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PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-
ASPARAGINE AND METAL-THREONINE COMPLEXES

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นัตติยา จินตนา : การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-แอสพาราจีนและสารประกอบเชิงซ้อนโลหะ-ทรีโอนีน (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ASPARAGINE AND METAL-THREONINE COMPLEXES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. นวลพรรณ จันทรศิริ, 105 หน้า.

งานวิจัยนี้เป็นการสังเคราะห์ตัวเร่งปฏิกิริยาสารประกอบเชิงซ้อนโลหะ-กรดแอมิโน (metal-amino acid complexes) ในรูปแบบของสารละลายในน้ำเพื่อใช้เป็นตัวเร่งปฏิกิริยาชนิดใหม่สำหรับการเตรียมโฟมพอลิยูรีเทนแบบแข็งด้วยตัวเร่งปฏิกิริยาสารประกอบเชิงซ้อนโลหะ-กรดแอมิโน เตรียมจากโลหะแอซิเตทและกรดแอมิโน โดยใช้น้ำเป็นตัวทำละลาย โลหะแอซิเตทที่ใช้ ได้แก่ ซิงค์แอซิเตทและคอปเปอร์แอซิเตท กรดแอมิโนที่ใช้ได้แก่แอสพาราจีนและทรีโอนีน ซึ่งกรดแอมิโนทั้งสองชนิดไม่มีกลิ่นและไม่เป็นพิษ การพิสูจน์เอกลักษณ์ของสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนด้วยยูวีวิสิเบิลสเปกโทรสโกปี อินฟราเรดสเปกโตรสโกปีและแมสสเปกโตรเมทรี สารประกอบเชิงซ้อนของโลหะ-กรดแอมิโนที่สังเคราะห์ คือ $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ และ $Cu(Thr)_2$ โดย Asn = แอสพาราจีน และ Thr = ทรีโอนีน ในรูปแบบสารละลายที่ละลายในน้ำและใช้เป็นตัวเร่งปฏิกิริยาสำหรับการเตรียมพอลิยูรีเทนโฟมแบบแข็ง ศึกษาประสิทธิภาพในการเร่งปฏิกิริยาของสารประกอบเชิงซ้อนของโลหะ-แอมิโนในรูปแบบสารละลายในน้ำจากเวลาที่ใช้ในการเกิดปฏิกิริยา ศึกษาสมบัติทางกายภาพและสมบัติเชิงกลของโฟมพอลิยูรีเทน เปรียบเทียบกับโฟมที่เร่งปฏิกิริยาด้วยไดเมทิลไซโคลเฮกซิลแอมีน จากผลการทดลองพบว่า สารประกอบของคอปเปอร์-ทรีโอนีนมีความว่องไวในการเร่งปฏิกิริยาสูงกว่าสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนชนิดอื่น

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NUTTIYA JINTANA: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-ASPARAGINE AND METAL-THREONINE COMPLEXES. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 105 pp.

This research aimed to synthesize metal-amino acid complexes in the form of aqueous solutions to serve as new catalysts for the preparation of rigid polyurethane foams. Aqueous solutions of metal-amino acid complexes were prepared from the reaction of metal acetates with amino acids and water was used as a solvent. Metal acetates employed were copper acetate and zinc acetate. Amino acids employed were asparagine (Asn) and threonine (Thr). Both amino acids are odorless and non-toxic. UV-Vis spectroscopy, FTIR spectroscopy and mass spectrometry were used to characterize metal-amino acid complexes. Metal-amino acid complexes, namely $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ and $Cu(Thr)_2$ (where Asn = asparagine and Thr = threonine), in the form of aqueous solutions were obtained and used as such catalysts for the preparation of polyurethane foam. Reaction times, physical properties and mechanical properties of the prepared foam were studied. The results were compared with RPUR foam catalyzed by DMCHA. The experimental results showed that $Cu(Thr)_2$ had the best catalytic activity among all metal-amino acid complexes.

Department: Chemistry   Student's Signature ....

Field of Study: Chemistry   Advisor's Signature ....

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จุฬาลงกรณ์มหาวิทยาลัย
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LIST OF ABBREVIATIONS

%	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
$^{\circ}C$	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
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 microscopy

SnOct	stannous octate
t	time
T_{max}	maximum core temperature
TEDA	triethylenediamine
TDI	toluene diisocyanate
trien	triethylenetetramine
UV	ultraviolet

CHAPTER I

INTRODUCTION

Polyurethane (PUR) is group of polymer which is widely used wherewith polyurethane foams can be divided to flexible polyurethane foams and rigid polyurethane foams (RPUR foams). RPUR foams are mainly used as thermal insulator in the building and refrigerator due to their good mechanical properties and low thermal conductivity [1, 2].

Rigid polyurethane foams are prepared by the exothermic polymerization reaction of di- or polyhydroxyl group of polyol with di- or polymeric isocyanate group in the presence of catalyst, surfactant and blowing agent. This reaction is called gelling reaction. When isocyanate group reacts with water to form carbamic acid which decomposes to give amine and release carbon dioxide (CO_2), this reaction gives air bubbles to rise up foam. This reaction is called blowing reaction and water is used as a blowing agent. Since gelling and blowing reactions are slow, appropriate catalysts are required to prepare polyurethane foams [3, 4]. Organotin, for example dibutyltin dilaurate (DBTDL), and tertiary amines, such as N,N-dimethylcyclohexylamine (DMCHA), are commonly used as commercial catalysts for RPUR foam preparation [5]. The disadvantage of organotin and tertiary amine catalysts are their toxicity and strong odor, respectively. Therefore, the development of new alternative catalysts is significant such as manganese complexes [6], zirconium complexes [7] and metal-amine complexes [8].

Metal-amino acid complexes have been used as animal nutrition [9], catalyst for regioselective synthesis of 1,4-disubstituted triazoles [10] and catalyst for thio-Michael reaction [11]. These complexes have never been used as catalysts in RPUR foams preparation. In the previous researches of our group, metal-amino acid

complexes were used as catalysts for the preparation of RPUR foams. These metal-amino acid complexes were MX_2; where M = Cu and Zn, X = valine, arginine, alanine and glycine) [12, 13]. The advantage of MX_2 is odorless. However, the catalytic activity of MX_2 was not good. Therefore, the aim of this research is the synthesis of metal-amino acid complexes with better catalytic activity.

Objective

The objective of this research was to synthesize metal-amino acid complexes in the form of aqueous solutions and used as catalysts for the preparation of rigid polyurethane foams without purification. These metal-amino acid complexes were odorless and were expected to have good catalytic activity. Metal-amino acid complexes synthesized were $Zn(Asn)_2$, $Cu(Asn)_2$, $Zn(Thr)_2$ and $Cu(Thr)_2$, where Asn = asparagine, Thr = threonine. The catalysts were easily prepared in one step from odorless and non-toxic amino acids. Water was used as a solvent in the preparation of catalysts, which has the advantages that water is non-toxic and acts as a blowing agent in the foaming reaction. Reaction times during RPUR foam preparation, physical and mechanical properties of RPUR foams were investigated and compared to the data which obtained from a commercial catalyst (DMCHA).

Scope of the research

The scopes of this research were to prepare RPUR foams using metal-asparagine and metal-threonine complexes as catalysts (Figure 1.1). The experiment was divided to 3 parts. The first part was the preparation RPUR foams catalyzed by N,N-dimethylcyclohexylamine (DMCHA) which is a commercial reference catalyst. The

RPUR foams were prepared by cup-test and molded methods. Then the reaction times during the foam rising were recorded, namely gel time, cream time, rise time and tack free time. RPUR foams obtained from cup test method were used for the investigation of height of foam, density, rise profile and temperature profile. FTIR spectroscopy was used to characterize RPUR foams. Physical and mechanical properties of RPUR foams obtained from molded method were used for the investigation of compression properties and morphology using scanning electron microscopy (SEM).

In the second part, metal-amino acid complexes were synthesized by the reaction between zinc acetate dihydrate [$Zn(OAc)_2.2H_2O$] or copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$] and asparagine (Asn) or threonine (Thr) using water as a solvent. The metal-amino acid complexes obtained were $Zn(Asn)_2$, $Cu(Asn)_2$, $Zn(Thr)_2$ and $Cu(Thr)_2$ (Figure 1.1). The complexes were characterized by UV-Vis, FTIR spectroscopy and mass spectrometry.

In the third part, RPUR foams were prepared by using aqueous solution of metal-amino acid complexes as catalysts. The preparation and investigation of RPUR foams were the same as RPUR foam catalyzed by DMCHA in the first part. Catalytic activity of the metal-amino acid complexes was compared with that of DMCHA.
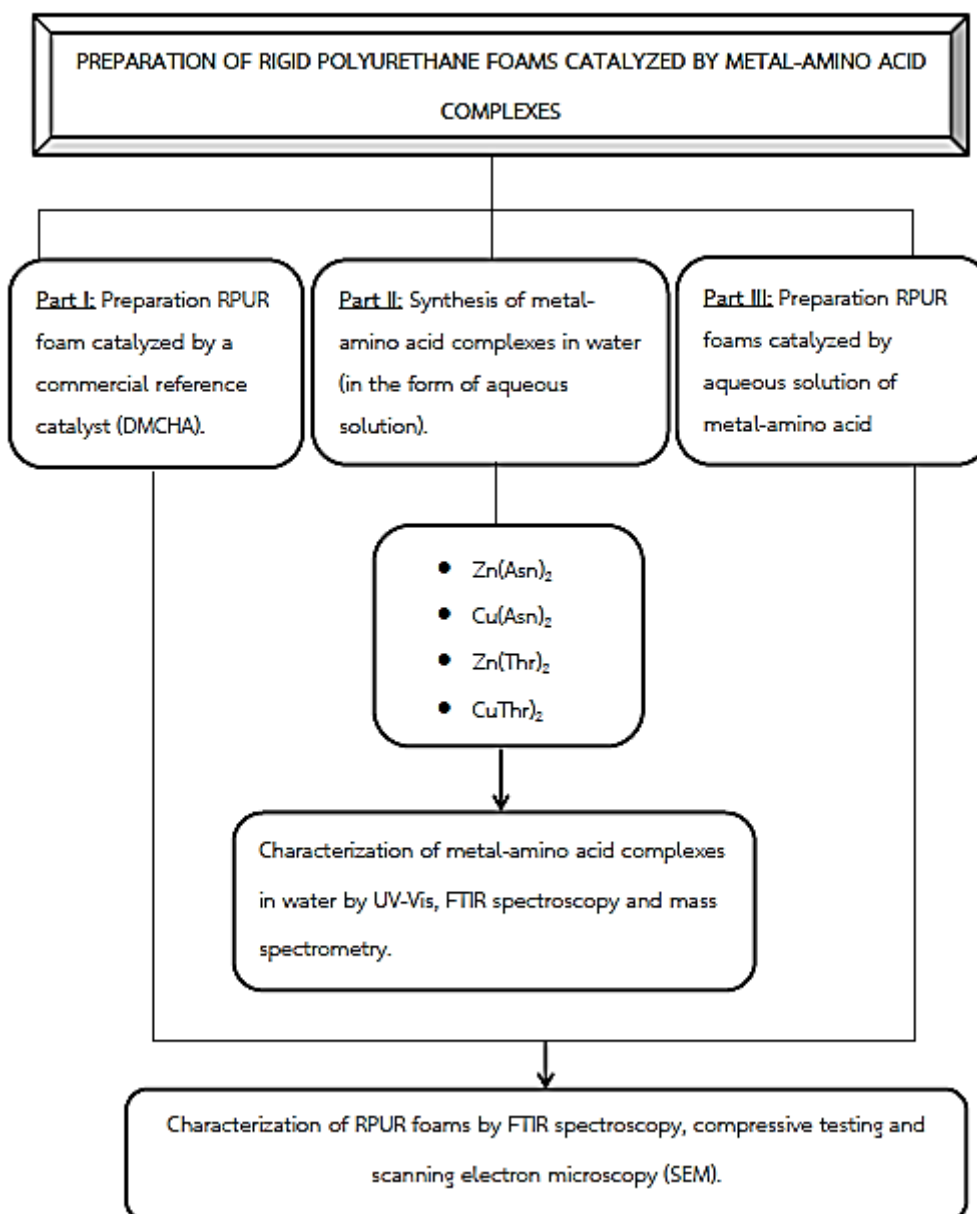
Figure 1.1 Scope of experiments

CHAPTER II

THEORY AND LITERATURE REVIEWS

The polymerization of polyurethane foams was obtained from polyol molecules containing di- or polyhydroxyl groups and isocyanate molecules with di- or polymeric isocyanate groups. Moreover, other components such as surfactants, blowing agents, catalysts and other additives were employed. Polyurethane foams can be divided to flexible polyurethane foams and rigid polyurethane foams (RPUR foams). RPUR foams are mainly used as thermal insulator in the building and refrigerator due to their good mechanical properties and low thermal conductivity[14].

2.1 Raw materials

The main raw materials used to prepare polyurethane foam are isocyanate and polyol, which undergo polymerization reaction to give the urethane linkage. Moreover, surfactants, blowing agents, catalysts and other additives were employed to modify the reaction process and the properties of rigid polyurethane foams. The physical and chemical characteristics of these compounds have influence the polymerization reaction and properties of RPUR foams [4].

2.1.1 Polyols

The polyols used for the preparation of RPUR foams are classified into two groups: (i) polyether polyols and (ii) polyester polyols. Commonly, polyols for RPUR foam have functionality 2.5-8.0, molecular weight of 150-1000 g/mol and hydroxyl value 250-1000 mgKOH/g [15]. The molecular weight and functionality of polyols determine the properties of RPUR foams. 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. This is because RPUR foams need the higher degree of crosslinking which contributes to the stiffness of polymer. Polyether polyols give more resilient foams with better hydrolysis resistance than polyester polyols then the polyester polyols give greater tensile strength and better resistance to oxidation and solvents than polyether polyols.

2.1.1.1 Polyether polyols

Polyether polyols are produced by the ring opening of alkylene oxides using a polyfunctional alcohol as initiator. The polyfunctional initiator compounds are ethylene glycol, glycerol, pentaerythritol, trimethylolpropane, sorbitol and sucrose (Table 2.1). Polyether polyols possess a wide range of functionality, and equivalent weight together with lower viscosity results in easier handling and cost effective production [15]. 90% of RPUR foam is produced from sucrose-based polyether polyols (Figure 2.1).
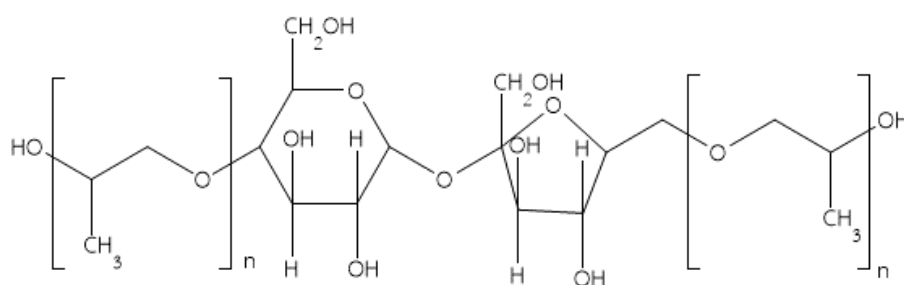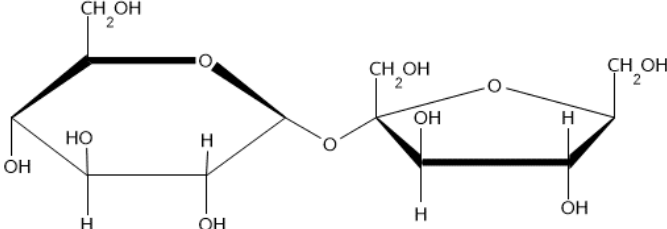
Figure 2.1 Structure of polyether sucrose-based polyol [poly(propyleneoxy sucrose)]

2.1.1.2 Polyester polyols

Polyester polyols are produced by polycondensation of a diacid with excess diols (and triols) such as adipic acid, sebacic acid and phthalic acid. The viscosity of polyester polyols is higher than polyether polyols [4]. Therefore, polyester polyols are usually used in flexible polyurethane foams more than polyether polyols.

Table 2.1 Polyfunctional initiator compounds used for preparing commercial

Hydroxylated compound	Chemical Structure	Functionality
Ethylene glycol (EG)	$HO-CH_2-CH_2-OH$	2
Glycerol		3
Trimethylol propane (TMP)		3
Pentaerythritol		4
Sorbitol		6
Sucrose		8

2.1.2 Diphenylmethane diisocyanate (MDI)

The main isocyanates used for preparation of RPUR foam are diphenylmethane diisocyanate (MDI) and their derivatives, because they have high reactivity in foaming reaction. MDI is obtained from the reaction of aniline and formaldehyde [16]. The types of MDI are divided into two types: polymeric MDI (PMDI) and purified monomeric MDI (pure MDI). Polymeric MDI contains 55% of 4,4'-diisocyanate and 2,4'-diisocyanate, 20-25% of triisocyanate and small quantities of the 2,2′-diisocyanate. Pure MDI is mainly used for elastomers and coatings [17]. The chemical structures of MDI isomer and polymeric MDI are shown in Figures 2.2-2.3.
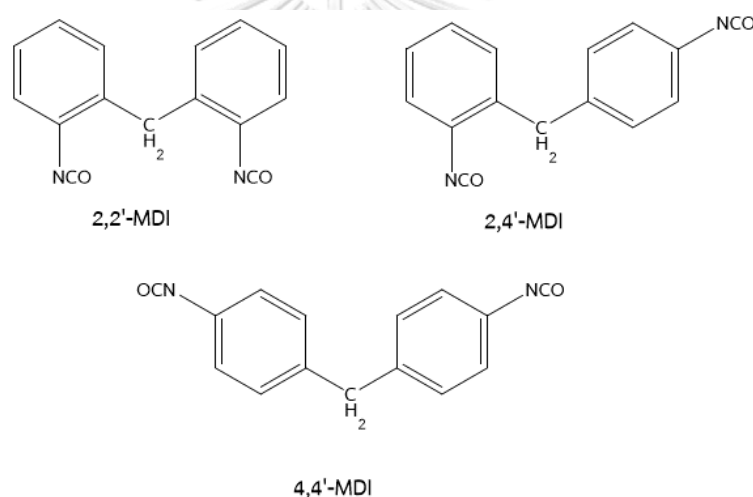
Figure 2.2 Isomeric structures of monomeric MDI
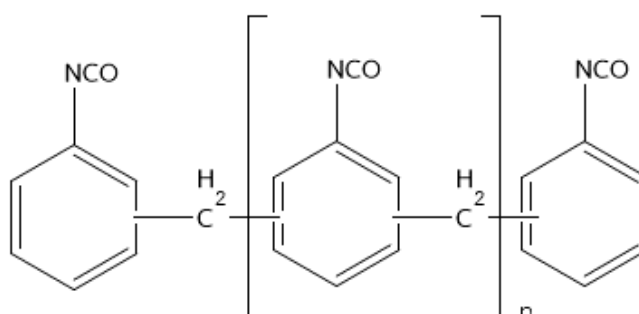
Figure 2.3 Structures of polymeric MDI (PMDI)

2.1.3 Surfactants

The surfactants most widely used in the polyurethane manufacturing are polydimethyl siloxane-polyether copolymer or silicone surfactants (Figure 2.4). Surfactants or surface-active materials are essential additive used in the PUR foam preparation. Surfactants assist in mixing incompatible components of the foam formation, controlling cell size of the foam cells by stabilizing the gas bubbles in the foaming process and reducing surface tension [18]. The silicone surfactants are usually added in the amount of 0.4-2.0% w/w of the polyol formulation [5].
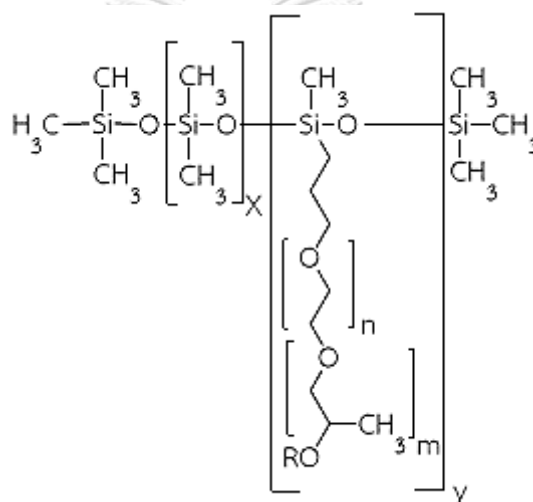
Figure 2.4 Structure of silicone surfactant used in the PUR foam preparation

2.1.4 Blowing agents

Types and contents of blowing agents considerably influence the properties of RPUR foams. Blowing agent was 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. The reaction between water and isocyanate produces CO_2 gas bubbles and gives a cellular structure via foaming process. The

reaction of water with isocyanates is exothermic reaction. The amount of water used for RPUR foam preparation is 3-5 parts of water per 100 parts of polyol.

Physical blowing agents are inert liquids that have low boiling points, low molecular weight and no reactivity to isocyanate groups. They can be evaporated by the heat of foaming reaction. Examples of Physical blowing agents are hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), chlorofluorocarbons (CFCs) and perfluorinated hydrocarbons (PFCs). They cause depletion of the ozone layer [5, 17].

2.1.5 Catalysts

Catalyst is an important component for RPUR foam preparation. Types and quantity of the catalysts influences the rate of reaction and the properties of RPUR foams. Normally, the amount of catalyst used is about 1-4 parts by weight (pbw) per 100 parts of polyol [19].

For RPUR foam preparation, a catalyst controls the reaction kinetics of two main types of reaction, which are (I) the blowing reaction of isocyanate with water (H_2O) to form carbon dioxide and polyurea, (II) the gelling reaction of isocyanate with polyol to form polyurethane. The most important catalysts such as tertiary amines, quaternary ammoninum salts, alkali metal carboxylates and organotin compounds as shown in Figure 2.5 and Table 2.2 [5].
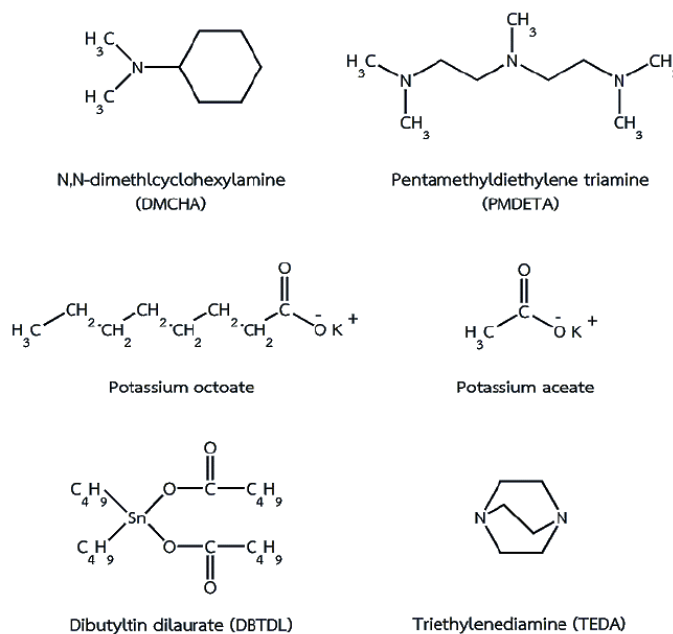
Figure 2.5 Structure of commercial catalysts used in RPUR foam preparation

Table 2.2 Commercial catalysts used for preparing RPUR foams[5]

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

2.2 Catalytic mechanisms

2.2.1 Amine catalysts

Tertiary amine catalysts have most widely used for polyurethane foam preparation. Two mechanisms have been proposed for tertiary amine catalysis [2].

The first mechanism proposed by Baker as shown in Scheme 2.1. The activation starts by the tertiary nitrogen atom of amine using its lone pair of electrons to coordinate with the positive electron charged carbon of the isocyanate group. The intermediate was formed. This intermediate then reacts with the active hydrogen from an alcohol to produce a urethane group.
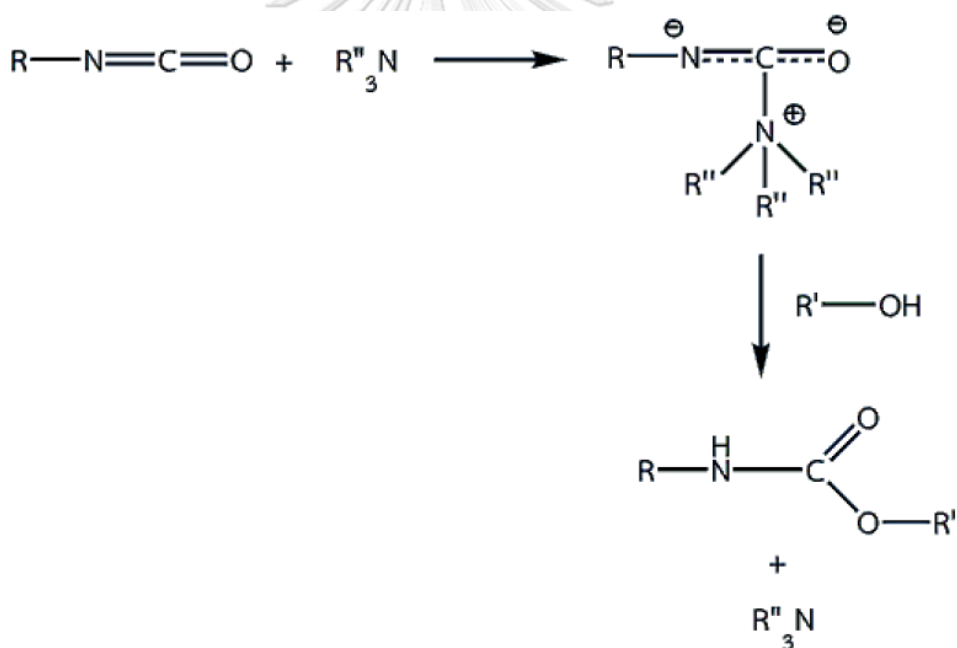
Scheme 2.1 Baker mechanism of amine catalysts

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

The activity of tertiary amine catalyst increases according to the basicity of the nitrogen atom and decreases according to increasing steric hindrance of amine.

R'—OH + R"$_3$N $\longrightarrow$ R"$_3$N$\cdots$H$\cdots$O—R' + R—N=C=O

R—N$\overset{\delta^{\ominus}}{=\!=\!=}C\overset{\delta^{\ominus}}{=\!=\!=}$O

R"$_3$N$\overset{}{\underset{\delta^{\oplus}}{\cdots\cdots}}H\cdots$O$\underset{\delta^{\oplus}}{}$—R'

R"$_3$N + R—N(H)—C(=O)—O—R'
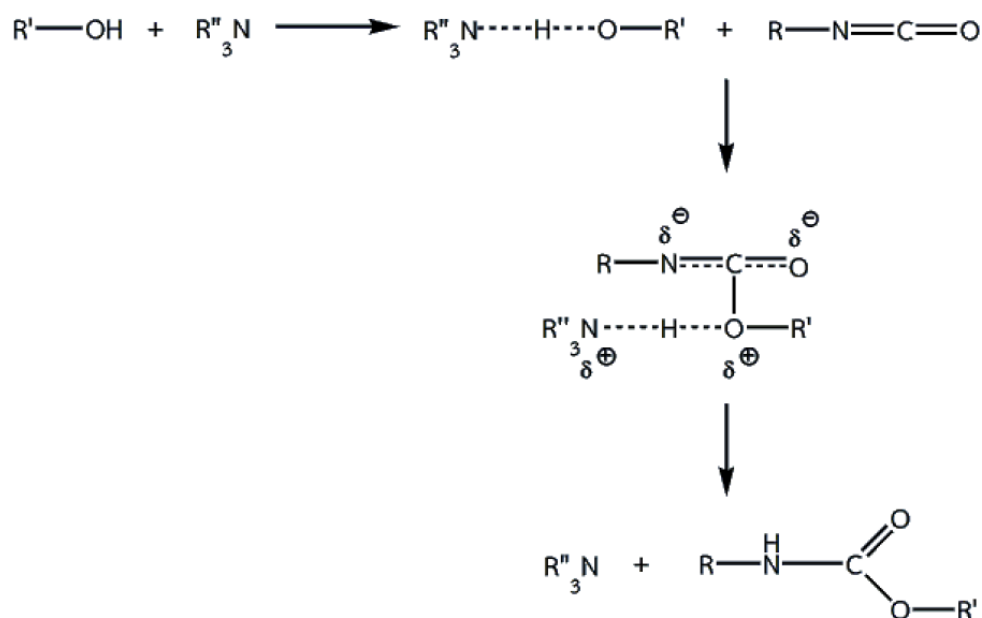
Scheme 2.2 Farka mechanism of amine catalysts

2.2.2 Organotin catalysts

The catalytic mechanism of tin (II) salt is shown in Scheme 2.3. The activation starts by organotin catalyst to coordinate with oxygen atom of isocyanate and polyol, which then gives the urethane product. The functions of organotin catalysts are to increase the positive electron to give the carbon atom of isocyanate and to cause the coordination between isocyanate and polyol.
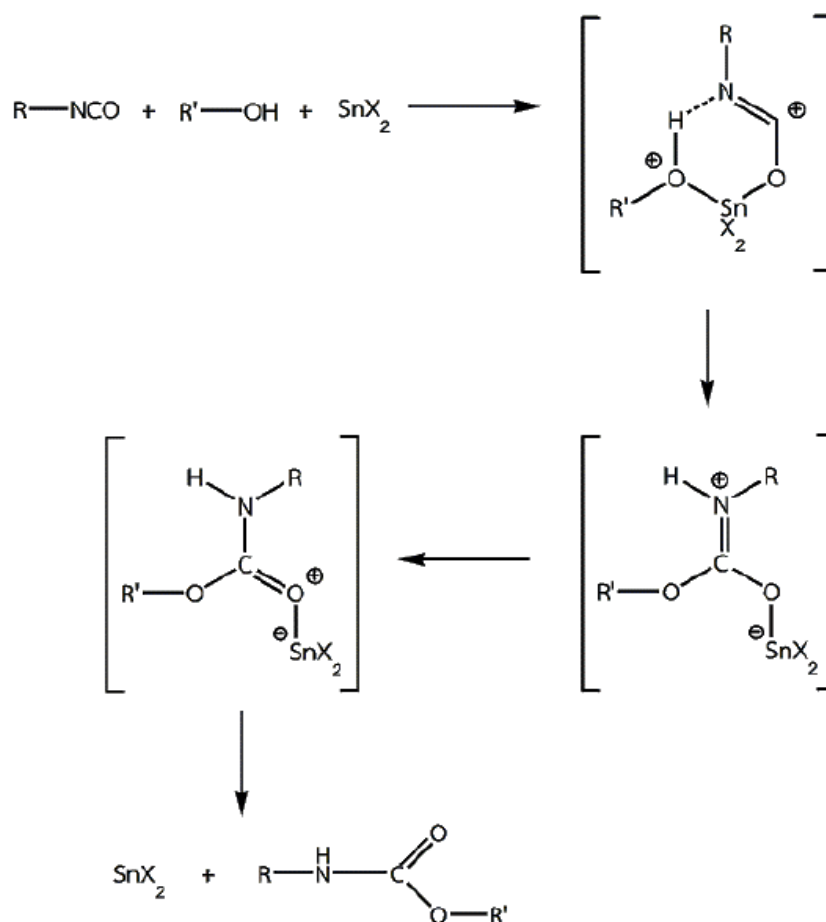
Scheme 2.3 Mechanism for tin (II) salts

2.3 Basic chemistry of urethane

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

2.3.1 Primary reactions of isocyanates

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

2.3.1.1 Reaction of isocyanate with polyol

The reaction between isocyanate and hydroxyl group in the preparation of polyurethane is called the "gelling reaction", which is the important reaction. It must be temperature controlled because it is an exothermic reaction. The chemical structure of the isocyanate and polyols affects the rate of polymerization. The catalyst is used to accelerate the reaction rate.

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

R—NCO   +   R'—OH   ⟶   urethane
isocyanate   hydroxyl
                   (polyol)
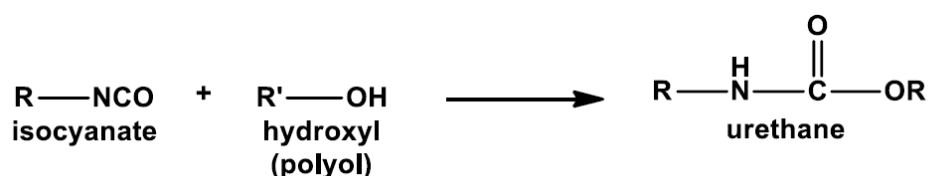
2.3.1.2 Reaction of isocyanate with water

The reaction between isocyanate and water produces unstable carbamic acid initially, which immediately decomposes to give amine and carbon dioxide. The carbon dioxide gas expands into the already present air bubbles. Therefore, this results in a rise of foam due to the increase in the bubble size. This reaction is called the "blowing reaction" because the CO_2 produced is used for rising the foam. The reaction rate is accelerated by a suitable choice of catalyst [15].

$$R\text{—}NCO \;+\; H_2O \;\longrightarrow\; \left[R\text{—}\underset{H}{N}\text{—}\overset{O}{C}\text{—}OH \right]$$

isocyanate   water   carbamic acid

$$\downarrow$$

$$R\text{—}NH_2 \;+\; CO_2$$

amine   carbon dioxide

2.3.2 Secondary reaction of isocyanate

2.3.2.1 Trimerization of isocyanates

Isocyanates can undergo secondary reaction under suitable conditions. For example, isocyanate trimer can only be formed on heating. The reaction of isocyanate trimer is accelerated by basic catalysts such as sodium and potassium salts of carboxylic acids [1].

$$3 \,(\text{"}R\text{—}NCO) \xrightarrow{\text{trimerization}}$$

isocyanate

isocyanurate

2.3.2.2 Reaction of isocyanate with amine

The reaction between isocyanate and amine produces the urea linkange. The reaction of isocyanate with primary amines occur approximately 100-

1000 times faster than that with primary alcohol. Hence, amines are used as chain-extenders and curing agents in polyurethane manufacture.

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

isocyanate   amine   Substituted urea
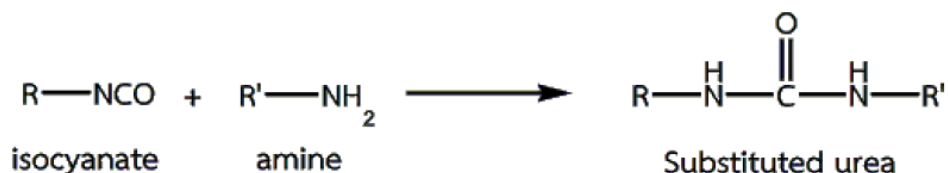
2.4 Formulations

The content of isocyanate needed to react with polyol and other reactive components in PUR formulation can be calculated to obtain chemically stoichiometric equivalents. This theoretical amount is known as the "isocyanate index". This Isocyanate index may be adjusted depending on the PUR system, properties required, ambient conditions and production scale.

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

The conventional way of calculating the ratio of the components required for PUR manufacture is to calculate the number of parts by weight (pbw) of the isocyanate required to react with 100 parts by weight of polyol and use the balanced amount of additives. Analytical data required for the calculation are the isocyanate value of the isocyanate and hydroxyl value, residual acid value and water content of the polyol and other reactive additives [1, 3].

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

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

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

Hydroxyl value (hydroxyl number; OHV)

The hydroxyl value or hydroxyl number is used as a measurement of concentration of isocyanate-reactive hydroxyl group per unit weight of the polyol and is expressed in mg KOH/g of polyol. The hydroxyl value is also defined as the milligrams of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound or polymer.

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

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

Acid value is also expressed as mg KOH/g of polyol and numerically equal to OHV in isocyanate usage.

Water content is the amount of the water reacting with two –NCO groups. Therefore, the equivalent weight of water is:

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

Isocyanate conversion (α),

The isocyanate conversion can be calculated by ATR-FTIR method, which is defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0:

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

Where:

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

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

2.5 Mechanical properties

Compressive properties are the important mechanical properties for RPUR foams. Compressive properties depend on density, type of foams and type of cell foams including closed cell and open cell structure as shown in Figures 2.6 and 2.7, respectively.

In the case of close cell foam, deformation involves cell wall bending and bucking, gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rapture.
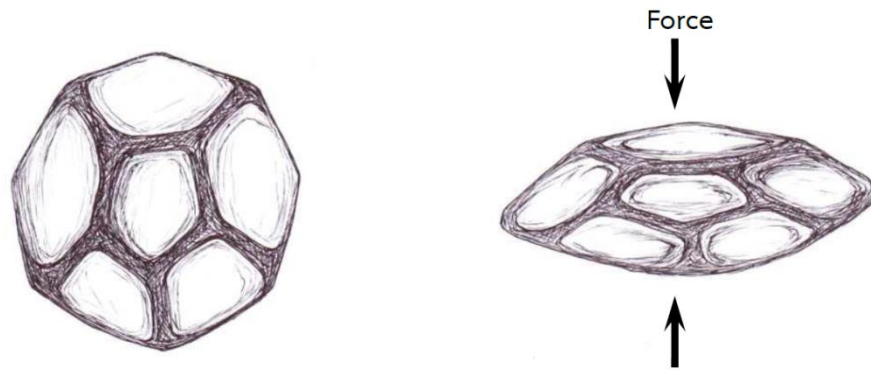
Figure 2.6 The deformation of closed cell foam [1]
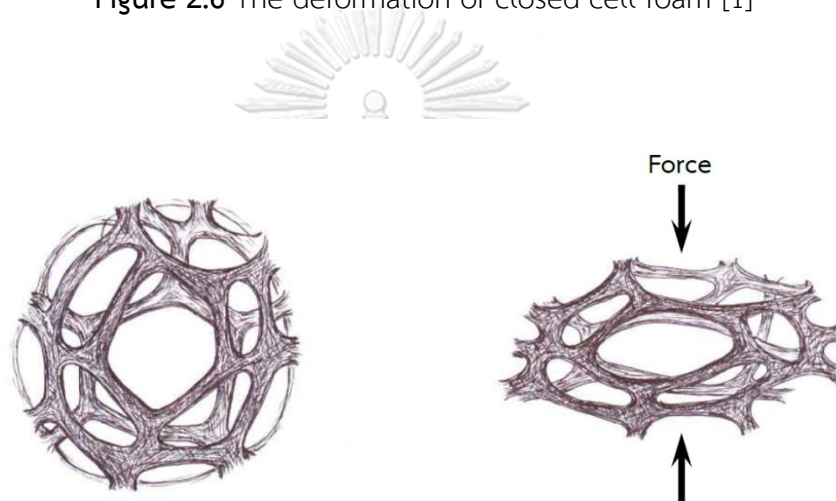
Figure 2.7 The deformation of open cell foam [1]

Closed cell of RPUR foams exhibited from very limited to no yielding behavior. Consequently, gas compression and matrix strength play important roles during the mechanical deformation of RPUR foams. In addition, cell rupture often occurs during the energy absorption process. The energy absorption characteristics of RPUR foam can be represented in terms of compression stress-strain curve. Figure 2.8 shows typical compressive stress-strain curve for RPUR foam.
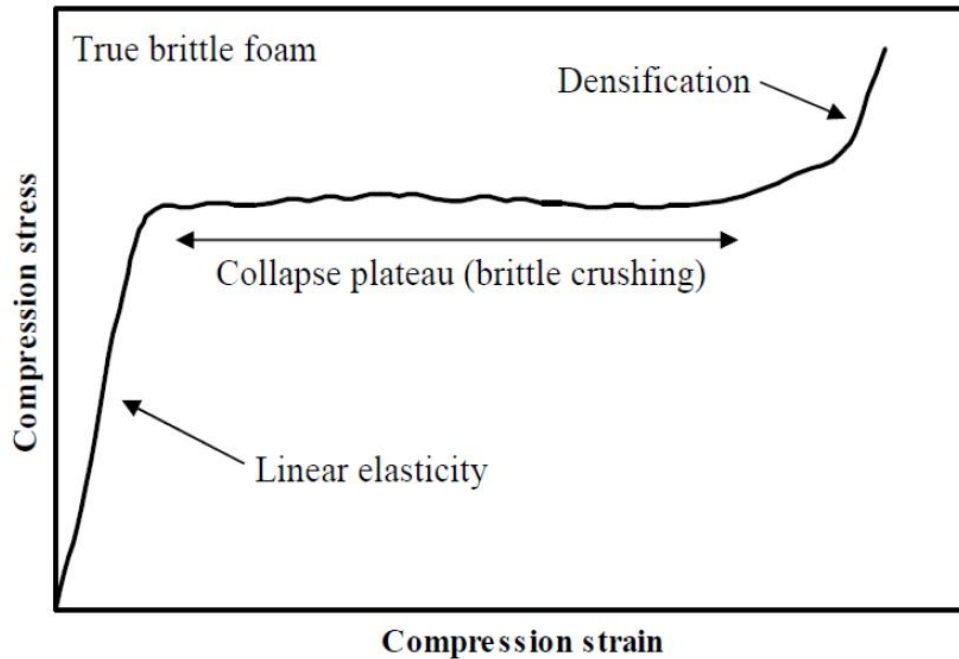
Figure 2.8 Typical compressive stress-strain curve for RPUR foam [1]

For RPUR foams, the compressive stress-strain curve is divided into three parts. (I) Initial linear elasticity is controlled by cell wall bending and by cell wall stretching due to the contained gas pressure. (II) The erratic nature of the collapse plateau corresponds to intermittent rupturing of individual cells. This is due to cell rupture in rigid foams, resilience is dramatically. (III) Densification, which occurs as foam density increase.

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 [20].

2.6 Literature reviews

The polymerization reactions of the RPUR foam are slow and therefore require a catalyst to accelerate the polymerization reactions. The commercial amine catalysts give faster reaction nevertheless it has strong odor in the working environment during the foam preparation. Thus, the development of a new catalyst having a high catalytic activity is necessary.

In 2009, Sardon and coworkers [7] used zirconium acetyl acetonate (Zr(acac)) and dibutyltin diacetate (DBTDA) as catalysts for synthesis of isophorone diisocyanate (IPDI) based waterborne polyurethanes that were synthesized using a two-step procedure as shown in Figure 2.9.
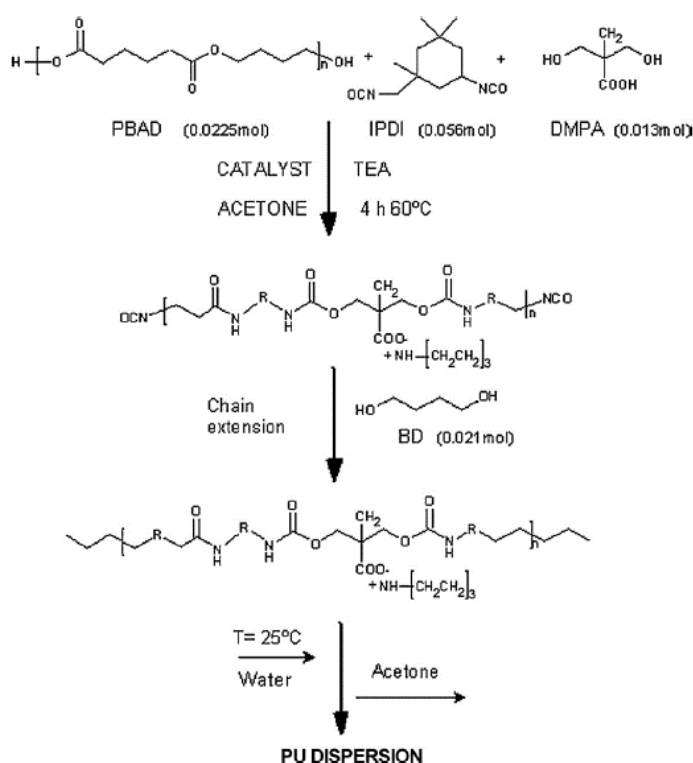
Figure 2.9 Process for obtaining waterborne polyurethanes [7]

*Isophorone diisocyanate (IPDI), trans-1,4-cyclohexylene diisocyanate, 1,3-bis(isocyanate methyl)-cyclohexane, 2,2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butanediol (BD), poly(1,4-butylene adipate) end-capped diol (Mn≈1000) (PBAD), triethylamine (TEA)

Liao and coworkers [22] synthesized neodymium chloride Schiff base complex and ethylene diamine using as catalyst for formation of water-blown semi-rigid polyurethane foam. This catalyst was good catalytic activity but neodymium is rare earth element.

From the previous works in our research group, Pengjam and coworkers [23] synthesized $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ complexes; where en = ethylenediamine and trien = triethylenetetramine. These complexes were used as catalysts for preparation of RPUR foams. It was found that $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ complexes showed comparable catalytic activity with the DMCHA.

Sridaeng and coworkers [8] synthesized metal-amine complexes, namely $Zn(acac)_2(en)$, $Cu(acac)_2(trien)$, $Zn(acac)_2(trien)$, $Cu(NO_3)_2(en)_2$, $Cu(NO_3)_2(trien)$ and $Cu(NO_3)_2(tetraen)$; where acac = acetylacetonate, en = ethylenediamine and trien = triethylenetetramine. These complexes were used in the preparation of RPUR foams. The results found that metal-amine complexes had weak odor than *N,N*-dimethylcyclohexylamine (DMCHA), which was a reference commercial catalyst. $Cu(acac)_2(trien)$ showed the better catalytic activity than other metal-amine complexes, but give the lower density and compressive stress than the RPUR foam prepared by DMCHA.

However, the amines used to synthesize metal-amine complexes in the previous research were toxic. This research is interested in using less toxic amino acid instead of amines. There are several researches that study about the synthesis and applications of metal-amino acid complexes as follows:

Kober and Sugiura [23] synthesized copper(II) amino acid complexes which were prepared from the reaction between copper(II) chloride and amino acids at low temperature and controlled pH using phenolphthalein as an indicator. The mole ratio of copper(II) : amino acid used was 1:2.

Graddon and Munday [24] prepared and studied the solubility of copper(II) amino acid complexes in water. The mole ratio of copper(II) : amino acid used was 1:2. Amino acids used were glycine, alanine, valine and proline. Copper(II) amino acid

complexes were prepared by addition of amino acids and sodium bicarbonate to aqueous solutions of copper(II) sulphate. These complexes were isolated as solids.

Di and coworkers [25] synthesized metal-amino acid complexes from zinc sulphate and L-amino acid (abbreviated as AA). The AA used were valine (Val), methionine (Met), histidine (His) and threonine (Thr). The mole ratio of $(ZnSO_4)$:(AA) was 1:1. Water and acetone were used as solvents. The complex formation is shown in the following reaction:

$$ZnSO_4 . 7H_2O \text{ (s)} + AA \text{ (s)} = Zn(AA)SO_4 . H_2O \text{ (s)} + 6H_2O \text{ (l)}$$

These complexes were isolated as white crystals, namely $Zn(Val)SO_4 \bullet H_2O$, $Zn(Met)SO_4 \bullet H_2O$, $Zn(His)SO_4 \bullet H_2O$ and $Zn(Thr)SO_4 \bullet H_2O$.

Zhang and coworkers [26] synthesized $[Cu(phen)(L\text{-}Thr)(H_2O)](ClO_4)$ complex; where phen = 1,10-phenanthroline, L-Thr = L-Threonine for investigated DNA nuclease activity of this complex. In the synthesis route, L-threonine and sodium hydroxide in water were mixed before added to aqueous solution of $Cu(NO_3)_2.3H_2O$. 1,10-phenanthroline were added for 3 h. at 60 $^{\circ}$C. Then $NaClO_4.H_2O$ was added at room temperature. Blue crystal of this complex were obtained.

Rumyantsev and coworkers [27] synthesized copper(II) amino acid complexes to study coordination interactions between these complexes with alkyl-substituted 2,2′-dipyrrolylmethene derivatives. The synthesis of copper(II) amino acid complexes were prepared using the same method of Kober and Sugiura [24].

Al-Jeboori and coworkers [28] synthesized metal-amino acid complexes $[M(L \bullet H_2O)_2$; where L = leucine, methionine and M = Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}] and studied their biological activity. The condition of synthesized complexes was in the presence of strong basis (NaOH) to obtain the ionization conditions of the amino acid at pH = 8-10.

Qadir and coworkers [9] synthesized of metal-amino acid complexes [M = Cu(II), Mg(II), Ca(II), Fe(II), Co(II) and Zn(II)]. The amino acids used were DL-alanine, L-glutamic acid and leucine. The mole ratio of metal:amino acid was 1:2 (Figure 2.10). The synthesis of metal-amino acid complexes of DL-Alanine and L-Glutamic used water as a solvent, while synthesis of metal-leucine complex used dimethyl sulfoxide (DMSO) as a solvent. Most of the amino acid complexes were formed at a pH of 4-6, However calcium and magnesium complexes were formed at a pH of 8-10. These complexes were obtained as white solids and used as nutritional supplements for animals.
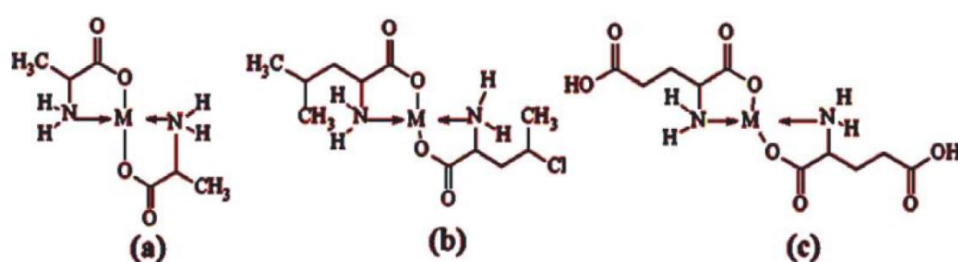
Figure 2.10 Proposed structures of metal (II) complexes [9]

Kidwai and coworkers [10] synthesized 1,4- disubstituted triazoles using bis[(L)prolinate-N,O]Zn complex as a catalyst. The bis[(L)prolinate-N,O]Zn complex synthesized from the reaction of zinc acetate (Zn(OAc)$_2$) with L-proline in methanol (MeOH). Bis[(L)prolinato-N,O]Zn complex was obtained as a white solid.

Darbem and coworkers [11] used bis[prolinate-N,O]Zn or Zn[Pro]$_2$ complex as a catalyst for the thio-Michael reaction (Figure 2.11). They proposed the catalytic mechanism of Zn[Pro]$_2$ complex as shown in Figure 2.12.
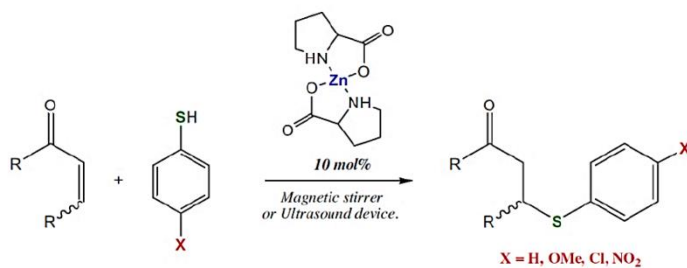
Figure 2.11 Thio-Michael reaction catalyzed by Zn[Pro]$_2$ complex [11]
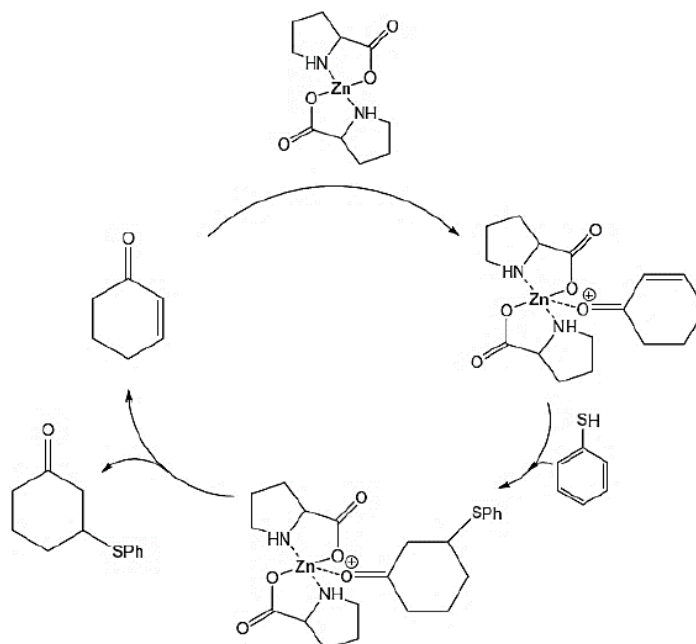
Figure 2.12 Mechanism of thio-Michael reaction catalyzed by Zn[Pro]$_2$ complex [11]

Sahoo and coworkers [29] synthesized Cu(II)/Glycine chelate complex using as catalyzed for the emulsion polymerization of acrylonitrile. They proposed the mechanism as follows:

1. chain initiation:

(a) Cu(II) + glycine $\rightleftharpoons$ complex I

(b) complex I + KHSO$_5$ $\rightleftharpoons$ complex II

(c) complex II + AN $\longrightarrow$ transient complex $\longrightarrow$ AN$^{\bullet}$ (M$^{\bullet}$)

2. Propagation:

$$M^{\bullet} \ + \ M \ \longrightarrow \ M^{\bullet}_2$$

$$M^{\bullet}_{n-1} + M \ \longrightarrow \ M^{\bullet}_n$$

3. termination:

$$M^{\bullet}_n \ + M^{\bullet}_m \ \longrightarrow \quad polymer$$

$$M^{\bullet}_n \ + Cu(II) \ complex \ \longrightarrow \ polymer \ + Cu(I) \ complex + H^+$$
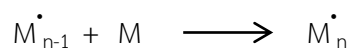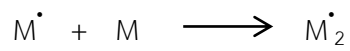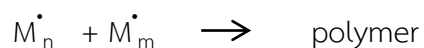
From the previous works in our research group, Keawmang and Nirapun [12, 13] synthesized metal-amino acid complexes for the preparation of RPUR foam as shown in Figures 2.13 and 2.14. The advantage of metal-amino acid complexes is they are odorless. However, the catalytic activity of these complexes was not good. Furthermore, some complex did not have good solubility in water. Therefore, the aim of this research is the synthesis of metal-amino acid complexes with better catalytic activity.
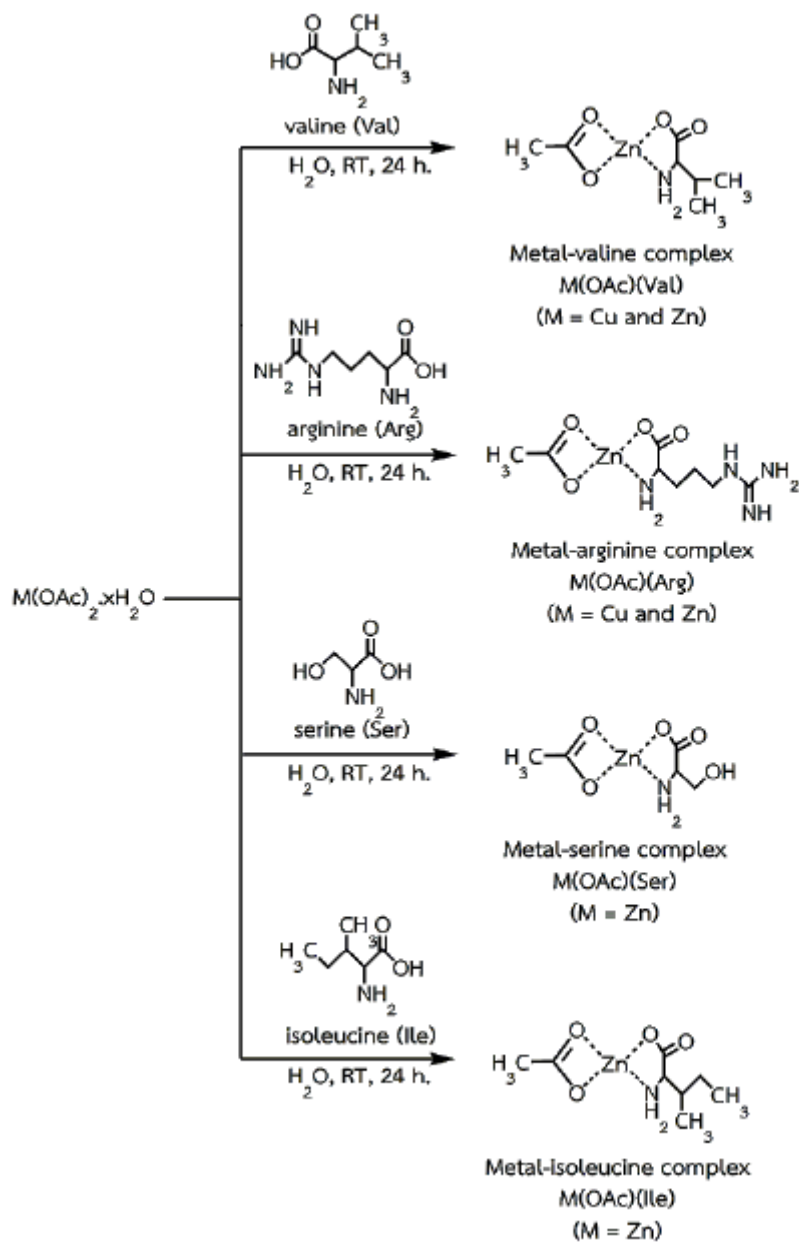
Figure 2.13 Synthesis of copper-amino acid and zinc-amino acid complexes [12]
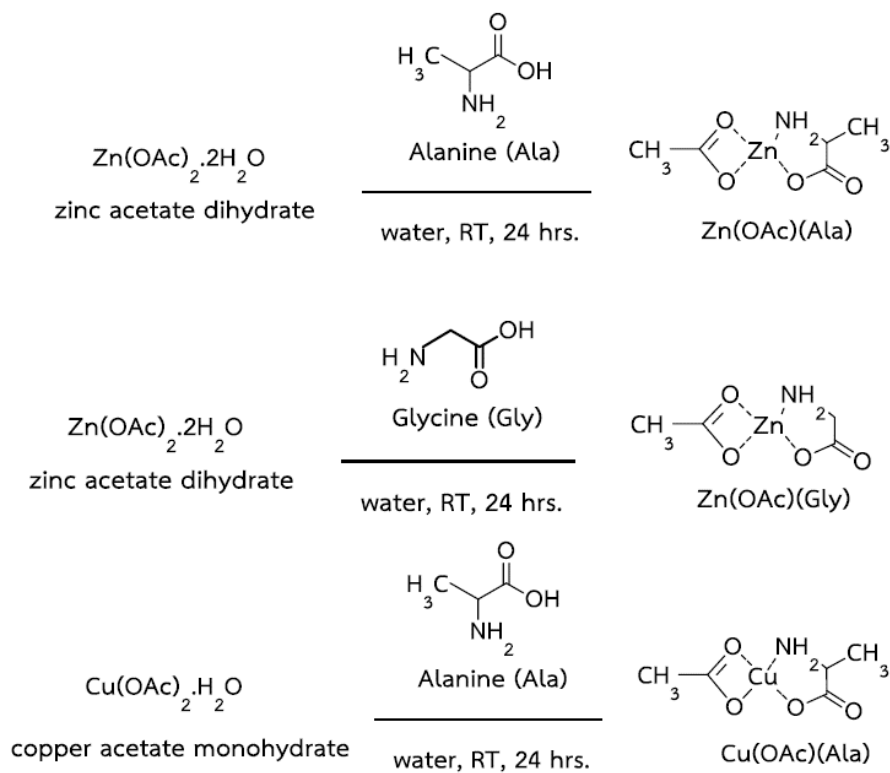
Figure 2.14 Synthesis of metal-amino acid complex aqueous solutions [13]

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and Raw materials

3.1.1 Synthesis of metal-amino acid complexes as aqueous solutions

Copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$] was obtained from Aldrich. Zinc acetate dihydrate [$Zn(OAc)_2.2H_2O$], L-Asparagine.H_2O (Asn) and L-Threonine (Thr) was obtained from Nacalai Tesque.

3.1.2 Preparation of rigid polyurethane foams (RPUR foams)

Polymeric MDI (4,4'- methane diphenyl diisocyanate; PMDI, Raycore[®] B9001, %NCO = 31.0 wt% and average functionality = 2.7), polyether polyol (Polimaxx[®] 4221, sucrose-based polyether polyol, hydroxyl value = 440 mgKOH/g and functionality = 4.3). Polysiloxane surfactant (Tegostab[®] B8460). N,N-dimethylcyclohexylamine (DMCHA, a commercial reference catalyst). They were supplied by IRPC Public Company Limited. Distilled water was used as a blowing agent.

3.2 Synthesis procedures

The metal-amino acid complexes were synthesized from the reaction between metal acetate [$M(OAc)_2$; where M = Zn and Cu] and amino acids (Asparagine and Threonine) using water as solvent (aqueous solution). The synthesis of metal-amino acid complexes was modified from a method reported in the literature [8, 12, 13]. The aqueous solution which contain 20 wt% of metal-amino acid complexes in water can be further used as a catalyst for RPUR foam preparation without

purification. The compositions of starting materials in the synthesis of all metal-amino acid complexes are shown in Table 3.1.

3.2.1 Synthesis of zinc-amino acid complexes as solution in water

3.2.1.1 Synthesis of zinc-asparagine complex [Zn(Asn)$_2$]

The mole ratio of zinc acetate dihydrate to asparagine was 1:1 (Scheme 3.1). The solution of 20 wt% Zn(Asn)$_2$ in water was synthesized by using the following method: a solution of asparagine (0.406 g, 2.75 mmol) in water (4 ml) was stirred at room temperature for 10 minutes. Zinc acetate dihydrate (0.594 g, 2.75 mmol) was added into the asparagine solution and the reaction mixture was stirred at room temperature for 24 hours. Zn(Asn)$_2$ at a concentration of 20 wt% solution in water was obtained as colorless liquid. In the addition, 11 wt% Zn(Asn)$_2$ and 33 wt% Zn(Asn)$_2$ were synthesized by using the same method for 20 wt% Zn(Asn)$_2$.
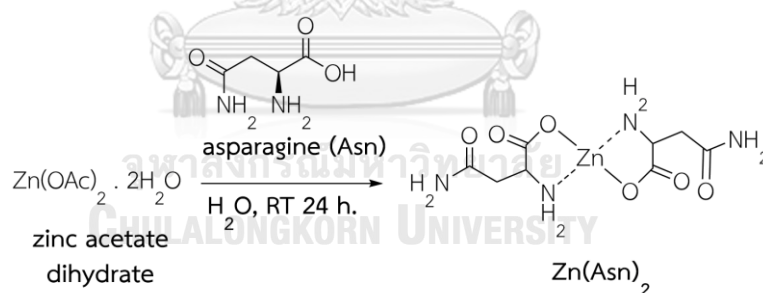
Scheme 3.1 Synthesis of zinc-asparagine complex [Zn(Asn)$_2$]

3.2.1.2 Synthesis of zinc-threonine complex [Zn(Thr)$_2$]

The mole ratio of zinc acetate dihydrate to threonine was 1:1 (Scheme 3.2). The solution of 20 wt% Zn(Thr)$_2$ in water was synthesized by using the following method: a solution of threonine (0.352 g, 2.95 mmol) in water (4 ml) was stirred at room temperature for 10 minutes. Zinc acetate dihydrate (0.648 g, 2.95

mmol) was added into the threonine solution and the reaction mixture was stirred at room temperature for 24 hours. $Zn(Thr)_2$ at a concentration of 20 wt% solution in water was obtained as colorless liquid. In the addition, 11 wt% $Zn(Thr)_2$ and 33 wt% $Zn(Thr)_2$ were synthesized by using the same method for 20 wt% $Zn(Thr)_2$.
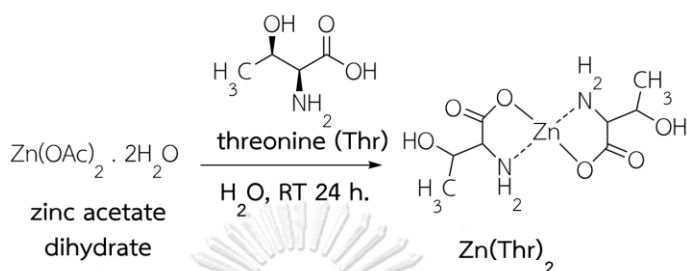
Scheme 3.2 Synthesis of zinc-threonine complex [$Zn(Thr)_2$]

3.2.2 Synthesis of copper-amino acid complexes as solution in water

3.2.2.1 Synthesis of copper-asparagine complex [$Cu(Asn)_2$]

The mole ratio of copper (II) acetate monohydrate to asparagine was 1:1 (Scheme 3.3). The solution of 20 wt% $Cu(Asn)_2$ in water was synthesized by using the following method: a solution of asparagine (0.429 g, 2.85 mmol) in water (4 ml) was stirred at room temperature for 10 minutes. Copper (II) acetate monohydrate (0.571 g, 2.85 mmol) was added into the asparagine solution and the reaction mixture was stirred at room temperature for 24 hours. $Cu(Asn)_2$ at a concentration of 20 wt% solution in water was obtained as thick blue viscous liquid. In the addition, 11 wt% $Cu(Asn)_2$ and 33 wt% $Cu(Asn)_2$ were synthesized by using the same method for 20 wt% $Cu(Asn)_2$.
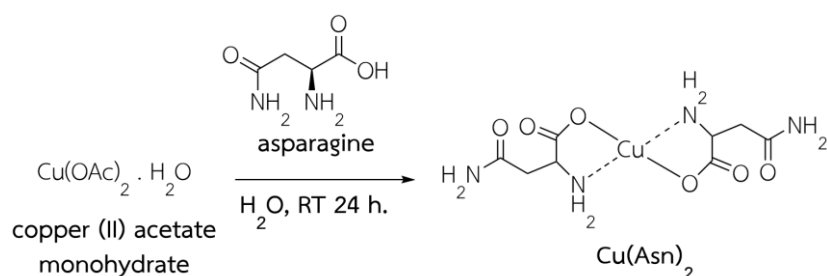
Scheme 3.3 Synthesis of copper-asparagine complex [Cu(Asn)$_2$]

3.2.2.2 Synthesis of copper-threonine complex [Cu(Thr)$_2$]

The mole ratio of copper (II) acetate monohydrate to Threonine was 1:1 (Scheme 3.4). The solution of 20 wt% Cu(Thr)$_2$ in water was synthesized by using the following method: a solution of Threonine (0.374 g, 3.14 mmol) in water (4 ml) was stirred at room temperature for 10 minutes. Copper (II) acetate monohydrate (0.626 g, 3.14 mmol) was added into the Threonine solution and the reaction mixture was stirred at room temperature for 24 hours. Cu(Thr)$_2$ at a concentration of 20 wt% solution in water was obtained as blue liquid. In the addition, 11 wt% Cu(Thr)$_2$ and 33 wt% Cu(Thr)$_2$ were synthesized by using the same method for 20 wt% Cu(Thr)$_2$.
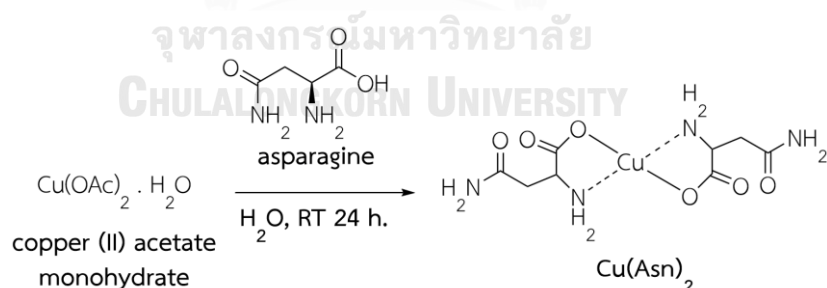
Scheme 3.4 Synthesis of copper- threonine complex [Cu(Thr)$_2$]

Table 3.1 Composition of starting materials in the synthesis of 11 wt% metal-amino acid complexes using water as a solvent

Metal-amino acid complexes	Mole ratio of metal acetate : amino acid	Metal acetate (g)		Amino acid (g)		Appearance
		$Zn(OAc)_2 \cdot 2H_2O$	$Cu(OAc)_2 \cdot H_2O$	Asparagine (Asn)	Threonine (Thr)	
Amount of H_2O 4 ml. Catalyst content in RPUR foam formulation = 0.5 pbw (11 wt% solution)						
$Zn(Asn)_2$	1:1	0.297	-	0.203	-	Homogeneous colorless liquid
$Zn(Thr)_2$	1:1	0.324	-	-	0.176	Homogeneous colorless liquid
$Cu(Asn)_2$	1:1	-	0.285	0.215	-	thick blue viscous liquid
$Cu(Thr)_2$	1:1	-	0.313	-	0.187	Homogeneous blue liquid

Table 3.2 Composition of starting materials in the synthesis of 20 wt% metal-amino acid complexes using water as a solvent

Metal-amino acid complexes	Mole ratio of metal acetate : amino acid	Metal acetate (g)		Amino acid (g)		Appearance
		$Zn(OAc)_2 \cdot 2H_2O$	$Cu(OAc)_2 \cdot H_2O$	Asparagine (Asn)	Threonine (Thr)	
Amount of H_2O 4 ml. Catalyst content in RPUR foam formulation = 1 pbw (20 wt% solution)						
$Zn(Asn)_2$	1:1	0.594	-	0.406	-	Homogeneous colorless liquid
$Zn(Thr)_2$	1:1	0.648	-	-	0.352	Homogeneous colorless liquid
$Cu(Asn)_2$	1:1	-	0.571	0.429	-	thick blue viscous liquid
$Cu(Thr)_2$	1:1	-	0.626	-	0.374	Homogeneous blue liquid

Table 3.3 Composition of starting materials in the synthesis of 33 wt% metal-amino acid complexes using water as a solvent

Metal-amino acid complexes	Mole ratio of metal acetate : amino acid	Metal acetate (g)		Amino acid (g)		Appearance
		$Zn(OAc)_2 \cdot 2H_2O$	$Cu(OAc)_2 \cdot H_2O$	Asparagine (Asn)	Threonine (Thr)	
Amount of H_2O 4 ml. Catalyst content in RPUR foam formulation = 2 pbw (33 wt% solution)						
$Zn(Asn)_2$	1:1	1.188	-	0.812	-	colorless liquid with white precipitate
$Zn(Thr)_2$	1:1	1.296	-	-	0.704	Homogeneous colorless liquid
$Cu(Asn)_2$	1:1	-	1.142	0.858	-	thick blue viscous liquid
$Cu(Thr)_2$	1:1	-	1.253	-	0.747	Homogeneous dark blue liquid

3.3 Preparation of rigid polyurethane (RPUR) foam

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 time, height of foam, density, rise profile, temperature profile and NCO conversion. FTIR spectroscopy was used to characterize RPUR foams. The reaction times of foam preparation were investigated ,namely gel time (which is the time while CO_2 is occurred then foam is rising), cream time (which is the time while polymerization of the reactants occurs), tack free time (which is the time when polymerization is completed) and rise time (which is the time while CO_2 is not generated). Physical and mechanical properties of RPUR foams obtained from molded method were used for the investigation of compression properties and morphology using scanning electron microscopy (SEM).

3.3.1 Rigid polyurethane (RPUR) foam preparation by cup test method

The formulation of RPUR foams preparation at NCO index of 100 is shown in Table 3.2. RPUR foam was prepared via two-step of mixing method as shown in Figure 3.3. In the first step, polyol, surfactant and catalysts (DMCHA or metal-amino acid complexes as aqueous solution) were mixed in a paper cup (700 ml) by hand mixing after that mixing by a mechanical stirrer at 2000 rpm for 20 seconds. In the case of DMCHA as catalyst, water was added before mixing in this step.

In the second step, PMDI was added into the paper cup from the first step, then the mixture was mixed again by the mechanical stirrer at 2000 rpm for 15 seconds then RPUR foam was allowed to rise freely at room temperature. The reaction times of foaming preparation were recorded. After that, the foams were kept for 48 hours at room temperature and then height of foam, density, the rise and temperature profile were measured from RPUR foams prepared by the cut test method. The apparent density was measured according to ASTM D 1622-09. The

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foam samples were sectioned into a cubic shape of 3.0 x 3.0 x 3.0 cm (length x width x thickness) (Figure 3.1).

Table 3.4 RPUR foam formulation at the NCO index of 100 (in parts by weight unit, pbw)

Formulation (NCO index = 100)	DMCHA (pbw)	Metal-amino acid solutions (pbw)
polyether polyol (Polimaxx® 4221)	100	100
Polysiloxane surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (water in the aqueous solution of metal-amino acid complexes acts as a blowing agent)	3.0	4.0
Catalyst	1.0	0.5, 1.0, 2.0
Polymeric diphenyl methane diisocyanate (PMDI, Raycore® B9001)	151.3	166.4
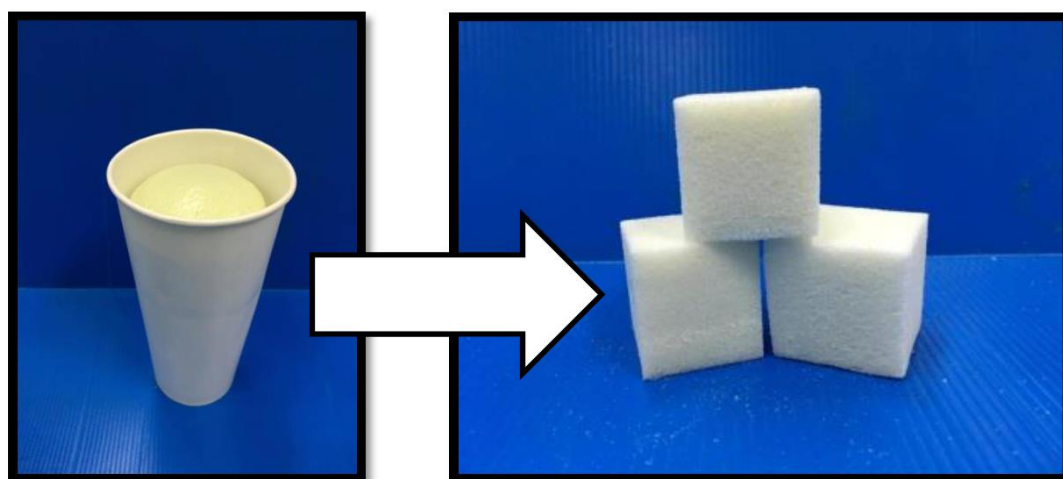
Figure 3.1 Samples for RPUR foam density measurements

3.3.2 Preparation of RPUR foams by plastic molded method

The amounts of all starting materials were increased to 5 times from cup test method and used the same mixing step as cup test method. The starting material were prepared in paper cup after that the mixture was poured into a plastic bag with the dimension of 10 × 10 × 10 cm (Figure 3.2) and allowed to rise freely at room temperature. The foams were kept for 48 hours. Then, the foam density was measured and these foams were used for investigation of the morphology using scanning electron microscopy (SEM) and mechanical properties by compression test.

Figure 3.2 RPUR foams prepared by plastic molded method
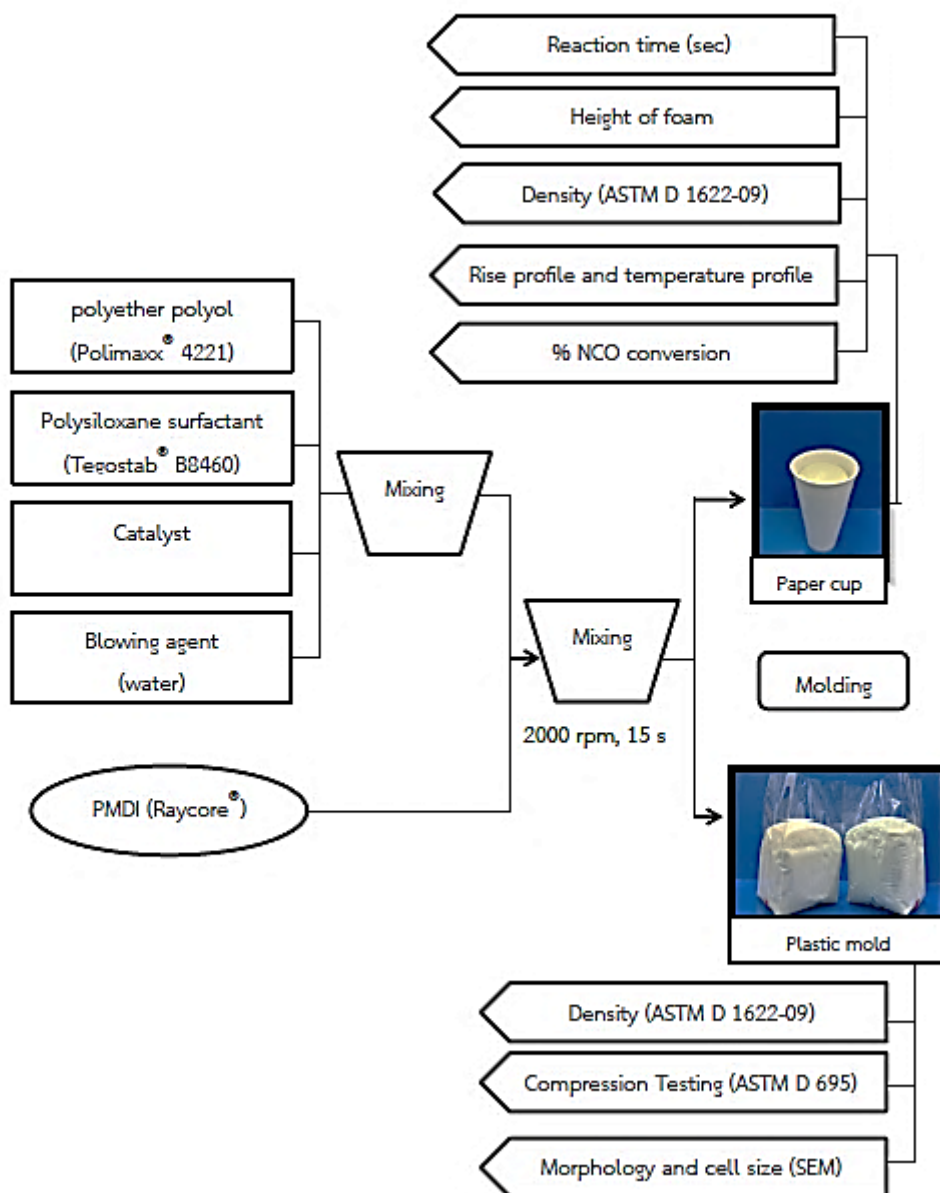
Figure 3.3 Process for preparation of rigid polyurethane foams

3.4 Characterization of metal-amino acid complexes

3.4.1 Ultraviolet-visible spectroscopy

UV-Vis spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer at room temperature. Absorption spectra were obtained and the samples were scan

over range 200-800 nm at a medium speed. Water is a solvent using in this characterization. Molar absorptivity (ε) was calculated using the following equation:

$$\varepsilon = A/bc$$

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

3.4.2 Infrared spectroscopy

The infrared spectroscopy was used to characterize metal-amino acid complexes and RPUR foams including NCO conversion.

Metal-amino acid complexes in aqueous solution were characterized by using Spectrum One PerkinElmer Fourier transform infrared (FTIR) spectrometer in ATR mode at room temperature. The sample was scanned over a range of 800-4000 cm^{-1} at a resolution of 4 cm^{-1} and number of scan 64. The IR bands given in Table 3.3 are used for the analysis. The measurement was controlled by Omnic software.

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Table 3.5 Characteristic IR bands of RPUR foam

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. Positive Ion Electrospray Ionization (Positive ESI) mass spectra were carried out using direct injection sample to Bruker Daltonics microTOF mass spectrometer. High resolution mass spectra were determined on Bruker Daltonics Data Analysis 3.3 with an electrospray ion source using water as a solvent.

3.5 Physical and Mechanical properties of RPUR foams

3.5.1 Reaction time

Digital Stopwatch was used to measure the reaction times namely, cream time, gel time, tack free time and rise time in accordance with ASTM D7487-13 [31].

3.5.2 The height of foam

The height of RPUR foam was measured from the bottom to the top in the direction of foam rising as shown in Figure 3.4.

Figure 3.4 Measurement of RPUR foam height

3.5.3 Density

Free rise density of RPUR foams was measured according to ASTM D 1622-09 [32]. 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.

3.5.4 Foaming temperature

A thermocouple Digicon DP-71 was used to record the foaming temperature of RPUR foams. Temperature data is presented by temperature profile.

3.5.5 Compression testing

The compression 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 [33]. 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.

3.5.6 Scanning electron microscopy (SEM)

The cell size and morphology of RPUR foams were measured on a LEO 1450 VP 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 10 kV

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of metal-amino acid complex aqueous solutions

Aqueous solutions of metal-amino acid complexes were synthesized from the reaction between metal acetate and amino acids using water as a solvent (Scheme 4.1). The metal acetates employed were zinc acetate dihydrate [$Zn(OAc)_2.2H_2O$] and copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$]. The amino acids employed were asparagine (Asn) and threonine (Thr). All metal-amino acid complex solutions in water (aqueous solution) were obtained as homogeneous solutions. They were easily prepared, odorless and had good solubility in starting material of RPUR foam formation. Therefore, they could be used as catalysts for RPUR foam preparation without purification.
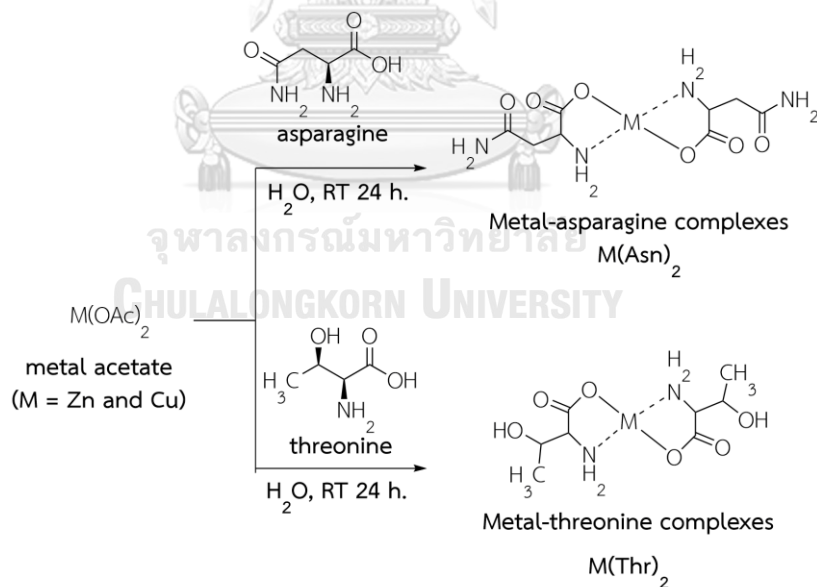
Scheme 4.1 Synthesis of zinc-amino acid and copper-amino acid complexes

4.1.1 Synthesis of zinc-amino acid complex aqueous solutions

Zinc-amino acid complexes were prepared from reaction between zinc acetate dihydrate with amino acids, namely asparagine (Asn) and threonine (Thr) using water as a solvent. Zinc-amino acid complexes were prepared as 11 wt% solution, 20 wt% solution and 33 wt% solution in water. The mole ratio of zinc acetate to amino acid employed was 1:1. The solutions of $Zn(Asn)_2$ and $Zn(Thr)_2$ were obtained as homogeneous colorless liquid as shown in Figures 4.1(a) and Figure 4.1(c), respectively.

4.1.2 Synthesis of copper-amino acid complex aqueous solutions

Copper-amino acid complexes were prepared from reaction between copper (II) acetate monohydrate with amino acids, namely asparagine (Asn) and threonine (Thr) using water as a solvent. Copper-amino acid complexes were prepared as 11 wt% solution, 20 wt% solution and 33 wt% solution in water. The mole ratios of copper (II) acetate to amino acid = 1:1 gave two copper-amino acid complexes, namely $Cu(Asn)_2$ and $Cu(Thr)_2$. The solutions of $Cu(Asn)_2$ and $Cu(Thr)_2$ were obtained as blue viscous liquid with precipitates and homogeneous blue liquid as shown in Figures 4.1(b) and 4.1(d), respectively.
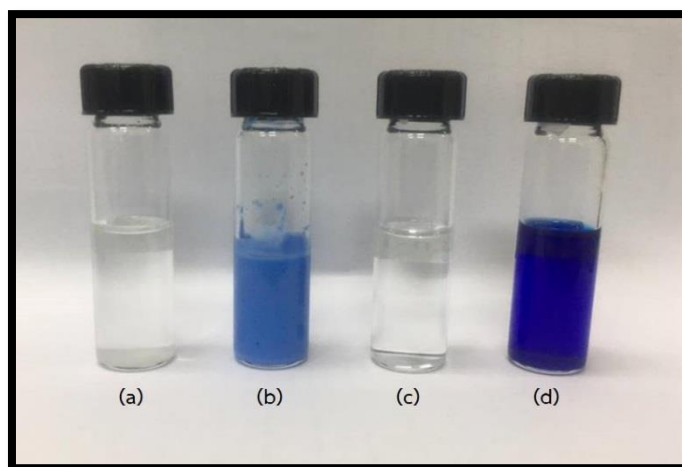
Figure 4.1 Metal-amino acid complexes 20 wt% in water (a) $Zn(Asn)_2$, (b) $Cu(Asn)_2$, (c) $Zn(Thr)_2$ and (d) $Cu(Thr)_2$

4.2 Characterization of zinc-amino acid complex aqueous solutions

4.2.1 IR spectroscopy of zinc-amino acid complex aqueous solutions

4.2.1.1 IR spectroscopy of zinc-asparagine complex [$Zn(Asn)_2$] aqueous solution

IR spectra of two starting materials used in the synthesis of $Zn(Asn)_2$ 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 asparagine [Figure 4.2(b)] exhibits absorption band at 3165 cm^{-1} (N-H stretching vibration), 1678 cm^{-1} (C=O asymmetric stretching), 1426 cm^{-1} (C=O symmetric stretching) and 1105 cm^{-1} (C-O stretching).

IR spectrum of $Zn(Asn)_2$ in aqueous solution was obtained as shown in Figure 4.2(c). $Zn(Asn)_2$ exhibited absorption band at 3269 cm^{-1} (N-H stretching and hydroxyl groups in water), at 1634 cm^{-1} (C=O asymmetric stretching) and 1416 cm^{-1} (C=O symmetric stretching). The asymmetric and symmetric C=O stretching peaks of

Zn(Asn)$_2$ in water shifted from those of Zn(OAc)$_2$, which indicated that the metal-amino acid complexes were formed.

Figure 4.2 IR spactra of (a) Zn(OAc)$_2$, (b) asparagine and (c) Zn(Asn)$_2$ aqueous solutions

4.2.1.2 IR spectroscopy of zinc-threonine complex [Zn(Thr)$_2$] aqueous solution

IR spectra of two starting materials used in the synthesis of Zn(Thr)$_2$ are described as follows: IR spectrum of Zn(OAc)$_2$ [Figure 4.3(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 threonine [Figure 4.3(b)] exhibits absorption band at 3024 cm^{-1} (N-H stretching vibration), 1620 cm^{-1} (C=O asymmetric stretching), 1414 cm^{-1} (C=O symmetric stretching) and 1105 cm^{-1} (C-O stretching).

IR spectrum of Zn(Thr)$_2$ in aqueous solution was obtained as shown in Figure 4.3(c). Zn(Thr)$_2$ exhibited absorption band at 3256 cm^{-1} (N-H stretching and hydroxyl groups in water), at 1633 cm^{-1} (C=O asymmetric stretching) and 1411 cm^{-1} (C=O symmetric stretching). The asymmetric and symmetric C=O stretching peaks of Zn(Thr)$_2$ in water shifted from those of Zn(OAc)$_2$, which indicated that the metal-amino acid complexes were formed.

Figure 4.3 IR spactra of (a) Zn(OAc)$_2$, (b) threonine and (c) Zn(Thr)$_2$ aqueous solutions

4.2.2 Positive ESI mass spectrometry of zinc-amino acid complex aqueous solutions

4.2.2.1 ESI mass spectrometry of zinc-asparagine complex [Zn(Asn)$_2$] aqueous solution

Mass spectrum of Zn(Asn)$_2$ is shown in Figure 4.4. The data of molecular ion peaks corresponding and m/z ratio are described in Table 4.1. The molecular ion peaks of Zn(Asn)$_2$ appeared at the m/z 384.9122 [Zn(Asn)$_2$+2H$_2$O+Na]$^+$, m/z 367.9313 [Zn(Asn)$_2$+H$_2$O+Na]$^+$, m/z 326.9029 [Zn(Asn)$_2$+H]$^+$. The unreacted Zn(OAc)$_2$ appeared at m/z 182.9653 [Zn(OAc)$_2$+H]$^+$.
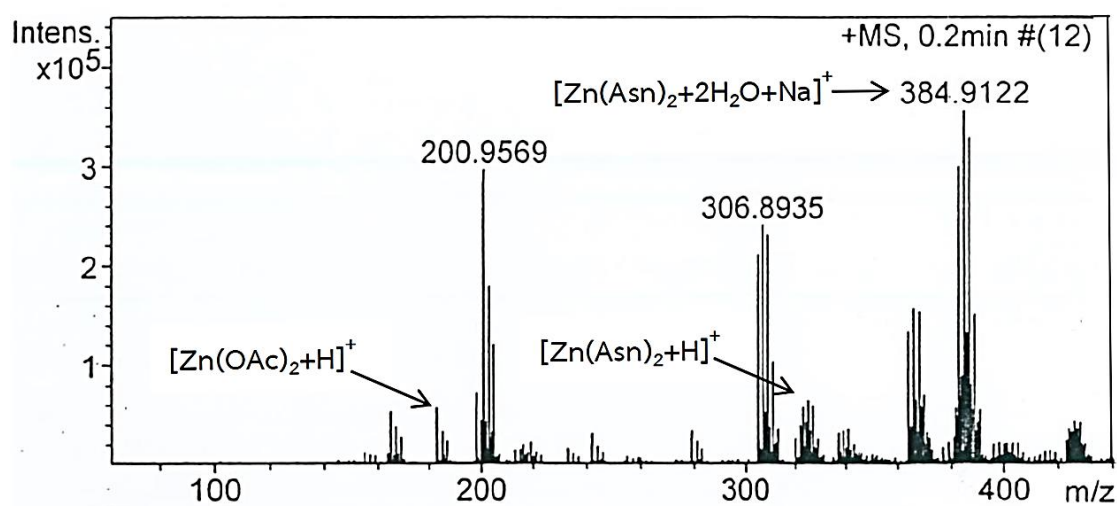
Figure 4.4 Positive ESI mass spectrum of Zn(Asn)$_2$ aqueous solution

4.2.2.2 ESI mass spectrometry of zinc-threonine complex [Zn(Thr)$_2$] aqueous solution

Mass spectrum of Zn(Thr)$_2$ is shown in Figure 4.5. The data of molecular ion peaks corresponding and m/z ratio are described in Table 4.1. The molecular ion peaks of Zn(Thr)$_2$ appeared at the m/z 365.9338 [Zn(Thr)$_2$+2H$_2$O+Na]$^+$ or [Zn(OAc)$_2$(Thr) +2H$_2$O+Na]$^+$ and m/z 306.8930 [Zn(Thr)$_2$+H]$^+$ or [Zn(OAc)$_2$(Thr)+H]$^+$.
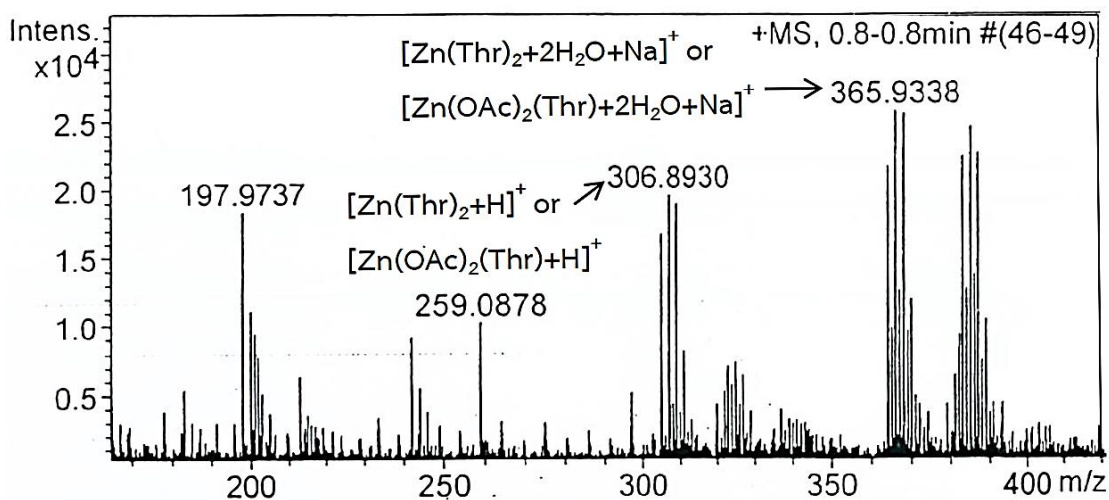
Figure 4.5 Positive ESI mass spectrum of Zn(Thr)$_2$ aqueous solution

From all previous results, the characterization of the zinc-amino acid complexes by IR spectroscopy and positive ESI mass spectrometry confirmed the formation of zinc-amino acid complexes.

Table 4.1 Molecular ion peaks of zinc-amino acid complex aqueous solutions

Molecular ion peak	m/z (Calculated)	m/z (Found)
[Zn(Asn)$_2$+H]$^+$	326.0205	326.9029
[Zn(Asn)$_2$+2H$_2$O+Na]$^+$	385.0314	384.9122
[Zn(Thr)$_2$+H]$^+$ or [Zn(OAc)$_2$(Thr)+H]$^+$	306.6324	306.8930
[Zn(Thr)$_2$+2H$_2$O+Na]$^+$ or [Zn(OAc)$_2$(Thr)+2H$_2$O+Na]$^+$	365.0879	365.9338

4.3 Characterization of copper-amino acid complex aqueous solutions

4.3.1 UV-visible spectroscopy of copper-amino acid complex aqueous solutions

UV-vis spectra of copper-amino acid complexes were obtained from their aqueous solutions as shown in Figure 4.6. Cu(OAc)$_2$ does not dissolve in water,

therefore, UV-vis spectrum of Cu(OAc)$_2$ was obtained from its methanolic solution. The absorption of Cu(Asn)$_2$ and Cu(Thr)$_2$ showed the maximum wavelength (λmax) at 223 and 220 nm, respectively and molar absorptivity (ε) of 2,583 and 2,342, respectively. These λmax shifted from that of Cu(OAc)$_2$, which appeared at 245 nm. These results suggested that the copper-amino acid complexes in water were formed.
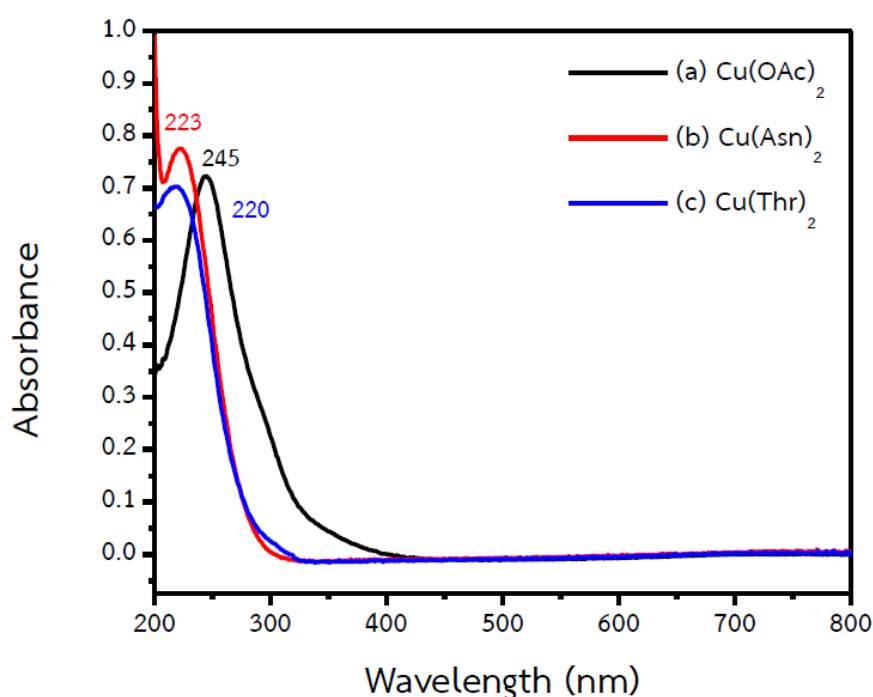
Figure 4.6 UV spectra of (a) Cu(OAc)$_2$, (b) Cu(Asn)$_2$ and (c) Cu(Thr)$_2$

4.3.2 IR spectroscopy of copper-amino acid complex aqueous solutions

4.3.2.1 IR spectroscopy of copper-asparagine complex [Cu(Asn)$_2$] aqueous solution

IR spectra of two starting materials used in the synthesis of Cu(Asn)$_2$ are described as follows: IR spectrum of Cu(OAc)$_2$ [Figure 4.7(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 asparagine [Figure 4.7(b)] exhibits absorption band at 3165 cm^{-1} (N-H stretching vibration), 1678 cm^{-1} (C=O asymmetric stretching), 1426 cm^{-1} (C=O symmetric stretching) and 1105 cm^{-1} (C-O stretching).

IR spectrum of Cu(Asn)$_2$ in aqueous solution was obtained as shown in Figure 4.7(c). Cu(Asn)$_2$ exhibited absorption band at 3325 cm^{-1} (N-H stretching and hydroxyl groups in water), at 1709 cm^{-1} (C=O asymmetric stretching) and 1413 cm^{-1} (C=O symmetric stretching). The asymmetric and symmetric C=O stretching peaks of Cu(Asn)$_2$ in water shifted from those of Cu(OAc)$_2$, which indicated that the metal-amino acid complexes were formed.
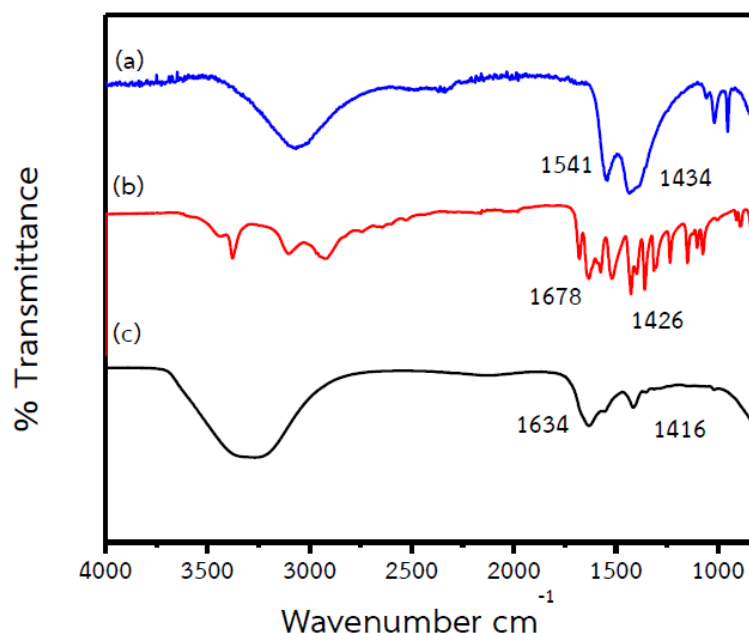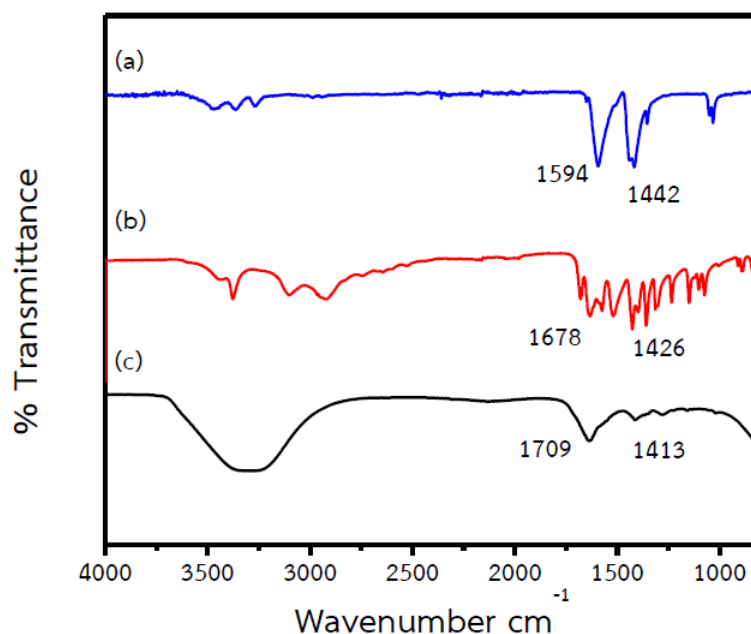

Figure 4.7 IR spactra of (a) Cu(OAc)$_2$, (b) asparagine and (c) Cu(Asn)$_2$ aqueous solutions

4.3.2.2 IR spectroscopy of copper-threonine complex [Cu(Thr)$_2$] aqueous solution

IR spectra of two starting materials used in the synthesis of Cu(Thr)$_2$ 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 threonine [Figure 4.8(b)] exhibits absorption band at 3024 cm^{-1} (N-H stretching vibration), 1620 cm^{-1} (C=O asymmetric stretching), 1414 cm^{-1} (C=O symmetric stretching) and 1105 cm^{-1} (C-O stretching).

IR spectrum of Cu(Thr)$_2$ in aqueous solution was obtained as shown in Figure 4.8(c). Cu(Thr)$_2$ exhibited absorption band at 3289 cm^{-1} (N-H stretching and hydroxyl groups in water), at 1631 cm^{-1} (C=O asymmetric stretching) and 1398 cm^{-1} (C=O symmetric stretching). The asymmetric and symmetric C=O stretching peaks of Cu(Thr)$_2$ in water shifted from those of Cu(OAc)$_2$, which indicated that the metal-amino acid complexes were formed.
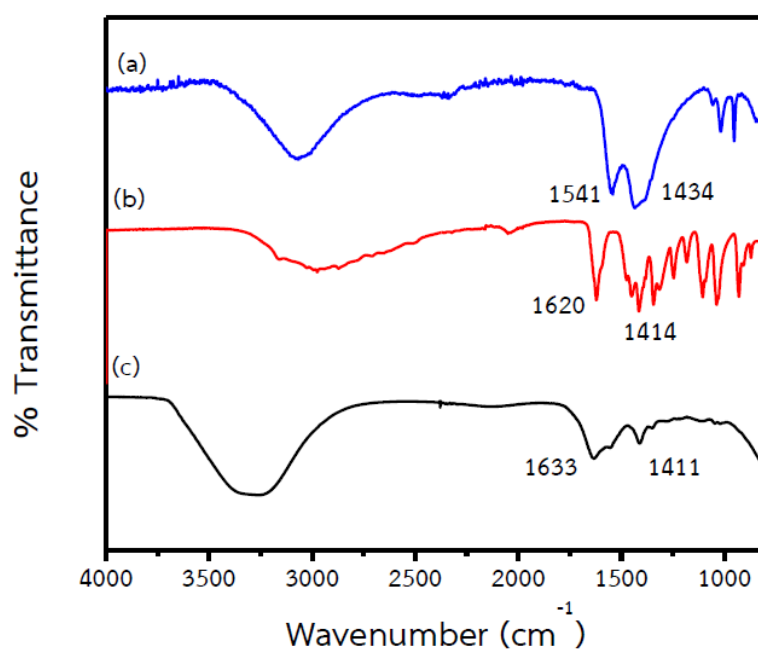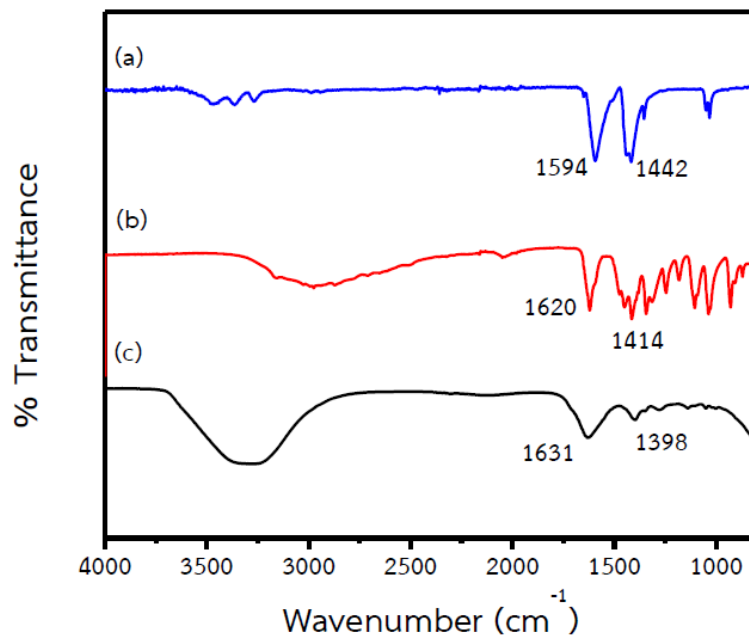
Figure 4.8 IR spactra of (a) Cu(OAc)$_2$, (b) threonine and (c) Cu(Thr)$_2$ aqueous solutions

4.3.3 Positive ESI mass spectrometry of copper-amino acid complex aqueous solutions

4.3.3.1 ESI mass spectrometry of copper-asparagine complex [Cu(Asn)$_2$] aqueous solution

Mass spectrum of Cu(Asn)$_2$ is show in Figure 4.9. The data of molecular ion peaks corresponding and m/z ratio are described in Table 4.2. The molecular ion peaks of Cu(Asn)$_2$ appeared at the m/z 383.8238 [Cu(Asn)$_2$+2H$_2$O+Na]$^+$, m/z 366.9493 [Cu(Asn)$_2$+H$_2$O+Na]$^+$, m/z 334.9240 [Cu(OAc)$_2$(Asn)+Na]$^+$ and m/z 326.8971 [Cu(Asn)$_2$+H]$^+$.
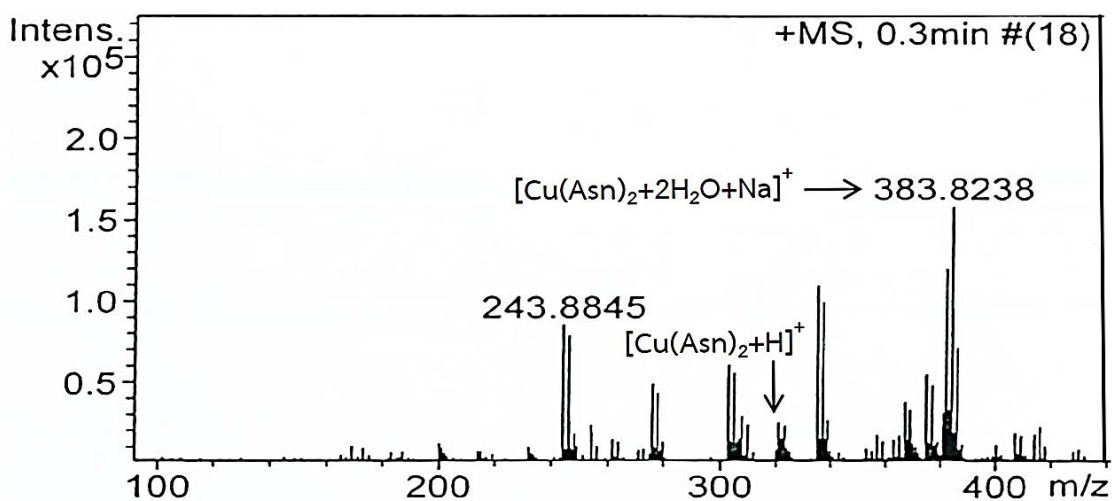
Figure 4.9 Positive ESI mass spectrum of Cu(Asn)$_2$ aqueous solution

4.3.3.2 ESI mass spectrometry of copper-threonine complex [Cu(Thr)$_2$] aqueous solution

Mass spectrum of Cu(Thr)$_2$ is show in Figure 4.10. The data of molecular ion peaks corresponding and m/z ratio are described in Table 4.2. The molecular ion peaks of Cu(Thr)$_2$ appeared at the m/z 361.9390 [Cu(Thr)$_2$+2H$_2$O+Na]$^+$ or [Cu(OAc)$_2$(Thr) +2H$_2$O+Na]$^+$, m/z 302.8983 [Cu(Thr)$_2$+H]$^+$ or [Cu(OAc)$_2$(Thr) +H]$^+$ and m/z 243.8838 [Cu(OAc)(Thr)+H]$^+$.
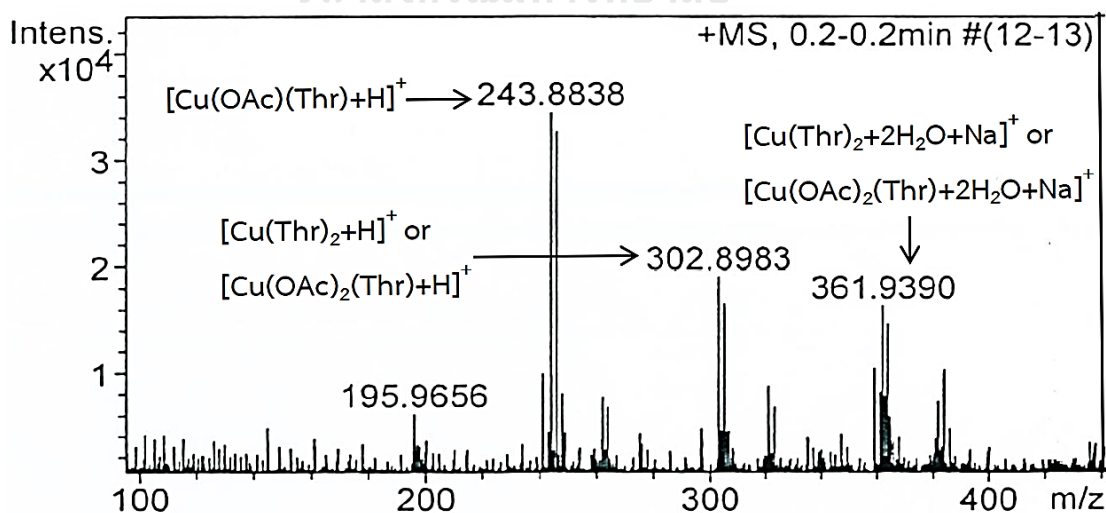
Figure 4.10 Positive ESI mass spectrum of Cu(Thr)$_2$ aqueous solution

Table 4.2 Molecular ion peaks of copper-amino acid complexes

Molecular ion peak	m/z (Calculated)	m/z (Found)
$[Cu(Asn)_2+H]^+$	326.7660	326.8971
$[Cu(Asn)_2+2H_2O+Na]^+$	384.0319	383.8238
$[Cu(OAc)(Thr)+H]^+$	243.0058	243.8838
$[Cu(Thr)_2+H]^+$ or $[Cu(OAc)_2(Thr)+H]^+$	302.7684	302.8983
$[Cu(Thr)_2+2H_2O+Na]^+$ or $[Cu(OAc)_2(Thr)+2H_2O+Na]^+$	361.0429	361.9390

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

4.4 Preparation of rigid polyurethane (RPUR) foams catalyzed by metal-amino acid complex aqueous solutions

4.4.1 Preparation of RPUR foams by cup test

RPUR foams obtained from cup test method (Figure 4.11) were used for the investigation of height of foams, reaction times, density, NCO conversion, rise profiles and temperature profiles. All properties of RPUR foams catalyzed by metal-amino acid complexes were compared with those catalyzed by DMCHA, which is a commercial catalyst.

Figure 4.11 RPUR foams prepared by using a 700 ml paper cups

4.4.1.1 Reaction time, height and density of RPUR foams

RPUR foams were prepared by using cup test method and using 20 wt% metal-amino acid complexes in water as catalysts (1 pbw) to investigate their reaction times and physical properties as shown in Table 4.3.

Table 4.3 Reaction time, height and density of RPUR foams prepared at the NCO index of 100 catalyzed by DMCHA and metal-amino acid complex aqueous solutions

Catalyst types	Cream time (sec)	Gel time (sec)	Rise time (sec)	Tack free time (sec)	Height (cm)	Density (Kg/m^3)
DMCHA (ref.)	19	33	90	99	14	39.93
Zn(Asn)$_2$	30	212	439	452	14	38.82
Zn(Thr)$_2$	30	132	241	263	14	38.62
Cu(Asn)$_2$	33	103	208	188	13	39.25
Cu(Thr)$_2$	46	107	158	144	14	39.24

The reaction times of RPUR foams catalyzed by metal-amino acid complexes compared with those catalyzed by DMCHA. It was found that the order of catalytic activity of metal-amino acid complexes was in the order DMCHA > Cu(Thr)$_2$ > Cu(Asn)$_2$ > Zn(Thr)$_2$ > Zn(Asn)$_2$. The aqueous solutions of Zn(Thr)$_2$, Cu(Asn)$_2$ and Cu(Thr)$_2$ showed good catalytic activity. Whereas Zn(Asn)$_2$ gives the lowest catalytic activity due to asparagine was less soluble in water and the unreacted Zn(OAc)$_2$ remained in solution (Figure 4.4). RPUR foams catalyzed by Cu(Asn)$_2$ and Cu(Thr)$_2$ gave the similar foam height and foam density to that catalyzed by DMCHA (Figure 4.14). RPUR foams catalyzed by metal-amino acid complexes were stable foams structure that would not collapse as shown in Figure 4.12.

From the reactivity results in Figure 4.13, the preparation of RPUR foams catalyzed by copper-amino acid complexes gave shorter rise time and tack free time than zinc-amino acid complexes, which suggested that the copper-amino acid complexes had better catalytic activity in blowing reaction and gelling reaction than zinc-amino acid complexes. In comparison between copper-asparagine complex and copper-threonine complex, Cu(Thr)$_2$ gave shorter rise time and tack free time than Cu(Asn)$_2$. This indicated that Cu(Thr)$_2$ had the highest catalytic activity.

Copper-amino acid complexes showed better catalytic activity than zinc-amino acid complexes because copper-amino acid complexes are better Lewis acid than zinc-amino acid complexes. Copper atom can have four, five or six coordinations while zinc atom prefers four coordinations. Therefore, copper atom in copper-amino acid complexes can act as better Lewis acid in coordination with isocyanate group in pMDI. This causes isocyanate group to have more positive charge and undergoes faster reaction with hydroxyl group in polyol to give urethane group.
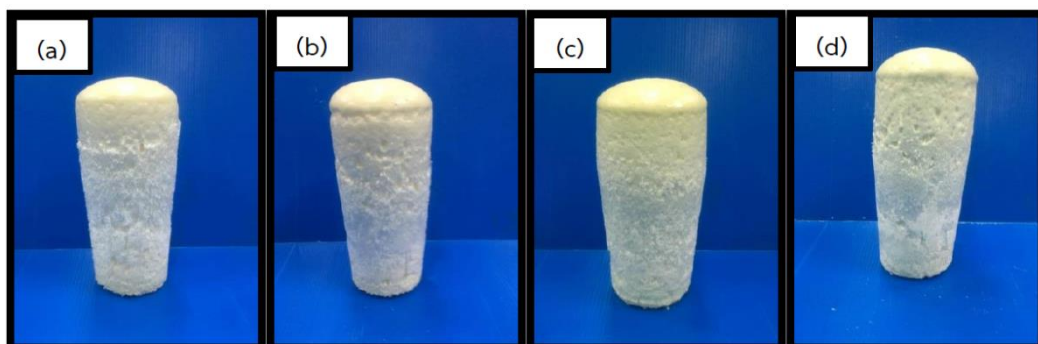
Figure 4.12 Appearances of RPUR foams catalyzed by (a) Zn(Asn)$_2$, (b) Zn(Thr)$_2$, (c) Cu(Asn)$_2$ and (d) Cu(Thr)$_2$
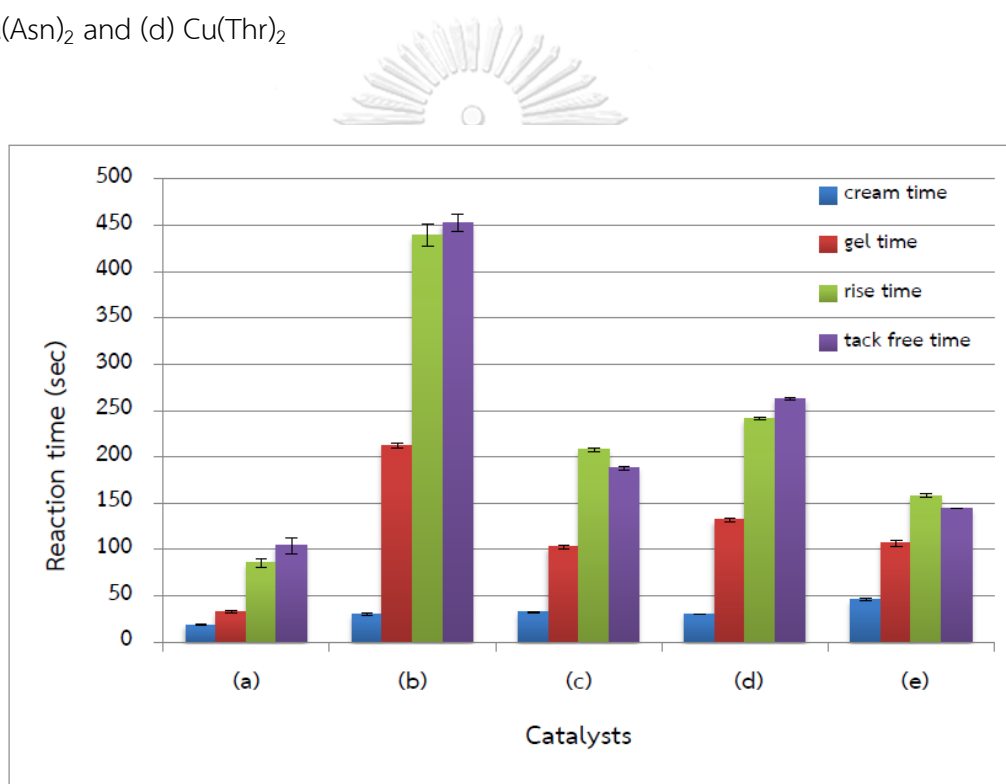
Figure 4.13 Reaction times of RPUR foams catalyzed by (a) DMCHA (b) Zn(Asn)$_2$, (c) Cu(Asn)$_2$, (d) Zn(Thr)$_2$ and (e) Cu(Thr)$_2$
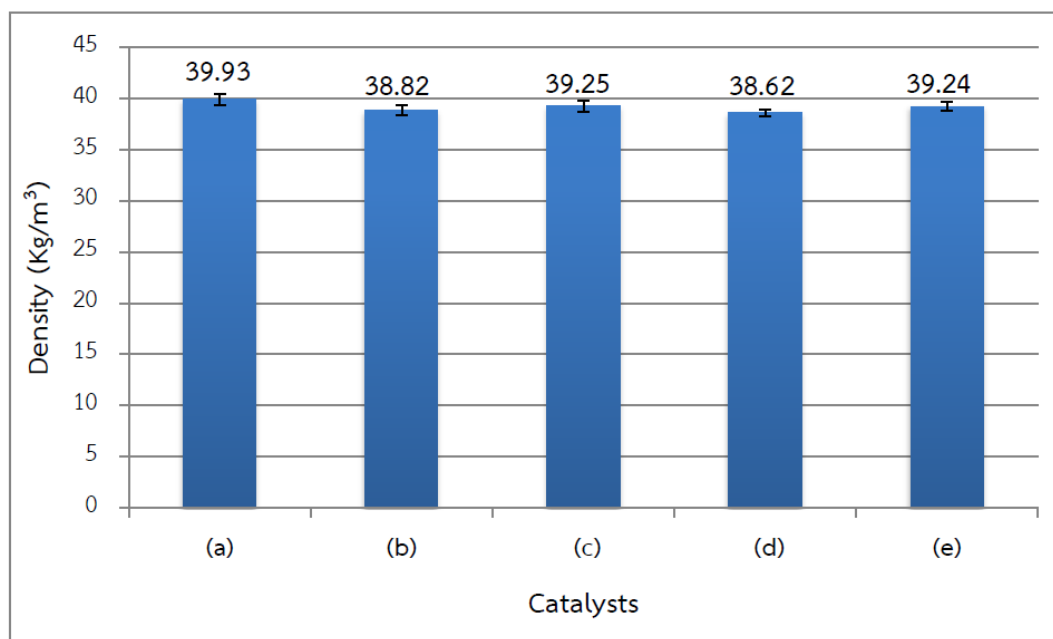
Figure 4.14 Density of RPUR foams catalyzed by (a) DMCHA (b) $Zn(Asn)_2$, (c) $Cu(Asn)_2$, (d) $Zn(Thr)_2$ and (e) $Cu(Thr)_2$ (Catalyst: 1 pbw, H_2O: 4 pbw)

4.4.1.2 Effect of catalyst contents in metal-amino acid complexes on reaction time of RPUR foams

The effect of catalyst contents in metal-amino acid complexes on reaction time of RPUR foams were investigated as shown in Figures 4.15-4.18. RPUR foams catalyzed by $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ and $Cu(Thr)_2$ were prepared at the catalyst contents of 0.5, 1.0 and 2.0 pbw. The reaction time decreased when the amount of catalyst was increased. The catalyst contents of 1.0 and 2.0 pbw gave almost the same reaction times. In addition, the holes at the bottom of RPUR foam samples were found and resulted in poor property of foams when 2.0 pbw of catalyst was used as shown in Figure 4.19. From this reason, the optimum catalyst content for the foam formulation was 1.0 pbw.
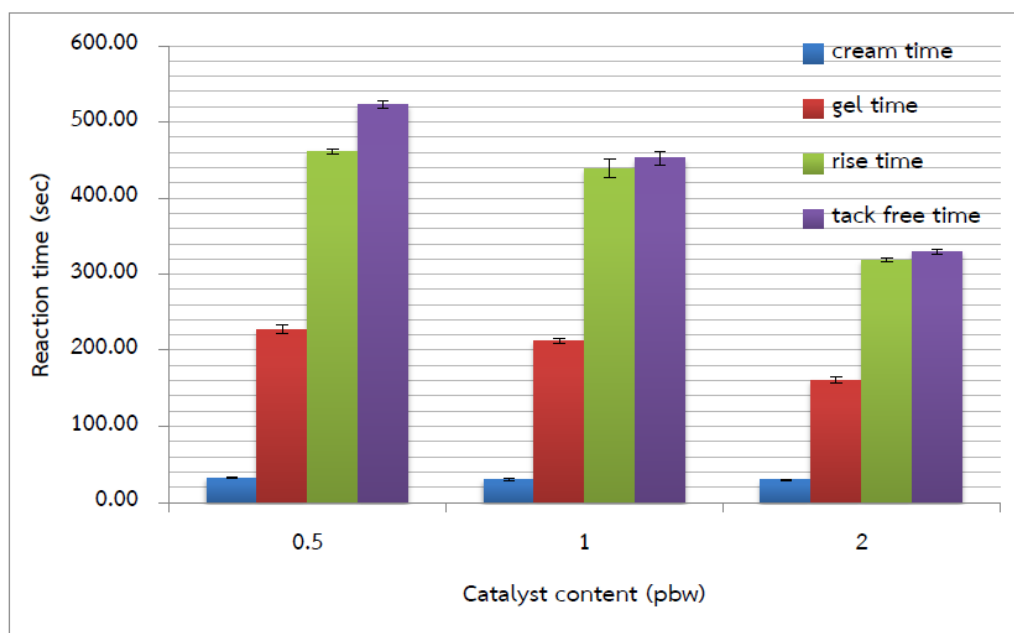
Figure 4.15 The effect of catalyst contents on reaction times of RPUR foams catalyzed by zinc-asparagine complex
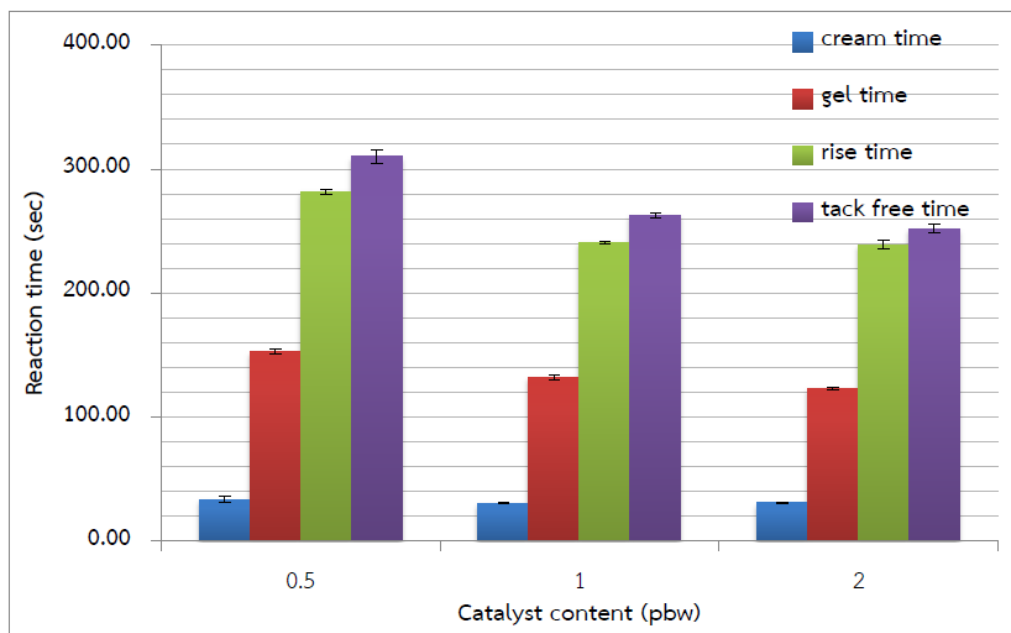
Figure 4.16 The effect of catalyst contents on reaction times of RPUR foams catalyzed by zinc-threonine complex
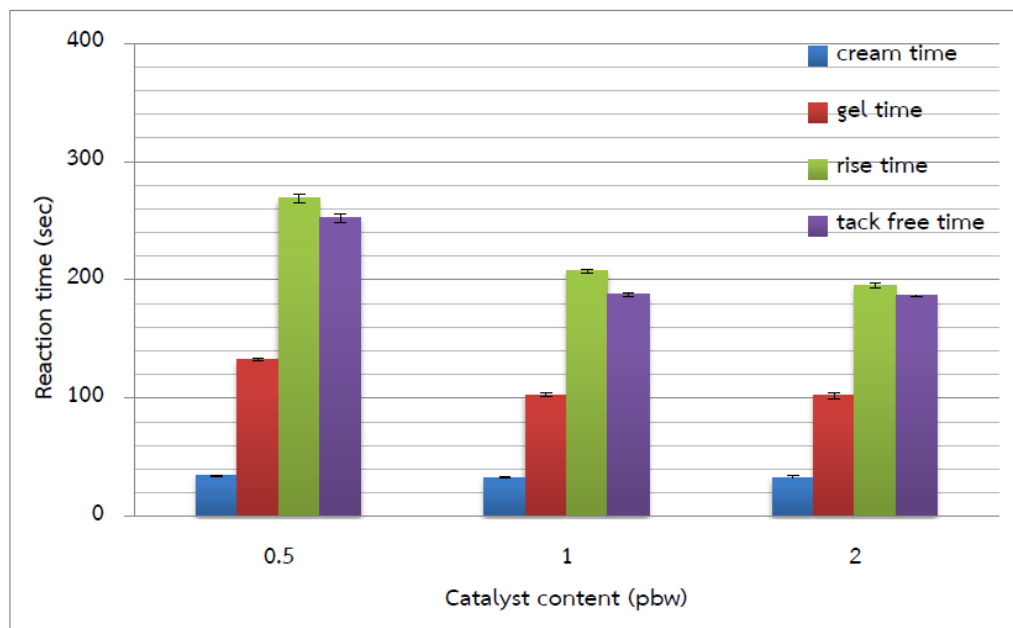
Figure 4.17 The effect of catalyst contents on reaction times of RPUR foams catalyzed by copper-asparagine complex
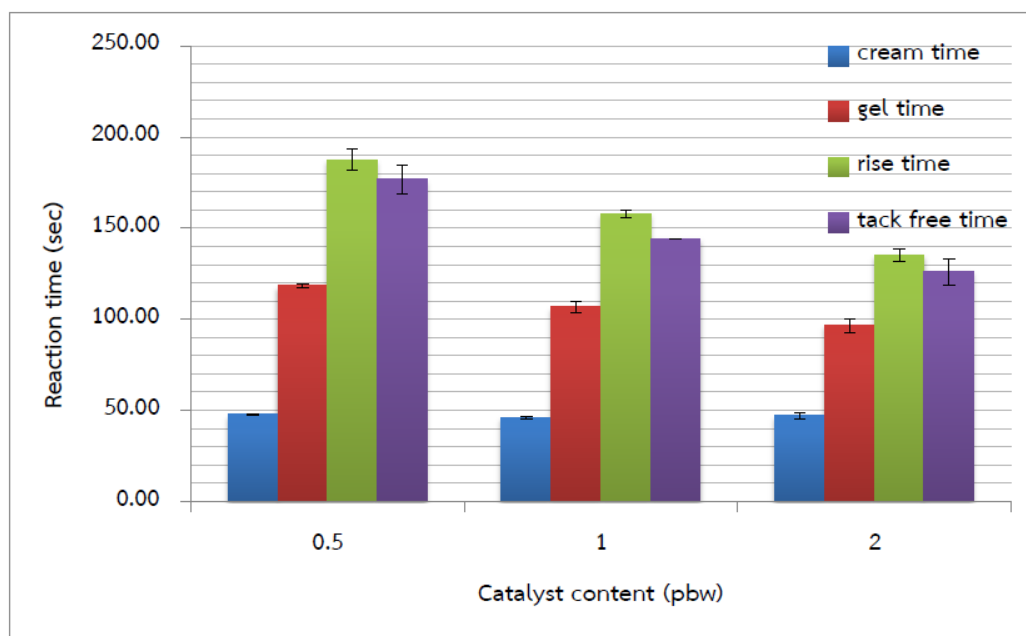
Figure 4.18 The effect of catalyst contents on reaction times of RPUR foams catalyzed by copper-threonine complex

Figure 4.19 RPUR foam catalyzed by Zn(Thr)$_2$ (2.0 pbw)

4.4.1.3 Effect of catalyst quantity on foam density

Effect of catalyst quantity on foam density is shown in Figure 4.20. The foam density decreased when the amount of catalyst was increased because increasing the amount of catalyst also increased the blowing reaction. RPUR foams catalyzed by amount of catalyst at 2.0 pbw gave better blowing reaction and lower foam density than those prepared from 1.0 and 0.5 pbw of catalyst (Figure 4.21). From these results, the amount of catalyst which was suitable for RPUR foam formulation was 1.0 pbw.
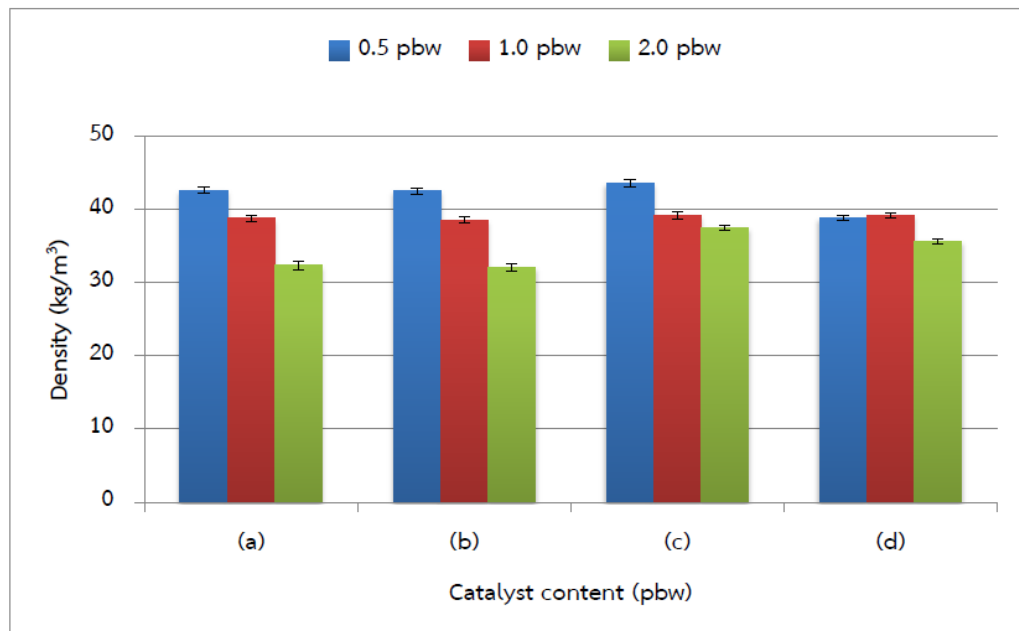
Figure 4.20 The effect of catalyst quantity on foam density catalyzed by (a) Zn(Asn)$_2$, (b) Zn(Thr)$_2$, (c) Cu(Asn)$_2$ and (d) Cu(Thr)$_2$

Figure 4.21 Appearance of RPUR foams prepared at different catalyst contents (a) 0.5 pbw, (b) 1.0 pbw and (c) 2.0 pbw

4.5 Rise profiles

Rise profiles of RPUR foams catalyzed by DMCHA, $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ and $Cu(Thr)_2$ were investigated as shown in Figure 4.22. Rise profiles data are the relationship between the height of foam in cup test method after mixing and the rise time. It was found that RPUR foams catalyzed by metal-amino acid complexes showed a short time to initiate the reaction which was cream time similar to the reaction of catalyzed by DMCHA. Copper-amino acid complexes gave a shorter rise time than zinc-amino acid complexes and DMCHA had a shorter rise time than copper-amino acid complexes. The order of catalytic activity of blowing reaction was in the order DMCHA > $Cu(Thr)_2$ > $Cu(Asn)_2$ > $Zn(Thr)_2$ > $Zn(Asn)_2$.
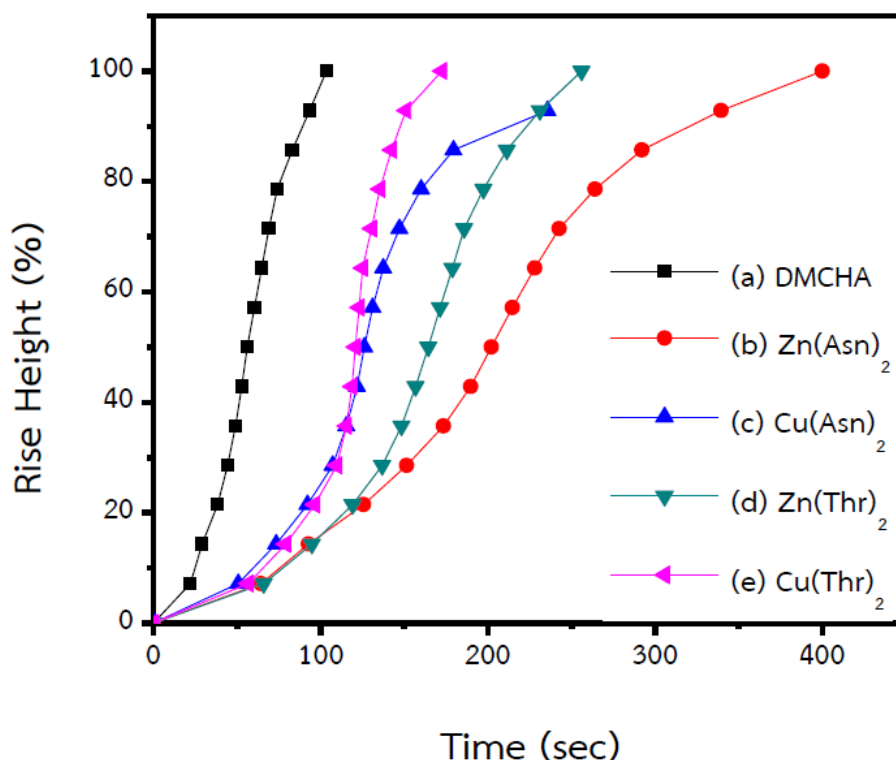
Figure 4.22 Rise profiles of RPUR foams catalyzed by (a) DMCHA (ref.), (b) $Zn(Asn)_2$, (c) $Cu(Asn)_2$, (d) $Zn(Thr)_2$ and (e) $Cu(Thr)_2$ (Catalyst: 1 pbw, H_2O: 4 pbw)

4.6 Temperature profiles

Temperature profiles of RPUR foams catalyzed by DMCHA, $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ and $Cu(Thr)_2$ were investigated as shown in Figure 4.23. It was found that the polymerization reaction was exothermic reaction which was due to the released heat of gelling reaction and blowing reaction. The maximum core temperature was in the range 96.4-133.3 $^{\circ}$C as shown in Table 4.4. 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 which except $Cu(Thr)_2$ 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. $Cu(Thr)_2$ gave the similar to the core temperature of catalyzed by DMCHA, which indicated that it had the highest catalytic activity as compared with other metal-amino acid complexes.
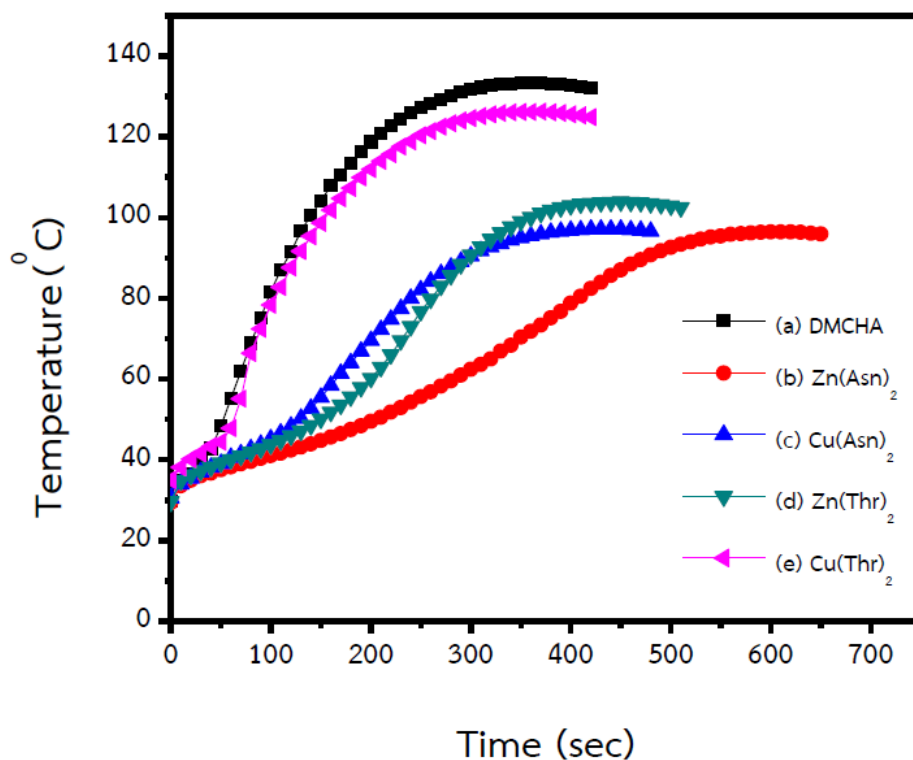
Figure 4.23 Temperature profiles of RPUR foams catalyzed by (a) DMCHA (ref.), (b) Zn(Asn)$_2$, (c) Cu(Asn)$_2$, (d) Zn(Thr)$_2$ and (e) Cu(Thr)$_2$

Table 4.4 The maximum core temperature of RPUR foams catalyzed by DMCHA, Zn(Asn)$_2$, Zn(Thr)$_2$, Cu(Asn)$_2$ and Cu(Thr)$_2$

Catalyst	Maximum core temperature (^{o}C)	Starting times (sec) at T_{max}*
DMCHA (ref.)	133.3	360
Zn(Asn)$_2$	96.4	610
Zn(Thr)$_2$	103.8	450
Cu(Asn)$_2$	97.1	440
Cu(Thr)$_2$	126.1	370

*T_{max} = The maximum core temperature

4.7 Proposed catalytic mechanism of copper(II)-Threonine complex (Cu(Thr)$_2$)

The reaction mechanism of RPUR foam catalyzed by Cu(Thr)$_2$ complex is proposed as shown in Scheme 4.2. The copper atom in Cu(Thr)$_2$ could act as a Lewis

acid and coordinate to the oxygen atom of the NCO group, which caused the NCO carbon to be more electrophilic. The nitrogen atom in copper(II)-threonine complexes interacted with the proton of the hydroxyl group and caused the hydroxyl oxygen to be more nucleophilic. The oxygen then reacted with the isocyanate group to give urethane linkage [22]. The catalytic mechanisms of other metal-amino acid complexes in this research were proposed to be similar to that of Cu(Thr)$_2$.
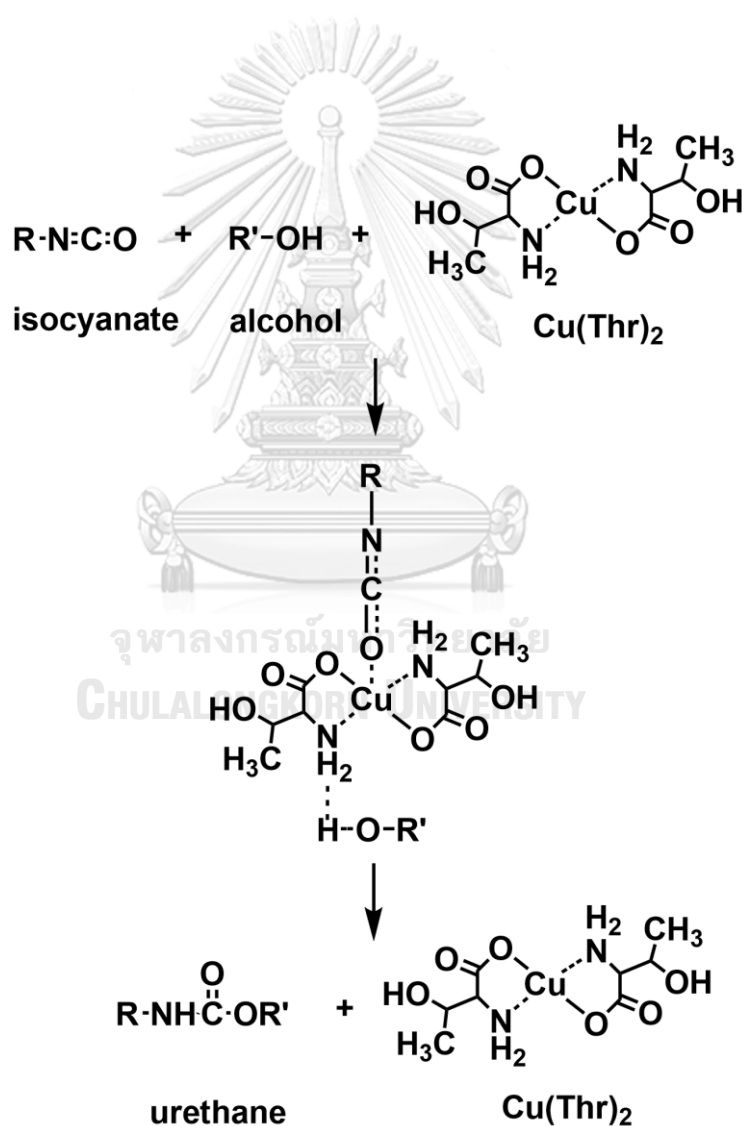
Scheme 4.2 Proposed catalytic mechanism of Cu(Thr)$_2$

4.8 Characterization of RPUR foams by ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was used to determine the progress of polymerization reaction of RPUR foam. 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.
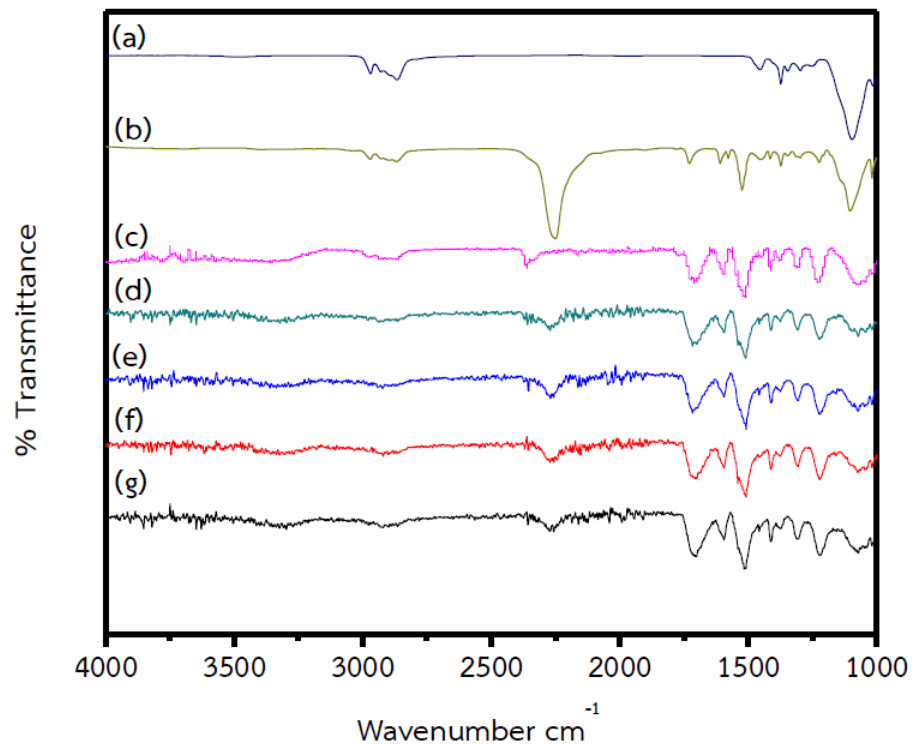
Figure 4.24 IR spectra of starting materials (a) polyether polyol, (b) polymeric MDI, RPUR foams catalyzed by (c) DMCHA, (d) Zn(Asn)$_2$, (e) Cu(Asn)$_2$, (f) Zn(Thr)$_2$ and (g) Cu(Thr)$_2$

4.9 NCO conversion of RPUR foams

The isocyanate (NCO) conversion of RPUR foams catalyzed by DMCHA and metal-amino acid complexes 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 [30].

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

where;

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

[Figure 4.24 (c-g)]

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

[Figure 4.24 (b)]

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

Table 4.5 Wavenumber of the functional groups used in calculation of NCO conversion

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

The NCO conversion of RPUR foams catalyzed by DMCHA and metal-amino acid complexes is shown in Table 4.6. It was found that RPUR foams catalyzed by DMCHA, Zn(Asn)$_2$, Zn(Thr)$_2$, Cu(Asn)$_2$ and Cu(Thr)$_2$ gave quantitative (approximately 99%) of NCO conversion. Therefore, the reaction of isocyanate with hydroxyl groups and water were completed. It could be concluded that all metal-amino acid complexes were good catalysts for preparation of RPUR foams.

Table 4.6 NCO conversion of RPUR foams catalyzed by DMCHA and metal-amino acid complexes (catalyst: 1 pbw, H_2O: 4 pbw)

Catalysts Types	Peak Area		NCO Conversion (%)
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	
DMCHA	0.127	2.465	99.95
Zn(Asn)$_2$	0.259	2.669	99.90
Zn(Thr)$_2$	0.114	2.107	99.95
Cu(Asn)$_2$	0.221	2.310	99.90
Cu(Thr)$_2$	0.145	2.344	99.94

4.10 Compressive properties of RPUR foams (molded method)

Compressive strength of RPUR foams is an important parameter for their application. The compression stress-strain curves of RPUR foams catalyzed by DMCHA and metal-amino acid complexes in parallel and perpendicular to the foam rising direction are shown in Figures 4.25 and 4.26, respectively. The compressive strength in parallel direction was higher than that of perpendicular direction (Figure 4.27 and Table 4.7). The compressive strength of RPUR foams catalyzed by different catalysts was DMCHA > Zn(Thr)$_2$ ≈ Cu(Thr)$_2$ > Zn(Asn)$_2$ ≈ Cu(Asn)$_2$ in parallel direction. In perpendicular direction, the compressive strength of RPUR foams catalyzed by different catalysts was DMCHA > Cu(Thr)$_2$ ≈ Zn(Thr)$_2$ ≈ Cu(Asn)$_2$ > Zn(Asn)$_2$.
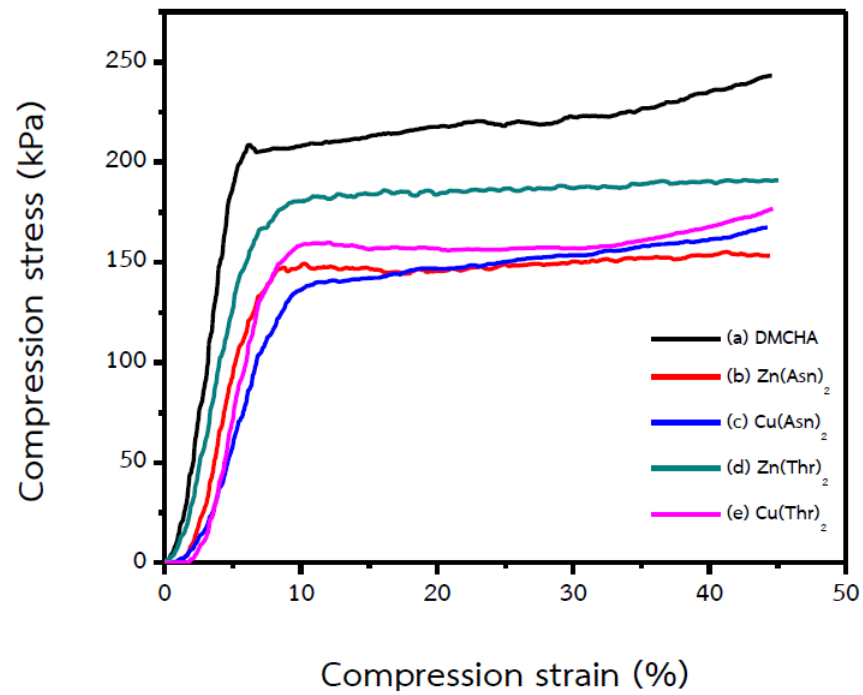
Figure 4.25 Stress-strain curves of RPUR foams catalyzed by (a) DMCHA, (b) $Zn(Asn)_2$, (c) $Cu(Asn)_2$, (d) $Zn(Thr)_2$ and (e) $Cu(Thr)_2$ in parallel to the foam rising direction
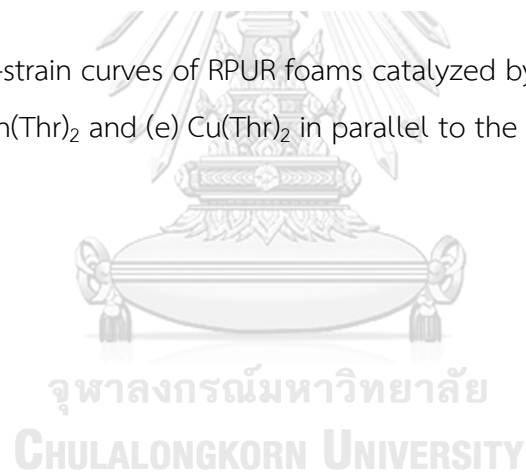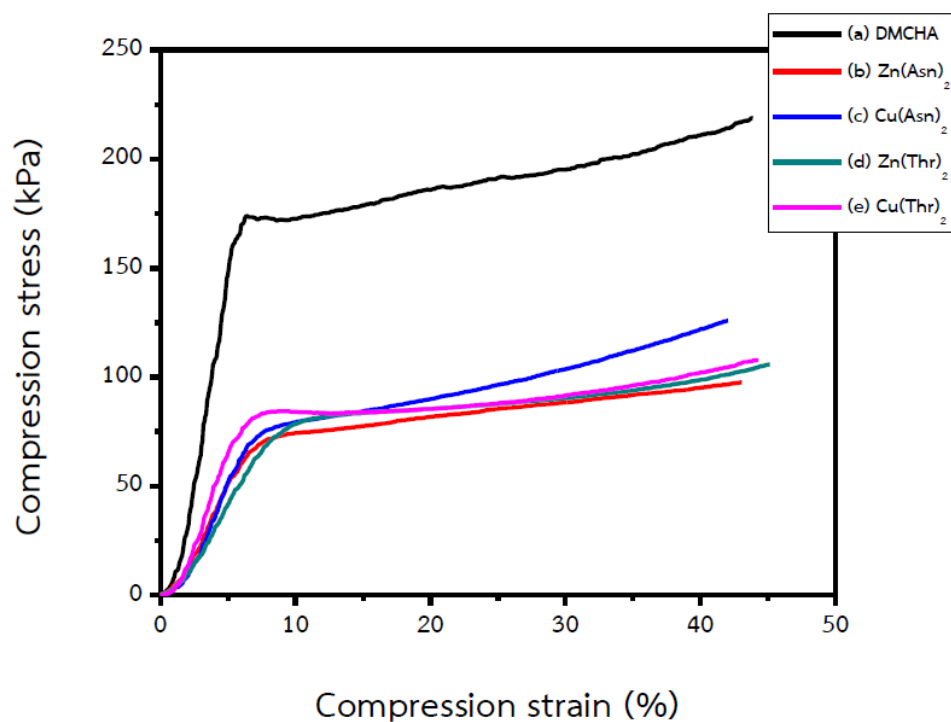
Figure 4.26 Stress-strain curves of RPUR foams catalyzed by (a) DMCHA, (b) $Zn(Asn)_2$, (c) $Cu(Asn)_2$, (d) $Zn(Thr)_2$ and (e) $Cu(Thr)_2$ in perpendicular to the foam rising direction
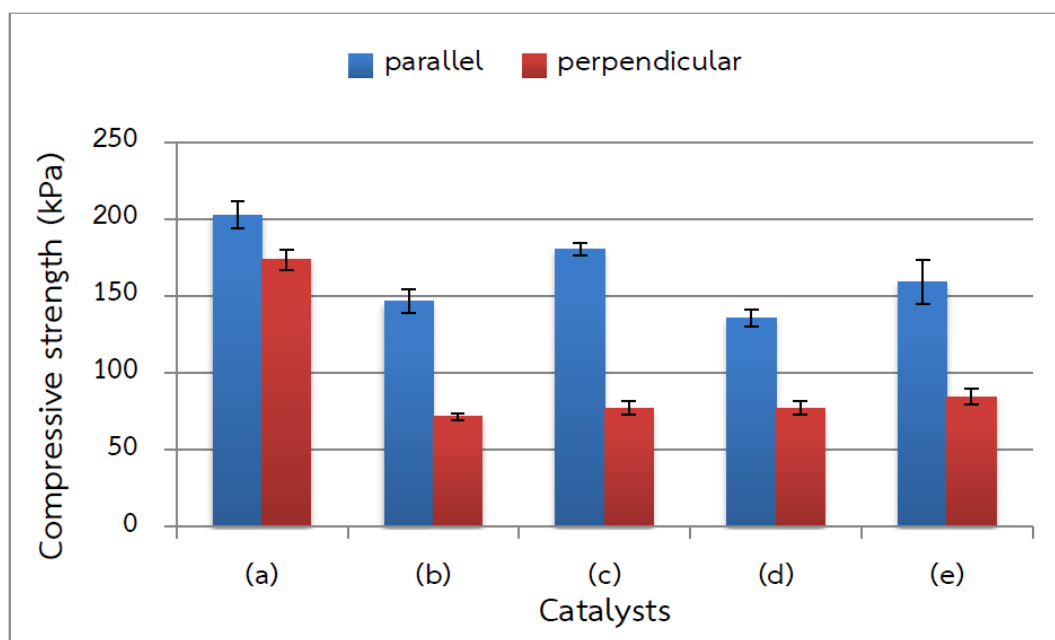
Figure 4.27 Compressive strength of RPUR foams catalyzed by (a) DMCHA, (b) $Zn(Asn)_2$, (c) $Zn(Thr)_2$, (d) $Cu(Asn)_2$ and (e) $Cu(Thr)_2$

Table 4.7 Compressive strength of RPUR foams

Catalysts	Compressive strength (kPa) in parallel direction	Compressive strength (kPa) in perpendicular direction
DMCHA (ref.)	202.9 ± 8.82	173.9 ± 6.61
Zn(Asn)$_2$	146.7 ± 7.43	71.7 ± 2.33
Zn(Thr)$_2$	180.6 ± 3.87	78.7 ± 4.14
Cu(Asn)$_2$	135.9 ± 5.78	77.2 ± 4.51
Cu(Thr)$_2$	159.2 ± 14.46	84.4 ± 5.15

4.11 RPUR foams morphology

The cell structure of RPUR foams was investigated by the SEM. RPUR foam catalyzed by Zn(Asn)$_2$, Zn(Thr)$_2$, Cu(Asn)$_2$ and Cu(Thr)$_2$ were prepared at the amount of catalyst of 1.0 pbw and blowing agent (H$_2$O) of 4 pbw. The samples were also studied in parallel and perpendicular direction of foam rising (Figures 4.28-4.37). The results revealed that the structure of all RPUR foams was closed-cell. The cell shapes were spherical and ellipsoidal in top view and side view, respectively, as shown in Figure 4.38 (a). 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 size w and cell size h (Figure 4.38 (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 w and cell size h (Figure 4.38 (b)), respectively. The data of averaged cell size of RPUR foams (Tables 4.8-4.9) revealed that cell size of RPUR foams catalyzed by different catalysts was in the order Zn(Asn)$_2$ > Cu(Asn)$_2$ > Zn(Thr)$_2$ > Cu(Thr)$_2$ > DMCHA in top view and Zn(Asn)$_2$ > Zn(Thr)$_2$ > Cu(Asn)$_2$ > Cu(Thr)$_2$ > DMCHA in side view. 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.
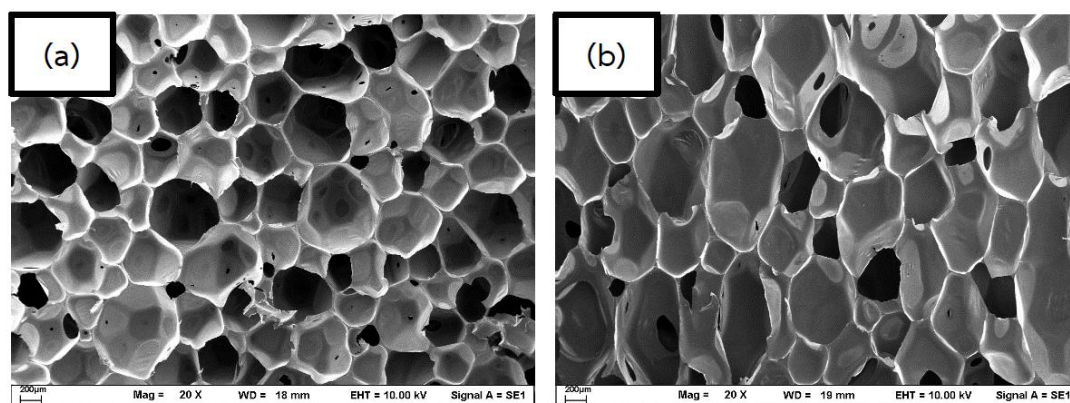
Figure 4.28 SEM of RPUR foams catalyzed by Zn(Asn)$_2$ (a) top view and (b) side view (20x)
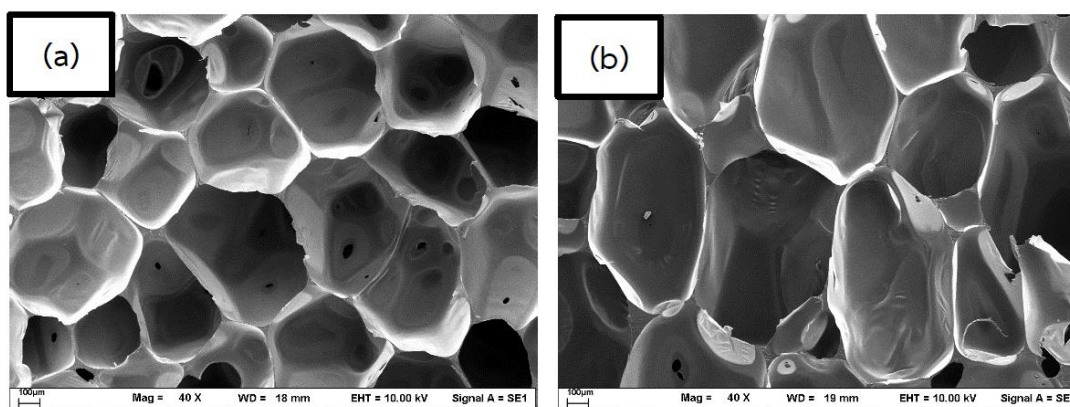
Figure 4.29 SEM of RPUR foams catalyzed by Zn(Asn)$_2$ (a) top view and (b) side view (40x)
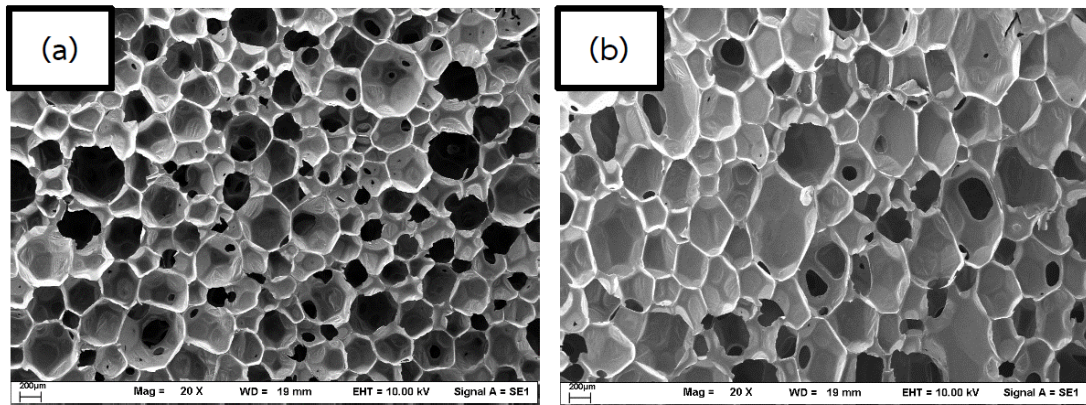
Figure 4.30 SEM of RPUR foams catalyzed by Cu(Asn)$_2$ (a) top view and (b) side view (20x)
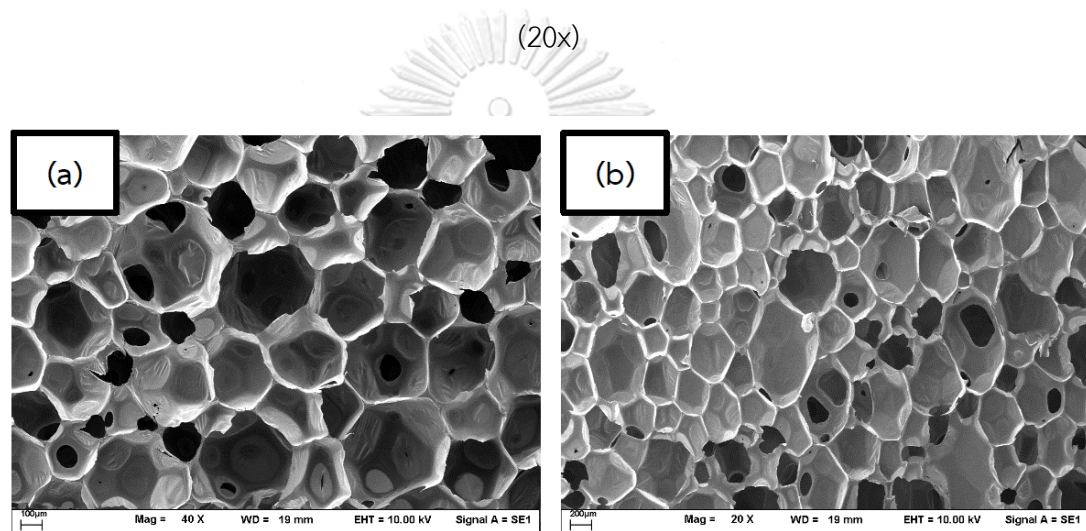
Figure 4.31 SEM of RPUR foams catalyzed by Cu(Asn)$_2$ (a) top view and (b) side view (40x)
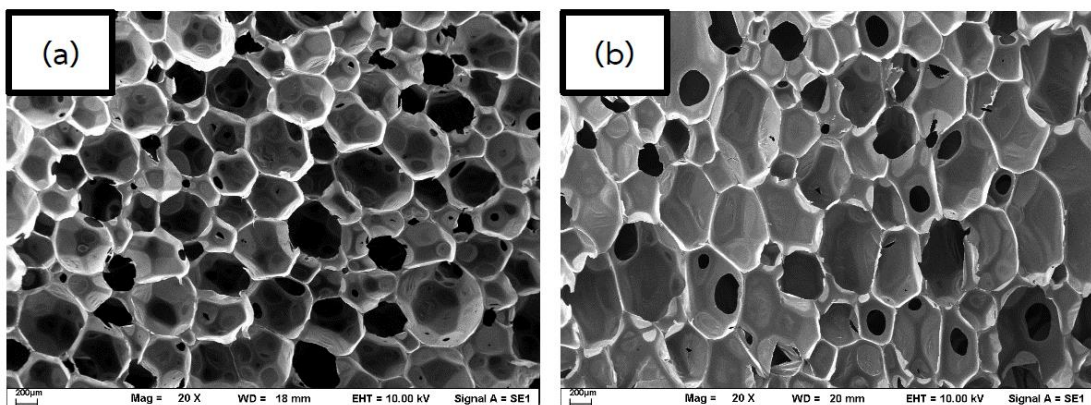
Figure 4.32 SEM of RPUR foams catalyzed by Zn(Thr)$_2$ (a) top view and (b) side view (20x)
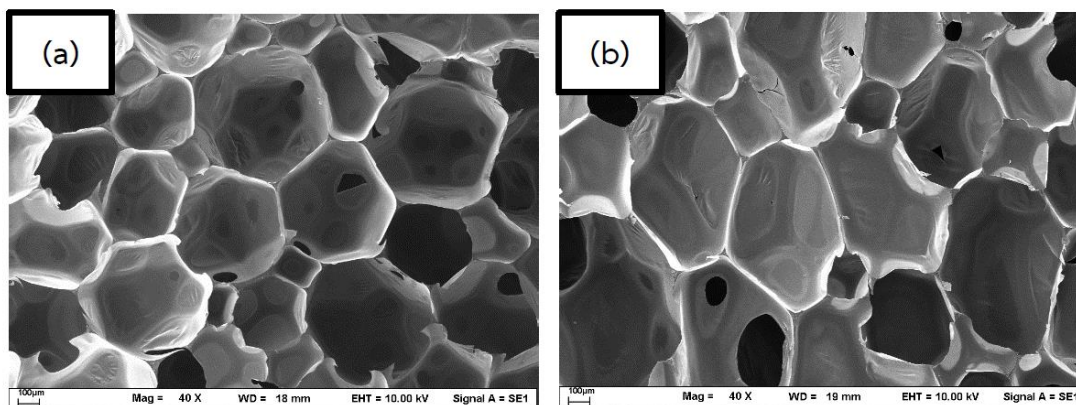
Figure 4.33 SEM of RPUR foams catalyzed by Zn(Thr)$_2$ (a) top view and (b) side view
(40x)
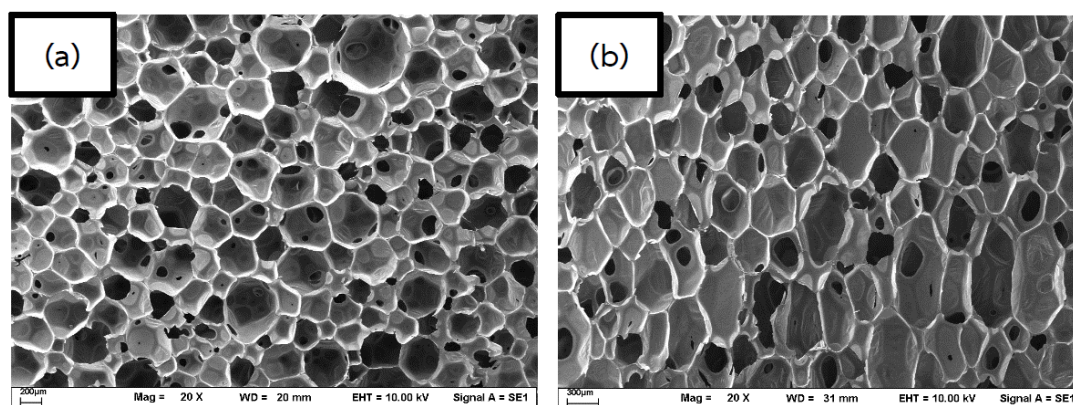
Figure 4.34 SEM of RPUR foams catalyzed by Cu(Thr)$_2$ (a) top view and (b) side view
(20x)
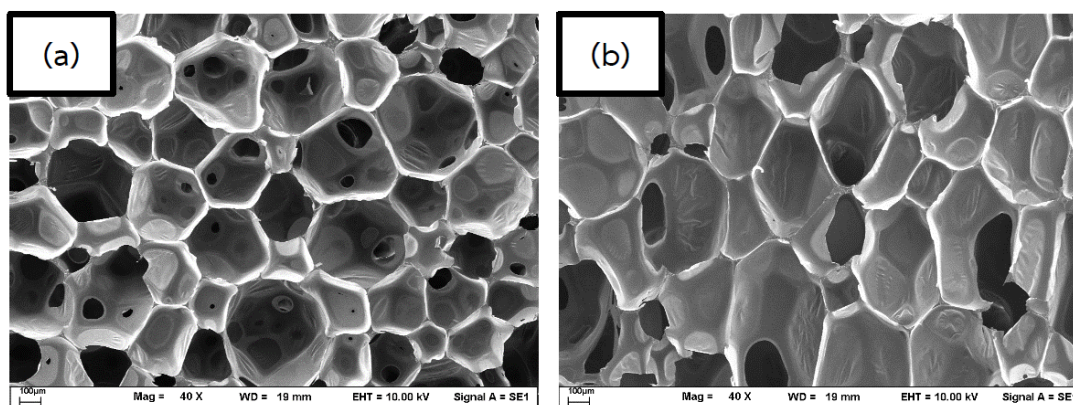
Figure 4.35 SEM of RPUR foams catalyzed by Cu(Thr)$_2$ (a) top view and (b) side view
(40x)
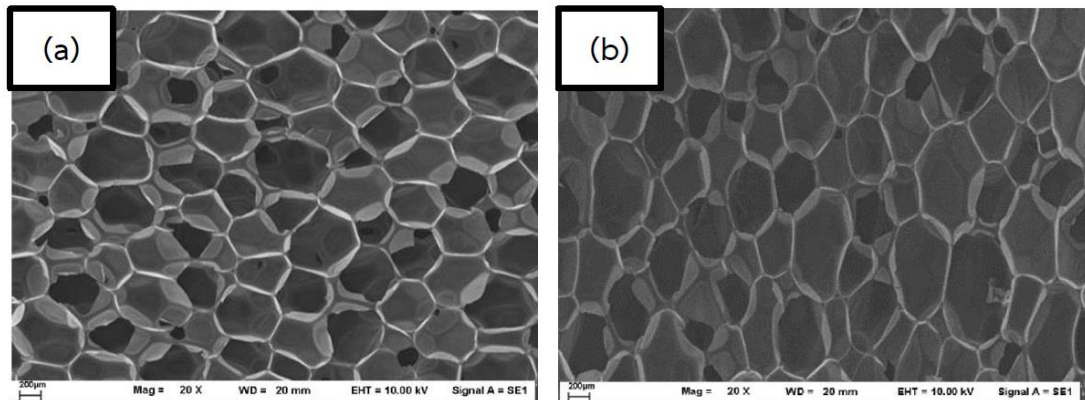
Figure 4.36 SEM of RPUR foams catalyzed by DMCHA (a) top view and (b) side view (20x)
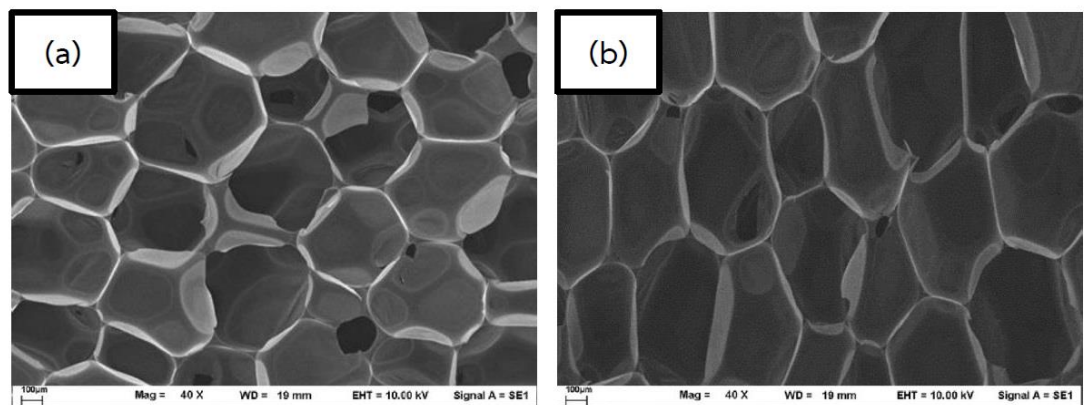
Figure 4.37 SEM of RPUR foams catalyzed by DMCHA (a) top view and (b) side view (40x)
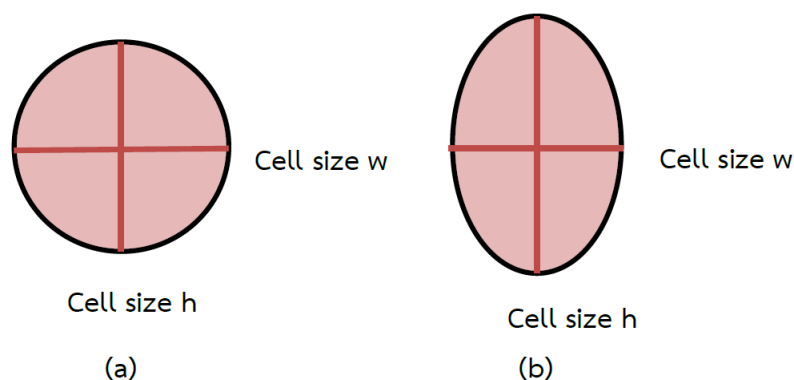
Figure 4.38 Measurement of cell size (a) Top view (b) Side view

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

Catalysts	Cell size (top view)	
	Cell size w (µm)	Cell size h (µm)
DMCHA (ref.)	355 ± 26.17	357 ± 24.23
Zn(Asn)$_2$	597 ± 58.13	618 ± 71.34
Cu(Asn)$_2$	436 ± 36.69	473 ± 58.33
Zn(Thr)$_2$	428 ± 45.35	399 ± 58.76
Cu(Thr)$_2$	373 ± 33.29	378 ± 33.29

Table 4.9 The cell size (side view) of RPUR foams catalyzed by DMCHA and metal-amino acid complexes

Catalysts	Cell size (side view)	
	Cell size w (µm)	Cell size h (µm)
DMCHA (ref.)	292 ± 30.68	417 ± 28.33
Zn(Asn)$_2$	701 ± 53.56	915 ± 45.16
Cu(Asn)$_2$	427 ± 40.58	579 ± 34.95
Zn(Thr)$_2$	652 ± 39.07	768 ± 45.37
Cu(Thr)$_2$	384 ± 27.39	581 ± 24.76

The external appearance of RPUR foams were obtained by cup test method. RPUR foams were cut as shown in Figures 4.39 a-c. External appearance of of RPUR foams is shown in Figures 4.40-4.44.
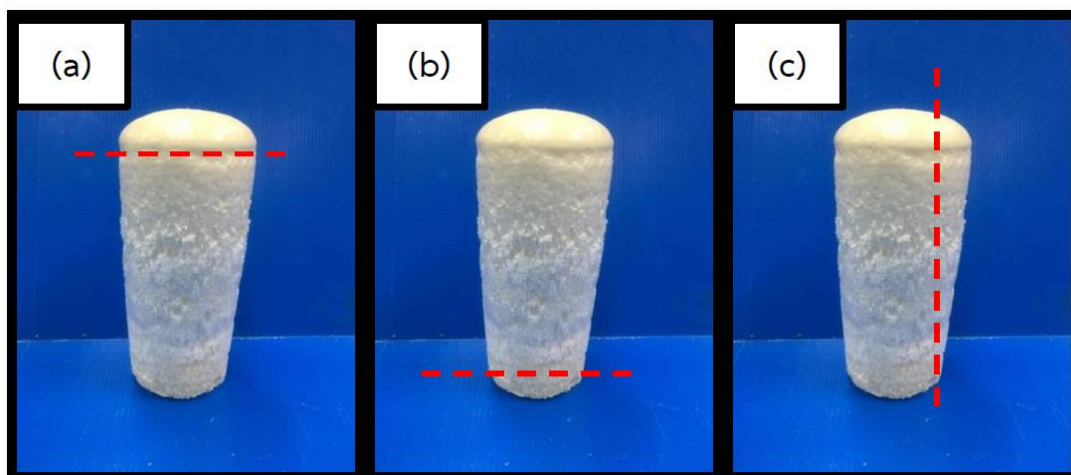
Figure 4.39 Cutting line for RPUR foam sample (a) top (b) bottom and (c) side of the sample
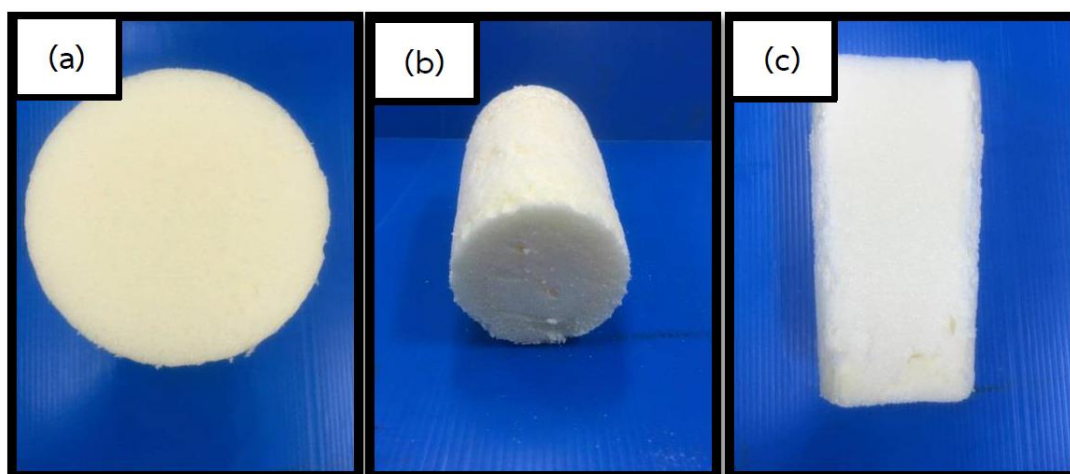
Figure 4.40 RPUR foams catalyzed by DMCHA
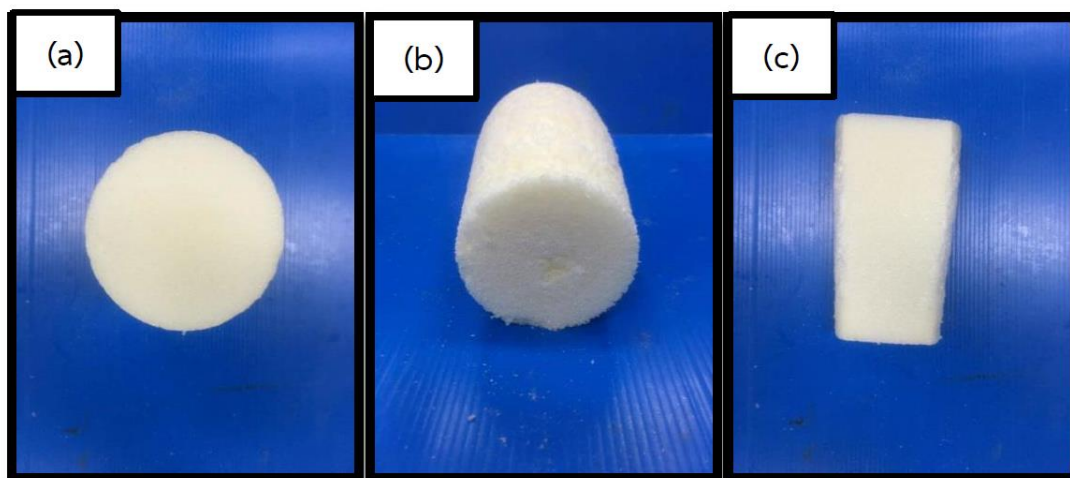
Figure 4.41 RPUR foams catalyzed by Zn(Asn)$_2$ (Catalyst: 1 pbw, H$_2$O: 4 pbw)
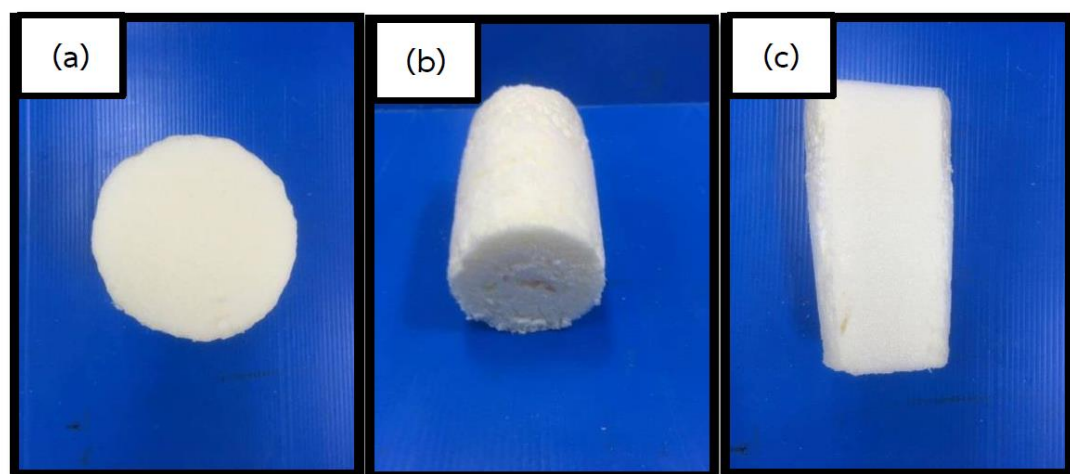
Figure 4.42 RPUR foams catalyzed by Zn(Thr)$_2$ (Catalyst: 1 pbw, H$_2$O: 4 pbw)
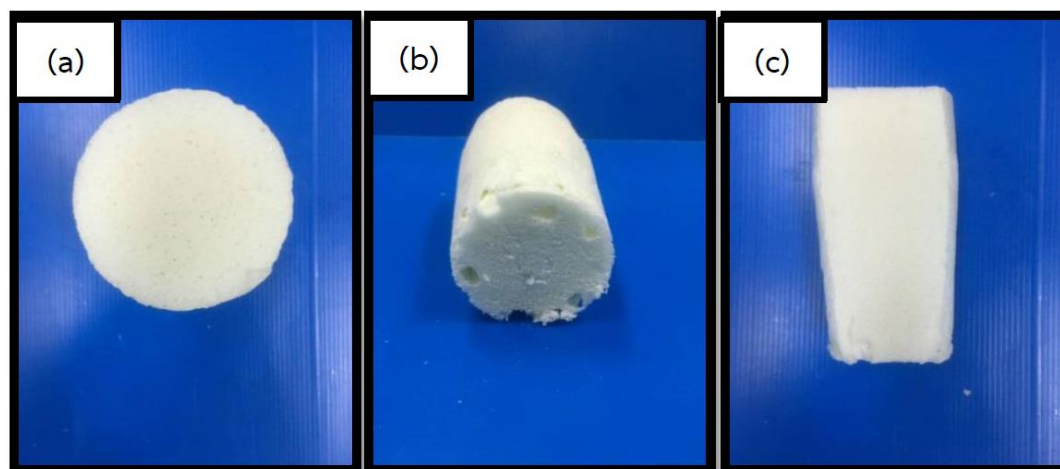
Figure 4.43 RPUR foams catalyzed by Cu(Asn)$_2$ (Catalyst: 1 pbw, H$_2$O: 4 pbw)
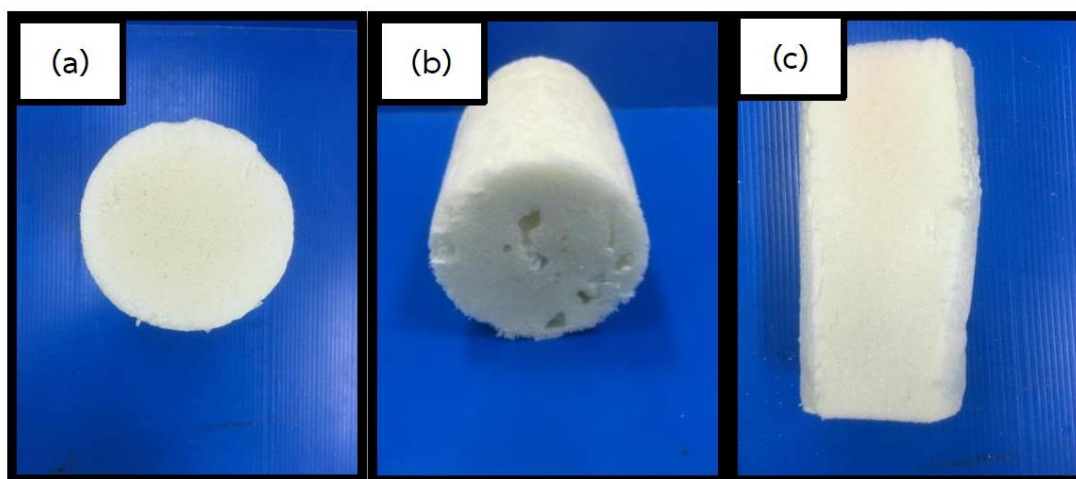
Figure 4.44 RPUR foams catalyzed by Cu(Thr)$_2$ (Catalyst: 1 pbw, H$_2$O: 4 pbw)

CHAPTER V

CONCLUSIONS

5.1 Conclusion

Metal-amino acid complexes, namely $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ and $Cu(Thr)_2$ $Zn(Asn)_2$, $Zn(Thr)_2$, $Cu(Asn)_2$ and $Cu(Thr)_2$, could be synthesized in water and were used as new catalysts for preparation of RPUR foams without purification. The solutions of metal-amino acid complexes were obtained as odorless liquids that could be easily dissolved in the starting materials used in foam formulations. The structure of metal-amino acid complexes were confirmed by UV visible spectroscopy, IR spectroscopy and mass spectrometry.

The catalytic activity of metal-amino acid complexes for RPUR foam preparation has been investigated and showed comparable catalytic activity to that obtained from a reference commercial catalyst (DMCHA). From the reaction times, RPUR foams prepared from metal-amino acid complexes showed the order of catalytic activity of DMCHA > $Cu(Thr)_2$ > $Cu(Asn)_2$ > $Zn(Thr)_2$ > $Zn(Asn)_2$. Furthermore, RPUR foam density obtained from $Cu(Thr)_2$ and $Cu(Asn)_2$ prepared at the mole ratio of copper acetate:amino acid = 1:1 at the amount of blowing agent = 4.0 pbw gave the similar foam height and foam density to RPUR foam catalyzed by DMCHA.

By varying the catalyst contents, it was found that the reaction time and foam density decreased when the amount of catalyst was increased. The optimum amount of catalyst in RPUR foam formulation was 1.0 pbw. Among all metal-amino acid complexes, $Cu(Thr)_2$ gave the highest catalytic activity.

Rise profile of RPUR foaming reaction catalyzed by copper-amino acid complexes gave shorter rise time than zinc-amino acid complexes and had similar

trend to RPUR foam catalyzed by DMCHA. From the slope of rise profile curve, The order of catalytic activity was DMCHA > $Cu(Thr)_2$ > $Cu(Asn)_2$ > $Zn(Thr)_2$ > $Zn(Asn)_2$.

The polymerization reaction was exothermic reaction which was due to the released heat of gelling reaction and blowing reaction. The maximum core temperature was in the range 96.4-133.3 $^{\circ}$C. This was appropriate foaming temperature since RPUR foams did not burn. $Cu(Thr)_2$ gave the similar to the core temperature and trend of catalyzed by DMCHA, which indicated that it had the high catalytic activity. RPUR foam catalyzed by $Cu(Thr)_2$ had the highest core temperature than those prepared from other metal-amino acid complexes.

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 the NCO index of 100. It could be concluded that all metal-amino acid complexes were good catalysts for preparation of RPUR foams.

From the compressive stress-strain curve, it was found that the compressive strength in parallel to the foam rising direction are higher than that in perpendicular to the foam rising direction. The compressive strength showed that RPUR foam catalyzed by DMCHA exhibited the higher compressive strength than that of the foam prepared from metal-amino acid complexes at both parallel and perpendicular to the foam rising direction. RPUR foam catalyzed by $Zn(Thr)_2$ had the highest compressive strength in comparison to those catalyzed by other metal-amino acid complexes.

Morphology of RPUR foams revealed that the structures of all RPUR foams had closed cell structure. The cells were spherical shape and ellipsoidal shape in parallel and perpendicular to the foam rising direction, respectively. RPUR foam catalyzed by $Cu(Thr)_2$ had the similar cell size with that catalyzed by DMCHA.

5.2 Suggestion for future work

The suggestion for future work is to use metal-amino acid complexes in the preparation of polyisocyanurate foam.

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APPENDIX

APPENDIX A

NCO index and NCO conversion calculations

NCO index calculation

Example Calculate the parts by weight (pbw) of PMDI (Raycore®B9001), molar mass = 365.8, functionality = 2.7 at an isocyanate index of 100 required to react with the following formulation:

Formulation (NCO index = 100)	parts by weight (pbw)	
polyether polyol (Polimaxx® 4221)	100	100
Polysiloxane surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (water in the aqueous solution of metal-amino acid complexes acts as a blowing agent)	3.0	4.0
Catalyst (metal-amino acid complexes or DMCHA)	1.0	0.5, 1.0, 2.0
Polymeric diphenyl methane diisocyanate (PMDI, Raycore® B9001)	?	?

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

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

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

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

Equivalent weight in the above formulation:

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

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

$$\text{Total equivalent weight} = \frac{100}{127.5} = 1.117$$

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

Therefore:

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

Where;

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

Thus: at isocyanate index = 100

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

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

Formulation (NCO index = 100)	parts by weight (pbw)	
polyether polyol (Polimaxx® 4221)	100	100
Polysiloxane surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (water in the aqueous solution of metal-amino acid complexes acts as a blowing agent)	3.0	4.0
Catalyst (metal-amino acid complexes or DMCHA)	1.0	0.5, 1.0, 2.0
Polymeric diphenyl methane diisocyanate (PMDI, Raycore® B9001)	151.3	166.4

NCO conversion calculation

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

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

Where:

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

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

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

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

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

Example Calculate the conversion of isocyanate (**α**) of rigid polyurethane foams catalyzed by Cu(Thr)$_2$ 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 = 0.062 = NCO^f

Thus:

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

$$= \left[1 - \frac{0.062}{98.0}\right] \times 100$$

$$\text{\% NCO conversion} = 99.94$$

Table A3 NCO conversion of RPUR foam catalyzed by $Cu(Thr)_2$ at NCO index 100 (catalyst = 1 pbw, H_2O = 4 pbw)

Catalysts	Peak Area			NCO
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	NCO^f (Ar-H = 1.0)	Conversion (%)
$Cu(Thr)_2$	0.145	2.344	0.062	99.94

Table A4 NCO conversion of RPUR foams catalyzed by DMCHA and metal-amino acid complexes at NCO index 100 (catalyst: 1 pbw, H_2O: 4 pbw)

Catalysts Types	Peak Area			NCO
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	NCO^f (Ar-H = 1.0)	Conversion (%)
DMCHA	0.127	2.465	0.052	99.95
$Zn(Asn)_2$	0.259	2.669	0.097	99.90
$Zn(Thr)_2$	0.114	2.107	0.054	99.95
$Cu(Asn)_2$	0.221	2.310	0.096	99.90
$Cu(Thr)_2$	0.145	2.344	0.062	99.94

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 (Polymaxx[®]4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Raycore[®]B9001)	151.3	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	19	0.55
Gel time	33	1.30
Rise time	90	2.00
Tack free time	99	4.00
Density (kg/m^3)	39.93	0.56
Mechanical properties		
Compressive strength (kPa) in parallel	202.9	8.82
Compressive strength (kPa) in perpendicular	173.9	6.61

Table B2 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by 20 wt% $Zn(Asn)_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	20 wt% $Zn(Asn)_2$	
Polyol (Polymaxx®4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore®B9001)	166.4	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	30	1.00
Gel time	212	2.52
Rise time	439	2.00
Tack free time	452	5.00
Density (kg/m^3)	38.82	0.49
Mechanical properties		
Compressive strength (kPa) in parallel	146.7	7.43
Compressive strength (kPa) in perpendicular	71.7	2.33

Table B3 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by 20 wt% Zn(Thr)$_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100 20 wt% Zn(Thr)$_2$	
Polyol (Polymaxx®4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore®B9001)	166.4	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	30	0.58
Gel time	132	1.73
Rise time	241	1.00
Tack free time	263	1.53
Density (kg/m^3)	38.62	0.36
Mechanical properties		
Compressive strength (kPa) in parallel	180.6	3.87
Compressive strength (kPa) in perpendicular	78.7	4.14

Table B4 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by 20 wt% Cu(Asn)$_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	20 wt% Cu(Asn)$_2$	
Polyol (Polymaxx®4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore®B9001)	166.4	
Efficiency parameters	**Data**	**S.D.**
Reaction times (sec)		
Cream time	33	0.58
Gel time	103	1.53
Rise time	208	1.53
Tack free time	188	1.53
Density (kg/m^3)	39.25	0.51
Mechanical properties		
Compressive strength (kPa) in parallel	135.9	5.78
Compressive strength (kPa) in perpendicular	77.2	4.51

Table B5 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by 20 wt% Cu(Thr)$_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	20 wt% Cu(Thr)$_2$	
Polyol (Polymaxx®4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore®B9001)	166.4	
Efficiency parameters	Data	S.D.
Reaction times (sec)		
Cream time	46	1.00
Gel time	107	3.21
Rise time	158	2.00
Tack free time	144	0.01
Density (kg/m^3)	39.24	0.40
Mechanical properties		
Compressive strength (kPa) in parallel	159.2	14.46
Compressive strength (kPa) in perpendicular	84.4	5.15

Table B6 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(Asn)$_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100			
	11 wt% Zn(Asn)$_2$		33 wt% Zn(Asn)$_2$	
Efficiency parameters	Data	S.D.	Data	S.D.
Reaction times (sec)				
Cream time	32	1.00	29	0.58
Gel time	228	5.86	161	4.04
Rise time	461	3.79	319	3.06
Tack free time	524	5.13	330	2.89
Density (kg/m^3)	42.66	0.46	32.40	0.56

Table B7 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(Thr)$_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100			
	11 wt% Zn(Thr)$_2$		33 wt% Zn(Thr)$_2$	
Efficiency parameters	Data	S.D.	Data	S.D.
Reaction times (sec)				
Cream time	33	2.08	31	0.58
Gel time	152	2.08	123	1.00
Rise time	282	2.00	239	3.61
Tack free time	310	5.51	252	3.61
Density (kg/m^3)	42.59	0.40	32.18	0.50

Table B8 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(Asn)_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100			
	11 wt% $Cu(Asn)_2$		33 wt% $Cu(Asn)_2$	
Efficiency parameters	Data	S.D.	Data	S.D.
Reaction times (sec)				
Cream time	35	0.58	33	1.53
Gel time	133	1.00	102	2.52
Rise time	269	3.61	196	2.08
Tack free time	252	3.79	187	0.58
Density (kg/m^3)	43.65	0.48	37.54	0.39

Table B9 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(Thr)_2$ at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100			
	11 wt% $Cu(Thr)_2$		33 wt% $Cu(Thr)_2$	
Efficiency parameters	Data	S.D.	Data	S.D.
Reaction times (sec)				
Cream time	48	0.58	47	2.00
Gel time	118	1.15	97	3.79
Rise time	187	5.86	135	3.61
Tack free time	177	7.64	126	7.00
Density (kg/m^3)	38.89	0.36	35.68	0.39

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