solid copper acetate and zinc acetate.

4.2.2.1 IR spectroscopy of copper-ethanolamine complex

IR spectrum of $Cu(OAc)_2$ is shown in Figure 4.8(a). It exhibited absorption band at 1594 cm^{-1} (C=O asymmetric stretching) and 1420 cm^{-1} (C=O symmetric stretching).

IR spectrum of $Cu(OAc)_2(EA)_2$ in ethylene glycol is shown in Figure 4.8(b). It exhibited absorption band at 1557 cm^{-1} (C=O asymmetric stretching) and 1403 cm^{-1} (C=O symmetric stretching).

The C=O stretching bands of carbonyl group in $Cu(OAc)_2(EA)_2$ in ethylene glycol were different from those of $Cu(OAc)_2$. It was found that the IR peaks of $Cu(OAc)_2(EA)_2$ shifted from those of $Cu(OAc)_2$ to lower energy because of the influence of ethanolamine coordination, which indicated that the copper-ethanolamine complex was formed.

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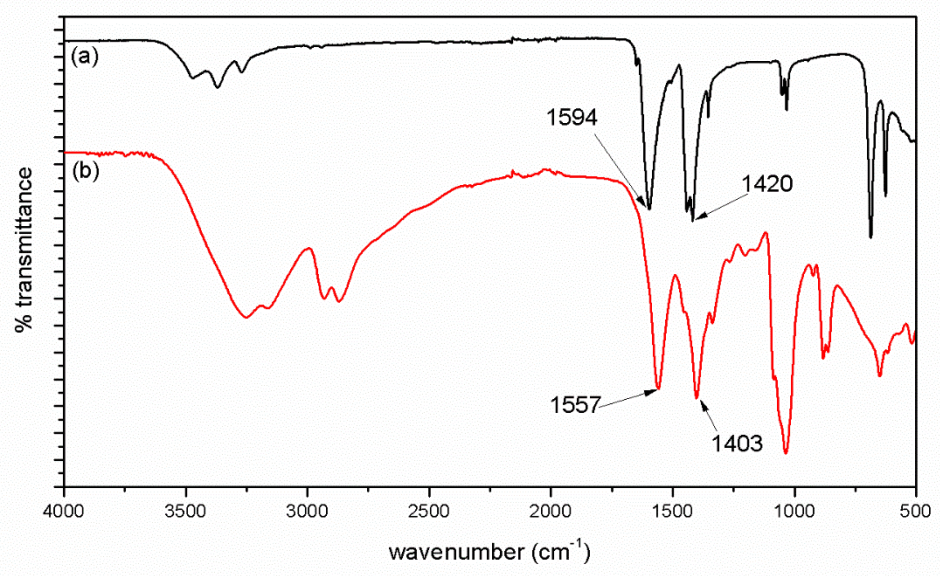

Figure 4.8 IR spectra of (a) $Cu(OAc)_2$ and (b) $Cu(OAc)_2(EA)_2$

4.2.2.2 IR spectroscopy of zinc-ethanolamine complex

IR spectrum of $Zn(OAc)_2$ is shown in Figure 4.9(a). It exhibited absorption band at 1558 cm^{-1} (C=O asymmetric stretching) and 1430 cm^{-1} (C=O symmetric stretching).

IR spectrum of $Zn(OAc)_2(EA)_2$ in ethylene glycol is shown in Figure 4.9(b). It exhibited absorption band at 1564 cm^{-1} (C=O asymmetric stretching) and 1403 cm^{-1} (C=O symmetric stretching).

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The C=O stretching bands of carbonyl group in $Zn(OAc)_2(EA)_2$ in ethylene glycol were different from those of $Zn(OAc)_2$. These IR data confirmed the formation of zinc-ethanolamine complex.

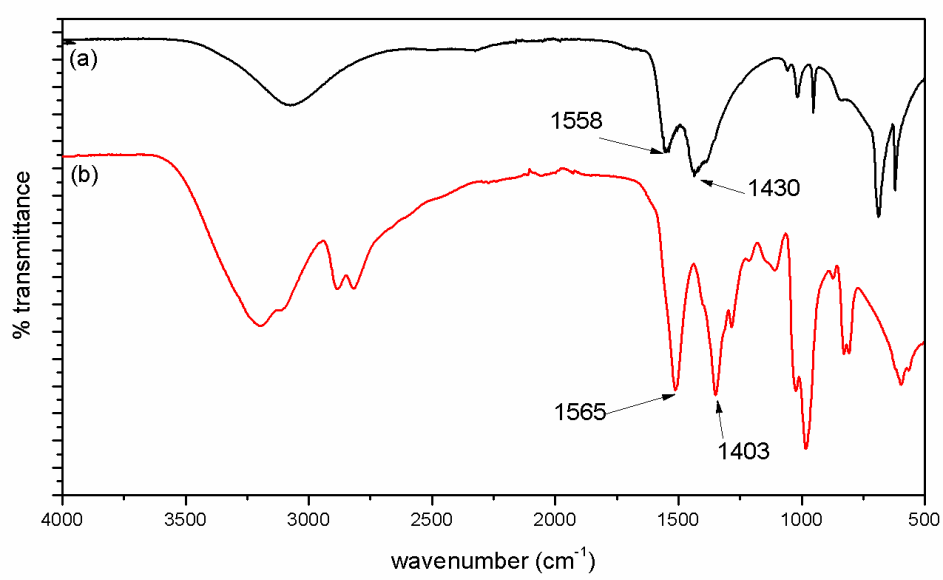

Figure 4.9 IR spectra of (a) $Zn(OAc)_2$ and (b) $Zn(OAc)_2(EA)_2$

4.2.3 Positive ESI mass spectrometry of metal-alkanolamine complexes

Mass spectrometry was also used to identify the structure and confirmed the complex formation of copper-ethanolamine and zinc-ethanolamine complexes. Mass spectra peak corresponded to the molecular weight of copper-ethanolamine and zinc-ethanolamine complexes.

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4.2.3.1 Mass spectrometry of copper-ethanolamine complex

Table 4.1 show the data of molecular ion peaks and their corresponding and m/z ratio, the molecular ion peaks of $Cu(OAc)_2(EA)_2$ is shown in Figure 4.10. $Cu(OAc)_2(EA)_2$ showed peaks at m/z 304.96 $[Cu(OAc)_2(EG)_2+H]^+$, m/z 305.99 $[Cu(OAc)_2(EG)(EA)+H]^+$, m/z 304.96 $[Cu(OAc)_2(EA)_2+H]^+$, m/z 246.94 $[Cu(OAc)(EA)_2+H]^+$ and m/z 245.93 $[Cu(OAc)(EG)(EA)+H]^+$. Therefore, copper-ethanolamine complex existed many forms in ethylene glycol solution.

Table 4.1 Molecular ion peak corresponding and m/z ratio of copper-ethanolamine complex

Molecular ion peak	m/z (Calculated)	m/z (Found)
$[Cu(OAc)_2(EG)_2+H]^+$	306.78	306.96
$[Cu(OAc)_2(EG)(EA)+H]^+$	305.79	305.99
$[Cu(OAc)_2(EA)_2+H]^+$	304.81	304.96
$[Cu(OAc)(EA)_2+H]^+$	246.73	246.94
$[Cu(OAc)(EG)(EA)+H]^+$	245.74	245.93

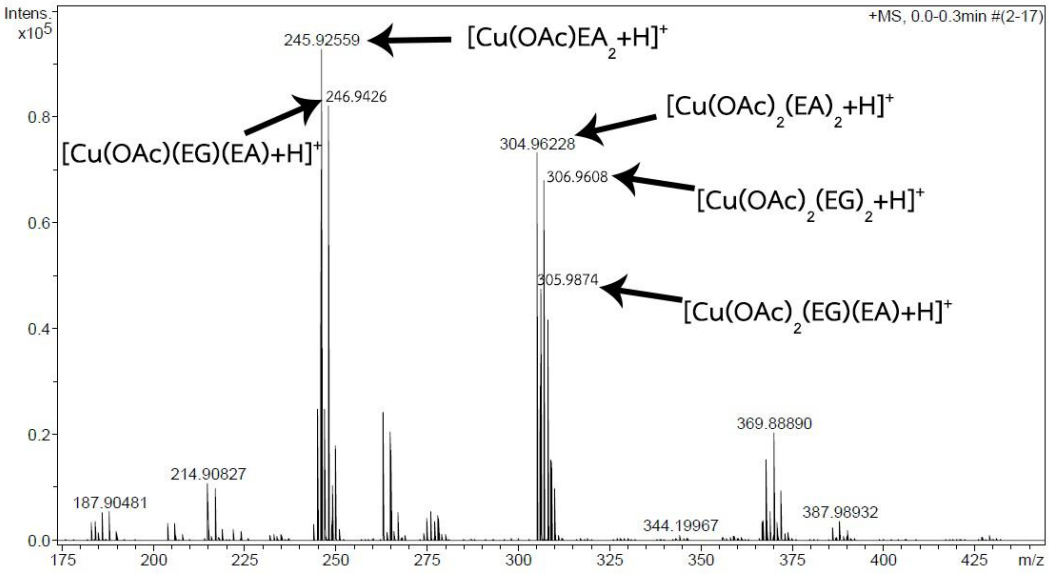

Figure 4.10 Mass spectrum of $Cu(OAc)_2(EA)_2$ in ethylene glycol

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4.2.3.2 Mass spectrometry of zinc-ethanolamine complex

Table 4.2 show the data of molecular ion peaks corresponding and m/z ratio, the molecular ion peaks of $Zn(OAc)_2(EA)_2$ is shown in Figure 4.11. $Zn(OAc)_2(EA)_2$ showed peaks at m/z 308.96 $[Zn(OAc)_2(EG)_2+H]^+$, m/z 307.93 $[Zn(OAc)_2(EG)(EA)+H]^+$, m/z 306.96 $[Zn(OAc)_2(EA)_2+H]^+$ and m/z 183.99 $[Zn(OAc)_2]^+$. Therefore, zinc-ethanolamine complex existed many forms in ethylene glycol solution.

Table 4.2 Molecular ion peak corresponding and m/z ratio of zinc-ethanolamine complex

Molecular ion peak	m/z (Calculated)	m/z (Found)
$[Zn(OAc)_2(EG)_2+H]^+$	308.64	308.96
$[Zn(OAc)_2(EG)(EA)+H]^+$	307.66	307.93
$[Zn(OAc)_2(EA)_2+H]^+$	306.67	306.96
$[Zn(OAc)_2]^+$	183.50	183.99

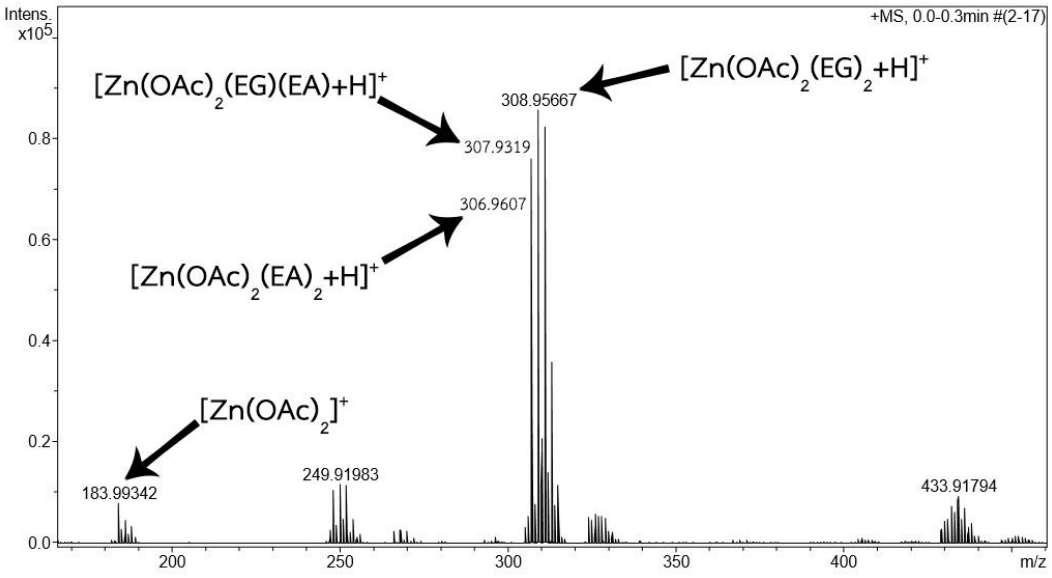

Figure 4.11 Mass spectrum of $Zn(OAc)_2(EA)_2$ in ethylene glycol

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The characterization of the metal-ethanolamine complexes by UV-visible spectroscopy, IR spectroscopy and mass spectrometry confirmed the formation of metal-ethanolamine complexes.

4.3 Preparation of rigid polyurethane (RPUR) foams

Metal-alkanolamine complexes used in the preparation of RPUR foams were 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) which had good solubility in ethylene glycol and gave homogeneous solutions.

4.3.1 Preparation of RPUR foams by cup test and molded method

The preparation of RPUR foam was done in two methods, namely cup test and molded method. The RPUR foam from cup-test method was used for investigation of reaction times, free rise density, rise profile, temperature profile and NCO conversion. The RPUR foam from molded method was used for investigation of compression properties and morphology.

4.3.1.1 Reaction times and density

The reaction scheme for the blowing and gelling reactions are shown in Scheme 4.1. The reaction times for polymerization of RPUR foam investigated were cream time (which is time while polyol and isocyanate mixture begins to change from the liquid state to a creamy and starts to expansion subsequently), gel time (which is the time while polymerization occurs and the foam start to stiffen), free rise time (which is the time while the foam reach to its maximum height) and tack free time (which is the time while the outer skin of the foam loses its stickiness or polymerization is completed). The target in this research was to increase gel time and decreased tack free time when compared with RPUR foams catalyzed by DMCHA.

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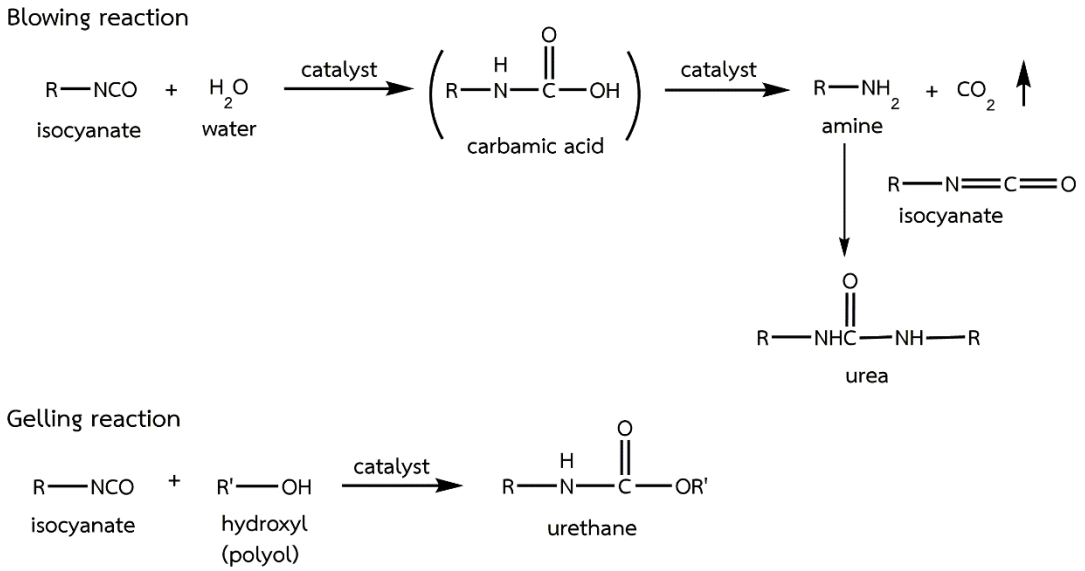
The RPUR foams density was measured in accordance with ASTM D 1622-09 [8]. The foam was cut into the size of 3.0 cm x 3.0 cm x 3.0 cm (length x width x thickness) as shown in Figure 4.12. The height of RPUR foam prepared by cup test was measured as shown in Figure 4.13.



Scheme 4.1 Blowing and gelling reactions of RPUR foam

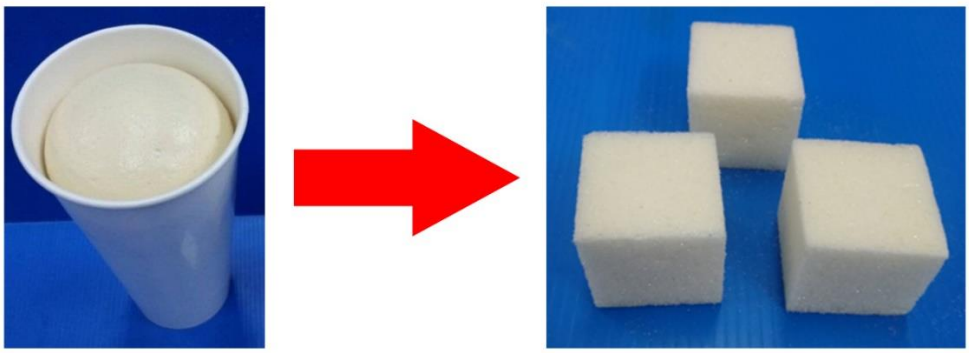


Figure 4.12 RPUR foam samples for foam density measurement

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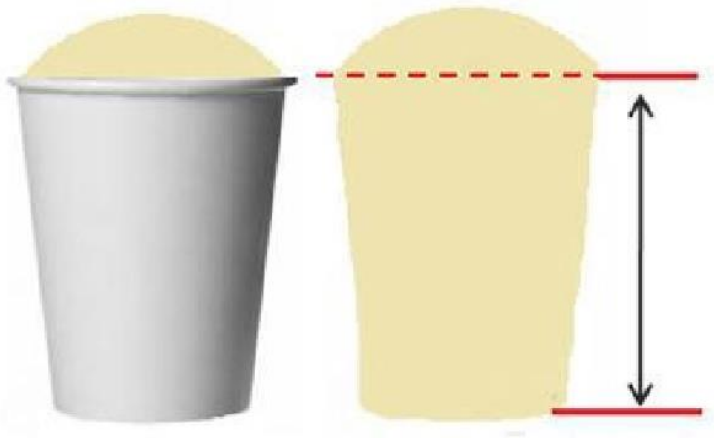

Figure 4.13 Measurement of RPUR foam height [1]

Table 4.3 shows the catalytic activity of RPUR foams catalyzed by 49% $Cu(OAc)_2(EA)_2$ in different ratio of $Cu(OAc)_2$:EA and 43 wt% $Cu(OAc)_2(EA)_2$ (1:4). It was found that the reaction times decreased when increasing the ratio of $Cu(OAc)_2$:EA. But the foams catalyzed by 49% $Cu(OAc)_2(EA)_2$ had wide density range because the complexes did not completely dissolve in ethylene glycol. 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) gave homogeneous solution and therefore it was used to prepared RPUR foam and compared the data with DMCHA.

Table 4.3 Reaction times, density and height of RPUR foams catalyzed by $Cu(OAc)_2(EA)_2$ prepared by cup test method

Catalysts	Cream time (sec)	Gel time (sec)	Rise time (sec)	Tack free time (sec)	Free rise density (kg/m^3)	Foam height (cm)
49 wt% $Cu(OAc)_2(EA)_2$ (1:1)	34	57	119	89	42 - 44	13.7
49 wt% $Cu(OAc)_2(EA)_2$ (1:2)	35	57	115	83	41 - 44	13.7
49 wt% $Cu(OAc)_2(EA)_2$ (1:3)	35	54	113	79	41 - 44	13.5
49 wt% $Cu(OAc)_2(EA)_2$ (1:4)	35	50	104	70	41 - 43	13.8
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	30	69	161	119	39.17	14.6

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Table 4.4 shows the catalytic activity of RPUR foams catalyzed by 48 wt% $Zn(OAc)_2(EA)_2$ in different ratio of $Zn(OAc)_2$:EA. It was found that RPUR foam catalyzed by 48 wt% $Zn(OAc)_2(EA)_2$ (1:4) gave homogeneous solution, however, the bottom part of RPUR foam had higher density than the upper part of RPUR foam. Therefore, 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) gave homogeneous solution and therefore it was used to prepared RPUR foam and compared the data with DMCHA.

Table 4.4 Reaction times, density and height of RPUR foams catalyzed by $Zn(OAc)_2(EA)_2$ prepared by cup test method

Catalysts	Cream time (sec)	Gel time (sec)	Rise time (sec)	Tack free time (sec)	Free rise density (kg/m^3)	Foam height (cm)
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	42	91	222	153	32.37	16.5
48 wt% $Zn(OAc)_2(EA)_2$ (1:4)	31	103	234	163	31 - 34	16.7

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The catalytic activity of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) were compared with that of DMCHA as shown in Table 4.5 and Figure 4.14. It was found that the gel time of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) (69 sec) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) (91 sec) was longer than that of DMCHA (32 sec). Rise time of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) (161 sec) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) (222 sec) was longer than that of DMCHA (101 sec). Tack free time of RPUR foams catalyzed by 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) (153 sec) is longer than that of DMCHA (120 sec), while RPUR foam prepared from 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) (119 sec) had similar tack free time to that prepared from DMCHA (120 sec).

According to the results from Table 4.5, The foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) had lower density (39.17 and 32.37 kg/m^3, respectively) than that catalyzed by DMCHA (42.17 kg/m^3).

Table 4.5 Reaction times, density and height of RPUR foams prepared by cup test method

Catalyst Types	Cream time (sec)	Gel time (sec)	Rise time (sec)	Tack free time (sec)	Free rise density (kg/m^3)	Foam height (cm)
DMCHA (ref.)	20	32	101	120	42.17	15.7
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	30	69	161	119	39.17	14.6
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	42	91	222	153	32.37	16.5

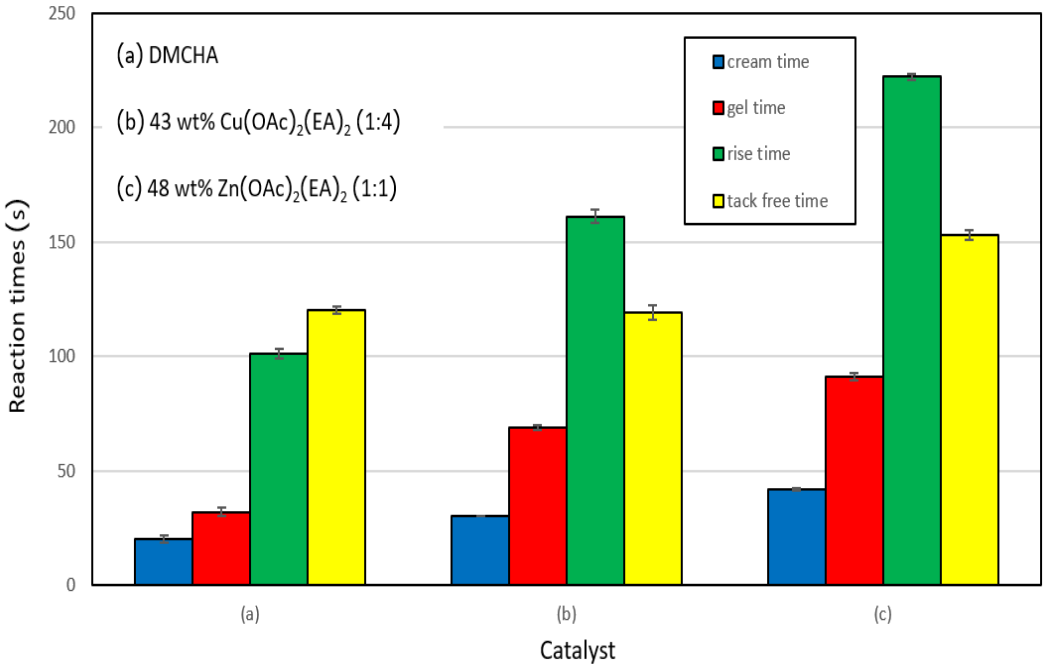

Figure 4.14 Reaction time of RPUR foams catalyzed by (a) DMCHA, (b) 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and (c) 48 wt% $Zn(OAc)_2(EA)_2$ (1:1).

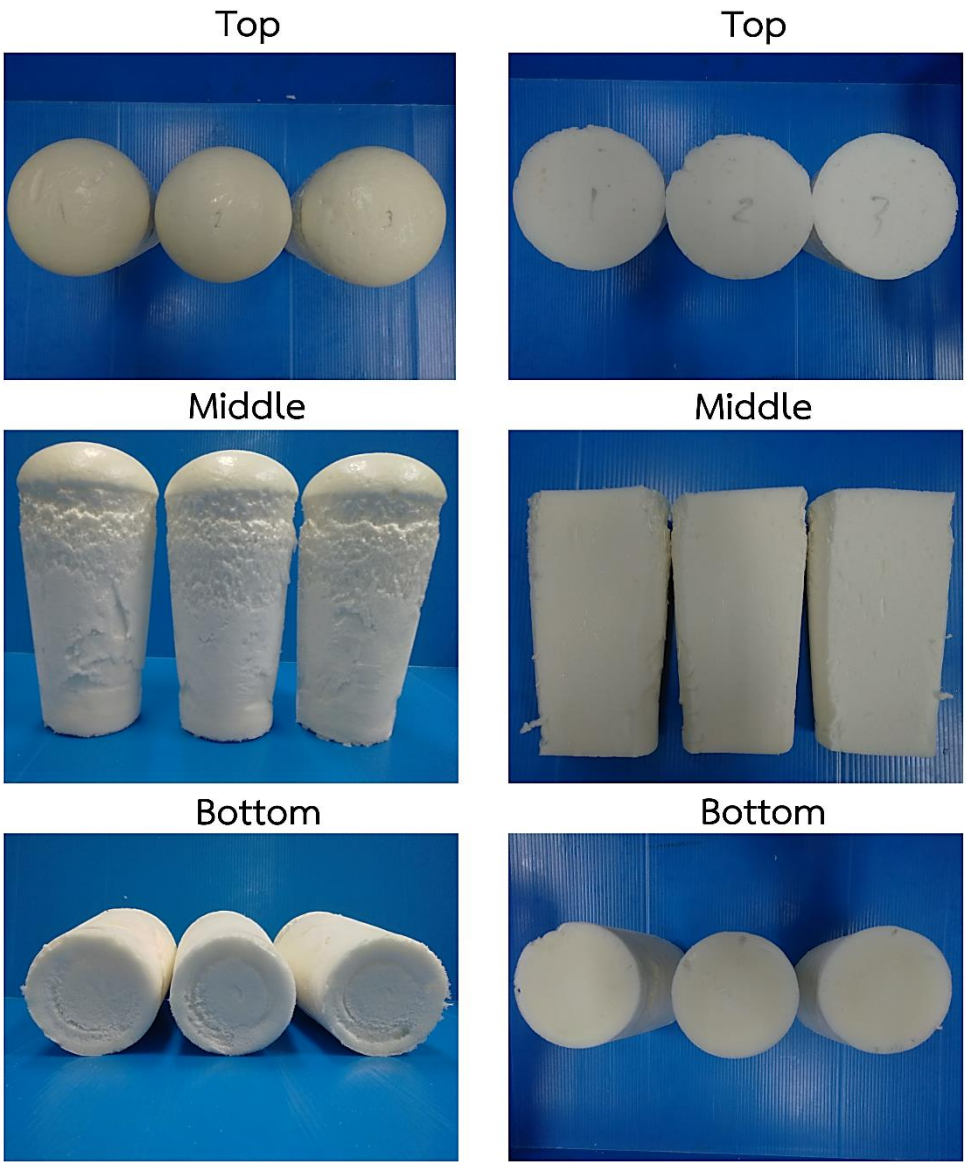

Figure 4.15 RPUR foams catalyzed by DMCHA

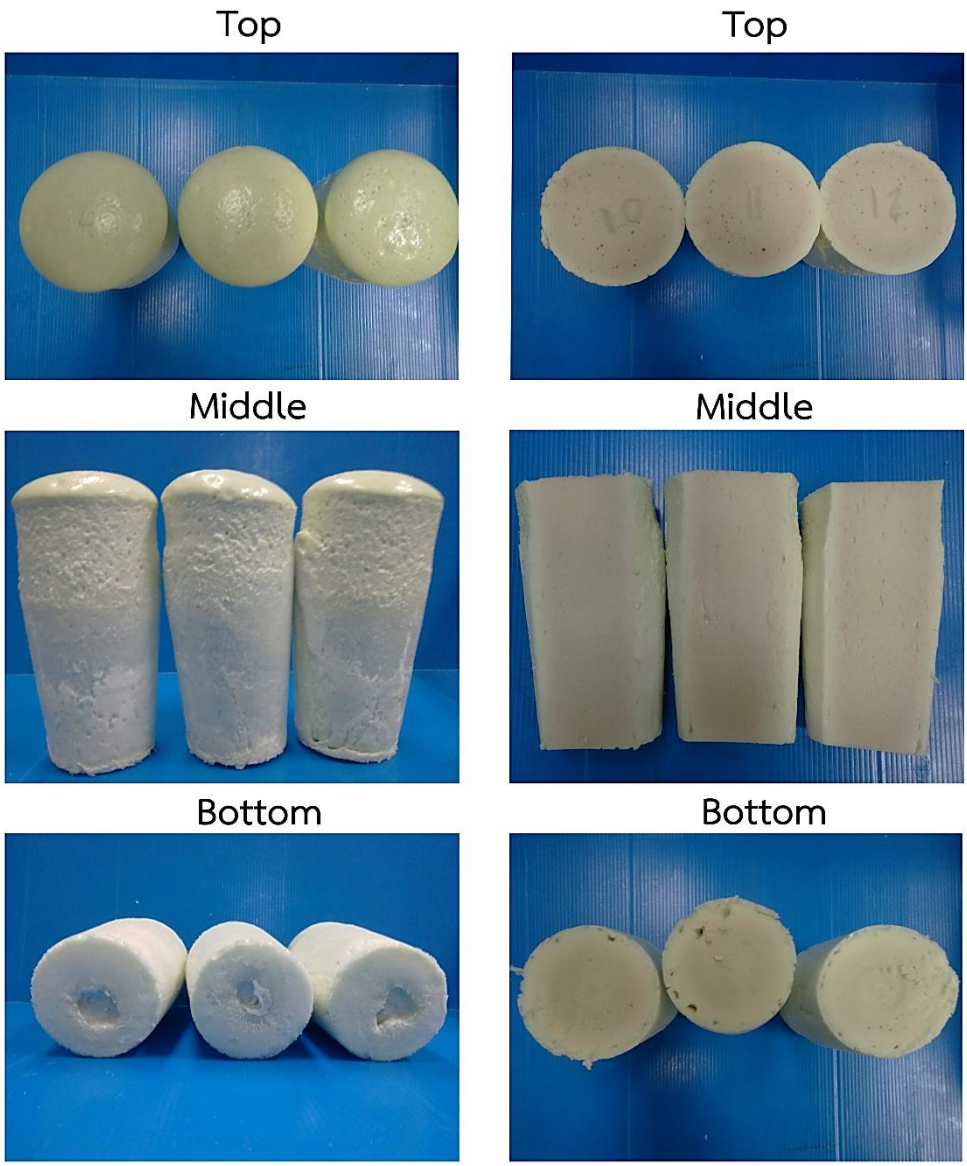

Figure 4.16 RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

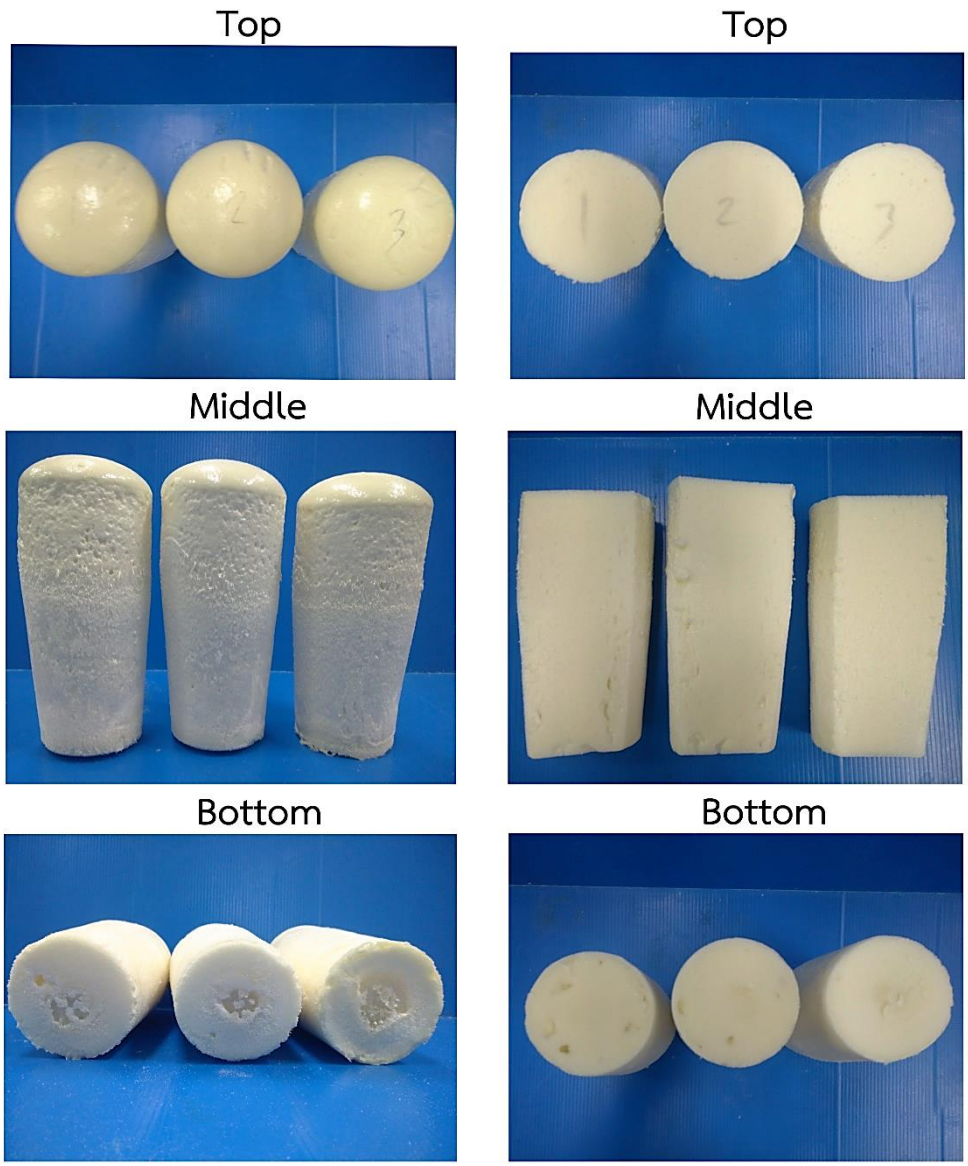

Figure 4.17 RPUR foams catalyzed by 48 wt% $Zn(OAc)_2(EA)_2$ (1:1)

4.3.1.2 Effect of catalyst contents on reaction time

43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) were chosen to investigate the effect of catalyst contents on reaction time as shown in Figures 4.18 and 4.22, respectively. The reaction times decreased when the amount of catalyst was increased. Although the catalyst content at 2.0 pbw gave faster reaction times, there are large holes at the bottom of the mold which resulted in poor property of foams. From these results, the optimum catalyst content for the foam formulation was 1.0 pbw.

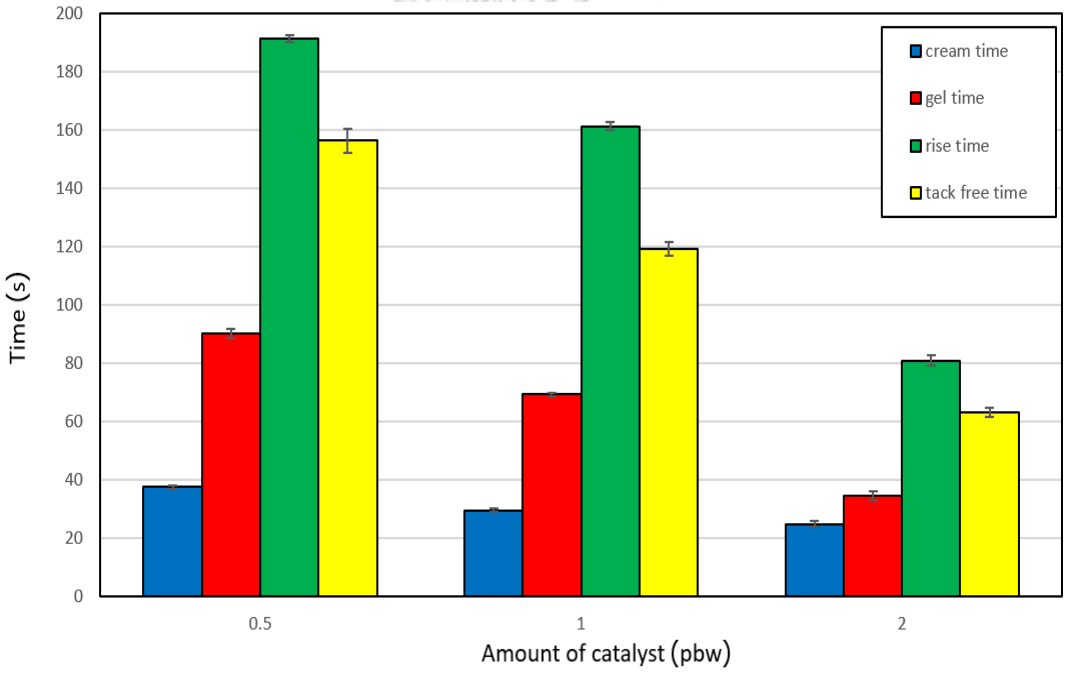

Figure 4.18 The effect of catalyst contents on reaction times of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

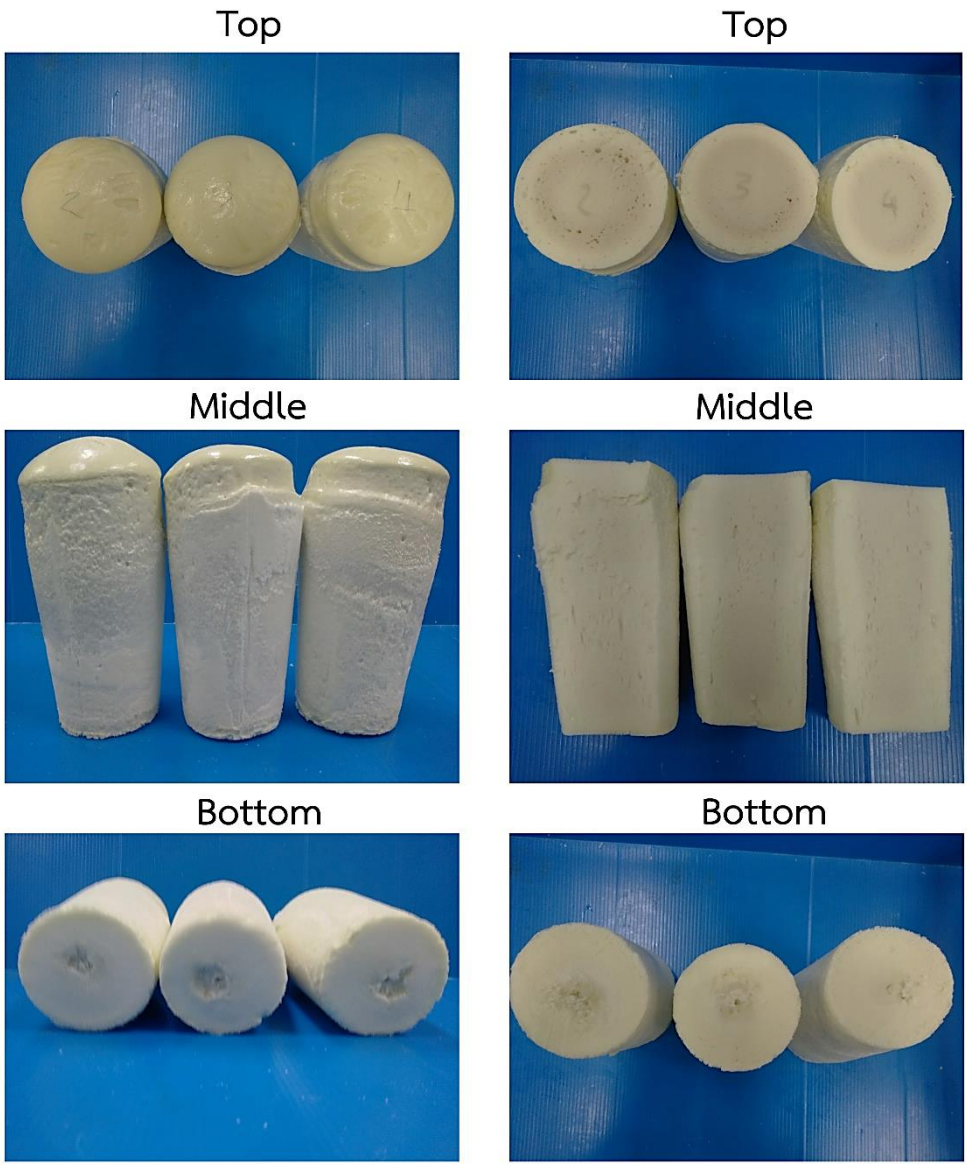

Figure 4.19 RPUR foams catalyzed by 0.5 pbw of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

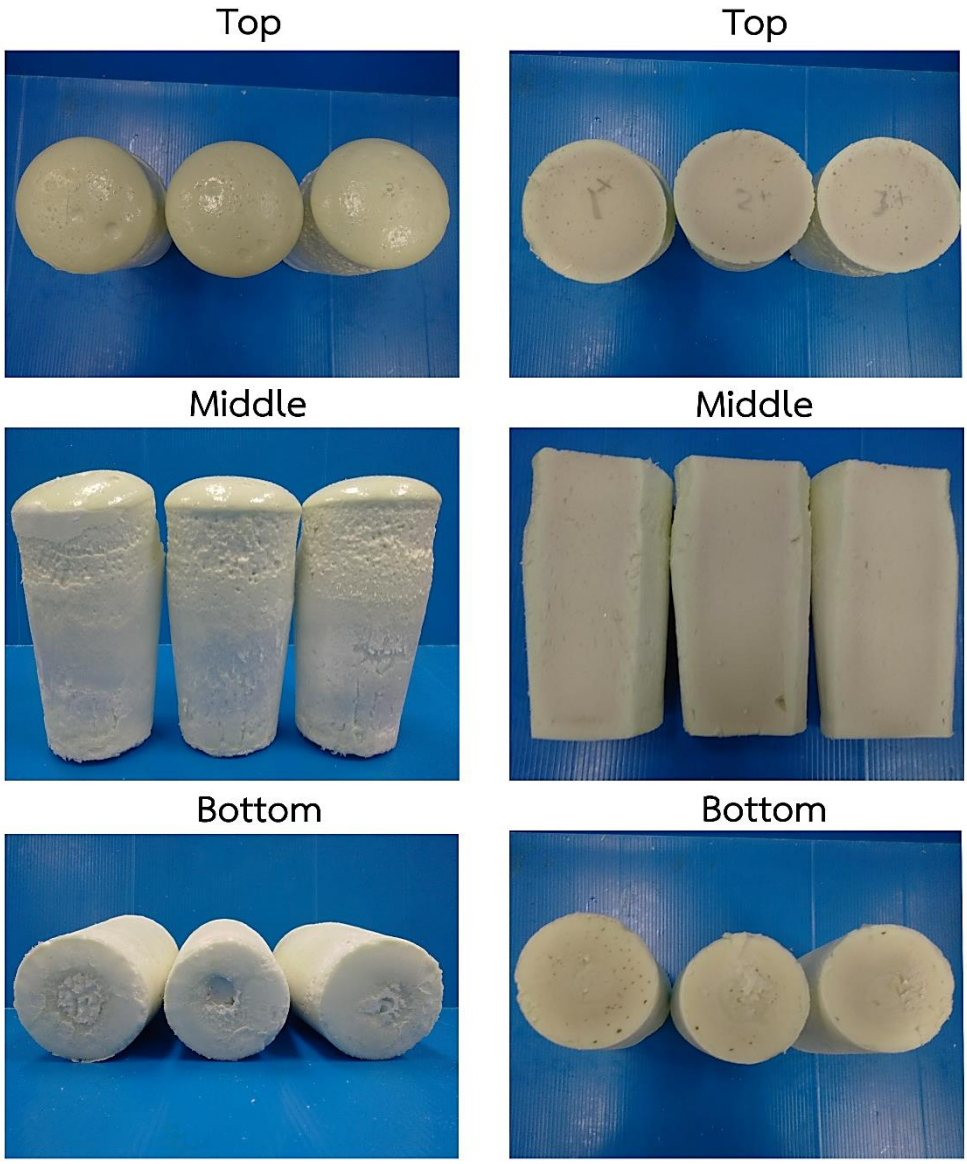

Figure 4.20 RPUR foams catalyzed by 1 pbw of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

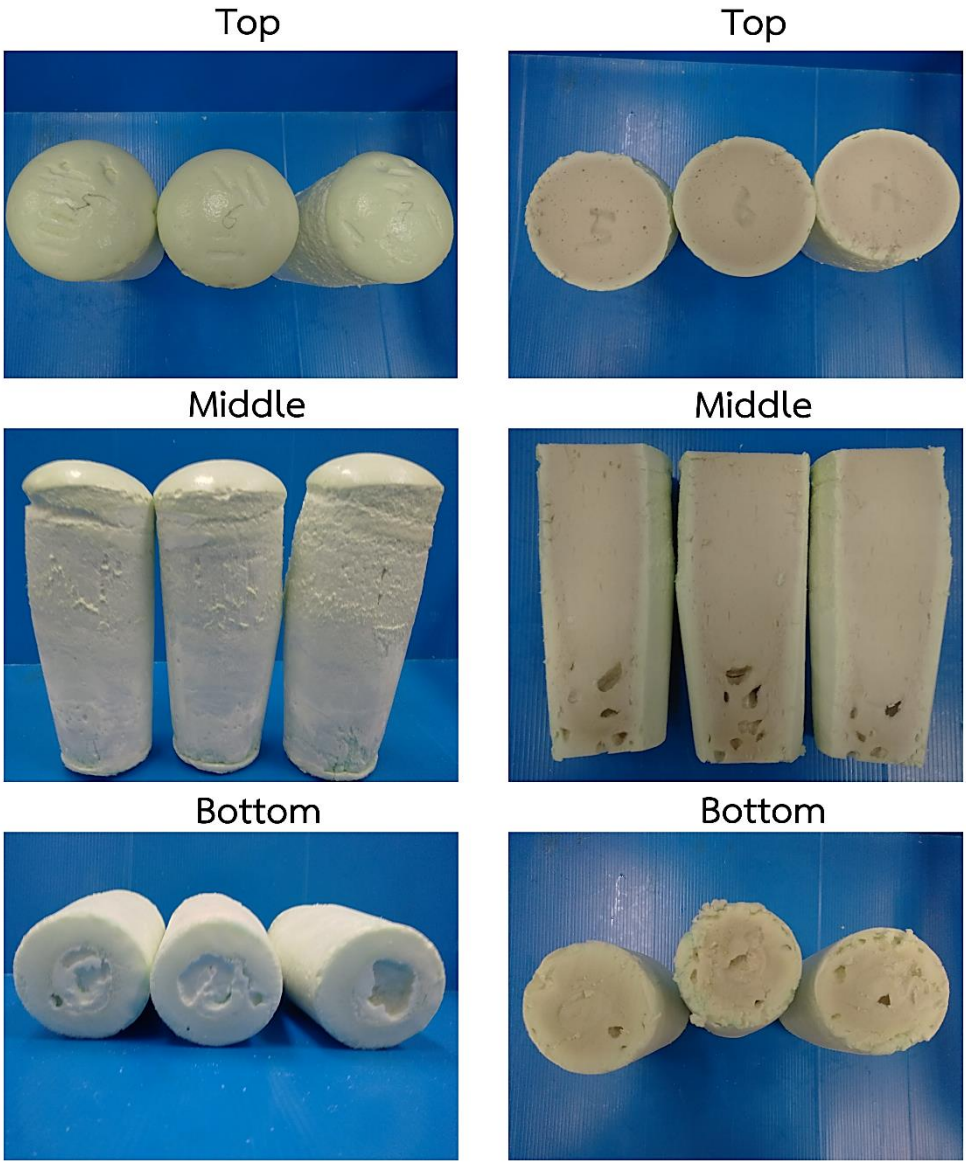

Figure 4.21 RPUR foams catalyzed by 2 pbw of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

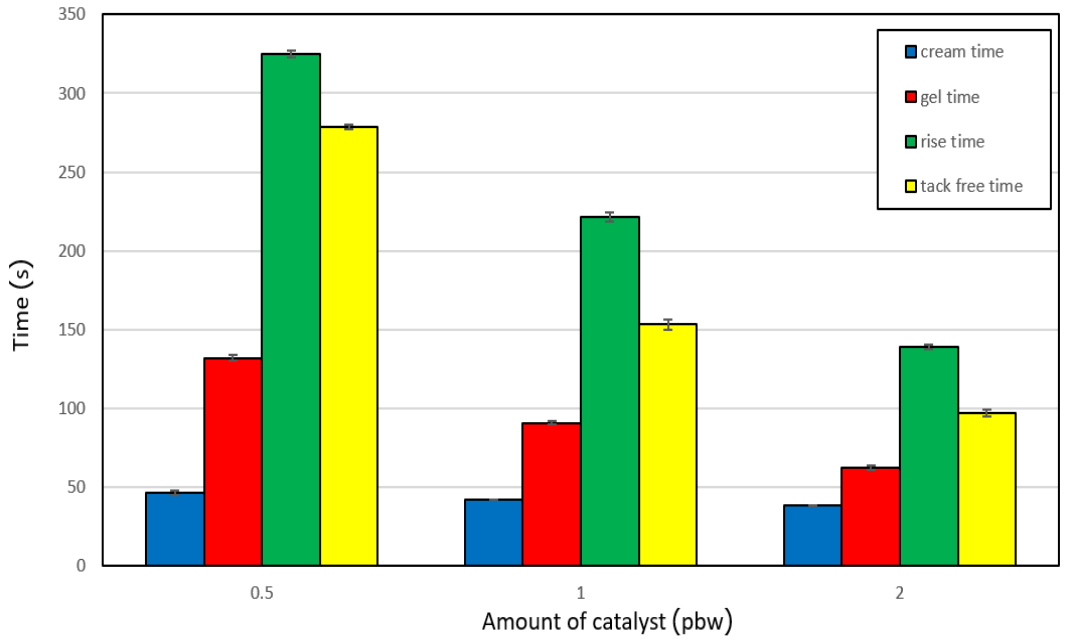

Figure 4.22 The effect of catalyst contents on reaction times of RPUR foams catalyzed by 43 wt% $Zn(OAc)_2(EA)_2$ (1:1)

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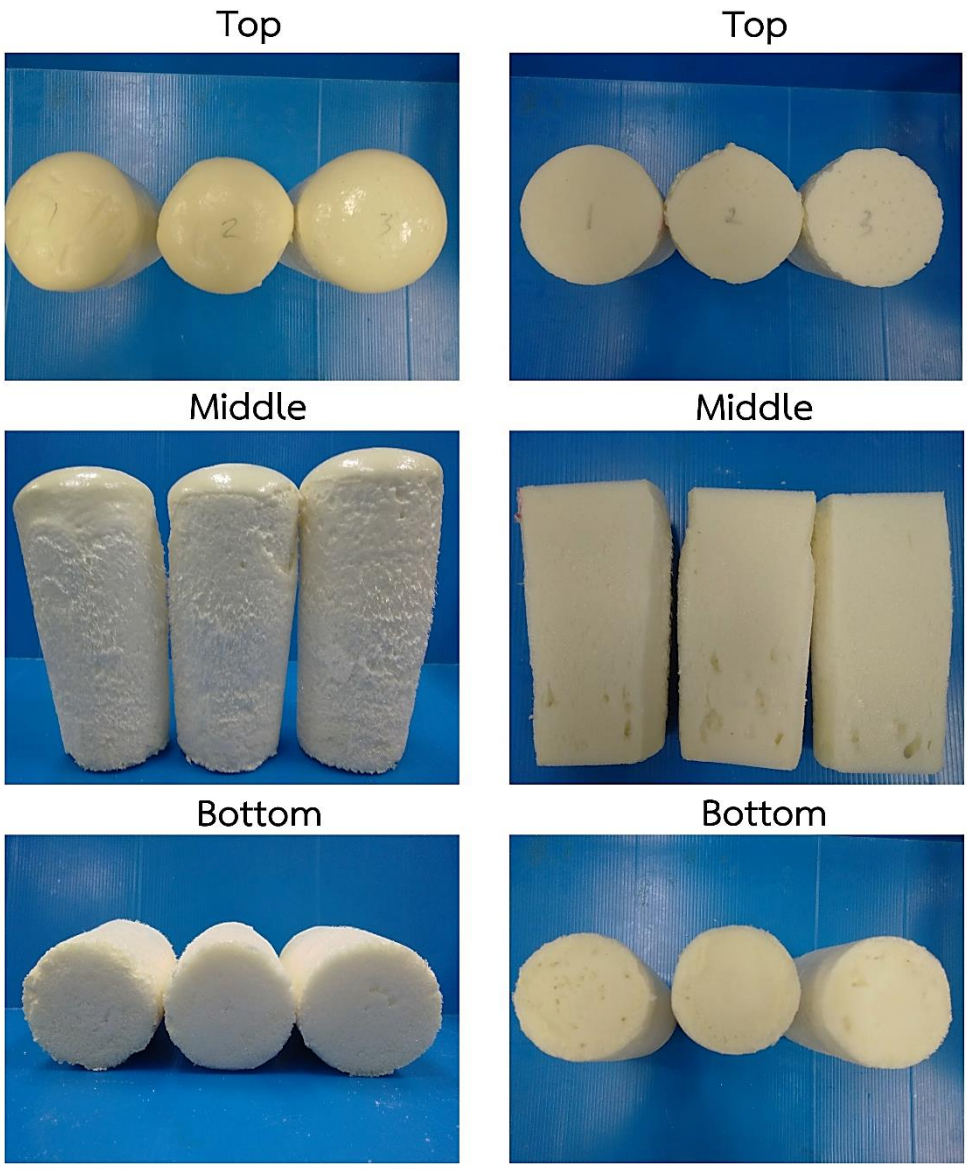

Figure 4.23 RPUR foams catalyzed by 0.5 pbw of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

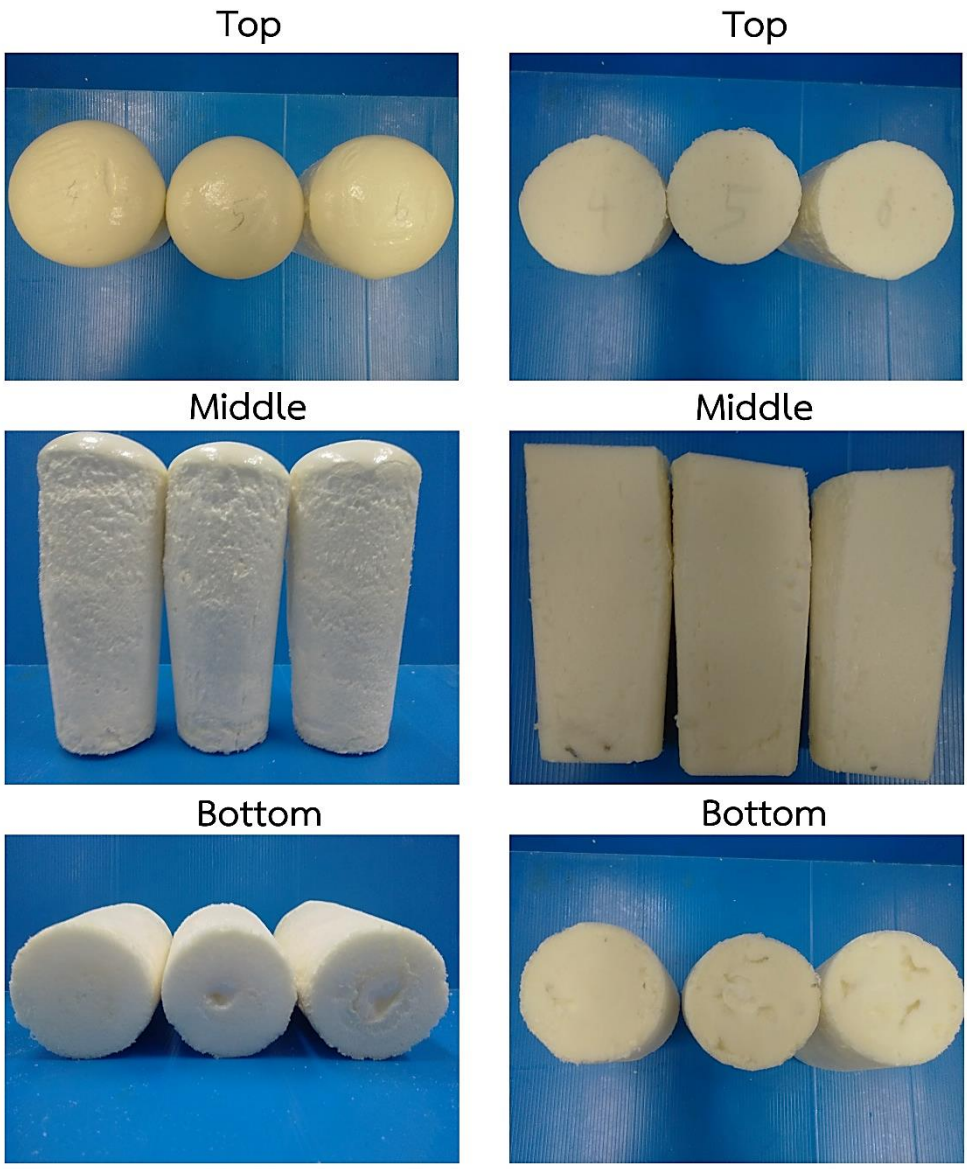

Figure 4.24 RPUR foams catalyzed by 1 pbw of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

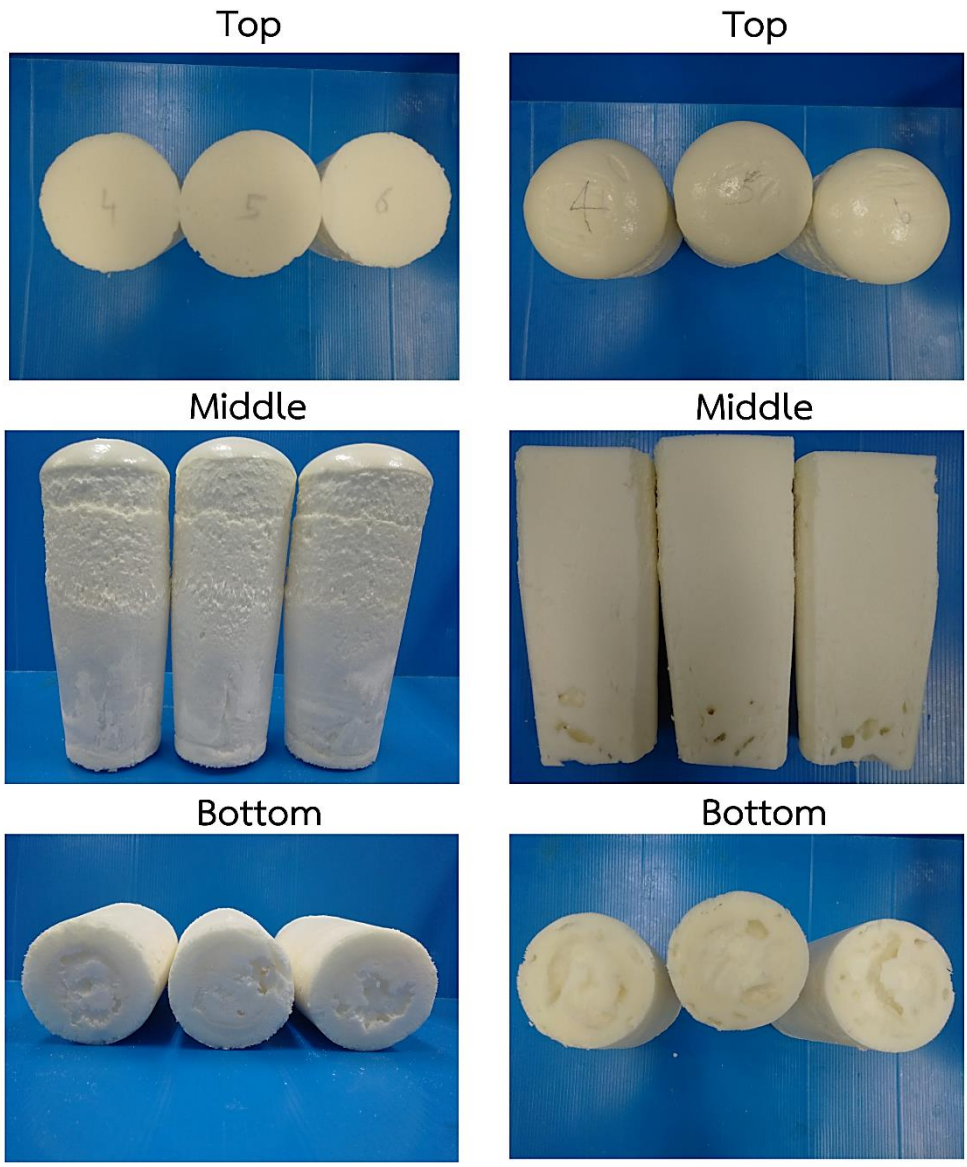

Figure 4.25 RPUR foams catalyzed by 2 pbw of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4)

4.3.1.3 Rise profile

Rise profiles of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) was investigated and compared with the foam catalyzed by DMCHA as shown in Figure 4.26. It was found that RPUR foams catalyzed by DMCHA had higher reactivity in blowing reaction than 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1).

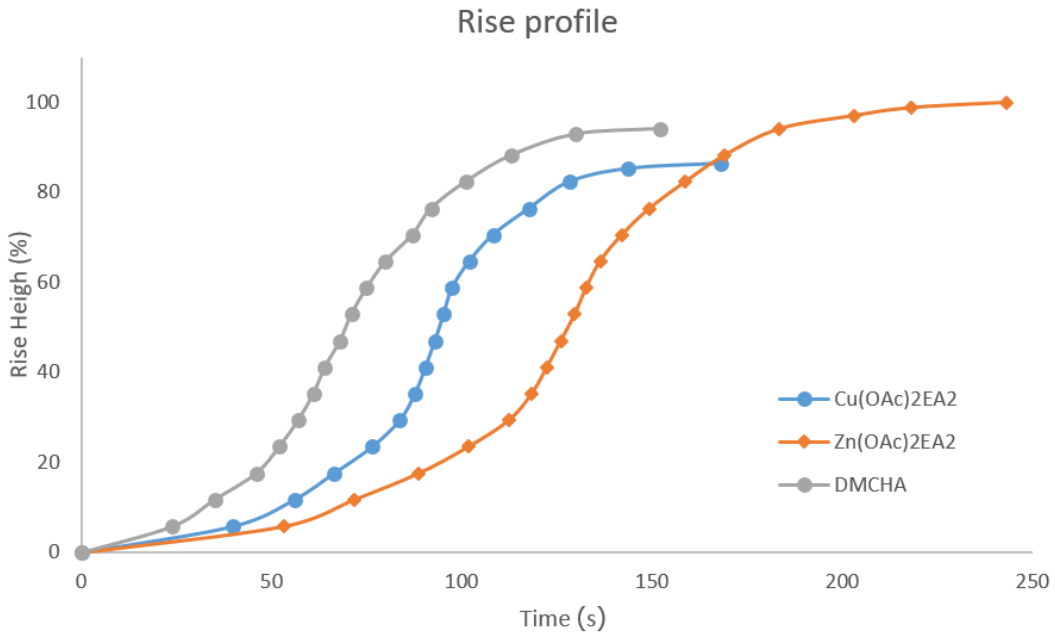

Figure 4.26 Rise profiles of RPUR foams catalyzed by (a) 43 wt% $Cu(OAc)_2(EA)_2$ (1:4), (b) 48 wt% $Zn(OAc)_2(EA)_2$ (1:1), (c) DMCHA

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4.3.1.4 Temperature profile

Temperature profiles of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) was investigated and compared with the foam catalyzed by DMCHA as shown in Figure 4.27. It was found that all of foams was exothermic reaction and similar temperature profiles. The maximum core temperature was in the range 114.5-117.5 °C (Table 4.6) which was appropriate for polymerization reaction of RPUR foams because the foam did not burn at this maximum temperature.

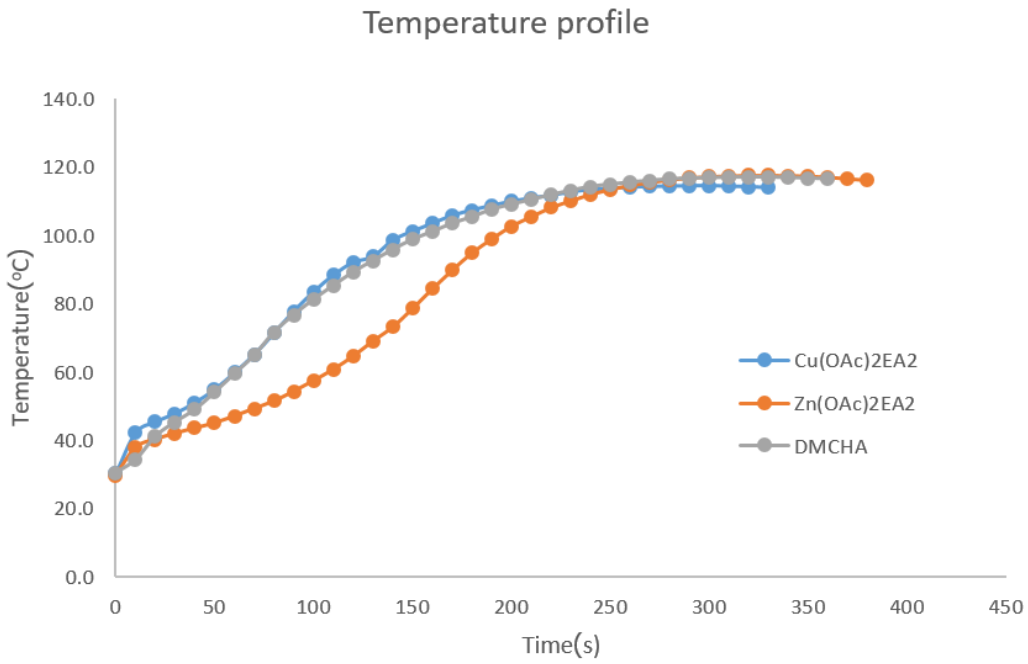

Figure 4.27 Temperature profiles of RPUR foams catalyzed by (a) 43 wt% $Cu(OAc)_2(EA)_2$ (1:4), (b) 48 wt% $Zn(OAc)_2(EA)_2$ (1:1), (c) DMCHA

Table 4.6 The maximum core temperature of RPUR foams catalyzed by metal-alkanolamine complexes, DMCHA.

Catalysts	Maximum core temperature (°C)	Starting times (sec) at T_{max}
DMCHA (ref.)	117.0	320
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	114.5	300
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	117.5	320

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4.3.2 Characterization of rigid polyurethane (RPUR) foams

ATR-FTIR spectroscopy was employed to study and investigate the polymerization reaction of RPUR foam system. IR spectra of polyether polyol, polymeric MDI and RPUR foam catalyzed by DMCHA, 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) are shown in Figures 4.28. Polyether polyol showed a broad band at 3409 cm^{-1}, which is due to the stretching vibration of hydroxyl groups. Polymeric MDI showed high intensity peak of free NCO absorption band at 2,277 cm^{-1}.

All RPUR foams show similar IR absorptions as the absorption bands at 3318-3332, 1705-1710 and 1075 cm^{-1} were NH stretching group, C=O stretching group of urethane and urea and C-O of urethane, respectively. From IR spectra as shown in Figure 4.27, it was found that the reactions of isocyanate with polyether polyol and water were completed by disappearance of isocyanate peak at 2277 cm^{-1}.

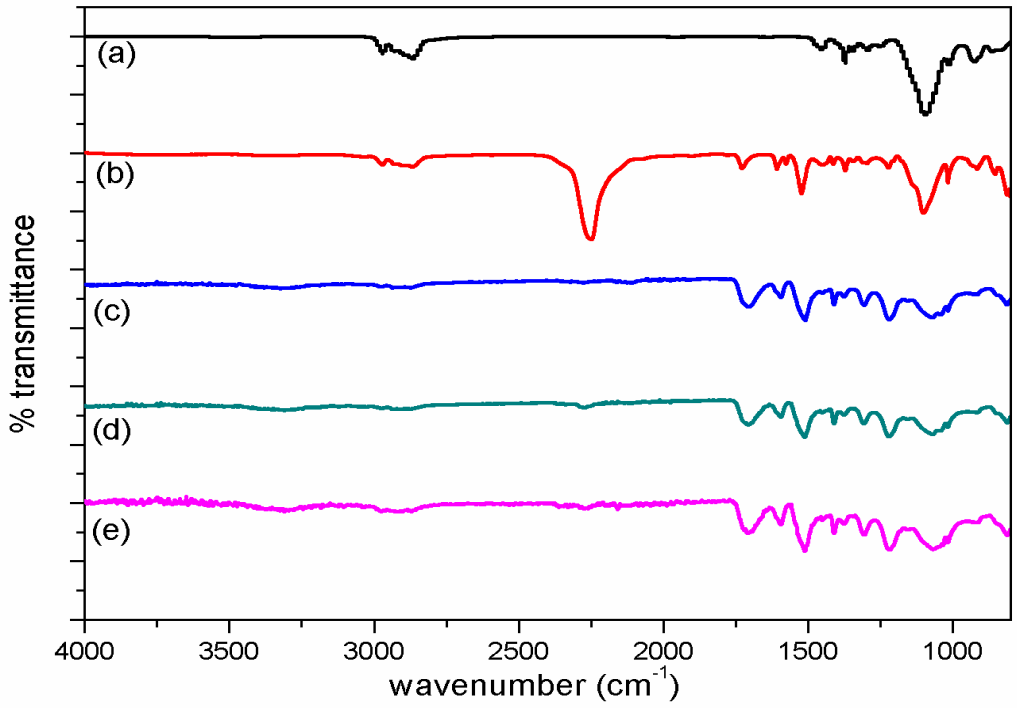

Figure 4.28 IR spectra of (a) polyether polyol (starting material), (b) polymeric MDI (starting material), RPUR foam catalyzed by (c) DMCHA (ref.), (d) 43 wt% $Cu(OAc)_2(EA)_2$ (1:4), (e) 48 wt% $Zn(OAc)_2(EA)_2$ (1:1).

4.3.3 NCO conversion of RPUR foams

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

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

where;

NCO^f = the peak area of isocyanate at time t [Figure 4.16 (c-e)]

NCO^i = the peak area of isocyanate at time 0 [Figure 4.16 (b)]

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

Polyisocyanurate : polyurethane (PIR:PUR) ratio was calculated from the peak area of isocyanate group and urethane group at 1415 and 1220 cm^{-1}, respectively (Table 4.7).

Table 4.7 Wavenumber of the functional groups used in calculation of NCO conversion

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

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Table 4.8 showed NCO conversion of RPUR foams catalyzed by DMCHA, 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1). It was found that all catalysts gave approximately more than 99% of NCO conversion. These results confirmed that the polymerization reactions were completed.

Table 4.8 NCO conversion of RPUR foams catalyzed by DMCHA, 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1).

Catalyst Types	Peak area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f Ar-H = 1		
DMCHA	0.242	2.269	1.027	5.591	0.107	99.9	0.184
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	0.1431	1.887	0.947	5.715	0.076	99.9	0.166
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	0.1552	2.21	1.184	6.902	0.070	99.9	0.172

4.3.4 Compressive properties of RPUR foams

The compression stress-strain curves of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) in perpendicular and parallel to the foam rising direction are demonstrated in Figure 4.29-4.30. From the results, the compressive strength of parallel to the foam rising direction was higher than that of perpendicular compression to the foam rising direction.

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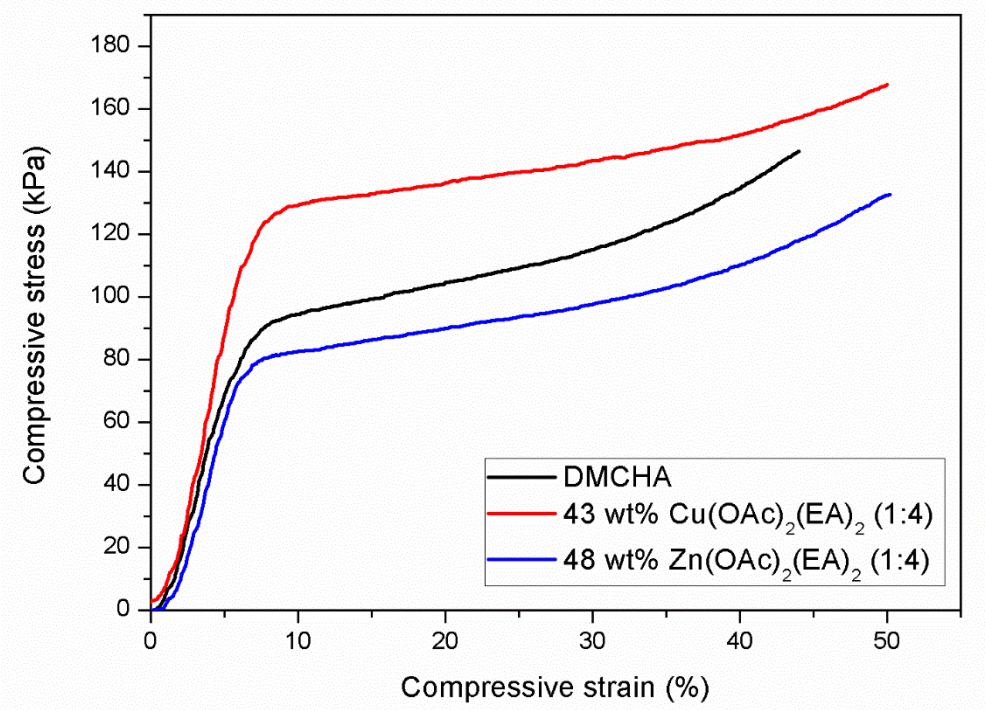

Figure 4.29 Compression stress-strain curves of RPUR foams in perpendicular to the foam rising direction

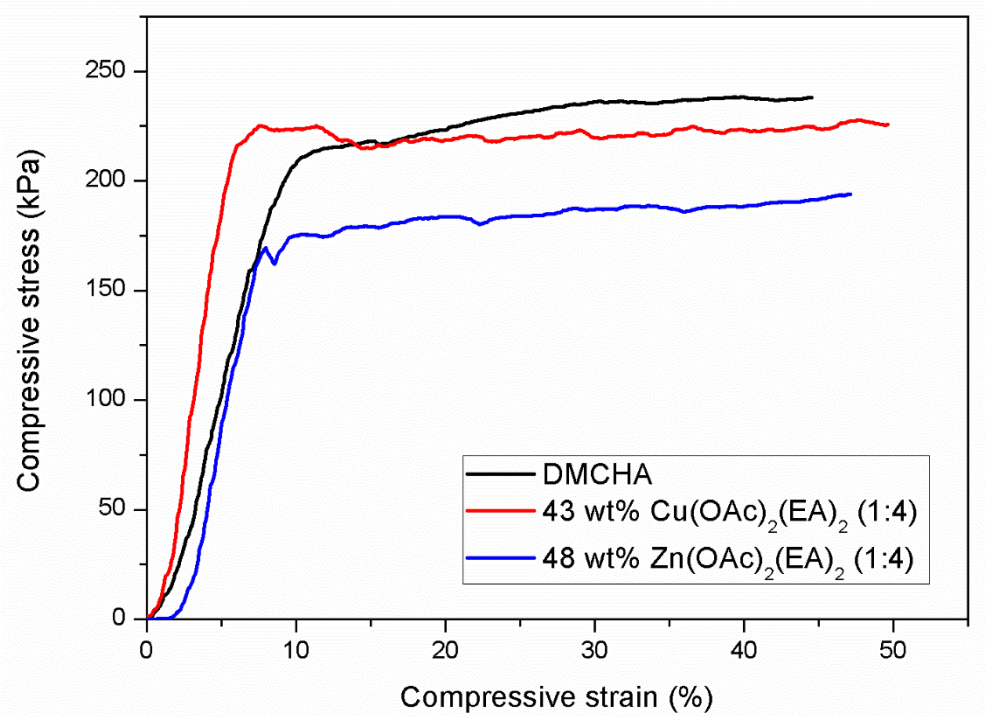

Figure 4.30 Compression stress-strain curves of RPUR foams in parallel to the foam rising direction

Table 4.9 Comparison of compressive strength of RPUR foams between parallel and perpendicular direction of foam rising

Catalyst Types	Compressive strength (kPa) in parallel	Compressive strength (kPa) in perpendicular
DMCHA	209.5	94.5
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	223.7	129.7
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	175.5	82.8

4.3.5 Morphology of RPUR foams

Morphology of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) in parallel and perpendicular to the foam rising direction was investigated and compared with the foam catalyzed by DMCHA as shown in Figures 4.31-4.33. The cell size of spherical cell and ellipsoidal cell were measured from cell-w and cell-h as shown in figure 4.34 (a) and figure 4.34 (b), respectively.

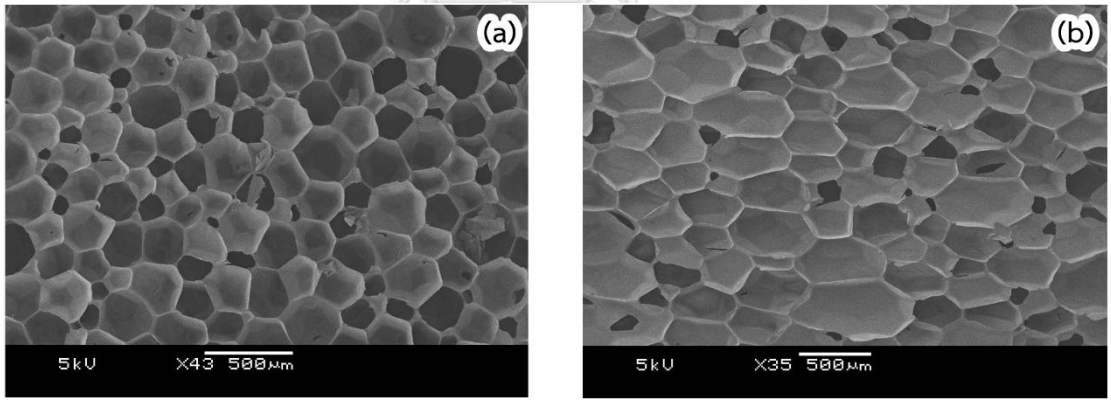

Figure 4.31 SEM of RPUR foam catalyzed by DMCHA (a) top view (43x), (b) side view (35x)

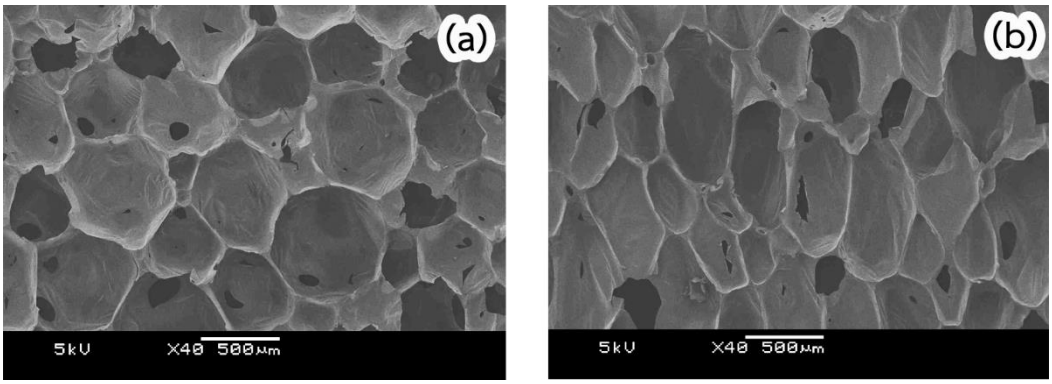

Figure 4.32 SEM of RPUR foam catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) (a) top view, (b) side view (40x)

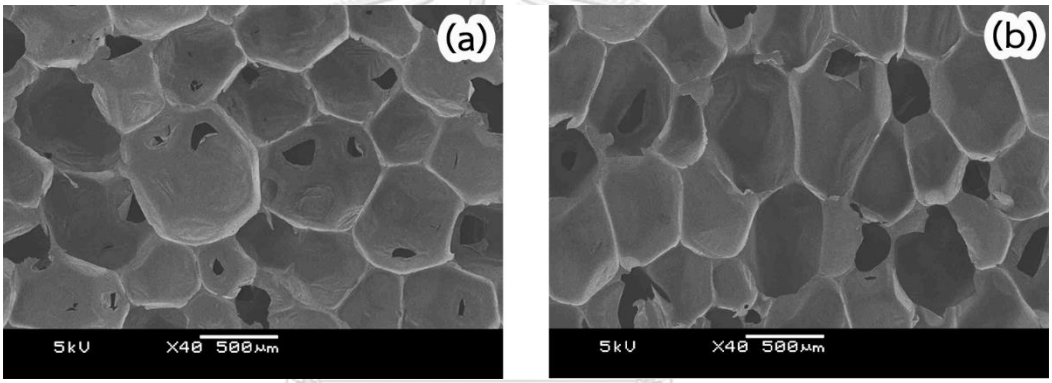

Figure 4.33 SEM of RPUR foam catalyzed by 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) (a) top view, (b) side view (40x)

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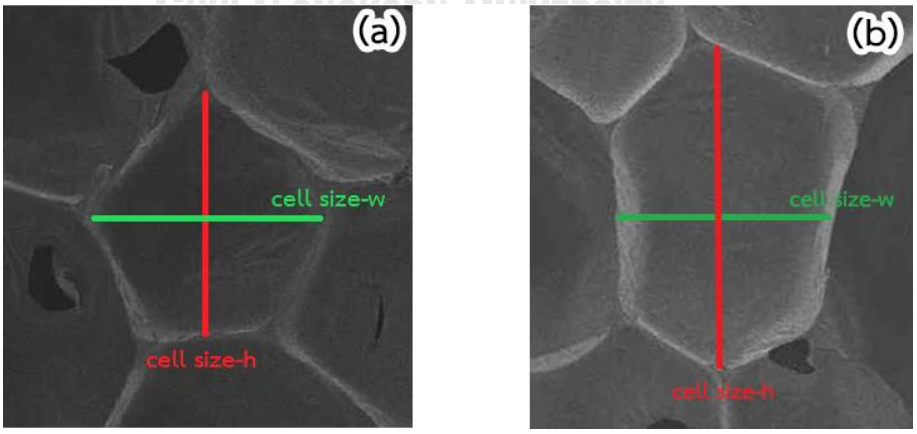

Figure 4.34 Measurement of cell size of RPUR foam

From SEM micrographs, it was found that RPUR foams prepared from DMCHA, 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) had closed cell. The cell morphology showed spherical shape and ellipsoidal shape in parallel and perpendicular direction, respectively. The average cell size of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) are shown in Table 4.10 and 4.11. The cell size in RPUR foam catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) was larger than RPUR foam catalyzed by DMCHA.

Table 4.10 The cell size (top view) of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1)

Catalyst Types	**Top view**	
	Cell size-w (μm)	**Cell size-h (μm)**
DMCHA	287 ± 38.08	288 ± 39.87
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	412 ± 43.26	879 ± 84.38
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	501 ± 47.09	774 ± 82.63

Table 4.11 The cell size (side view) of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1)

Catalyst Types	**Side view**	
	Cell size-w (μm)	**Cell size-h (μm)**
DMCHA	285 ± 33.96	371 ± 52.63
43 wt% $Cu(OAc)_2(EA)_2$ (1:4)	540 ± 92.82	578 ± 88.17
48 wt% $Zn(OAc)_2(EA)_2$ (1:1)	626 ± 109.57	651 ± 74.63

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CHAPTER V
CONCLUSION

5.1 Conclusion

Metal-alkanolamine complexes, namely $Cu(OAc)_2(EA)_2$ (1:1), $Cu(OAc)_2(EA)_2$ (1:2), $Cu(OAc)_2(EA)_2$ (1:3), $Cu(OAc)_2(EA)_2$ (1:4), $Zn(OAc)_2(EA)_2$ (1:1), $Zn(OAc)_2(EA)_2$ (1:2), $Zn(OAc)_2(EA)_2$ (1:3) and $Zn(OAc)_2(EA)_2$ (1:4) were prepared as solutions in ethylene glycol at different concentrations (wt%). It was found that 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) were obtained as homogeneous solutions. Therefore, 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) were used as catalysts for preparation of RPUR foams without purification. UV-visible spectroscopy, FTIR spectroscopy and mass spectrometry confirmed the complex formation.

Copper-ethanolamine complex showed better catalytic activity than zinc-ethanolamine complex because copper-ethanolamine complex is better Lewis acid than zinc-ethanolamine complex. Copper atom can have four, five or six coordinations while zinc atom prefers four coordinations. Therefore, copper atom in copper-ethanolamine complex can act as better Lewis acid in coordination with isocyanate group in pMDI. This cause isocyanate group to have more positive charge and undergoes faster reaction with hydroxyl group in polyol to give urethane group.

The catalytic activity of 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) for RPUR foam preparation has been investigated and compared with that of DMCHA. RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) gave longer gel time, tack free time and rise time as compare with DMCHA. Therefore, $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ are suitable for RPUR foam applications which require longer gel time.

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Rise profile of RPUR foaming reaction catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) had similar trend to that of DMCHA. $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ gave longer reaction time than DMCHA. The polymerization reaction of RPUR foams is exothermic and the maximum core temperature during foaming reaction was in the range of 114.5-117.5 °C, which was appropriate for polymerization of RPUR foam since the foam did not burn or decompose at this temperature range. The NCO conversion was approximately more than 99% at the NCO index of 105. Thus, these complexes were good catalysts for preparation of RPUR foams.

The compressive properties of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) showed compressive strength lower than that catalyzed by DMCHA. Their compressive strength in parallel to the foam rising direction were higher than that in perpendicular direction, which indicated that RPUR foams were anisotropic materials and having ellipsoid cell shape.

Morphology of RPUR foams indicated that the cell structure of RPUR foams catalyzed by 43 wt% $Cu(OAc)_2(EA)_2$ (1:4), 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) and DMCHA are closed cell. The shapes of foam cells in perpendicular to the foam rising direction and parallel to the foam rising direction were spherical and ellipsoidal, respectively.

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5.2 Suggestion for future work

The suggestion for future work is to use 43 wt% $Cu(OAc)_2(EA)_2$ (1:4) and 48 wt% $Zn(OAc)_2(EA)_2$ (1:1) in ethylene glycol solutions with other commercial catalysts, such as potassium octoate, for the preparation of polyisocyanurate foams.

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APPENDIX

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APPENDIX A

NCO index and NCO conversion calculations

NCO index calculation

For example Calculate the parts by weight (pbw) of PMDI (Raycore® B9001), molar mass = 365.8, functionality = 2.7 at an isocyanate index of 105 and amount of H_2O of 3 and 4 pbw required to react with the following formulation:

Starting materials	Formulation (parts by weights, pbw)[a]	
	1	2
Polyol (Polymaxx® 4221)	100.0	100.0
Surfactant (Tegostab® B8460)	2.5	2.5
Catalysts (DMCHA or metal-alkanolamine complexes in ethylene glycol)	1.0	1.0
Blowing agent (distilled water)	3.0	4.0
PMDI (Raycore® B9001)	?	?

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Equivalent weight of Polymaxx® 4221 $= \frac{56.1}{440} \times 1000 = 127.5$

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

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

Equivalent weight of ethanolamine $= \frac{61}{2} = 30.5$

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

Equivalent in the above formulation:

$$\text{Polyol (Polymaxx® 4221)} = \frac{\mathbf{100}}{\mathbf{127.5}} = 0.784$$

$$\text{Water (blowing agent)} = \frac{\mathbf{4.0}}{\mathbf{9.0}} = 0.444$$

$$\text{Ethylene glycol (solvent)} = \frac{\mathbf{0.9352}}{\mathbf{31}} = 0.030$$

$$\text{Ethanolamine (solvent)} = \frac{\mathbf{0.3796}}{\mathbf{30.5}} = 0.012$$

Total equivalent weight = 1.270

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

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$$\text{PMDI (pbw)} = 1.270 \times \frac{\textbf{PMDI molar mass}}{\textbf{functionality}} = 1.270 \times \frac{\mathbf{365.8}}{\mathbf{2.7}} = 172.1$$

Where;

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

Thus:

at Isocyanate index = 105;

$$\text{Isocyanate actual} = \frac{\mathbf{172.1}}{\mathbf{100}} \times 105 = 180.7 \text{ pbw}$$

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

Starting materials	Formulation (parts by weights, pbw)[a]	
	1	2
Polyol (Polymaxx® 4221)	100.0	100.0
Surfactant (Tegostab® B8460)	2.5	2.5
Catalysts (DMCHA or metal-alkanolamine complexes in ethylene glycol)	1.0	1.0
Blowing agent (distilled water)	3.0	4.0
PMDI (Raycore® B9001)	164.9	180.7

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, as shown in the following equation:

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

where;

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

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

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

Table A2 Free NCO absorbance peak area in PMDI (Raycore® B9001) from IR-ATR

PMDI (Raycore® B9001) spectra	NCO absorbance peak area normalized @ 1.0 Ar-H peak area
1	98.02
2	97.95
3	98.11
Average (NCO^i)	98.0

Conversion of isocyanate (%)

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

NCO^i = 98.0

NCO^f = 0.1067

α = [1 – (0.1067/98.0)] x 100 = 99.9

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APPENDIX B

Synthesis of Metal-alkanolamine complexes

74%	1:1	1:2	1:3	1:4	43%	1:1	1:2	1:3	1:4
$EA_{รวม}$	0.140	0.280	0.420	-	$EA_{รวม}$	-	-	-	0.328
EA	0.140	0.280	0.280	-	EA	-	-	-	0.164
EA_{ex}	-	-	0.140	-	EA_{ex}	-	-	-	0.164
EG	0.400	0.260	0.120	-	EG	-	-	-	0.404
Cu	0.460	0.460	0.460	-	Cu	-	-	-	0.268
62%					30%				
$EA_{รวม}$	0.12	0.234	0.351	0.468	$EA_{รวม}$	0.07	-	-	-
EA	0.12	0.234	0.234	0.234	EA	0.07	-	-	-
EA_{ex}	-	-	0.117	0.234	EA_{ex}	-	-	-	-
EG	0.50	0.383	0.266	0.149	EG	0.70	-	-	-
Cu	0.38	0.383	0.383	0.383	Cu	0.23	-	-	-
56%					20%				
$EA_{รวม}$	-	-	-	0.376	$EA_{รวม}$	0.047	-	-	-
EA	-	-	-	0.188	EA	0.047	-	-	-
EA_{ex}	-	-	-	0.188	EA_{ex}	-	-	-	-
EG	-	-	-	0.200	EG	0.800	-	-	-
Cu	-	-	-	0.306	Cu	0.153	-	-	-
49%					48%	Zn complexes			
$EA_{รวม}$	0.094	0.188	0.282	0.376	$EA_{รวม}$	0.087	0.174	0.261	0.348
EA	0.094	0.188	0.188	0.188	EA	0.087	0.174	0.174	0.174
EA_{ex}	-	-	0.094	0.188	EA_{ex}	-	-	0.087	0.174
EG	0.600	0.506	0.412	0.318	EG	0.600	0.513	0.426	0.339
Cu	0.306	0.306	0.306	0.306	Zn	0.313	0.313	0.313	0.313

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Calculated mole ratio of metal-alkanolamine complexes

$Cu(OAc)_2 \cdot H_2O$ Mw = 199.63 g/mol $Zn(OAc)_2 \cdot 2H_2O$ Mw = 219.50 g/mol

Ethanolamine(EA) Mw = 61.08 g/mol

74% $Cu(OAc)_2 \cdot H_2O$ = 0.46 g = 0.46/199.63= 2.304 mmol

EA = 0.28 g = 0.28/61.08 = 4.584 mmol

62% $Cu(OAc)_2 \cdot H_2O$ = 0.383 g = 0.383/199.63 = 1.919 mmol

EA = 0.234 g = 0.234/61.08 = 3.831 mmol

56% $Cu(OAc)_2 \cdot H_2O$ = 0.306 g = 0.306/199.63 = 1.533 mmol

EA = 0.188 g = 0.188/61.08 = 3.078 mmol

49% $Cu(OAc)_2 \cdot H_2O$ = 0.306 g = 0.306/199.63 = 1.533 mmol

EA = 0.188 g = 0.188/61.08 = 3.078 mmol

43% $Cu(OAc)_2 \cdot H_2O$ = 0.268 g = 0.268/199.63 = 1.342 mmol

EA = 0.164 g = 0.164/61.08 = 2.685 mmol

30% $Cu(OAc)_2 \cdot H_2O$ = 0.230 g = 0.230/199.63 = 1.152 mmol

EA = 0.070 g = 0.070/61.08 = 1.146 mmol

20% $Cu(OAc)_2 \cdot H_2O$ = 0.153 g = 0.153/199.63 = 0.766 mmol

EA = 0.047 g = 0.047/61.08 = 0.769 mmol

48% $Zn(OAc)_2 \cdot 2H_2O$ = 0.313 g = 0.313/199.63 = 1.425 mmol

EA = 0.174 g = 0.174/61.08 = 2.849 mmol

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Calculated amount of Catalyst and Isocyanate were used

43% Cu complex [Cu : 4EA]

NCO index calculation

Equivalent weight of polyol = (MW x 1000)/functional = (56.1 x 1000)/490 = 114.49

Equivalent weight of water = MW/functional = 18/2 = 9

Equivalent weight of EG = MW/functional = 62/2 = 31

Equivalent weight of EA = MW/functional = 61/2 = 30.5

Equivalent in the above formulation

Polyol = pbw/Eq = 100/114.49 = 0.8734

H2O = 4/9 = 0.4444

EG = 1.154/31 = 0.0302

EA = 0.703/30.5 = 0.0124

Total Eq weight

= 0.8734+0.4444+0.0302+0.0124

= 1.3604

Isocyanate were used

= (total Eq x Mw)/functional

= (1.3604 x 340)/2.7

= 171.309

Index 100 used 17.13 per cup

Index 105 used (171.309 x105)/100 = 179.874

Isocyanate were used 17.99 per cup

Amount of catalyst

Used cat. 1 pbw

Complex Cu 0.804 g

EA 0.492 g

EA_{ex} 0.492 g

EG 1.212 g

Pbw of complex, EG, EA_{ex}

Solution 3 g; Cu cpx 1.296 g

EA_{ex} 0.492 g

EG 1.212 g

Cu 1.296 g = 1 pbw

EA_{ex} 0.492 g = 0.3796 pbw

EG 1.212 g = 0.9352 pbw

Cu cpx 1.296 g in solution 3 g

Cu cpx 0.1 g(pbw) used 0.23 g

Conclude amount of reactant in cup test

Polyol = 10 g Surfactant = 0.25 g Catalyst [43% $Cu(OAc)_2(EA)_2$ (1:4)] = 0.23 g

H_2O = 0.4 g Isocyanate = 17.99 g

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48% Zn complex [Zn : 4EA]

NCO index calculation

Equivalent weight of polyol = (MW x 1000)/functional = (56.1 x 1000)/490 = 114.49

Equivalent weight of water = MW/functional = 18/2 = 9

Equivalent weight of EG = MW/functional = 62/2 = 31

Equivalent weight of EA = MW/functional = 61/2 = 30.5

Equivalent in the above formulation

Polyol = pbw/Eq = 100/114.49 = 0.8734

H2O = 4/9 = 0.4444

EG = 0.696/31 = 0.0225

EA = 0.357/30.5 = 0.0117

Total Eq weight

= 0.8734+0.4444+0.0225+0.0117

= 1.352

Isocyanate were used

= (total Eq x Mw)/functional

= (1.352 x 340)/2.7

= 170.252

Index 100 used 17.03 per cup

Index 105 used (170.252 x105)/100 = 178.765

Isocyanate were used 17.88 per cup

Amount of catalyst

Used cat. 1 pbw

Complex Zn 0.313 g

EA 0.174 g

EA_{ex} 0.174 g

EG 0.339 g

Pbw of complex, EG, EA_{ex}

Solution 1 g; Cu cpx 0.487 g

EA_{ex} 0.174 g

EG 0.339 g

Zn 0.487 g = 1 pbw

EA_{ex} 0.339 g = 0.696 pbw

EG 0.174 g = 0.357 pbw

Zn cpx 0.487 g in solution 3 g

Zn cpx 0.1 g(pbw) used 0.21 g

Conclude amount of reactant in cup test

Polyol = 10 g Surfactant = 0.25 g Catalyst [48% $Zn(OAc)_2(EA)_2$ (1:4)] = 0.21 g

H_2O = 0.4 g Isocyanate = 17.88 g

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