

การเตรียมโพลีเมอร์แบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-วาเลินและโลหะ-อาร์
จีนีน



บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559
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PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-
VALINE AND METAL-ARGININE COMPLEXES

Miss Woranut Keawmang



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2016

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Thesis Title	PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL- VALINE AND METAL- ARGININE COMPLEXES
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Field of Study	Petrochemistry and Polymer Science
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วรรณุช แก้วเม่ง : การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะ-วาเลอีนและโลหะ-อาร์จินีน (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-VALINE AND METAL-ARGININE COMPLEXES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. นवलพรรณ จันทร์ศิริ, 113 หน้า.

งานวิจัยนี้เป็นการพัฒนาตัวเร่งปฏิกิริยาชนิดใหม่สำหรับการเตรียมพอลิยูรีเทนโฟมแบบแข็งคือ สารประกอบเชิงซ้อนโลหะ-กรดแอมิโน ซึ่งไม่มีกลิ่นเหม็นและมีความเป็นพิษต่ำ สารประกอบเชิงซ้อนของโลหะ-กรดแอมิโนที่สังเคราะห์ คือ $\text{Cu}(\text{OAc})(\text{Val})$, $\text{Cu}(\text{OAc})(\text{Arg})$, $\text{Zn}(\text{OAc})(\text{Val})$, $\text{Zn}(\text{OAc})(\text{Arg})$, $\text{Zn}(\text{OAc})(\text{Ser})$ และ $\text{Zn}(\text{OAc})(\text{Ile})$ โดย OAc = แอซิเตท, Val = วาเลอีน, Arg = อาร์จินีน, Ser = ซีรีน และ Ile = ไอโซลิวซีน สังเคราะห์ในรูปแบบสารละลายของสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนที่ละลายในน้ำ นำสารละลายของสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนนี้มาใช้เป็นตัวเร่งปฏิกิริยาสำหรับการเตรียมพอลิยูรีเทนโฟมแบบแข็งโดยไม่ต้องทำให้บริสุทธิ์ พิสูจน์เอกลักษณ์ของสารประกอบเชิงซ้อนซิงก์-กรดแอมิโนโดยใช้แมสสเปกโตรเมตรีและอินฟราเรดสเปกโตรสโกปี ศึกษาประสิทธิภาพในการเร่งปฏิกิริยาของสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนจากเวลาที่ใช้ในการเกิดปฏิกิริยาของการเกิดโฟม ตรวจสอบสมบัติทางกายภาพและสมบัติทางเชิงกลของพอลิยูรีเทนโฟมแบบแข็ง เปรียบเทียบกับพอลิยูรีเทนโฟมที่เร่งปฏิกิริยาด้วยไดเมทิลไฮโคลเฮกซิลแอมินซึ่งเป็นตัวเร่งปฏิกิริยาทางการค้า จากผลการทดลองพบว่า สารประกอบเชิงซ้อน $\text{Zn}(\text{OAc})(\text{Val})$ มีความว่องไวในการเร่งปฏิกิริยาสูงกว่าสารประกอบเชิงซ้อนโลหะ-กรดแอมิโนชนิดอื่น และให้พอลิยูรีเทนโฟมที่มีความหนาแน่น สมบัติทางกายภาพและสมบัติทางเชิงกลคล้ายกับพอลิยูรีเทนโฟมแบบแข็งที่เตรียมจากไดเมทิลไฮโคลเฮกซิลแอมิน

สาขาวิชา ปีโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต

ปีการศึกษา 2559

ลายมือชื่อ อ.ที่ปรึกษาหลัก

5772132023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: RIGID POLYURETHANE FOAM / METAL-AMINO ACID COMPLEX / CATALYST

WORANUT KEAWMANG: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY METAL-VALINE AND METAL-ARGININE COMPLEXES. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph.D., 113 pp.

This research studied new catalysts for rigid polyurethane foam (RPUR foam) preparation, namely metal-amino acid complexes, which are odorless and low toxicity. The metal-amino acid complexes synthesized were $\text{Cu}(\text{OAc})(\text{Val})$, $\text{Cu}(\text{OAc})(\text{Arg})$, $\text{Zn}(\text{OAc})(\text{Val})$, $\text{Zn}(\text{OAc})(\text{Arg})$, $\text{Zn}(\text{OAc})(\text{Ser})$ and $\text{Zn}(\text{OAc})(\text{Ile})$; where OAc = acetate, Val = valine, Arg = arginine, Ser = serine and Ile = isoleucine. The synthesis was done to obtain aqueous solution of metal-amino acid complexes in water. These metal-amino acid complexes were used as catalysts in the preparation of rigid polyurethane foams without purification. Characterization of zinc-amino acid complexes was done using mass spectrometry and FTIR spectroscopy. The catalytic activity of metal-amino acid complexes was studied by investigation of the reaction time of the foam formation. Physical and mechanical properties of RPUR foams were investigated. The results were compared with those catalyzed by dimethylcyclohexylamine (DMCHA), which is a commercial catalyst. The experimental results $\text{Zn}(\text{OAc})(\text{Val})$ showed the best catalytic activity among all metal-amino acid complexes. $\text{Zn}(\text{OAc})(\text{Val})$ gave polyurethane foam having density, physical and mechanical properties similar to that catalyzed by dimethylcyclohexylamine.

Field of Study: Petrochemistry and
Polymer Science

Student's Signature

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Academic Year: 2016

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Associate Professor Dr. Nuanphun Chantarasiri for kindness, invaluable advice, supervision and constant encouragement throughout the course of this research. I would like to thank Assistant Professor Dr. Duangruthai Sridaeng, for kindness and valuable suggestions.

I also would like to thank my committee members, Professor Dr. Suda Kiatkamjornwong and Dr. Duangamol Tungasmita, for valuable comments and suggestions.

Definitely, this research cannot be completed without kindness and helpful of many organizations. Firstly, I wish to express thanks to IRPC Public Company Limited for supplying the chemicals used in the preparation of rigid polyurethane foams. Special thanks are due to Program of Petrochemistry and Polymer Science, Chulalongkorn University; Department of chemistry, Faculty of Science, Chulalongkorn University and Scientific and Technological Research Equipment Center, Chulalongkorn University.

Furthermore, I would like to thank my friends and all members of Supramolecular Chemistry Research Unit for their encouragement, advice and generous helps. Finally, I would like to express my deepest gratitude to my family, especially my father and mother for their love, supports and encouragement.

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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
$^{\circ}\text{C}$	degree Celsius (centigrade)
CO_2	carbondioxide gas
CFCs	chlorofluorocarbons
$\text{Cu}(\text{OAc})_2$	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
Tmax	maximum core temperature
TEDA	triethylenediamine
TDI	toluene diisocyanate
trien	triethylenetetramine
UV	ultraviolet



CHAPTER I

INTRODUCTION

Polyurethane foams (PUR foams) have an important role in many industries. They are used in the manufacture for a variety of applications such as car seating, car exterior panels, bedding, buoyancy in boats, housings for electronic equipment, shoe and boot soles [1]. PUR foam can be subdivided into three types, namely flexible foam, semi-rigid foam and rigid foam [2].

Rigid polyurethane (RPUR) foams are widely used materials due to their light weight, low thermal conductivity and high compressive-strength properties. They are used as packaging materials, furniture and the insulation of refrigerators, coolers, freezers, building engineering and construction [3, 4]. RPUR foams are synthesized by the polymerization reaction between di- or polyisocyanate group in polymeric methylene diphenyl diisocyanate (PMDI) and di- or polyhydroxyl group in polyol to form urethane linkages. This reaction is called the “gelling reaction”. When water is used as a blowing agent, the reaction of isocyanate with water gives carbamic acid, which decomposes to give amine and carbon dioxide gas (CO_2). Carbon dioxide expands as air bubbles to result a rise of foam. This reaction is called the “blowing reaction”. Nevertheless, the gelling and blowing reactions are slow. Catalyst is an essential component for RPUR foam preparation.

The commercial catalysts used for RPUR foam preparation are *N,N*-dimethylcyclohexylamine (DMCHA) and 1,4-diazabicyclo[2,2,2]octane (DABCO) [5]. These commercial catalysts have good catalytic activity, but they have strong odor and emit odor in the working environment during the foam preparation. Therefore, new catalysts are necessary to replace these commercial catalysts.

From the previous researches in our group, copper-amine complexes were synthesized and used as catalysts in RPUR foam preparation. The copper-amine complexes investigated were $\text{Cu}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$, where OAc = acetate,

en = ethylenediamine and trien = triethylenetetramine. These catalysts had good catalytic activity and odorless when compared to DMCHA [6]. However, the amines used in the synthesis of metal-amine complexes are toxic. Therefore, this research is interested in the synthesis of metal-amino acid complexes from less toxic amino acids.

Objectives of the research

The objective of this research was to synthesize metal-amino acid complexes in the form of solution in water that could be used as catalysts in the preparation of RPUR foam without purification. Metal-amino acid complexes synthesized were Cu(OAc)(Val), Cu(OAc)(Arg), Zn(OAc)(Val), Zn(OAc)(Arg), Zn(OAc)(Ser) and Zn(OAc)(Ile), where OAc = acetate, Val = valine, Arg = Arginine, Ser = serine and Ile = isoleucine. It was expected that metal-amino acid complexes could be easily prepared, odorless, have good solubility as starting materials of RPUR foam formulation and had good catalytic activity.

Scope of the research

The scopes of this research can be divided into two parts (Figure 1.1). In the first part, metal-amino acid complexes were synthesized in the form of solution in water (aqueous solution). Metal acetates used were copper acetate [Cu(OAc)₂] and zinc acetate [Zn(OAc)₂]. Amino acids used were valine (Val), arginine (Arg), serine (Ser) and isoleucine (Ile). The concentrations of metal-amino acid complexes in water and the mole ratios of metal:amino acid were varied. Mass spectrometry and FTIR spectroscopy were used to characterize metal-amino acid complexes.

In the second part, RPUR foams were prepared by using aqueous solution of metal-amino acid complexes as catalysts. RPUR foams were prepared using cup test method and plastic mold. The reaction times, foaming temperature, free rise density, height of foams and NCO conversion of RPUR foams prepared by cup test method

were investigated. The RPUR foams prepared in plastic mold were used to investigate density, mechanical properties and morphology.

The reaction time, physical and mechanical properties of RPUR foam prepared by using the metal-amino acid complexes as catalysts were compared with those catalyzed by DMCHA, which is used as a reference commercial catalyst.



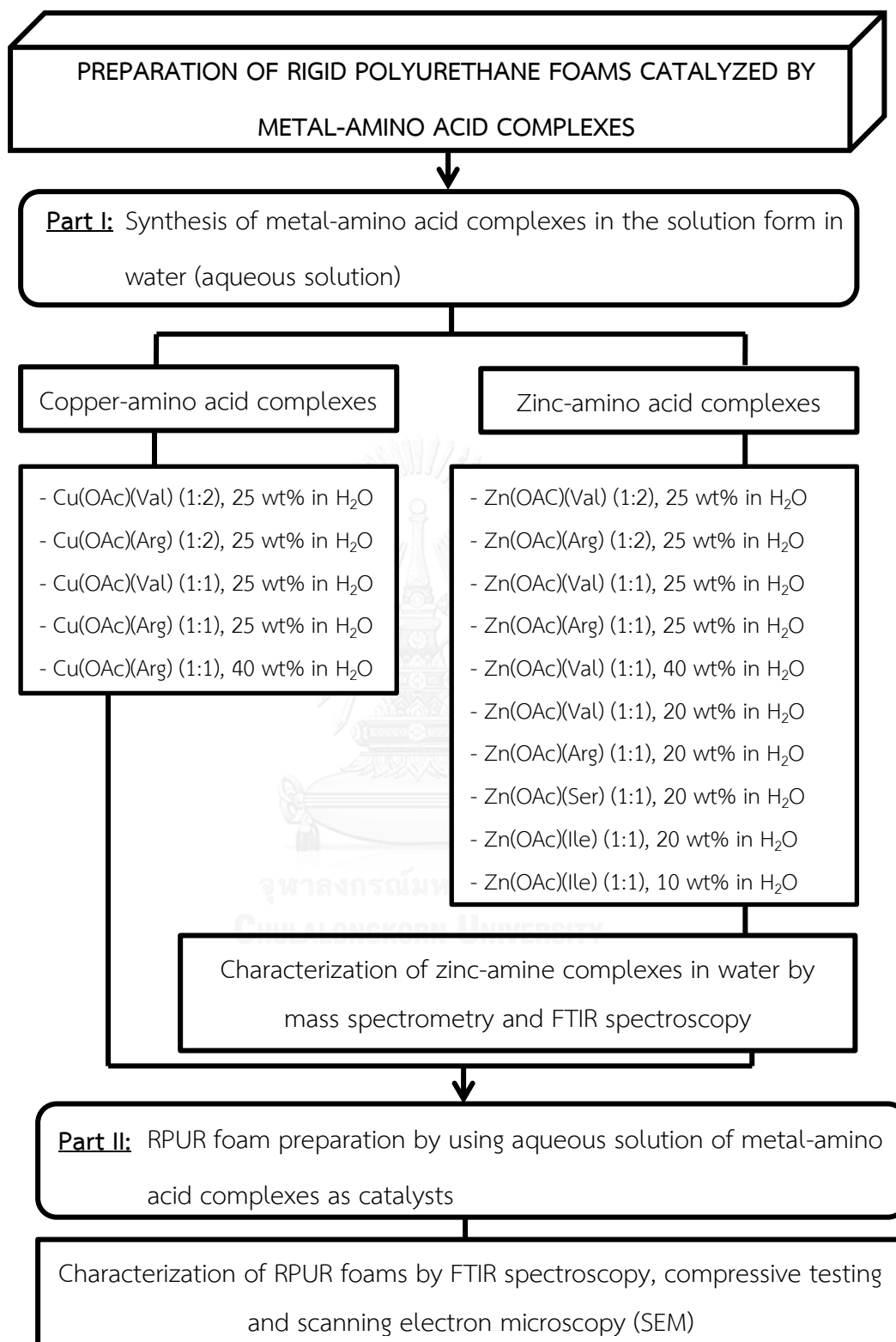


Figure 1.1 Scope of experiments

CHAPTER II

THEORY AND LITERATURE REVIEW

Polyurethane foams (PUR foams) were discovered by Otto Bayer and co-worker in 1937 at the I.G. Farbenn industries in Leverkusen, Germany. They made polyurethane foams by polyaddition processes [1, 7]. The polymerization of polyurethane foams was obtained from polyol molecules containing two or more hydroxyl groups and isocyanate molecules with two or more isocyanate groups. Moreover, other components such as surfactants, blowing agents, catalysts and other additives were employed. The properties of PUR foams can be modified in widely range, which depends on types of starting materials in foam formulation. The types of PUR foams can be subdivided into three types: flexible foam, semi-rigid foam and rigid foam [2].

Rigid polyurethane (RPUR) foams are widely used as building engineering, construction insulation and in the insulation of refrigerators, coolers, pipes. Other applications for RPUR foams are packaging materials and molded furniture, because of their low thermal conductivity and good mechanical properties [4, 7].

2.1 Raw materials

The main raw materials used to prepare polyurethane foam are isocyanate and polyol 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 [8].

2.1.1 Diphenylmethane diisocyanate (MDI)

The major isocyanates are aromatic isocyanates and aliphatic isocyanates [1]. The two aromatic isocyanates were used for the production of rigid polyurethane foams because it has high reactivity in foaming reaction [9]. Diphenylmethane diisocyanate or methylene diphenylene diisocyanate (MDI) are two aromatic isocyanate compounds. MDI is obtained from the reaction of aniline and formaldehyde [10]. 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. Polymeric MDI is dark brown liquid at room temperature. Pure MDI is a white to pale yellow solid of melting point about 38 °C, which obtained from the distillation process of polymeric MDI and used for elastomer and coating [11]. The chemical structures of each MDI isomer and polymeric MDI are shown in Figures 2.1 and 2.2, respectively.

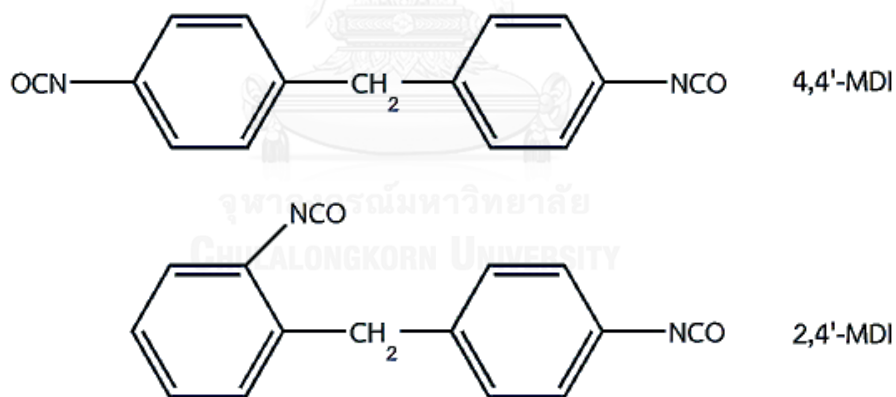


Figure 2.1 Isomeric structures of monomeric MDI

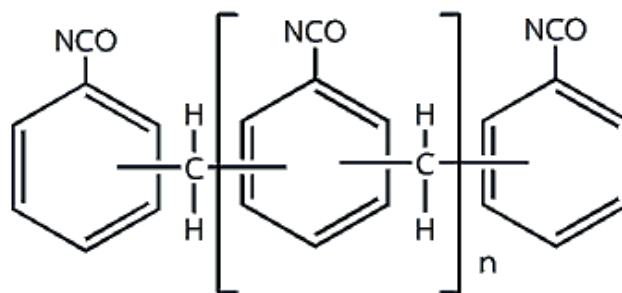


Figure 2.2 Structures of polymeric MDI (PMDI)

2.1.2 Polyols

The polyols used for the production of PUR foams are classified in two types, namely polyether polyols and polyester polyols. The molecular weight and functionality of polyols determined the properties of PUR foams. Polyols used in flexible polyurethane foams and rigid polyurethane foams have different properties. Flexible polyurethane foams need lower functionality and higher molecular weight polyols. RPUR foams need higher functionality and lower molecular weight polyols in order to get the higher degree of crosslinking which contributes to the stiffness of polymer. Polyols used for RPUR foam preparation have molecular weight of 150-1000 g/mol, functionality 2.5-8.0 and hydroxyl value of 250-1000 mgKOH/g [12].

2.1.2.1 Polyether polyols

Polyether polyols are produced by the ring opening of alkylene oxides using a polyfunctional as initiator. The polyfunctional initiator compounds are ethylene glycol, glycerol, pentaerythritol, trimethylolpropane, sorbitol and sucrose (Table 2.1). Polyether polyols have wide range of functionality and equivalent weight together with the low viscosity and production cost is cheaper but lower oxidation resistance than that polyester polyols [11]. The molecular weight of polyether polyols used for making RPUR foams are 500 g/mol in order to reduce the distance between crosslinking. Most polyols used in manufacturing PUR foams are polyether polyols because of low cost

and ease of handling (low viscosity) [1, 2]. An example polyether polyols is shown in Figure 2.3.

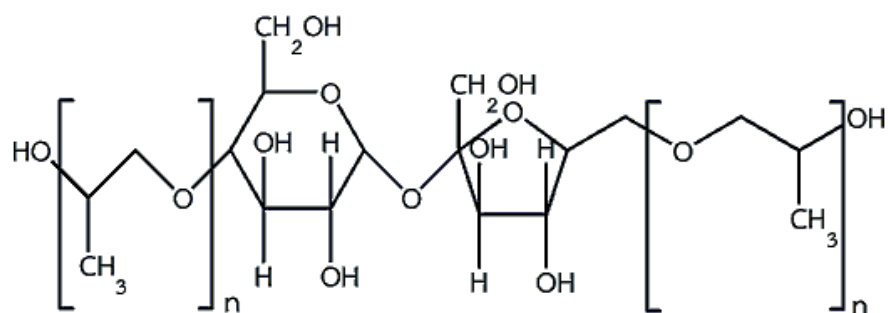
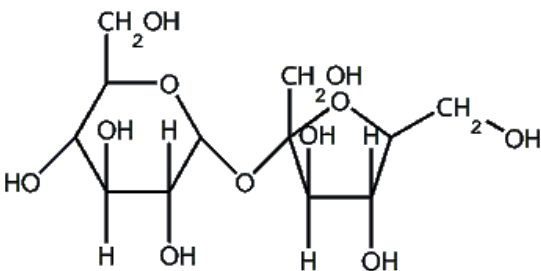


Figure 2.3 Structure of polyether sucrose-based polyol [poly(propyleneoxy sucrose)]



Table 2.1 Polyfunctional initiator compounds used for preparing commercial polyols

Hydroxylated compound	Chemical Structure	Functionality
Ethylene glycol (EG)	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	2
Glycerol	$\begin{array}{c} \text{H}_2\text{C}-\text{OH} \\ \\ \text{HC}-\text{OH} \\ \\ \text{H}_2\text{C}-\text{OH} \end{array}$	3
Trimethylol propane (TMP)	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{HC}-\text{CH}_2-\text{OH} \\ \\ \text{H}_2\text{C}-\text{CH}_2-\text{OH} \end{array}$	3
Pentaerythritol	$\begin{array}{c} \text{H}_2\text{C}-\text{OH} \\ \\ \text{HO}-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{H}_2\text{C}-\text{OH} \end{array}$	4
Sorbitol	$\text{HO}-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2-\text{OH}$	6
Sucrose		8

2.1.2.2 Polyester polyols

Polyester polyols are produced by condensation or step-growth polymerization reactions between diols (and triol) and dicarboxylic acid such as adipic acid, sebacic acid and three isomeric phthalic acids. Polyester polyols give polyurethane foams with good mechanical properties and resistance to oils, solvents and oxidation. However, they are more expensive, more viscous and therefore not easy to handle. Consequently, they are only used in application that need their superior properties. In addition, polyester polyols can be used to produce both flexible and RPUR foams [9].

2.1.3 Surfactants

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 [13]. The surfactants most widely used in the polyurethane manufacturing are polydimethyl siloxane-polyether copolymer or silicone surfactants. (Figure 2.4). The silicone surfactants are usually added in the amount of 0.4-2.0% w/w of the polyol formulation.

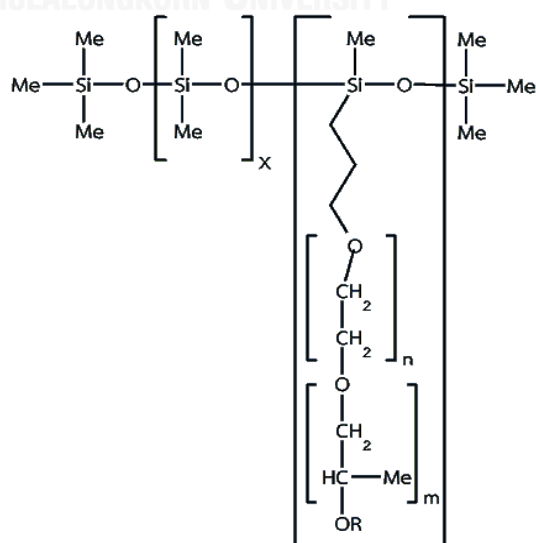


Figure 2.4 Structure of silicone surfactant used in the PUR foam preparation

2.1.4 Blowing agents

Polyurethane foams are produced by using blowing agents which create gas bubbles in the reaction mixture. Types and amounts of blowing agents are considerably influenced to the properties of PUR foam. Blowing agents used for PUR foam preparation are divided in two types, namely physical and chemical blowing agents.

Chemical blowing agents are chemical compound that react with isocyanate groups to generate carbon dioxide (CO₂) gas and give cellular structure of foams. Water is one of the most widely used chemical blowing agents used for the foaming reaction. The reaction of water with isocyanates is exothermic reaction. The amount of water used for PUR foam preparation is 3-5 parts of water per 100 parts of polyol.

Physical blowing agents are inert liquids that have low molecular weight, low boiling points and no reactivity to isocyanate groups. They can be evaporated by the heat of foaming reaction. Examples of physical blowing agents are chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and perfluorinated hydrocarbons (PFCs). They cause depletion of the ozone layer. Therefore, the use of environmentally friendly blowing agents has become an important in the preparation of PUR foams. Water and cyclopentane have replaced such environmentally hazardous blowing agents [11, 14].

2.1.5 Catalysts

Catalyst is important in RPUR foam preparation. It accelerates the reaction of isocyanates with water and with polyols. Catalysts used for RPUR foam preparation are tertiary amines, quaternary ammonium salts, alkali metal carboxylates and organotin compounds (Table 2.2 and Figure 2.5) [15]. Types and amount of the catalysts influence the rate of reaction and the properties of RPUR foams. Generally, the amount of catalyst is used about 1-4 parts by weight per 100 parts of polyol [3].

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 [14].

Table 2.2 Commercial catalysts used for preparing RPUR foams [15]

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

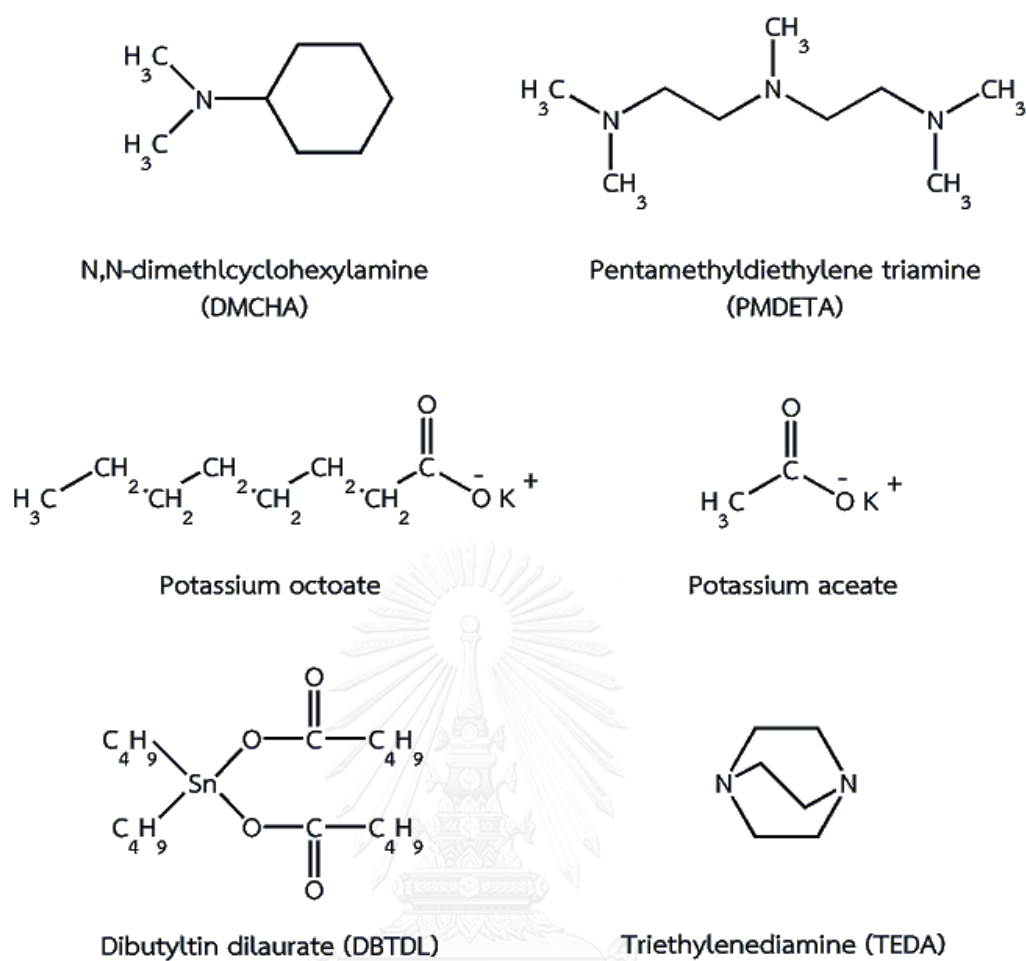


Figure 2.5 Structure of commercial catalysts used in RPUR foam preparation

When the catalyst too strongly promotes the blowing reaction, much of the CO_2 gas will be evolved before sufficient reaction of isocyanate with polyol occurs. The CO_2 gas will bubble out of the formulation, resulting in collapse of the foam. If a catalyst too strongly promotes the gelling reaction, most CO_2 gas will be generated after a significant degree of polymerization has occurred. This results in RPUR foam having high density, broken or poorly defined cells or other undesirable features.

2.1.6 Additives

2.1.6.1 Flame retardants

The addition of flame retardants to polyurethane foams reduces the level of fire, flame and smoke combustion products. The addition of small amounts (up to 2 parts per hundred of polyol) of flame retardant has little or no effect on foam physical properties, but adverse effects are noticeable when higher amounts are used. The fire retardants used for polyurethane system are chlorinated phosphate ester [1, 2].

2.1.6.2 Fillers

Particulate fillers for polyurethane system are used to reduce cost, increase compression resistance, compressive strength and weight of seat cushion. Reinforcing fibrous fillers are used to increase stiffness, heat resistance and tensile strength. Typical fillers such as calcium carbonate, barium sulphate, carbon fibers and carbon black [1, 2].

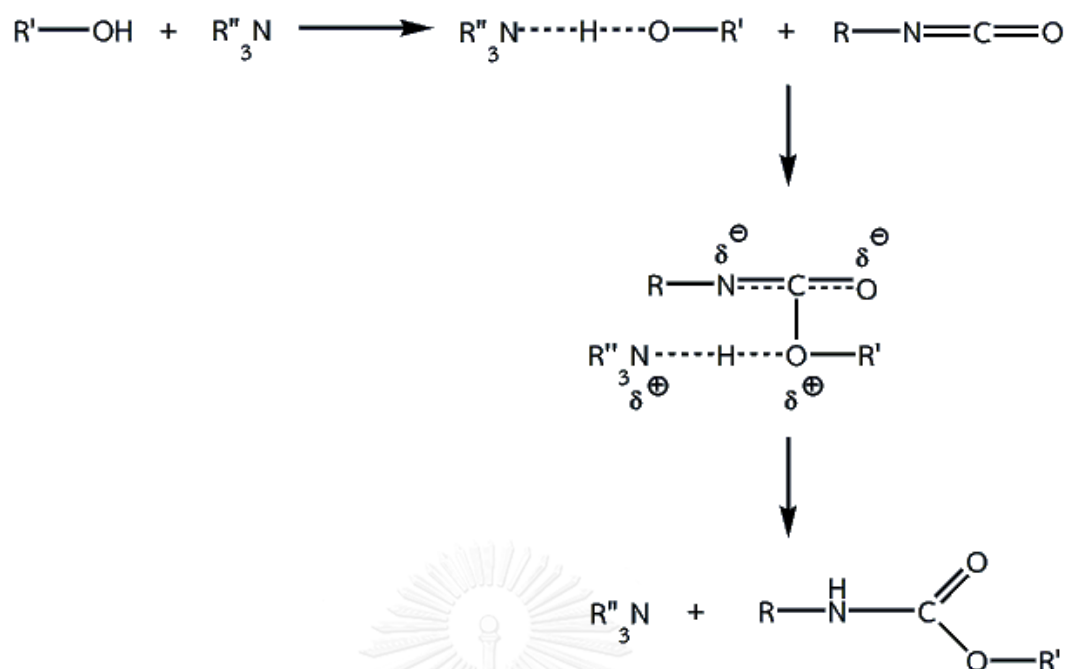
2.1.6.3 Coloring Materials

Pigments used must be inert to isocyanates and stable at the reaction temperature. Pigments can be inorganic or organic in nature. The inorganic pigments include titanium dioxide, chromium oxide, carbon black and iron oxide. The organic pigments often include phthalocyanines and dioxazines [1, 2].

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 [5]. The first mechanism proposed by Baker as shown in Scheme 2.1. The activation starts by the tertiary nitrogen of amine using its lone pair of electrons to coordinate with the positive electron charged carbon of the isocyanate group, then the complex

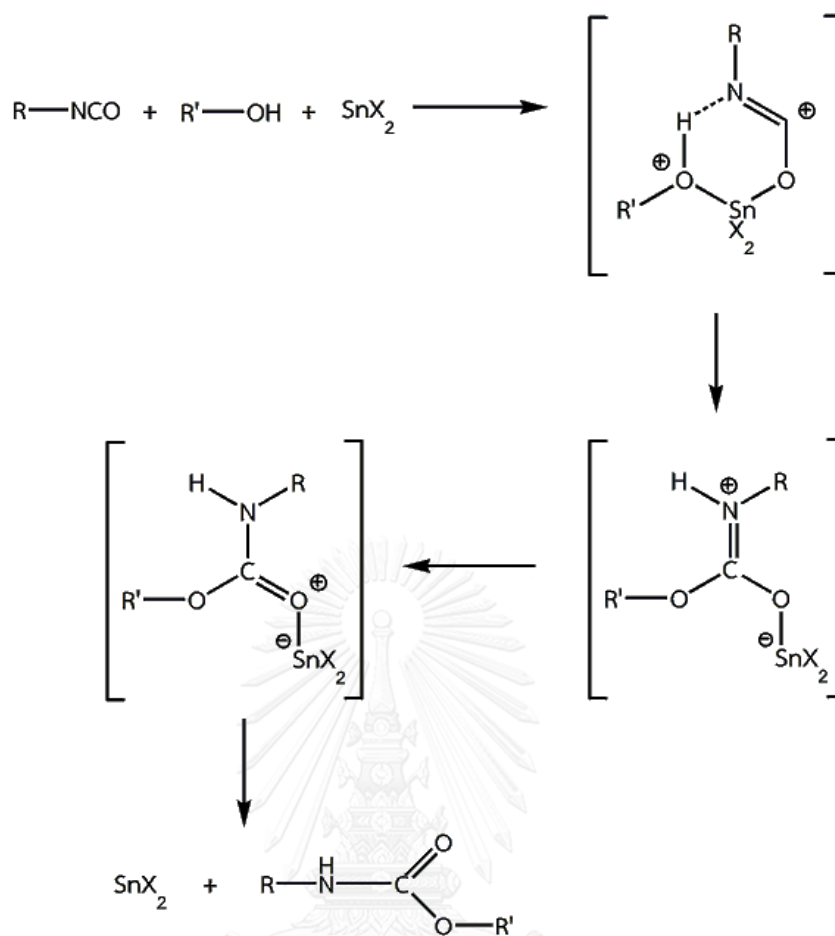


Scheme 2.2 Farka mechanism of amine catalysts

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

2.2.2 Organotin catalysts

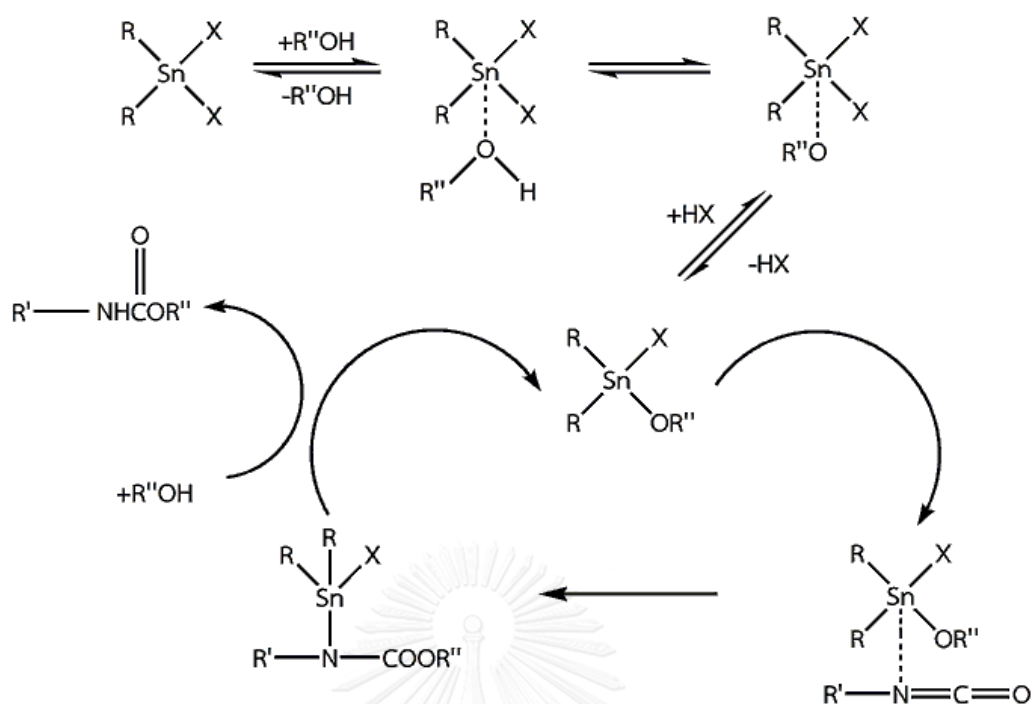
The catalytic mechanism of tin (II) salt is shown in Scheme 2.3. The activation starts by organotin catalyst to coordinate with oxygen atom of isocyanate and polyol, which then gives the urethane product. The functions of organotin catalysts are to increase the positive electron to give the carbon atom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



Scheme 2.3 Mechanism of tin (II) salt catalysts

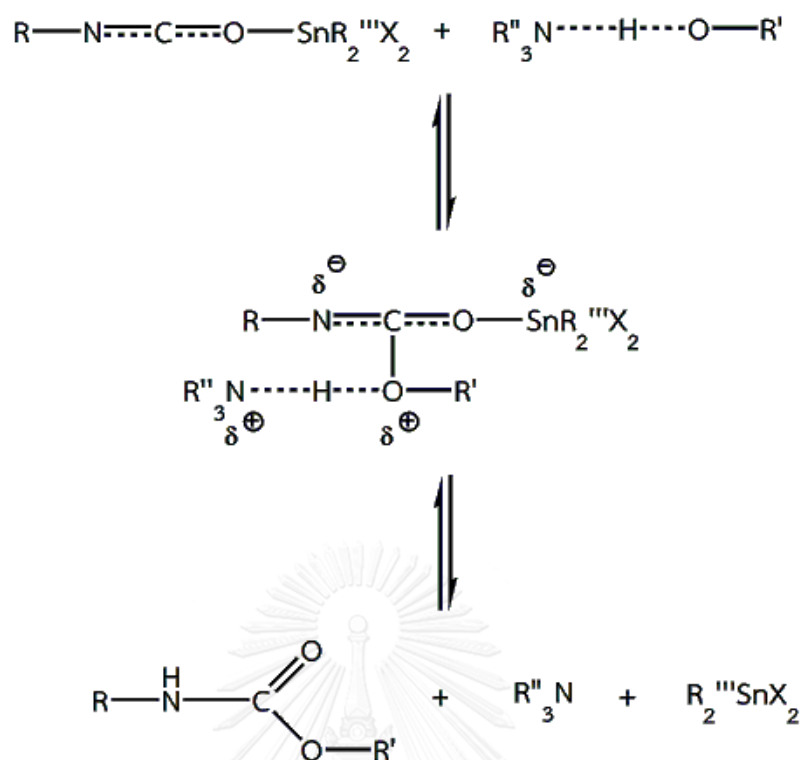
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The catalytic mechanism of tin (IV) catalysts, such as dialkyltin dicarbonates and dialkyltin dialkylthiolates (Scheme 2.4), is the reaction of the tin with a polyol to form a tin alkoxide, which can then react with the isocyanate to form a complex.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



Scheme 2.4 Mechanism of tin (IV) salt catalysts

When tin compound and amines are used as the catalyst mixtures, a synergistic effect of these two catalysts is observed (Scheme 2.5). The tin compound coordinated to the oxygen atom of the isocyanate group contribute to activate the electrophilic nature of the carbon. While amine coordinated to the hydrogen of the OH group and forms a transition state to activate urethane formation reaction.



Scheme 2.5 Mechanism of tin-amine synergism

2.3 Basic urethane chemistry

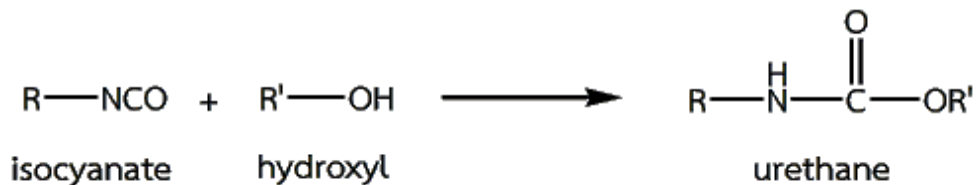
The reaction in polyurethane formation is the exothermic reaction between di- or polyfunctional isocyanate and di- or polyfunctional hydroxyl group. For simplicity, the basic principle of urethane chemistry is explained below using monofunctional reagents.

2.3.1 Primary reaction of isocyanates

2.3.1.1 Reaction of isocyanate with polyol

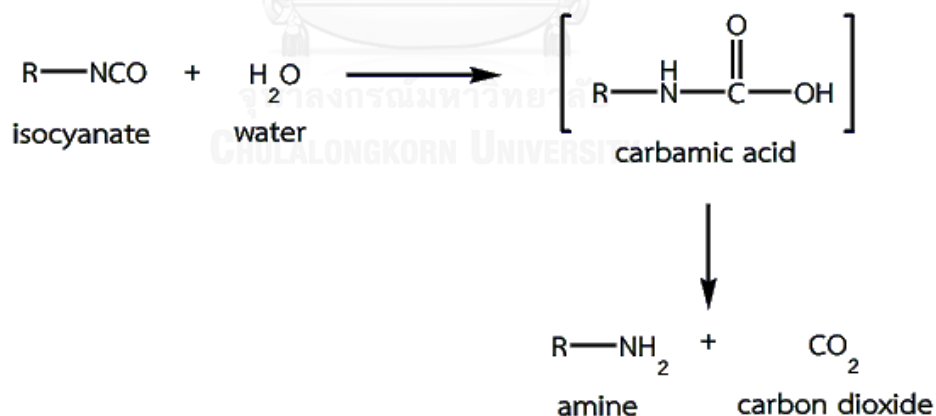
The reaction between isocyanate and hydroxyl group in the manufacture of polyurethane is called the “gelling reaction”, which is the important reaction. This reaction is an exothermic reaction. The chemical structure of the isocyanate and

polyols affects the rate of polymerization. The catalyst is used to accelerate the reaction rate.



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 CO₂ produced is used for blowing the foam. The reaction rate is accelerated by a suitable choice of catalyst [5].



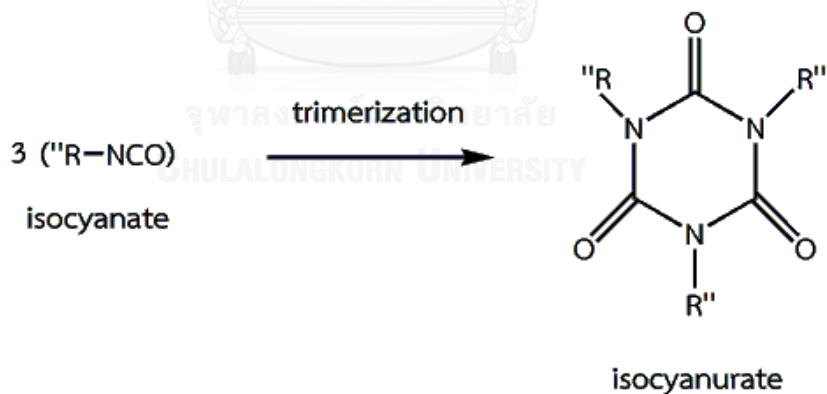
2.3.1.3 Reaction of isocyanate with amine

The reaction between isocyanate and amine produces the urea linkage. 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.



2.3.2 Secondary reaction of isocyanate

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 [2].



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, 2].

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

$$\begin{aligned} \text{Isocyanate value} = \% \text{ NCO group} &= \frac{42 \times \text{functionality}}{\text{molar mass}} \times 100 \\ &= \frac{4200}{\text{equivalent weight}} \end{aligned}$$

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.

$$\begin{aligned} \text{Hydroxyl value} &= \frac{56.1 \times \text{functionality}}{\text{molar mass}} \times 1000 \\ &= \frac{56.1}{\text{equivalent weight}} \times 1000 \end{aligned}$$

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:

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

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 most important mechanical properties for PUR foams. Compressive properties depend on density, type of base polymer and the predominance of either open or closed cells.

Open cell foam relies on cell walls bending and bucking, which is essentially a reversible process as shown in Figure 2.6. Besides, the cells more compacted during compression, the escape of air through and out of the foam will become increasingly more difficult. The entrapped air will therefore offers some resistance to foam deformation during the final stages of compression.

For close cell foam, deformation involves cell wall bending and bucking, gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rupture as shown in Figure 2.7.

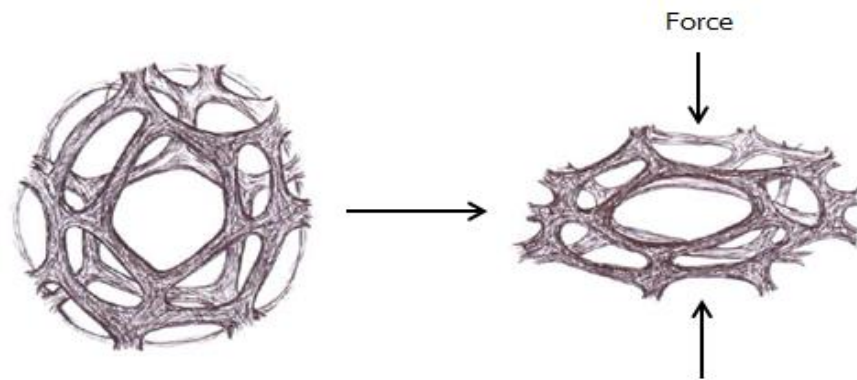


Figure 2.6 Open cell deformation [2]

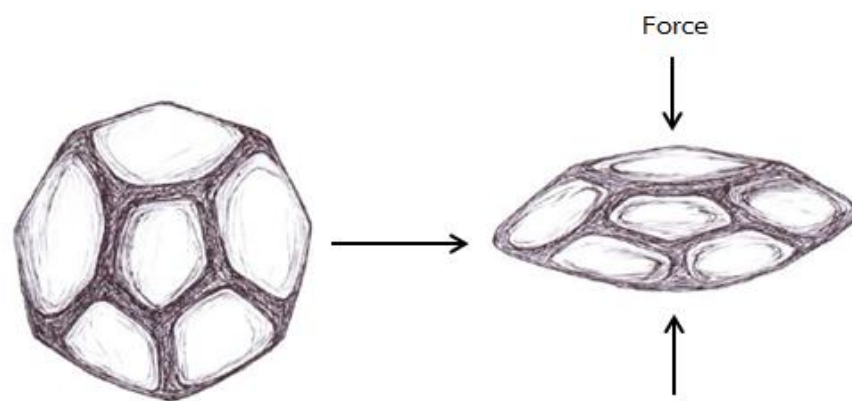


Figure 2.7 Closed cell deformation [2]

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. Besides, 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.

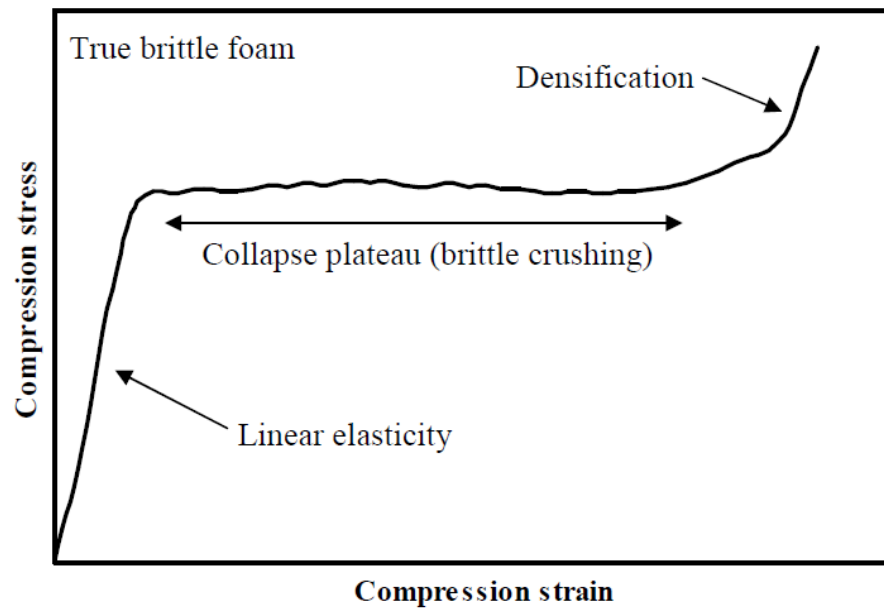


Figure 2.8 Typical compressive stress-strain curve for RPUR foam [16]

For RPUR foams, the compressive strain-strain curve is divided in three parts. (I) 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.

The compressive strength of RPUR foams is usually reported at some definite deformation (5 or 10%). The compressive strength of the foam cell in the direction of foam rise is higher than that in the direction of perpendicular to the foam rise [16].

2.6 Literature reviews

The starting materials used in the preparation of polyurethane foams can be divided into three parts, namely polyol, isocyanate and blowing agent (H_2O). 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 but it has strong odor and emits odor in the working environment during the foam preparation. A new catalyst is necessary to replace these commercial catalysts. The previous researches had studied and developed the new catalysts for polyurethane foam preparation which are described as follows:

From the previous works in our research group, Sridaeng and coworkers [17] 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 metal-amine complexes were used in the preparation of RPUR foam. 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 did the RPUR foam prepared by DMCHA.

Pengjam and coworkers [6] synthesized $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ complexes (where en = ethylenediamine and $trien$ = triethylenetetramine). These copper-amine 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.

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:

Di and coworkers [18] synthesized metal-amino acid complexes from zinc sulphate and L- α -amino acid (abbreviated as AA). The AA used were valine (Val), methionine (Met), histidine (His) and threonine (Thr). The mole ratio of (ZnSO₄):(AA) was 1:1. Water and acetone were used as solvents. The complex formation is shown in the following reaction:



These complexes were isolated as white crystals, namely Zn(Val)SO₄ · H₂O, Zn(Met)SO₄ · H₂O, Zn(His)SO₄ · H₂O and Zn(Thr)SO₄ · H₂O.

Chen and coworkers [19] prepared the metal-amino acid complex of zinc acetate dehydrate and L- α -methionine. Water and acetone were used as solvents at the volume ratio of water:acetone = 1:25. The zinc acetate-methionine complex was isolated as a white solid. The complex formation is shown below:



Nishat and coworkers [20] prepared metal-glycine complexes from the reactions of metal acetates [M(OAc)₂ where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] with glycine using ethanol as a solvent. The mole ratio of metal acetate:glycine used was 1:2 (Figure 2.9).

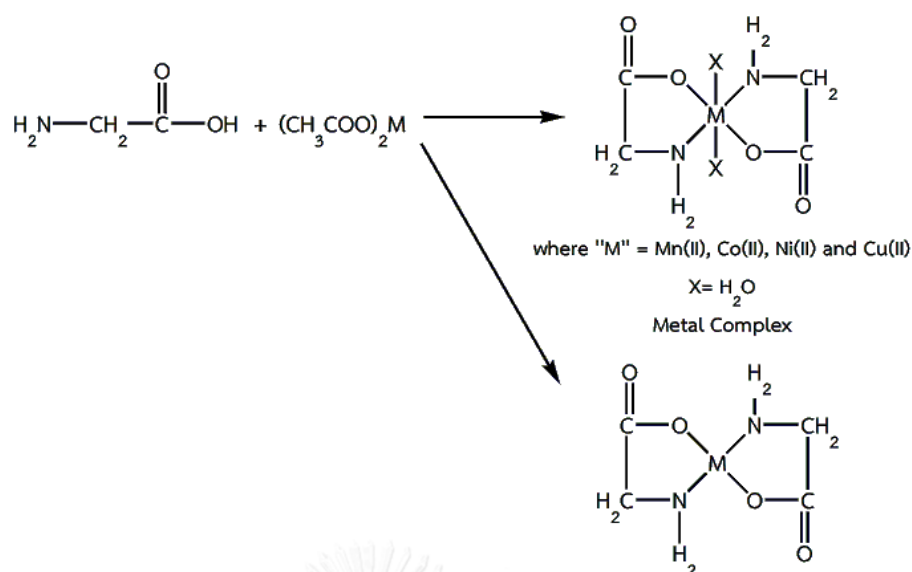


Figure 2.9 Synthesis of metal- glycine complex [20]

Graddon and coworkers [21] prepared and studied the solubility of copper(II) sulphate- α -amino acid complexes in water. The mole ratio of copper(II) sulphate: α -amino-acid used was 1:2. Amino acids used were glycine, α -alanine, valine and leucine. They found that the solubility of copper(II) sulphate- α -amino acid complexes decreased when α -amino acid had the length of alkyl chain attached to carbon atom over two carbon atoms. This was because alkyl groups hindered the interaction of water molecules with copper atom.

Herlinger and coworkers [22] investigated the structure of bis(amino acidato)copper(II) complexes in aqueous solution state and solid state. Bis(amino acidato)copper(II) complexes studied were Cu(gly)₂, Cu(DL-ala)₂, Cu(L-ala)₂, Cu(DL- α -ABA)₂, Cu(DL-ile)₂, Cu(L-ile)₂, Cu(DL-val)₂, Cu(L-val)₂, Cu(DL-leu)₂, Cu(L-leu)₂, Cu(DL-phe)₂ and Cu(L-phe)₂ (gly = glycine, ala = alanine, ABA = DL- α -Amino-*n*-butyric, ile = isoleucine, val = valine, leu = leucine and phe = phenylalanine). They found that these complexes had a trans structure, except Cu(gly)₂, Cu(L-ala)₂, Cu(L-ile)₂, Cu(DL-ile)₂ and Cu(DL-phe)₂ which had a cis structure.

Lv and coworkers [23] synthesized metal-valine complexes from copper(II) perchlorate hexahydrate $[\text{Cu}(\text{ClO}_4)_2]$ and cobalt(II) perchlorate hexahydrate $[\text{Co}(\text{ClO}_4)_2]$ with L-valine using potassium hydroxide (KOH) and methanol (MeOH) as a solvent (Figure 2.10). Cu(II)-L-valine and Co(II)-L-valine complexes were characterized by X-ray diffraction (XRD) and found that they had the crystal system as orthorhombic and monoclinic, respectively.

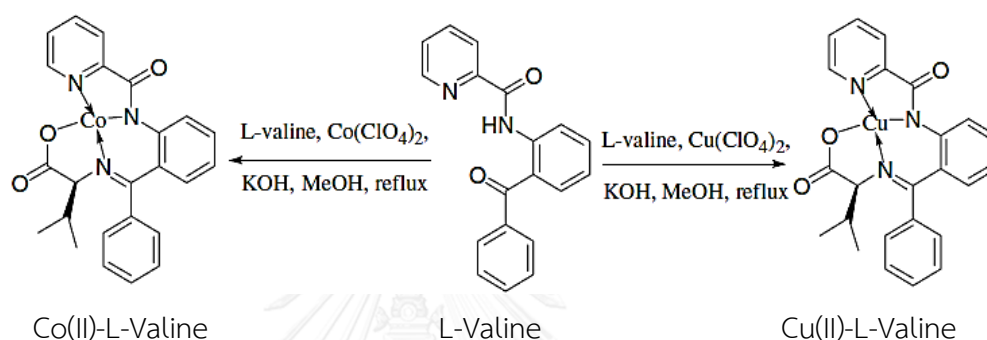


Figure 2.10 Synthesis of Cu(II)-L-valine and Co(II)-L-valine complexes [23]

Many researches used metal-amino acid complexes as catalysts for the various reactions as follows:

Chen and coworkers [24] synthesized copper-amino acid complexes from copper(II) bromide (CuBr), copper(II) dibromide (CuBr_2), copper(I) chloride (CuCl), arginine, guanine, adenine, cytosine and histidine using water as a solvent to obtain aqueous solution of copper-amino acid complexes. It was found that the solution of these copper-amino acid complexes could be used as catalysts for poly(2,6 dimethyl-1,4-phenylene oxide) synthesis and Cu(II)-arginine showed the best catalytic activity.

Valodkar and coworkers [25] prepared copper(II) acetate-L-Valine complexes on poly(styrene-divinyl benzene) [poly(S-DVB)] as a polymer support, namely $\text{Cu}(\text{L-Val})_2(\text{OAc})_2$ -poly(S-DVB) and $\text{Cu}(\text{L-Val})_2$ -poly(S-DVB) complexes. They were used for catalytic oxidation polymerization of benzyl alcohols and cyclohexanol. It was found that these catalysts could be recycled without any loss in activity.

Kidwai and coworkers [26] synthesized 1,4- disubstituted triazoles using $\text{bis}[(\text{L})\text{prolinate-N,O}]\text{Zn}$ complex as a catalyst. The $\text{bis}[(\text{L})\text{prolinate-N,O}]\text{Zn}$ complex synthesized from the reaction of zinc acetate ($\text{Zn}(\text{OAc})_2$) with L-proline in methanol (MeOH). $\text{Bis}[(\text{L})\text{prolinate-N,O}]\text{Zn}$ complex was obtained as a white solid.

Darbem and coworkers [27] used $\text{bis}[(\text{L})\text{prolinate-N,O}]\text{Zn}$ or $\text{Zn}[\text{Pro}]_2$ complex as a catalyst for the thio-Michael reaction (Figure 2.11). They proposed the catalytic mechanism of $\text{Zn}[\text{Pro}]_2$ complex as shown in Figure 2.12.

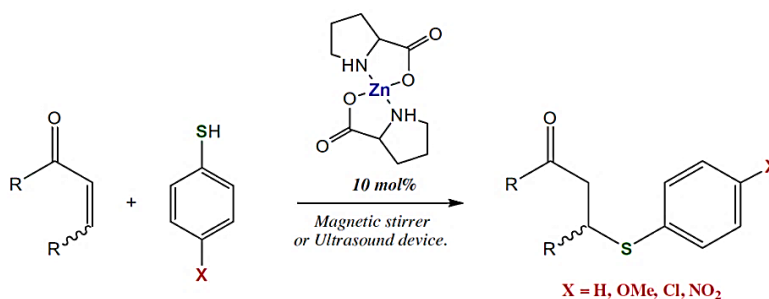


Figure 2.11 Thio-Michael reaction catalyzed by $\text{Zn}[\text{Pro}]_2$ complex [27]

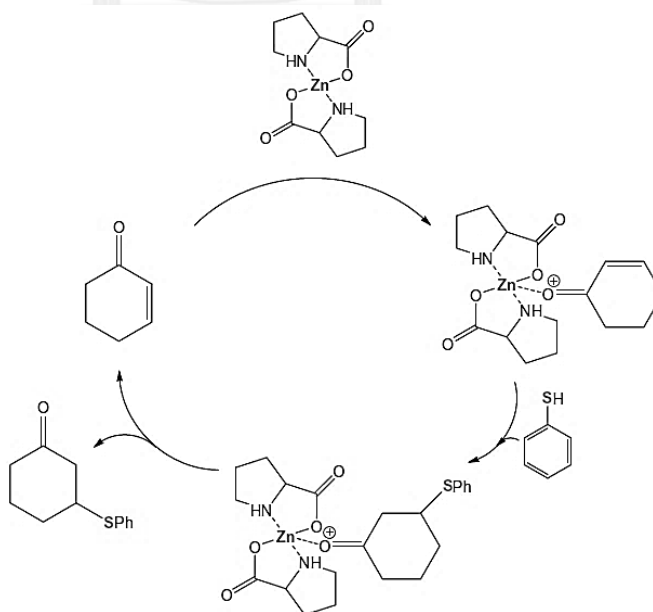


Figure 2.12 Mechanism of thio-Michael reaction catalyzed by $\text{Zn}[\text{Pro}]_2$ complex [27]

Qadir and coworkers [28] synthesized of metal-amino acid complexes [M = 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. 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. These complexes were obtained as white solids and used as nutritional supplements for animals.

The previous researches have been success to synthesis metal-amino acid complexes. The metal-amino acid complexes have been used as catalysts in different reactions and the metal-amino acid complexes have good catalytic activity.

Therefore, in this research, we were interested to synthesize the metal-amino acid complexes in the form of solution in water (aqueous solution) that could be used as catalysts in the preparation of rigid polyurethane foam (RPUR foam) without purification. The solution of metal-amino acid complexes was expected to be easily prepared, odorless, good solubility in RPUR foam formulation. Water in the aqueous solution of metal-amino acid complexes also acts as a blowing reagent in RPUR foam formulation.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and Raw materials

3.1.1 Synthesis of metal-amino acid complexes

Copper (II) acetate monohydrate $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$ was obtained from Aldrich. Zinc acetate dihydrate $[\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}]$ was obtained from Aldrich and Nacalai Tesque, respectively. DL-Valine (Val) and L-Arginine (Arg) were obtained from Aldrich. L-Serine (Ser) and L-(+)-Isoleucine (Ile) were obtained from Nacalai Tesque.

3.2.1 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'-dimethyl cyclohexylamine (DMCHA, a commercial reference catalyst). They were supplied by IRPC Public Company Limited. Distilled water was used as a blowing agent.

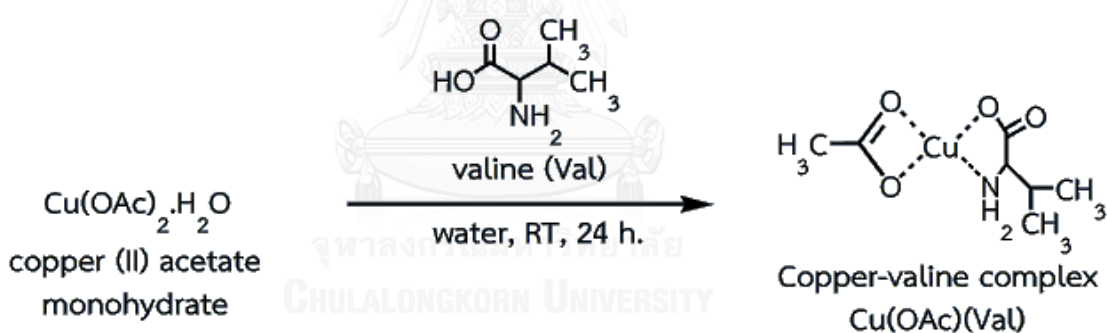
3.2 Synthesis procedures

Metal-amino acid complexes were synthesized from the reaction between metal acetate $[\text{M}(\text{OAc})_2]$ and amino acids in the form of solution in water (aqueous solution). The synthesis of metal-amino acid complexes was modified from a method reported in the literature [6, 29]. The aqueous solution of metal-amino acid complexes 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 in water are shown in Table 3.1.

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

3.2.1.1 Synthesis of copper-valine complex [Cu(OAc)(Val) (1:1) and Cu(OAc)(Val) (1:2)]

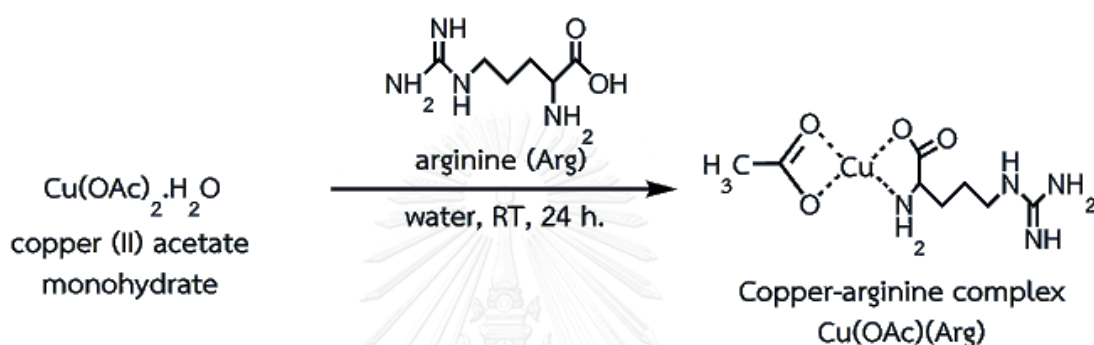
The mole ratio of copper (II) acetate monohydrate to valine was 1:1 (Scheme 3.1). The solution of Cu(OAc)(Val) in water was synthesized by using the following method: a solution of valine (0.370 g, 3.15 mmol) in water (3 ml) was stirred at room temperature for 10 minutes. Copper (II) acetate monohydrate (0.630 g, 3.15 mmol) was then added into the valine solution and the reaction mixture was stirred at room temperature for 24 hours. Cu(OAc)(Val) (1:1) at a concentration of 25 wt% solution in water was obtained as blue liquid with blue precipitate. Cu(OAc)(Val) (1:2) was synthesized by using the same method for Cu(OAc)(Val) (1:1) employing the mole ratio of copper acetate monohydrate:valine = 1:2.



Scheme 3.1 Synthesis of copper-valine complex [Cu(OAc)(Val)]

3.2.1.2 Synthesis of copper-arginine complex [Cu(OAc)(Arg) (1:1) and Cu(OAc)(Arg) (1:2)]

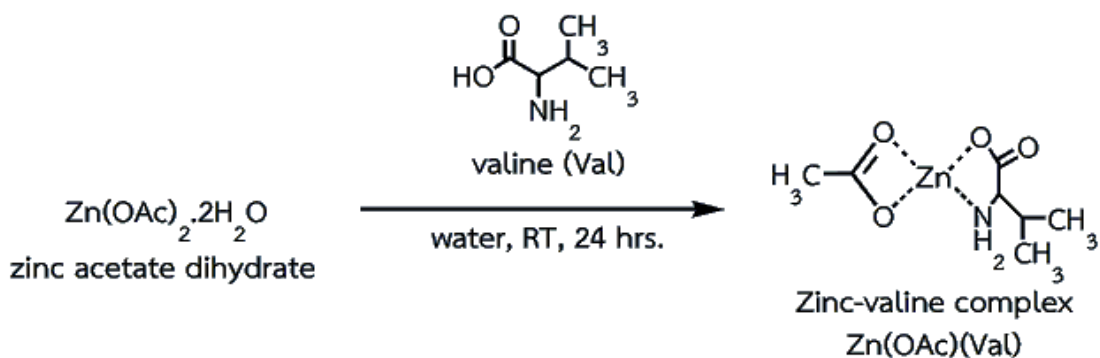
The solutions of Cu(OAc)(Arg) were synthesized by using the mole ratios between Cu(OAc)₂·H₂O:arginine = 1:1 and 1:2 (Scheme 3.2). The solutions of copper-arginine complex were obtained, namely Cu(OAc)(Arg) (1:1) and Cu(OAc)(Arg) (1:2). Copper-arginine complex were synthesized by using the same method for Cu(OAc)(Val) (1:1).



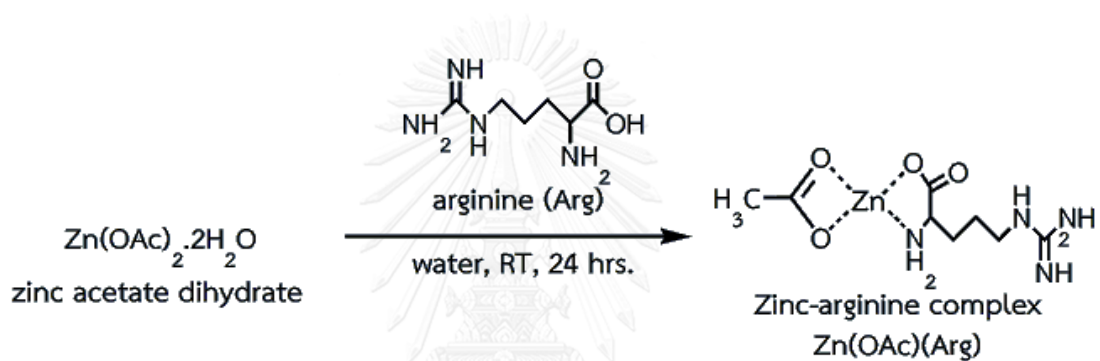
Scheme 3.2 Synthesis of copper-arginine complex [Cu(OAc)(Arg)]

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

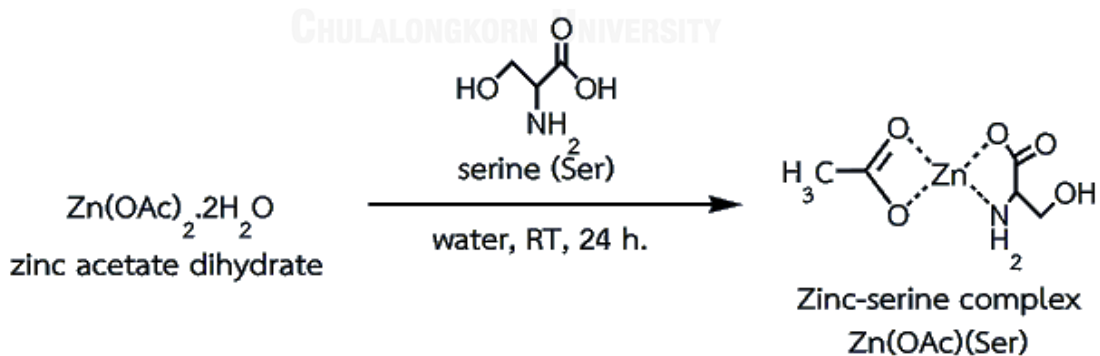
All zinc-amino acid complexes were synthesized by using the same method for Cu(OAc)(Val) (1:1). The mole ratios of zinc acetate dihydrate:amino acid employed were 1:1 and 1:2. The synthesis of zinc-valine complex [Zn(OAc)(Val)], zinc-arginine complex [Zn(OAc)(Arg)], zinc-serine complex [Zn(OAc)(Ser)] and zinc-isoleucine complex [Zn(OAc)(Ile)] are shown in Schemes 3.3-3.6, respectively.



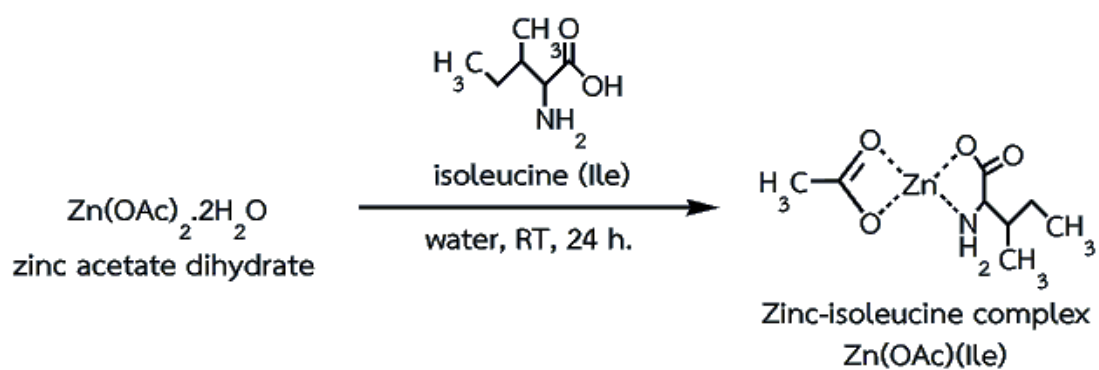
Scheme 3.3 Synthesis of zinc-valine complex [Zn(OAc)(Val)]



Scheme 3.4 Synthesis of zinc-arginine complex [Zn(OAc)(Arg)]



Scheme 3.5 Synthesis of zinc-serine complex [Zn(OAc)(Ser)]



Scheme 3.6 Synthesis of zinc-isoleucine complex $[\text{Zn}(\text{OAc})(\text{Ile})]$



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

Metal-amino acid complexes	Mole ratios of metal acetate:amino acid	Wt% of metal-amino acid complexes in H ₂ O	M(OAc) ₂ · xH ₂ O (g, mmol)	Amino acid (g, mmol)	Appearance
Amount of H ₂ O 3 ml. Catalyst content in RPUR foam formulation = 1 pbw					
Cu(OAc)(Val) (1:2)	1:2	25	0.460, 2.304	0.540, 4.609	Blue liquid with blue precipitate
Cu(OAc)(Arg) (1:2)	1:2	25	0.364, 1.82	0.636, 3.65	Homogeneous blue liquid
Cu(OAc)(Val) (1:1)	1:1	25	0.630, 3.15	0.370, 3.15	Blue liquid with blue precipitate
Cu(OAc)(Arg) (1:1)	1:1	25	0.534, 2.67	0.466, 2.67	Homogeneous blue liquid
Cu(OAc)(Arg) (1:1)	1:1	40	1.068, 5.34	0.932, 5.35	Homogeneous blue liquid
Zn(OAc)(Val) (1:2)	1:2	25	0.484, 2.20	0.516, 4.40	Colorless liquid with precipitate
Zn(OAc)(Arg) (1:2)	1:2	25	0.386, 1.76	0.614, 3.52	Homogeneous white viscous liquid
Zn(OAc)(Val) (1:1)	1:1	25	0.652, 2.97	0.348, 2.97	Homogeneous colorless liquid
Zn(OAc)(Arg) (1:1)	1:1	25	0.558, 2.53	0.442, 2.53	Homogeneous white viscous liquid
Zn(OAc)(Val) (1:1)	1:1	40	1.304, 5.94	0.696, 5.94	Colorless liquid with precipitate

Table 3.1 (continued) Composition of starting materials in the synthesis of metal-amino acid complexes using water as a solvent

Metal-amino acid complexes	Mole ratios of metal acetate:amino acid	Wt% of metal-amino acid complexes in H ₂ O	M(OAc) ₂ · xH ₂ O (g, mole)	Amino acid (g, mole)	Appearance
Amount of H ₂ O 4 ml. Catalyst content in RPUR foam formulation = 1 pbw					
Zn(OAc)(Val) (1:1)	1:1	20	0.652, 2.97	0.348, 2.97	Homogeneous colorless liquid
Zn(OAc)(Arg) (1:1)	1:1	20	0.558, 2.53	0.442, 2.53	Homogeneous white viscous liquid
Zn(OAc)(Ser) (1:1)	1:1	20	0.676, 3.07	0.324, 3.07	Homogeneous colorless liquid
Zn(OAc)(Ile) (1:1)	1:1	20	0.626, 2.85	0.374, 2.85	Colorless liquid with precipitate
Zn(OAc)(Ile) (1:1)	1:1	11	0.313, 1.42	0.187, 1.42	Homogeneous colorless liquid

M = Cu and Zn, OAc = acetate, Val = valine, Arg = arginine, Ser = serine and Ile = isoleucine

3.3 Rigid polyurethane (RPUR) foams preparations

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

The formulations used for RPUR foams preparation at NCO index of 100 are shown in Tables 3.2 and 3.3. RPUR foam samples were prepared by using a two-step of mixing method as shown in Figure 3.3. In the first mixing step, polyol, surfactant and catalysts (metal-amino acid complexes as aqueous solution or DMCHA) were mixed in a 700 ml paper cup by hand mixing until homogeneous followed by mixing with a mechanical stirrer at 2000 rpm for 20 seconds. In the second mixing step, polymeric MDI was added into the mixed polyol from the first mixing, then the mixture was mixed again by the mechanical stirrer at 2000 rpm for 15 seconds. During the polymerization of RPUR foams, the reaction times, namely cream time (the time at which the mixture of raw materials change from a liquid state to cream and the foam started to rise), gel time (the time at which the foam started to harden), rise time (the time at which the foam stopped rising and the generated CO₂ gas stops) and tack free time (the time at which polymerization reaction is completed and the surface of foam is not sticky) were measured. After that, the foams were kept at room temperature for 48 hours to complete the polymerization reactions before measuring height, density and NCO conversion. In addition, the rise and temperature profile were measured from RPUR foams prepared by the cut test method. The appearance of RPUR foams prepared by the cup test method is shown in Figure 3.1.



Figure 3.1 RPUR foams prepared by the cup test method and catalyzed by Zn(OAc)(Val) (1:1)

3.3.2 Preparation of rigid polyurethane (RPUR) foam by plastic mold method

The preparation of RPUR foams by mold method were prepared by using a plastic bag with the dimension of 10 x 10 x 10 cm. All of the starting materials were mixed in paper cup as described in 3.3.1, then was poured into a plastic bag and allowed to rise freely at room temperature. The RPUR foams were kept at room temperature for 48 h to complete the polymerization reactions before measuring density, mechanical properties and morphology. The appearance of RPUR foams prepared by the cup test method is shown in Figure 3.2.



Figure 3.2 RPUR foams prepared by plastic mold method and catalyzed by Zn(OAc)(Val) (1:1)

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

Foam formulation NCO Index = 100	parts by weight (pbw)	
	DMCHA	Metal-amino acid complexes
-Polyether polyol (Polimaxx [®] 4221)	100	100
-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	3.0, 4.0
-Catalyst (metal-amino acid complexes or DMCHA)	1.0	1.0, 0.5
-Polymeric MDI (PMDI, Raycore [®] B9001)	151.3	151.3, 166.4

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

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

Foam formulation NCO Index = 100	Weight (g)	
	DMCHA	Metal-amino acid complexes
-Polyether polyol (Polimaxx [®] 4221)	10.0	10.0
-Surfactant (Tegostab [®] B8460)	0.25	0.25
-Blowing agent (water in the aqueous solution of metal-amino acid complexes acts as a blowing agent)	0.3	0.3, 0.4
-Catalyst (metal-amino acid complexes or DMCHA)	0.1	0.1, 0.05
-Polymeric MDI (PMDI, Raycore [®] B9001)	15.13	15.13, 16.64

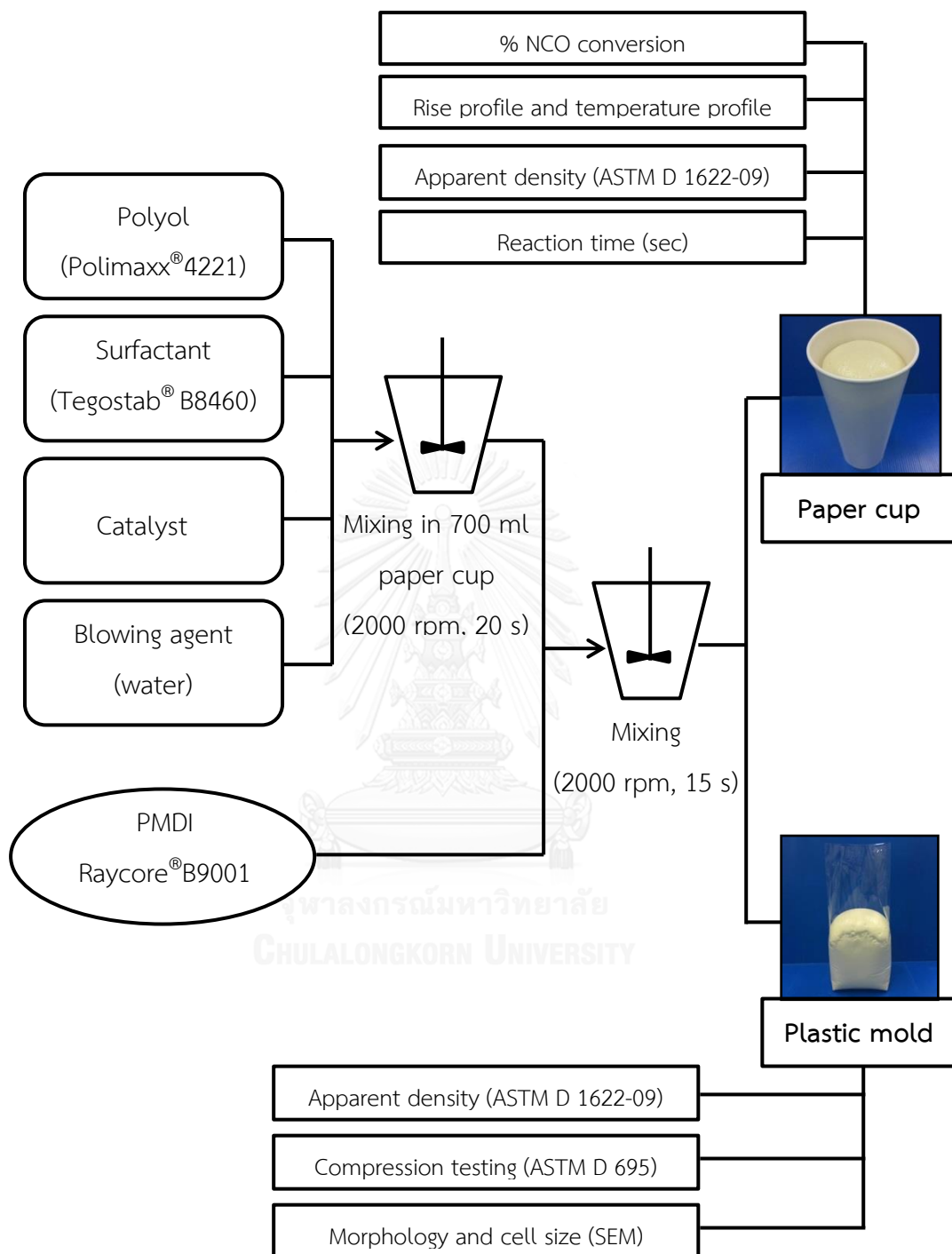


Figure 3.3 Process for preparation of rigid polyurethane foams

3.4 Characterizations of zinc-amino acid complexes and RPUR foams

3.4.1 Infrared spectroscopy

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

Zinc-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.

Zinc-amino acid complexes in solid form and RPUR foams were characterized by using a Nicolet 6700 FTIR spectrometer in the 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 60. The IR bands are used for the analysis shown in Table 3.4. The measurement was controlled by Omnic software.

Table 3.4 Characteristic IR bands of RPUR foam [30]

Functional group	Vibration mode	IR peak (cm^{-1})
NCO	NCO antisymmetric stretching	2180-2310
CO	C=O (urethane, urea, isocyanurate, allophanate, Biuret, etc.)	1620-1760
Amide	C-N stretching (urethane, urea)	1155-1245
Reference	Non-reaction groups in polyol and isocyanate	935-1050

3.4.2 Mass spectrometry (MS)

Mass spectrometry was used to confirm that the complex formations by produces spectra of mass-to-charge ratio of charge particle. Positive Ion Electrospray Ionization (Positive ESI) mass spectra were carried out using Bruker Daltonics microOTOF mass spectrometer. Samples were prepared by 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, rise time and tack free time in accordance with ASTM D7487-13 [31].

3.5.2 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.

3.5.3 Foaming temperature

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

3.5.4 Scanning electron microscope (SEM)

The morphology and cell size of RPUR foams were measured on a JSM-6480 LV scanning electron microscope (SEM). The sample foams were cut from surface in both parallel and perpendicular to the foaming directions and coating with gold before

scanning in order to provide an electrically conductive surface. The accelerating voltage was 15 kV.

3.5.5 Compressive testing

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise directions were performed using universal testing machine (Lloyd/LRX) according to ASTM D 695 [33]. The size of samples was 5.0 x 5.0 x 5.0 cm (length x width x thickness). The rate of crosshead movement was fixed at 50 mm/min and the preload cell used was 0.100 N.

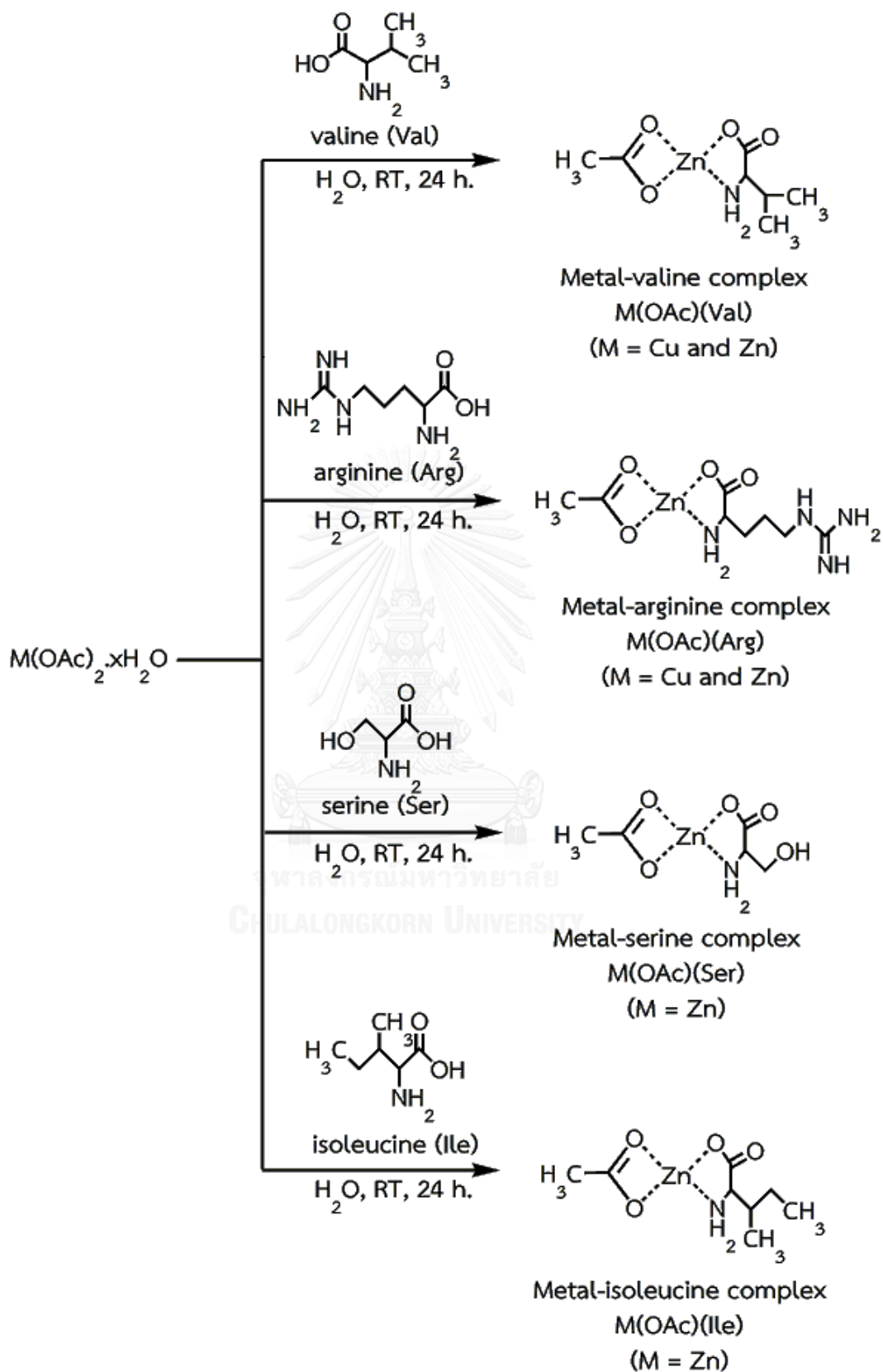


CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of metal-amino acid complexes

Metal-amino acid complexes were synthesized from the reaction between metal and amino acids. The metals used were copper(II) acetate monohydrate $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$ and zinc(II) acetate dihydrate $[\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}]$. The amino acids used were valine (Val), arginine (Arg), serine (Ser), and isoleucine (Ile). The synthesis of metal-amino acid complexes used water as a solvent to give aqueous solution of metal-amino acid complexes (scheme 4.1). All metal-amino acid complexes were odorless, could be easily prepared, had good solubility in starting material of RPUR foam formation and could be used as catalysts for RPUR foam preparation without purification.



Scheme 4.1 Syntheses of copper-amino acid and zinc-amino acid complexes

4.1.1 Synthesis of copper-amino acid complexes

Copper-amino acid complexes were prepared from reaction between copper(II) acetate monohydrate with amino acids, namely valine (Val) and arginine (Arg). Water was used as a solvent and copper-amino acid complexes were prepared as 25 wt% solution in water. The reactions of copper(II) acetate monohydrate with amino acids at the mole ratios of copper acetate to amino acid = 1:2 and 1:1 gave four copper-amino acid complexes, namely Cu(OAc)(Val) (1:2), Cu(OAc)(Arg) (1:2), Cu(OAc)(Val) (1:1) and Cu(OAc)(Arg) (1:1). The solutions of Cu(OAc)(Val) (1:2) and Cu(OAc)(Val) (1:1) were not homogeneous. They were obtained as blue liquid with blue precipitate as shown in Figures 4.1(a) and 4.2(a), respectively, whereas Cu(OAc)(Arg) (1:2) and Cu(OAc)(Arg) (1:1) were obtained as homogeneous blue liquid as shown in Figures 4.1(b) and 4.2(b), respectively.

Moreover, the complex of Cu(OAc)(Arg) (1:1) was prepared as 40 wt% solution in water for the study of solubility and catalyst activity. The solution of 40 wt% Cu(OAc)(Arg) (1:1, 2 pbw) was obtained as homogeneous blue liquid as shown in Figure 4.2(c).

4.1.2 Synthesis of zinc-amino acid complexes

Zinc-amino acid complexes were prepared from the reaction between zinc acetate dihydrate with two amino acids, namely valine (Val) and arginine (Arg). The mole ratio of zinc to amino acid used was 1:2. For the reactions between zinc acetate dihydrate with amino acids, namely valine (Val), arginine (Arg) serine (Ser), and isoleucine (Ile), the mole ratios of zinc to amino acid used were 1:1.

At 25 wt% solution in water, zinc-amino acid complexes prepared at the mole ratio of zinc to amino acid (Val and Arg) = 1:2 and 1:1 gave four zinc-amino acid complexes, namely Zn(OAc)(Val) (1:2) or Zn(Val)₂, Zn(OAc)(Arg) (1:2), Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1). The solutions of Zn(OAc)(Val) (1:2), Zn(OAc)(Arg) (1:2), Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) were obtained as colorless liquid with

precipitate, homogeneous white viscous liquid, homogeneous colorless liquid and homogeneous white viscous liquid, respectively, as shown in Figures 4.3 and 4.4.

At 20 wt% solution in water, zinc-amino acid complexes prepared at the mole ratio of zinc to amino acid (Val, Arg, Ser and Ile) = 1:1 gave four zinc-amino acid complexes, namely Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1). The solutions of Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) were obtained as homogeneous colorless liquid, homogeneous white viscous liquid, homogeneous colorless liquid and colorless liquid with precipitate, respectively, as shown in Figure 4.5.

The solution of Zn(OAc)(Ile) (1:1) at a concentration of 20 wt% solution in water was not homogeneous. Therefore, 11 wt% solution of Zn(OAc)(Ile) (1:1) in water was prepared. The solution of 11 wt% Zn(OAc)(Ile) (1:1) in water were obtained as homogeneous colorless liquid as shown in Figure 4.5(e).

Moreover, The complex of Zn(OAc)(Val) (1:1) was prepared as 40 wt% solution in water for the study solubility and catalyst activity. The solution of Zn(OAc)(Val) (1:1) in water was obtained as colorless liquid with precipitate as shown in Figure 4.4(c).

IR spectroscopy and positive ESI mass spectrometry were used to identify the structure of zinc-amino acid complexes.

Table 4.1 Appearances of metal-amino acid complex

Metal-amino acid complexes	Concentration (wt% in H ₂ O)	Appearance	Figure
Cu(OAc)(Val) (1:2)	25	Blue liquid with blue precipitate	4.1 a
Cu(OAc)(Arg) (1:2)	25	Homogeneous blue liquid	4.1 b
Cu(OAc)(Val) (1:1)	25	Blue liquid with blue precipitate	4.2 a
Cu(OAc)(Arg) (1:1)	25	Homogeneous blue liquid	4.2 b
Cu(OAc)(Arg) (1:1)	40	Homogeneous blue liquid	4.2 c
Zn(OAc)(Val) (1:2)	25	Colorless liquid with precipitate	4.3 a
Zn(OAc)(Arg) (1:2)	25	Homogeneous white viscous liquid	4.3 b
Zn(OAc)(Val) (1:1)	25	Homogeneous colorless liquid	4.4 a
Zn(OAc)(Arg) (1:1)	25	Homogeneous white viscous liquid	4.4 b
Zn(OAc)(Val) (1:1)	40	Colorless liquid with precipitate	4.4 c
Zn(OAc)(Val) (1:1)	20	Homogeneous colorless liquid	4.5 a
Zn(OAc)(Arg) (1:1)	20	Homogeneous white viscous liquid	4.5 b
Zn(OAc)(Ser) (1:1)	20	Homogeneous colorless liquid	4.5 c
Zn(OAc)(Ile) (1:1)	20	Colorless liquid with precipitate	4.5 d
Zn(OAc)(Ile) (1:1)	11	Homogeneous colorless liquid	4.5 e

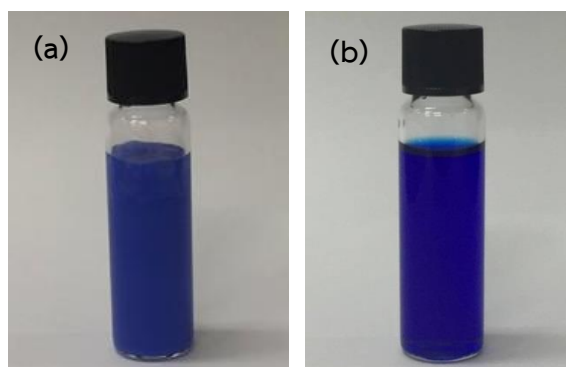


Figure 4.1 Copper-amino acid complex aqueous solutions (a) $\text{Cu}(\text{OAc})(\text{Val})$ (1:2) (25 wt%) and (b) $\text{Cu}(\text{OAc})(\text{Arg})$ (1:2) (25 wt%)

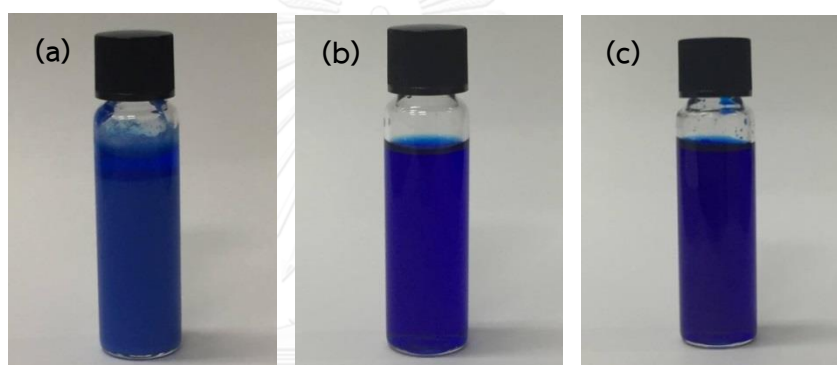


Figure 4.2 Copper-amino acid complex aqueous solutions (a) $\text{Cu}(\text{OAc})(\text{Val})$ (1:1) (25 wt%), (b) $\text{Cu}(\text{OAc})(\text{Arg})$ (1:1) (25 wt%) and (c) $\text{Cu}(\text{OAc})(\text{Arg})$ (1:1) (40 wt%)

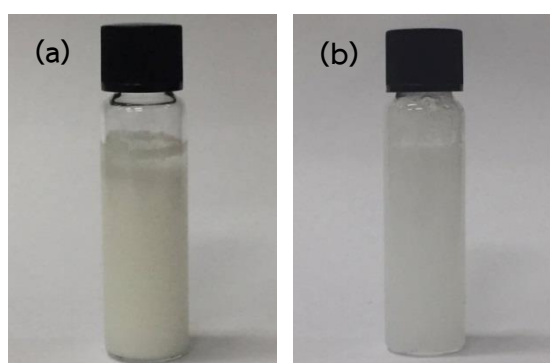


Figure 4.3 Zinc-amino acid complex aqueous solutions (a) $\text{Zn}(\text{OAc})(\text{Val})$ (1:2) (25 wt%) and (b) $\text{Zn}(\text{OAc})(\text{Arg})$ (1:2) (25 wt%)

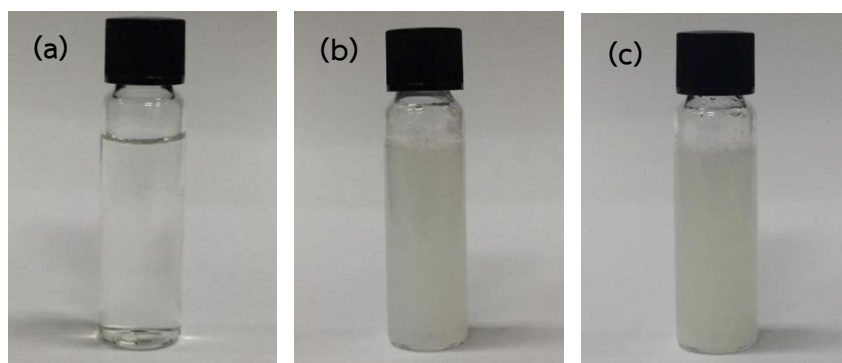


Figure 4.4 Zinc-amino acid complex aqueous solutions (a) Zn(OAc)(Val) (1:1) (25 wt%), (b) Zn(OAc)(Arg) (1:1) (25 wt%) and (c) Zn(OAc)(Val) (1:1) (40 wt%)

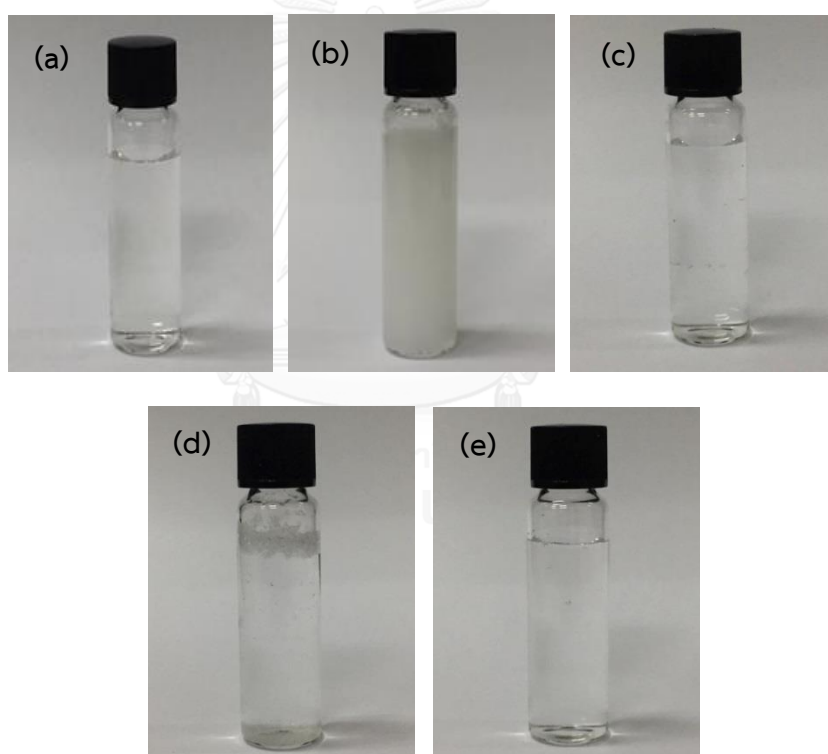


Figure 4.5 Zinc-amino acid complex aqueous solutions (a) Zn(OAc)(Val) (1:1) (20 wt%), (b) Zn(OAc)(Arg) (1:1) (20 wt%), (c) Zn(OAc)(Ser) (1:1) (20 wt%), (d) Zn(OAc)(Ile) (1:1) (20 wt%) and (e) Zn(OAc)(Ile) (1:1) (11 wt%)

4.2 Characterization zinc-amino acid complexes synthesized in water

The aqueous solutions of zinc-amino acid complexes were homogeneous and therefore characterization could be done by using IR spectroscopy and mass spectrometry. The aqueous solutions of copper-amino acid complexes were not homogeneous and therefore characterization could not be done.

4.2.1 IR spectroscopy of zinc-amino acid complexes

4.2.1.1 IR spectroscopy of zinc-valine complex [Zn(OAc)(Val)]

The IR spectra of Zn(OAc)(Val) (1:1) is shown in Figure 4.6. IR spectrum of Zn(OAc)(Val) (1:1) was obtained by using two methods.

Zn(OAc)(Val) (solid) was prepared in the form of a solution in water and dried by freeze drying method to obtain Zn(OAc)(Val) in a solid form. IR spectrum of Zn(OAc)(Val) (solid) is shown in Figure 4.6(c). It exhibited absorption bands at 3123 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl group in water), 2960 cm^{-1} (C-H stretching), 1541 cm^{-1} (C=O asymmetric stretching), 1409 cm^{-1} (C=O symmetric stretching), 1327 cm^{-1} (C-N stretching) and 1018 cm^{-1} (C-O stretching).

In the second method, IR spectrum of Zn(OAc)(Val) (solution) was obtained from aqueous solution. IR spectrum of Zn(OAc)(Val) (solution) is shown in Figure 4.6(d). It exhibited absorption bands at 3277 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl group in water), 2980 cm^{-1} (C-H stretching), 1595 cm^{-1} (C=O asymmetric stretching), 1410 cm^{-1} (C=O symmetric stretching), 1357 cm^{-1} (C-N stretching) and 1018 cm^{-1} (C-O stretching).

The C=O stretching of carbonyl group in Zn(OAc)(Val) (solid) and Zn(OAc)(Val) (solution) were different. Zn(OAc)(Val) (solid) gave the same peaks as Zn(OAc)₂, which normally appears as absorption bands around at 1541 cm^{-1} (asymmetric C=O) and 1434 cm^{-1} (symmetric C=O). These IR data indicated that the Zn(OAc)(Val) (solid) might decompose to give starting materials during freeze drying process. The IR

peak of Zn(OAc)(Val) (solution) was shifted from those of Zn(OAc)₂ and valine, which indicated that the complex was formed in aqueous solution.

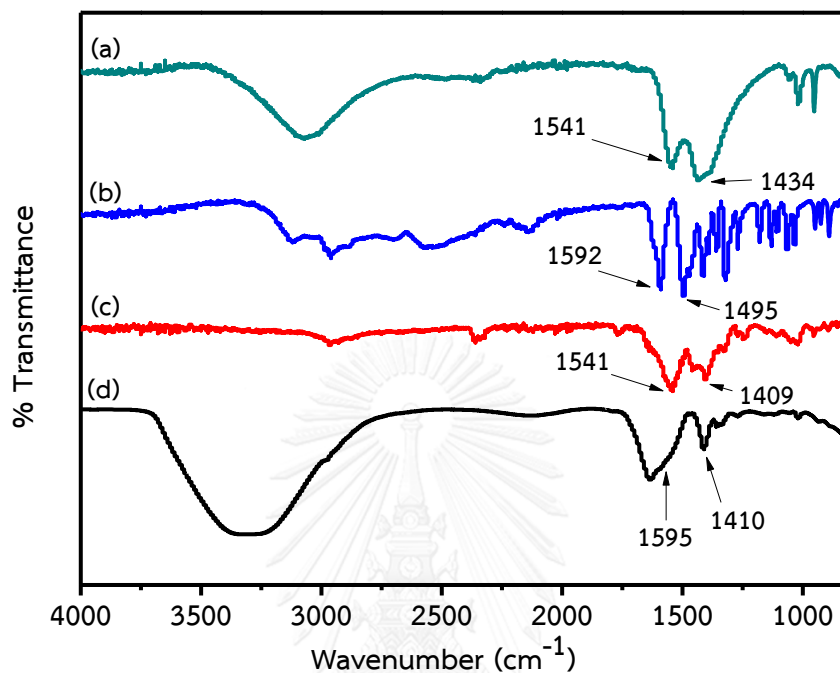


Figure 4.6 IR spectra of (a) Zn(OAc)₂, (b) Valine, (c) Zn(OAc)(Val) (1:1) (solid) and (d) Zn(OAc)(Val) (1:1) (solution)

4.2.1.2 IR spectroscopy of zinc-arginine complex [Zn(OAc)(Arg)]

The IR spectra of Zn(OAc)(Arg) (1:1) is shown in Figure 4.7. IR spectrum of Zn(OAc)(Arg) (solid) was obtained by freeze drying of Zn(OAc)(Arg) aqueous solution. IR spectrum of Zn(OAc)(Arg) (solid) is shown in Figure 4.7(c). It exhibited absorption band at 3276 cm⁻¹ (could be attributed to N-H stretching vibration and hydroxyl group in water), 2961 cm⁻¹ (C-H stretching), 1541 cm⁻¹ (C=O asymmetric stretching), 1396 cm⁻¹ (C=O symmetric stretching), 1339 cm⁻¹ (C-N stretching) and 1016 cm⁻¹ (C-O stretching). The C=O stretching of carbonyl group in Zn(OAc)(Arg) (solid) were the same as typical Zn(OAc)₂ peaks normally appears as absorption band around at 1541 cm⁻¹ (asymmetric

C=O). Zn(OAc)(Arg) (solid) decomposed to give the starting material during the freeze drying process.

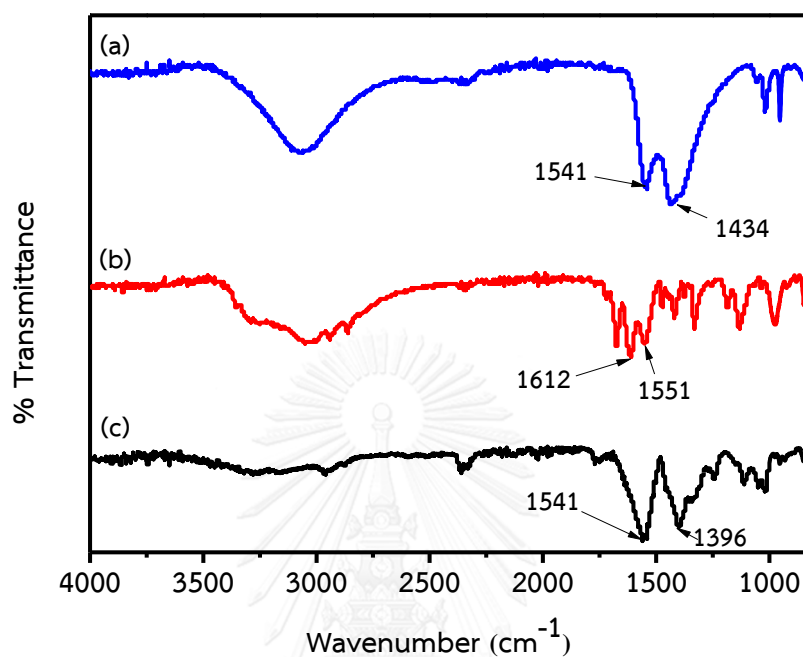


Figure 4.7 IR spectra of (a) Zn(OAc)₂, (b) Arginine and (c) Zn(OAc)(Arg) (1:1) (solid)

4.2.1.3 IR spectroscopy of zinc-serine complex [Zn(OAc)(Ser)]

The IR spectra of Zn(OAc)(Ser) (1:1) is shown in Figure 4.8. IR spectrum of Zn(OAc)(Ser) (1:1) (solid) was obtained by freeze drying of Zn(OAc)(Ser) aqueous solution. IR spectrum of Zn(OAc)(Ser) solid is shown in Figure 4.8(c). It exhibited absorption band at 3267 cm⁻¹ (could be attributed to N-H stretching vibration and hydroxyl group in water), 2957 cm⁻¹ (C-H stretching), 1541 cm⁻¹ (C=O asymmetric stretching), 1401 cm⁻¹ (C=O symmetric stretching), 1335 cm⁻¹ (C-N stretching) and 1027 cm⁻¹ (C-O stretching). The C=O stretching of carbonyl group in Zn(OAc)(Ser) (solid) were the same as typical Zn(OAc)₂ peaks normally appears as absorption band around at 1541 cm⁻¹ (asymmetric C=O) and 1434 cm⁻¹ (symmetric C=O). Zn(OAc)(Ser) (solid) decomposed to give the starting material during the freeze drying process.

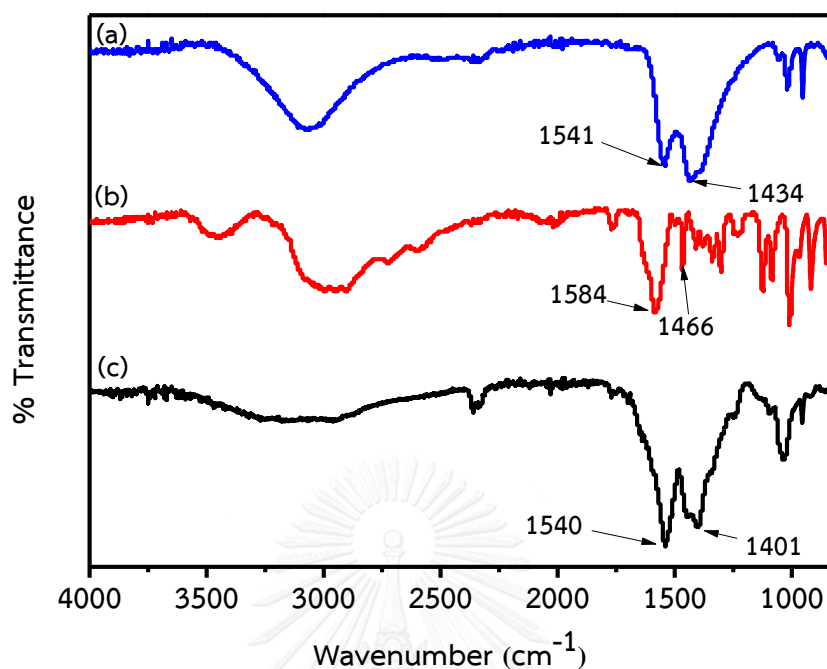


Figure 4.8 IR spectra of (a) $\text{Zn}(\text{OAc})_2$, (b) Serine and (c) $\text{Zn}(\text{OAc})(\text{Ser})$ (1:1) (solid)

4.2.1.4 IR spectroscopy of zinc-isoleucine complex [$\text{Zn}(\text{OAc})(\text{Ile})$]

The IR spectra of $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) is shown in Figure 4.9. IR spectrum of $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) (solid) was obtained by freeze drying of $\text{Zn}(\text{OAc})(\text{Ile})$ aqueous solution. IR spectrum of $\text{Zn}(\text{OAc})(\text{Ile})$ (solid) is shown in Figure 4.9(c). It exhibited absorption band at 3151 cm^{-1} (could be attributed to N-H stretching vibration and hydroxyl group in water), 2960 cm^{-1} (C-H stretching), 1541 cm^{-1} (C=O asymmetric stretching), 1394 cm^{-1} (C=O symmetric stretching), 1327 cm^{-1} (C-N stretching) and 1034 cm^{-1} (C-O stretching). The C=O stretching of carbonyl group in $\text{Zn}(\text{OAc})(\text{Ile})$ (solid) were the same as typical $\text{Zn}(\text{OAc})_2$ peaks normally appears as absorption band around at 1541 cm^{-1} (asymmetric C=O) and 1434 cm^{-1} (symmetric C=O). $\text{Zn}(\text{OAc})(\text{Ile})$ (solid) decomposed to give the starting materials during the freeze drying process.

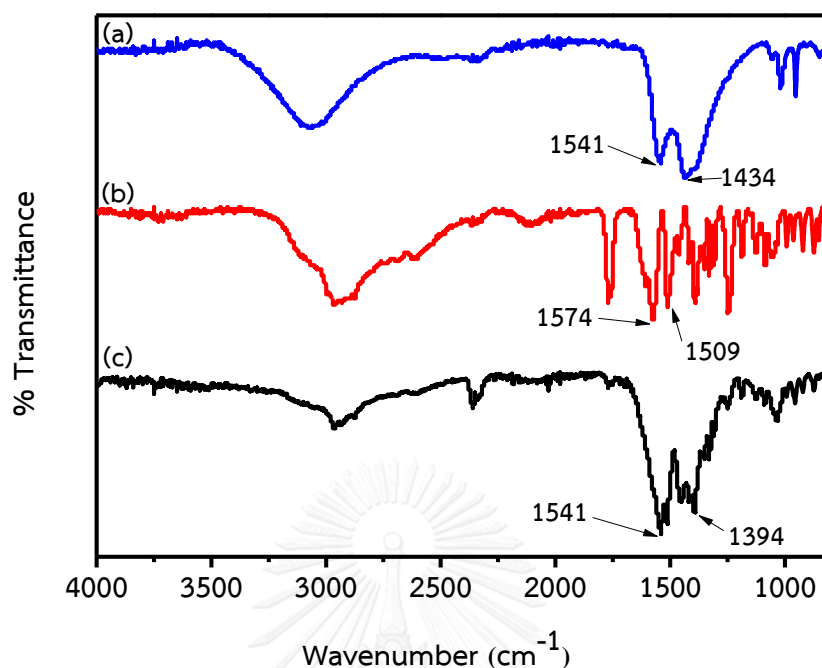


Figure 4.9 IR spectra of (a) $\text{Zn}(\text{OAc})_2$, (b) Isoleucine and (c) $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) (solid)

4.2.2 Positive ESI mass spectrometry of zinc-amino acid complex

Positive ESI mass spectrometry was also used to identify the structure and molecular weight of zinc-amino acid complexes. Positive ESI mass spectra were obtained from aqueous the solution of zinc-amino acid complexes. The molecular ion peaks of $\text{Zn}(\text{OAc})(\text{Val})$ (1:1), $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) and $\text{Zn}(\text{OAc})(\text{Ser})$ (1:1) are shown in Figures 4.10, 4.13 and 4.16, respectively. The data of molecular ion peaks corresponding and m/z ratio are described in Table 4.2. The molecular ion peaks of $\text{Zn}(\text{OAc})(\text{Val})$ (1:1) appeared at the m/z 240.0274 $[\text{Zn}(\text{OAc})(\text{Val})+\text{H}]^+$ and m/z 297.0875 $[\text{Zn}(\text{Val})_2+\text{H}]^+$. The molecular ion peaks of $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) appeared at m/z 254.0387 $[\text{Zn}(\text{OAc})(\text{Ile})+\text{H}]^+$ and m/z 325.1113 $[\text{Zn}(\text{Ile})_2+\text{H}]^+$. The molecular ion peak of $\text{Zn}(\text{OAc})(\text{Ser})$ (1:1) appeared at m/z 227.9862 $[\text{Zn}(\text{OAc})(\text{Ser})+\text{H}]^+$. The molecular ion peaks of zinc-amino acid complexes corresponded to the molecular weight of zinc-amino acid complexes obtained from the calculation, which indicated that the zinc-amino acid complexes were formed. Therefore, zinc-valine and zinc-isoleucine

complexes exist in two forms, $\text{Zn(OAc)(Val)/Zn(Val)}_2$ and $\text{Zn(OAc)(Ile)/Zn(Ile)}_2$ (Figures 4.10 and 4.13, respectively). Zinc-serine complex exists in one form, Zn(OAc)(Ser) as shown in Figure 4.16.

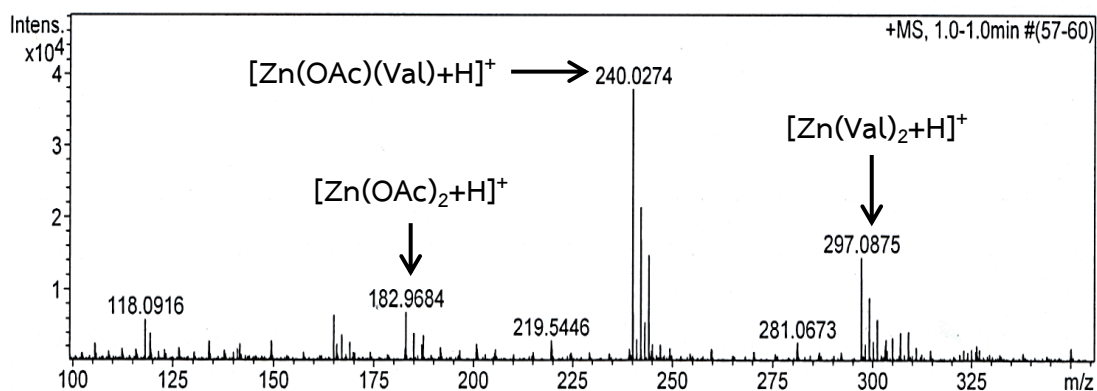


Figure 4.10 Positive ESI mass spectrum of Zn(OAc)(Val) (1:1)

The structures of Zn(OAc)(Val) and Zn(Val)_2 are shown in Figures 4.11 and 4.12, respectively.

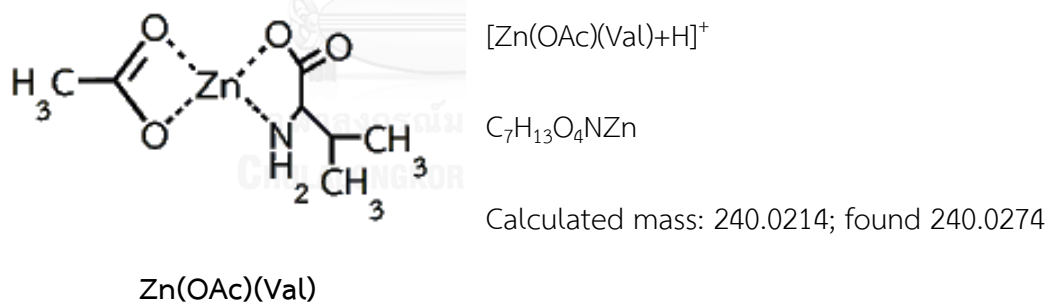
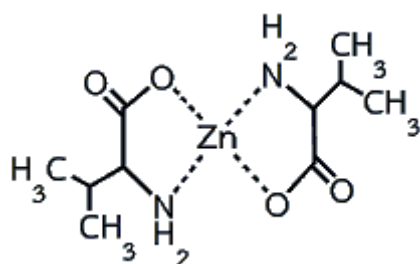


Figure 4.11 Structure, molecular formula and molecular weight of $[\text{Zn(OAc)(Val)+H}]^+$


 $[\text{Zn}(\text{Val})_2+\text{H}]^+$
 $\text{C}_{14}\text{H}_{26}\text{O}_8\text{N}_2\text{Zn}$

Calculated mass: 297.0792; found 297.0875

 $\text{Zn}(\text{Val})_2$

Figure 4.12 Structure, molecular formula and molecular weight of $[\text{Zn}(\text{Val})_2+\text{H}]^+$

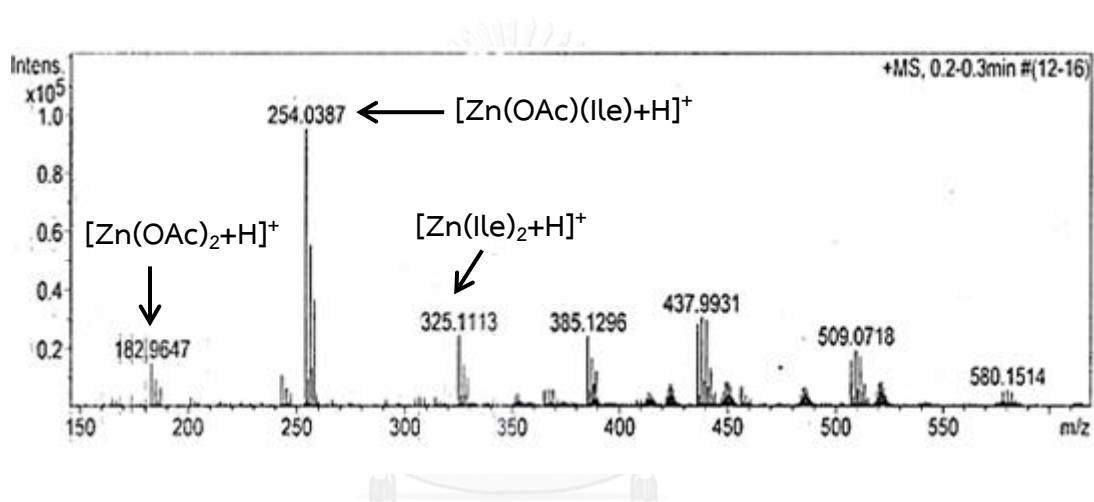
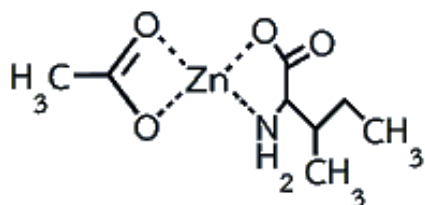


Figure 4.13 Positive ESI mass spectrum $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1)

The structures of $\text{Zn}(\text{OAc})(\text{Ile})$ and $\text{Zn}(\text{Ile})_2$ are shown in Figures 4.14 and 4.15, respectively.


 $[\text{Zn}(\text{OAc})(\text{Ile})+\text{H}]^+$
 $\text{C}_8\text{H}_{15}\text{O}_4\text{NZn}$

Calculated mass: 254.0370; found 254.0387

 $\text{Zn}(\text{OAc})(\text{Ile})$

Figure 4.14 Structure, molecular formula and molecular weight of $[\text{Zn}(\text{OAc})(\text{Ile})+\text{H}]^+$

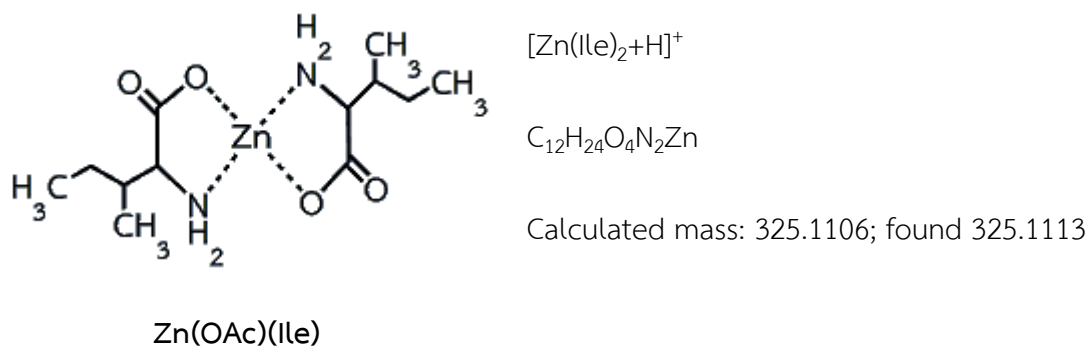


Figure 4.15 Structure, molecular formula and molecular weight of [Zn(Ile)₂+H]⁺

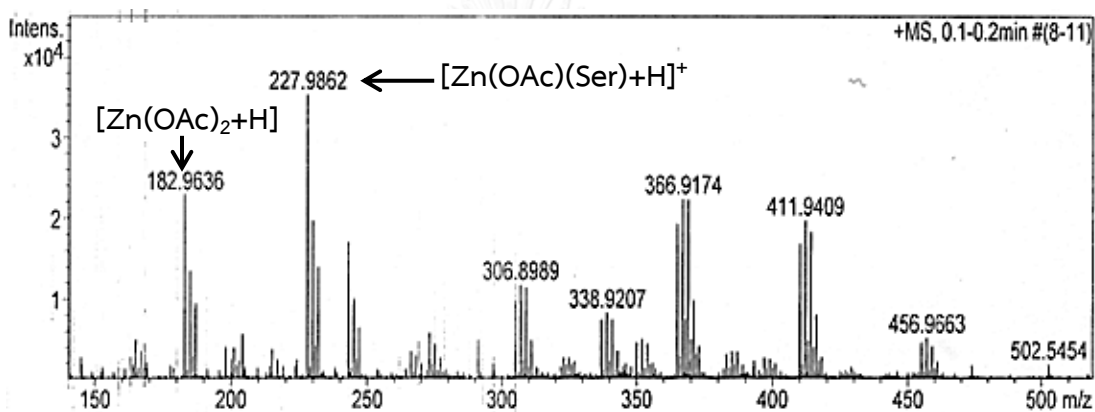


Figure 4.16 Positive ESI mass spectrum Zn(OAc)(Ser) (1:1)

The structures of Zn(OAc)(Ser) is shown in Figure 4.17.

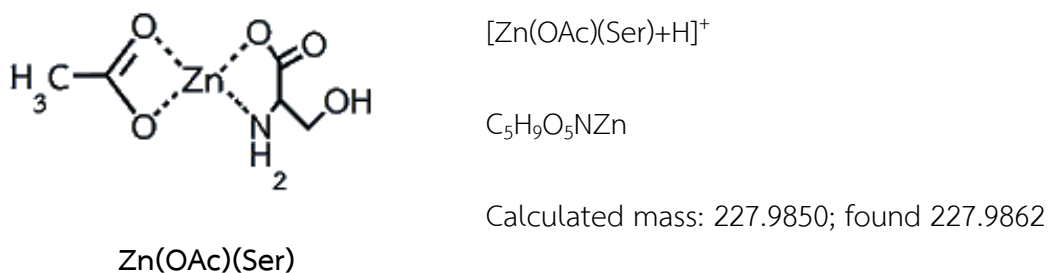


Figure 4.17 Structure, molecular formula and molecular weight of [Zn(OAc)(Ser)+H]⁺

Table 4.2 Molecular ion peaks of zinc-amino acid complexes

Molecular ion peak	m/z (Calculated)	m/z (Found)
$[\text{Zn}(\text{OAc})(\text{Val})+\text{H}]^+$	240.0214	240.0274
$[\text{Zn}(\text{Val})_2+\text{H}]^+$	297.0792	297.0875
$[\text{Zn}(\text{OAc})(\text{Ile})+\text{H}]^+$	254.0370	254.0387
$[\text{Zn}(\text{Ile})_2+\text{H}]^+$	325.1106	325.1113
$[\text{Zn}(\text{OAc})(\text{Ser})+\text{H}]^+$	227.9850	227.9862



4.3 Preparation of rigid polyurethane (RPUR) foam catalyzed by metal-amino acid complexes

4.3.1 Reaction time, density and height of RPUR foams

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

Catalyst types	Blowing agent (pbw)	Amount of catalyst (pbw)	Cream time (sec)	Gel time (sec)	Rise time (sec)	Tack free time (sec)	Density (Kg/m ³)	Height (cm)
DMCHA (ref.)	3	1	22	34	107	135	37.96	14.1
Cu(OAc)(Val) (1:2)	3	1	22	192	460	524	49.23	10.5
Cu(OAc)(Arg) (1:2)	3	1	24	153	408	508	54.28	9.8
Cu(OAc)(Val) (1:1)	3	1	33	100	205	208	42.53	12.7
Cu(OAc)(Arg) (1:1)	3	1	28	154	327	417	47.99	10.5
Cu(OAc)(Arg) (1:1)	3	2	28	174	399	486	46.25	10.7
Zn(OAc)(Val) (1:2)	3	1	23	143	380	455	43.40	11.3
Zn(OAc)(Arg) (1:2)	3	1	22	191	711	1088	54.99	9.5
Zn(OAc)(Val) (1:1)	3	1	22	92	208	233	38.94	13.8
Zn(OAc)(Arg) (1:1)	3	1	22	137	468	743	46.31	10.0
Zn(OAc)(Val) (1:1)	3	2	22	102	213	239	43.24	12.3
Zn(OAc)(Val) (1:1)	4	1	22	97	217	222	37.95	14.1
Zn(OAc)(Arg) (1:1)	4	1	22	132	395	408	39.68	13.5
Zn(OAc)(Ser) (1:1)	4	1	22	128	323	342	38.91	13.9
Zn(OAc)(Ile) (1:1)	4	1	22	66	142	142	31.46	16.9
Zn(OAc)(Ile) (1:1)	4	1	22	105	254	274	38.99	13.7

4.3.1.1 Effect of mole ratio of starting materials in synthesis of metal-amino acid complexes on reaction time and density of RPUR foams

The effect of mole ratio of starting materials in synthesis of metal-amino acid complexes on reaction time of RPUR foams was investigated. RPUR foams were prepared at the amount of blowing agent (H_2O) = 3 pbw. For copper-amino acid complexes, the variation of mole ratio between copper acetate :amino acids (Val and Arg) at 1:2 and 1:1 showed that the reaction time decreased when the amount of amino acids decreased. This was because the solubility of copper-amino acid complexes in water increased. It was found that RPUR foams catalyzed by Cu(OAc)(Val) (1:2) and Cu(OAc)(Arg) (1:2) gave the longer tack free time than did Cu(OAc)(Val) (1:1) and Cu(OAc)(Arg) (1:1). Cu(OAc)(Val) (1:1) give the shorter tack free time than other copper-amino acid complexes but gave the longer tack free time than DMCHA. In comparison, between Cu(OAc)(Val) (1:1) and Cu(OAc)(Arg) (1:1), Cu(OAc)(Arg) (1:1) had the better solubility in water but gave the longer tack free time than did Cu(OAc)(Val) (1:1) because of the result of steric hindrance [21]. RPUR foams catalyzed by Cu(OAc)(Val) (1:2) and Cu(OAc)(Val) (1:1) had holes at the bottom of the foam samples but the holes were not found in RPUR foams catalyzed by Cu(OAc)(Arg) (1:2) and Cu(OAc)(Arg) (1:1).

For the effect of mole ratio in zinc-amino acid complexes on reaction time of RPUR foams as shown in Figure 4.19, the trends were the same as those of copper-amino acid complexes. RPUR foams catalyzed by Zn(OAc)(Val) (1:2) and Zn(OAc)(Arg) (1:2) gave the longer tack free time than did Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1). The complex of Zn(OAc)(Val) (1:1) gave the shorter tack free time than did other zinc-amino acid complexes but they gave the longer tack free time than did DMCHA. RPUR foam catalyzed by Zn(OAc)(Val) had holes at the bottom of the foam samples. RPUR foams catalyzed by Zn(OAc)(Val) (1:2), Zn(OAc)(Arg) (1:2) and Zn(OAc)(Arg) (1:1) did not have holes at the bottom of the foam samples.

Therefore, the best mole ratio of metal acetate:amino acid in the synthesis of metal-amino acid complexes was 1:1. The effect of different types of metal acetates

and amino acids in metal-amino acid complexes on the reaction times of RPUR foams is shown in Figure 4.20. RPUR foams catalyzed by Cu(OAc)(Val) (1:1) showed the shorter tack free time than did other metal-amino acid complexes but gave the longer cream time than did other metal-amino acid complexes. However, Cu(OAc)(Val) was not soluble in water. Therefore, Zn(OAc)(Val) (1:1) was the optimum catalyst, which had a short tack free time, soluble in water and gave foam density (38.94 Kg/m^3) similar to those catalyzed by DMCHA (37.96 Kg/m^3) as shown in Figure 4.21. However, RPUR foams catalyzed by Zn(OAc)(Val) (1:1) gave the longer tack free time than that catalyzed by DMCHA.

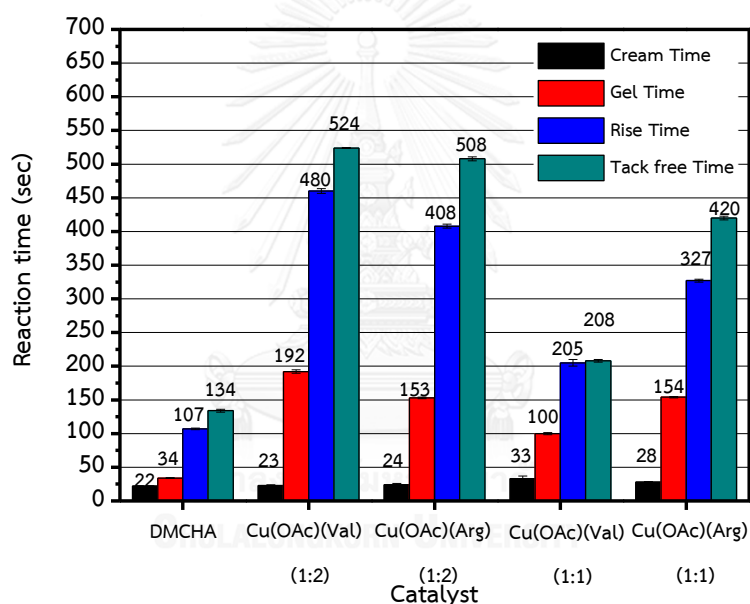


Figure 4.18 Effect of mole ratio on reaction time of RPUR foams catalyzed by DMCHA, Cu(OAc)(Val) (1:2), Cu(OAc)(Arg) (1:2), Cu(OAc)(Val) (1:1) and Cu(OAc)(Arg) (1:1) at the amount of blowing agent of 3.0 pbw

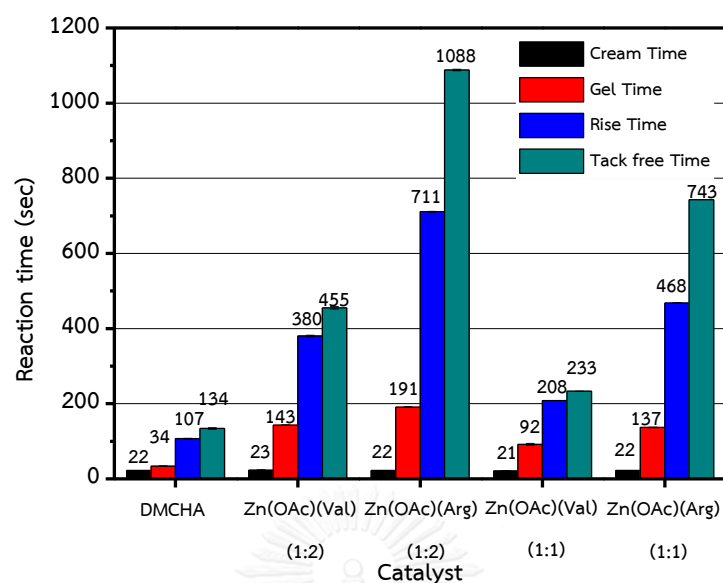


Figure 4.19 Effect of mole ratio on reaction time of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:2), Zn(OAc)(Arg) (1:2), Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 3.0 pbw

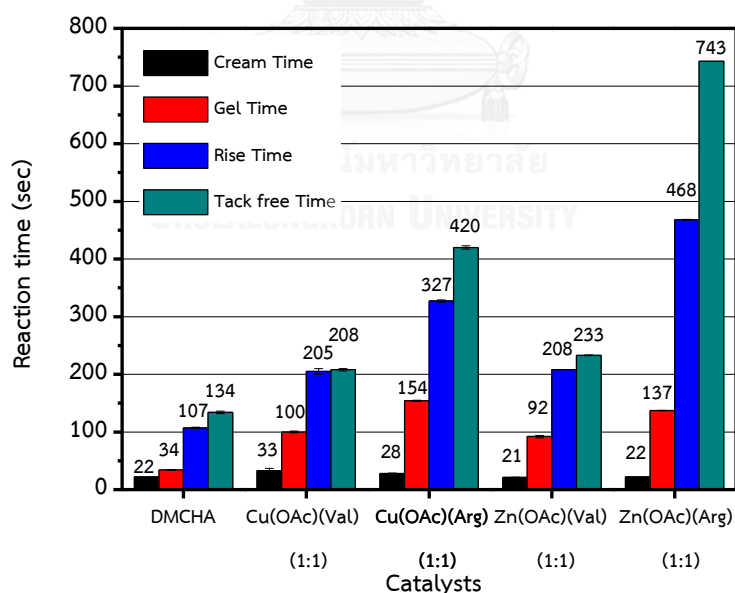


Figure 4.20 Effect of difference in types of metal acetates and amino acids in metal-amino acid complexes on reaction time of RPUR foams catalyzed by DMCHA, Cu(OAc)(Val) (1:1), Cu(OAc)(Arg) (1:1), Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 3.0 pbw

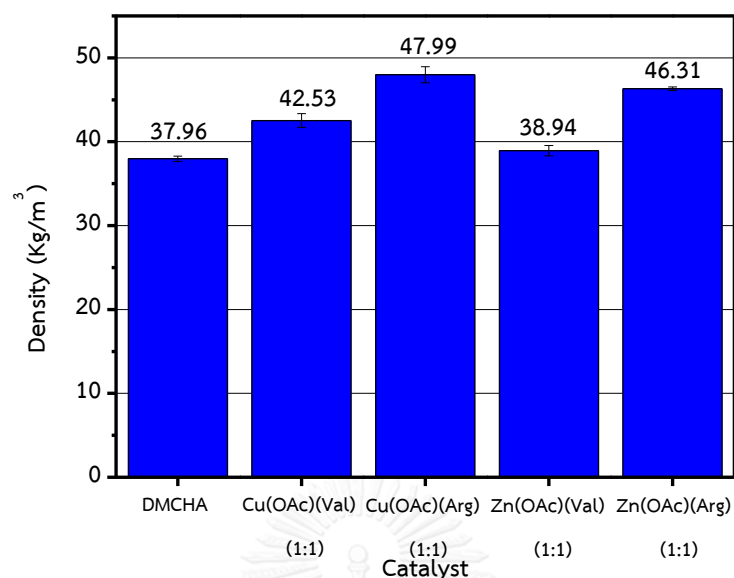


Figure 4.21 Effect of difference in types of metal acetates and amino acids in metal-amino acid complexes on foam density of RPUR foams catalyzed by DMCHA, Cu(OAc)(Val) (1:1), Cu(OAc)(Arg) (1:1), Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 3.0 pbw

4.3.1.2 Effect of concentration of zinc-isoleucine complexes on reaction time of RPUR foams

The effect of concentration of zinc-isoleucine complexes on reaction time of RPUR foams were investigated as shown in Figure 4.22. The zinc-isoleucine complexes prepared at a mole ratio of zinc:isoleucine were 1:1, by using the amount of blowing agent 4.0 pbw. It was found that RPUR foams catalyzed by Zn(OAc)(Ile) (1:1) (20 wt%) gave the shorter tack free time than did Zn(OAc)(Ile) (1:1) (11 wt%). But Zn(OAc)(Ile) (1:1) (20 wt%) was not soluble in water, RPUR foam had low density (31.46 Kg/m³) and large holes at the bottom of foam. RPUR foams catalyzed by Zn(OAc)(Ile) (1:1) (20 wt%) and Zn(OAc)(Ile) (1:1) (11 wt%) gave the longer tack free time than that catalyzed by DMCHA.

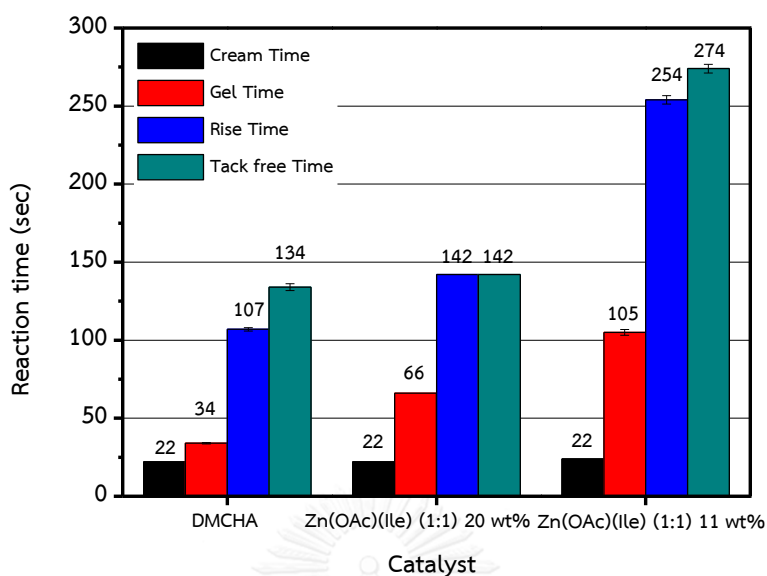


Figure 4.22 Effect of concentration on reaction time of RPUR foams catalyzed by DMCHA, Zn(OAc)(Ile) (1:1) (20 wt%) and Zn(OAc)(Ile) (1:1) (11 wt%) at the amount of blowing agent of 4.0 pbw

4.3.1.3 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 Figure 4.23. RPUR foams catalyzed by Cu(OAc)(Arg) (1:1) and Zn(OAc)(Val) (1:1) at the catalyst contents of 1 and 2 pbw gave almost the same reaction times. The holes at the bottom of RPUR foam samples were found when 2 pbw of catalyst was used. Therefore, the increase of catalyst contents was not suitable for RPUR foams preparation.

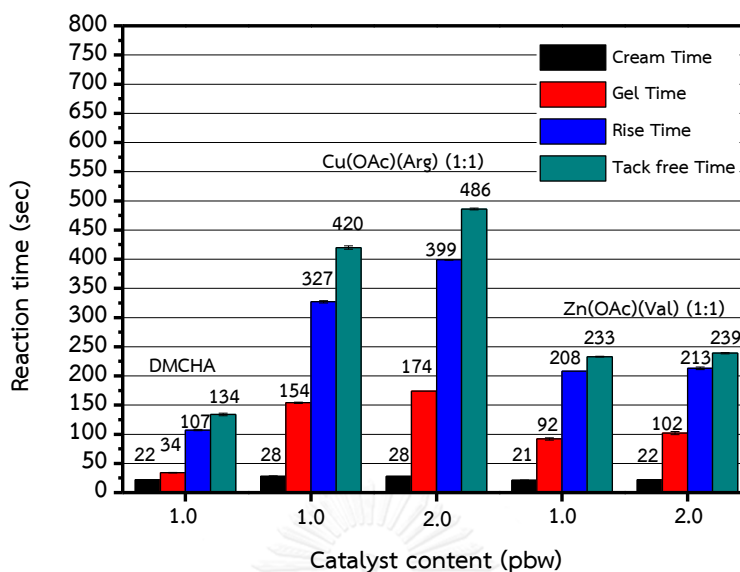


Figure 4.23 Effect of catalyst content on reaction time of RPUR foams catalyzed by DMCHA, Cu(OAc)(Arg) (1:1) and Zn(OAc)(Val) (1:1) at the amount of blowing agent of 3.0 pbw

4.3.1.4 Effect of blowing agent (water) quantity in zinc-amino acid complexes on reaction time of RPUR foams

Water was used as a solvent in the synthesis of metal-amino acid complex solution and also was a blowing agent in RPUR foam formulation. The effect of blowing agent quantity in zinc-amino acid complex aqueous solutions on the reaction time of RPUR foams was investigated as shown in Figure 4.24. Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) were prepared by using the amount of blowing agent 3.0 and 4.0 pbw. It was found that the reaction time decreased when the amount of blowing agent increased. This was because the solubility of zinc-amino acid complexes in water was increased. RPUR foams catalyzed by Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 4.0 pbw gave the shorter tack free time than those catalyzed by Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 3.0 pbw.

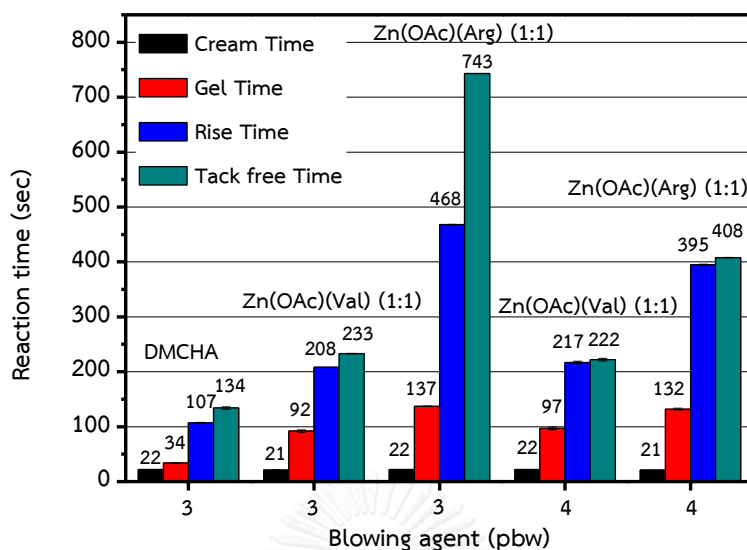


Figure 4.24 Effect of blowing agent quantities on reaction time of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 3.0 and 4.0 pbw

4.3.1.5 Effect of blowing agent (water) quantity in zinc-amino acid complexes on density of RPUR foams

Water was used as a solvent in the synthesis of metal-amino acid complex solution and also was a blowing agent in RPUR foam formulation. The effect of blowing agent quantity in zinc-amino acid complexes on density of RPUR foams were investigated as shown in Figure 4.25. Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) were prepared by using the amount of blowing agent 3.0 and 4.0 pbw. It was found that the density of RPUR foams decreased when the amount of blowing agent increased. Water could react with isocyanate group to generate CO₂ gas. Therefore, the blowing agent at 4.0 pbw generate more CO₂ than 3.0 pbw. RPUR foams catalyzed by Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1) at the amount of blowing agent of 4.0 pbw had higher foam heights and less foam density than those prepared at the amount of blowing agent of 3.0 pbw. Zn(OAc)(Val) (1:1) with the amount of blowing agent 4.0 pbw gave similar

foam density (37.95 kg/m^3) to that catalyzed by DMCHA (37.96 kg/m^3). From these results, the amount of blowing agent 4.0 pbw was suitable for RPUR foam formulation.

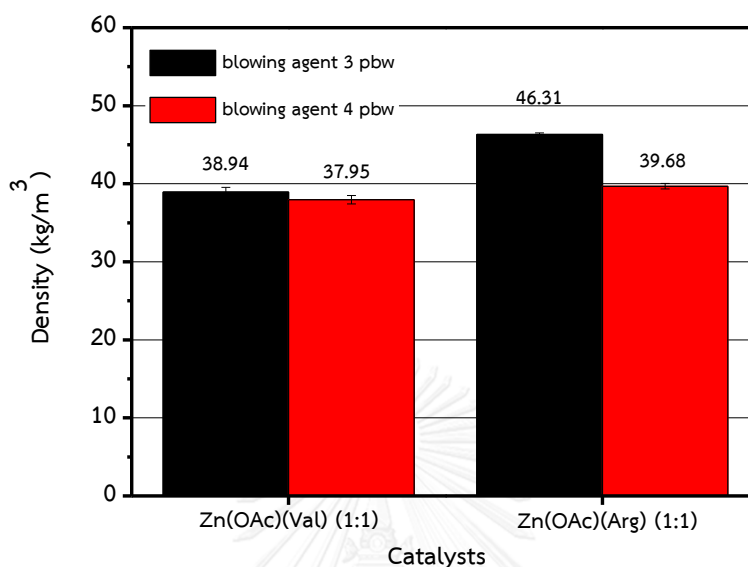


Figure 4.25 Effect of blowing agent quantity on density of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1) and Zn(OAc)(Arg) (1:1)

4.3.1.6 Effect of amino acid on the reaction time of RPUR foams catalyzed by zinc-amino acid complexes

From previous results, it was found that the mole ratio of zinc acetate:amino acid at 1:1 and the amount of blowing agent of 4.0 pbw were suitable for RPUR foam formulation. The effect of different amino acids in zinc-amino acid complexes on reaction time of RPUR foams were investigated as shown in Figure 4.26. It was found that the reaction time of RPUR foams catalyzed by zinc-amino acid complexes was DMCHA < Zn(OAc)(Val) (1:1) < Zn(OAc)(Ile) (1:1) < Zn(OAc)(Ser) (1:1) < Zn(OAc)(Arg) (1:1). This result indicated that the formation of Zn(OAc)(Val) (1:1) complex is effective. Valine is a small molecule which has less steric hindrance and therefore Zn(OAc)(Val) (1:1) had good catalytic property. Zn(OAc)(Arg) (1:1) gave the longest tack

free time because the solution of Zn(OAc)(Arg) (1:1) was homogeneous white viscous liquid and arginine had steric hindrance [21].

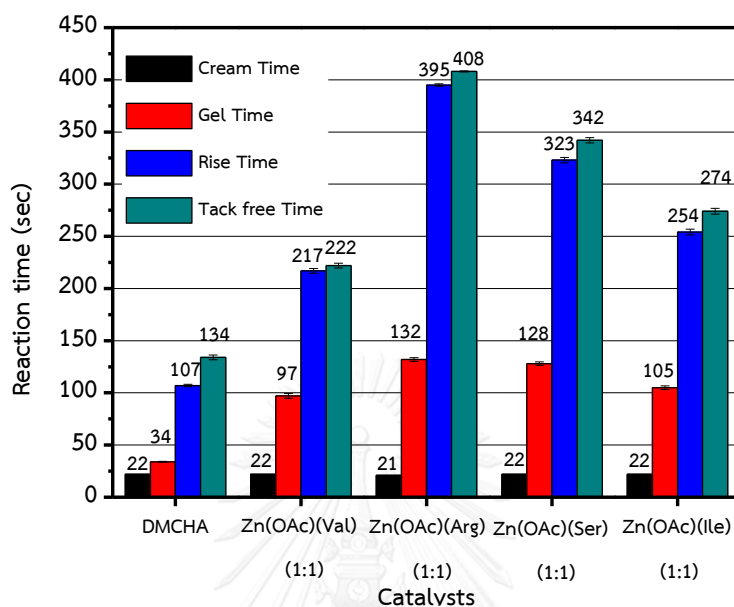


Figure 4.26 Reaction time of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

4.3.1.7 Density and height of RPUR foams catalyzed by zinc-amino acid complexes

Density and height of RPUR foams catalyzed by zinc-amino acid complexes were investigated as shown in Figures 4.27 and 4.28, respectively. The zinc-amino acid complexes were prepared by using the amount of blowing agent of 4.0 pbw. It was found that foam density decreased when foam heights increased. RPUR foams catalyzed by Zn(OAc)(Val) (1:1) gave similar foam density (37.95 kg/m^3) and height (14.1 cm) to those catalyzed by DMCHA (37.96 kg/m^3 , 14.1 cm).

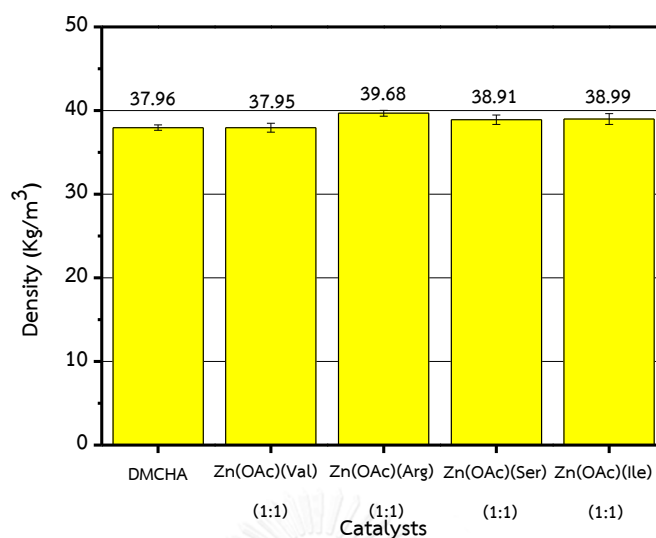


Figure 4.27 Density of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

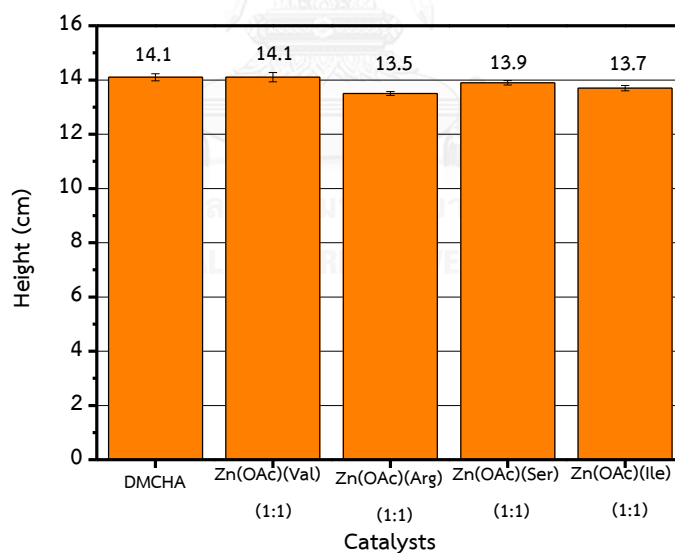


Figure 4.28 Height of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

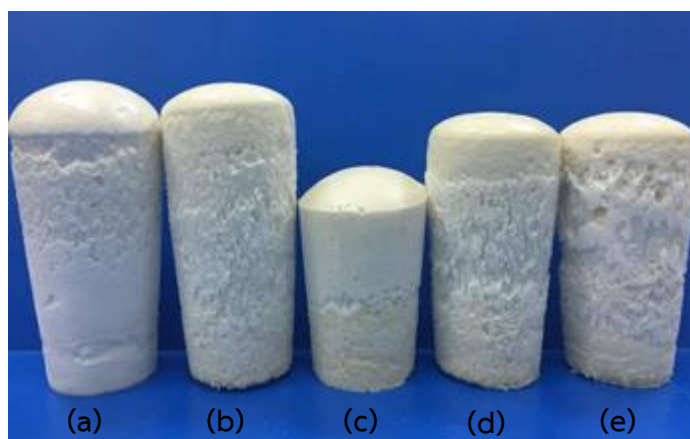


Figure 4.29 Appearance of RPUR foams catalyzed by (a) DMCHA, (b) Zn(OAc)(Val) (1:1), (c) Zn(OAc)(Arg) (1:1), (d) Zn(OAc)(Ser) (1:1) and (e) Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

4.3.2 Rise profiles

Rise profiles of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) the amount of blowing agent 4.0 pbw were investigated as shown in Figure 4.30. Rise profiles gave the data that agreed with the reaction time in Table 4.3. It was found that RPUR foams catalyzed by zinc-amino acid complexes showed a short time to initiate the reaction (which were cream time) similar to the reaction of catalyzed by DMCHA. DMCHA showed a very fast rise curve in the later stage (which were gel time and rise time), while zinc-amino acid complexes had a longer rise curve in the latter stage.

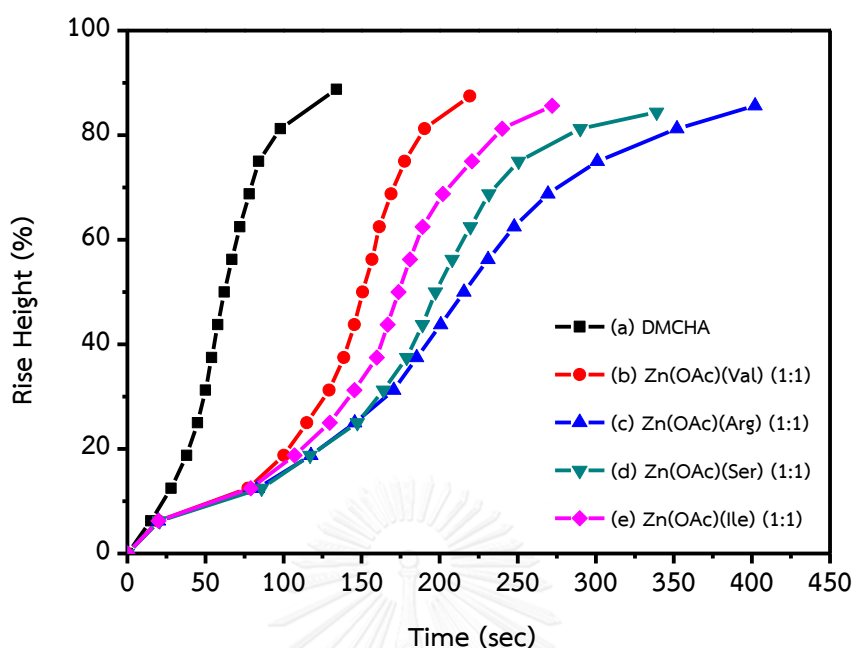
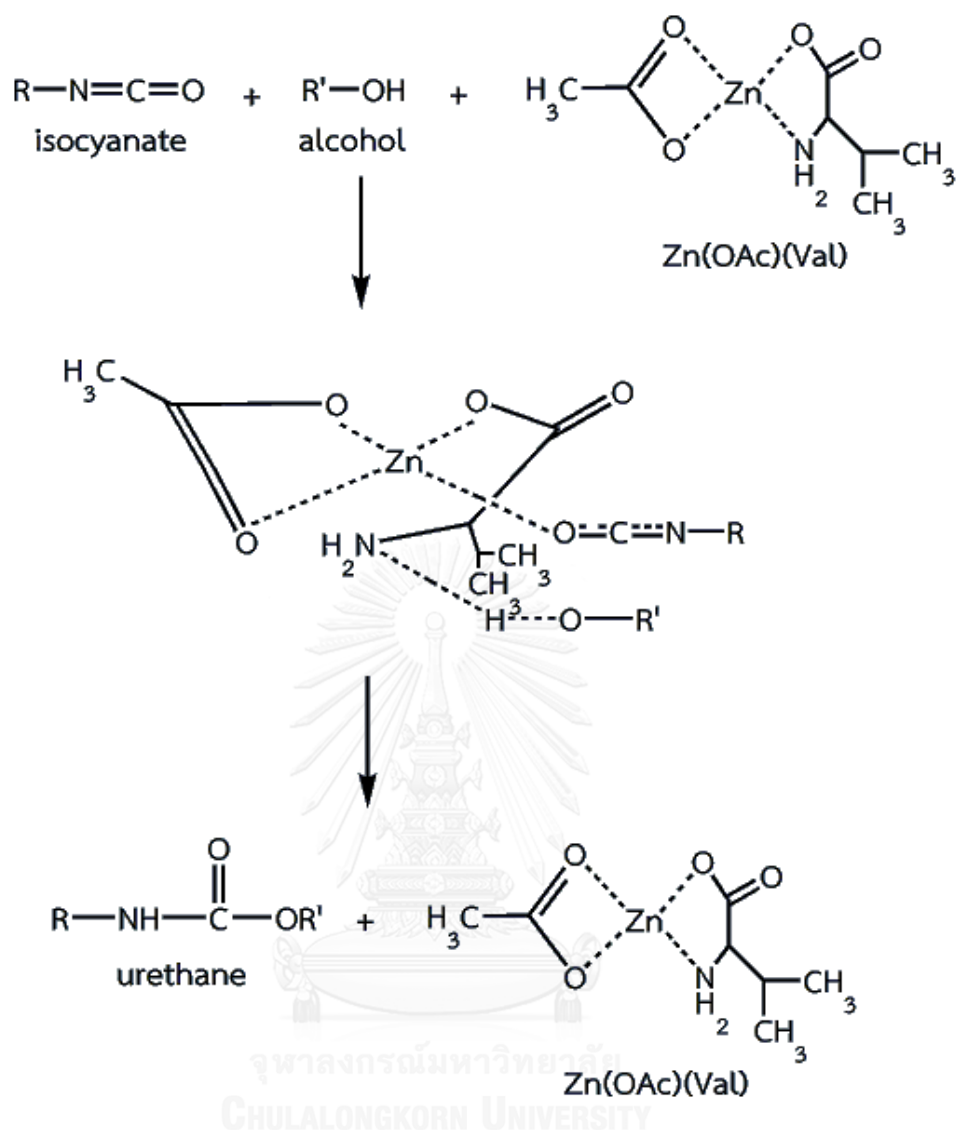


Figure 4.30 Rise profiles of RPUR foams catalyzed by (a) DMCHA, (b) Zn(OAc)(Val) (1:1), (c) Zn(OAc)(Arg) (1:1), (d) Zn(OAc)(Ser) (1:1) and (e) Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

4.3.3 Proposed catalytic mechanism of zinc-valine complex

The reaction mechanism of RPUR foam catalyzed by Zn(OAc)(Val) (1:1) complex is proposed as shown in Scheme 4.2. The zinc atom in Zn(OAc)(Val) 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 zinc-valine 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 [6]. The catalytic mechanisms of other metal-amino acid complexes in this research were proposed to be similar to that of Zn(OAc)(Val) (1:1).



Scheme 4.2 Catalytic mechanism of $\text{Zn}(\text{OAc})(\text{Val})$ (1:1)

4.3.4 Foaming Temperature

Temperature profiles of RPUR foams catalyzed by DMCHA, $\text{Zn}(\text{OAc})(\text{Val})$ (1:1), $\text{Zn}(\text{OAc})(\text{Arg})$ (1:1), $\text{Zn}(\text{OAc})(\text{Ser})$ (1:1) and $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) at the amount of blowing agent of 4.0 pbw were investigated as shown in Figure 4.31. It was found that the polymerization reaction was exothermic reaction which was the released heat of gelling reaction and blowing reaction. The maximum core temperature was in the range 95.4-129.7 °C as shown in Table 4.4.

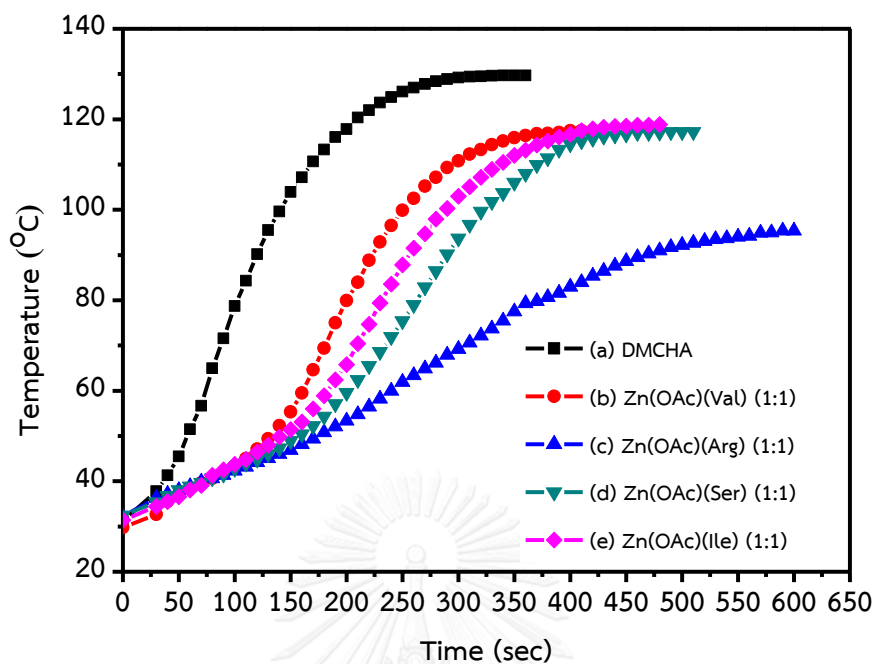


Figure 4.31 Temperature profiles of RPUR foams catalyzed by (a) DMCHA, (b) Zn(OAc)(Val) (1:1), (c) Zn(OAc)(Arg) (1:1), (d) Zn(OAc)(Ser) (1:1) and (e) Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

Table 4.4 The maximum core temperature of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

Catalysts	Maximum core temperature (°C)	Starting time at Tmax
DMCHA	129.7	360
Zn(OAc)(Val) (1:1)	117.5	420
Zn(OAc)(Arg) (1:1)	95.4	600
Zn(OAc)(Ser) (1:1)	117.2	510
Zn(OAc)(Ile) (1:1)	118.8	480

4.3.5 Characterization of RPUR foams

ATR-FTIR spectroscopy was used to investigate the polymerization of RPUR foam system. IR spectra of polyether polyol, polymeric MDI and RPUR foams catalyzed by DMCHA and zinc-amino acid complexes are shown in Figure 4.32. IR spectra of polyether polyol showed the broad band at 3409 cm^{-1} (stretching vibration of hydroxyl groups). Polymeric MDI showed high intensity of isocyanate absorption band at 2277 cm^{-1} .

All RPUR foams exhibited absorption band at $3324\text{-}3341\text{ cm}^{-1}$ (NH stretching of urethane and urea), $1701\text{-}1706\text{ cm}^{-1}$ (C=O stretching of urethane and urea), $1071\text{-}1079\text{ cm}^{-1}$ (C-O of urethane) and $1507\text{-}1509\text{ cm}^{-1}$ (could be attributed to N-H-bending vibration and C-N stretching vibration of urethane and urea groups). The band at $1221\text{-}1222\text{ cm}^{-1}$ was associated with the characteristic stretching vibration of C-N-H bond of urethane and urea [34].

From IR spectra of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1), the peak of isocyanate at 2277 cm^{-1} disappeared, which indicated that the reaction of isocyanate with hydroxyl groups and water were completed. Except for RPUR foams catalyzed by Zn(OAc)(Arg) (1:1) from which the peak of isocyanate at 2277 cm^{-1} could be observed. This indicated that Zn(OAc)(Arg) was not a good catalyst for RPUR foam preparation.

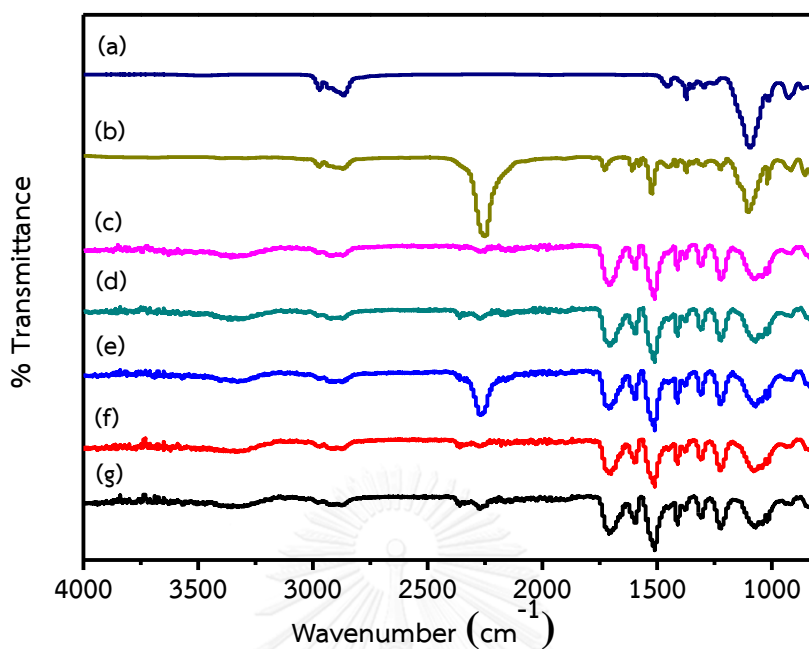


Figure 4.32 IR spectra of starting materials (a) polyether polyol, (b) polymeric MDI, RPUR foams catalyzed by (c) DMCHA, (d) Zn(OAc)(Val) (1:1), (e) Zn(OAc)(Arg) (1:1), (f) Zn(OAc)(Ser) (1:1) and (g) Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw

4.3.6 Isocyanate (NCO) conversion of RPUR foams

The peak area of the functional groups from IR spectra of polymeric MDI and RPUR foams catalyzed by DMCHA and zinc-amino acid complexes in Figure 4.32 were used in the calculation % NCO conversion.

The NCO conversion was defined as the ratio between isocyanate peak area at time 0 and isocyanate peak area at time t as shown in following equation.

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

Where:

NCO^f = the area of isocyanate absorbance peak area at time t (Figures 4.32 c-g)

NCO^i = the area of isocyanate absorbance peak area at initial time 0 (Figures 4.32 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	$\text{N}=\text{C}=\text{O}$
Phenyl	1595	Ar-H
Urethane	1220	-C-O-

The NCO conversion of RPUR foams catalyzed by DMCHA and zinc-amino acid complexes at the amount of blowing agent of 4.0 pbw is shown in Table 4.6. It was found that RPUR foams catalyzed by DMCHA, $\text{Zn}(\text{OAc})(\text{Val})$ (1:1), $\text{Zn}(\text{OAc})(\text{Ser})$ (1:1) and $\text{Zn}(\text{OAc})(\text{Ile})$ (1:1) gave approximately 99% of NCO conversion at which indicated that the reaction of isocyanate with hydroxyl groups and water were completed. Except for RPUR foams catalyzed by $\text{Zn}(\text{OAc})(\text{Arg})$ (1:1), which gave approximately 96% of NCO conversion. This indicated that the reaction of isocyanate with hydroxyl groups and water were not completed.

Table 4.6 NCO conversion of RPUR foams catalyzed by DMCHA and zinc-amino acid complexes at the amount of blowing agent of 4.0 pbw

Catalysts Types	Peak Area		NCO Conversion (%)
	NCO 2277 cm ⁻¹	Ar-H 1595 cm ⁻¹	
DMCHA	0.590	2.597	99.77
Zn(OAc)(Val) (1:1)	0.682	2.584	99.73
Zn(OAc)(Arg) (1:1)	10.064	2.583	96.02
Zn(OAc)(Ser) (1:1)	0.731	2.365	99.68
Zn(OAc)(Ile) (1:1)	0.683	2.485	99.72

4.4 Compressive properties of RPUR foams

The compression stress-strain curves of RPUR foams catalyzed by DMCHA and zinc-amino acid complexes at the amount of blowing agent of 4.0 pbw in parallel and perpendicular to the foam rising direction are shown in Figures 4.33 and 4.34, respectively. The compressive strength in parallel direction was higher than that of perpendicular direction, which indicated that all RPUR foams were anisotropic materials. The foam cells were elongated in the direction of the rise. The compressive properties depend on direction of measurement, which could be explained by the foam cell model as shown Figure 4.40. The compressive strength of RPUR foams catalyzed by different catalysts was DMCHA > Zn(OAc)(Val) (1:1) > Zn(OAc)(Ile) (1:1) > Zn(OAc)(Ser) (1:1) > Zn(OAc)(Arg) (1:1) in both parallel and perpendicular direction.

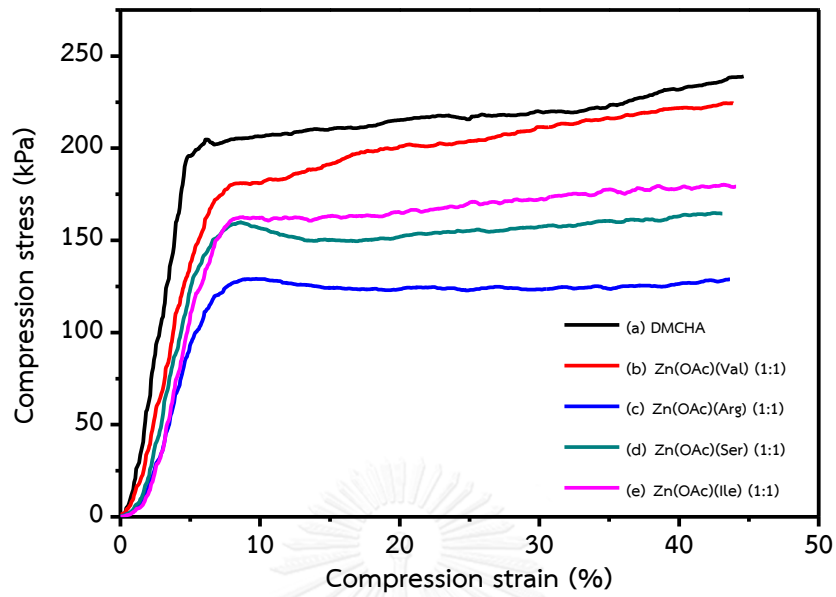


Figure 4.33 Compression stress-strain curves of RPUR foams in parallel to the foam rising direction

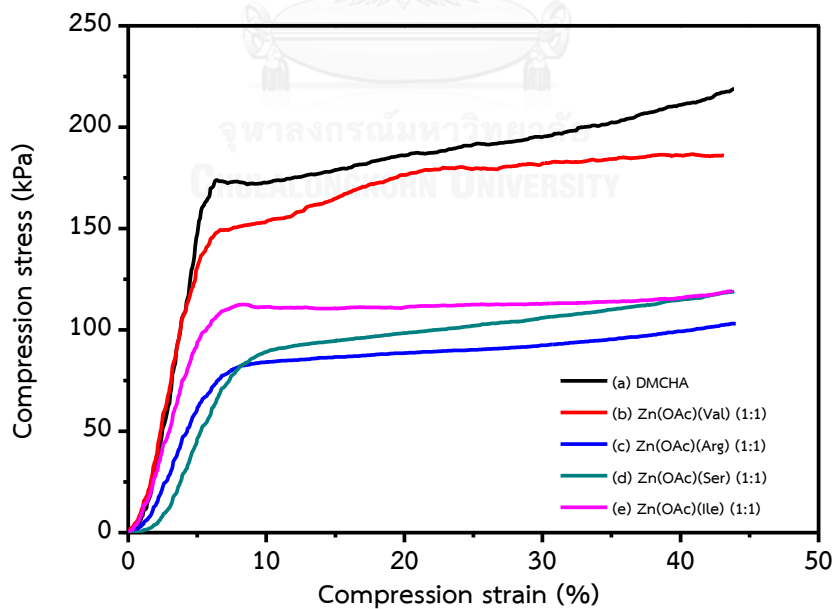


Figure 4.34 Compression stress-strain curves of RPUR foams in perpendicular to the foam rising direction

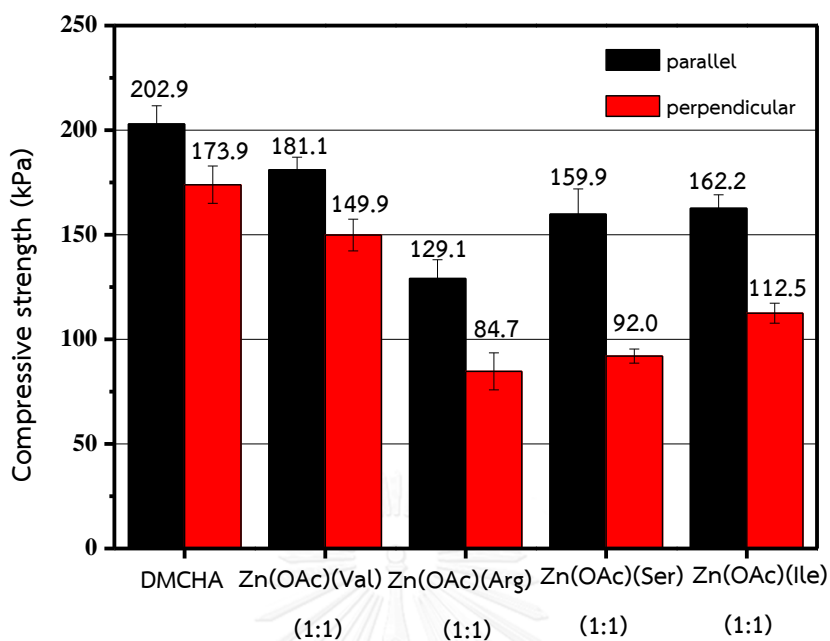


Figure 4.35 Compressive strength of RPUR foams

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(OAc)(Val) (1:1)	181.1 ± 5.94	149.9 ± 7.60
Zn(OAc)(Arg) (1:1)	129.1 ± 9.30	84.7 ± 8.85
Zn(OAc)(Ser) (1:1)	159.9 ± 11.98	92.0 ± 3.41
Zn(OAc)(Ile) (1:1)	162.6 ± 6.48	112.5 ± 4.83

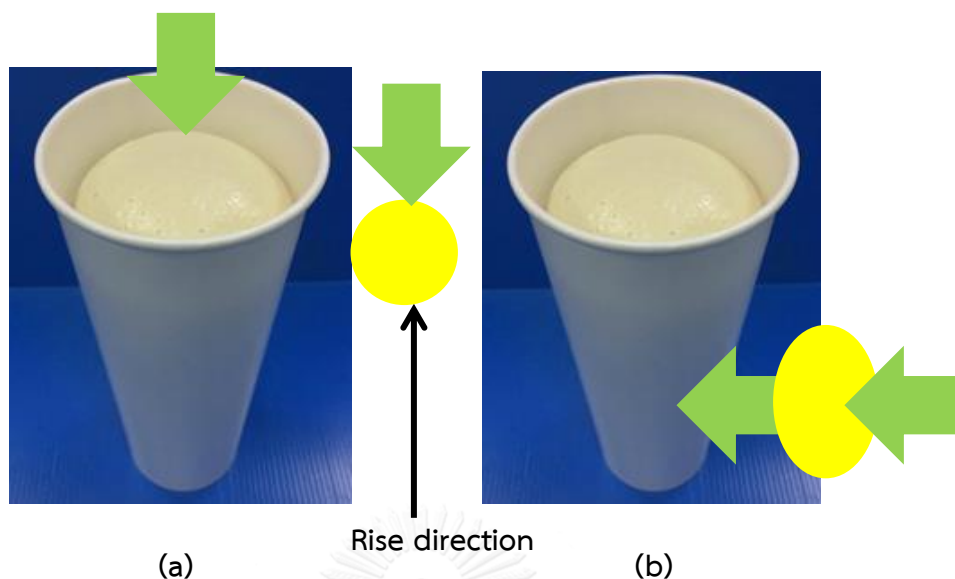


Figure 4.36 (a) Spherical cells, equal properties in all directions; (b) ellipsoid cells, which properties depend on direction

4.5 RPUR foams morphology

Morphology of RPUR foams catalyzed by DMCHA and zinc-amino acid complexes at the amount of blowing agent of 4.0 pbw in parallel and perpendicular to the foam rising direction are shown in Figures 4.37-4.46. The cell structure of all RPUR foams were closed cell. The cell shape of foams shown in (a) top view and (b) side view were spherical and ellipsoid, respectively. The average cell size of RPUR foams catalyzed by DMCHA, Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) are shown in Tables 4.8 and 4.9. The average cell size of RPUR foams for spherical shape and ellipsoidal shape was measured from cell size₁ and cell size₂ (Figure 4.47 (a) and 4.47 (b), respectively). It was found that the average cell size in top view and side view of RPUR foams obtained from different catalysts were DMCHA < Zn(OAc)(Val) (1:1) < Zn(OAc)(Ile) (0.5:0.5) < Zn(OAc)(Ser) (1:1) < Zn(OAc)(Arg) (1:1). Therefore, the small cell size of RPUR foams gave more compressive strength.

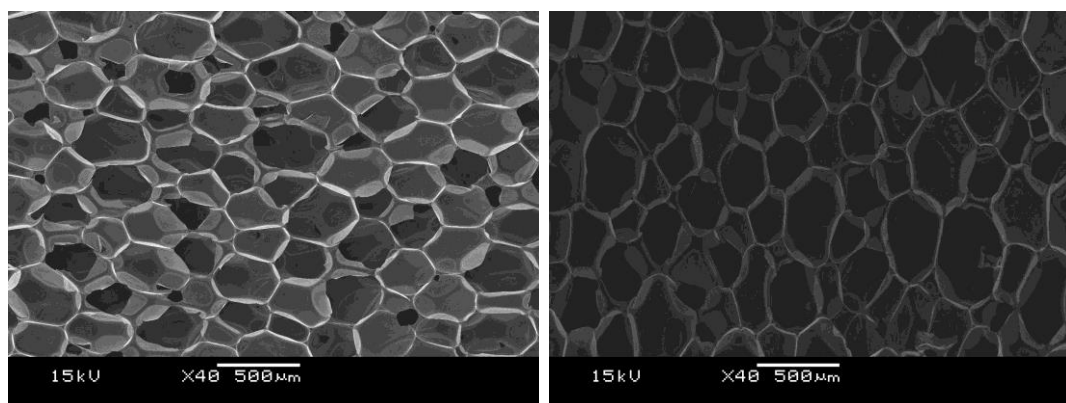


Figure 4.37 SEM of RPUR foams catalyzed by DMCHA (a) top view and (b) side view (40x)

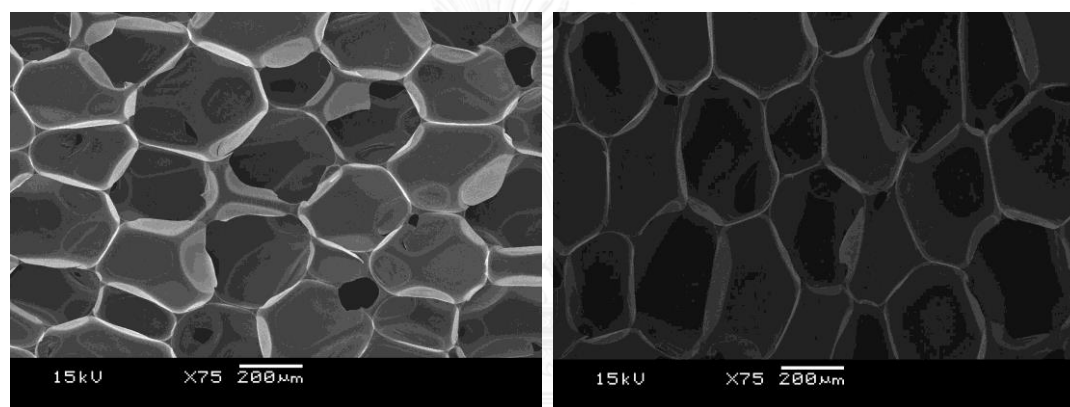


Figure 4.38 SEM of RPUR foams catalyzed by DMCHA (a) top view and (b) side view (75x)

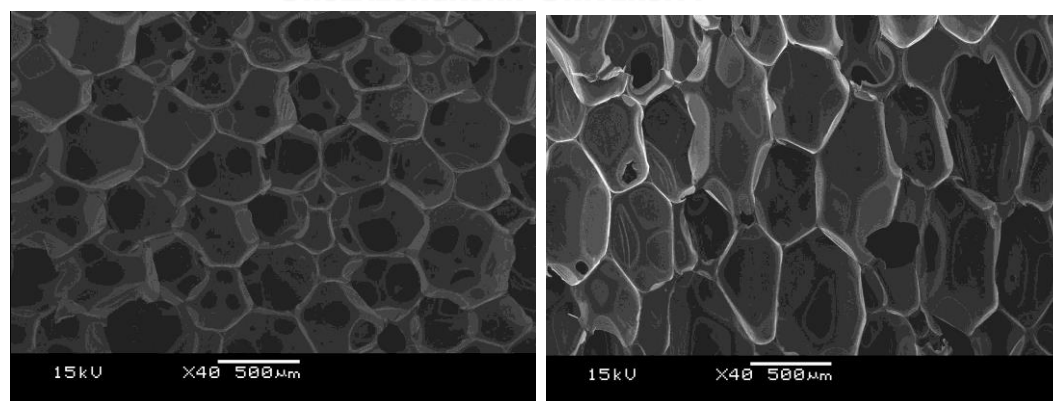


Figure 4.39 SEM of RPUR foams catalyzed by Zn(OAc)(Val) (1:1) (a) top view and (b) side view (40x)

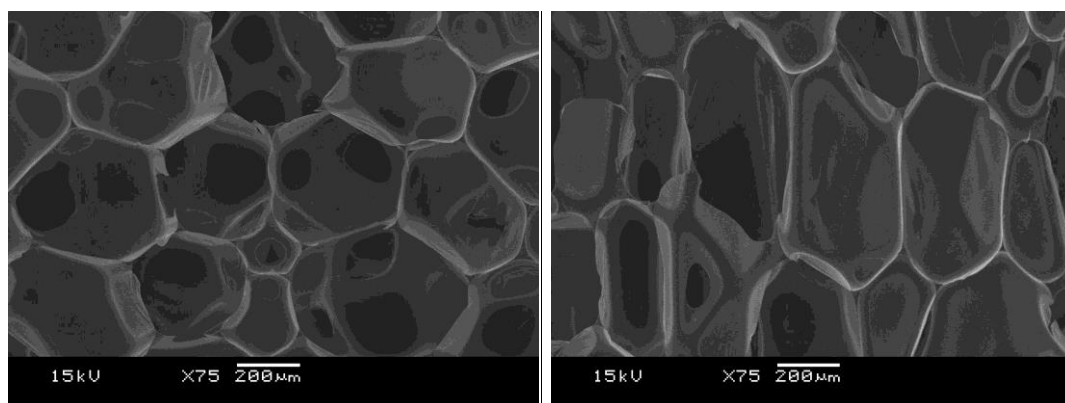


Figure 4.40 SEM of RPUR foams catalyzed by Zn(OAc)(Val) (1:1) (a) top view and (b) side view (75x)

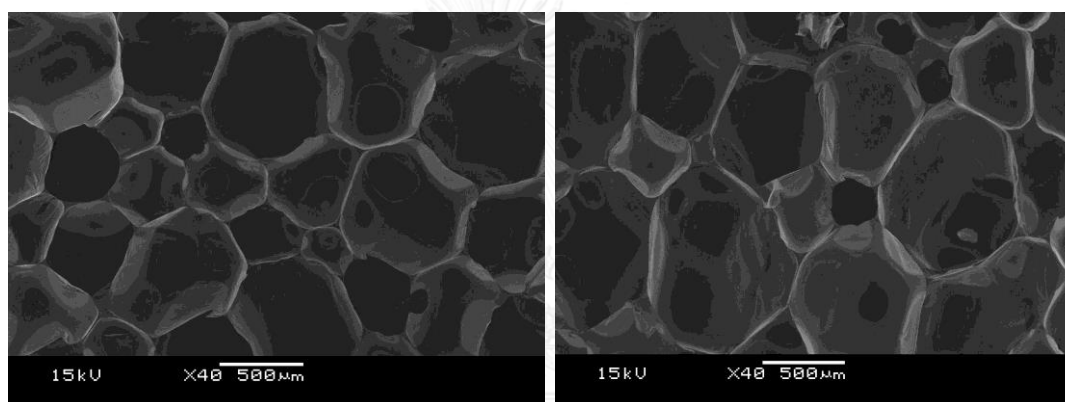


Figure 4.41 SEM of RPUR foams catalyzed by Zn(OAc)(Arg) (1:1) (a) top view and (b) side view (40x)

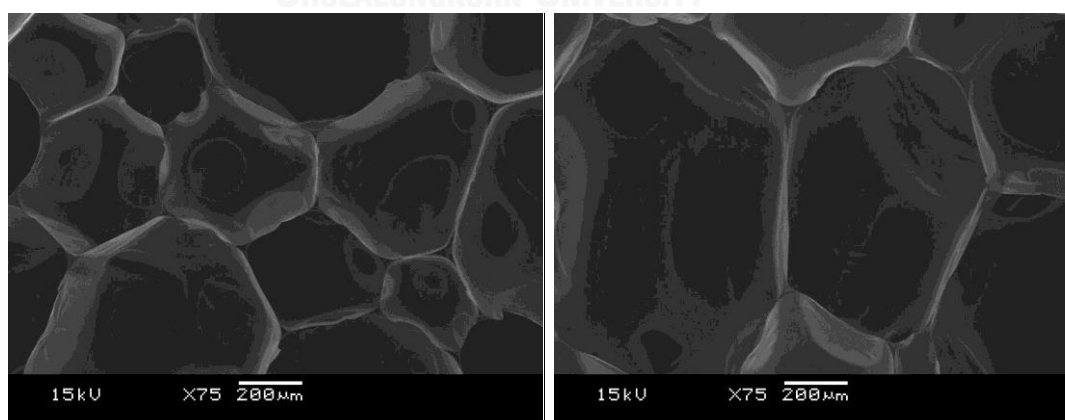


Figure 4.42 SEM of RPUR foams catalyzed by Zn(OAc)(Arg) (1:1) (a) top view and (b) side view (75x)

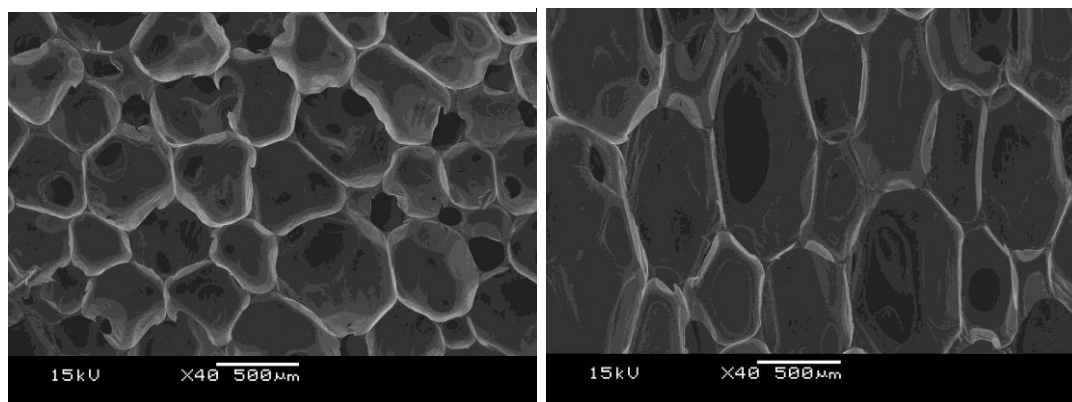


Figure 4.43 SEM of RPUR foams catalyzed by Zn(OAc)(Ser) (1:1) (a) top view and (b) side view (40x)

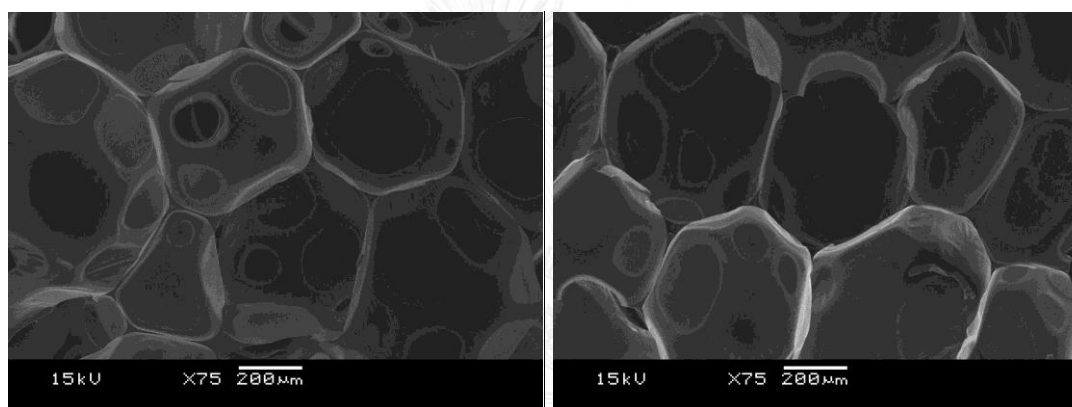


Figure 4.44 SEM of RPUR foams catalyzed by Zn(OAc)(Ser) (1:1) (a) top view and (b) side view (75x)

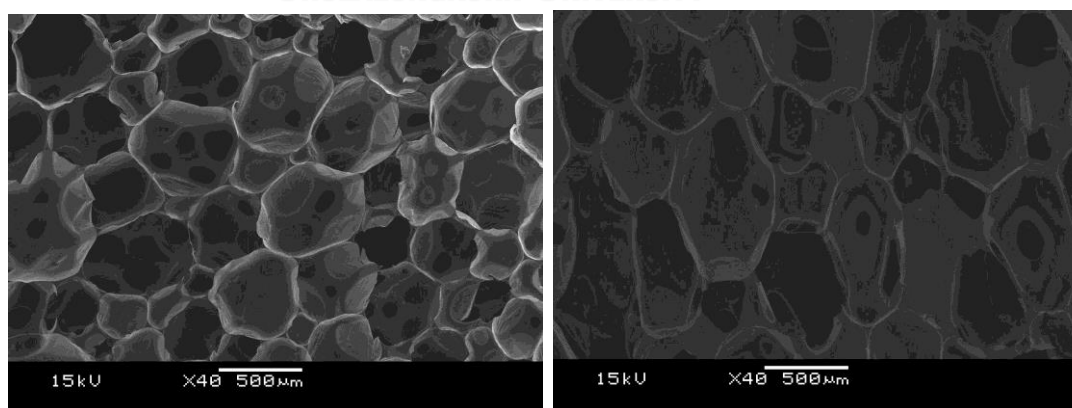


Figure 4.45 SEM of RPUR foams catalyzed by Zn(OAc)(Ile) (1:1) (a) top view and (b) side view (40x)

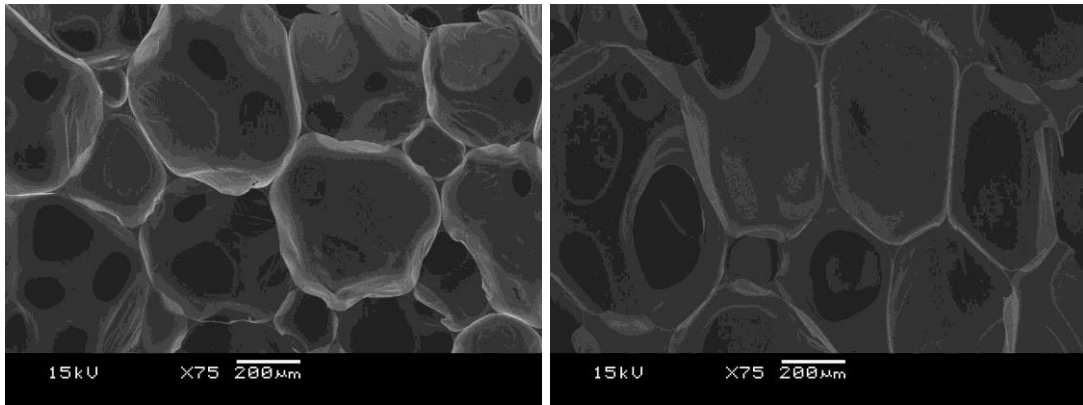


Figure 4.46 SEM of RPUR foams catalyzed by Zn(OAc)(Ile) (1:1) (a) top view and (b) side view (75x)

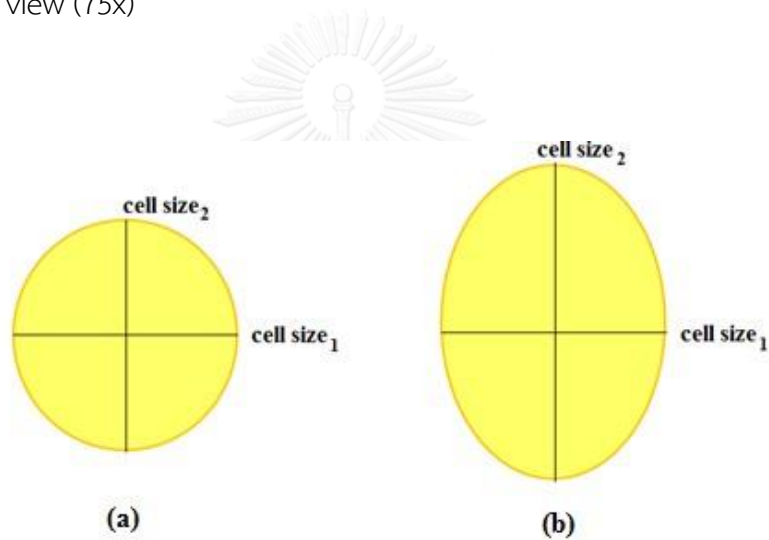


Figure 4.47 Measurement of cell size of PRUR foams (a) spherical shape and (b) ellipsoid shape

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

Catalysts	Top view	
	Cell size1 (μm)	Cell size2 (μm)
DMCHA (ref.)	358 ± 40.19	354 ± 35.43
Zn(OAc)(Val) (1:1)	377 ± 96.35	382 ± 115.52
Zn(OAc)(Arg) (1:1)	538 ± 147.19	483 ± 140.87
Zn(OAc)(Ser) (1:1)	423 ± 147.57	399 ± 141.89
Zn(OAc)(Ile)(1:1)	387 ± 139.88	392 ± 119.03

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

Catalysts	Side view	
	Cell size1 (μm)	Cell size2 (μm)
DMCHA (ref.)	289 ± 59.86	408 ± 67.83
Zn(OAc)(Val) (1:1)	328 ± 114.98	577 ± 101.02
Zn(OAc)(Arg) (1:1)	574 ± 119.19	740 ± 156.50
Zn(OAc)(Ser) (1:1)	419 ± 111.99	675 ± 129.46
Zn(OAc)(Ile)(1:1)	352 ± 127.86	588 ± 109.53

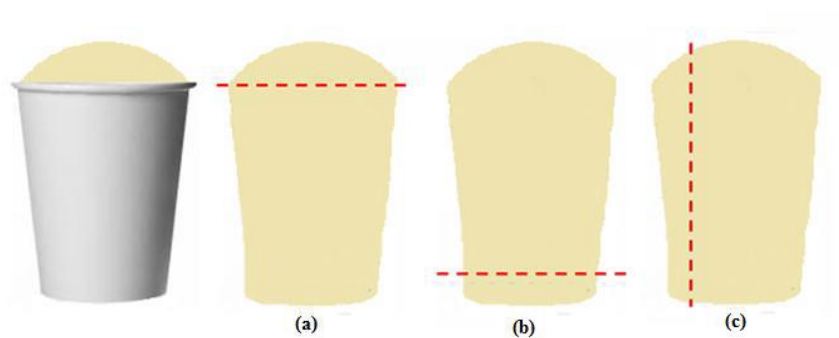


Figure 4.48 Cutting line for RPUR foams

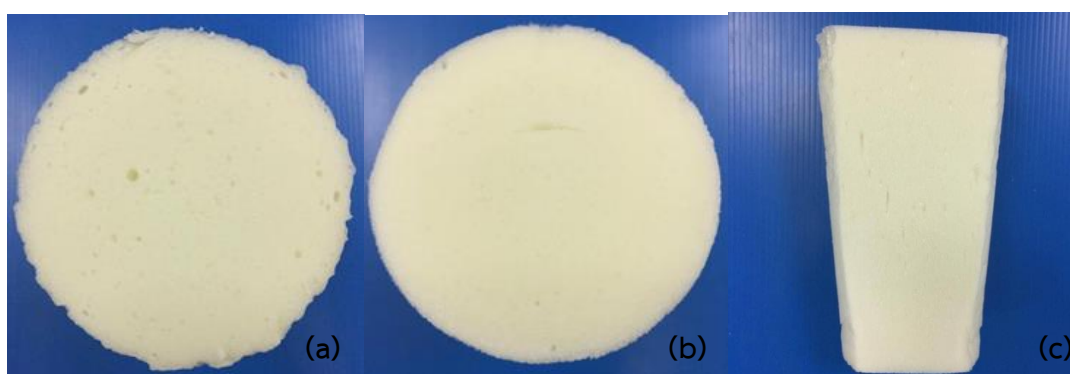


Figure 4.49 RPUR foams catalyzed by DMCHA (a) top; (b) bottom; (c) side of the foam sample



Figure 4.50 RPUR foams catalyzed by Zn(OAc)(Val) (1:1) (a) top; (b) bottom; (c) side of the foam sample

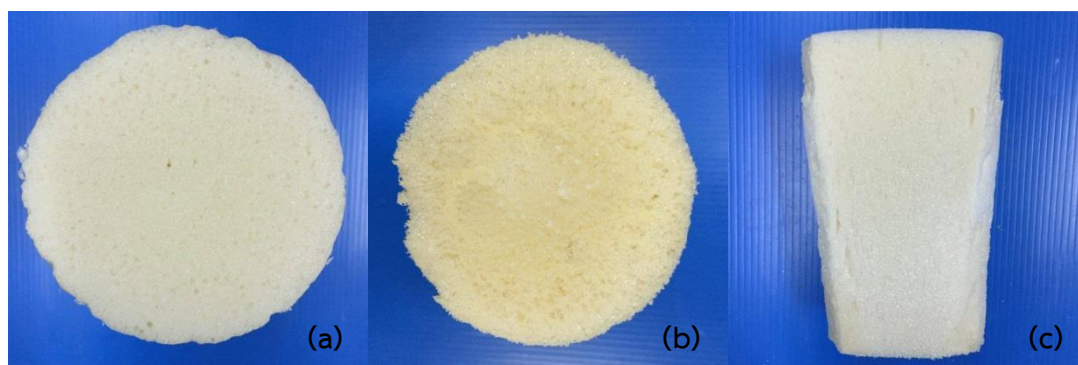


Figure 4.51 RPUR foams catalyzed by Zn(OAc)(Arg) (1:1) (a) top; (b) bottom; (c) side of the foam sample

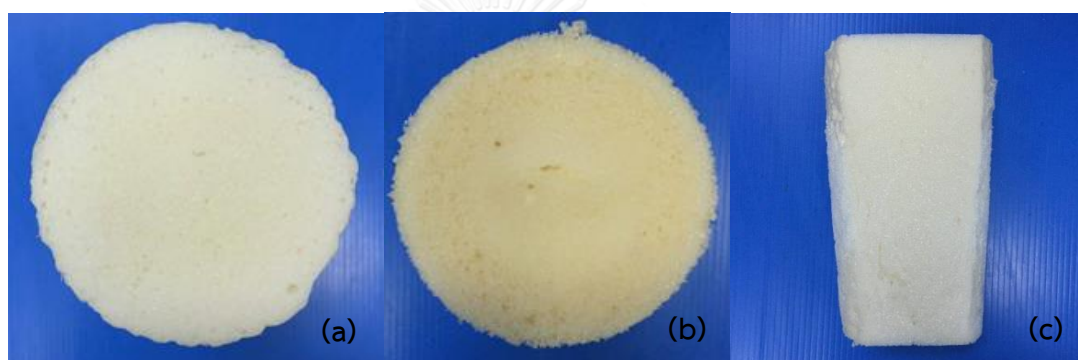


Figure 4.52 RPUR foams catalyzed by Zn(OAc)(Ser) (1:1) (a) top; (b) bottom; (c) side of the foam sample

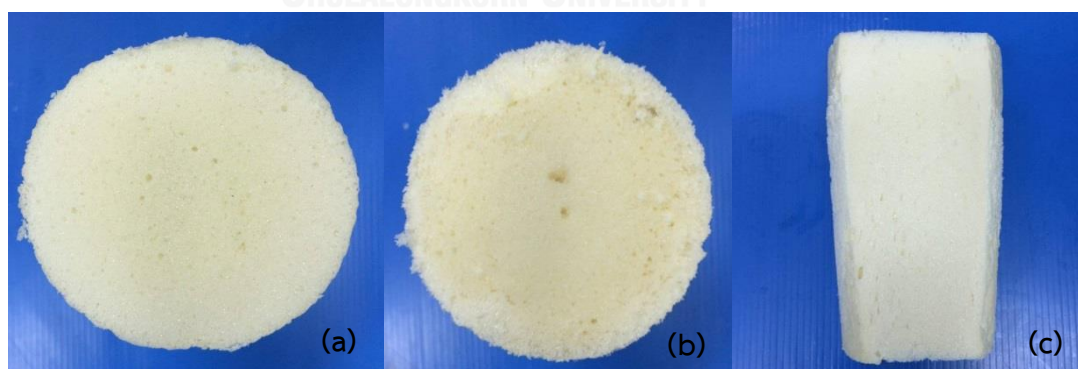


Figure 4.53 RPUR foams catalyzed by Zn(OAc)(Ile) (1:1) (a) top; (b) bottom; (c) side of the foam sample

CHAPTER V

CONCLUSION

5.1 Conclusion

Metal-amino acid complexes could be synthesized in water. The mole ratio of metal acetate to amino acid at 1:1 was suitable for the preparation of metal-amino acid complex aqueous solutions at the concentration of 20 wt%. The aqueous solutions of metal-amino acid complexes were obtained as odorless liquid and could be easily dissolved in the starting materials of RPUR foam formulation. Water in the aqueous solutions of metal-amino acid complexes also functioned as a blowing agent in RPUR foam formulation. Therefore, the aqueous solutions of metal-amino acid complexes could be used as catalysts for preparation of RPUR foams without purification. IR spectroscopy and mass spectrometry were used to characterize the zinc-amino acid complexes.

RPUR foam catalyzed by metal-amino acid complexes had longer the reaction times and therefore less catalytic activity of the RPUR foam catalyzed by DMCHA. It was found that RPUR foam catalyzed by zinc-valine complex at the mole ratio of metal acetate to amino acid = 1:1 and the amount of blowing 4.0 pbw (20 wt% concentration of metal-amino acid complexes in water) gave similar foam density to RPUR foam catalyzed by DMCHA.

Rise profile of RPUR foams catalyzed by Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1), Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) at the amount of blowing agent 4.0 pbw had shorter cream time at the initial of reaction time and a slow rise curve in the later stage. While DMCHA showed very fast reaction time since the initial reaction until the end of reaction.

The polymerization of RPUR foams is an exothermic reaction. The maximum core temperature during foaming reaction of Zn(OAc)(Val) (1:1), Zn(OAc)(Arg) (1:1),

Zn(OAc)(Ser) (1:1) and Zn(OAc)(Ile) (1:1) at the amount of blowing agent of 4.0 pbw was 95.4-129.7 °C. The NCO conversion was studied by ATR-FTIR spectroscopy. It was found that RPUR foams catalyzed by zinc-amino acid complexes had NCO conversion higher than 99%, which indicated that zinc-amino acid complexes have good catalytic activity in both gelling and blowing reactions.

From the result of compressive stress-strain curve, it was found that compressive strength of RPUR foams in the parallel direction to foam rising direction are higher than that in perpendicular direction. RPUR foams catalyzed by zinc-amino acid complexes gave less compressive strength than RPUR foams catalyzed by DMCHA.

Morphology of RPUR foams indicated that all cell structures of RPUR foams were closed cell. The foam cells in the top view (perpendicular to the foam rising direction) were spherical shape. The foam cells in side view (parallel to the foam rising direction) were ellipsoid shape. These results indicated that RPUR foams were anisotropic materials. The RPUR foams catalyzed by zinc-amino acid complexes gave more average cell size than RPUR foam catalyzed by DMCHA. These results agreed with the compressive strength data because the large cell size of foams gave less compressive strength.

5.2 Suggestion for future work

The suggestion for future work is the preparation metal complexes using other amino acids and use as catalysts for RPUR foam preparation.

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APPENDIX

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APPENDIX A

NCO index and NCO conversion calculations

NCO index calculation

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

Foam formulation NCO Index = 100	parts by weight (pbw)	
-Polyether polyol (Polimax®4221)	100	100
-Surfactant (Tegostab® B8460)	2.5	2.5
-Blowing agent (water)	3.0	4.0
-Catalyst (metal-amino acid complexes or DMCHA)	1.0	1.0, 0.5
-Polymeric MDI (PMDI, Raycore®B9001)	?	?

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

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

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

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

Equivalent weight in the above formulation:

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

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

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

For stoichiometric equivalence, PMDI pbw is total equivalent \times 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;

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

Therefore:

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)

Foam formulation NCO Index = 100	parts by weight (pbw)	
-Polyether polyol (Polimax [®] 4221)	100	100
-Surfactant (Tegostab [®] B8460)	2.5	2.5
-Blowing agent (water)	3.0	4.0
-Catalyst (metal-amino acid complexes or DMCHA)	1.0	1.0, 0.5
-Polymeric MDI (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:

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

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) and PIR: PUR of rigid polyurethane foams catalyzed by Zn(OAc)(Val) (1:1) catalyst at NCO index 100

Conversion of isocyanate (%)

Data at **Table A2**

Absorbance peak area of initial NCO = 98.0 = NCOⁱ

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 = 0.227 = NCO^f

Therefore:

$$\begin{aligned} \text{Isocyanate conversion (\%)} &= \left[1 - \frac{\text{NCO}^f}{\text{NCO}^i} \right] \times 100 \\ &= \left[1 - \frac{0.227}{98.0} \right] \times 100 \end{aligned}$$

$$\% \text{ NCO conversion} = 99.73$$

Table A3 NCO conversion of RPUR foam catalyzed by Zn(OAc)(Val) (1:1) at NCO index 100 (catalyst = 1 pbw, H₂O = 4 pbw)

Catalyst	Peak Area			NCO Conversion (%)
	NCO 2277 cm ⁻¹	Ar-H 1595 cm ⁻¹	NCO ^f (Ar-H = 1.0)	
Zn(OAc)(Val) (1:1)	0.682	2.584	0.263	99.73

Table A4 NCO conversion of RPUR foam catalyzed by different catalysts at the NCO index 100 (catalyst = 1 pbw, H₂O = 4 pbw)

Catalyst	Peak Area			NCO Conversion (%)
	NCO 2277 cm ⁻¹	Ar-H 1595 cm ⁻¹	NCO ^f (Ar-H = 1.0)	
DMCHA (ref.)	0.590	2.597	0.227	99.77
Zn(OAc)(Val) (1:1)	0.682	2.584	0.263	99.73
Zn(OAc)(Arg) (1:1)	10.064	2.583	3.896	96.02
Zn(OAc)(Ser) (1:1)	0.731	2.365	0.309	99.68
Zn(OAc)(Ile) (1:1)	0.683	2.485	0.274	99.72

APPENDICE 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.
<i>Reaction times (sec)</i>		
Cream time	22	0
Gel time	34	0.45
Tack free time	134	2.19
Rise time	107	1.10
Density (kg/m ³)	37.96	0.32
<i>Mechanical properties</i>		
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 Cu(OAc)(Val) at the NCO index 100 and the amount of blowing agent of 3.0 pbw

Cu(OAc)(Val)	The mole ratios of metal acetate:amino acid			
	1:2		1:1	
Efficiency parameters	Data	S.D.	Data	S.D.
<i>Reaction times (sec)</i>				
Cream time	23	1.15	33	4.04
Gel time	192	2.52	100	1.53
Tack free time	460	3.46	205	5.00
Rise time	524	0.58	208	2.00
Density (kg/m ³)	49.23	0.78	42.53	0.81

Table B3 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Cu(OAc)(Arg) at the NCO index 100 and the amount of blowing agent of 3.0 pbw

Cu(OAc)(Arg)	The mole ratios of metal acetate:amino acid			
	1:2		1:1	
Efficiency parameters	Data	S.D.	Data	S.D.
<i>Reaction times (sec)</i>				
Cream time	24	2.00	28	0.58
Gel time	153	1.15	154	1.00
Tack free time	408	2.89	327	2.08
Rise time	508	2.89	420	2.89
Density (kg/m ³)	54.28	0.75	47.99	0.95

Table B4 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Cu(OAc)(Arg) (1:1, 40 wt%) at the NCO index 100 and the amount of blowing agent of 3.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	Cu(OAc)(Arg) (1:1, 40 wt%)	
Polyol (Polymaxx [®] 4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore [®] B9001)	166.4	
Efficiency parameters	Data	S.D.
<i>Reaction times (sec)</i>		
Cream time	28	0
Gel time	174	0
Tack free time	399	0.58
Rise time	486	1.73
Density (kg/m ³)	46.25	0.77

Table B5 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Val) at the NCO index 100 and the amount of blowing agent of 3.0 pbw

Zn(OAc)(Val)	The mole ratios of metal acetate:amino acid			
	1:2		1:1	
Efficiency parameters	Data	S.D.	Data	S.D.
<i>Reaction times (sec)</i>				
Cream time	23	1.15	21	0.58
Gel time	143	0.58	92	2.08
Tack free time	380	2.00	208	0
Rise time	455	3.46	233	0.58
Density (kg/m ³)	43.40	1.00	38.94	0.61

Table B6 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Arg) at the NCO index 100 and the amount of blowing agent of 3.0 pbw

Zn(OAc)(Arg)	The mole ratios of metal acetate:amino acid			
	1:2		1:1	
Efficiency parameters	Data	S.D.	Data	S.D.
<i>Reaction times (sec)</i>				
Cream time	22	0	22	0
Gel time	191	1.00	137	0.58
Tack free time	711	1.15	468	0.58
Rise time	1088	2.25	743	0
Density (kg/m ³)	54.99	0.81	46.31	0.21

Table B7 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Val) (1:1,40 wt%) at the NCO index 100 and the amount of blowing agent of 3.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	Zn(OAc)(Val) (1:1, 40 wt%)	
Polyol (Polymaxx [®] 4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	3.0	
PMDI (Raycore [®] B9001)	151.3	
Efficiency parameters	Data	S.D.
<i>Reaction times (sec)</i>		
Cream time	22	0
Gel time	102	2.89
Tack free time	213	2.08
Rise time	239	1.15
Density (kg/m ³)	43.24	1.00

Table B8 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Val) (1:1) at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	Zn(OAc)(Val) (1:1)	
Polyol (Polymaxx [®] 4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore [®] B9001)	166.4	
Efficiency parameters	Data	S.D.
<i>Reaction times (sec)</i>		
Cream time	22	0
Gel time	97	2.31
Tack free time	217	2.31
Rise time	222	2.31
Density (kg/m ³)	37.95	0.53
<i>Mechanical properties</i>		
Compressive strength (kPa) in parallel	181.1	5.94
Compressive strength (kPa) in perpendicular	149.9	7.60

Table B9 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Arg) (1:1) at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	Zn(OAc)(Arg) (1:1)	
Polyol (Polymaxx [®] 4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore [®] B9001)	166.4	
Efficiency parameters	Data	S.D.
<i>Reaction times (sec)</i>		
Cream time	21	0
Gel time	132	1.79
Tack free time	395	1.10
Rise time	408	0.45
Density (kg/m ³)	39.68	0.35
<i>Mechanical properties</i>		
Compressive strength (kPa) in parallel	129.1	9.30
Compressive strength (kPa) in perpendicular	84.7	8.85

Table B10 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Ser) (1:1) at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Formulations (pbw)	Catalyst at NCO index 100	
	Zn(OAc)(Ser) (1:1)	
Polyol (Polymaxx [®] 4221)	100	
Catalyst	1.0	
Surfactant	2.5	
Blowing agent	4.0	
PMDI (Raycore [®] B9001)	166.4	
Efficiency parameters	Data	S.D.
<i>Reaction times (sec)</i>		
Cream time	22	0
Gel time	128	1.67
Tack free time	323	2.74
Rise time	342	2.51
Density (kg/m ³)	38.91	0.56
<i>Mechanical properties</i>		
Compressive strength (kPa) in parallel	159.9	11.98
Compressive strength (kPa) in perpendicular	92.0	3.41

Table B11 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by Zn(OAc)(Ile) at the NCO index 100 and the amount of blowing agent of 4.0 pbw

Zn(OAc)(Ile)	The concentration of metal-amino acid complexes			
	20 wt% in H ₂ O		11 wt% in H ₂ O	
Efficiency parameters	Data	S.D.	Data	S.D.
<i>Reaction times (sec)</i>				
<i>Cream time</i>	22	0	22	0.00
<i>Gel time</i>	66	0	105	1.79
<i>Tack free time</i>	142	0	254	2.74
<i>Rise time</i>	142	0	274	2.74
Density (kg/m ³)	37.97	0.99	38.99	0.64
<i>Mechanical properties</i>				
Compressive strength (kPa) in parallel	-	-	162.6	6.48
Compressive strength (kPa) in perpendicular	-	-	112.5	4.83

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