การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-ไกลซีนและโลหะ-อะลานีน

นางสาวจิระประภา นิราพันธ์

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สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-GLYCINE AND METAL-ALANINE COMPLEXES

Miss Jiraprapa Nirapun

จุฬาลงกรณ์มหาวิทยาลัย
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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 2016

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Thesis Title	PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-GLYCINE AND METAL-ALANINE COMPLEXES
By	Miss Jiraprapa Nirapun
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Nuanphun Chantarasiri, Ph.D.

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จิระประภา นิราพันธ์ : การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-ไกลซีนและโลหะ-อะลานีน (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-GLYCINE AND METAL-ALANINE COMPLEXES) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. นวลพรรณ จันทรศิริ, 88 หน้า.

ในงานวิจัยนี้รายงานการเตรียมโฟมพอลิยูรีเทนแบบแข็งซึ่งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-กรดแอมิโน กรดแอมิโนที่ใช้ คือ ไกลซีนและอะลานีน ซึ่งละลายน้ำได้ดี จึงสามารถเกิดปฏิกิริยากับโลหะแอซิเทต ได้เป็นสารละลายของสารประกอบเชิงซ้อนโลหะ-กรดอะมิโนในน้ำ ข้อดีของตัวเร่งปฏิกิริยานี้ คือ สารละลายของสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนในน้ำไม่มีกลิ่นเหม็นและกรดแอมิโนไม่มีความเป็นพิษ ตรวจสอบเอกลักษณ์ของสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนด้วยยูวี-วิสิเบิลสเปกโทรสโคปี อินฟราเรดสเปกโตรสโกปีและแมสสเปกโตรเมทรี การเตรียมโฟมพอลิยูรีเทนแบบแข็งเตรียมได้จากปฏิกิริยาพอลิเมอไรเซชันระหว่างสารประกอบพอลิเมอริกเมทิลีนไดฟีนิลไดไอโซไซยาเนตกับพอลิออล ที่ค่าดัชนีไอโซไซยาเนตเท่ากับ 100 ศึกษาเวลาที่ใช้ในการเกิดปฏิกิริยาพอลิเมอไรเซชัน สมบัติทางกายภาพ และสมบัติเชิงกลของพอลิยูรีเทนโฟมแบบแข็งที่เตรียมได้ เปรียบเทียบกับข้อมูลจากตัวเร่งปฏิกิริยาทางการค้า คือ ไดเมทิลไซโคลเฮกซิลแอมีน จากผลการทดลองพบว่า สารประกอบเชิงซ้อนคอปเปอร์-อะลานีน เป็นตัวเร่งปฏิกิริยาที่ดีที่สุด โฟมพอลิยูรีเทนแบบแข็งที่เตรียมจากสารประกอบเชิงซ้อนคอปเปอร์-อะลานีน มีสมบัติทางกายภาพและสมบัติเชิงกลที่ใกล้เคียงกับโฟมที่เตรียมจากไดเมทิลไซโคลเฮกซิลแอมีน

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สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต .....

ปีการศึกษา 2559 ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

5771941223 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: POLYURETHANE / FOAMS / CATALYST / AMINO ACID

JIRAPRAPA NIRAPUN: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-GLYCINE AND METAL-ALANINE COMPLEXES. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 88 pp.

In this study, rigid polyurethane foams were synthesized by using the metal-amino acid complexes as catalysts. The amino acids used were glycine and alanine, which are water soluble amino acid. Therefore, they can form complexes with metal acetate in water to give aqueous solution of metal-amino acid complexes. The advantages of this catalysts are the aqueous solution of metal-amino acid complexes do not have odor and the amino acids are non-toxic. The chemical structure of metal-amino acid complexes were characterized by using UV-visible spectroscopy, FTIR spectroscopy and mass spectrometry. Rigid polyurethane (RPUR) foams were prepared by the reaction between polymeric methanediphenyl diisocyanate and polyol at the isocyanate index of 100. The reaction times of foam formation, physical properties and mechanical properties of RPUR foams were investigated and compared with those obtained from a commercial catalyst. The results revealed copper-alanine complex was the best catalyst. Rigid polyurethane foam prepared from copper-alanine complex had comparable physical and mechanical properties to that prepared from dimethylcyclohexylamine.

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Field of Study:	Petrochemistry and Polymer Science	Student's Signature	.....
		Advisor's Signature	.....
Academic Year:	2016		

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Associate Professor Dr. Nuanphun Chantarasiri for helpful suggestion, supervision and guidance throughout the course of this research, and Dr. Duangruthai Sridaeng, assistant-advisor, for the inestimable suggestion.

Besides my advisor, I would like to thank my thesis committee members, Prof.Dr. Suda Kiatkamjornwong, Dr. Duangamol Tungasmita for their valuable suggestions and insightful comments.

Definitely, this research cannot be completed without kindness and helpful of many people such as Huntsman (Thailand) Ltd. and IRPC Public Company Limited for supplying the chemicals used in this research. I would like to acknowledge the 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 would like to acknowledge friends and all members of Supramolecular Chemistry Research Unit for their encouragement and generous helps. Finally, I would like to thank my family for their constant love, encouragement and support.

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%	percentage
ε	molar absorptivity
α	isocyanate conversion
λ_{max}	maximum absorption peak
ATR-IR	attenuated total reflectance-infrared
ASTM	American Society for Testing and Material
cm	centimeter
cm^{-1}	unit of wavenumber
^{o}C	degree Celsius (centrigrade)
CO_2	carbondioxide gas
CFCs	chlorofluorocarbons
$Cu(OAc)_2$	copper acetate
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

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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
PIR	poly(isocyanurate-urethane)
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
Tmax	maximum core temperature
TEDA	triethylenediamine
TDI	toluene diisocyanate

trien	triethylenetetramine
UV	ultraviolet

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CHAPTER I
INTRODUCTION

Polyurethane foams (PUR foams) are produced by the addition polymerization between isocyanate (–NCO) and hydroxyl (–OH) compounds. PUR foams can be classified into three main types: flexible foams, semi-rigid foams and rigid foams [1]. The cell structure depends on the process used for the preparation of polyurethane foams. Flexible polyurethane foam are open-cell structure. Therefore, flexible polyurethane foam is used in cushioning, carpet padding and bedding [2, 3]. Rigid polyurethane foam (RPUR foam) has closed cell structure. RPUR foam is a solid foam material which is used as thermal insulation panel, and construction due to their good insulation materials, low thermal conductivity and low density [4, 5].

The main starting materials used to prepare polyurethane foams are polyisocyanate, polyol, blowing agent, catalyst and surfactant [3, 6]. Two important reactions in the preparation of polyurethane foam are gelling and blowing reactions. Gelling reaction is the reaction between isocyanate (–NCO) and hydroxyl (–OH) compounds to form a urethane group. Blowing reaction is the reaction between isocyanate compounds and water to produce primary amine and carbon dioxide gas, which acts as a blowing agent.

The gelling and blowing reactions must be accelerated by the addition of catalysts such as tertiary amines and organotin compounds because the reaction of isocyanate group with hydroxyl group is slow [7, 8]. Common commercial catalysts used for preparation of RPUR foams are N,N-dimethylcyclohexylamine (DMCHA) and dibutyltin dilaurate (DBTDL) [8]. These catalysts have good catalytic activity but they have odors and toxicity.

Our research group reported the synthesis of copper-amine complexes which could be used as catalysts for RPUR foams preparation, namely $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien). These catalysts have weak odor as compared to DMCHA. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien), could be prepared as solution of copper-amine complexes in ethylene glycol which could be used as catalysts for the preparation of FPUR foam without purification [9].

Objective of the research

The objective of this research was to develop new catalysts, namely metal-amino acid complexes, for the preparation of RPUR foams. The aqueous solution of metal-glycine [M(OAc)(Gly)] and metal-alanine [M(OAc)(Ala)] complexes (where M= Cu and Zn, OAc = acetate, Gly= Glycine, Ala= Alanine) were prepared and used as catalysts in the preparation of RPUR foams. Amino acids are biochemical compounds containing amine ($-NH_2$) and carboxyl (-COOH) functional groups. Glycine and alanine are non-toxic and soluble in water which indicate that they can form complex with the metal ion in water. Reaction times, physical and mechanical properties of RPUR foam were studied and compared to the data obtained from a commercial catalyst (DMCHA).

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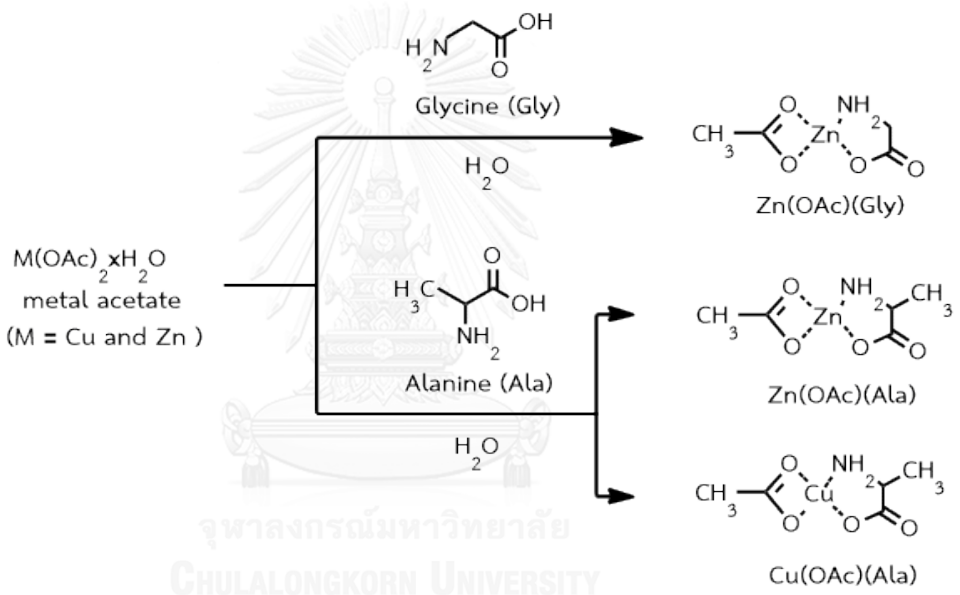
Scope of the research

The experiment can be divided into 2 parts. In the first part, metal-amino acid complexes were synthesized by the reaction between copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$] or zinc acetate dihydrate [$Zn(OAc)_2.2H_2O$] and glycine or alanine. Metal-amino acid complex solutions in water, namely Zn(OAc)(Ala) Zn(OAc)(Gly) and Cu(OAc)(Ala), were obtained (Scheme 1.1). The mole ratios between metal acetate to amino acid were varied at 1:1 and 1:2. The complexes were characterized by UV-Vis, FTIR spectroscopy and mass spectrometry.

In the second part, RPUR foams were prepared using the aqueous solution of metal-amino acid complexes as catalysts. The RPUR foams were prepared by cup-test and molded methods. RPUR foams obtained from cup test method were used for the investigation of reaction times, rise profile, temperature profile, density and NCO conversion. RPUR foams obtained from molded method were used for the investigation of compression properties and morphology. Catalytic activity of the metal-amino acid complexes was compared with that of N,N-dimethylcyclohexylamine (DMCHA), which is a commercial catalyst.



Scheme 1.1 Synthesis of metal-glycine [M(OAc)(Gly)] and metal-alanine [M(OAc)(Ala)] complexes in water (aqueous solutions)

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CHAPTER II
THEORY AND LITERATURE REVIEWS

Polyurethane (PUR) foams are polymers made by addition polymerization. The reaction to give polyurethane is done by reacting isocyanate (-NCO) compounds with hydroxyl (-OH) compounds. Catalyst, surfactant and blowing agent are also added. The specific properties of PUR foams depend on the starting materials in the foam formulation. PUR foams can be both rigid and flexible foams. They are used in many applications such as coating, construction and thermal insulation [3].

Rigid polyurethane (RPUR) foams are good thermal insulation materials that show low thermal conductivity, sound insulation property, low water absorption and light weight (due to their low density). They are also used in many applications such as packaging materials, cold storage and thermal insulation [4, 5].

2.1 Raw materials

The main starting materials for makingthe polyurethane foams are isocyanate and polyols that contains two or more than two founction groups. Surfactants, catalysts, blowing agent are added. Physical properties, thermal stability, density, strength, flowability combustibility and other properties of RPUR foams are controlled by the efficiency in process of reaction and reactants [10].

2.1.1 Isocyanates

Diphenylmethane diisocyanate (MDI) and its derivatives are the major building block for preparing RPUR foams due to the relatively high reactivity of MDI. MDI consists of two forms: purified monomeric MDI and polymeric MDI (PMDI). Pure MDI is the most widely used and also known as 4,4'-diphenylmethane diisocyanate (4,4′-MDI. Polymeric

MDI (PMDI) is a mixture of MDI which contains both 4,4′-MDI and 2,4′-MDI. The chemical structures of MDI monomer and polymeric MDI are shown in Figures 2.1-2.2.

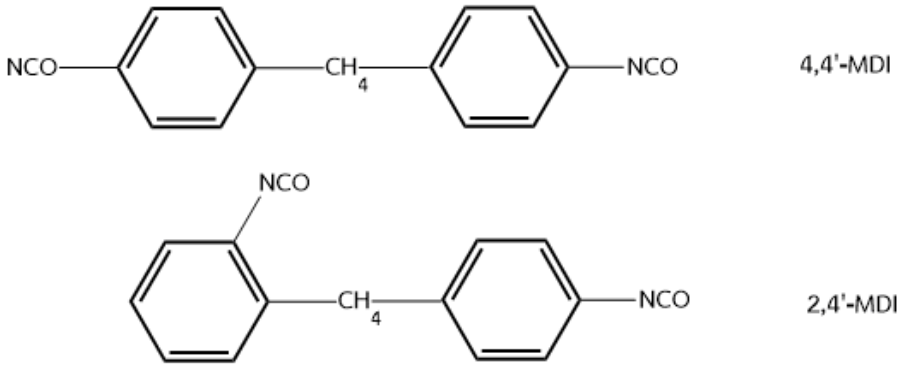

Figure 2.1 Structures of MDI

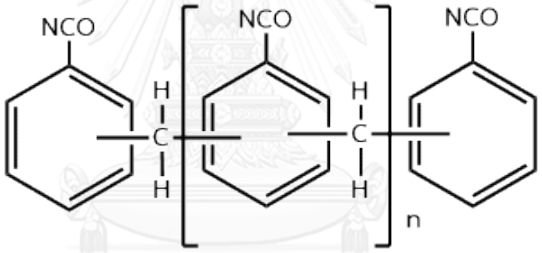

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Figure 2.2 Structure of PMDI

2.1.2 Polyols

The reaction of polyurethane foam is done by reacting isocyanates with polyols, which have compounds hydroxyl groups. The properties of final RPUR foams depend on the structures of polyols. The polyols can be classified into two groups: (i) polyester polyols and (ii) polyether polyols. Polyether polyols have higher hydrolysis resistance and mechanical properties than that of polyester polyols. Production of RPUR foams uses high functionality and low- molecular weight polyols while the production of flexible polyurethane (FPUR) foams uses low functionality and low-molecular weight polyols.

Polyether polyols are prepared by the ring-opening reaction of ethylene or propylene oxides. Glycerol, ethylene glycol, trimethylolpropane, sucrose, and sorbital are used as the polyfunctional initiator [2].

Polyether polyols used in polyurethane (PUR) foams are prepared by condensation polymerization between diacid with two –COOH groups and diol with two –OH groups. Polyester polyols are more viscous than that of polyether polyols. They are difficult to manage when compared with polyether polyol [11].

2.1.3 Surfactants

Polydimethylsiloxane-polyether copolymers or silicone surfactants (Figure 2.3) are the most widely used surfactants for RPUR foam preparation [7]. Surfactants help in improving compatibility of raw materials in the foam formulation. Surfactants control the size of the cell structure by stabilizing the gas bubbles formed during formation of PUR foams and they stabilize the rising foam by reducing stress concentrations in the thinning cell-walls [12].

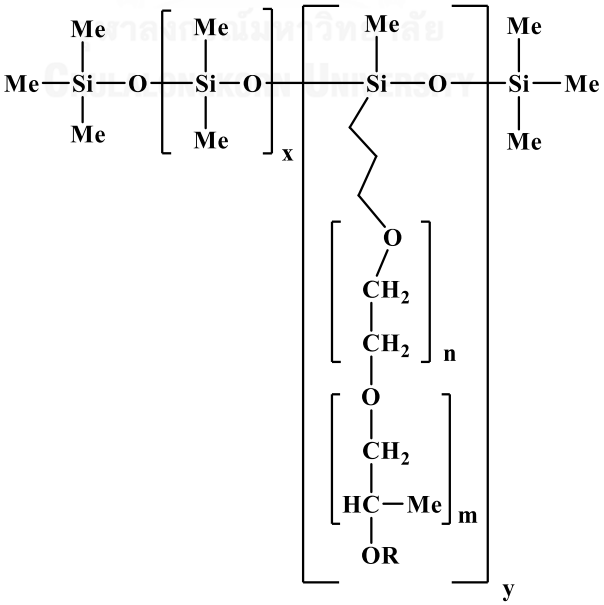

Figure 2.3 Structure of silicone surfactants

2.1.4 Blowing agents

Blowing agent are classified into two types: (i) physical blowing agents and (ii) chemical blowing agents. Chemical blowing agent reacts with isocyanate group to release gas upon thermal decomposition. The most common chemical blowing agent is water, which reacts with the isocyanates. The water/isocyanate reaction produces CO_2 gas bubbles and gives a cellular structure via foaming process. When water is used as the blowing agent, it is generally used in the amounts from 3 to 5 parts by weight per 100 parts by weight of polyol. Chemical blowing agents are typically used to obtain high and medium density foams. The physical blowing agents are liquids which have low boiling points and evaporate into gas when heated from exothermic foaming reaction. The examples of physical blowing agents are chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrocarbons, such as pentane, isopentane and cyclopentane [1, 7].

2.1.5 Catalysts

Catalyst selectivity impacts the reaction balance of the overall reactivity of an isocyanate with water, and specific reactions. The common examples of catalysts used with PUR foams are tertiary amines, quaternary amines, organometallic compounds and carboxylic acid salts.

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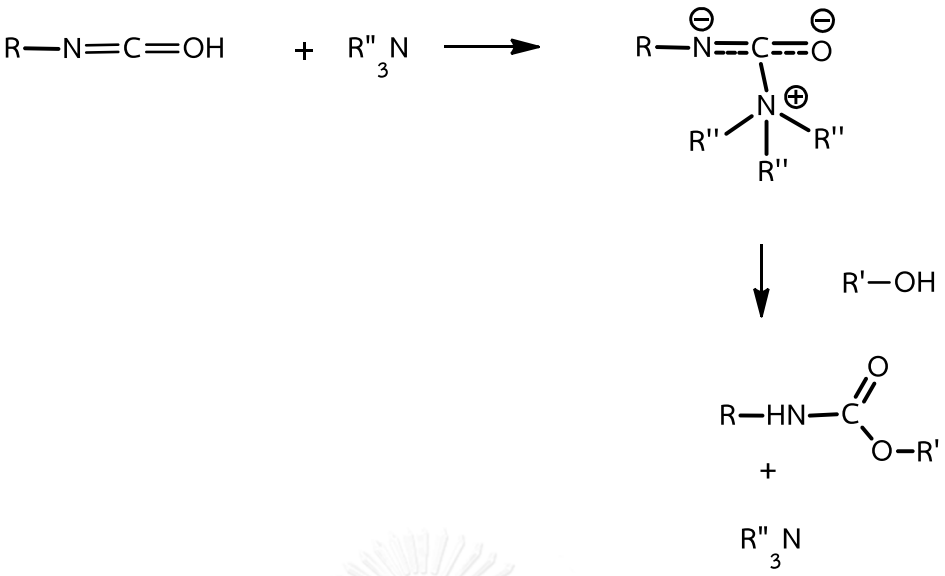
2.1.5.1 Amine catalysts

Tertiary amine catalysts are the most widely used in the preparation of polyurethane foams. The two main types of mechanisms have been proposed[2]. The first mechanism proposed by Baker is shown in Scheme 2.1. The nitrogen atom of amines has a lone pair of electrons to coordinate on the positive charge of the carbon atom in the isocyanate group. The catalytic tertiary amine activate the electrophilic nature of the carbon. Therefore, polyols contain reactive hydroxyl (OH) groups that can react with isocyanate carbon easily.



Scheme 2.1 Baker mechanism of amine catalysts

The second mechanism has been proposed by Farka as shown in Scheme 2.2. The nitrogen atom of tertiary amine can coordinate with the hydrogen atom of hydroxyl (OH) groups. Thus, the reaction of hydroxyl (OH) groups and isocyanate are more easily formed.

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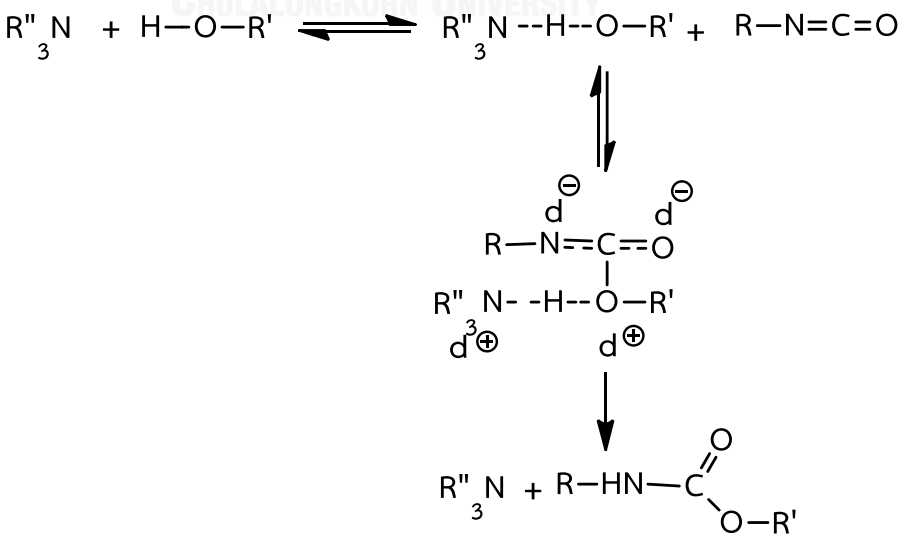
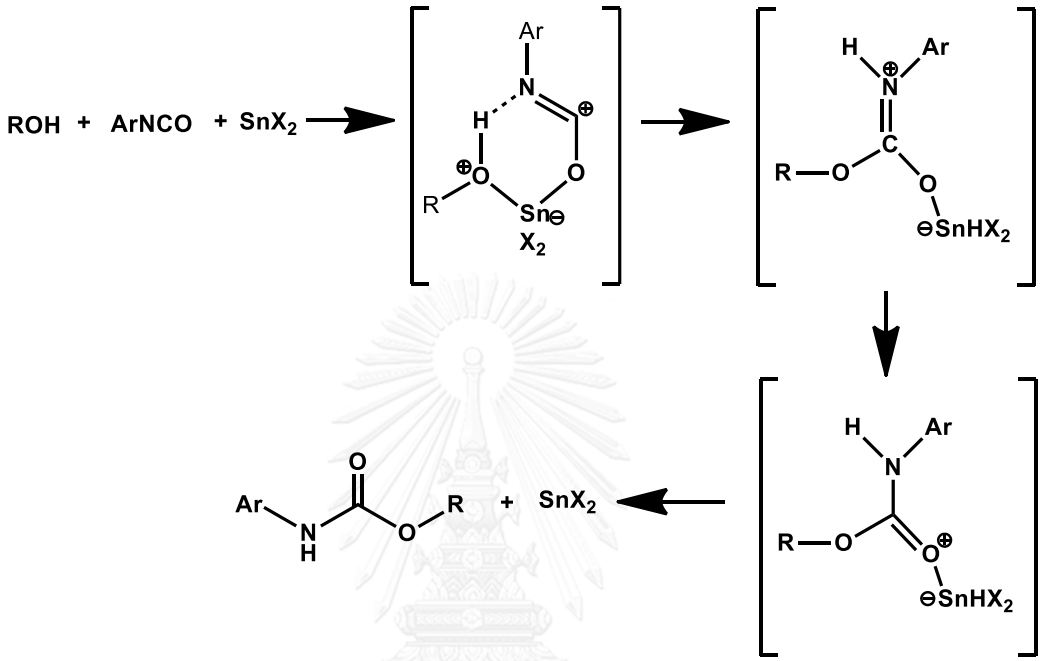


Scheme 2.2 Farka mechanism of amine catalysts

2.1.5.2 Organotin catalysts

The proposed mechanism of tin (II) salt catalyst is shown in Scheme 2.3. The iscocyanate, polyol and tin (II) salt catalyst form a ternary complex, which make urethane product.



Scheme 2.3 Mechanism for tin (II) salts

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2.2 Basic urethane chemistry [3]

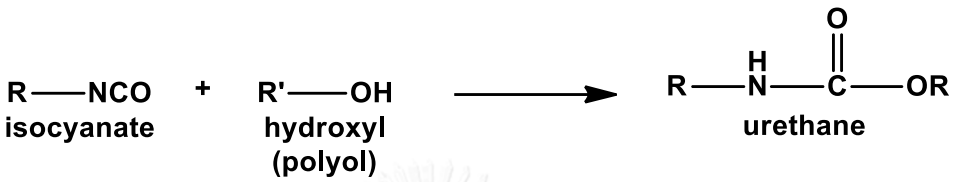
The basic principle of urethane chemistry is described below using a monofunctional reagents.

2.2.1 Primary reactions of isocyanates

Primary addition reactions of isocyanate with hydroxyl (OH) groups and water yields urethane, carbon dioxide (CO_2) and substituted urea.

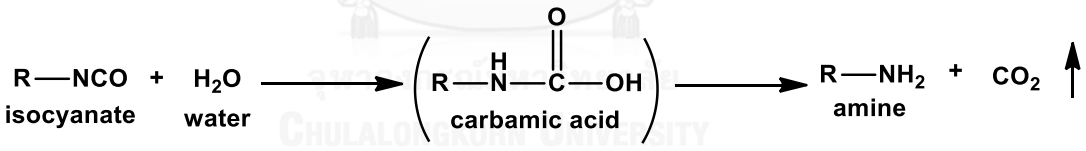
2.2.1.1 Reaction of isocyanate with polyol

The reaction of isocyanate and hydroxyl groups is known as a gelling (or polymerization) reaction. It is an exothermic reaction. The rate of the polymerization reaction is mainly affected by chemical structure of the isocyanate and polyols. For example, the steric hindrance in isocyanate groups and the type of hydroxyl group. The rate of a chemical reaction can be accelerated by using catalysts.



2.2.1.2 Reaction of isocyanate with water

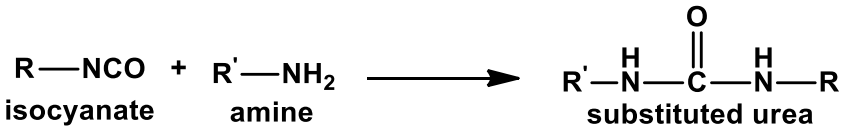
This is known as a blowing reaction. Isocyanate reacts with water to form unstable carbamic acid which then decomposes into an amine and carbon dioxide. The carbon dioxide diffuses and the resulting in a rise of foam. The density of foam is affected by blowing reaction. The reaction rate is also accelerated by catalyst [3].



2.2.2 Secondary reactions of isocyanates

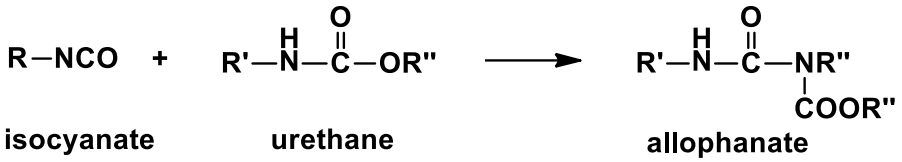
2.2.2.1 Reaction of isocyanate with amine

The chemical reaction between isocyanate and amine gives a urea linkage. Amine can be used as chain-extender in the production of polyurethane foams.



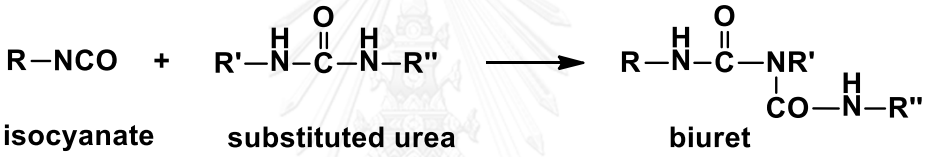
2.2.2.2 Reaction of isocyanate with urethane

The nitrogen atom of the urethane reacts with the isocyanate group, resulting in a allophanate.



2.2.2.3 Reaction of isocyanate with urea

A biuret is formed by the reaction between isocyanate and nitrogen atom of substituted urea.



2.3 Mechanical properties

One of the most important mechanical properties of RPUR foams is the compressive properties. Compressive deformation behavior and energy absorption characteristic of foam depend mainly on foam density and cell types which can be either “open” or “closed” cells.

Flexible polyurethane foams are open-cell foams. The deformation involves cell wall bending and bucking, gas compression, cell wall stretching yielding (reversible). It becomes 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 considerably during the final compression stage (Figure 2.4).

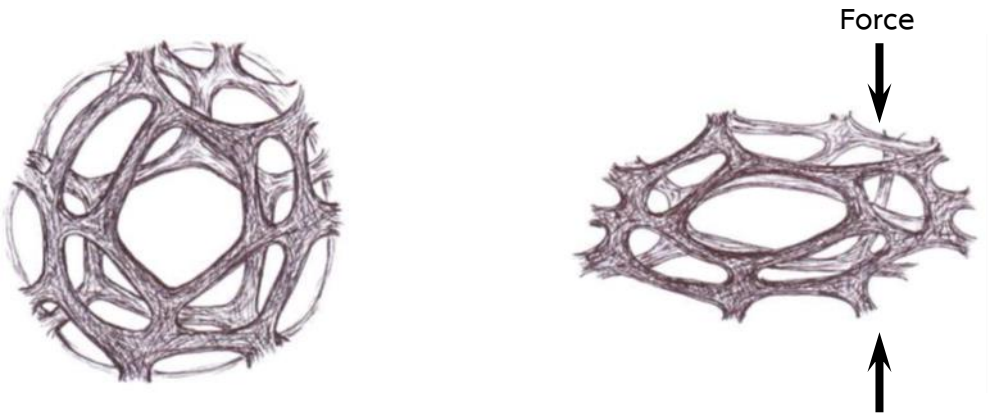


Figure 2.4 The deformation behaviour of an open-cell foam [2]

Rigid polyurethane foams are closed- cell foams. Free air flow is not a consideration in closed cell foams. The deformation involves cell wall bending and bucking, gas compression, cell wall stretching/ yielding (non- reversible) . Severe compression causes cell rapture. (Figure 2.5) [2].

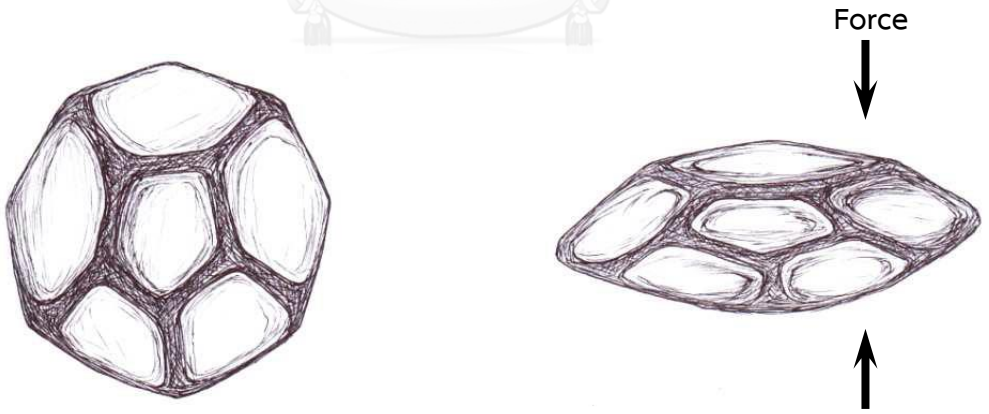


Figure 2.5 The deformation behaviour of an closed cell foam.[2]

Closed cell RPUR foams exhibit from very limited to no yielding behavior. Thus, gas compression and matrix strength play an important role during in the mechanical deformation of RPU) foams. During the process, cell rupture often occurs during the energy absorption process. The energy-absorbing characteristics of RPUR foams can be represented in the compression stress–strain curve (Figure 2.6).

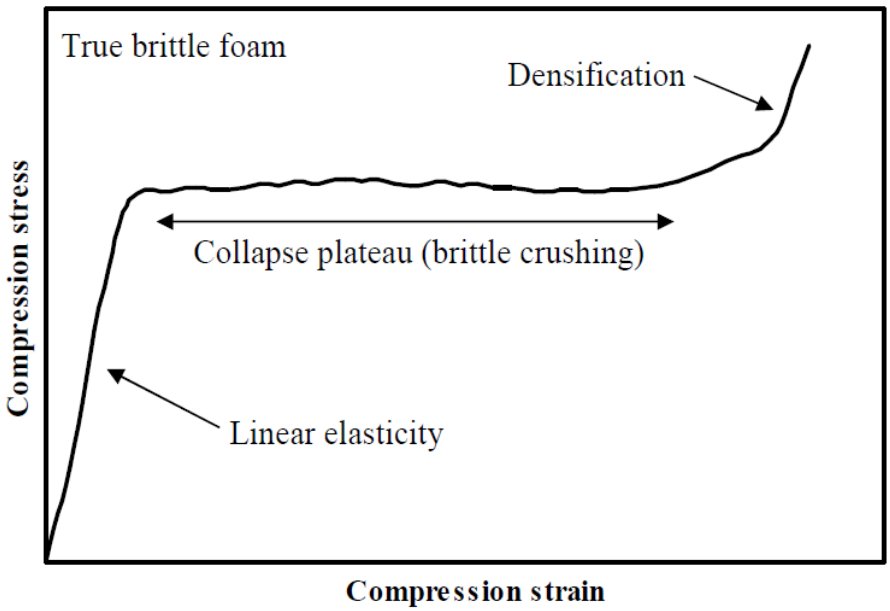


Figure 2.6 Typical shape of the compression stress-strain curve for RPUR foams [13]

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For rigid foams, elements of true crushing of brittle foams 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 that the cell rupture in rigid foams, resilience has therefore dramatically affected. Foams can generally resist only single impacts.

Typically, the compressive strength of RPUR foam is usually reported at some definite deformation (5 or 10%). RPUR foam was tested parallel and perpendicular. 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 [14].

2.4 Literature reviews

2.4.1 Literature reviews about use of transition metal complexes as catalysts in the preparation of RPUR foams.

The previous works in our research group focused on using copper-amine as catalysts in the preparation of RPUR foams as described below.

Pengjam et al. [15] synthesized copper-amine complexes, $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) where OAc = acetate; en = ethylenediamine; trien = triethylenetetramine, as pure compounds. The synthesis was done using acetone as a solvent and acetone was removed to obtain pure metal complexes. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) can be used as catalysts instead of N,N-dimethylcyclohexylamine (DMCHA). DMCHA used for RPUR foams production emitted strong odor while copper-amine complexes have weak odor.

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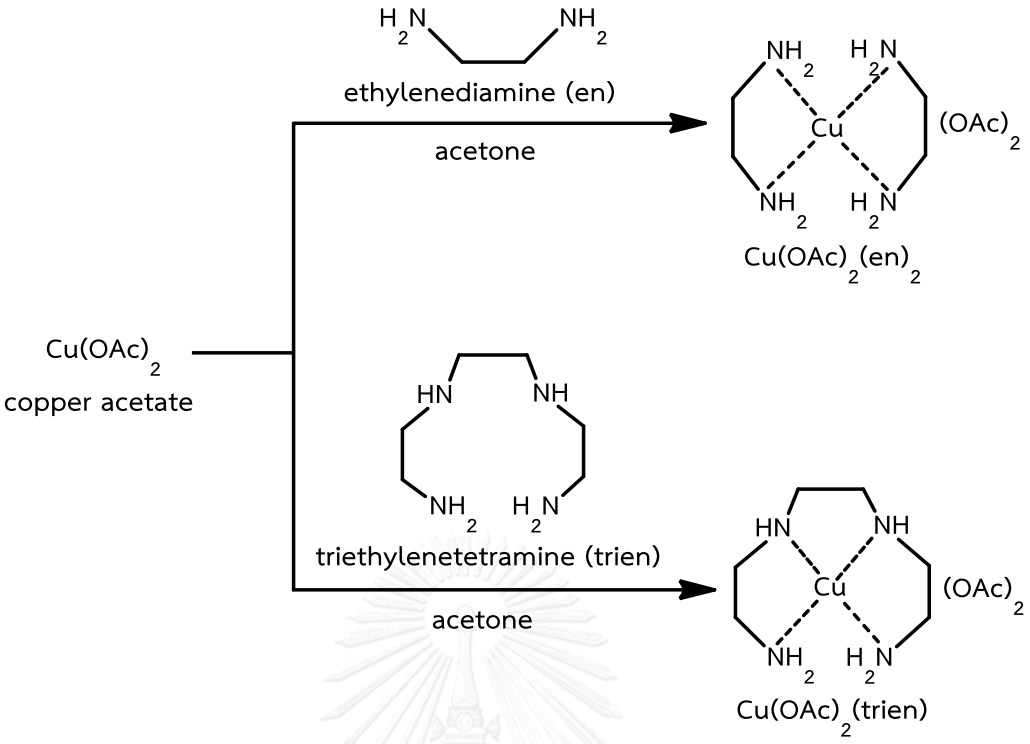
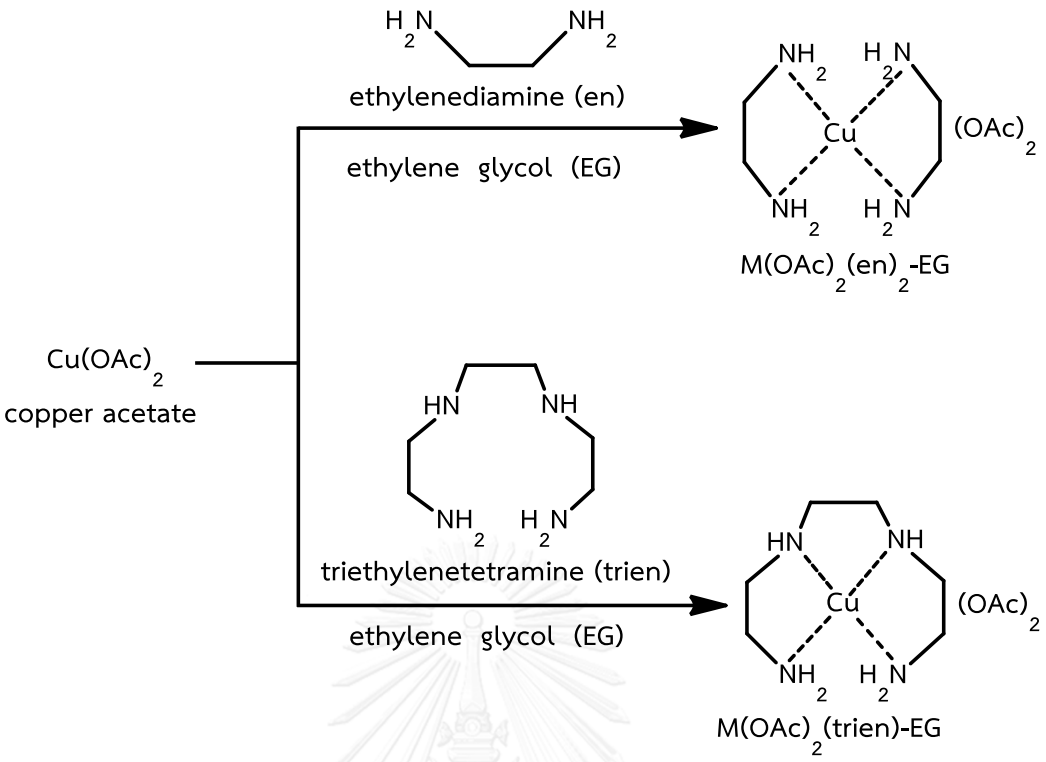


Scheme 2.4 Synthesis of copper-amine complexes as pure compounds [15]

Sridaeng et al. [16] synthesized $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) in the form of solutions in ethylene glycol (EG), namely, $Cu(OAc)_2(en)_2$-EG and $Cu(OAc)_2$(trien)-EG (Scheme 2.5). The solution of copper-amine complexes in ethylene glycol were odorless and could be used as catalysts for the preparation of flexible polyurethane foams foam without purification. The catalytic mechanism of copper-amine complexes is proposed that the activation starts by the copper atom coordinated by oxygen atom of the isocyanate group. The nitrogen atom of amine interacting with the proton of hydroxyl group to form a complex intermediate. As a result, the oxygen atom of the hydroxyl group reacts with the isocyanate group easier to produce a urethane group (Scheme 2.7).



Scheme 2.5 Synthesis of copper-amine complexes in the form of solutions in ethylene glycol (EG) [16]

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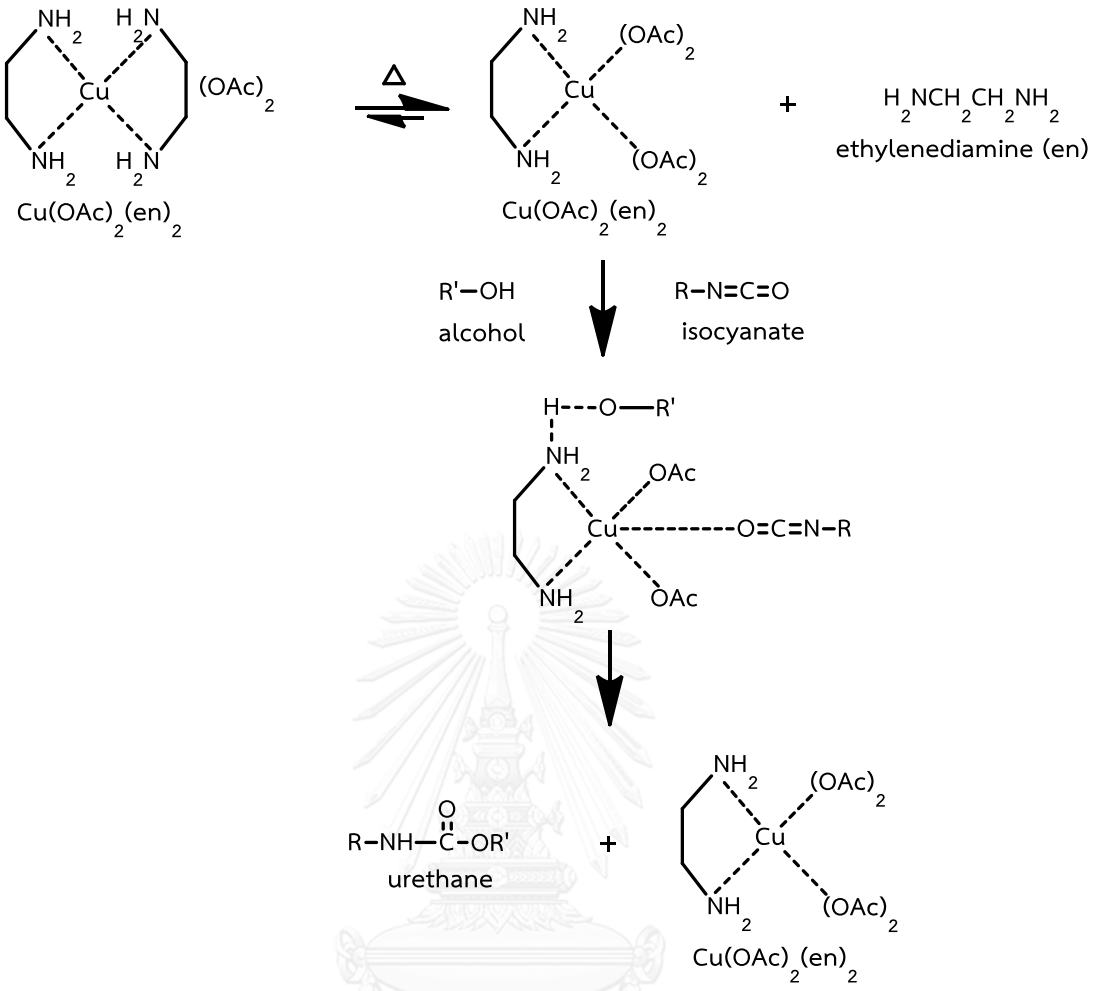

Scheme 2.6 The urethane reaction mechanism catalyzed by $Cu(OAc)_2(en)_2$ [16]

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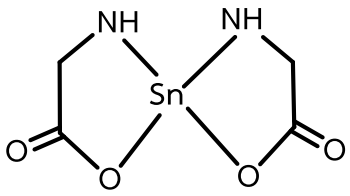
2.4.2 Literature reviews about synthesis of metal amino acid complexes

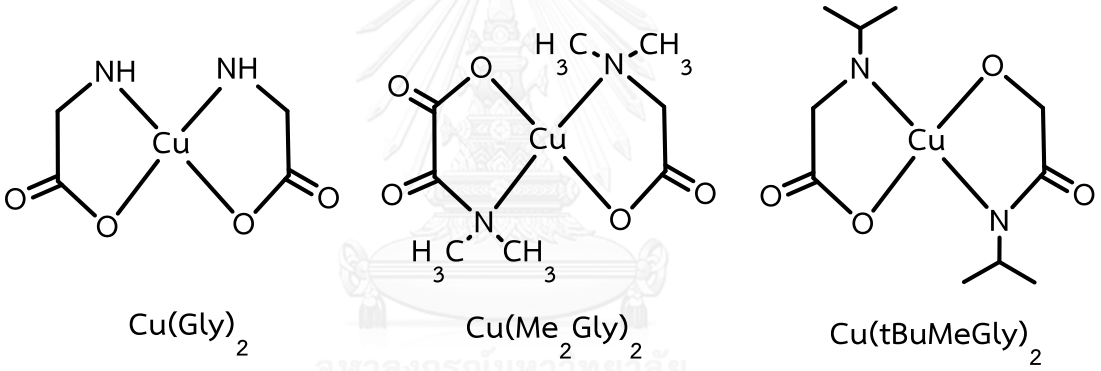
Novikova et al. [17] synthesized tin-glycine complex [$Sn(Gly)_2 \cdot H_2O$] and characterized by TGA, IR and Raman spectroscopy. It was found that glycine molecule is coordinated to Sn(II) as bidentate chelating ligand by oxygen atom from the carboxyl group and nitrogen atom of a glycine molecule (Figure 2.7).



$Sn(Gly)_2$

Figure 2.7 Structure of tin-glycine complex [$Sn(Gly)_2 \cdot H_2O$]

Sabolovic et al. [18] studied the structure of copper-amino acid complexes, namely $Cu(Gly)_2$,$Cu(Me_2Gly)_2$ and$Cu(tBuMeGly)_2$ using the B3LYP method (Figure 2.8).



$Cu(Gly)_2$ $Cu(Me_2Gly)_2$ $Cu(tBuMeGly)_2$

Figure 2.8 Structure of $Cu(Gly)_2$,$Cu(Me_2Gly)_2$ and$Cu(tBuMeGly)_2$

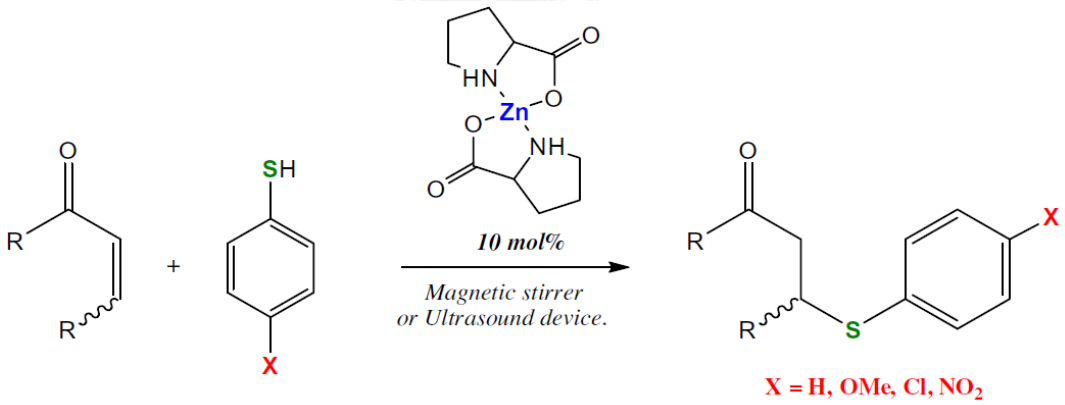
Kober et al. [19] synthesized copper amino-acid complexes (CuA_2) using $CuCl_2$ and $Cu(OH)_2$. as a reactant. A is amino acids, namely glycine, alanine, aminobutyric acid, valine, aminocaproic acid, isoleucine, proline, phenylalanine, phenylglycine, tyrosine, tryptophane, asparagine, sarcosine, lysine, arginine and histidine.

Graddon et al. [20] synthesized copper amino-acid complexes using $CuSO_4$. Amino acid used were glycine, alanine, valine and leucine. Water was used as a solvent. The solid copper amino-acid complexes were obtained.

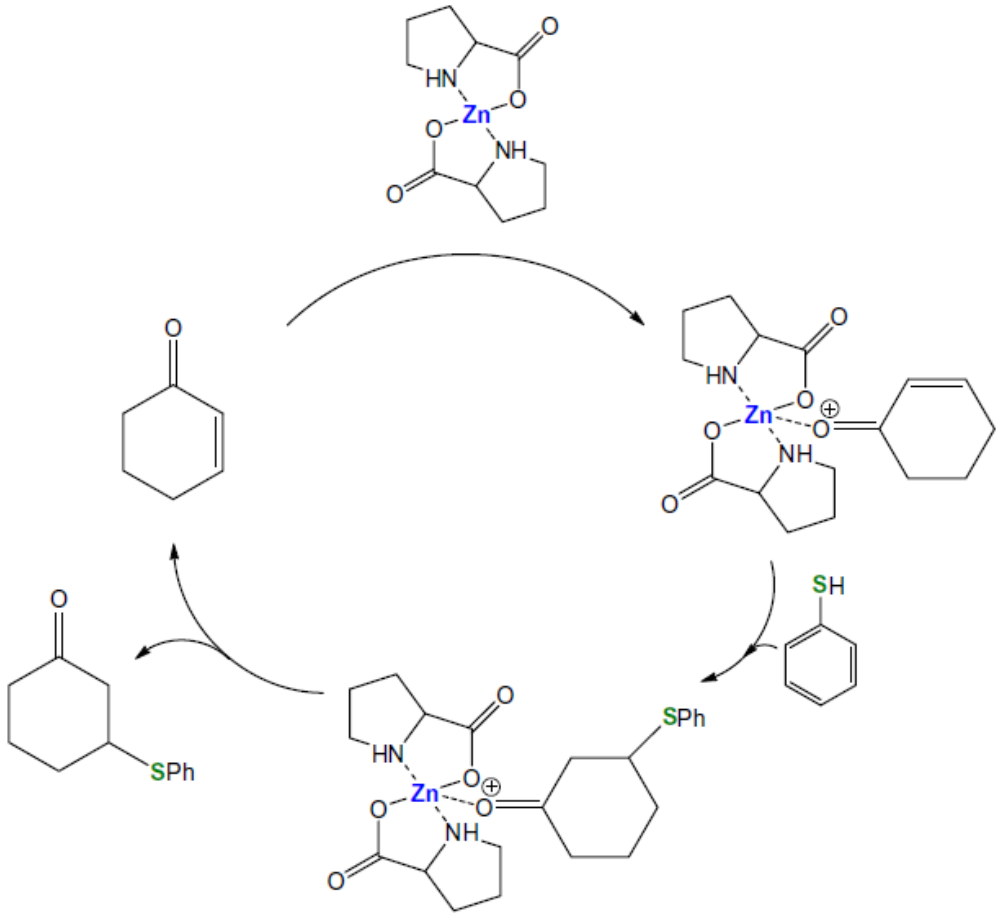
Qadir et al. [21] synthesized copper amino-acid complexes (MA_2) for animal nutrition. The metals (M) used were Fe, Cu, Zn, Co, Ca and Mg. The amino acids (A) used were alanine, glutamic acid and leucine. It was found that metal-Alanine and metal-glutamic acid complexes were water soluble. While metal-leucine was soluble in dimethylsulfoxide (DMSO). The other complexes were insoluble in both water and DMSO.

Sahoo et al. [22] used the copper(II) salts, amino acid and potassium monopersulfate ($KHSO_5$) as the catalysts for the emulsion polymerization of acrylonitrile. The Cu(II) salts used were $CuSO_4$, $Cu(NO_3)_2$, $CuCl_2$ and $Cu(OAc)_2$. The amino acids used were glycine, alanine and leucine.

Darbem et al. [23] studied bis[prolinate-N,O]Zn or Zn[Pro]$_2$ complex as a catalyst for the thio-Michael reaction (Scheme 2.7).This paper proposed a mechanism as shown in Scheme 2.8.



Scheme 2.7 Thio-Michael reaction using Zn[Pro]$_2$ a as catalyst [23]



Scheme 2.8 Plausible mechanism for Zn [Pro]$_2$ catalyzed the thio-Michael reaction [23]

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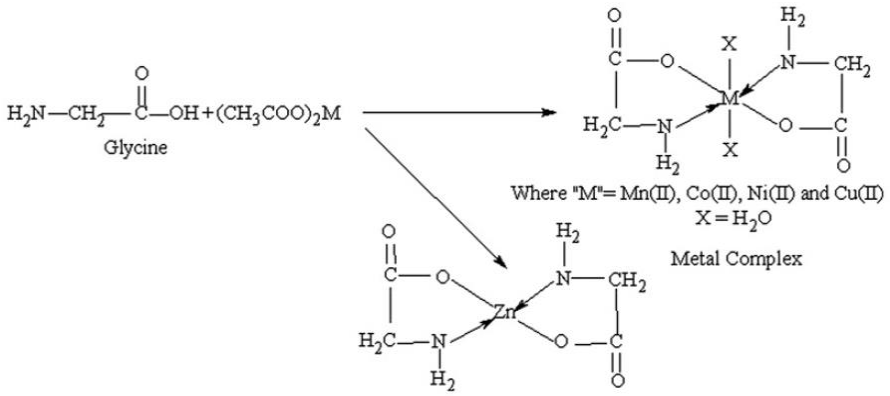
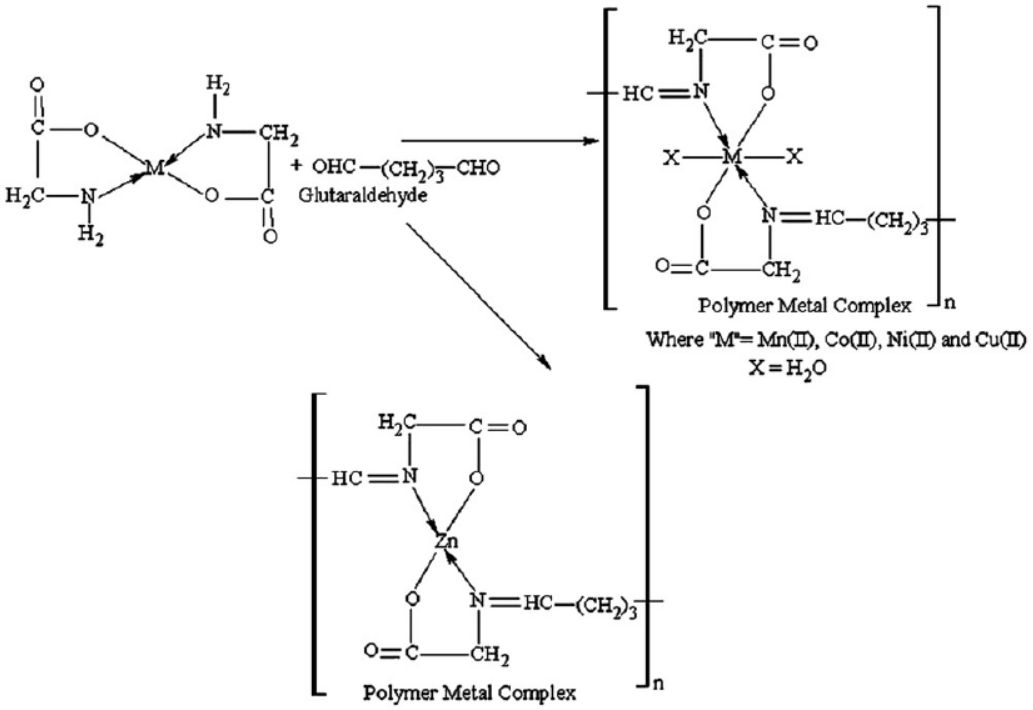
Kidwai et al. [24] synthesized 1,4-disubstitutedtriazoles using bis[(L)prolinato-N,O]Zn complex as a catalyst. The zinc amino complex was prepared from zinc acetate [$Zn(OAc)_2$], proline and triethylamine in methanol.

Nishat et al. [25] metal-glycine complexes by the reaction of glycine with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in 1 : 2 molar ratio using ethanol as solvent (Scheme 2.9). Metal-glycine complexes was then underwent condensation polymerization with glutaraldehyde to give polymer metal complexes (Scheme 2.10).



Scheme 2 9 Synthesis of metal-glycine complexes [25]



Scheme 2.10 Synthesis of polymer metal complex [25]

Herlinger et al. [26] studied the infrared spectra of bis(amino acidato)-copper(II) complexes. The amino acid used were glycine, L- and DL-alanine, DL-a-amino-n-butyric acid, L- and DLvaline, L- and DL-leucine, L- and DL-isoleucine, L- and DL-phenylalanine.

The purpose of this research was to develop new catalysts for the preparation of RPUR foams. The aqueous solution of metal-glycine M(OAc)(Gly) and metal-alanine M(OAc)(Ala) complexes were used as catalysts (where M= Cu, Zn, OAc = acetate, Gly= Glycine, Ala= Alanine). Glycine and alanine are non-toxic and have good solubility in water. Therefore, they can form complex with the metal ion in water. The reaction time, physical and mechanical properties of RPUR foam were studied and compared with the results obtained from the commercial catalyst (DMCHA)

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CHAPTER III
EXPERIMENTAL

3.1 Chemicals

3.1.1 Synthesis of metal-amino acid complexes in aqueous solutions

Copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$] and zinc acetate dihydrate [$Zn(OAc)_2.2H_2O$] were obtained from Aldrich. The other chemicals, namely alanine and glycine were obtained from Aldrich. All chemcals were used without purification.

3.1.2 Preparation of rigid polyurethane (RPUR) foams

Polymeric MDI (4,4'-methane diphenyl diisocyanate; PMDI, Raycore® B 9001, %NCO = 31.0 wt % and average functionality = 2.7), sucrose-based polyether polyol (Polimaxx® 4221, hydroxyl value (OHV) = 440 mg of KOH/g and functionality = 4.3), polysiloxane surfactant (Tegostab® B8460) and N,N-dimethylcyclohexylamine (DMCHA; reference commercial catalyst) were supplied by IRPC Public Company Limited. Distilled water was used as a chemical blowing agent.

3.2 Synthetic procedures

Synthesis of metal-amino acid complexes were carried out using water as a solvent to obtain the solutions of metal-amino acid complexes in water. The preparation of metal-amino acid complexes was performed according to the previous report [15]. Metal-amino acid complexes aqueous solutions were used as catalysts for the preparation of RPUR foams.

3.2.1 General procedure for the synthesis of metal-amino acid complex aqueous solutions

Metal-amino acid complex aqueous solutions namely, Zn(OAc) (Ala) , Zn(OAc)(Gly) and Cu(OAc)(Ala) were synthesized using mole ratios of metal(II) acetate [$M(OAc)_2.xH2O$] : amino acid = 1:2 and 1:1 as reported in Table 3.1 and Scheme 3.1.

The aqueous solutions of metal-amino acid complexes were obtained as 20 wt% and 25 wt% solutions and used as catalysts for the preparation of FPUR foams without purifications.

Aqueous solutions of metal-amino acid complexes [Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala)] were prepared by using the following procedure: Metal(II) acetate was added to water and the solution stirred for 10 minutes at room temperature. Amino acid was then added and the reaction mixture was then stirred at room temperature for 24 hours. All aqueous solution of metal-amino acid complexes were obtained as homogeneous and odorless solutions.

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Table 3.1 Composition of starting materials in the synthesis of metal-amino acid complex aqueous solutions

Metal-amino acid complexes	Mole ratios of $M(OAc)_2.xH_2O$: amino acid	Amount of $Cu(OAc)_2.H_2O$	Amount of $Zn(OAc)_2.2H_2O$	Amount of Amino acids		Amount of water / wt% in water	Appearances
				Glycine	Alanine		
Zn(OAc)(Ala)	1:2	-	0.552 g, 2.51 mmol	-	0.448 g, 5.03 mmol	3 ml / 25 wt%	colorless solution
Zn(OAc)(Ala)	1:2	-	0.552 g, 2.51 mmol	-	0.448 g, 5.03 mmol	4 ml / 20 wt%	colorless solution
Zn(OAc)(Ala)	1:1	-	0.711 g, 3.24 mmol	-	0.289 g, 3.24 mmol	3 ml / 25 wt%	colorless solution
Zn(OAc)(Ala)	1:1	-	0.711 g, 3.24 mmol	-	0.289 g, 3.24 mmol	4 ml / 20 wt%	colorless solution
Zn(OAc)(Gly)	1:2	-	0.594 g, 2.71 mmol	0.406 g, 5.41 mmol	-	3 ml / 25 wt%	colorless solution with precipitate
Zn(OAc)(Gly)	1:2	-	0.594 g, 2.71 mmol	0.406 g, 5.41 mmol	-	4 ml / 20 wt%	colorless solution
Zn(OAc)(Gly)	1:1	-	0.745 g, 3.40 mmol	0.255 g, 3.40 mmol	-	3 ml / 25 wt%	colorless solution

Table 3.1 Composition of starting materials in the synthesis of metal-amino acid complex aqueous solutions (cont.)

Metal-amino acid complexes	Mole ratios of $M(OAc)_2.xH_2O$: amino acid	Amount of $Cu(OAc)_2.H_2O$	Amount of $Zn(OAc)_2.2H_2O$	Amount of Amino acids		Amount of water / wt% in water	Appearances
				Glycine	Alanine		
Zn(OAc)(Gly)	1:1	-	0.745 g, 3.40 mmol	0.255 g, 3.40 mmol	-	4 ml / 20 wt%	colorless solution
Cu(OAc)(Ala)	1:2	0.528 g, 2.64 mmol	-	-	0.472 g, 5.30 mmol	3 ml / 25 wt%	blue solution
Cu(OAc)(Ala)	1:2	0.528 g, 2.64 mmol	-	-	0.472 g, 5.30 mmol	4 ml / 20 wt%	blue solution
Cu(OAc)(Ala)	1:1	0.528 g, 2.64 mmol	-	-	0.309 g, 3.46 mmol	3 ml / 25 wt%	blue solution
Cu(OAc)(Ala)	1:1	0.528 g, 2.64 mmol	-	-	0.309 g, 3.46 mmol	4 ml / 20 wt%	blue solution

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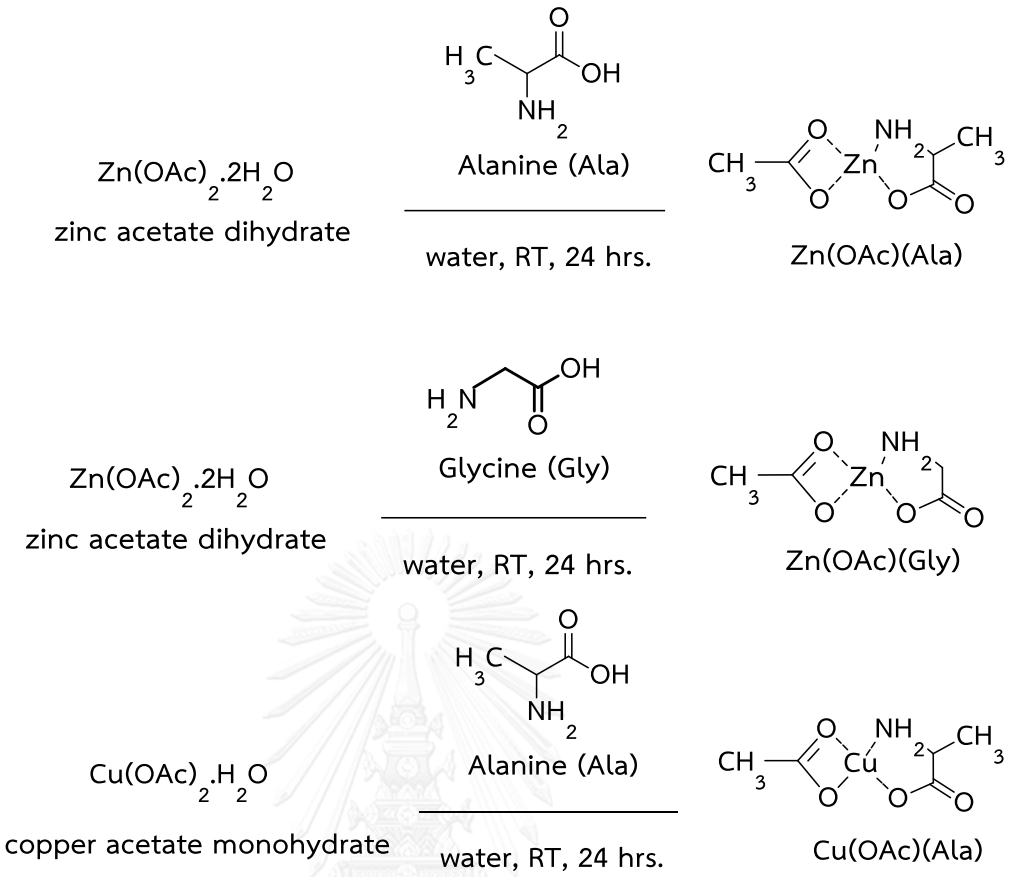

Scheme 3 1 Synthesis of metal-amino acid complex aqueous solutions

3.3 Rigid polyurethane (RPUR) foam preparation

RPUR foams were prepared by two steps of mixing using two methods namely, cup-test and molded methods. The RPUR foams preparation procedure catalyzed by Zn(OAc)(Gly), Zn(OAc)(Ala), Cu(OAc)(Ala) and a reference commercial catalyst (DMCHA) is illustrated in Figure 3.1. RPUR foam preparation using cup test method were used for the investigation of reaction times, rise profile, temperature profile, density and NCO conversion. RPUR foam preparation using molded method was used for the investigation of morphology and compressive properties.

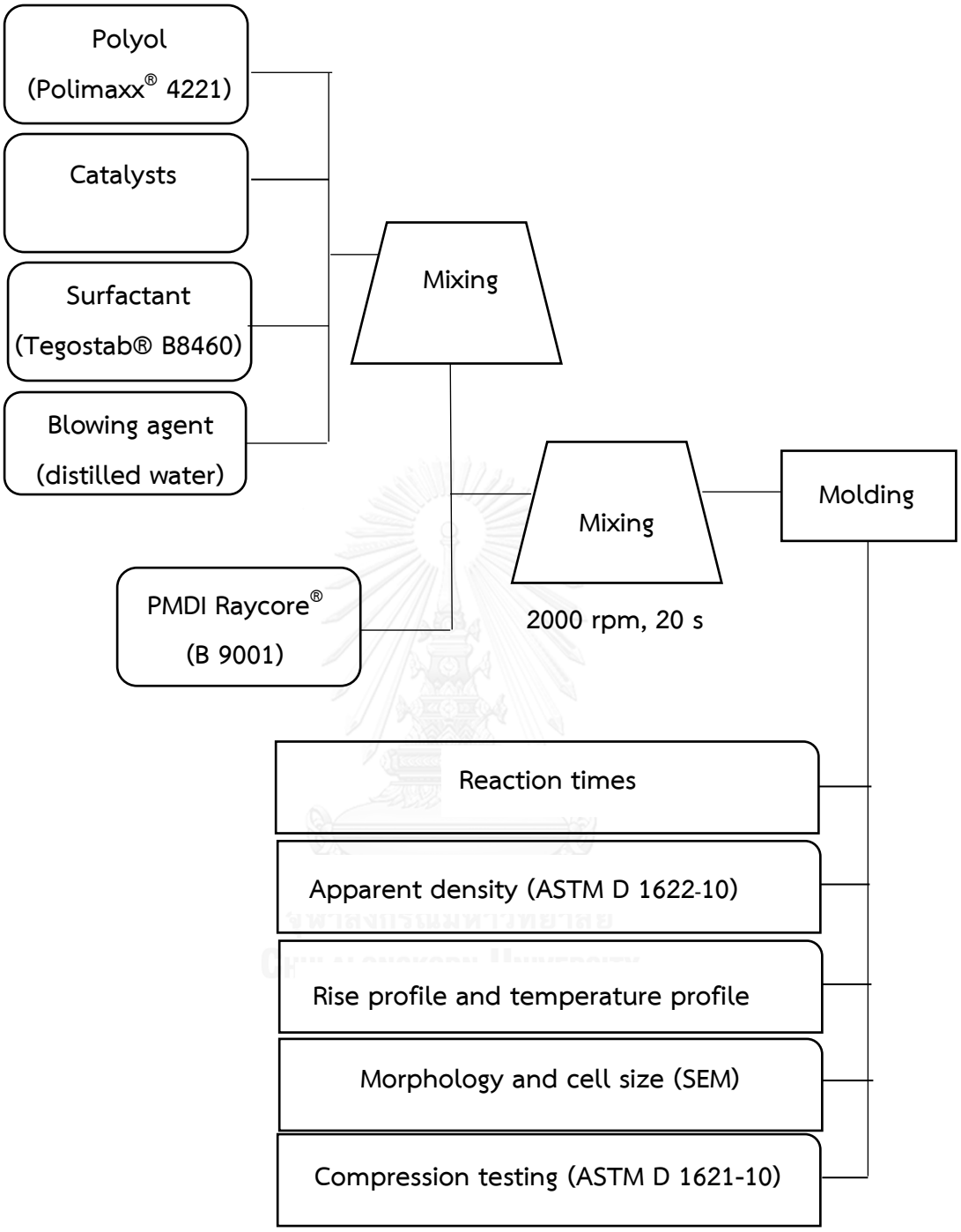

Figure 3.1 Process of preparation of rigid polyurethane foams

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

RPUR foams samples were prepared at room temperature according to the formulation as shown in Table 3.2. The isocynate index used was 100. In the first step, polyol, catalysts (DMCHA or metal-amino acid complex aqueous solution), surfactant were mixed together in a paper cup (700 ml) by mechanical stirrer at 2000 rpm for 20 s. Water in metal-amino acid complex aqueous solution served as a blowing agent. In the second step, polymeric MDI was added into the mixed polyol from first mixing. Then, the mixing was stirred using mechanical stirrer at 2000 rpm for 20 seconds. During the polymerization reactions, cream time (the time of the beginning of blowing reaction), gel time (the time while RPUR foam begins to change its state from liquid to gel), rise time (the time of the foam stop rising which CO_2 generation stops) and tack-free time (the time while polymerization is completed and the surface of RPUR foam does not stick to the material) were investigated. The foams were kept at room temperature for 48 hours. Physical and mechanical characteristics of RPUR foam were analyzed. In this study, the apparent density was measured according to ASTM D 1622-09. .After foam preparation, the samples were sectioned into a cubic shape of 3.0 x 3.0 x 3.0 cm (length x width xthickness) (Figure 3.2). The height of RPUR foam was measured from the bottom to the topin the direction of foam risingas shown in Figure 3.3.

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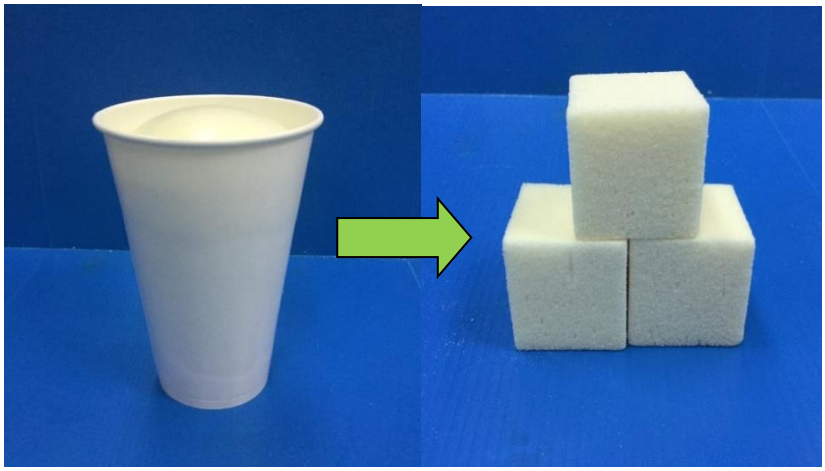

Figure 3.2 Samples for RPUR foam density measurements

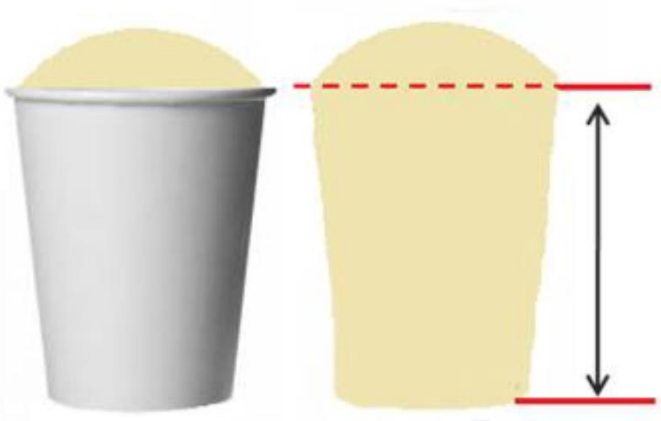

Figure 3.3 Measurement of RPUR foam height

3.3.2 Preparation of RPUR foams by molded method

After the final mixing step of the starting materials in a paper cup as described in 3.3.1, the mixture was poured into a 10 × 10 × 10 cm (length x width x height) plastic bag and allowed to rise freely at room temperature (Figure 3.4). The foams were kept for 48 hours. Then, they were used for investigating the mechanical properties and morphology.

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Figure 3.4 Measurement of RPUR foam prepared by using a mold test method

Table 3.2 RPUR foam formulations

Chemicals	**pbw (parts by weight)**	
Polyether polyol Polimaxx® 4221; OH-number = 440 mg KOH/g; functionality = 4.3)	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5
Blowing agent (H_2O in metal-amino acid complex aqueous solution served as a blowing agent)	3	4
Catalyst (DMCHA or metal-amino acid complex aqueous solution)	1	1
Polymeric MDI (PMDI, Raycore® B 9001; %NCO = 31.0; functionality = 2.7)	151.3	166.4

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3.4 Characterization of copper-amino acid complexes

3.4.1 Ultraviolet-visible spectroscopy

The UV- Vis spectra were acquired using a Varian Cary 50 UV- Vis spectrophotometerat room temperature, The samples were recorded as absorption spectra of metal amino acid complexs in the range of 200-800nm at a medium speed. Water is a solvent using in this characterization.

3.4.2 Infrared spectroscopy

Metal- amino acid complexs and polyurethane foams catalyzed by Zn(OAc)(Ala),Zn(OAc)(Gly) and Cu(OAc)(Ala) 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 3.3 are used for the analysis.The measurement was controlled by Omnic software.

Table 3.3 Characteristic IR bands of RPUR foam [27]

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

3.4.3 Mass spectrometry (MS)

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

3.5 Physical and Mechanical properties of RPUR foams

3.5.1 Reaction times

The reaction times namely, cream time, gel time tack free time and rise time were investigated by using a digital stopwatch in accordance with ASTM D7487-13 [28].

3.5.2 Temperature

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

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3.5.3 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 x width x thickness) and the average values of three samples were reported.

The free rise density of RPUR foams was measured in accordance with ASTM D 1622-09 [29]. The size of specimen was 3.0 cm x 3.0 cm x 3.0 cm (width x length x thickness) and the average values of three samples was reported.

3.5.4 Compressive testing

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise direction were carried out by using universal testing machine (Lloyd/LRX) according to ASTM D 695 [30]. The specimen size of samples was 5.0 x 5.0 x 5.0 cm (length x width x thickness) dimension, the rate of crosshead movement was fixed at 50 mm/min and the preload cell used was 0.100 N.

3.5.5 Scanning electron microscopy (SEM)

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

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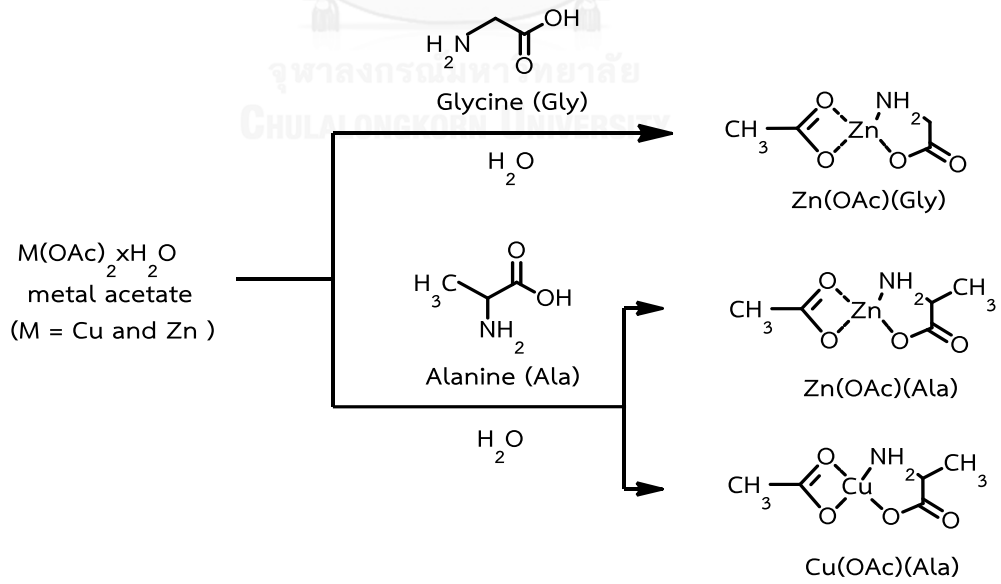
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of zinc-alanine [Zn(OAc)(Ala)], zinc-glycine [Zn(OAc)(Gly)] and copper-alanine [Cu(OAc)(Ala)] complexes as aqueous solutions

Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala) were prepared for using as catalysts in the preparation of RPUR foams. All metal complexes were prepared using water as a solvent to obtain aqueous solution of metal complexes (Scheme 4.1) [15]. It was found that metal-amino acid complexes could be successfully prepared using water as a solvent. These metal-amino acid complex aqueous solutions could be used as catalysts in the preparation of RPUR foams without purification. The aqueous solution of Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala) are colorless and blue solutions as shown in Figure 4.1 (a-c), respectively.



Scheme 4.1 Synthesis of zinc-alanine [Zn(OAc)(Ala)], zinc-glycine [Zn(OAc)(Gly)] and copper-alanine [Cu(OAc)(Ala)] complexes as aqueous solutions

(a) (b) (c)

Figure 4.1 The aqueous solution of (a) Zn(OAc)(Ala), (b) Zn(OAc)(Gly) and (c) Cu(OAc)(Ala)

4.1.1 Synthesis of zinc-alanine complexes in aqueous solutions [Zn(OAc)(Ala)]

The Zn(OAc)(Ala) was prepared by the action of zinc acetate dihydrate [Zn(OAc) $2.H_2O$] and alanine in water. It was found that Zn(OAc)(Ala) was obtained as colorless solutionas shown in Figure 4.1(a). Moreover, this complex could be mixed with the other substrates for preparing RPUR foam. The characterization of Zn(OAc)(Ala) was carried out using FTIR spectroscopy and Mass Spectrometry (MS).

4.1.2 Characterization of zinc-alanine complex [Zn(OAc)(Ala)]

4.1.2.1 IR spectroscopy of Zn(OAc)(Ala)

IR spectra of two starting materials used in the synthesis of Zn(OAc)(Ala) are described as follows: IR spectrum of $Zn(OAc)_2$ [Figure 4.2(a)] exhibits absorption band at 3062 cm^{-1} (N-H stretching vibration and hydroxyl groups in water), 1541 cm^{-1} (C=O asymmetric stretching), 1434 cm^{-1} (C=O symmetric stretching) and at 1019 cm^{-1} (C-O stretching). IR spectrum of alanine [Figure 4.2(b)] exhibits absorption band at 3073 cm^{-1} (N-H stretching vibration), 1589 cm^{-1} (C=O asymmetric stretching), 1408 cm^{-1} (C=O symmetric stretching), 1277 cm^{-1} C-N stretching) and 1014 cm^{-1} (C-O stretching).

IR spectrum of Zn(OAc)(Ala) was obtained in the form of solid by freeze drying of Zn(OAc)(Ala) aqueous solution as shown in Figure 4.2(c). Zn(OAc)(Ala) exhibited absorption band at 3095 cm^{-1} (N-H stretching and hydroxyl groups in water), 2980 cm^{-1} (C-H stretching), at 1538 cm^{-1} (C=O asymmetric stretching), 1447 cm^{-1} (C=O symmetric stretching), at 1352 cm^{-1} (C-N stretching) and 1025 cm^{-1} (C-O stretching). The asymmetric and symmetric C=O stretching peaks of Zn(OAc)(Ala) in water and $Zn(OAc)_2$ appeared at the similar position. This could not confirm that Zn(OAc)(Ala) was formed. Therefore, mass spectrometry was used to confirm the formation of Zn(OAc)(Ala).

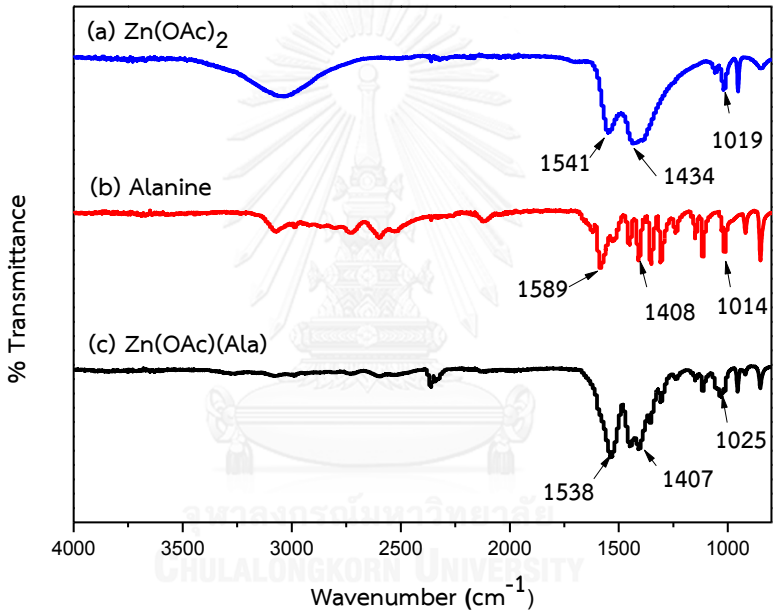


Figure 4.2 IR spectra of (a) $Zn(OAc)_2$ (b) Alanine (c) Zn(OAc)(Ala) (freeze drying)

4.1.2.2 Positive electrospray ionization mass spectrometry (ESI MS) of Zn(OAc)(Ala)

Mass spectrum of Zn(OAc)(Ala) aqueous solution is shown in Figure 4.3. The molecular ion peak of $[Zn(OAc)(Ala)+H]^+$ was found at *m/z* 211.99, which indicated the formation of Zn(OAc)(Ala) complex (Figure 4.4). The molecular ion peak of $[Zn(Ala)_2+H]^+$ was found at *m/z* 241.02, which indicated the formation of $Zn(Ala)_2$

complex (Figure 4.4). The molecular ion peak of zinc acetate, which was a starting material in the symthesis of Zn(OAc)(Ala), was found as $[Zn(OAc)_2+H]^+$ at *m/z* 182.96. Therefore, MS data indicated that Zn(OAc)(Ala) complex could be formed in water.

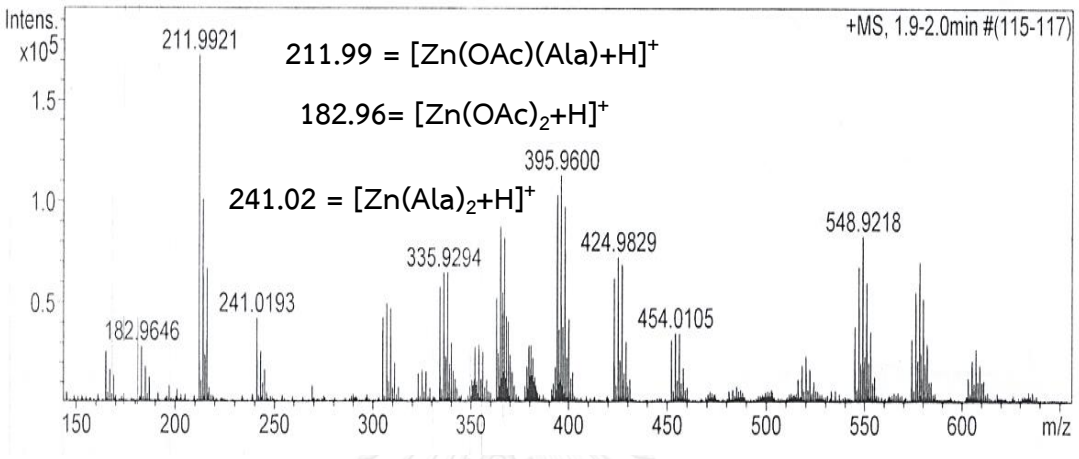


Figure 4.3 Positive ESI MS of Zn(OAc)(Ala)

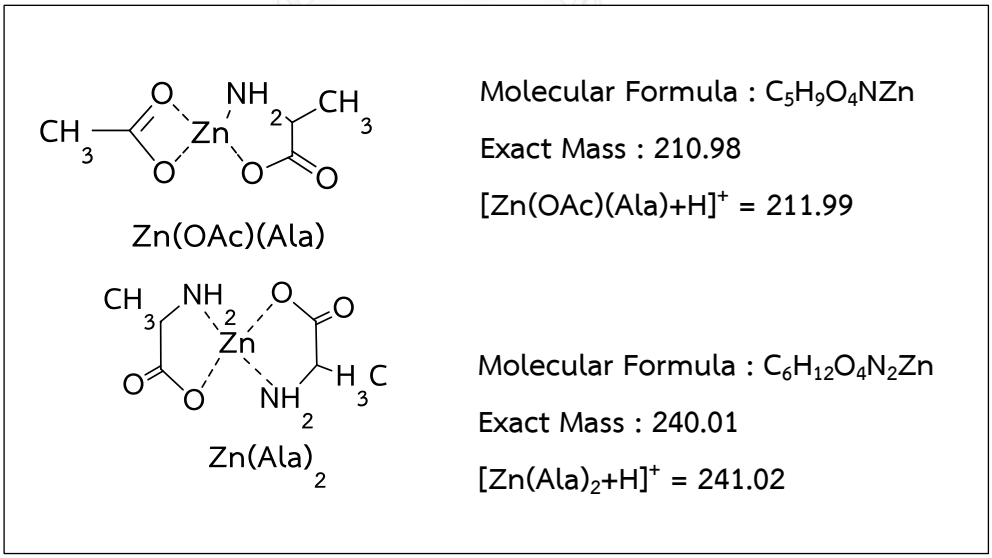


Figure 4.4 Structure, molecular formula and mass of Zn(OAc)(Ala) and $Zn(Ala)_2$

4.1.3 Synthesis of zinc-glycine complexes in aqueous solutions [Zn(OAc)(Gly)]

The Zn(OAc)(Gly) was prepared by the action of zinc acetate dihydrate [Zn(OAc) 2.H_2O] and glycine in water. It was found that Zn(OAc)(Ala) was obtained as colorless solution as shown in Figure 4.1(b). Moreover, this complex could be mixed with the other substrates for preparing RPUR foam. The characterization of Zn(OAc)(Gly) were carried out using FTIR spectroscopy and Mass Spectrometry (MS).

4.1.4 Characterization of zinc-glycine complex [Zn(OAc)(Gly)]

4.1.4.1 IR spectroscopy of Zn(OAc)(Gly)

IR spectra of two starting materials used in the synthesis of Zn(OAc)(Gly) are described as follows: IR spectrum of $Zn(OAc)_2$ [Figure 4.5(a)] exhibits absorption band at 3062 cm^{-1} (N-H stretching vibration and hydroxyl groups in water), 1541 cm^{-1} (C=O asymmetric stretching), 1434 cm^{-1} (C=O symmetric stretching) and at 1019 cm^{-1} (C-O stretching). IR spectrum of glycine [Figure 4.5(b)] exhibits absorption band at 3165 cm^{-1} (N-H stretching vibration), 1581 cm^{-1} (C=O asymmetric stretching), 1496 cm^{-1} (C=O symmetric stretching), 1335 cm^{-1} C-N stretching) and 1105 cm^{-1} (C-O stretching).

IR spectrum of Zn(OAc)(Ala) was obtained in the form of solid by freeze drying of Zn(OAc)(Ala) aqueous solution as shown in Figure 4.5(c). Zn(OAc)(Gly) exhibited absorption band at 3177 cm^{-1} (N-H stretching and hydroxyl groups in water), 2986 cm^{-1} (C-H stretching), at 1538cm^{-1} (C=O asymmetric stretching), 1443 cm^{-1} (C=O symmetric stretching), at 1331 cm^{-1} (C-N stretching) and 1027 cm^{-1} (C-O stretching). The asymmetric and symmetric C=O stretching peaks of Zn(OAc)(Gly) in water and $Zn(OAc)_2$ appeared at the similar position. This could not confirm that Zn(OAc)(Gly) was formed. Therefore, mass spectrometry was used to confirm the formation of Zn(OAc)(Gly).

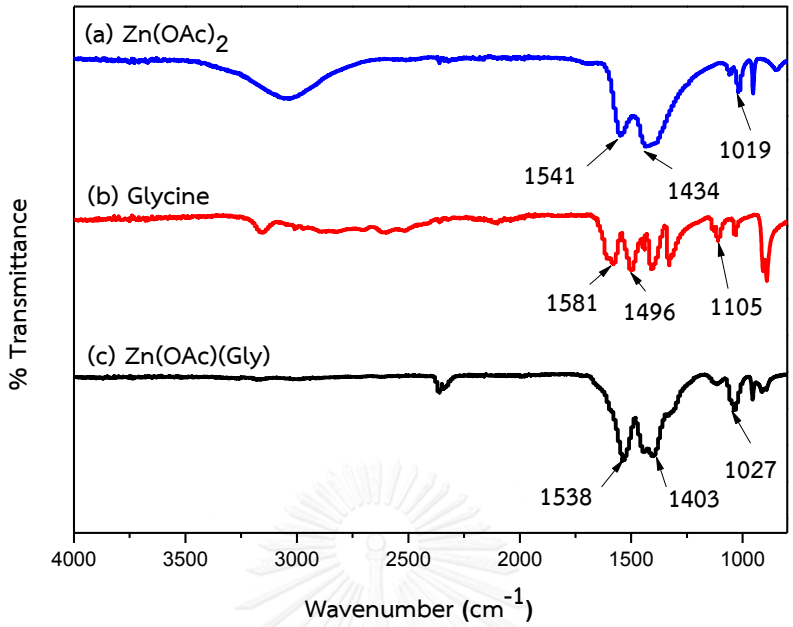


Figure 4.5 IR spectra of (a) $Zn(OAc)_2$ (b) Glycine (c) Zn(OAc)(Gly) (freeze drying)

4.1.4.2 Positive electrospray ionization mass spectrometry (ESI MS) of Zn(OAc)(Gly)

Mass spectrum of Zn(OAc)(Gly) aqueous solution is shown in Figure 4.6. The molecular ion peak of $[Zn(OAc)(Ala)+H]^+$ was found at *m/z* 197.97, which indicated the formation of Zn(OAc) (Gly) complex (Figure 4.7). The molecular ion peak of $[Zn(Gly)_2+H]^+$ was not found at *m/z* 241.02, which indicated the formation of $Zn(Gly)_2$ complex (Figure 4.7). The molecular ion peak of zinc acetate, which was a starting material in the symthesis of Zn(OAc)(Gly), was found as $[Zn(OAc)_2+H]^+$ at *m/z* 182.96. Therefore, MS data indicated that Zn(OAc)(Gly) complex could be formed in water.

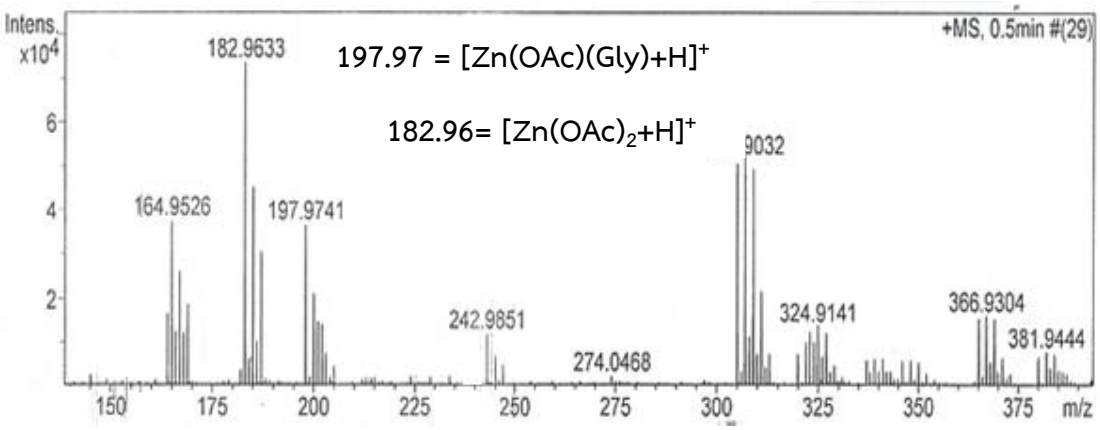


Figure 4.6 Positive ESI MS of Zn(OAc)(Gly)

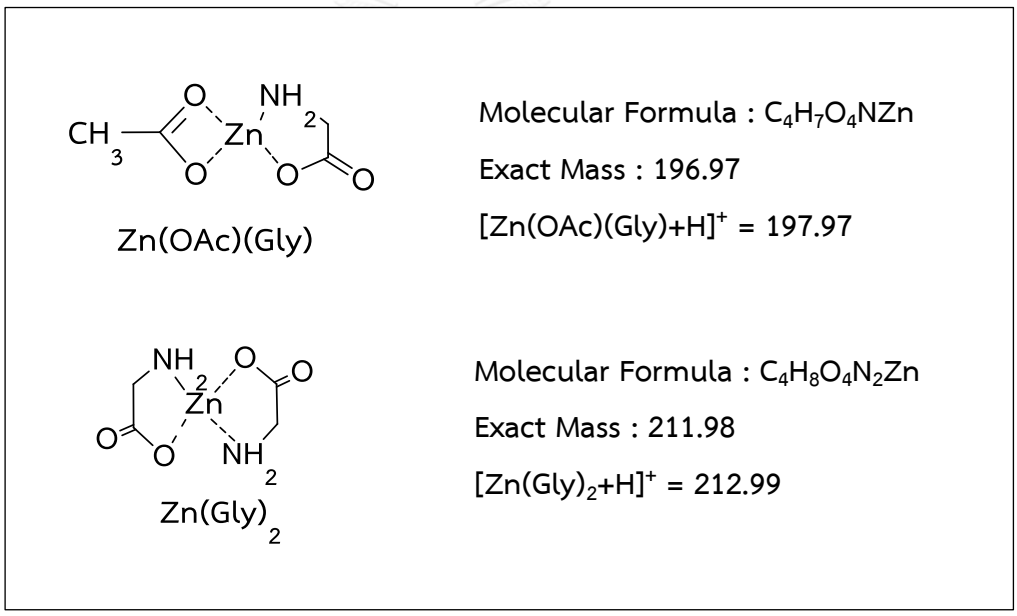


Figure 4.7 Structure of Zn(OAc)(Gly) and $Zn(Gly)_2$

4.1.5 Synthesis of copper-alanine complexes in aqueous solutions [Cu(OAc)(Ala)]

The Cu(OAc)(Ala) is prepared by the action of copper acetate monohydrate [$Cu(OAc)_2.H_2O$] and alanine in water gave aqueous solutions. It was found that Cu(OAc)(Ala) in water was obtained as blue-violet solution as shown in Figure 4.1(c). It

could be mixed with other substrates in the preparation of RPUR foam. We characterized by FTIR spectroscopy and Mass Spectrometry (MS).

4.1.6 Characterization of copper-alanine complex [CuOAc)(Ala)]

4.1.6.1 IR spectroscopy of Cu(OAc)(Ala)

IR spectra of two starting materials used in the synthesis of Cu(OAc)(Ala) are described as follows: IR spectrum of $Cu(OAc)_2$ [Figure 4.8(a)] exhibits absorption band at 3376 cm^{-1} (N-H stretching vibration and hydroxyl groups in water), 1594 cm^{-1} (C=O asymmetric stretching), 1442 cm^{-1} (C=O symmetric stretching) and at 1033 cm^{-1} (C-O stretching). IR spectrum of alanine [Figure 4.8(b)] exhibits absorption band at 3073 cm^{-1} (N-H stretching vibration), 1589 cm^{-1} (C=O asymmetric stretching), 1408 cm^{-1} (C=O symmetric stretching), 1277 cm^{-1} C-N stretching) and 1014 cm^{-1} (C-O stretching).

IR spectrum of Cu(OAc)(Ala) was obtained in the form of solid by freeze drying of Cu(OAc)(Ala) aqueous solution as shown in Figure 4.8(c). Cu(OAc)(Ala) exhibited absorption band at 3264 cm^{-1} (N-H stretching and hydroxyl groups in water), 2926 cm^{-1} (C-H stretching), at 1538 cm^{-1} (C=O asymmetric stretching), 1394 cm^{-1} (C=O symmetric stretching), at 1394 cm^{-1} (C-N stretching) and 1122 cm^{-1} (C-O stretching).

IR spectrum of Cu(OAc)(Ala) was obtained in the form of aqueous solution as shown in Figure 4.8(d). Cu(OAc)(Ala) exhibited absorption band at 3272 cm^{-1} (N-H stretching and hydroxyl groups in water), 2983 cm^{-1} (C-H stretching), at 1599 cm^{-1} (C=O asymmetric stretching), 1400 cm^{-1} (C=O symmetric stretching), at 1397 cm^{-1} (C-N stretching) and 1114 cm^{-1} (C-O stretching). The asymmetric and symmetric C=O stretching peaks of Cu(OAc)(Ala) in water and $Cu(OAc)_2$ appeared at the different positions. This could confirm that Cu(OAc)(Ala) was formed.

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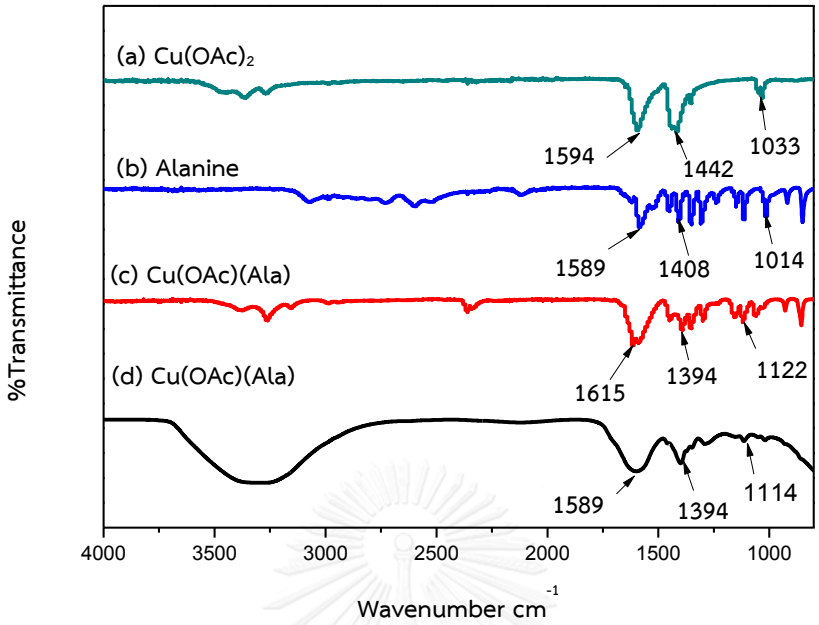

Figure 4.8 IR spectra of (a) $Cu(OAc)_2$; (b) Alanine; (c) Cu(OAc)(Ala) (freeze drying) and (d) Cu(OAc)(Ala) (solution)

4.1.6.2 Positive electrospray ionization mass spectrometry (ESI MS) of Cu(OAc)(Ala)

Mass spectrum of Cu(OAc)(Ala) aqueous solution is shown in Figure 4.9. The molecular ion peak of $[Cu(OAc)(Ala)+H]^+$ was found at *m/z* 210.99, which indicated the formation of Cu(OAc)(Ala) complex (Figure 4.10). The molecular ion peak of $[Cu(Ala)_2+H]^+$ was not found at *m/z* 240.02, which indicated the formation of $Cu(Ala)_2$ complex (Figure 4.10). The molecular ion peak of copper acetate, which was a starting material in the synthesis of Cu(OAc)(Ala), was not found as $[Cu(OAc)_2+H]^+$ at *m/z* 181.96. Therefore, MS data indicated that Cu(OAc)(Ala) complex could be formed in water.

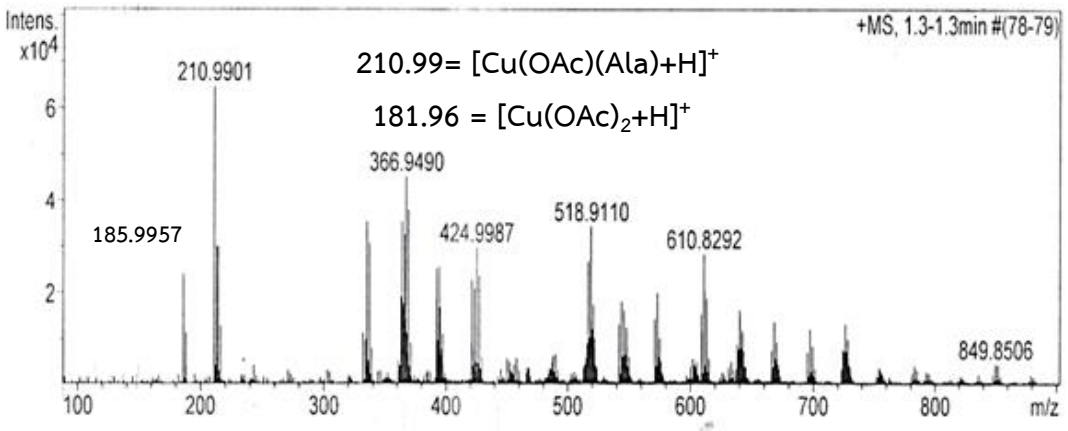

Figure 4.9 Positive ESI MS of Cu(OAc)(Ala)

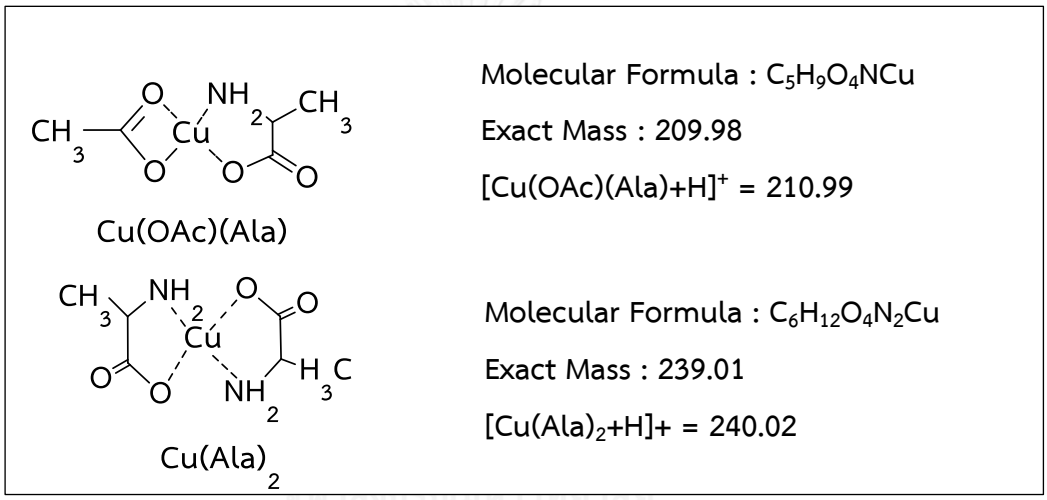

Figure 4.10 Structure of Cu(OAc)(Ala) and $Cu(Ala)_2$

The MS data confirmed the structure of metal-amino acid complexes, namely Zn(OAc)(Gly), Zn(OAc)(Ala) and Cu(OAc)(Ala). Table 4.1 summerizes the MS data.

Table4.1 Molecular ion peaks of Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala)

Molecular ion peak	*m/z* (Calculated)	*m/z* (Found)
$[Zn(OAc)(Ala)+H]^+$	211.9901	211.9921
$[Zn(OAc)(Gly)+H]^+$	197.9745	197.9741
$[Cu(OAc)(Ala)+H]^+$	210.9906	210.9901

4.1.6.3 UV-visible spectroscopy of Cu(OAc)(Ala)

UV–vis absorption spectra of $Cu(OAc)_2$ and Cu(OAc)(Ala) are shown in Figure 4.11. Cu(OAc)(Ala) complex gives the maximum wavelength at 215 nm, which was shifted from the maximum wavelenth of $Cu(OAc)_2$ at 228 nm. These results suggested that Cu(OAc)(Ala) complex was formed in water.

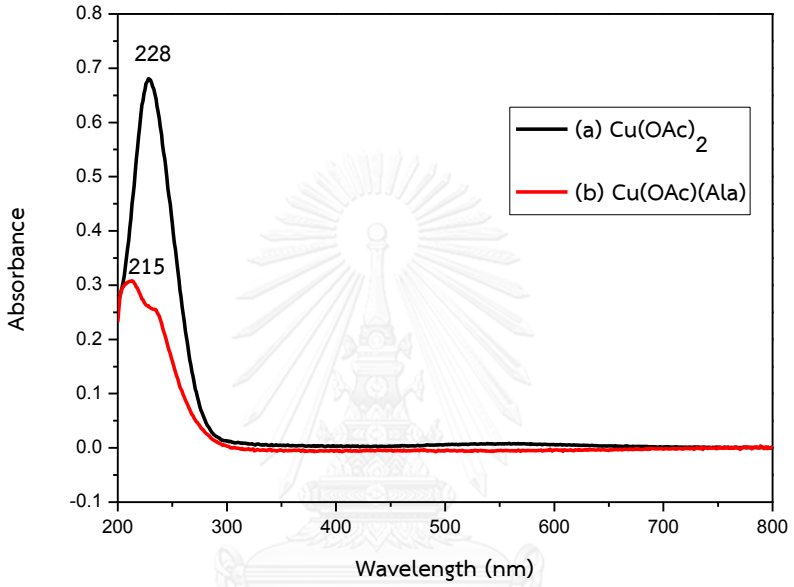

Figure 4.11 UV spectra of (a) $Cu(OAc)_2$; (b) Cu(OAc)(Ala)

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4.2 Rigid polyurethane (RPUR) foam preparations

Rigid polyurethane foams were prepared by using Zn(OAc)(Gly), Zn(OAc)(Ala) and Cu(OAc)(Ala) as catalysts. In the synthesis of metal-amino acid complexes, the mole ratio of metal(II) acetate : amino acid employed was 1:1 and 1:2. The amount of water used as a solvent in the synthesis of metal-amino acid complexes was varied to obtain the amount of water as a blowing agent in RPUR foam formulation at 3 and 4 pbw.

4. 2. 1 Reaction times of RPUR foams catalyzed by metal-amino acids prepared at different mole ratios of metal(II) acetate monohydrate : amino acid and different amounts of blowing agent (water)

RPUR foams were prepared by using cup test method to investigate their reaction times and physical properties as shown in Table 4.2 and Figures 4.12-4.15.

In the first step of investigation, the mole ratio between metal(II) acetate monohydrate : amino acid was varied at 1:2 and 1:1 at the amount of blowing agent (water) of 3 pbw. It was found that the order of catalytic activity of metal-amino acid complexes was in the order of DMCHA > Cu(OAc)(Ala) > Zn(OAc)(Ala) > Zn(OAc)(Gly). The reaction times of RPUR foams catalyzed by metal-amino acid complexes at the mole ratio of metal(II) acetate : amino acid = 1:1 gave the shorter reaction time than those catalyzed by metal-amino acid complexes at the mole ratio of metal(II) acetate : amino acid = 1:2. These results indicated that the mole ratio metal(II) acetate : amino acid = 1:1 gave the best catalytic activity.

In the second step of investigation, the amount of blowing agent (water) was varied from 3 pbw to 4 pbw. It was found that the order of catalytic activity of metal-amino acid complexes was in the order DMCHA > Cu(OAc)(Ala) > Zn(OAc)(Ala) > Zn(OAc)(Gly). Metal-amino acid complexes prepared at the mole ratio of metal(II) acetate : amino acid = 1:1 gave better catalytic activity than those prepared at the mole ratio of metal(II) acetate: amino acid = 1:2.

Metal-amino acid complexes prepared at the mole ratio of metal(II) acetate monohydrate : amino acid = 1:1 gave better catalytic activity since their structures obtained from the MS data were Zn(OAc)(Gly), Zn(OAc)(Ala) and Cu(OAc)(Ala). The complex formation of Cu(OAc)(Ala) and Zn(OAc)(Ala) occurred effectively since the peaks of copper acetate and zinc acetate starting material were not observed in the mass spectrum. The complex formation of Zn(OAc)(Gly) was not effective since the peak of zinc acetate starting material was observed in the mass spectrum. Therefore, Zn(OAc)(Gly) had less catalytic activity than Zn(OAc)(Ala).

Table 4.2 Reaction times of RPUR foams catalyzed by metal-amino acids prepared at the mole ratio of metal(II) acetate monohydrate : amino acid = 1:1 and 1:2 and the amount of blowing agent was 3 and 4 pbw

Catalyst	**Cream time (sec)**	**Gel time (sec)**	**Rise time (sec)**	**Tack free time (sec)**	**Density (kg/m^3)**	**Height (cm)**
DMCHA (reference catalyst)	22	38	127	152	39.2	14.5
Zn(OAc)(Ala)(1:2) [H_2O =3 pbw]	33	91	298	363	37.2	13.6
Zn(OAc)(Ala)(1:2) [H_2O =4 pbw]	34	84	260	319	41.9	14.2
Zn(OAc)(Ala)(1:1) [H_2O =3 pbw]	30	82	295	351	42.3	12.7
Zn(OAc)(Ala)(1:1) [H_2O =4 pbw]	22	63	233	243	35.2	14.9
Zn(OAc)(Gly)(1:2) [H_2O =3 pbw]	34	158	555	647	44.1	12.2

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Table 4.2 Reaction times of RPUR foams catalyzed by metal-amino acids prepared at the mole ratio of metal(II) acetate monohydrate : amino acid = 1:1 and 1:2 and the amount of blowing agent was 3 and 4 pbw (cont.)

Catalyst	Cream time (sec)	Gel time (sec)	Rise time (sec)	Tack free time (sec)	Density (kg/m^3)	Height (cm)
Zn(OAc)(Gly) (1:2) [H_2O =4 pbw]	34	83	359	424	42.2	13.1
Zn(OAc)(Gly)(1:1) [H_2O =3 pbw]	27	100	343	408	41.4	12.5
Zn(OAc)(Gly)(1:1) [H_2O =4 pbw]	24	72	336	376	39.4	13.0
Cu(OAc)(Ala)(1:2) [H_2O =3 pbw]	29	97	287	344	67.0	9.0
Cu(OAc)(Ala)(1:2) [H_2O =4 pbw]	32	89	240	299	48.6	11.7
Cu(OAc)(Ala)(1:1) [H_2O =3 pbw]	28	81	285	337	46.2	11.5
Cu(OAc)(Ala)(1:1) [H_2O =4 pbw]	22	42	178	195	40.7	13.0

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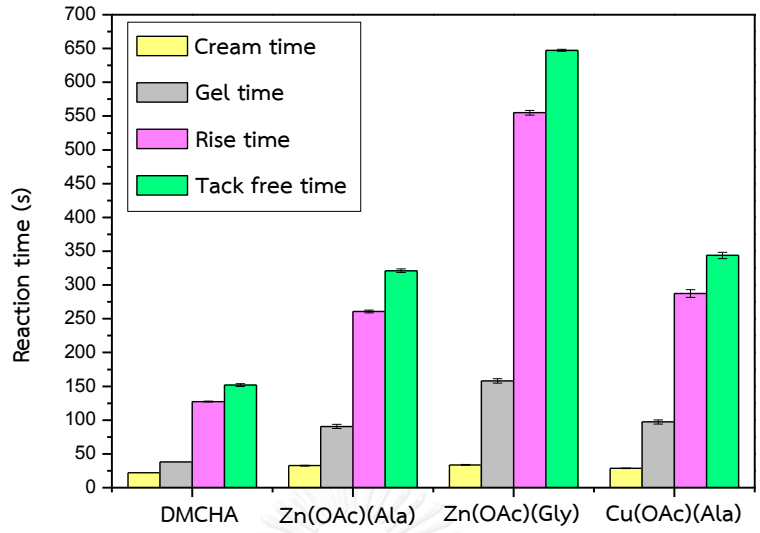

Figure 4.12 Reaction times of RPUR foams catalyzed by DMCHA and metal-amino acid complexes prepared at the mole ratio of metal(II) acetate : amino acid = 1:2 and the amount of blowing agent was 3 pbw

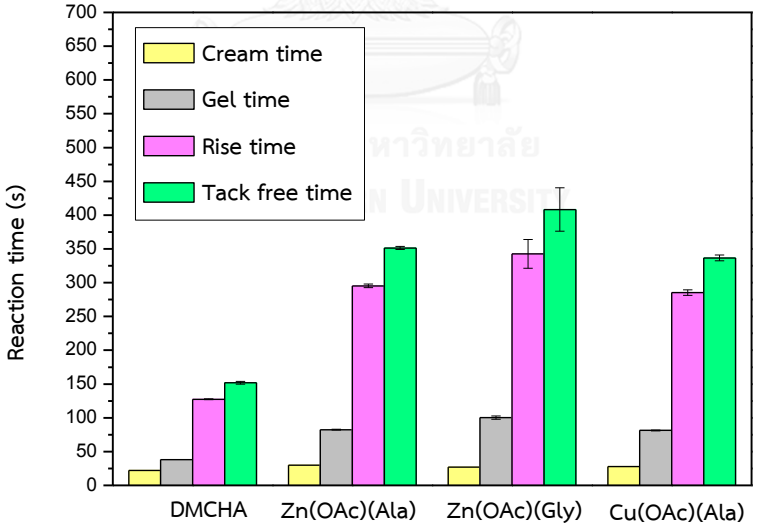

Figure 4.13 Reaction time of RPUR foams catalyzed by DMCHA and metal-amino acid complexs prepared at the mole ratio of metal(II) acetate : amino acid = 1:1 and the amount of blowing agent was 3 pbw

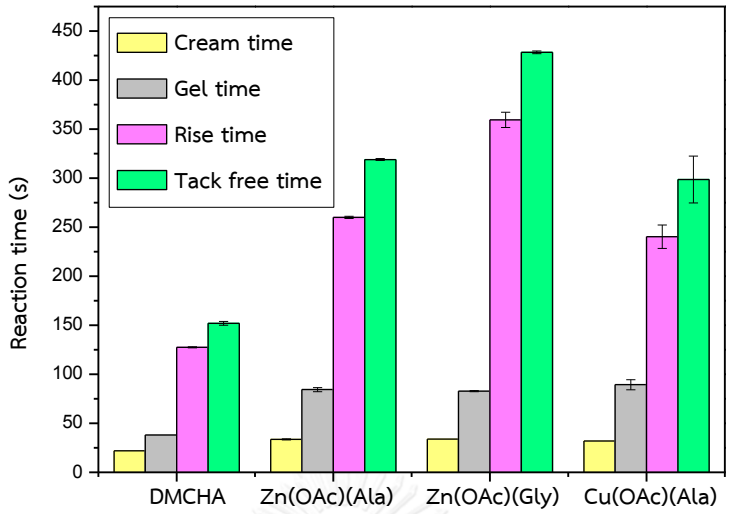

Figure 4.14 Reaction time of RPUR foams catalyzed by DMCHA and metal-amino acid complexs prepared at the mole ratio of metal(II) acetate : amino acid = 1:2 and the amount of blowing agent was 4 pbw

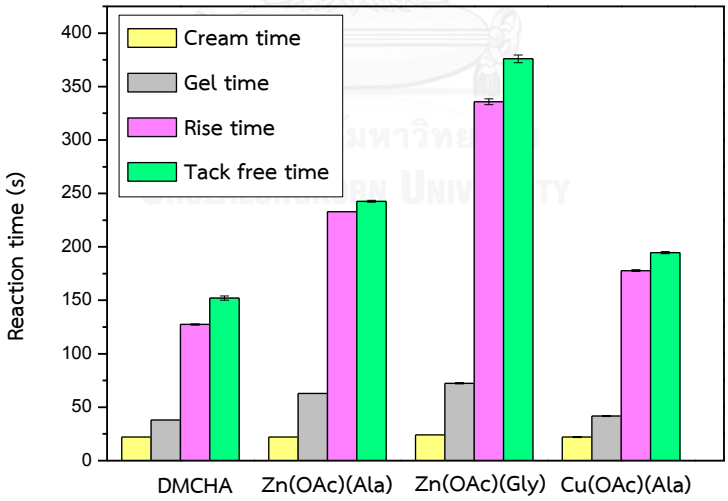

Figure 4.15 Reaction time of RPUR foams catalyzed by DMCHA and metal-amino acid complexs prepared at the mole ratio of metal(II) acetate : amino acid = 1:1 and the amount of blowing agent was 4 pbw

4.2.2 Density of RPUR foams catalyzed by metal-amino acids prepared at the mole ratio of metal(II) acetate monohydrate : amino acid = 1:1 and 1:2 and the amount of blowing agent was 3 and 4 pbw.

In this study, water was the chemical blowing agent which expanded RPUR foams by CO_2 gas generated by the reaction between water and isocyanate group, and this reaction is exothermic [6, 31]. Increasing blowing agent content would reduce the density of RPUR foams since there was more CO_2 amount in the system. It was found that the density of RPUR foams decreased with increasing blowing agent content (Figures 4.16-4.19).

RPUR foams catalyzed by Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala) prepared from the mole ratio of metal(II) acetate : amino acid = 1:1 at the blowing agent amount of 4 pbw gave suitable foam density for application. The density of RPUR foams catalyzed by Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala) were 35.2, 39.4 and 40.7 kg/m^3, respectively, which was closed to that of DMCHA (39.2 kg/m^3).

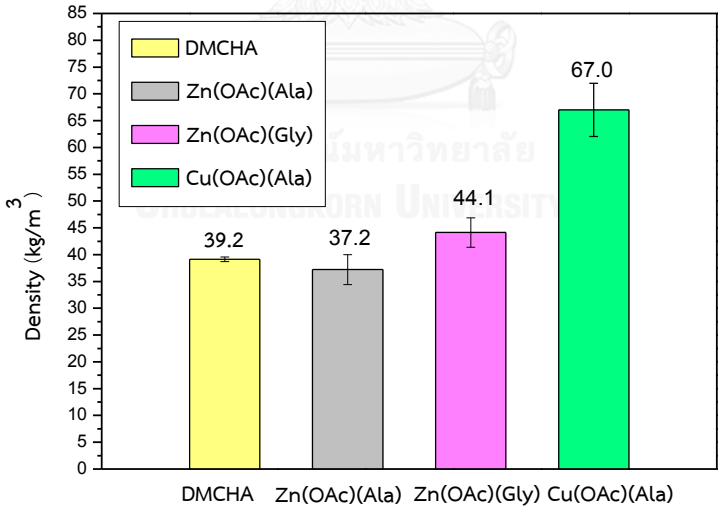

Figure 4.16 Density of RPUR foams catalyzed by DMCHA and metal- amino acid complexes prepared at the mole ratio of metal(II) acetate : amino acid = 1:2 and the amount of blowing agent was 3 pbw

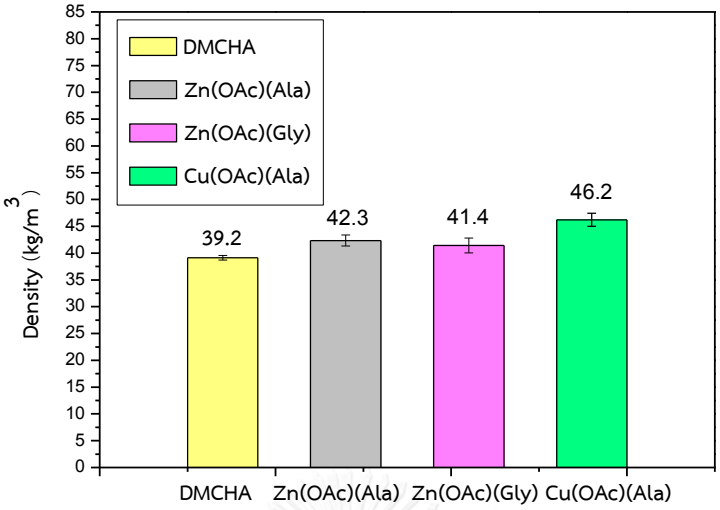

Figure 4.17 Density of RPUR foams catalyzed by DMCHA and metal- amino acid complexes prepared at the mole ratio of metal(II) acetate : amino acid = 1:1 and the amount of blowing agent was 3 pbw

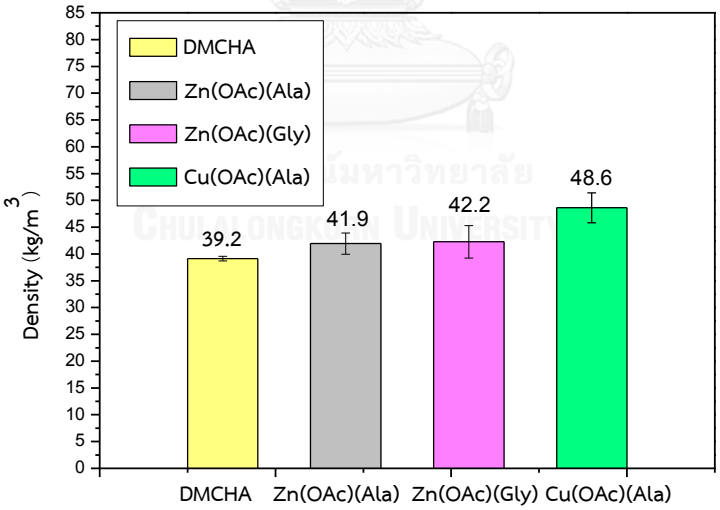

Figure 4.18 Density of RPUR foams catalyzed by DMCHA and metal- amino acid complexes prepared at the mole ratio of metal(II) acetate : amino acid = 1:2 and the amount of blowing agent was 4 pbw

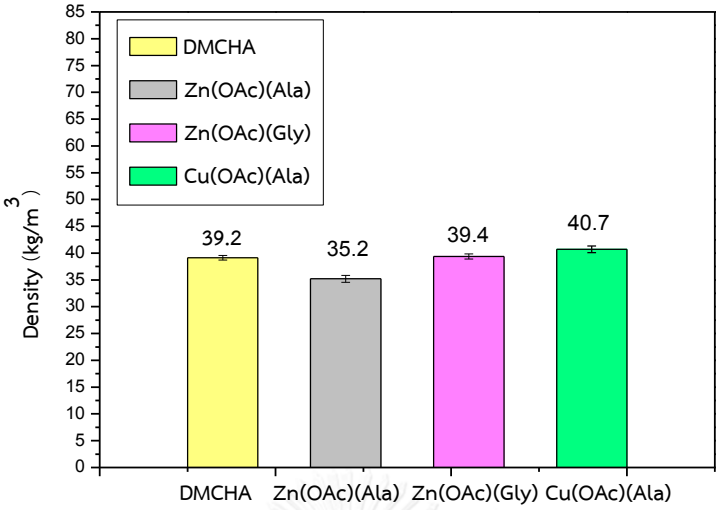

Figure 4.19 Density of RPUR foams catalyzed by DMCHA and metal-amino acid complexes prepared at the mole ratio of metal(II) acetate : amino acid was 1:1 and the amount of blowing agent was 4 pbw

4.3 Rise profiles

Rise profiles were obtained from RPUR foams prepared by cup test method. The catalysts employed were DMCHA and metal-amino acid complexes. Rise time is the time of blowing reaction occurs until CO_2 production stops. The beginning of blowing reaction is cream time. Characteristics of the rise curve of RPUR foams catalyzed by metal-amino acid complexes were compared that catalyzed by DMCHA as shown in Figure 4.20. Rise profiles of RPUR foams catalyzed by metal-amino acid complexes showed a longer initial of reaction time than that of DMCHA. The order of catalytic activity of blowing reaction was in the order DMCHA > Cu(OAc)(Ala) > Zn(OAc)(Ala) > Zn(OAc)(Gly).

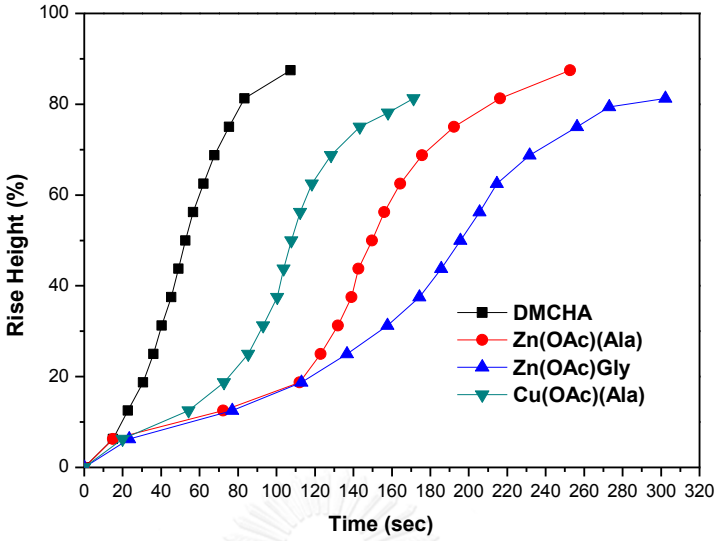

Figure 4.20 Rise profiles of RPUR foams catalyzed by (a) DMCHA; (b) Zn(OAc)(Ala); (c) Zn(OAc)(Gly) and (d) Cu(OAc)(Ala) at the amount of blowing agent = 4 pbw

4.4 Temperature profiles

Tempeature profiles were obtained from RPUR foams prepared by cup test method. The catalysts employed were DMCHA and metal-amino acid complexes. Characteristics of the rise profiles of RPUR foams catalyzed by metal-amino acid complexes were compared that catalyzed by DMCHA as shown in Figure 4.21.

The results revealed that the polymerization reaction was exothermic and all RPUR foams had the same temperature profiles. The maximum core temperature in the polymerization reaction was in the range 113.9 –126.6 °C (Table 4.3). The range of optimum temperature for polymerization reaction was suitable for application since RPUR foams did not decompose because of the heat accumulated inside. The temperature profiles of RPUR foams catalyzed by metal-amino acid complexes showed longer initial of reaction time than that catalyzed by DMCHA. It indicated that the RPUR foams catalyzed by metal-amino acid complexes had longer cream time and gel time than that catalyzed by DMCHA.

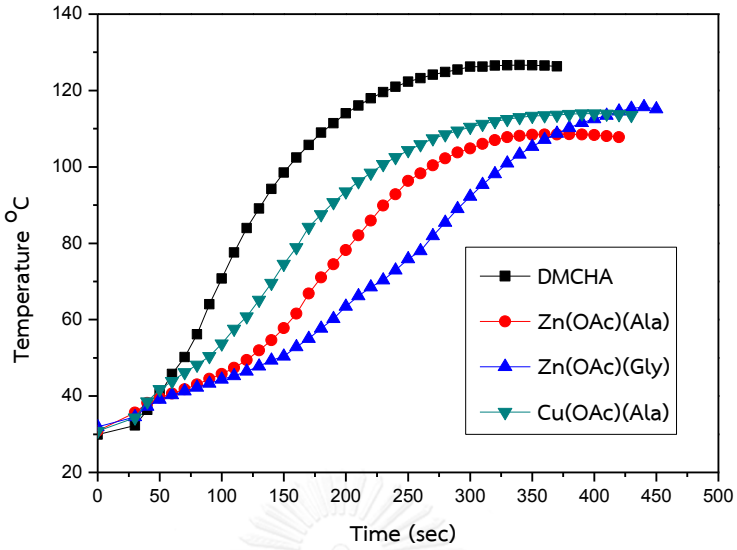

Figure 4.21 Temperature profiles of RPUR foams catalyzed by (a) DMCHA; (b) Zn(OAc)(Ala); (c) Zn(OAc)(Gly) and (d) Cu(OAc)(Ala) at the amount of blowing agent = 4 pbw

Table 4.3 The maximum core temperature of RPUR foams catalyzed by DMCHA, Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala)

Catalysts	Maximum core temperature (oC)	Starting times (sec) at T_{max}
DMCHA	126.6	340
Zn(OAc)(Ala)	108.6	380
Zn(OAc)(Gly)	115.7	440
Cu(OAc)(Ala)	113.9	390

4.5 Characterization of RPUR foams by ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was used to determine the polymerization of RPUR foam system. IR spectra of starting materials, namely polyether polyol, polymeric MDI and RPUR foams catalyzed by DMCHA and metal-amino acid complexes are presented in Figure 4.22. The peaks of polyether polyol showed a broad band at 3409 cm^{-1}, which were attributed to the stretching vibration of hydroxyl groups. Polymeric MDI showed high intensity of free NCO absorption band at 2277 cm^{-1}. All FTIR spectra of RPUR foams showed similar peaks as follows: 3341 cm^{-1} (N-H stretching of urethane and urea), 1710 cm^{-1} (C=O stretching of urethane and urea), 1075 cm^{-1} (C-O of urethane), 1511 cm^{-1} (N-H bending and C-N stretching of urethane and urea and 1220 cm^{-1} (C-N-H stretching vibration of urethane and urea).

IR spectra of RPUR foams catalyzed by DMCHA and metal-amino acid complexes showed small NCO peak around 2277 cm^{-1}, indicating that the reactions of isocyanate with hydroxyl groups and water were completed.

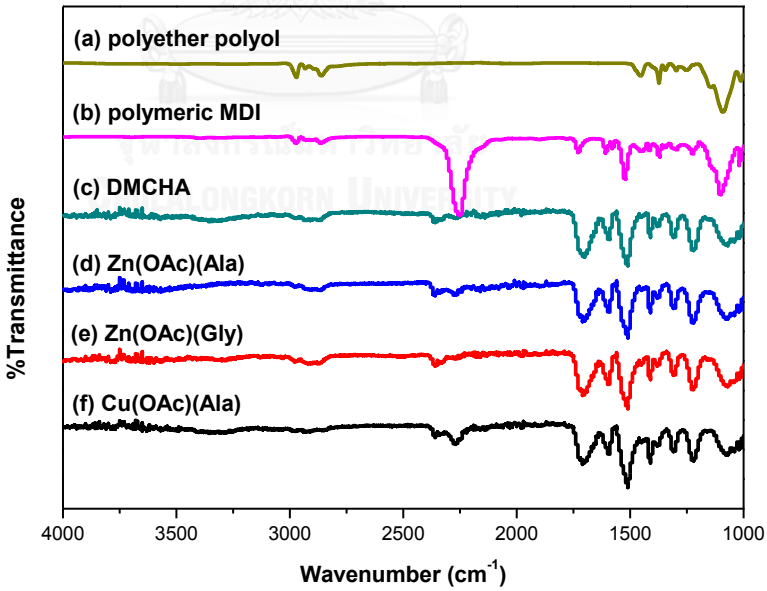

Figure 4.22 IR spectra of starting materials (a) polyether polyol; (b) polymeric MDI, RPUR foams catalyzed by (c) DMCHA; (d) Zn(OAc)(Ala) ; (e) Zn(OAc)(Gly) and (f) Cu(OAc)(Ala)

4.6 NCO conversion of RPUR foams

The isocyanate (NCO) conversion of RPUR foams catalyzed by DMCHA and copper-amino acid complexs is presented in Table 4.5.The NCO conversion defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0 as shown in the following equation.

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

where;

NCO^{f} = the area of the absorption peak by the isocyanate group at time t [Figure 4.27 (c-f)]

NCO^{i} = the area of the absorption peak by the isocyanate group at time 0 [Figure 4.27 (b)]

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

Table 4.4 Wavenumber of 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-

The results of NCO conversion (%) of RPUR foams catalyzed by DMCHA and metal-amino acid complexs are shown in Table 4.5. These findings indicate that all catalysts were approximately NCO conversion (%) was more than 99% at NCO index 100. Therefore, the results indicated that the polymerization reactions of RPUR foam were completed.

Table 4.5 NCO conversion (%) of RPUR foams catalyzed by DMCHA and metal-amino acid complexes

Catalysts	Peak Area		NCO conversion (%)
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	
DMCHA	0.173	2.841	99.94
Zn(OAc)(Ala)	0.081	3.171	99.97
Zn(OAc)(Gly)	0.239	2.773	99.91
Cu(OAc)(Ala)	0.558	2.473	99.72

4.7 Compressive properties of RPUR foams

The results of compression tests for RPUR foam catalyzed by DMCHA, Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala) are shown in Figures 4.23-4.24. It was found that foam samples in the parallel to the foam rising direction had compressive strength higher than those in perpendicular direction. Therefore, all RPUR foams were anisotropic materials as regards to their mechanical properties, which the compressive strength of the foams depend on direction of measurement. RPUR foams catalyzed by DMCHA showed higher compressive strength than those prepared from metal amino acid complexes in both parallel and perpendicular direction of foam rising. The compressive strength of RUPR foams catalyzed by different catalysts was in the order DMCHA > Cu(OAc)(Ala). RPUR foam catalyzed by Cu(OAc)(Ala) had higher density than those catalyzed by Zn(OAc)(Gly) and Zn(OAc)(Ala). In addition, the cell size of RPUR foam catalyzed by Cu(OAc)(Ala) was smaller than that those catalyzed by Zn(OAc)(Gly) and Zn(OAc)(Ala). The high compressive strength of RPUR foam catalyzed by Cu(OAc)(Ala) resulted from small cell size and high density.

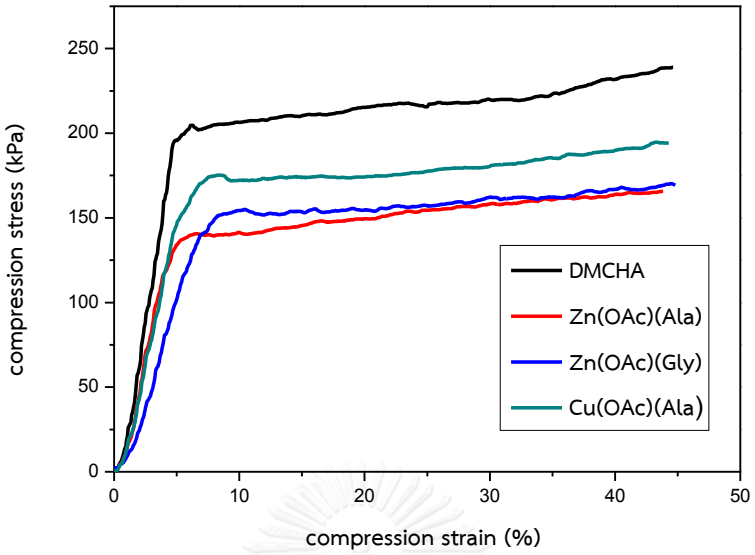

Figure 4.2 3 Stress- strain curves of RPUR foams catalyzed by (a) DMCHA; (b) Zn(OAc)(Ala); (c) Zn(OAc)(Gly) and (d) Cu(OAc)(Ala) prepared at the amount of blowing agent of 4 pbw, parallel to the foam rising direction.

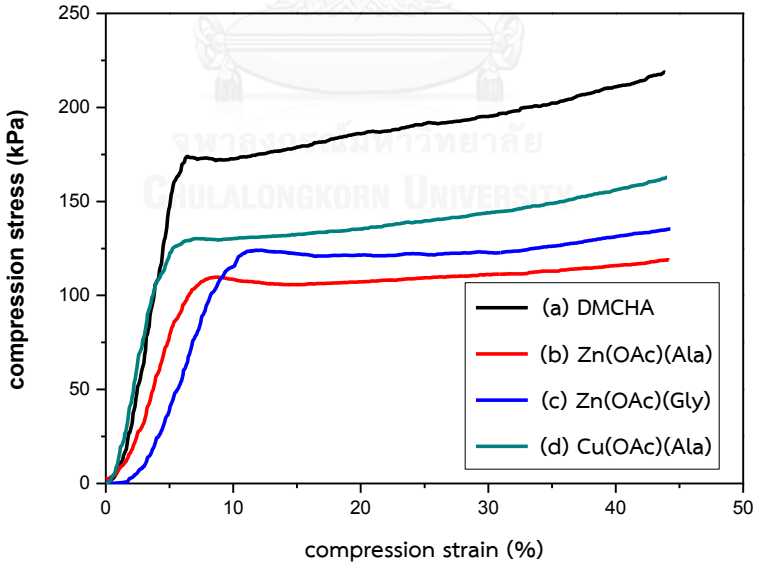

Figure 4.24 Stress-strain curves of RPUR foams catalyzed by (a) DMCHA; (b) Zn(OAc)(Ala); (c) Zn(OAc)(Gly) and (d) Cu(OAc)(Ala) prepared at the amount of blowing agent of 4 pbw, perpendicular to the foam rising direction.

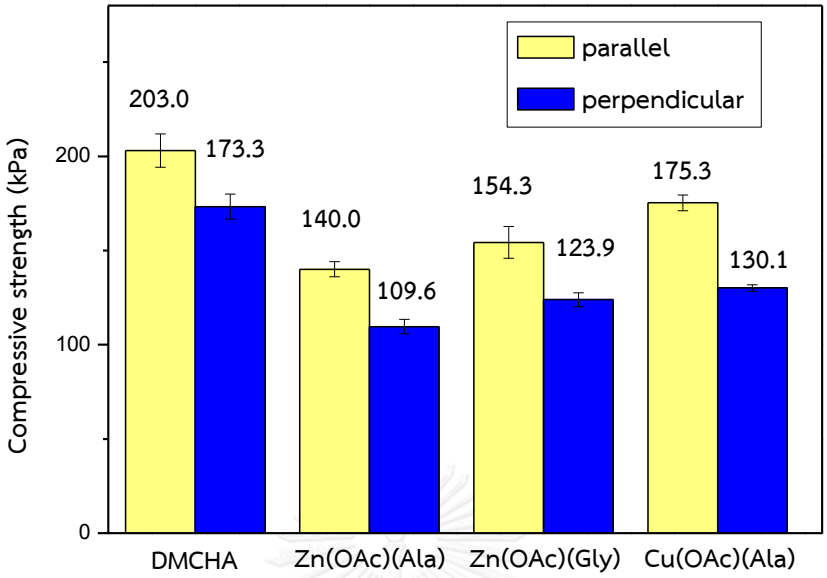

Figure 4.25 Comparison of parallel and perpendicular compressive strength of RPUR foams

Table 4.6 Compressive strength of RPUR foams

Catalysts	Compressive strength (kPa) in parallel direction	Compressive strength (kPa) in perpendicular direction
DMCHA	203.0 ± 8.83	173.3 ± 6.61
Zn(OAc)(Ala)	140.0 ± 4.03	109.6 ± 3.85
Zn(OAc)(Gly)	154.3 ± 8.42	123.9 ± 3.68
Cu(OAc)(Ala)	175.3 ± 4.23	130.1 ± 1.73

4.8 Morphology of RPUR foams at the blowing agent (H_2O) was 4 pbw

The cell structure of RPUR foams was investigated by the SEM. RPUR foam catalyzed by Zn(OAc)(Ala), Zn(OAc)(Gly) and Cu(OAc)(Ala) were prepared at the amount of blowing agent (H_2O) of 4 pbw. The samples were also studied in parallel and perpendicular direction of foam rising (Figures 4.26-4.33). The results revealed that the structure of all RPUR foams was closed-cell. The cells shape were spherical and ellipsoidal in top view and side view, respectively, as shown in Figure 4.34 (a). This revealed that RUPR foams were anisotropic materials. The average cell diameter of RPUR foams is shown in Tables 4.6-4.7. In the study of spherical shape, the measurement of the transverse and the longitudinal directions were expressed as cell size1 and cell size2 (Figure 4.34 a). In the study of elliptical shape, the measurement of the transverse (long length) and the longitudinal (short length) directions were expressed as cell size 1 and cell size 2 (Figure 4.34 b), respectively. The data of averaged cell size of RPUR foams (Tables 4.6-4.7) revealed that cell size of RPUR foams catalyzed by different catalysts was in the order DMCHA <Cu(OAc)(Ala)<Zn(OAc)(Ala) < Zn(OAc)(Gly). These results agree with the compressive strength data that RPUR foam catalyzed by DMCHA gave more strength than RPUR foams catalyzed by metal-amino acid complexes.

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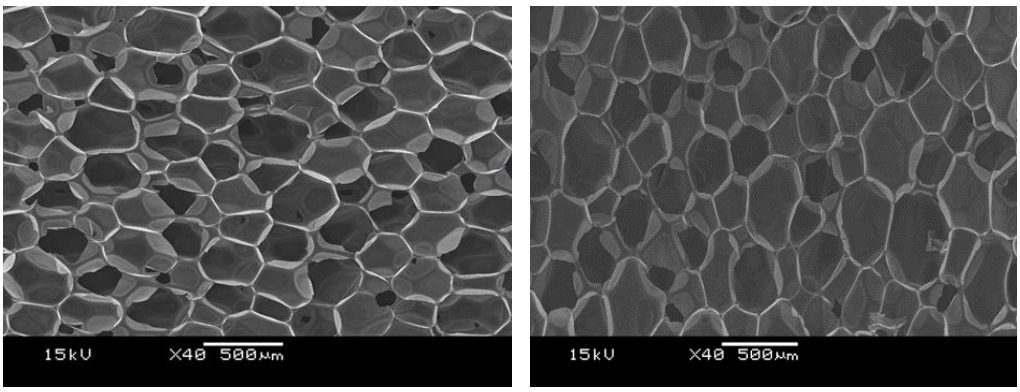
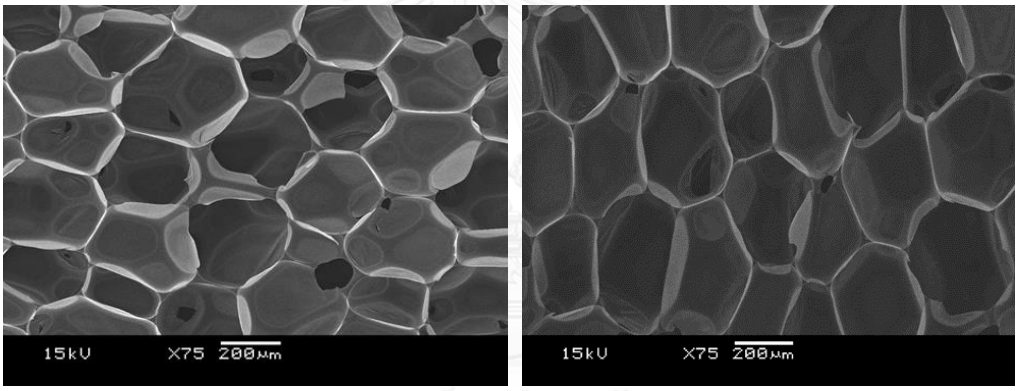


(a) (b)

Figure 4.26 SEM images of RPUR foam catalyzed by DMCHA: (a) top view; (b) side view (40x)



(a) (b)

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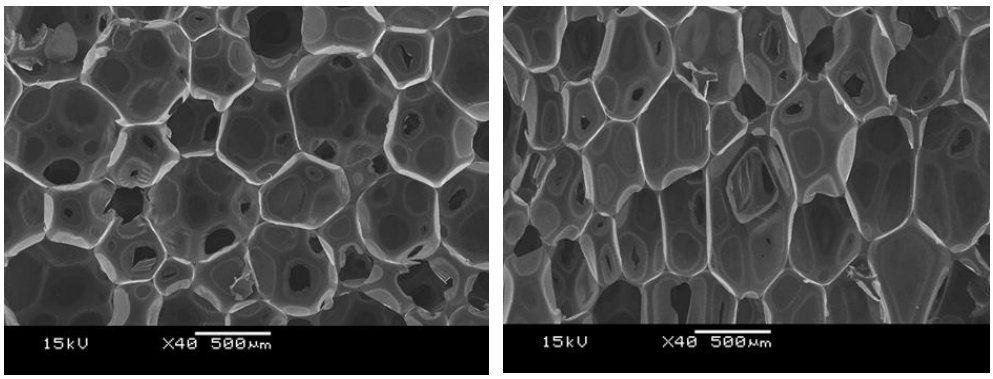
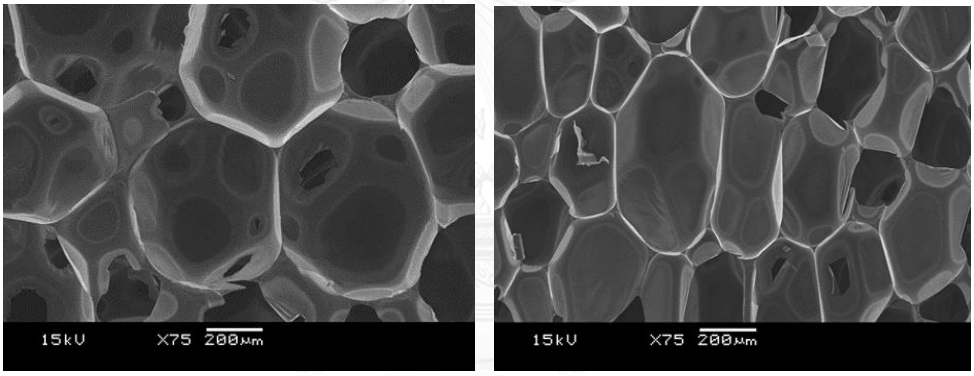
Figure 4.27 SEM images of RPUR foam catalyzed by DMCHA: (a) top view; (b) side view (75x)



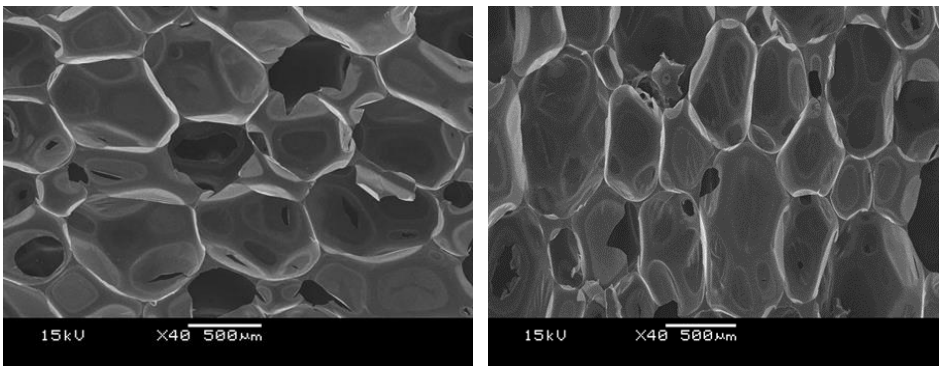
(a) (b)

Figure 4.28 SEM images of RPUR foam catalyzed by Zn(OAc)(Ala): (a) top view; (b) side view (40x)



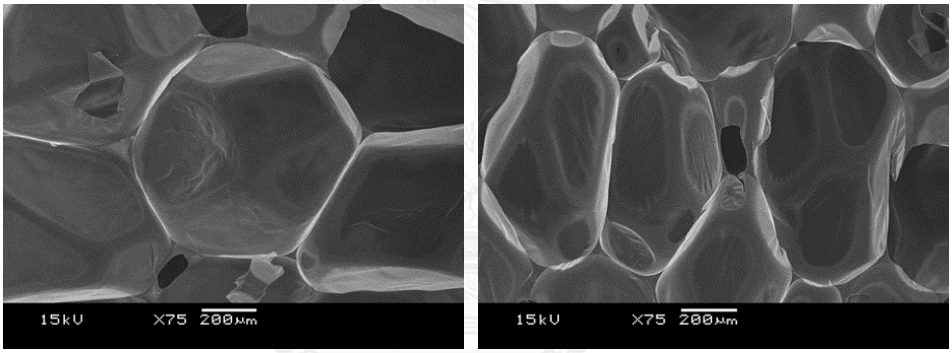
(a) (b)

Figure 4.29 SEM images of RPUR foam catalyzed by Zn(OAc)(Ala): (a) top view; (b) side view (75x)



(a) (b)

Figure 4.30 SEM images of RPUR foam catalyzed by Zn(OAc)(Gly): (a) top view; (b) side view (40x)



(a) (b)

Figure 4.31 SEM images of RPUR foam catalyzed by Zn(OAc)(Gly): (a) top view; (b) side view (75x)

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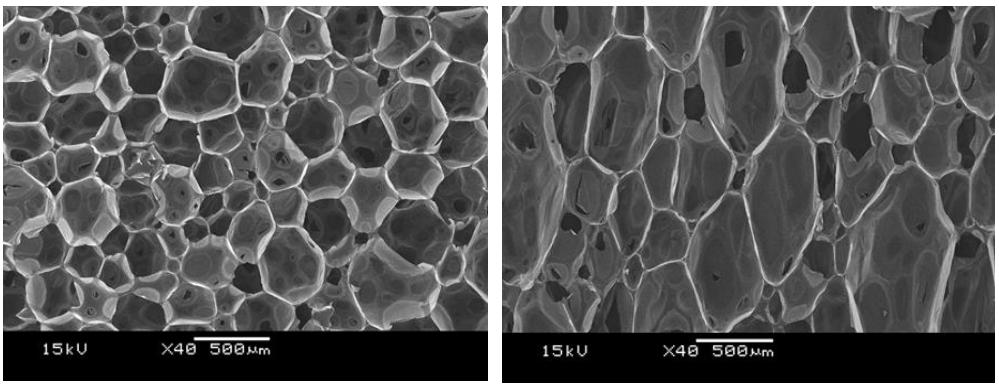
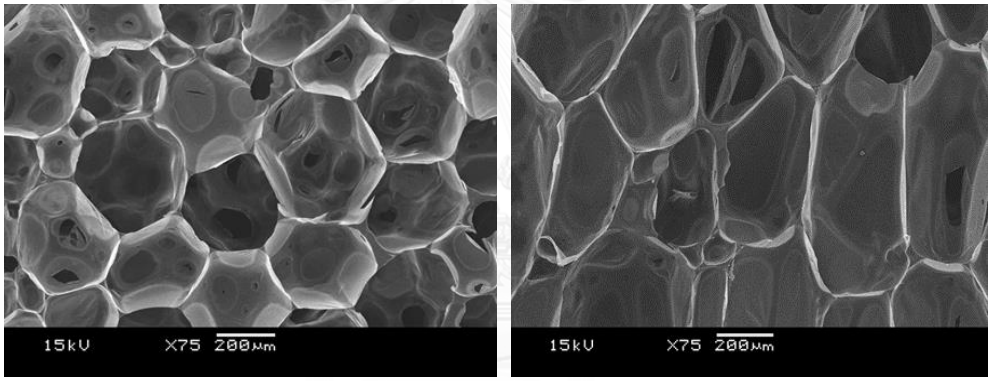


(a) (b)

Figure 4.32 SEM images of RPUR foam catalyzed by Cu(OAc)(Ala): (a) top view; (b) side view (40x)



(a) (b)

Figure 4.33 SEM images of RPUR foam catalyzed by Cu(OAc)(Ala): (a) top view; (b) side view (75x)

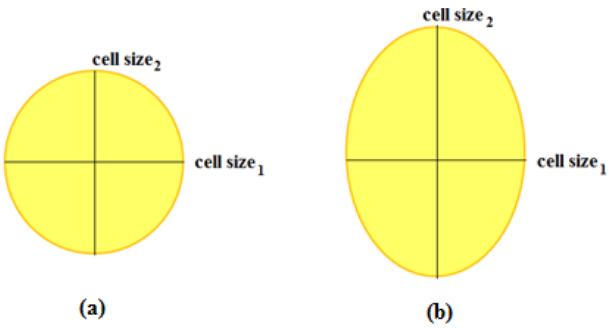


Figure 4.34 Measurement of cell size (a) Top view (b) Side view

Table 4.7 The cell size (top view) of RPUR foams catalyzed by DMCHA and metal-amino acid complexes

catalysts	Top view	
	Cell size$_1$ (μm)	Cell size$_2$ (μm)
*DMCHA (ref.)	358.6 ± 40.19	354.8 ± 35.43
Zn(OAc)(Ala)	561.7 ± 49.34	574.2 ± 73.47
Zn(OAc)(Gly)	707.8 ± 58.44	716.8 ± 63.73
Cu(OAc)(Ala)	365.3 ± 67.48	358.2 ± 75.80

Table 4.8 The cell size (side view) of RPUR foams catalyzed by DMCHA and metal-amino acid complexes

catalysts	Side view	
	Cell size$_1$ (μm)	Cell size$_2$ (μm)
*DMCHA (ref.)	289.3 ± 59.86	408.1 ± 67.83
Zn(OAc)(Ala)	508.5 ± 86.65	621.8 ± 115.34
Zn(OAc)(Gly)	743.1 ± 48.20	847.7 ± 56.24
Cu(OAc)(Ala)	312.6 ± 111.09	431.6 ± 103.56

The average cell sizes of RPUR foams are shown in Tables 4.7 and 4.8. The results showed that cell size of RPUR foams on the top view was smaller than that of the side view. From small to large cell size, The order of cell size of RPUR foams catalyzed by different catalysts is DMCHA < Cu(OAc)(Ala) < Zn(OAc)(Ala) < Zn(OAc)(Gly).

The external appearance of RPUR foams obtained by cup test method. RPUR foams were cut as shown in Figures 4.35 a-c. External appearance of of RPUR foams is shown in Figures 4.36-4.48.

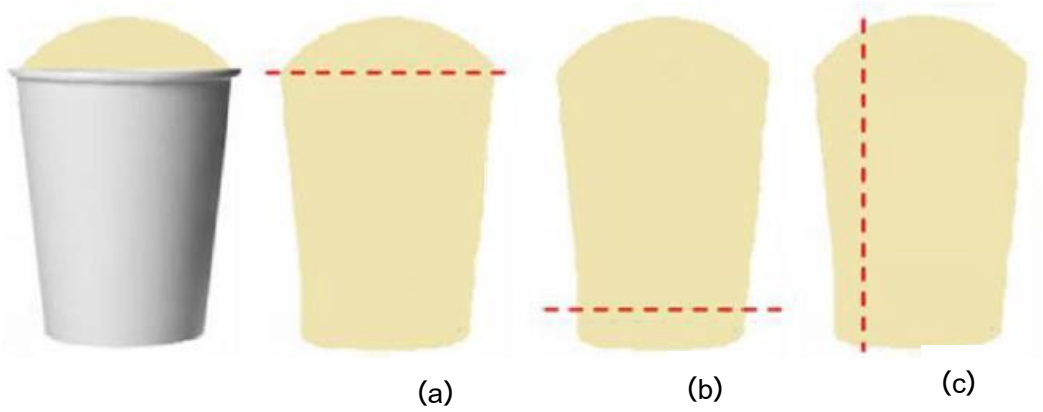


Figure 4.35 Cutting line for RPUR foam samples (a) top (b) bottom and (c) side of the sample

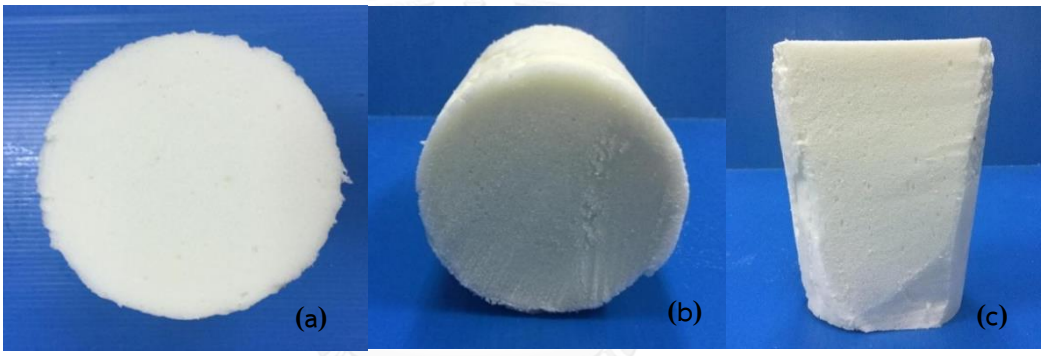


Figure 4.36 RPUR foams catalyzed by DMCHA

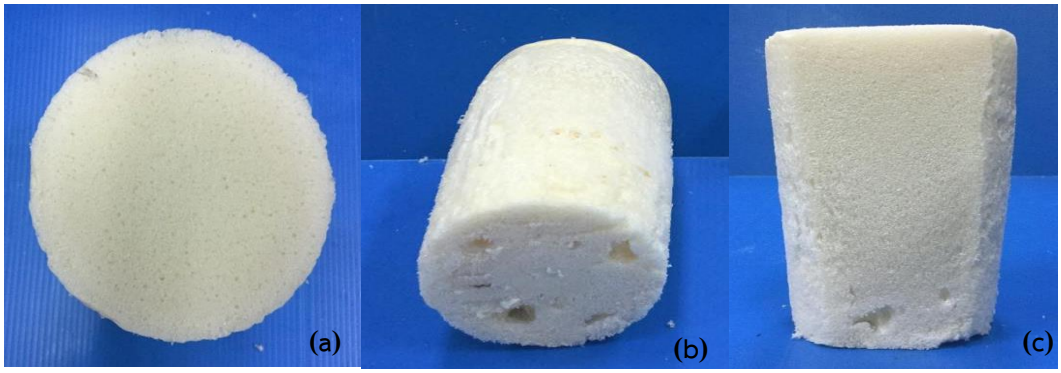


Figure 4.37 RPUR foams catalyzed by Zn(OAc)(Ala) (1:2); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 3 pbw.

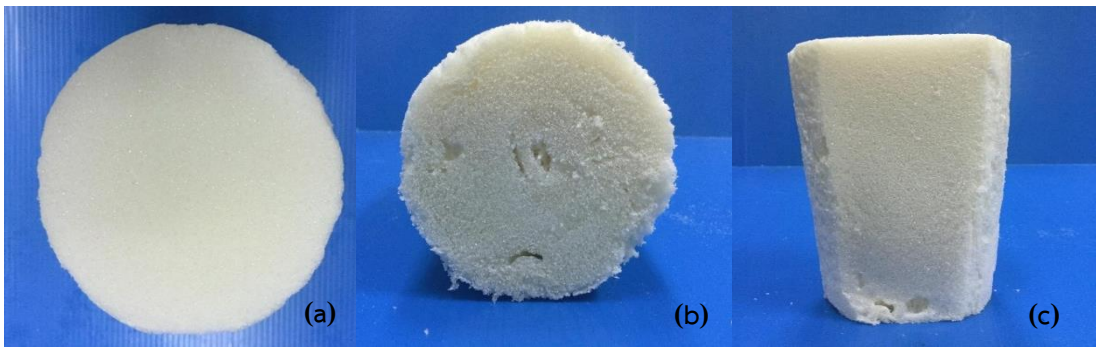


Figure 4.38 RPUR foams catalyzed by Zn(OAc)(Ala) (1:1); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 3 pbw.

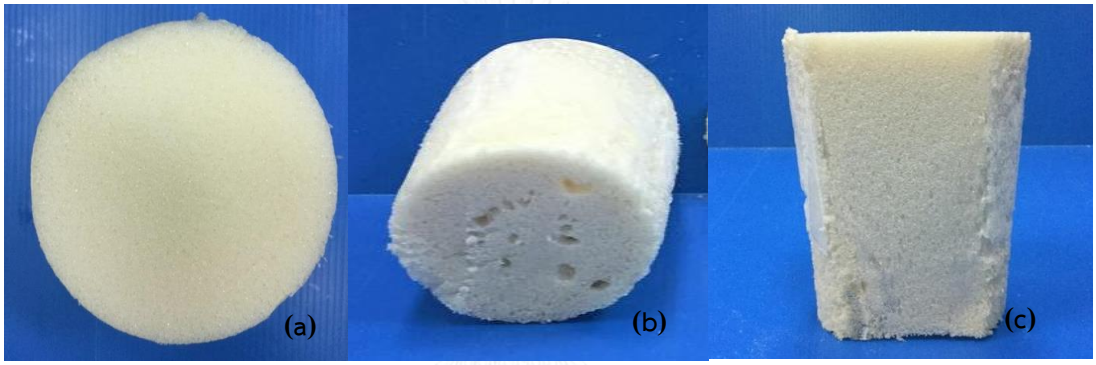


Figure 4.39 RPUR foams catalyzed by Zn(OAc)(Gly) (1:2); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 3 pbw.

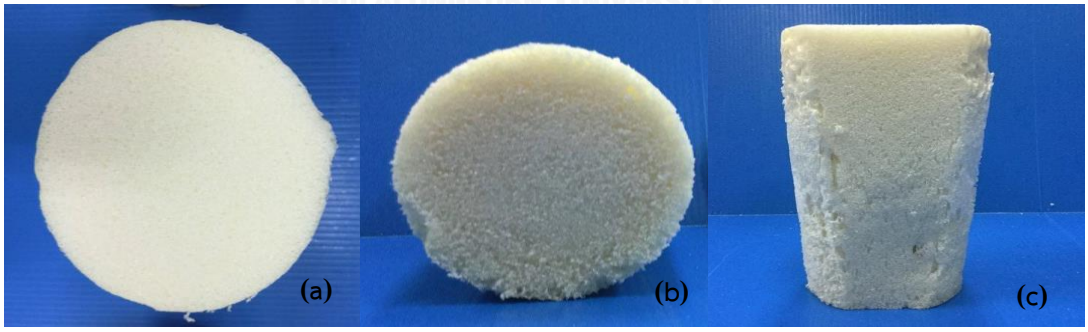


Figure 4.40 RPUR foams catalyzed by Zn(OAc)(Gly) (1:1); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 3 pbw.

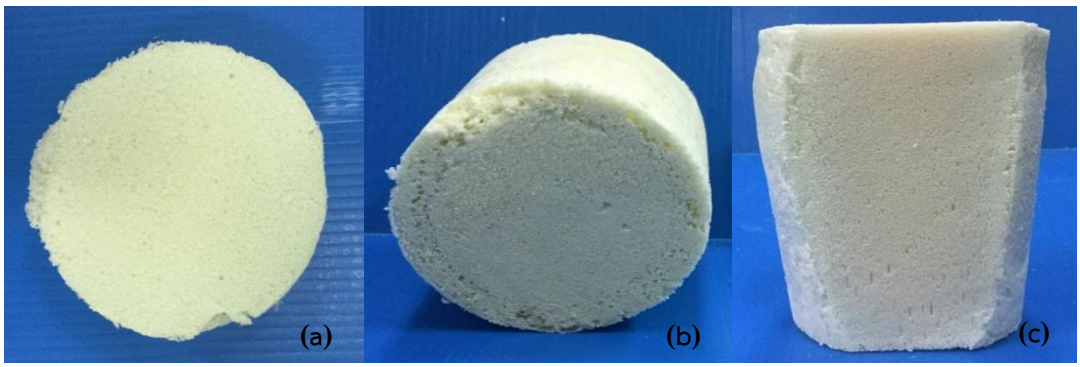


Figure 4.41 RPUR foams catalyzed by Cu(OAc)(Ala) (1:2); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 3 pbw.

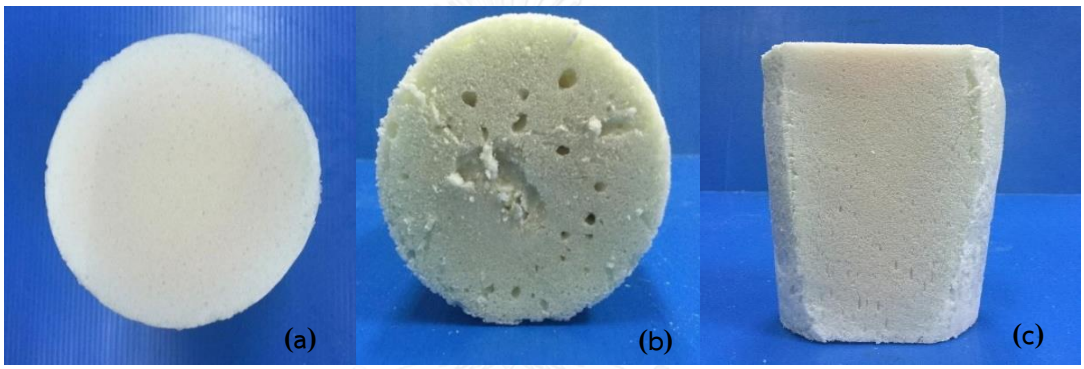


Figure 4.42 RPUR foams catalyzed by Cu(OAc)(Ala) (1:1); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 3 pbw.

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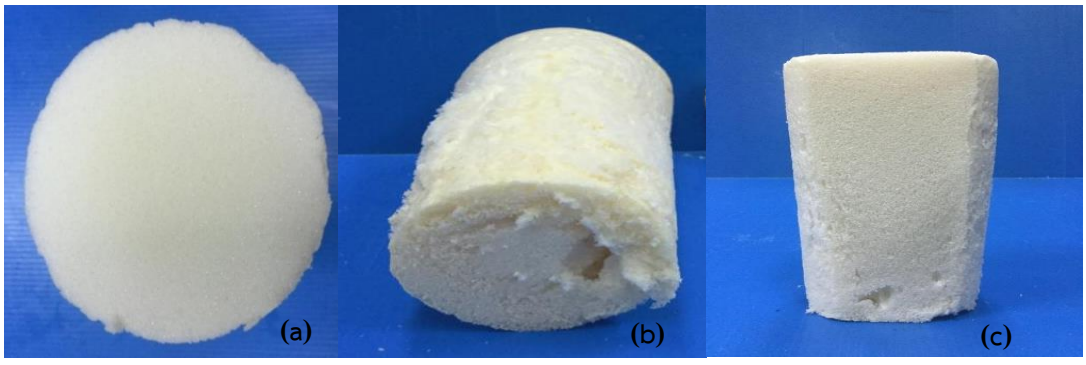

Figure 4.43 RPUR foams catalyzed by Zn(OAc)(Ala) (1:2); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 4 pbw.

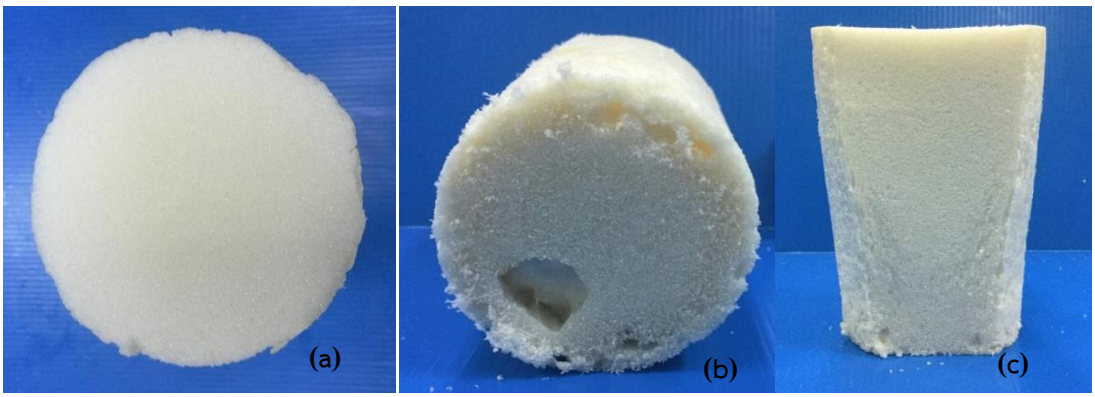

Figure 4.44 RPUR foams catalyzed by Zn(OAc)(Ala) (1:1); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 4 pbw.

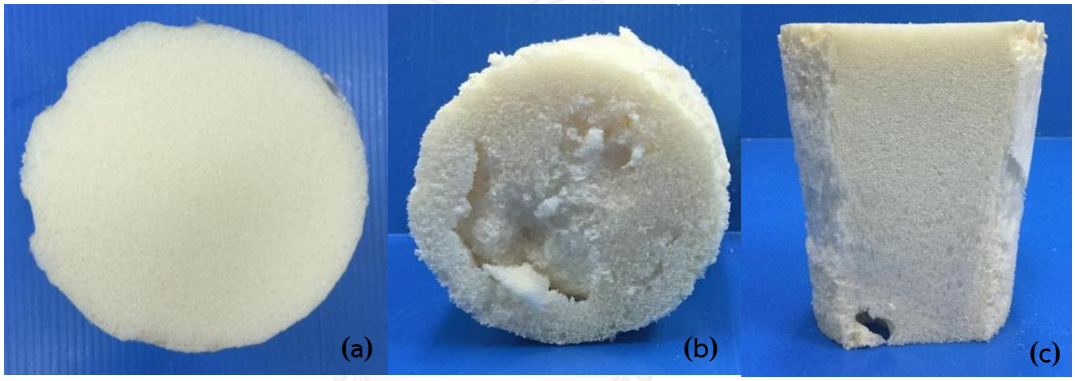

Figure 4.45 RPUR foams catalyzed by Zn(OAc)(Gly) (1:2); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 4 pbw.

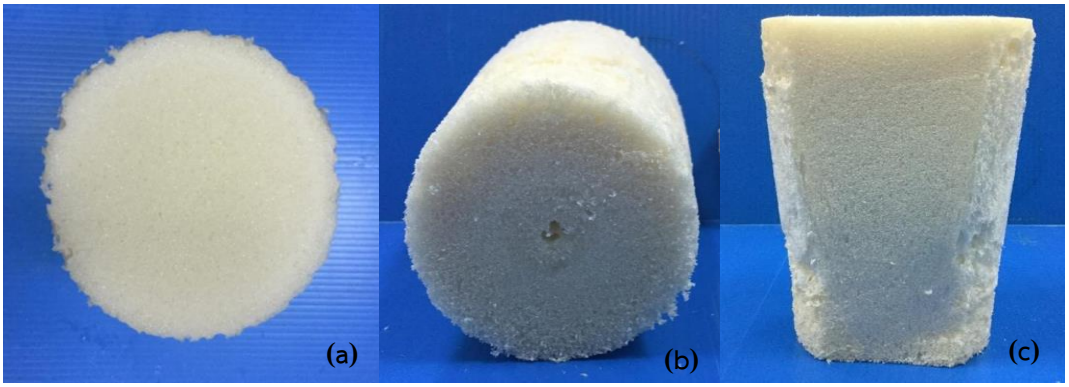

Figure 4.46 RPUR foams catalyzed by Zn(OAc)(Gly) (1:1); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 4 pbw.

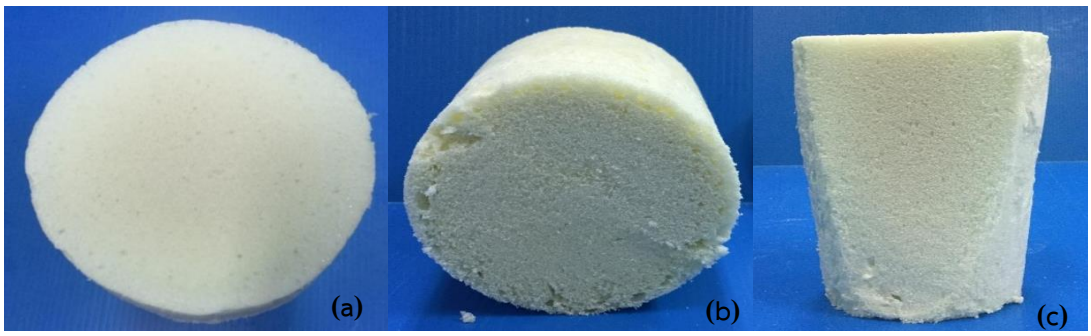

Figure 4.47 RPUR foams catalyzed by Cu(OAc)(Ala) (1:2); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 4 pbw.

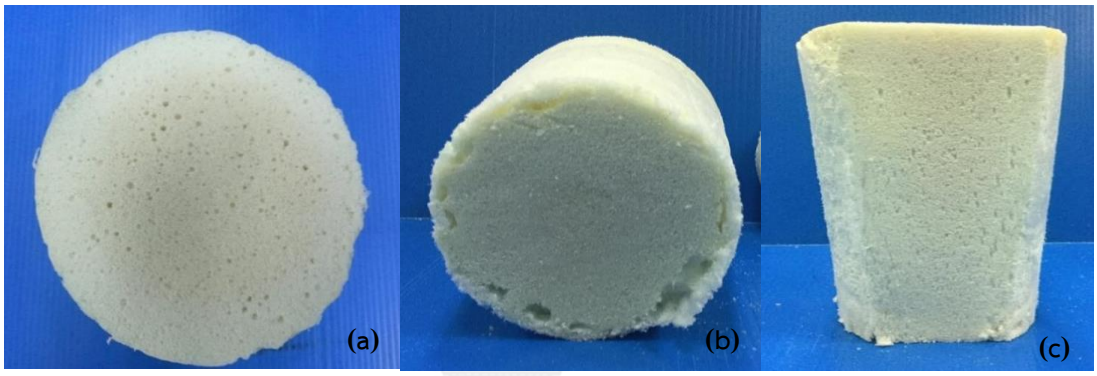

Figure 4.48 RPUR foams catalyzed by Cu(OAc)(Ala) (1:1); the amount of catalyst = 1 pbw and the amount of blowing agent (H_2O) = 4 pbw

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CHAPTER V
CONCLUSION

5.1 Conclusion

The solutions of metal- amino acid complexes, namely Zn(OAc) (Ala) , Zn(OAc)(Gly), and Cu(OAc)(Ala) in water were used as catalysts for rigid polyurethane foam preparation. The solutions of metal-amino acid complexes were obtained as odorless liquids that could be easily dissolved in the other starting materials used in foam formulations. The formation of a complexes were confirmed by UV visible spectroscopy, IR spectroscopy and mass spectrometry.

From the reaction times, RPUR foams prepared from metal- amino acid complexes showed the order of catalytic activity of Cu(OAc)(Ala) > Zn(OAc)(Ala) > Zn(OAc)(Ala). Metal-amino acid complexes prepared at the mole ratio of metal acetate : amino acid = 1:1 gave shorter reaction time and therefore better catalytic activity than those prepared at the 1:2 mole ratio. The catalytic activities and RPUR foam density obtained from Cu(OAc)(Ala) prepared at the mole ratio = 1:1 at the amount of blowing agent = 4 pbw were comparable to those obtained from a reference commercial catalyst (DMCHA).

Rise profile of RPUR foaming reaction catalyzed by metal- amino acid complexes were compared with that of DMCHA. From the slope of rise profile curve, the order of catalytic activity was DMCHA > Cu(OAc)(Ala) > Zn(OAc)(Ala) > Zn(OAc)(Gly).

The polymerization reaction was exothermic and all foams had the same temperature profiles. The maximum core temperature of foaming reaction was in the range 108.6-126.6°C. This was appropriate foaming temperature since RPUR foams did not burn. The NCO conversion (%) was investigated by ATR-FTIR spectroscopy and it was found that the NCO conversion for all catalysts was more than 99% at NCO index of 100.

The results of compressive strength showed that RPUR foam catalyzed by DMCHA exhibited the higher compressive strength than that of the foam prepared from a metal amino acid complexes at both parallel and perpendicular to the foam rising direction. The compressive strength of foam catalyzed by Cu(OAc)(Ala) (175.3 kPa) were comparable to that prepared from DMCHA (203.0 kPa).

Morphology of RPUR foams revealed that the structure of all RPUR foams are closed-cell. The cells were spherical shape and ellipsoidal shape in parallel and perpendicular to the foam rising direction, respectively. This results revealed that the foams were anisotropic materials.

5.2 Suggestion for future work

The suggestion for future work is to use other amino acids for synthesizing other metal amino acid complexes.

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APPENDIX

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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	pbw (parts by weight)	
	Blowing agent = 3	Blowing agent = 4
Polyether polyol (Polimaxx® 4221; OH-number = 440 mg KOH/g; functionality = 4.3)	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5
Blowing agent (H_2O)	3	4
Catalyst	1	1
Polymeric MDI (PMDI, Raycore® B9001; %NCO = 31.0; functionality = 2.7)	151.3	166.4

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

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

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

Equivalent in the above formulation:

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

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

Total equivalent weight = 1.117

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

Thus:

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

where;

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

Therefore:

at isocyanate index = 100

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

at Blowing agent = 4 pbw

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

$$\text{Water} = \frac{4.0}{9.0} = 0.444$$

Total equivalent weight = 1.228

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Thus:

$$\text{PMDI (pbw)} = 1.228 \times \frac{\text{PMDI molar mass}}{\text{functionality}} = 1.228 \times \frac{365.8}{2.7} = 166.4$$

where;

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

Therefore:

at isocyanate index = 100

$$\text{Isocyanate actual} = \frac{166.4}{100} \times 100 = 166.4 \text{ pbw}$$

Table A1 Isocyanate quantity at different blowing agent

Chemicals	**pbw (parts by weight)**	
	Blowing agent = 3	**Blowing agent = 4**
Polyether polyol (Polimaxx® 4221; OH-number = 440 mg KOH/g; functionality = 4.3)	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5
Blowing agent (H_2O)	3	4
Catalyst	1	1
Polymeric MDI (PMDI, Raycore® B9001; %NCO = 31.0; functionality = 2.7)	151.3	166.4

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NCO conversion calculation

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

$$\text{Isocyanate conversion (\%)} = 1 - \left[\frac{NCO^f}{NCO^i}\right] x100$$

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)

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

Table A 2 Free NCO absorbance peak area in PMDI (Suprasec®5005) from IRATR

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

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Example Calculate the conversion of isocyanate (α) of rigid polyurethane foams catalyzed by Zn(OAc)(Ala) catalyst at NCO index 100

Conversion of isocyanate (%)

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 = 0.0255 = NCO^f

Thus, conversion of isocyanate (%) = $1-\left[\frac{NCO^f}{NCO^i}\right]x100$

$= 1-\frac{0.0255}{98}x100$

$= 99.97$

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Table A3 NCO conversion of RPUR foam catalyzed by Zn(OAc)(Ala) 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)	
Zn(OAc)(Ala)	0.081	3.171	0.0255	99.97

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	0.173	2.841	0.0609	99.94
Zn(OAc)(Ala)	0.081	3.171	0.0255	99.97
Zn(OAc)(Gly)	0.239	2.773	0.0862	99.91
Cu(OAc)(Ala)	0.558	2.473	0.2774	99.72

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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 (Polimaxx® 4221)	100.0	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Raycore® B9001)	151.4	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	22	0
Gel time	38	0
Tack free time	152	2
Rise time	127.4	0.55
Density (kg/m^3)	39.2	0.43
Mechanical properties		
Compressive strength (kPa) in parallel	203.0	8.83
Compressive strength (kPa) in perpendicular	173.3	6.61

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Table B2 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Gly) at the NCO index 100

Formulations (pbw)	**Zn(OAc)(Gly) [H_2O =3 pbw]**				**Zn(OAc)(Gly) [H_2O =4 pbw]**			
	1:1		**1:2**		**1:1**		**1:2**	
Polyol (Polimaxx® 4221)	100.0		100.0		100.0		100.0	
Catalyst	1.0		1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5		2.5	
Blowing agent	3.0		3.0		4.0		4.0	
PMDI ((Raycore® B9001)	151.4		151.4		166.4		166.4	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times (sec)								
Cream time	27	0	34	0.58	24	0	34	0
Gel time	100	2.52	158	3.46	72	0.55	83	0.58
Tack free time	408	32.33	647	1.53	376	3.61	424	1.53
Rise time	343	21.46	555	3.46	336	2.68	359	7.77
Density (kg/m^3)	41.41	1.39	44.11	2.74	39.4	0.47	42.23	3.04
Mechanical properties								
Compressive strength (kPa) in parallel	-	-	-	-	154.3	8.42	-	-
Compressive strength (kPa) in perpendicular	-	-	-	-	123.9	3.68	-	-

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Table B3 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Ala) at the NCO index 100

Formulations (pbw)	**Zn(OAc)(Ala) [H_2O =3 pbw]**				**Zn(OAc)(Ala) [H_2O =4 pbw]**			
	1:1		**1:2**		**1:1**		**1:2**	
Polyol (Polimaxx® 4221)	100.0		100.0		100.0		100.0	
Catalyst	1.0		1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5		2.5	
Blowing agent	3.0		3.0		4.0		4.0	
PMDI (Raycore® B9001)	151.4		151.4		166.4		166.4	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times (sec)								
Cream time	30	0	33	0.58	22	0	34	0.58
Gel time	82	0.58	91	3.21	63	0	84	2.08
Tack free time	351	2.31	363	13.20	242.6	0.89	319	1
Rise time	295	2.52	298	6.51	233	0	260	1
Density (kg/m^3)	42.3	1.04	37.2	2.78	35.2	0.65	41.9	1.99
Mechanical properties								
Compressive strength (kPa) in parallel	-	-	-	-	140.0	4.03	-	-
Compressive strength (kPa) in perpendicular	-	-	-	-	109.6	3.85	-	-

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Table B4 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Cu(OAc)(Ala) at the NCO index 100

Formulations (pbw)	**Cu(OAc)(Ala) [H_2O =3 pbw]**				**Cu(OAc)(Ala) [H_2O =4 pbw]**			
	1:1		**1:2**		**1:1**		**1:2**	
Polyol (Polimaxx® 4221)	100.0		100.0		100.0		100.0	
Catalyst	1.0		1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5		2.5	
Blowing agent	3.0		3.0		4.0		4.0	
PMDI (Raycore® B9001)	151.4		151.4		166.4		166.4	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times (sec)								
Cream time	28	0	29	0.58	22	0.5	32	0
Gel time	81	0.58	97	3.06	42	0.45	89	5.13
Tack free time	337	4.16	344	4.73	195	0.89	299	23.97
Rise time	285	4.04	287	5.86	178	0.84	240	11.93
Density (kg/m^3)	46.2	1.21	67.0	4.96	40.7	**0.62**	48.6	2.80
Mechanical properties								
Compressive strength (kPa) in parallel	-	-	-	-	175.3	4.23	-	-
Compressive strength (kPa) in perpendicular	-	-	-	-	130.1	1.73	-	-

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