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นางสาวอลิษา ลิ้มศิรินาวา

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สาขาวิชาเคมี ภาควิชาเคมี
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PREPARATION OF RIGID POLYURETHANE FOAMS USING METAL ACETYLACETONATE-AMINE CATALYSTS

Miss Alisa Limsirinawa

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
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Thesis Title PREPARATION OF RIGID POLYURETHANE FOAMS USING METAL ACETYLACETONATE-AMINE CATALYSTS
By Miss Alisa Limsirinawa
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Thesis Advisor Associate Professor Nuanphun Chantarasiri, Ph. D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.... Chairman

(Assistant Professor Warinthorn Chavasiri, Ph. D.)

.... Thesis Advisor

(Associate Professor Nuanphun Chantarasiri, Ph. D.)

.... Examiner

(Professor Thawatchai Tuntulani, Ph. D.)

.... Examiner

(Associate Professor Polkit Sangvanich, Ph. D.)

.... External Examiner

(Duangruthai Sridaeng, Ph. D.)

อลิยา ลิ้มศิรินาวา : การเตรียมโฟมพอลิยูรีเทนแบบแข็งโดยใช้ตัวเร่งปฏิกิริยาโลหะแอซีทิลแอซีโทเนต-แอมีน. (PREPARATION OF RIGID POLYURETHANE FOAMS USING METAL ACETYLACETONATE-AMINE CATALYSTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. นวลพรรณ จันทรศิริ, 96 หน้า.

งานวิจัยนี้สนใจที่จะ พัฒนาตัวเร่งปฏิกิริยาสำหรับ การเตรียมโฟมพอลิยูรีเทนแบบแข็ง โดยสังเคราะห์สารประกอบเชิงซ้อนของโลหะ-แอมีนจากปฏิกิริยาระหว่างเกลือแอซีทิลแอซีโทเนตของโลหะ [M(acac)$_2$] กับแอมีน แล้วนำมาใช้เป็นตัวเร่งปฏิกิริยาเตรียมโฟมพอลิยูรีเทนแบบแข็ง นำตัวเร่งปฏิกิริยาที่สังเคราะห์ได้มาพิสูจน์เอกลักษณ์ด้วยเทคนิคอินฟราเรดสเปกโทรสโกปี ยูวี-วิสสิเบิลสเปกโทรสโกปี แมสสเปกโทรเมทรี และวิเคราะห์หาธาตุองค์ประกอบ ข้อดีของสารประกอบเชิงซ้อนของโลหะ-แอมีน คือ มีกลิ่นเหม็นน้อยกว่าไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA) ซึ่งเป็นตัวเร่งปฏิกิริยาทางการค้าที่ใช้ ทั่วไป ในการเตรียม โฟมพอลิยูรีเทนแบบแข็ง ทำการเตรียมโฟมที่ดัชนีไอโซไซยาเนตเท่ากับ 100 และ 150 ศึกษาเวลาในการเกิดปฏิกิริยาในระหว่างการเตรียมโฟม ศึกษาความสมบูรณ์ในการเกิดปฏิกิริยาพอลิเมอไรเซชันโดยใช้เทคนิคเอทีอาร์-อินฟราเรดสเปกโทรสโกปี ด้วยค่าการเปลี่ยนแปลงของปริมาณหมู่ไอโซไซยาเนต วิเคราะห์และเปรียบเทียบความหนาแน่นของโฟมพอลิยูรีเทนแบบแข็งที่ได้ จากผลการทดลองพบว่าโฟมพอลิยูรีเทนแบบแข็งที่เตรียมจากสารประกอบเชิงซ้อนโลหะ- แอมีน มีเวลาของการเกิดปฏิกิริยา สมบัติทางกายภาพ และสมบัติเชิงกลของดีเทียบเท่ากับโฟมพอลิยูรีเทนแบบแข็งที่เตรียมจากตัวเร่งปฏิกิริยาทางการค้าคือ ไดเมทิลไซโคลเฮกซิลแอมีน

ภาควิชา..........เคมี.................. ลายมือชื่อนิสิต..
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ALISA LIMSIRINAWA: PREPARATION OF RIGID POLYURETHANE FOAMS USING METAL ACETYLACETONATE-AMINE CATALYSTS. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph. D., 96 pp.

This work is interested in the development of catalysts for rigid polyurethane foam preparation. Metal-amine complexes have been synthesized from metal acetylacetonate [$M(acac)_2$] and amines then use as catalysts in the preparation of rigid polyurethane foams. The metal-amine complexes synthesized were characterized using FTIR spectroscopy, UV-visible spectroscopy, mass spectrometry and elemental analysis. It was found that the metal-amine complexes are much less smelly as compared to dimethylcyclohexylamine (DMCHA), which is a commercial catalyst commonly used in the preparation of rigid polyurethane foams. The foams were prepared using the isocyanate index of 100 and 150. The reaction times during the foam preparation were investigated. The completeness of polymerization reaction was studied using ATR-IR spectroscopy by following isocyanate conversion. The densities of the rigid polyurethane foams were determined and compared. The experimental results showed that the reaction times, physical and mechanical properties of the foams prepared by use of the metal-amine complexes were comparable to those prepared from dimethylcyclohexylamine.

Department : Chemistry	Student's Signature
Field of Study : Chemistry	Advisor's Signature
Academic Year : 2012	

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

%	percentage
ε	molar absorptivity
ATR-IR	Attenuated Total Reflectance-Infrared
acac	acetylacetonate
CFCs	chlorofluorocarbons
cm	centimeter
cm^{-1}	unit of wavenumber
^{o}C	degree Celsius (centrigrade)
CO_2	carbon dioxide
DBTDL	dibutyltin dilaurate
DMCHA	N,N-dimethylcyclohexylamine
EA	Elemental Analysis
EG	ethyleneglycol
en	ethylenediamine
FAAS	flame atomic spectroscopy
FTIR	Fourier Transform Infrared Spectrophotometer
g	gram
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
IDT	Initial Decomposition Temperature
K Ac	potassium acetate
KOH	potassium hydroxide
K Oct	potassium octoate
kg	kilogram
kV	kilovolt
M	metal
$M(OAc)_2$	metal acetate
m^3	cubic meter
MDI	4,4'-methane diphenyl diisocyanate
MeOH	methanol

mA	milliampere
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mmol	millimole
N	newton unit
NCO	isocyanate
OH	hydroxyl
OHV	hydroxyl value
pbw	part by weight
PFCs	perfluorinated hydrocarbons
PIR	polyisocyanurate
pentaen	pentaethylenehexamine
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PU	polyurethane
PUR	polyurethane
PS	polystyrene
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
ref	reference
SEM	Scanning Electron Microscope
Sn Oct	stannous octoate
t	time
TDI	toluene diisocyanate
TEDA	triethylenediamine
TGA	Thermogravimetric Analysis
TMP	trimethylol propane
T_{max}	maximum core temperature
tetraen	tetraethylenepentamine
trien	triethylenetetramine
UV	ultraviolet

CHAPTER I

INTRODUCTION

Polyurethane foams are now playing an important role in many industries from construction to cars and furniture to footwear. Also, polyurethane foams can be divided into three major classes, namely flexible, semi-rigid and rigid foams.

Rigid polyurethane (RPUR) foams are one of the most versatile polymers that have been used in a wide range of areas. Because of their light weight, low thermal conductivity, good mechanical resistance and strength at low density, these foams are applied in many thermal insulation products such as refrigerators, freezers, refrigerated trucks, refrigerated warehouses, refrigerated containers, building and construction, chemical plants, portable ice boxes and water heaters [1-3].

RPUR foam is usually synthesized by the reaction of diisocyanate with hydroxyl compound or polyols, which is an exothermic reaction. Other components such as surfactant, blowing agent and catalyst are also employed to regulate the properties of the foam [4-5].

Catalyst is one component which played a vital role in RPUR foam system since the reaction between isocyanate and hydroxyl group is slow [6]. Nowadays, tin compounds and tertiary amines are mainly used as catalyst because of their excellent catalytic activity. However, tin compound is highly toxic and amine has strong odor. Accordingly, new catalysts or catalytic systems are needed to replace these catalysts [7].

The research in our group involves the synthesis of the complexes between metal(II)acetate and amine as the new catalysts for the RPUR foam preparation. It was found that those complexes showed comparable catalytic activity to the commercial catalyst: dimethylcyclohexylamine (DMCHA). However, some complexes gave fast reaction times, namely cream time and gel time, and caused difficulties in the RPUR foam preparation. Hence, the new catalysts were developed in this research.

Objectives

This work focused on the synthesis of metal-amine complexes and used as catalysts for RPUR foam preparation. It was expected that the obtained complexes presented good solubility, good catalytic activity and are less smelly. Consequently, we investigated the physical and mechanical properties of the foams, and reaction times during the foam rising. Variation of catalyst types, the content of catalysts and blowing agent and isocyanate index in the foam formulation was studied.

Scope of the research

The scopes of this research were the synthesis of the metal-amine complexes from metal acetylacetonate [$M(acac)_2$] and amine, using methanol or water as solvents. The synthesized metal-amine complexes were characterized by FTIR spectroscopy, UV-visible spectroscopy, flame atomic absorption spectroscopy (FAAS), elemental analysis and mass spectrometry.

Next, rigid polyurethane foams were prepared using these metal-amine complexes as catalysts. The reaction times during foam preparation were recorded, namely gel time, cream time, tack free time and rise time. Later, the RPUR foams were characterized by ATR-FTIR spectroscopy, compression testing, scanning electron microscopy (SEM) and thermogravimetry (TGA).

Physical and mechanical properties of the RPUR foams were determined at various NCO indexes, catalyst content, blowing agent amount and catalyst types. The obtained results in RPUR foam preparation using the obtained catalysts were compared with those of commercial catalyst, DMCHA, which is used as a reference catalyst.

CHAPTER II

THEORY AND LITERATURE REVIEWS

Polyurethane foams are produced by using polyols and isocyanate compounds as the main components and other components such as surfactant, blowing agent and catalyst are also employed to regulate the properties of the foam. They can be made into different kinds of forms divided to flexible, semi-rigid and rigid foams.

In terms of rigid polyurethane (RPUR) foams, they are one of the most versatile polymers that have been used in a wide range of areas. Because of their light weight, low thermal conductivity and good mechanical resistance, they are used as insulation to packaging and commercial refrigeration, and building engineering applications [5, 8].

2.1 Raw materials

For the manufacture of rigid polyurethane (RPUR) foams, the main polymer-forming reaction takes place between polyfunctional isocyanates and polyhydroxyl compounds or polyols, forming the urethane linkage. The physical and chemical character, structure, and molecular size of these compounds influence the polymerization reaction, as well as final physical properties of polyurethane. In the presence of excess isocyanate groups, further reactions occur to produce allophanates, isocyanurates and other secondary products [9]. In addition, additive such as catalysts, surfactants, blowing agents and fillers are used to control and modify the reaction process and performance characteristics of the polyurethane foam.

2.1.1 Isocyanates

The major isocyanate employed is aromatic isocyanates because foaming reactions require high reactivity, and aliphatic isocyanates react slowly with OH groups [6]. The two aromatic isocyanates used for the production of almost all rigid polyurethane foams are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) in oligomeric type [10]. Variation of polyurethane properties can be achieved by variation of the types of isocyanate used [2].

2.1.1.1 Toluene diisocyanate (TDI), TDI is manufactured by phosgenation of diaminotoluene, which is obtained by the reduction of nitrotoluene. TDI is a colourless liquid commercially available as a mixture of 2,4- and 2,6-isomers in the ratio of 80:20 or 65:35. Its main use is in the production of flexible polyurethane foams [2, 10]. The use of TDI in rigid polyurethane foams is limited by its high isocyanate content and high vapor pressure. Elimination of operator exposure to TDI vapor requires well-designed ventilating systems. These two factors restrict TDI-based rigid foams to insulation of refrigerator or freezer cabinets and to other in-plant operations [9]. Therefore, it is pretty a difficult material to handle on site, in transport and in the laboratory and consequently its usage has been limited in favor of MDI which has a lower volatility.

2.1.1.2 Diphenylmethane diisocyanate (MDI), MDI is obtained by the phosgenation of the condensation product of aniline with formaldehyde [11]. MDI is availible in two types, purifide monomeric and polymeric MDI. They contains both 4,4′-isomer and 2,4′-isomer and different grades may have different ratios of these two. Their average functionality is in a range of 2.3 to 3.0. Pure MDI (or monomeric MDI) is obtained by the distillation of a crude reaction product and is used for elastomers and coatings [2]. Polymeric MDI (Figure 2.1) is a yellow to dark brown material, liquid at room temperature. The higher functionality of polymeric MDI facilitating the production of a rigid, crosslinked, network coupled with the highly aromatic character which contributes to flame resistance, makes polymeric MDI (PMDI) the isocyanate of choice for most rigid polyurethane foams [10].

Of all the commercially available isocyanates, MDI is the one that produces polyurethanes which yellow fastest on exposure to light. This is because the urethanes derived from it can easily oxidize through a radical mechanism to produce a quinine-imide, conjugated structure, which is a yellow chromophore [12]. The viscosity of polymeric MDI increases with increasing molecular weight and polymeric isocyanate content. Moreover, the selection of polymeric MDI may obtain the different kinds of polyurethanes due to different range of functionality, structure and compositions.

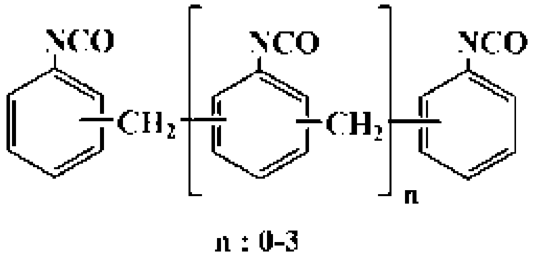


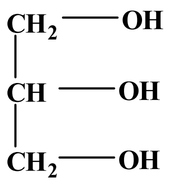
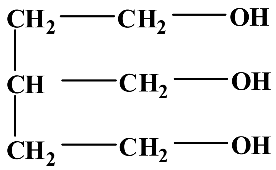
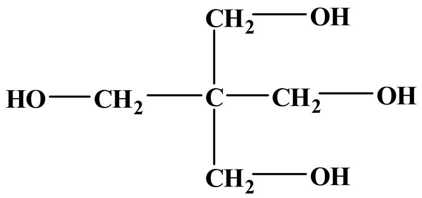
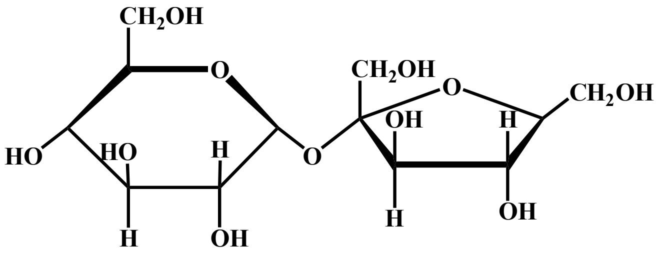
Figure 2.1 The chemical structures of polymeric MDI.

2.1.2 Polyols

The polyol used for the manufacture of RPUR foams are usually either polyether or polyester type polyols. In general, rigid foam polyol have molecular weight of 150-1000 g/mol, functionality 2.5-8.0 and hydroxyl value 250-1000 mg KOH/g. The segment length between junction points this effectively produces more tightly crosslinked networks [13]. Generally, polyethers give softer, more resilient foams with better hydrolysis resistance than polyesters, while the polyester-based foams may be expect to have greater tensile strength and better resistance to oils, solvents and oxidation [14]. Polyether polyols for RPUR foams are produced using high functionality initiators such as glycerol, sorbitol and sucrose. Some polyol characteristics are shown in Table 2.1.

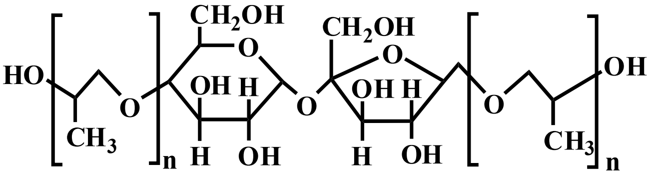
The lower functionality and higher molecular weight polyols are used in the production of flexible polyurethane foams. On the other hand, rigid foams need the higher functionality and lower molecular weight polyols in order to get the higher degree of crosslinking which contributes to the stiffness of polymer. It is necessary to utilize various polyols produce polyurethane with desired properties.

Table 2.1 Functionality of some common polyols [10]

Hydroxylated Compound	**Chemical Structure**	**Functionality**
Ethylene glycol (EG)	$HO-CH_2-CH_2-OH$	**2**
Glycerol	 $HO-CH_2-CH(OH)-CH_2-OH$	**3**
Trimetylol propane (TMP)	 $HO-CH_2-CH_2-CH_2-CH(CH_2-OH)-CH_2-CH_2-OH$	**3**
Pentaerythritol	 $HO-CH_2-C(CH_2-OH)_2-CH_2-OH$	**4**
Sorbitol	$HO-CH_2-(CHOH)_4-CH_2-OH$	**6**
Sucrose		**8**

2.1.2.1 Polyether polyols

Polyether polyols are produced by the ring opening of alkylene oxides using a polyfunctional as starter or initiator. The polyfunctional starter compounds are mainly ethylene glycol, trimethylolpropane, glycerol, pentaerythritol, sorbitol and sucrose. Sucrose is an ideal for a rigid polyol starter because of its low cost, ready availability and high functionality [12]. The advantages of polyether polyols over polyester polyols are various functionality, equivalent weight can be widely changed, the viscosity is lower than polyester, production cost is cheaper and the functionality and equivalent weight of polyether polyols can be widely varied. A disadvantage is lower oxidation resistance than that of polyester foams [2]. In RPUR foam production, polyether polyol based sucrose (Figure 2.2) is approximately 90% of used polyols due to their low cost and ease of handling (low viscosity).



Poly (propyleneoxy) sucrose

Figure 2.2 Structure of polyether polyol-based sucrose [poly(propyleneoxy sucrose)]

2.1.2.2 Polyester polyols

Polyester polyols are produced by condensation reactions between diols (and triol) and dicarboxylic acid such as adipic acid, sebacic acid and three isomeric phthalic acids. They were used to a significant extent in the early development period of RPUR foams but were later discontinued except for special applications owing to their high cost coupled with generally low functionality, high viscosity and low dimensional stability of the resulting foam [10]. Moreover, the polyester polyols tenderly produce foams with better mechanical properties due to their more reaction and are less soluble in organic solvents. In addition, they are more expensive, more viscous and therefore not easy to handle. As a consequence, they are only used in applications that require their superior properties. Therefore, the use of polyesters in RPUR foams was traditionally very limited compared with polyether polyols.

2.1.3 Surfactants

Surfactants are essential additives used in the manufacture of all polyurethane foams. The surfactants most commonly used in the polyurethane industry are polydimethyl siloxane-polyethyl copolymers. Since the late 1950s, these so called "silicone surfactants" almost completely replaced other organic, nonionic surfactants which were previously used before [15]. In polyurethane foaming, they are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and sub-surface voids. They carry out two roles: first, they help in mixing incompatible components by lowering the surface tension of the emerging gas-liquid interface, and presumably also by emulsifying the polyol-isocyanate interface; and second, they have a critical role in stabilizing the early foaming stages of the foam structure until sufficient polymerization has occurred to form a self-supporting cell wall of polymer network. The most important function of the surfactant in foams is bubble stabilization [12].

Today, the largest commercial application of silicone surfactants is their use as additives for the production of polyurethane foam. They are typically added in amounts of 0.4–2.0% w/w of the polyol formulation. To meet specific processing needs of different foam systems, the molecular structure may be tuned by the length and varying the composition of the polydimethylsiloxane backbone or the number, length, and composition of the pendant polyether chains [15].

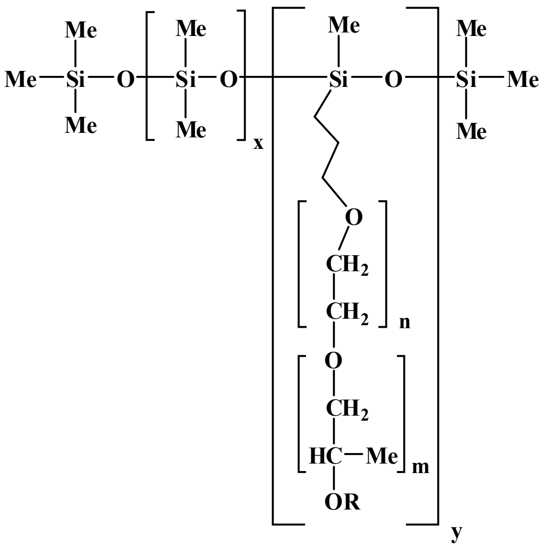


Figure 2.3 Structure of silicone surfactants [15]

2.1.4 Blowing agents

The properties of RPUR foams are considerably influenced by the type and content of the blowing agents. The two kinds of blowing agent used for the production of polyurethane foams are chemical blowing agent and physical blowing agent.

Chemical blowing agents are chemical compounds that react with isocyanate groups to generate carbon dioxide gas. Water is one of the most widely used chemical blowing agents and has been used since the beginning of the polyurethane foam industry for both flexible and rigid foams. Physical blowing agents are inert liquids that have low boiling points and nonreactivity to isocyanate groups; they evaporate by the exotherm of foaming reaction [2, 15]. The physical blowing agents, e.g. chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorinated hydrocarbons (PFCs), have been suggested to contribute to the depletion of the ozone layer and the use has been regulated in many countries. Thus, water has replaced such environmentally hazardous blowing agents [16].

Owing to the ban of use of CFCs, the use of water as a blowing agent is being developed. However, the use of water alone has some disadvantages, e.g. increased use of water results in higher reaction exotherm, which is the cause of scorching or fire, system viscosity is high, so the flowability of foaming systems in the mold becomes worse [2].

Water reacts with an isocyanate and produces unstable carbamic acid initially, which immediately decomposes into an amine and carbon dioxide (CO_2) as blowing gas. In general, water concentrations are 3-5 parts of water per 100 parts of polyol. The reaction of water with an isocyanate is exothermic and results in the formation of active urea sites which form crosslinks via hydrogen bonding. To reduce the high crosslink density, auxiliary blowing agents are used to produce low density foams with a softer feel than water-blown foams and to produce closed cell flexible foams. Next, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane foam [16].

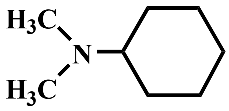
2.1.5 Catalysts

The kinetic rate of reactions of rigid polyurethane foams formation mainly depends on the rates of the blowing and gelling reaction which are controlled by catalysts. The rate of foam formation is also affected by a higher ratio of isocyanate to polyol or an increase in the temperature of the ingredients. Thus, RPUR foam formation is influenced by the quantity of the catalyst, the contents of the isocyanate and polyol, and the temperature of the ingredients. Normally, the catalyst composition is used in amounts of about 1- 4 parts by weight per 100 parts polyol to produce the necessary catalytic response [17].

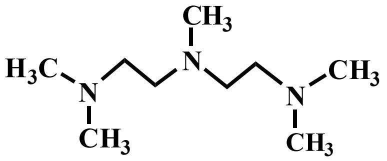
For RPUR foam preparation, three kinds of reactions, which are the blowing reaction of isocyanate with H_2O to form CO_2 and polyurea, the gelling reaction of isocyanate with polyol to form polyurethane and the trimerization of isocyanate, are employed. In preparing formulations, catalysts are thought to balance these reactions, although synergistic effects of certain catalyst combinations are known as well where most important catalysts are shown in Table 2.2 and Figure 2.4 [15].

Table 2.2 Frequently used catalysts in RPUR foams [15]

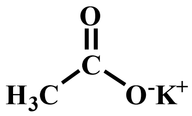
Catalyst Type	Code	Perceived Action
Tertiary amines		
Pentamethyldiethylene triamine	PMDETA	Blowing
Triethylenediamine	TEDA	Gelling
Dimethylcyclohexylamine	DMCHA	Blowing/ Gelling
Alkali metal carboxilates		
Potassium acetate	K Ac	Gelling/ Trimer formation
Potassium octoate	K Oct	Gelling/ Trimer formation
Tin compounds		
Stannous octoate	Sn Oct	Gelling
Dibutyltin dilaurate	DBTDL	Gelling



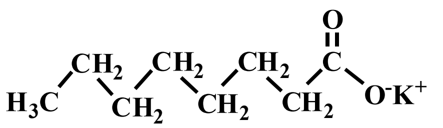
N,N-dimethylcyclohexylamine
(DMCHA)



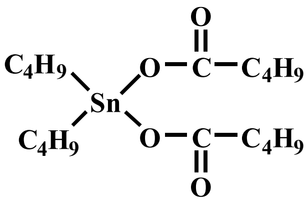
Pentamethyldiethylene triamine
(PMDETA)



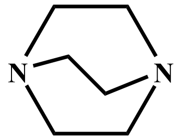
Potassium acetate



Potassium octoate



Dibutyltin dilaurate (DBTDL)



Triethylenediamine (TEDA)

Figure 2.4 Commercial catalysts used in RPUR foams

The ability of the catalyst to selectively promote either gelling or blowing reaction is an important consideration in selecting a catalyst for the production of RPUR foam. If a catalyst too strongly promotes the blowing reaction, much of the CO_2 gas will be evolved before sufficient reaction of isocyanate with polyol has occurred, and the CO_2 gas will bubble out of the formulation, resulting in collapse of the foam. Hence, the foam of poor quality will be produced. On the contrary, if a catalyst promotes the gelling reaction to a too high degree, a substantial portion of the CO_2 gas will be evolved after a significant degree of polymerization has occurred. Again, the poor quality foam, this time characterized by high density, broken or poorly defined cells, or other undesirable features, will be produced.

Generally, tin catalysts accelerate mainly isocyanate-polyol reaction and they are considered “gelling catalysts”. In contrast, tertiary amine catalysts promote mainly the isocyanate-water reaction, which generates CO_2 and they are considered “blowing catalysts”. Besides, tertiary amines are catalyzed both the blowing and gelling reaction, whereas tin catalysts catalyzed mainly isocyanate-polyol reaction [2, 11, 18].

However, tertiary amine catalysts generally are malodorous and offensive and many have high volatility due to their low molecular weight. Release of tertiary amines during foam processing may present significant safety and toxicity problems, and release of residual amines from consumer products is generally undesirable [19].

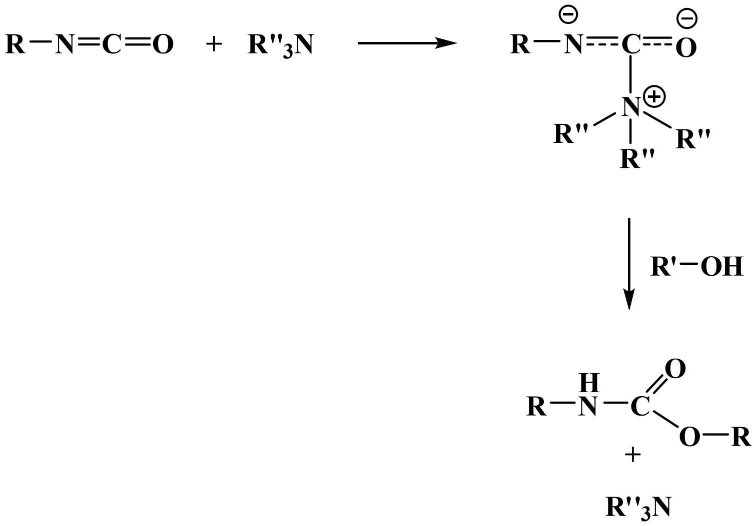
Tertiary amine and tin compound are combined in most applications, not only to provide the desired balance of gelling reaction and blowing reaction but also to tune these reactions to the needs of production equipment [14]. Catalyst mixtures are generally needful to control the balance of the polymerization and the gas generation reactions which both are exothermic reactions. Getting the suitable balance of polymerization and foaming is a major importance in the production of closed cell foam.

2.2 Reaction mechanisms

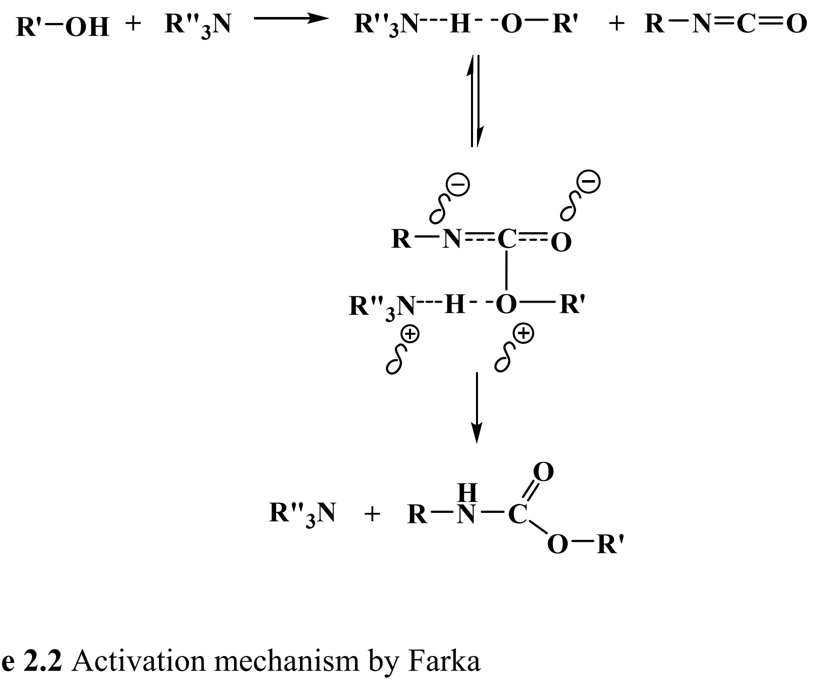
2.2.1 Amine catalysts

For tertiary amine catalysts, two mechanisms have been proposed [4]. The first mechanism proposed by Baker is outlined in Scheme 2.1. The activation starts by the tertiary amine using its lone pair of electrons to coordinate to the positive electron charged carbon of the NCO group contribute to activate the electrophilic nature of the carbon. Thus, OH group of polyols can attach to the isocyanate more easily.

The second mechanism proposed by Farka is depicted in Scheme 2.2, supported in the more recent literature [19]. The activation starts by the tertiary amine coordinates to the hydrogen of the OH group and forms a transition state to activate urethane formation reaction. It is said that the tertiary amine can be tuned by maximizing its ability to form a hydrogen bond with alcohol, thereby activating the O–H bond which it can attach to the isocyanate more easily.



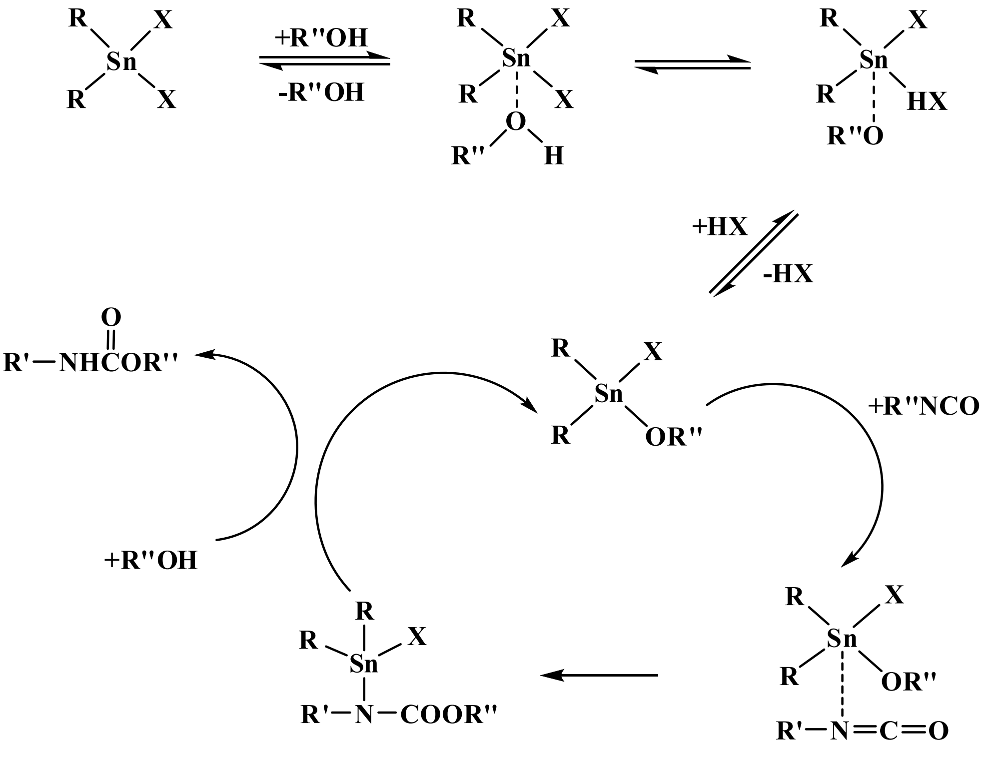
Scheme 2.1 Activation mechanism by Baker



Scheme 2.2 Activation mechanism by Farka

2.2.2 Organotin catalysts

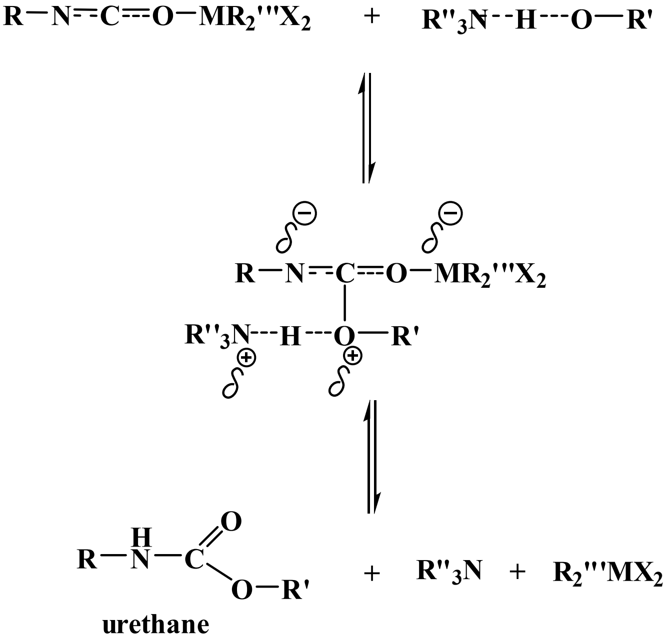
For the tin IV catalysts, the mechanism proposed is illustrated in Scheme 2.3, dialkyltin dicarbonates and dialkyltin dialkylthiolates, is the reaction of the tin with a polyol forming a tin alkoxide, which can then react with the isocyanate to form a complex. Transfer of the alkoxide anion onto the coordinated isocyanate affords an N-stannylurethane, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide. In other words, tin coordinate to the nitrogen of the NCO group contribute to activates the electrophilic nature of the carbon. Thus, OH group of polyols can attach to the isocyanate more easily.



Scheme 2.3 Mechanism of tin (IV) salts catalyst

2.2.3 Metal-amine catalysts

The mechanism proposed for a synergy between metal and amine catalysts is outlined in Scheme 2.4. The metal coordinate to the oxygen of the NCO group contribute to activate the electrophilic nature of the carbon corresponding with amine coordinate to the hydrogen of the OH group and forms a transition state to activate urethane formation reaction.



Scheme 2.4 Mechanism of metal-amine synergism

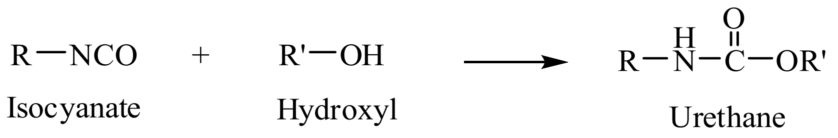
2.3 Basic Chemistry

Polyurethanes are special group of heterochain polymers, characterized by the structure of -[OCONH-R-NHCOO-R’-]$_n$-, based on the high reactivity of the isocyanate group with compound containing active hydrogen. The urethane groups (-NHCOO-) are esters of carbamic acid, a theoretically unstable acid [20]. Generally, the most important reaction in polyurethane formation is an exothermic reaction [21]. In simple terms, the basic principle of urethane chemistry is described below using monofunctional reagents.

2.3.1 Primary reaction of isocyanates

2.3.1.1 Reaction with polyol

This reaction is the most important reaction in the manufacture of polyurethanes that leads to production of carbamate, which is called a urethane in the case of high molecular weight polymers.

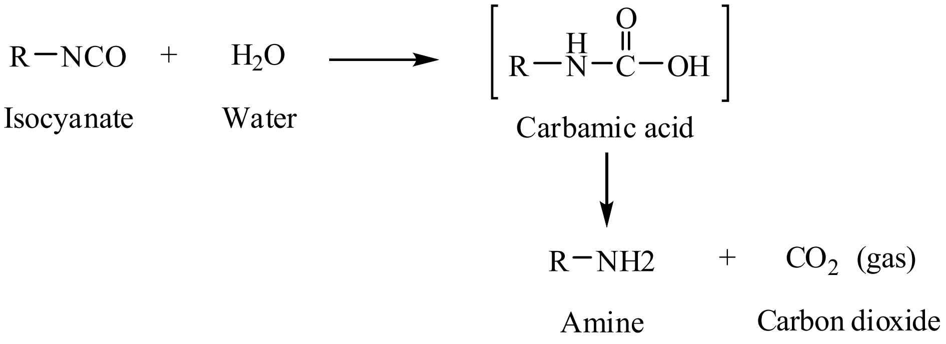


$$R-NCO + R'-OH \longrightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OR'$$

For polyurethane foam system, this reaction is called the “gelling reaction”. Due to it is an exothermic reaction, the temperature must be controlled. The rate of polymerization is affected by the chemical structure of the isocyanate and polyols and the catalyst is used to accelerate the reaction rate.

2.3.1.2 Reaction with water

Isocyanate reacts with water and produces unstable carbamic acid initially, which immediately decomposes into an amine and carbon dioxide. This carbon dioxide gas diffuses into the already present air bubbles, and this result in a rise of foam due to the increase in the bubble size [4, 17].

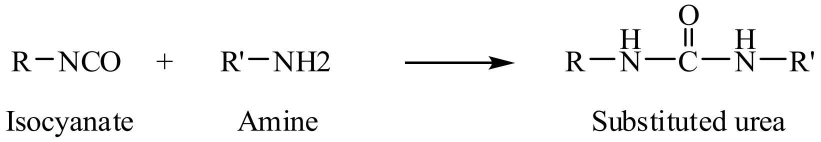


$$R-NCO + H_2O \longrightarrow \left[R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OH \right] \longrightarrow R-NH2 + CO_2 \text{ (gas)}$$

This reaction is called the “blowing reaction” because the carbon dioxide gas produced is used for blowing the foam. The reaction rate is accelerating by suitable choice of catalyst system.

2.3.1.3 Reaction with amines

The reaction between isocyanate and amine forms the urea linkange. In general, reactions of unhindered isocyanates with primary amines occur approximately 100-1000 times faster than with primary alcohols [21]. Thus, amines are usually used as chain-extenders and curing agents in polyurethane manufacture.



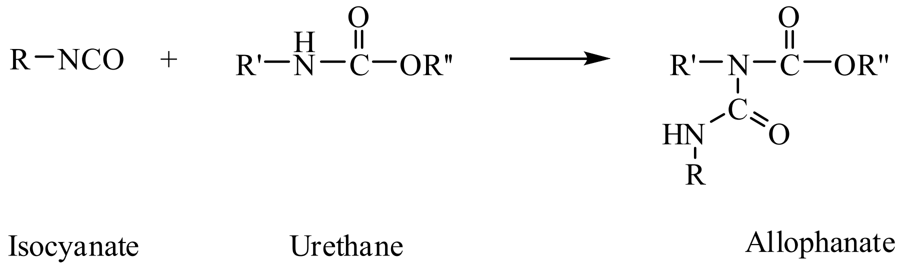
$$R{-}NCO + R'{-}NH2 \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R'$$

2.3.2 Secondary reaction of isocyanates

Isocyanate may react, under suitable conditions, with the active hydrogen atoms of urethane and urea linkages from the primary reactions as follows:

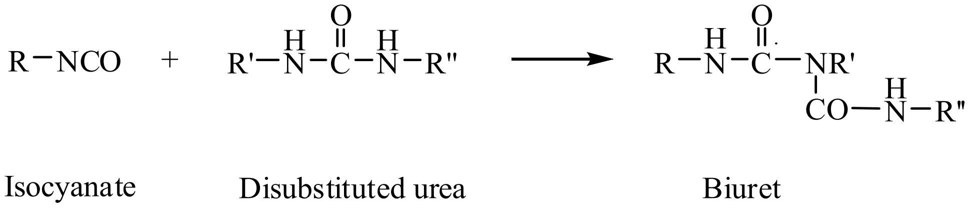
2.3.2.1 Reaction with urethane

For this reaction, the hydrogen on the nitrogen atom of the urethane group is capable of reacting with additional isocyanate to generate an allophanate [2]. However, the formation of the allophanate is high temperature and reversible reaction. If actually formed, the allophanate linkage would serve to cross-link the polymer further. In addition, the typical catalysts used in polyurethane foam formulations do not promote this reaction and the high internal temperatures of the foam bun would favor its immediate decomposition.



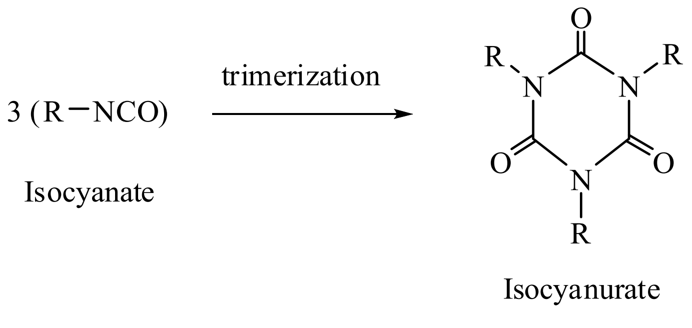
2.3.2.2 Reaction with urea

For the biuret formation, similarly to the allophanate formation, especially when an excess of isocyanate is used, a hydrogen atom from the disubstituted urea reacts with a free isocyanate group to generate a biuret. Formation of allophanates and biurets in polyurethane are conceptual method of cross-linking the polymer. However, reactions of isocyanates with urea groups are significantly faster and occur at lower temperature than that with urethane groups [20].



2.3.2.3 Trimer formation

The trimerization of isocyanate, resulting in forming isocyanurates, which leads to creates high temperature resistant cellular structural units [22]. Generally, isocyanate trimer can be formed on heating either aliphatic or aromatic isocyanates. This reaction is accelerated by basic catalysts such as sodium and potassium salts of carboxylic acids [21].



2.4 Formulations

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

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

Generally, the conventional way of calculating the ratio of the components required for polyurethane manufacture is to calculate the number of part by weight of the isocyanate needed to react with 100 parts by weight of polyol and use balanced amount of additives. The analytical data need 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 [6, 21].

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

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

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

Hydroxyl value (hydroxyl number; OHV)

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

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

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

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

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

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

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

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

where;

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

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

2.5 Mechanical properties

The compressive strength of the polyurethane foam measures the degree of deformation, that will occur when a pressure are put to the foam sample and the higher the compressive strength, the lower the tendency of the foam to shrink of expand [12].

Compressive strength is the value of the compressive force at 10 percent strain divided by the initial surface area of the test specimen. As a general rule, if the maximum compressive force is reached before the strain of the sample reached 10 percent, the compressive force will be recorded. In addition, the slope of the initial straight-line part of the stress-strain curve represents the elastic part of the deformation. Consequently, the ratio between stress and strain is called the Young's modulus [12].

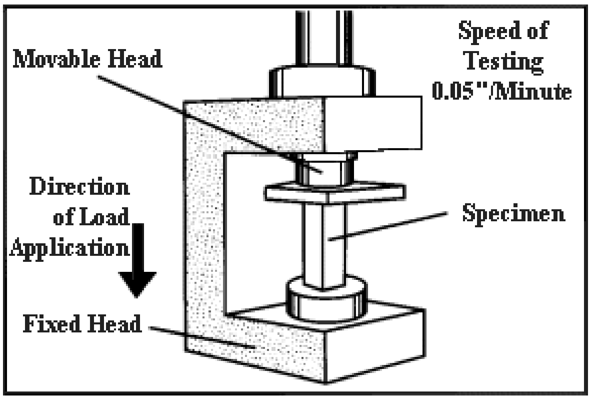


Figure 2.5 An example instrument for compressive strength test [23]

In this research, the compressive strength of RPUR foam can be determined according to ASTM D1621-10 [24]. An example universal testing machine for rigid polyurethane foam is shown in Figure 2.5 and the compressive strength test of the foam sample in parallel and perpendicular to the foam rise direction were analyzed using this machine. The energy absorption characteristics of foam can be represented in term of compression stress-strain curves as shown in Figure 2.6.

Furthermore, the compressive strength of RPUR foam mainly depends on density, type of base polymer and the predominance of either open or closed cells. Consequently, the compressive strength of RPUR foam increases with increasing density and when the foam cells are in the direction of rise, the compressive strength perpendicular to rise will be lower than the one parallel to rise [12]. Moreover, most rigid polyurethane foams are anisotropic cells which they are stronger in the direction of foam rise. The anisotropic character is normally more pronounced in molded items or panels where the foam rises through a long vertical distance [14].

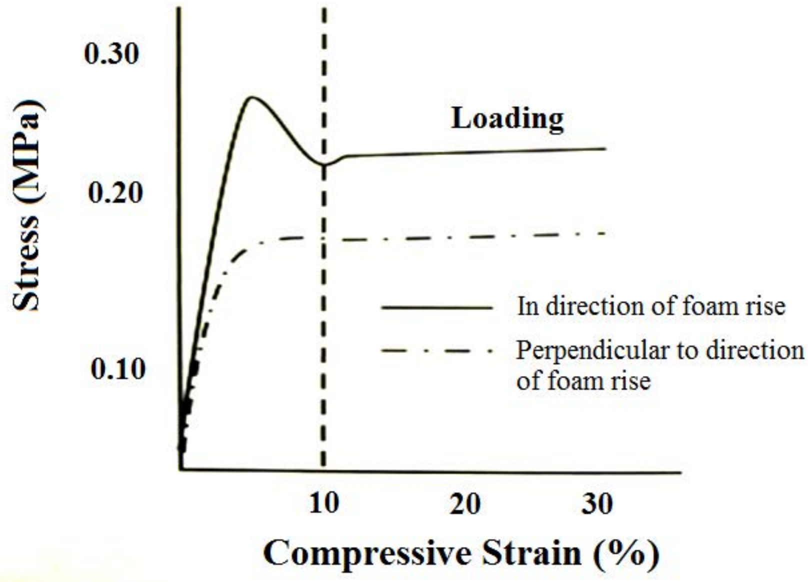


Figure 2.6 Typical stress-strain curve obtained during compression [12].

2.6 Literature reviews

There are many reports concerning the effect of surfactants, blowing agents and catalysts on the properties of rigid polyurethane (RPUR) foam. But fewer reports focus on the synthesis of the new catalyst for rigid polyurethane foam system.

Seo and coworkers [5] disclosed the study of the effects of surfactant and blowing agent quantity on the properties of the rigid polyurethane foams. Amine was used as a catalyst, and distilled water used as blowing agent. The results showed that the cell size was decreased with an increase in surfactant. With increasing the distilled water, the density and mechanical strength of the foam was decreased.

Xiaobin and coworkers [25] pointed out that water content have the effect on the density and suggested water played an important role in determining the properties of polyurethane foams. In connection with this, Singh and coworkers [17] commented that the density decreased with an increase in the water content. Moreover, they found that the rate of RPUR foam formation (mainly measured from the cream time, gel time and tack-free time) increased with increase in the catalyst (tin and triethylenediamine) and water content. So far, many excellent research works have reviewed to accelerate the gelling and blowing reaction from the mixed catalyst between tin and amine [17, 26-27]. From these reports, they suggested that the amine catalyst mainly accelerated the blowing reaction, as confirmed by the faster cream time, and the tin catalyst accelerated the gelling reaction, as confirmed by the faster gel time and tack-free time.

Seo and coworkers [26] prepared RPUR foams from polymeric MDI, polyether polyols, silicone surfactant, distilled water and amine catalysts. The results show that the types of blowing or gelling catalysts affect the kinetic rate of RPUR foam. An increase in the quantity of the catalyst results in the kinetic rate, density and compressive strength of RPUR foam. In addition, with increasing OH value and functionality of polyols, the density and compressive strength also increased. According to the survey conducted by Lim and coworkers [28], the closed cell content and compressive strength of the foam increased with increase in the OH value due to the increased crosslink density.

Han and coworkers [29] disclosed the effect of silicone surfactant on cell size of polyurethane foam. Scanning electron microscopy results revealed an optimum concentration of the surfactant is about 1.5 to 2.5 pbw. The optimum of surfactant demonstrated a smaller cell size, together with the lower thermal conductivity of the RPUR foams. On the other hand, the smaller cell size improved the thermal insulation property of the foam.

Lim and coworkers [30] investigated the effect of surfactant quantity on the reactivity and properties of the RPUR foams. It was observed that cream time, gel time and tack-free time increased with the content of surfactant increasing because of the increased stability of reaction mixture and rising bubbles. It was also shown that cell size decreased and closed cell content increased at low surfactant concentrations.

Jackovich and coworkers [31] proved the effect of processing temperature (24, 40, 65 and 85°C) on the density of RPUR foam. An increase in the processing temperature results in a decrease in foam density.

Effects of foam density on the morphological, mechanical and thermal properties of the water blown RPUR foam were reported by Thirumal and coworkers [32]. The results indicated that the mechanical strength increased with the increase in density of the foams. Although, when the density increased, the thermal conductivity was decreased. Furthermore, the thermal stability decreased with decrease in density, because of the formation of biuret and allophanate in lowest density.

In the manufacture of RPUR foams, the combination of many kinds of each component was commonly used to develop the polyurethane foam system. White and coworkers [33] focus on the formulation of RPUR foam by using polyols blends, many types of blowing agents and mixed catalysts. It was considered that all developed RPUR foam had an excellent dimensional stability and thermal insulation.

Moore and coworkers [34] studied the use of a variety of Mannich polyols in order to reduce blowing agent and catalyst consumption. This report claimed that the increase in Mannich polyol levels could be used to significantly speed up the reaction profile of RPUR system.

Recently, there has been interest in the development of vegetable oil based polyurethanes [35-37]. Yang and coworkers [38] investigated an approach to incorporate modified epoxidized soybean oil polyol as a replacement for petroleum-based polyether polyol. The catalyst used for the production of polyurethane was tertiary amine. The results showed that soy polyols played significant role in improving the foam properties.

Catalyst is one component which played an important role in RPUR foam system since the reaction between isocyanate and hydroxyl group is slow [6]. Thus, tin compounds and tertiary amine are mainly used as catalyst because of their excellent catalytic activity. However, tin is highly toxic and amine has strong odor. Accordingly, a new catalyst or catalytic system is needed to replace these catalysts.

In order to resolve this problem, many research efforts have been developing the catalyst for polyurethane system. Sardon and coworkers [39] disclosed about the catalytic activity of tin compounds and zirconium acetylacetonate [$Zr(acac)_2$] in the polymerization of waterborne polyurethane. $Zr(acac)_2$ is much less toxic than comparable tin compounds. For this work, when $Zr(acac)_2$ is used in the presence of triethylamine (TEA), $Zr(acac)_2$ shows a higher catalytic activity than tin compounds. The results confirmed that zirconium compound was a good alternative to replace tin catalyst.

Kurnoskin [40-41] synthesized of metal-containing epoxy polymers with the complexes of metals (Cu^{2+}, Zn^{2+}, Mn^{4+}, Fe^{3+}, Ni^{2+} and Cd^{2+}) and aliphatic amines (ethylenediamine, diethylenetriamine, triethylenetetramine and cycloethylated diethylenetriamine). The reactivity of the metal complexes depended on their structures.

Metal acetylacetonates [$M(acac)_2$] are widely used in the urethane forming reaction [42]. The attractiveness of acetylacetonates as potential initiators of large-scale synthesis is also increased by their availability, relatively low price, less toxic and easy storage [43]. For example, copper(II) acetylacetonate [$Cu(acac)_2$] is a soluble copper catalyst that has been widely employed in many types of reactions. The easy access and low cost of this metal compound, together with its varied applications as catalyst, make $Cu(acac)_2$ a powerful reagent in organic synthesis [44-46].

Inoue and coworkers [47] prepared the complexes metal acetylacetonate [M(acac)$_n$; M = Mn, Fe, Co, Ni and Cu] and tertiary amines then used as the catalysts for the reactions between hexamethylene diisocyanate (HDI) and diethylene glycol. It was found that these complexes showed catalytic activity comparable to dibutyltin dilaurate (DBTDL) catalyst, which was a reference commercial catalyst. However, these complexes are only used in polyurethane formation from HDI and diethylene glycol, and there was no report in the use of these metal complex catalysts in RPUR foams systems.

From the work in our group, Pengjam [48] synthesized the complexes between metal(II)acetate and amine and used as the new catalysts in RPUR foam preparation. It was found that copper complexes showed comparable catalytic activity to the DMCHA, which was a reference commercial amine catalyst.

In manufacturing of RPUR foams, tin and amine catalysts generally used together to balance the gelling and blowing reactions. However, tin is toxic to human beings and amine has strong odor. Herein, we were interested to synthesize metal-amine complexes to accelerate both gelling and blowing reactions that can be used instead of amine catalyst. These metal-amine complexes could be easily prepared from inexpensive starting materials and have no odor. The obtained results in RPUR foam preparation using the synthesized catalysts were compared with those of commercial amine catalyst, DMCHA, which is used as a reference catalyst.

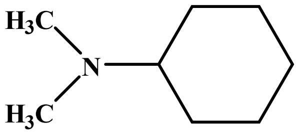


Figure 2.7 Structure of N, N-dimethylcyclohexyl amine (DMCHA) (a reference commercial amine catalyst) [1]

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and raw materials

3.1.1 Metal-amine complexes synthesis

Copper(II) acetylacetonate [Cu(acac)$_2$], zinc(II) acetylacetonate [Zn(acac)$_2$], ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pentaethylenehexamine (pentaen) were obtained from TCI, Fluka and Aldrich. Methanol was standard analytical grade and used without further purification.

3.1.2 Foam preparation

In this work, polyol (Daltolac$^{®}$ R180, sucrose-based polyether polyol) used to prepare rigid polyurethane foam was supplied by Huntsman (Thailand) CO., Ltd. The specifications of Daltolac$^{®}$ R180 are as follows: functionality = 4.3, acid number (mgKOH/g) =0.1, viscosity at 25 °C = 5345 cP, water content = 0.050%, hydroxyl number = 438.39.

Polymeric MDI (4,4'-methane diphenyl diisocyanate; PMDI, Suprasec$^{®}$-5005, %NCO = 31.0 wt %, average functionality = 2.7), polysiloxane surfactant (Tegostab$^{®}$ B8460) and a reference catalyst (N,N-dimethylcyclohexylamine; DMCHA) were supplied by Huntsman (Thailand) CO., Ltd. Distilled water was used as a chemical blowing agent.

3.2 Synthetic procedures

Metal-amine complexes were prepared from the reaction between metal acetylacetonate [M(acac)$_2$] and amine, using methanol or water as a solvent [49]. In the case of the synthesis using methanol as a solvent, methanol was removed from the metal-amine complex before using in the preparation of RPUR foam. For the synthesis in water, an aqueous solution containing metal-amine complex was obtained, which can be further used as a catalyst for RPUR foam preparation without purification. The reactivity in foaming reaction of the complexes synthesized in methanol and water were compared. M(acac)$_2$ used in this study were Cu(acac)$_2$ and

$Zn(acac)_2$. Amines used in this study were ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pentaethylenehexamine (pentaen). Compositions of starting materials in the preparation of all metal-amine complexes in methanol are shown in Table 3.1.

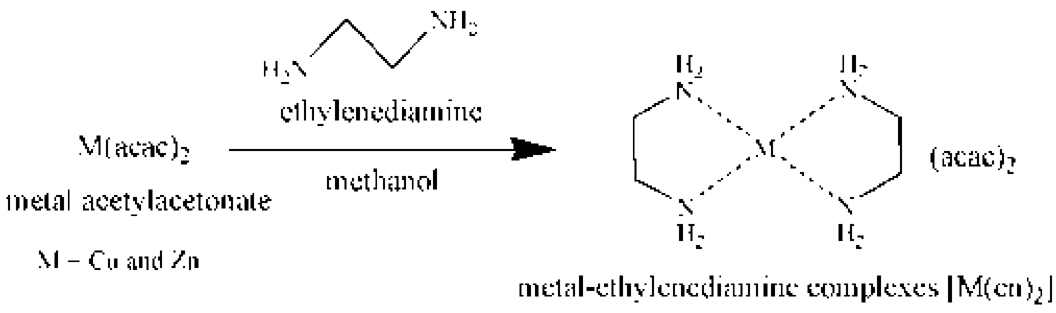
Table 3.1 Composition of starting materials in the preparation of metal-amine complexes prepared at $M(acac)_2$:amine mole ratio of 1:1 using methanol as a solvent

Metal complexes	**Weight of composition**		**Yield (%)**	**Appearance**
	$M(acac)_2$ (g, mmol)	**amine (mL, mmol)**		
$Cu(en)_2$	0.685, 2.61	0.35, 5.22	81	Blue powder
Cu(trien)	0.642, 2.45	0.37, 2.45	95	Blue viscous liquid
Cu(tetraen)	0.580, 2.22	0.42, 2.22	87	Blue viscous liquid
Cu(pentaen)	0.530, 2.02	0.52, 2.02	85	Dark blue viscous liquid
$Zn(en)_2$	0.687, 2.60	0.35, 5.20	79	White powder
Zn(trien)	0.643, 2.44	0.36, 2.44	82	Yellow viscous liquid
Zn(tetraen)	0.582, 2.21	0.42, 2.21	92	Yellow viscous liquid
Zn(pentaen)	0.532, 2.02	0.51, 2.02	90	Yellow viscous liquid

en = ethylenediamine, trien = triethylenetetramine, tetraen = tetraethylenepentamine, pentaen = pentaethylenehexamine

3.2.1 Synthesis of metal-amine complexes in methanol

3.2.1.1 Metal-ethylenediamine complexes [$M(en)_2$]

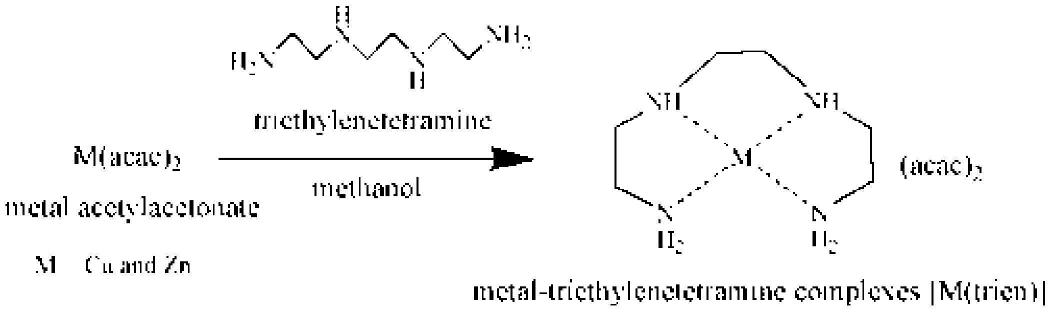


Scheme 3.1 Synthesis of metal-ethylenediamine complexes

The preparation of Cu(en)$_2$ was done as follows: a solution of ethylenediamine (0.35 mL, 5.24 mmol) in methanol (25 mL) was stirred at room temperature. Copper(II) acetylacetonate (0.6853 g, 2.61 mmol) was added to the ethylenediamine solution. After the reaction mixture was stirred at room temperature for overnight, the solution was evaporated and dried under vacuum to remove methanol. Cu(en)$_2$ was obtained as a blue powder (0.81 g, 81%): IR (KBr, cm^{-1}); 3275 (N-H stretching), 2922 (C-H stretching), 1580 (C=O asymmetric stretching), 1507 (C=O symmetric stretching), 1354 (C-N stretching), 1016 (C-O stretching). UV; λ_{max} (MeOH) = 296 nm, molar absorptivity (ε) = 5,160. Anal. Calcd. For $CuC_{14}O_4H_{32}N_4$: C 43.79; H 8.40; N 14.59; found C 42.86; H 6.27; N 13.73. AAS. Calcd. For $CuC_{14}O_4H_{32}N_4$: Cu 16.55; found Cu 13.51.

Zn(en)$_2$ was prepared using the same procedure as described above. Zn(en)$_2$ was obtained as a white powder (0.79 g, 79%): IR (KBr, cm^{-1}); 3318 (N-H stretching), 2972 (C-H stretching), 1602 (C=O asymmetric stretching), 1507 (C=O symmetric stretching), 1320 (C-N stretching), 1124 (C-O stretching). UV; λ_{max}(MeOH) = 288 nm, molar absorptivity (ε) = 980. Zn(en)$_2$ shown *m/z* = 348.286. Anal. Calcd. For $ZnC_{12}O_4H_{24}N_2$: C 44.25; H 7.43; N 8.60; found C 44.50; H 7.31; N 8.74. AAS. Calcd. For $ZnC_{12}O_4H_{24}N_2$: Zn 20.08; found Zn 20.16.

3.2.1.2 Metal-triethylenetetramine complexes [M(trien)]



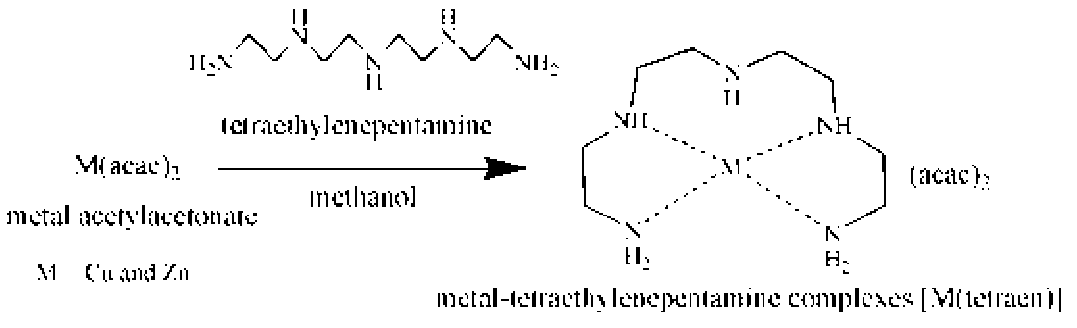
Scheme 3.2 Synthesis of metal-triethylenetetramine complexes

Metal-triethylenetetramine complexes were prepared using similar procedure as described above. Cu(trien) was obtained as a blue viscous liquid (0.95 g, 95%): IR (KBr, cm^{-1}); 3450 (N-H stretching), 2931 (C-H stretching), 1584 (C=O asymmetric stretching), 1531 (C=O symmetric stretching), 1350 (C-N stretching), 1018 (C-O stretching). UV; λ_{max} (MeOH) = 273 nm, molar absorptivity (ε) = 5,220.

Cu(trien) shown *m/z* = 408.508. Anal. Calcd. For $CuC_{16}O_4H_{34}N_4$: C 46.87; H 8.36; N 13.66; found C 44.58; H 5.44; N 2.71. AAS. Calcd. For $CuC_{16}O_4H_{34}N_4$: Cu 15.50; found Cu 14.67.

Zn(trien) was obtained as a yellow viscous liquid (0.82 g, 82%): IR (KBr, cm^{-1}); 3300 (N-H stretching), 2978 (C-H stretching), 1616 (C=O asymmetric stretching), 1504 (C=O symmetric stretching), 1323 (C-N stretching), 1127 (C-O stretching). UV; λ_{max}(MeOH) = 278 nm, molar absorptivity (ε) = 1,125. Zn(trien) shown *m/z* = 434.414. Anal. Calcd. For $ZnC_{16}O_4H_{34}N_4$: C 46.66; H 8.32; N 13.60; found C 46.78; H 8.17; N 13.70. AAS. Calcd. For $ZnC_{16}O_4H_{34}N_4$: Zn 15.88; found Zn 15.52.

3.2.1.3 Metal-tetraethylenepentamine complexes [M(tetraen)]

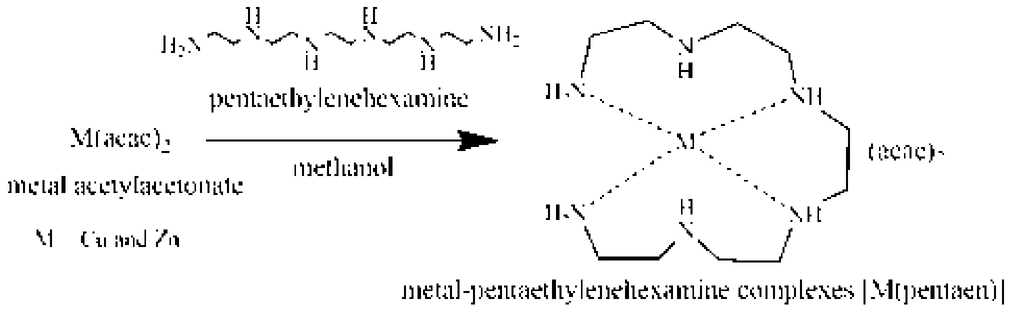


Scheme 3.3 Synthesis of metal-tetraethylenepentamine complexes

Metal-tetraethylenepentamine complexes were prepared using similar procedure as described above. Cu(tetraen) was obtained as a blue viscous liquid (0.87 g, 87%): IR (KBr, cm^{-1}); 3300 (N-H stretching), 2928 (C-H stretching), 1570 (C=O asymmetric stretching), 1488 (C=O symmetric stretching), 1332 (C-N stretching), 1011 (C-O stretching). UV; λ_{max} (MeOH) = 290 nm, molar absorptivity (ε) = 4,625.

Zn(tetraen) was obtained as a yellow viscous liquid (0.92 g, 92%): IR (KBr, cm^{-1}); 3263 (N-H stretching), 2937 (C-H stretching), 1592 (C=O asymmetric stretching), 1510 (C=O symmetric stretching), 1317 (C-N stretching), 1119 (C-O stretching). UV; λ_{max} (MeOH) = 292 nm, molar absorptivity (ε) = 1,240.

3.2.1.4 Metal-pentaethylenehexamine complexes [M(pentaen)]



Scheme 3.4 Synthesis of metal-pentaethylenehexamine complexes

Metal-pentaethylenehexamine complexes were prepared using similar procedure as described above. Cu(pentaen) was obtained as a dark blue viscous liquid (0.85 g, 85%): IR (KBr, cm^{-1}); 3290 (N-H stretching), 2947 (C-H stretching), 1568 (C=O asymmetric stretching), 1484 (C=O symmetric stretching), 1342 (C-N stretching), 1018 (C-O stretching). UV; λ_{max} (MeOH) = 290 nm, molar absorptivity (ε) = 6,773.

Zn(pentaen) was obtained as a yellow viscous liquid (0.90 g, 90%): IR (KBr, cm^{-1}); 3250 (N-H stretching), 2925 (C-H stretching), 1602 (C=O asymmetric stretching), 1490 (C=O symmetric stretching), 1315 (C-N stretching), 1112 (C-O stretching). UV; λ_{max} (MeOH) = 289 nm, molar absorptivity (ε) = 1,625.

3.2.2 Synthesis of metal-amine complexes in water

3.2.2.1 Metal-ethylenediamine complexes [M(en)$_2$_Water]

The preparation of Cu(en)$_2$_Water was done as follows: copper (II) acetylacetonate (0.6853 g, 2.61 mmol) and polysiloxane surfactant (Tegostab® B8460) (2.5 ml) were dissolved in 3 mL of distilled water at room temperature and the solution was stirred for 30 minutes. Ethylenediamine (0.35 mL, 5.24 mmol) was then added dropwise and the solution was stirred at room temperature for overnight. Then the metal-amine complex solution was used in the preparation of rigid polyurethane foam without purification. Cu(en)$_2$_Water aqueous solution was obtained as a blue solution. UV; λ_{max} (MeOH) = 296 nm, molar absorptivity (ε) =

2,030. $Zn(en)_2$_Water was prepared using similar procedure as described above. $Zn(en)_2$_Water aqueous solution was obtained as a white solution. UV; λ_{max} (MeOH) = 288 nm, molar absorptivity (ε) = 830.

3.2.2.2 Metal-triethylenetetramine complexes [M(trien)_Water]

M(trien)_Water was prepared using similar procedure as described above. Then the M(trien)_Water aqueous solution was used in the preparation of rigid polyurethane foam without purification. Cu(trien)_Water aqueous solution was obtained as a blue solution. UV; λ_{max} (MeOH) = 273 nm, molar absorptivity (ε) = 3,180. Zn(trien)_Water aqueous solution was obtained as a yellow solution. UV; λ_{max} (MeOH) = 278 nm, molar absorptivity (ε) = 970.

3.2.2.3 Metal-tetraethylenepentamine complexes [M(tetraen)_Water]

M(tetraen)_Water was prepared using similar procedure as described above. Then the M(tetraen)_Water aqueous solution was used in the preparation of rigid polyurethane foam without purification. Cu(tetraen)_Water aqueous solution was obtained as a blue solution. UV; λ_{max} (MeOH) = 290 nm, molar absorptivity (ε) = 2,455. Zn(tetraen)_Water aqueous solution was obtained as a yellow solution. UV; λ_{max} (MeOH) = 292 nm, molar absorptivity (ε) = 1,010.

3.2.2.4 Metal-pentaethylenehexamine complexes [M(pentaen)_Water]

M(pentaen)_Water was prepared using similar procedure as described above. Then the M(pentaen)_Water aqueous solution was used in the preparation of rigid polyurethane foam without purification. Cu(pentaen)_Water aqueous solution was obtained as a dark blue solution. UV; λ_{max} (MeOH) = 290 nm, molar absorptivity (ε) = 4,395. Zn(pentaen)_Water aqueous solution was obtained as a yellow solution. UV; λ_{max} (MeOH) = 289 nm, molar absorptivity (ε) = 1,100.

3.3 Rigid polyurethane (RPUR) foam preparations

RPUR foam samples were synthesized using a two- step method (Figure 3.1). The formulations used for foam preparation are presented in Tables 3.2 and 3.3. In the first mixing step, the polyol, catalysts (metal-amine complexes or DMCHA), surfactant, and blowing agent (water) were mixed in a 700-mL paper cup. In the second mixing step, PMDI was added to the mixed polyol from the first mixing then the mixture were mixed in homogeneous mixture by mechanical stirrer at 2000 rpm for 20 seconds. The same speed was maintained for all formulations. The foam was allowed to rise freely, and during the foaming reaction, cream time (the time when the foam started to rise), gel time (the time when the foam mixture started to gel), tack-free time (the time when polymerization reaction is completed) and rise time (the time when the foam stopped rising which is the time when CO_2 generation stops) were measured. After that, the foams were kept at room temperature for 48 hours and then physical and mechanical characterizations were carried out.

Table 3.2 RPUR foam formulations at different NCO indexes (in parts by weight unit, pbw)

Formulations (pbw)	**NCO index**	
	100	**150**
Polyol (Daltolac® R180)	100	100
Catalysts (metal-amine complexes or DMCHA)	1.0	1.0
Surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (H_2O)	3.0	3.0
Polymeric MDI (PMDI, Suprasec®-5005)	151	227

Table 3.3 RPUR foam formulations at different NCO indexes (in gram unit, cup test)

Formulations (g)	**NCO index**	
	100	**150**
Polyol (Daltolac® R180)	10.0	10.0
Catalysts (metal-amine complexes or DMCHA)	0.1	0.1
Surfactant (Tegostab® B8460)	0.25	0.25
Blowing agent (H_2O)	0.30	0.30
Polymeric MDI (PMDI, Suprasec®-5005)	15.1	22.7

RPUR foams were prepared at the NCO indexes of 100 and 150. The NCO index is a measure of excess NCO used relative to the theoretical equivalent amount required to react with polyol and blowing agent (water).

Since the RPUR foams obtained from different catalysts have similar IR spectra, therefore, only the IR data of the RPUR foams obtained from the Cu(trien) catalyst are shown as follows: IR (ATR-IR, cm^{-1}); 3320 (N-H), 2907, 2874 (C-H), 2272 (free NCO), 1711 (C=O), 1595 (Ar-H), 1512 (N-H), 1413 (C-N isocyanurate), 1306 (C-H), 1220, 1075 (C-O urethane).

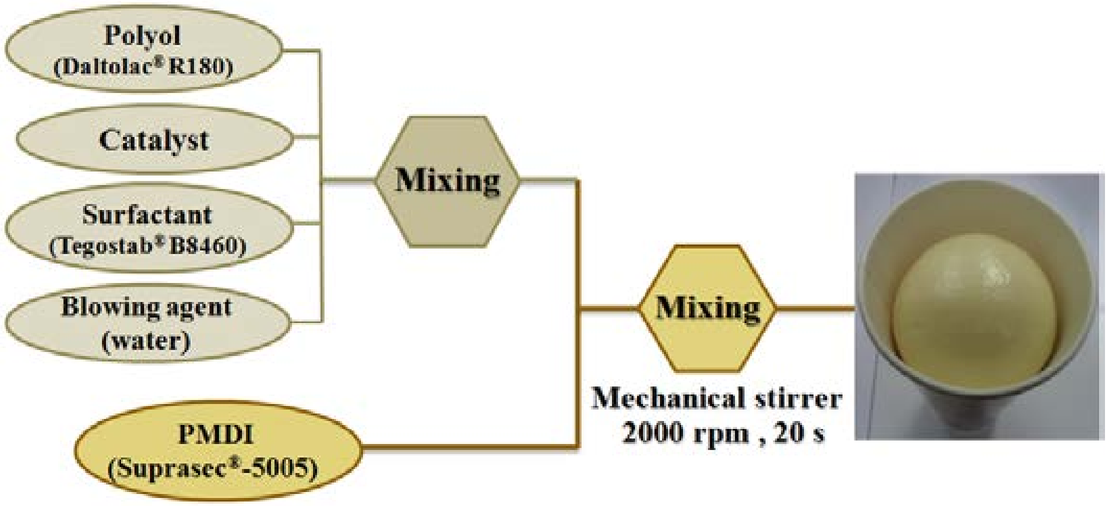


Figure 3.1 Process of preparation of rigid polyurethane foam

3.4 Instrumentation

3.4.1 Infrared spectroscopy

Fourier transform infrared (FTIR) spectrometer was used to study of functional groups on metal-amine complexes as catalyst and RPUR foams. The IR spectra were performed on a Nicolet 6700 FTIR spectrometer using ATR probe at room temperature. The samples were scanned over a range of 700-4000 cm^{-1} at a resolution of 4 cm^{-1} and a number of scan was 64. It is important that the samples are pressed, reproducibly and with a constant pressure, against the IR-transmitting ATR crystal. The ATR crystal is integrated into the beam of an ATR-IR spectrometer (Nicolet 6700) in such a way that IR light is passed through the crystal by means of total reflection. ATR occurs on the measuring surface that is in contact with the foam sample. The IR bands given in Table 3.4 are used for the analysis. The measurement was controlled by Omnic software.

Table 3.4 Characteristic IR bands of RPUR foam [50]

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
Isocyanurate	Ring deformation and CH$_2$-deformation in PMDI	1370-1443
Amide	C-N stretching (urethane, urea)	1155-1245
Reference	Non-reactive groups in polyol and isocyanate	935-1050

3.4.2 Ultraviolet-visible spectroscopy

UV-visible spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions highly conjugated organic compounds. UV-Vis spectra were recorded on ultraviolet and visible spectrophotometer at room temperature. Absorption spectra were obtained on Varian Cary 50 UV-Vis spectrophotometer. The samples were scan over range 200-500 nm at a medium speed.

3.4.3 Mass spectrometry (MS)

Mass spectrometry (MS) is an analytical technique that measures the mass-to-charge ratio of charge particles. MALDI-TOF mass spectra were carried out on Bruker Daltonics MALDI-TOF using 2-cyano-4-hydroxy cinnamic acid (CCA) as matrix. High resolution mass spectra were determined on Bruker Daltonics Data Analysis 3.3 with an electrospray ion source using methanol as a solvent.

3.4.4 Flame atomic spectroscopy (FAAS)

Flame atomic spectroscopy (FAAS) is a spectroanalytical produre for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state using a flame (Perkin-Elmer : AAnalyst 100)

3.4.5 Atomic absorption spectrometry (EA)

For organic chemists, element analysis or “EA” almost always refers to %C, %H and %N analysis; the determination of the percentage weights of carbon, hydrogen and nitrogen of a sample. Elemental analysis was carried out using a Perkin-Elmer EP 2400 analyzer.

3.4.6 Digital Stopwatch

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

3.4.7 Thermocouple

Thermocouple is a widely used type of temperatures sensor for measurement. The foaming temperatures were recorded by dual thermocouple, Digicon DP-71.

3.5 Physical and Mechanical properties of RPUR foam

3.5.1 Density

The apparent density of RPUR foams were measured according to ASTM D 1622-09 [51] by cutting into cubic shape with 3.0 cm x 3.0 cm x 3.0 cm dimensions. The mass density or density of material is defined as its mass per until volume. In the test, the specimen is carefully measured the geometry and accurately weighed. The average values of three samples were reported. Since, polyurethane foam physical properties as a function of foam density. This property is important because of its direct relationship with both cost and load bearing.

3.5.2 Scanning electron microscope (SEM)

The morphology and cell size of RPUR foam samples were studied with a Hitachi/S-4800 scanning electron microscope (SEM). A slice of foam samples was prepared for SEM analysis by coating with gold before scanning in both parallel and perpendicular to the rising direction to provide an electrically conductive surface. The accelerating voltage was 20 kV.

3.5.3 Compressive testing

The compressive strength test of foams in parallel and perpendicular to the foam rise direction were analyzed using universal testing machine (Lloyd/LRX) according to ASTM D 1621-09 [24]. The size of the specimen was 3.0 x 3.0 x 3.0 cm (width x length x thickness) dimension, the rate of crosshead movement was fixed at 2.54 mm/min and the preload cell used was 0.100 N.

3.5.4 Thermalgravimetric analysis (TGA)

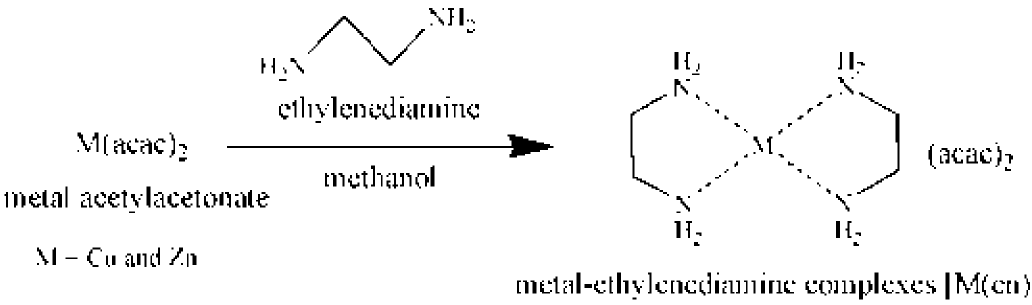
Thermalgravimetric analysis (TGA) was used to investigate the thermal stability of RPUR foam. Thermal stability was examined using a Mettler-Toledo, Model TGA/DSC1 with robot, thermogravimetric analyzer. All samples were heated from 50^{o}C to 750^{o}C at heating rate of 10^{o}C/min under nitrogen atmosphere. The result of thermal stability was report in percentage weight residue of foams. The decomposition temperature was analyzed by the software of the instrument.

CHAPTER IV

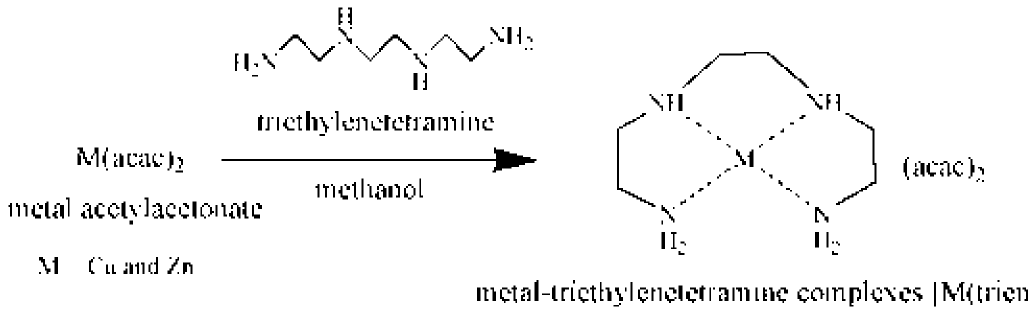
RESULTS AND DISCUSSION

4.1 Synthesis of the metal-amine complexes

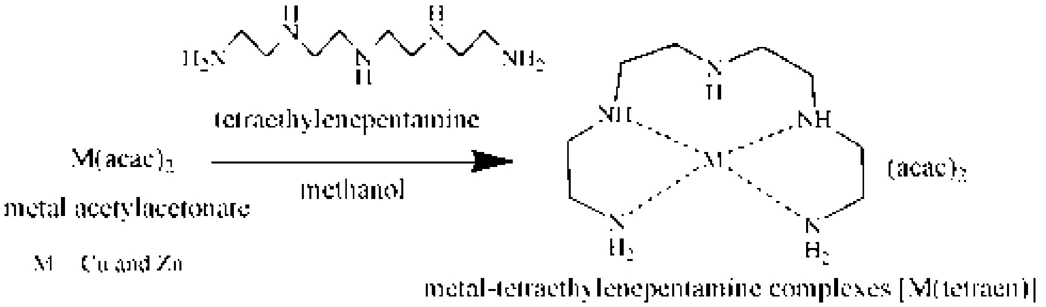
The reactions between metal acetylacetonate and amine gave metal-amine complexes as shown in Schemes 4.1-4.4. Metal-amine complexes were synthesized using methanol as a solvent. Methanol was removed from the metal-amine complexes under vacuum before using in the preparation of RPUR foam. The metal-amine complexes were odorless and could be easily dissolved in the polyol/ water/surfactant mixture, whereas copper acetylacetonate and zinc acetylacetonate were not soluble. Furthermore, the metal-amine complexes were synthesized using water as a solvent to obtained metal-amine complexes in aqueous solution which were then used in the preparation of RPUR foam without purification.



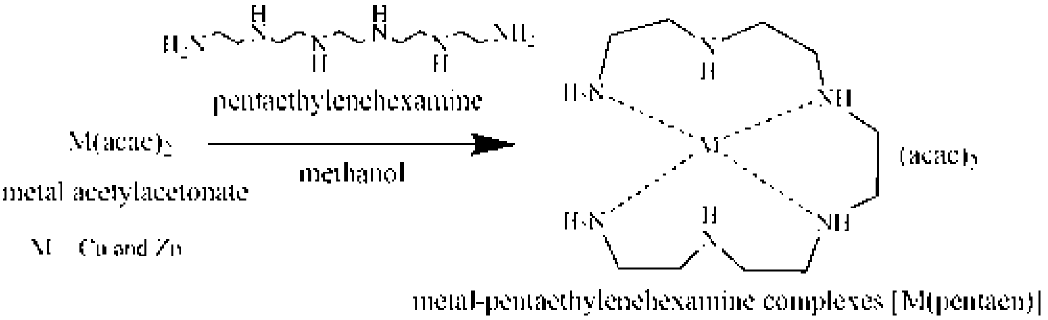
Scheme 4.1 Synthesis of metal-ethylenediamine complexes



Scheme 4.2 Synthesis of metal-triethylenetetramine complexes



Scheme 4.3 Synthesis of metal-tetraethylenepentamine complexes



Scheme 4.4 Synthesis of metal-pentaethylenehexamine complexes

4.2 Characterization of copper-amine complexes

4.2.1 IR spectroscopy of copper-amine complexes

IR spectra of copper-amine complexes are shown in Figures 4.1 and 4.2. They exhibited absorption bands at 3275-3450 cm^{-1} (N-H stretching), 2922-2947 cm^{-1} (C-H stretching), 1570-1584 cm^{-1} (C=O asymmetric stretching), 1484-1531 cm^{-1} (C=O symmetric stretching), 1332-1354 cm^{-1} (C-N stretching) and 1011-1018 cm^{-1} (C-O stretching). Asymmetric C=O stretching in $Cu(en)_2$ and Cu(trien) appeared as absorption bands at 1580 and 1584 cm^{-1}, respectively. Symmetric C=O stretching in $Cu(en)_2$ and Cu(trien) appeared at 1507 and 1531 cm^{-1}, respectively. These C=O stretching bands were different from those of $Cu(acac)_2$, which appeared as absorption bands around at 1575 cm^{-1} (asymmetric C=O) and 1522 cm^{-1} (symmetric C=O). These IR data suggested that the $Cu(en)_2$ and Cu(trien) complexes were formed since IR peak of the complexes shifted from those of $Cu(acac)_2$. For Cu(tetraen) and

Cu(pentaen), their asymmetric C=O stretching peaks appeared at 1570 and 1568 cm^{-1}, respectively. Symmetric C=O peaks appeared at 1488 and 1484 cm^{-1}, respectively. It was found that the IR peak of Cu(tetraen) and Cu(pentaen) shifted from those of Cu(acac)$_2$, which indicated that the complexes were formed.

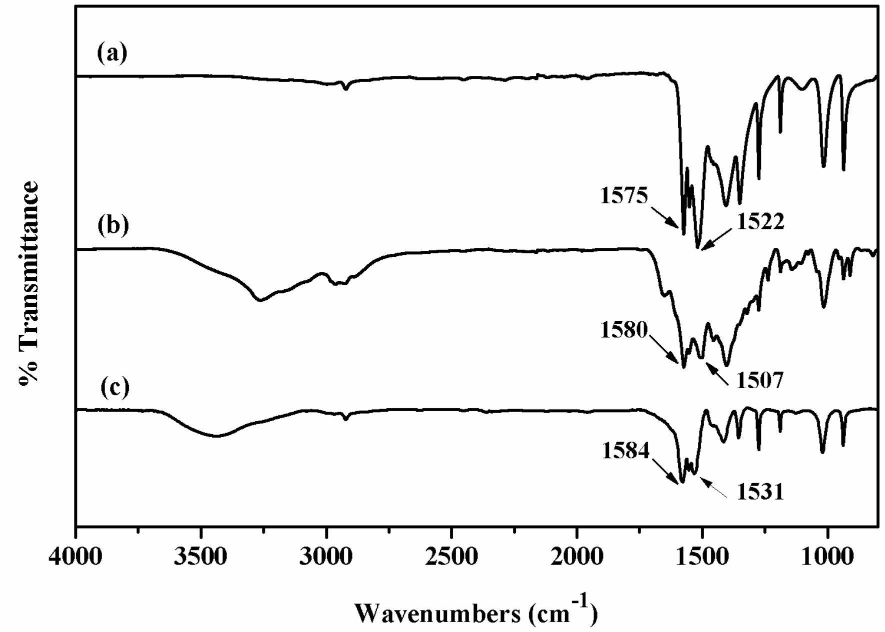


Figure 4.1 IR spectra of (a) Cu(acac)$_2$; (b) Cu(en)$_2$; (c) Cu(trien)

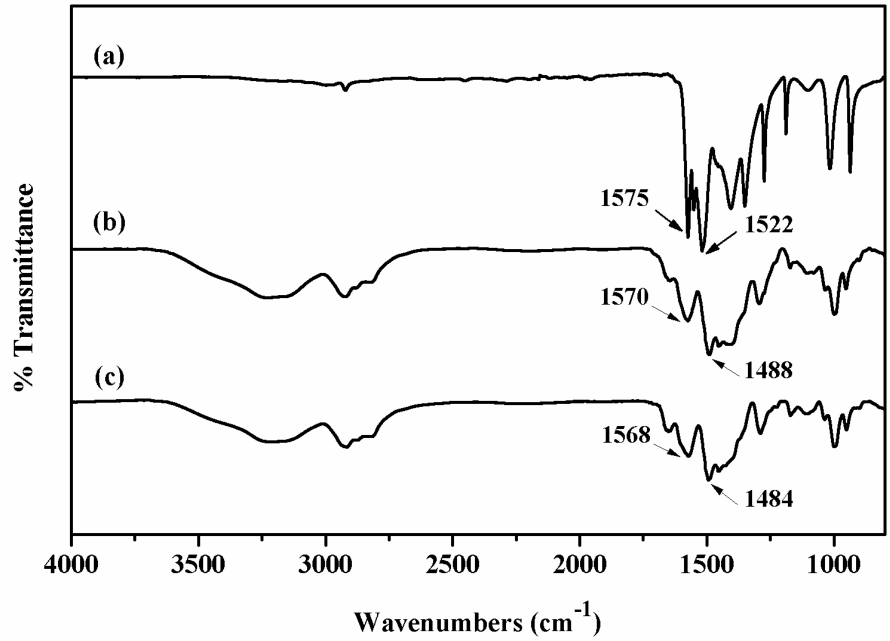


Figure 4.2 IR spectra of (a) Cu(acac)$_2$; (b) Cu(tetraen); (c) Cu(pentaen)

4.2.2 UV-visible spectroscopy of copper-amine complexes

UV-visible spectra of copper-amine complexes are shown in Figures 4.3-4.6. The absorption of $Cu(en)_2$, Cu(trien), Cu(tetraen) and Cu(pentaen) appeared at 296, 273, 290 and 289 nm, respectively. The complexes synthesized in methanol and those synthesized in water gave the same maximum wavelength. These peaks shifted from those of $Cu(acac)_2$, which appeared at 292 nm. These result suggested the complex formation.

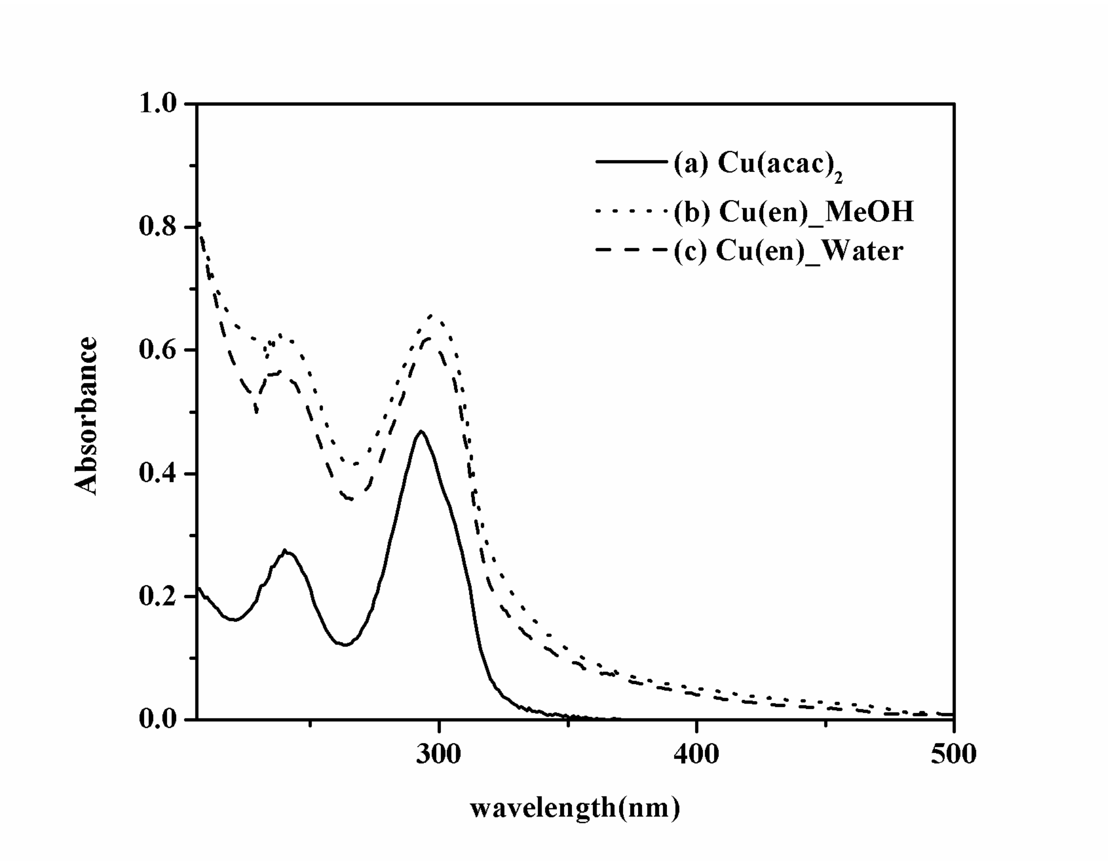


Figure 4.3 UV-vis spectra of (a) $Cu(acac)_2$; (b) Cu(en)_MeOH and (c) Cu(en)_Water

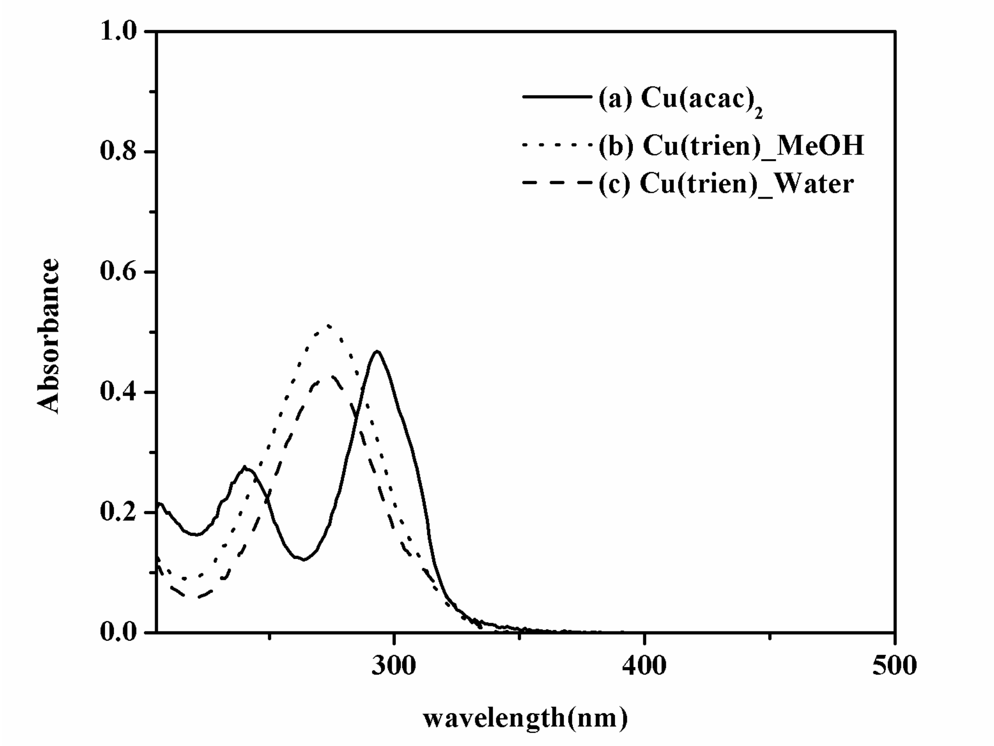


Figure 4.4 UV-vis spectra of (a) $Cu(acac)_2$; (b) Cu(trien)_MeOH and (c) Cu(trien)_Water

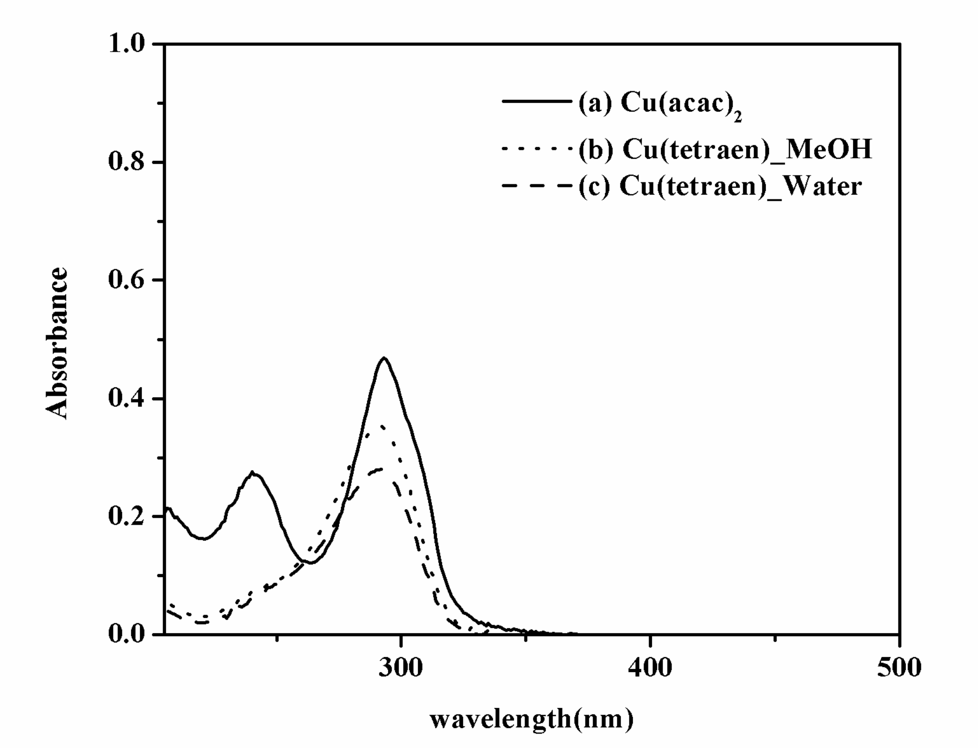


Figure 4.5 UV-vis spectra of (a) $Cu(acac)_2$; (b) Cu(tetraen)_MeOH and (c) Cu(tetraen)_Water

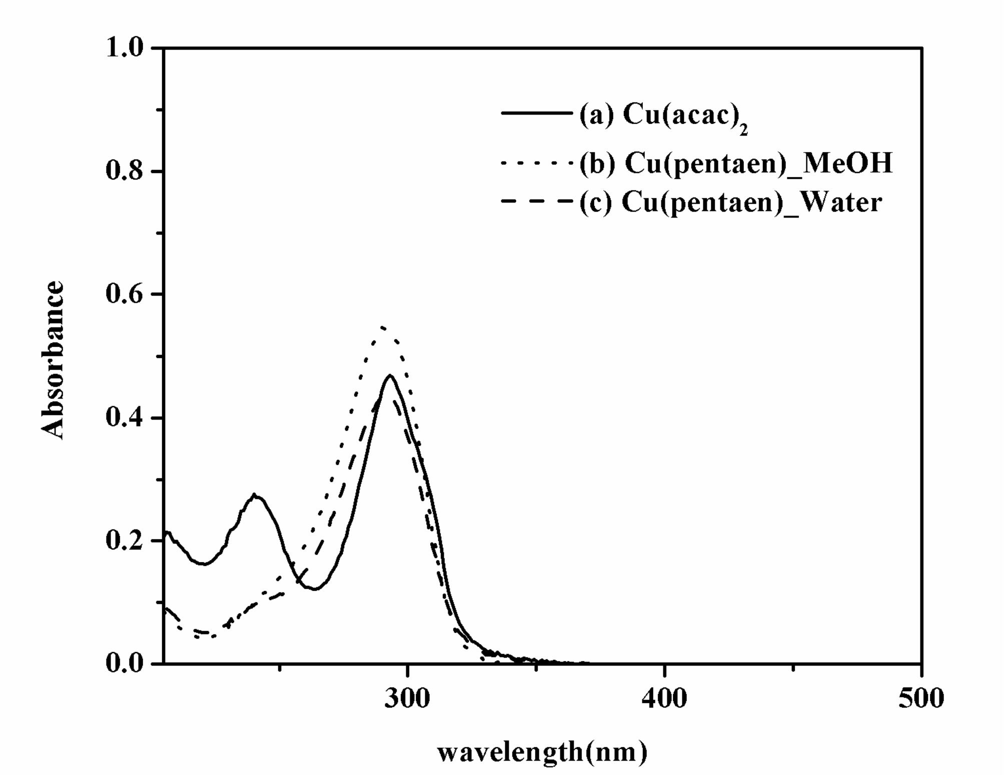


Figure 4.6 UV-vis spectra of (a) Cu(acac)$_2$; (b) Cu(pentaen)_MeOH and (c) Cu(pentaen)_Water

4.2.3 Determination of copper amount in copper-amine complexes by flame atomic spectroscopy (FAAS)

The amount of copper in copper-amine complexes was determined using FAAS (Table 4.1). This result indicates that the experimental value and the calculated value were different.

Table 4.1 FAAS data of copper-amine complexes

Catalyst	Elements determined	Experimental (%)	Calculated (%)
Cu(en)$_2$	Cu	13.51	16.55
Cu(trien)	Cu	14.67	15.50

4.2.4 Elemental analysis of copper-amine complexes

Elemental analysis (%C, %H and %N) of copper-amine complexes is shown in Table 4.2. This result indicates that there was inconsistency between the experimental value and the calculated value.

Table 4.2 Elemental analysis (%C, %H, and %N) of copper-amine complexes

Catalyst	Elements determined	Experimental (%)	Calculated (%)
$Cu(en)_2$	%C	42.86	43.79
	%H	6.27	8.40
	%N	13.73	14.59
Cu(trien)	%C	44.58	46.87
	%H	7.68	8.36
	%N	15.08	13.66

4.2.5 Mass spectrometry of copper-amine complexes

The molecular ion peak of Cu(trien) at *m/z* = 426.369 corresponding to $[^{63}Cu(acac)_2(trien)+H_2O]^+$ and *m/z* = 449.376 corresponding to the form of $[^{63}Cu(acac)_2(trien)+H_2O+Na]^+$ are observed in the MALDI-TOF mass spectrum (Figure 4.7).

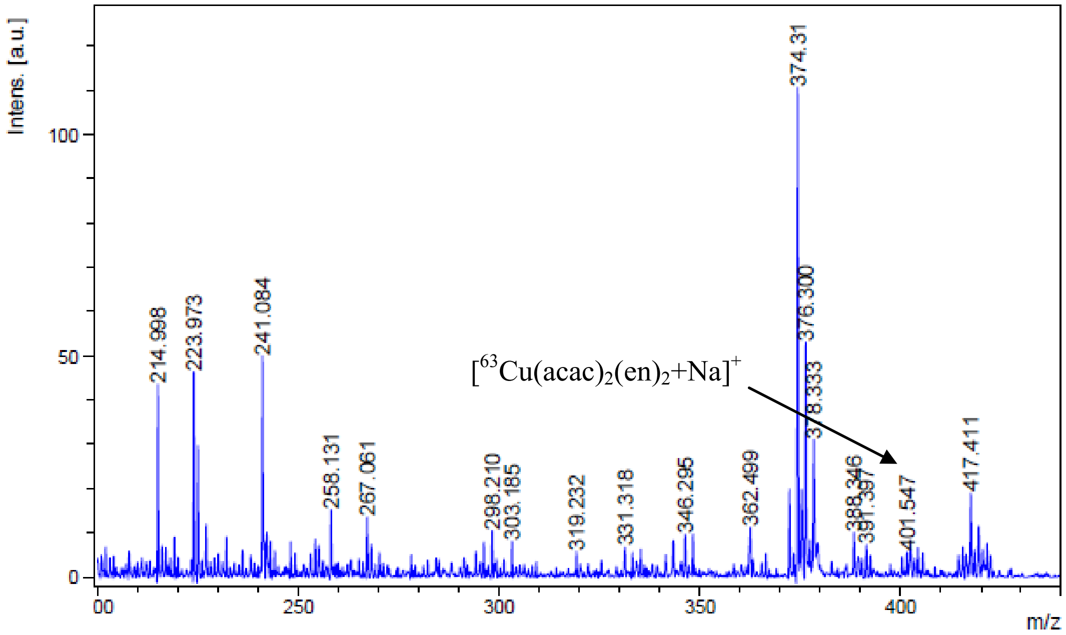


Figure 4.7 Mass spectrum (MALDI-TOF) of $Cu(en)_2$

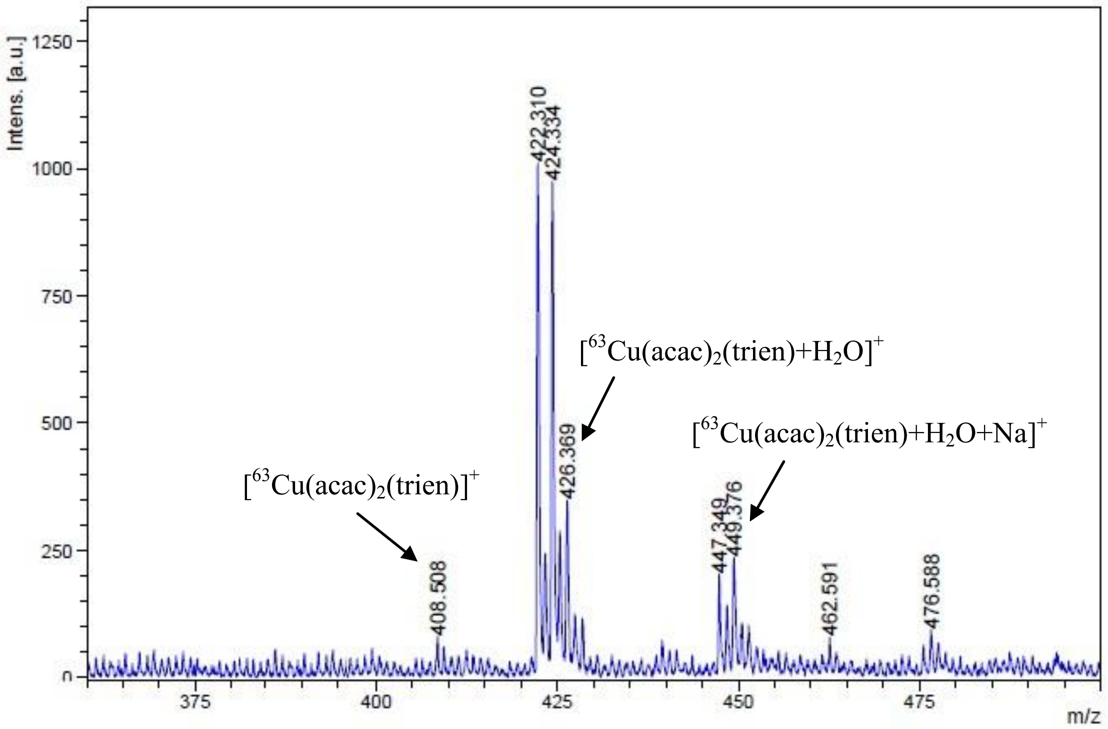


Figure 4.8 Mass spectrum (MALDI-TOF) of Cu(trien)

4.3 Characterization of zinc-amine complexes

4.3.1 IR spectroscopy of zinc-amine complexes

The IR spectra of zinc-amine complexes are shown in Figures 4.9 and 4.10. They exhibited absorption bands at 3250-3318 cm^{-1} (N-H stretching), 2925-2978 cm^{-1} (C-H stretching), 1592-1616 cm^{-1} (C=O asymmetric stretching), 1490-1510 cm^{-1} (C=O symmetric stretching), 1315-1323 cm^{-1} (C-N stretching) and 1112-1127 cm^{-1} (C-O stretching). Asymmetric C=O stretching in $Zn(en)_2$ and Zn(trien) appeared at 1602 and 1616 cm^{-1}, respectively. Symmetric C=O stretching in $Zn(en)_2$ and Zn(trien) appeared at 1507 and 1504 cm^{-1}, respectively. These C=O peaks were different from those of $Zn(acac)_2$ normally appears as absorption band around 1593 cm^{-1} (asymmetric C=O) and 1514 cm^{-1} (symmetric C=O). It was found that the IR peak of $Zn(en)_2$ and Zn(trien) complexes shifted from those of $Zn(acac)_2$, which indicated that the complexes were formed. For Zn(tetraen) and Zn(pentaen), their asymmetric C=O stretching peaks appeared at 1592 and 1602 cm^{-1}, respectively. Symmetric C=O peaks appeared at 1510 and 1490 cm^{-1}, respectively. These C=O stretching bands were different from those of $Zn(acac)_2$. The IR data suggested that Zn(tetraen) and

Zn(pentaen) complexes were formed since IR peak of these complexes shifted from those of Zn(acac)$_2$.

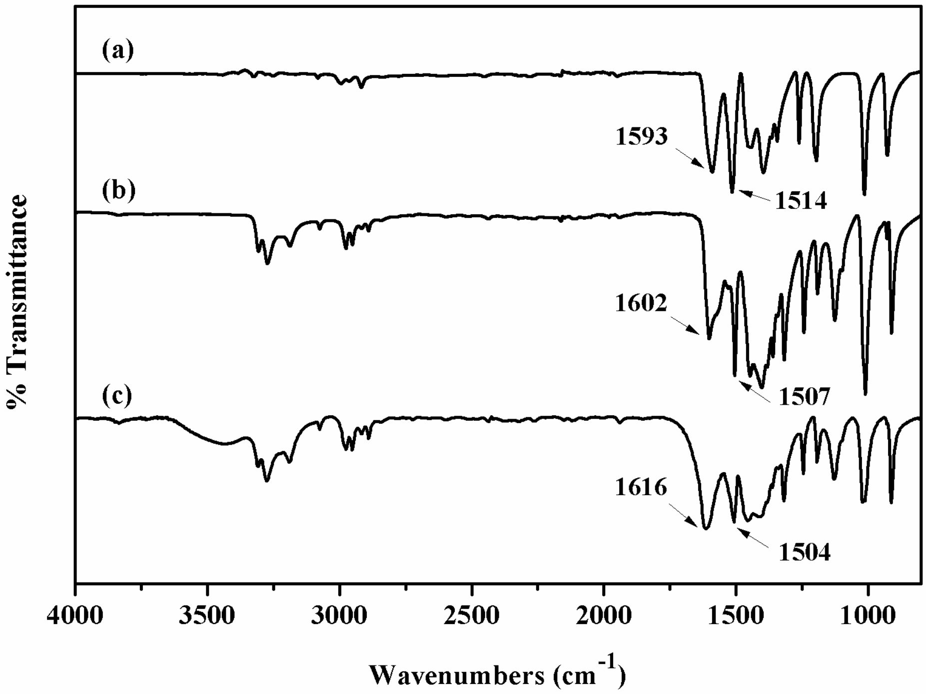


Figure 4.9 IR spectra of (a) Zn(acac)$_2$; (b) Zn(en)$_2$ and (c) Zn(trien)

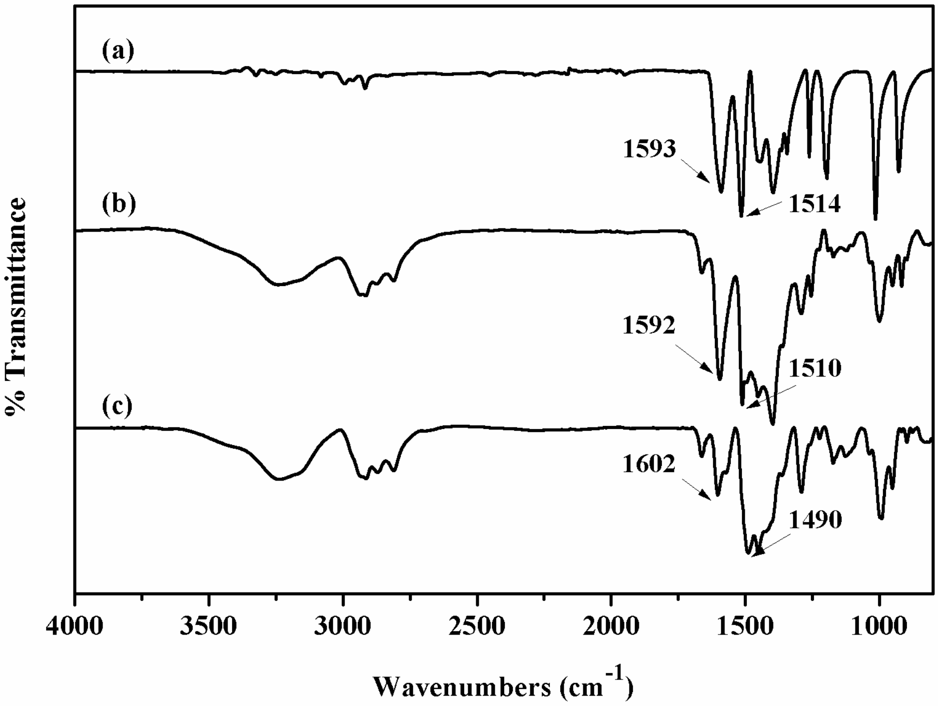


Figure 4.10 IR spectra of (a) Zn(acac)$_2$; (b) Zn(tetraen) and (c) Zn(pentaen)

4.3.2 UV-visible spectroscopy of zinc-amine complexes

UV-visible spectra of zinc-amine complexes are shown in Figures 4.11-4.14. The absorption of $Zn(en)_2$, Zn(trien), Zn(tetraen) and Zn(pentaen) appeared at 288, 278, 292 and 289 nm, respectively. The complexes synthesized in methanol and those synthesized in water gave the same maximum wavelength. Their maximum wavelengths slightly shifted from typical maximum wavelength of $Zn(acac)_2$ at 285 nm, which confirmed the complex formation.

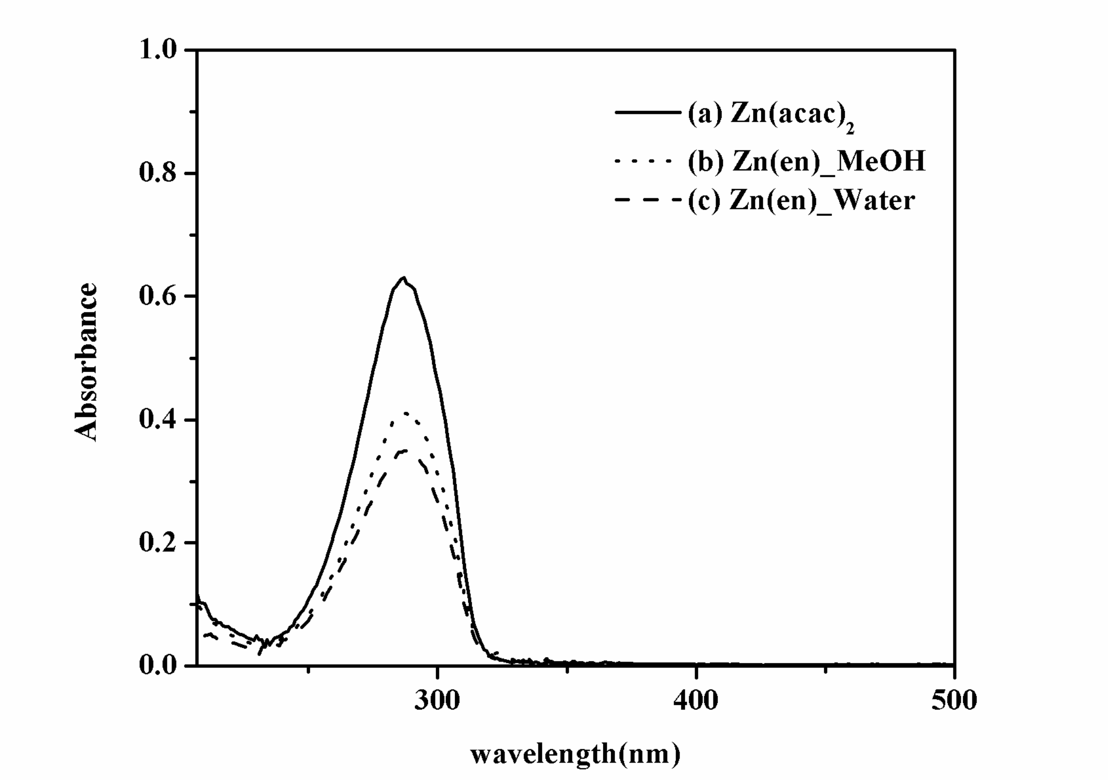


Figure 4.11 UV-vis spectra of (a) $Zn(acac)_2$; (b) Zn(en)_MeOH and (c) Zn(en)_Water

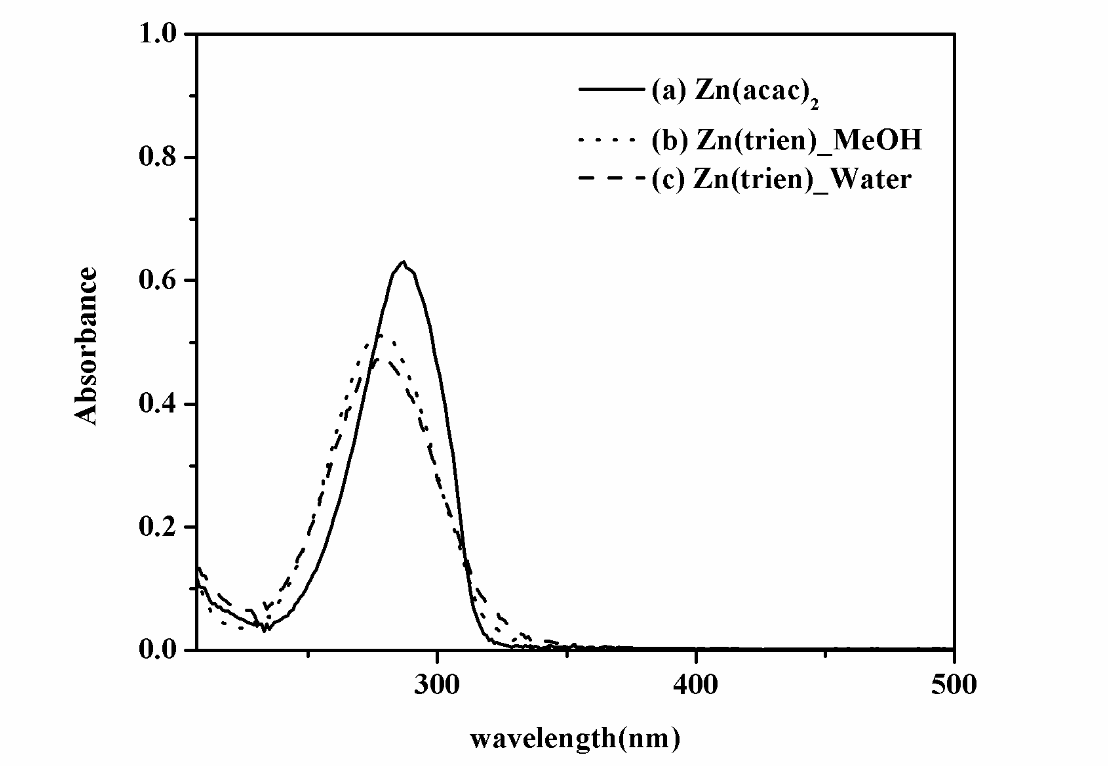


Figure 4.12 UV-vis spectra of (a) Zn(acac)$_2$; (b) Zn(trien)_MeOH and (c) Zn(trien)_Water

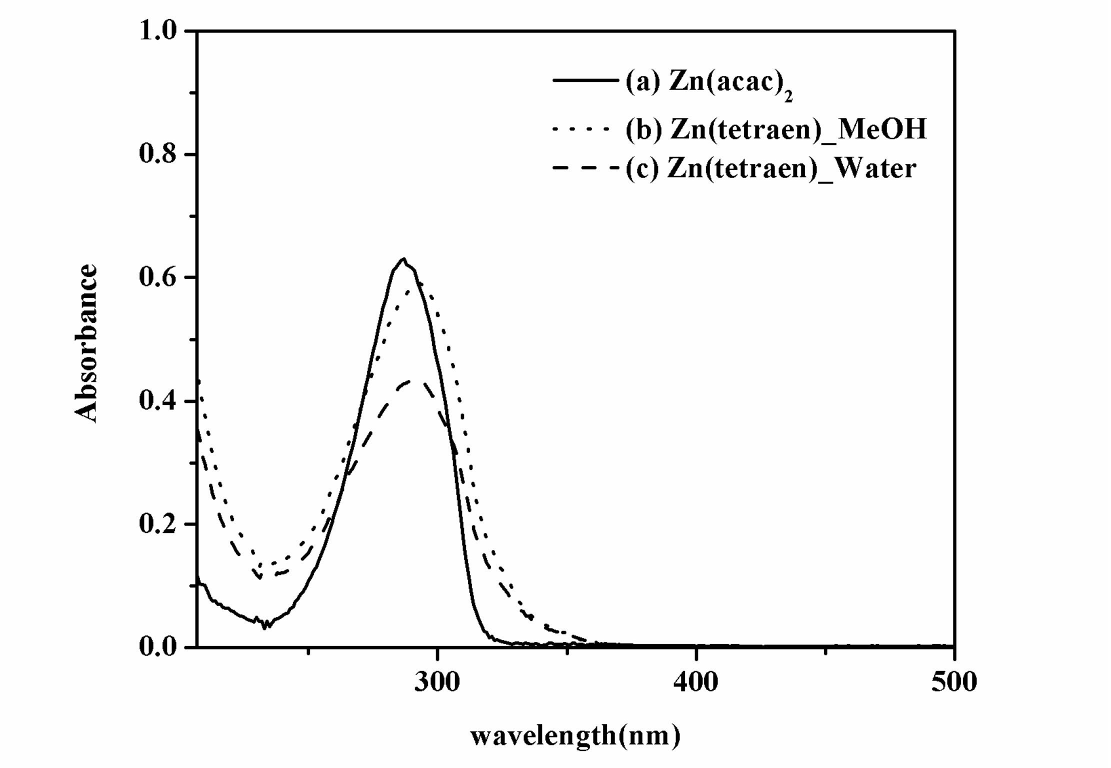


Figure 4.13 UV-vis spectra of (a) Zn(acac)$_2$; (b) Zn(tetraen)_MeOH and (c) Zn(tetraen)_Water

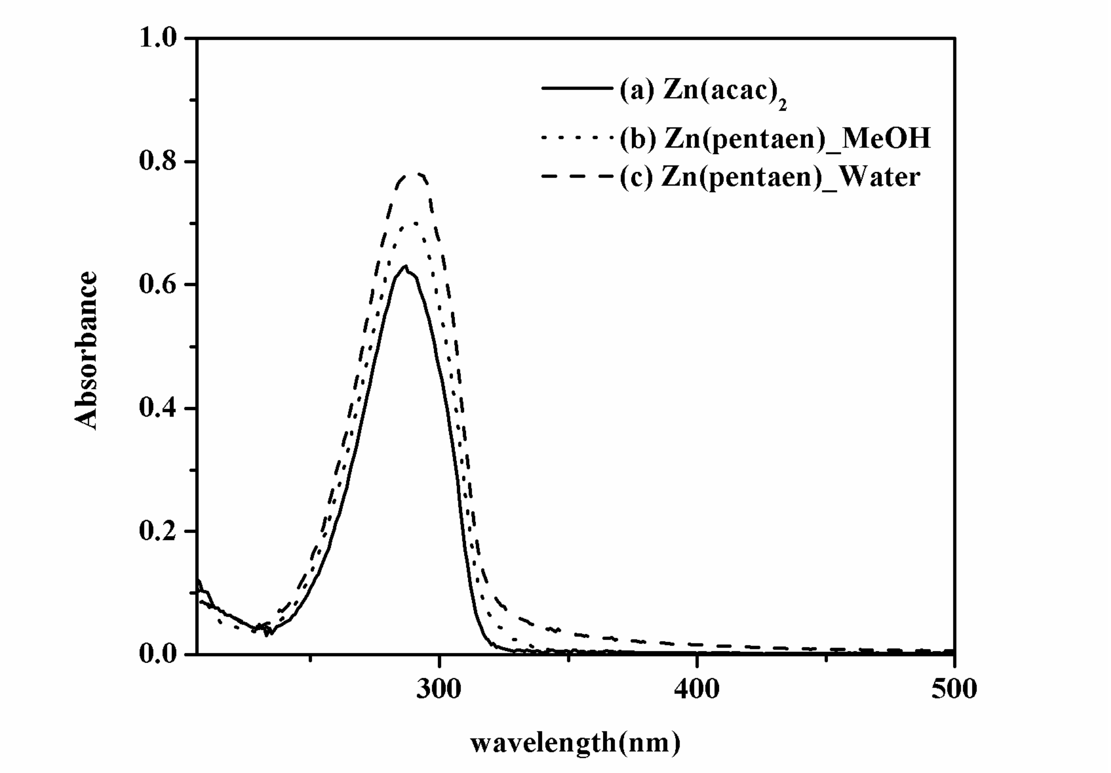


Figure 4.14 UV spectra of (a) Zn(acac)$_2$; (b) Zn(pentaen)_MeOH and (c) Zn(pentaen)_Water

4.3.3 Determination of zinc amount in zinc-amine complexes by flame atomic spectroscopy (FAAS)

FAAS results in determination of zinc amount in zinc-amine complexes (Table 4.3) indicate that there is the consistency between the experimental value and the calculated value. It confirmed the structure of the zinc-amine complexes (Schemes 4.1-4.2).

Table 4.3 FAAS results of zinc-amine complexes

Catalyst	Elements determined	Experimental (%)	Calculated (%)
Zn(en)$_2$	Zn	20.16	20.08
Zn(trien)	Zn	15.52	15.88

4.3.4 Elemental analysis of zinc-amine complexes

Elemental analysis (%C, %H and %N) of zinc-amine complexes showed the results in agreement with the calculated values (Table 4.4).

Table 4.4 Elemental analysis (%C, %H, and %N) of zinc-amine complexes

Catalyst	Elements determined	Experimental (%)	Calculated (%)
$Zn(en)_2$	%C	44.50	44.25
	%H	7.31	7.43
	%N	8.74	8.60
Zn(trien)	%C	46.78	46.66
	%H	8.17	8.32
	%N	13.70	13.60

4.3.5 Mass spectrometry of zinc-amine complexes

The molecular ion peak at *m/z* = 348.286 corresponding to $[^{64}Zn(acac)_2(en)_2+Na]^+$ (Figure 4.15) and *m/z* = 434.414 corresponding to $[^{64}Zn(acac)_2(trien)+Na]^+$ (Figure 4.16) are observed in the MALDI-TOF mass spectrum.

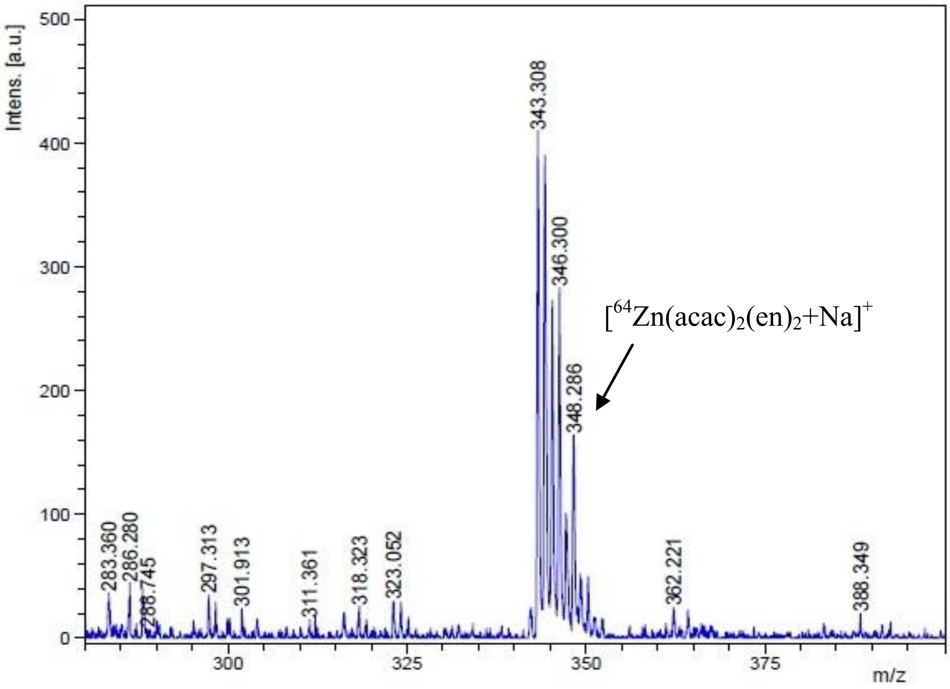


Figure 4.15 Mass spectrum (MALDI-TOF) of $Zn(en)_2$

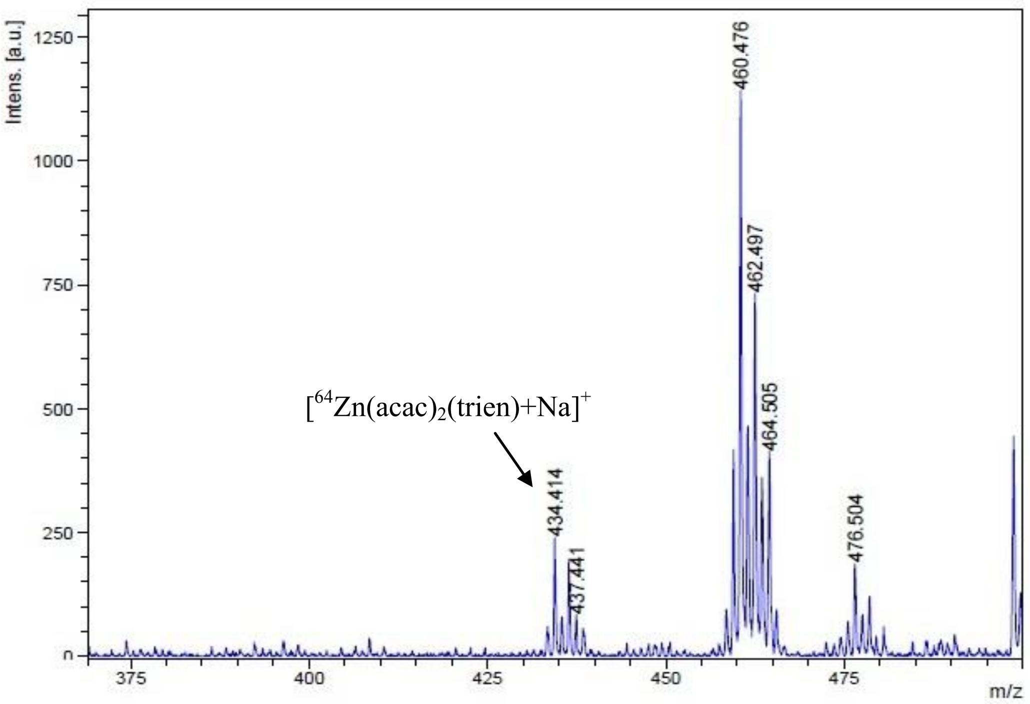


Figure 4.16 Mass spectrum (MALDI-TOF) of Zn(trien)

4.4 Preparation of rigid polyurethane (RPUR) foams

4.4.1 Preparation of RPUR foams catalyzed by metal-amine complexes

The metal-amine complexes synthesized in methanol were separated and dried under vacuum to remove methanol before using as catalysts in the preparation of RPUR foams. The metal-amine complexes synthesized in water gave aqueous solution of metal-amine complexes and therefore they were used as catalysts in the preparation of RPUR foams without purification. RPUR foams catalyzed by metal-amine complexes were prepared by mechanical mixing technique in two steps of the mixing. In the first mixing step, polyol, catalysts (metal-amine complexes or DMCHA), surfactant and blowing agent (water) were mixed in 700-mL paper cup. In the second mixing step, isocyanate was added to the polyol mixture from the first mixing, then the mixture were mixed to obtained homogeneous mixture for 20 seconds using a 2000 rpm mechanical stirrer. The foam was allowed to rise freely, and during the foaming reaction, cream time, gel time, tack-free time and rise time were measured. After that, the foams were kept at room temperature for 48 hours before carrying out physical and mechanical analysis. The foam formulation is shown in Table 4.5.

Table 4.5 RPUR foam formulations catalyzed by metal-amine complexes at different NCO indexes.

Formulations (pbw*)	**NCO index**	
	100	**150**
Polyol (Daltolac® R180)	100	100
Catalyst (metal complexes or DMCHA)	1.0	1.0
Surfactant (Tegostab® B8460)	2.5	2.5
Water (blowing agent)	3.0	3.0
PMDI (Suprasec® 5005)	151	227

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

4.4.2 Reaction times

The reaction times measured were cream time (the time when the foam started to rise), gel time (the time when the foam mixture started to gel), tack free time (the time when polymerization reaction is completed) and rise time (the time when the foam stopped rising which is the time when CO_2 generation stops). The reaction times of RPUR foams catalyzed by metal-amine complexes synthesized in methanol were compared to those catalyzed by metal-amine complexes synthesized in water. The obtained results are also compared with commercial catalyst (DMCHA).

The reaction times of RPUR foam catalyzed by metal-amine complexes synthesized in methanol are shown in Table 4.6 and those synthesized in water are shown in Table 4.7. It was found that the metal-amine complexes synthesized in methanol and those synthesized in water gave the similar reactivity results. Therefore, the preparation of metal complexes in water had advantage because foam formulation had water which was blowing agent. The preparation of metal complexes in water is more convenient than the preparation in methanol since the solution of metal complexes in water can be further used in the preparation of polyurethane foam without purification.

Table 4.6 Reaction times of RPUR foams prepared at NCO indexes of 100 catalyzed by metal-amine complexes synthesized in methanol.

Catalysts types	Cream time (min)	Gel time (min)	Tack free time (min)	Rise time (min)	Density (kg/m^3)	Volume (V)
DMCHA (ref.)	0:22	0:32	3:07	2:21	39.7	7.5/8V
Cu(en)	0:24	0:46	1:40	1:54	35.5	7/8V
Cu(trien)	0:26	1:06	2:25	2:38	38.0	7/8V
Cu(tetraen)	0:26	1:20	2:51	3:14	38.2	6.5/8V
Cu(pentaen)	0:24	1:15	2:42	3:03	38.8	6.5/8V
Zn(en)	0:30	1:33	6:06	5:01	39.0	6/8V
Zn(trien)	0:25	1:02	3:49	3:02	35.5	7/8V
Zn(tetraen)	0:29	1:10	5:25	4:49	36.0	6.5/8V
Zn(pentaen)	0:28	1:08	5:29	4:34	38.0	6.5/8V

Table 4.7 Reaction times of RPUR foams prepared at NCO indexes of 100 catalyzed by metal-amine complexes synthesized in water.

Catalysts types	Cream time (min)	Gel time (min)	Tack free time (min)	Rise time (min)	Density (kg/m^3)	Volume (V)
DMCHA (ref.)	0:22	0:32	3:07	2:21	39.7	7.5/8V
Cu(en)	0:25	0:36	1:30	1:41	34.7	7/8V
Cu(trien)	0:24	1:03	2:01	2:35	37.4	7/8V
Cu(tetraen)	0:25	1:16	2:48	3:06	36.2	6.5/8V
Cu(pentaen)	0:23	0:58	2:06	2:20	37.7	6.5/8V
Zn(en)	0:22	0:46	5:04	3:55	36.0	7/8V
Zn(trien)	0:29	1:07	3:45	3:30	34.9	7/8V
Zn(tetraen)	0:28	1:08	5:20	4:40	35.4	6.5/8V
Zn(pentaen)	0:27	1:04	5:11	4:25	37.5	6.5/8V

From the reactivity results in Figures 4.17-4.18, the copper-amine complexes showed comparable catalytic activity to DMCHA since copper-amine complexes and DMCHA gave similar tack free time. When using copper-amine complexes as a catalyst, tack free time was shorter than rise time. This result was good for foam preparation since the foam continued to rise when the polymerization reaction was almost completed. This gave stable foam structure that would not collapse.

Both copper-amine and zinc-amine complexes were good catalyst since their tack free times were short. The tack free time corresponded to gelling reaction, which was the reaction between isocyanate and hydroxyl group to form urethane groups. Since copper-amine complexes gave shorter tack free time than zinc-amine complexes, this indicated that copper-amine complexes had better catalytic activity in gelling reaction than zinc-amine complexes.

Furthermore, rise profile of RPUR foams prepared from copper-amine complexes and zinc-amine complexes showed similar trend to that of DMCHA (Figure 4.19). DMCHA is a tertiary amine-based catalyst and has strong catalytic activity towards both blowing and gelling reactions [19]. The metal-amine complexes showed longer initial time than DMCHA and exhibited a fast rise curve in the latter stage.

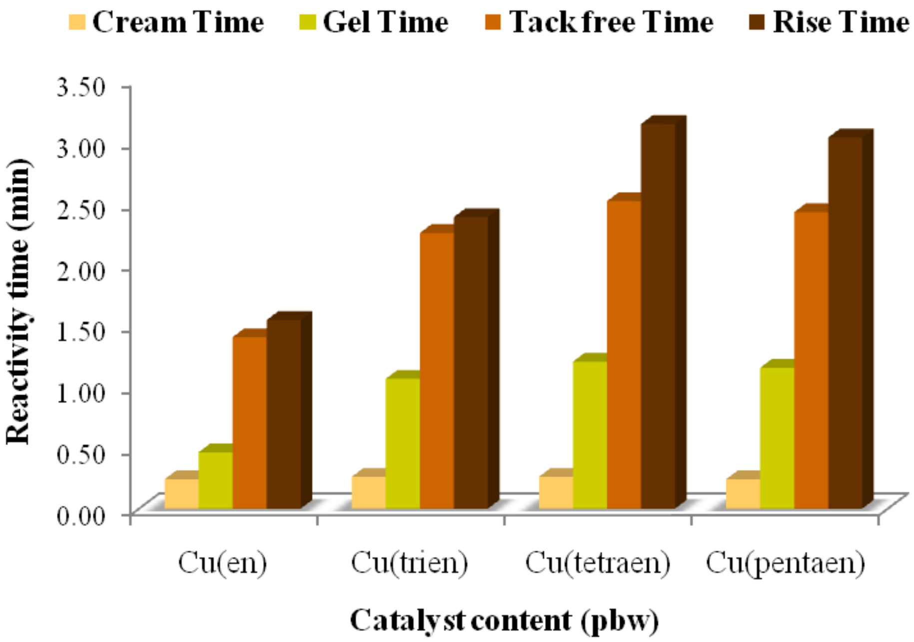


Figure 4.17 Reaction times of RPUR foams catalyzed by copper-amine complexes.

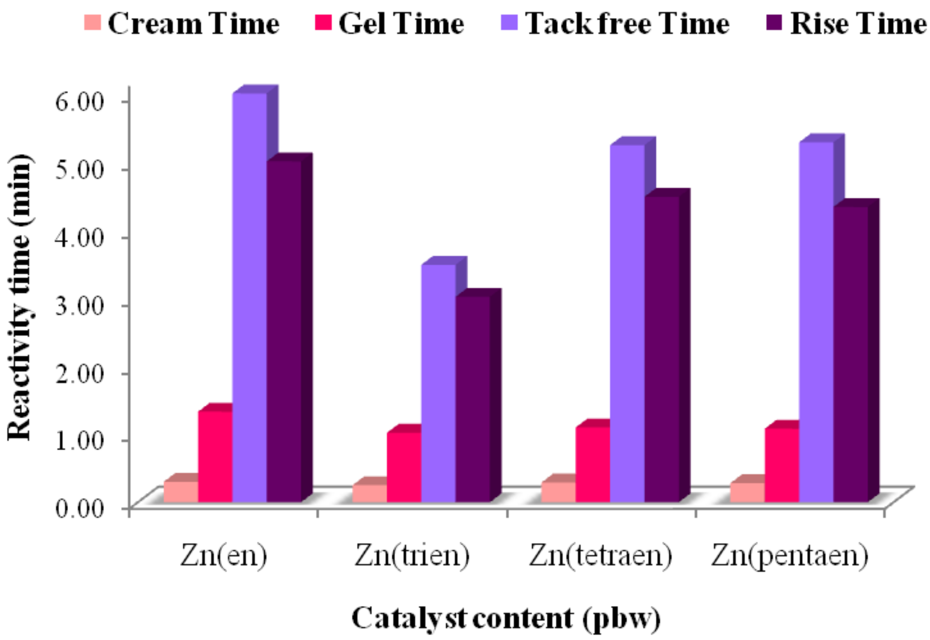


Figure 4.18 Reaction times of RPUR foams catalyzed by zinc-amine complexes.

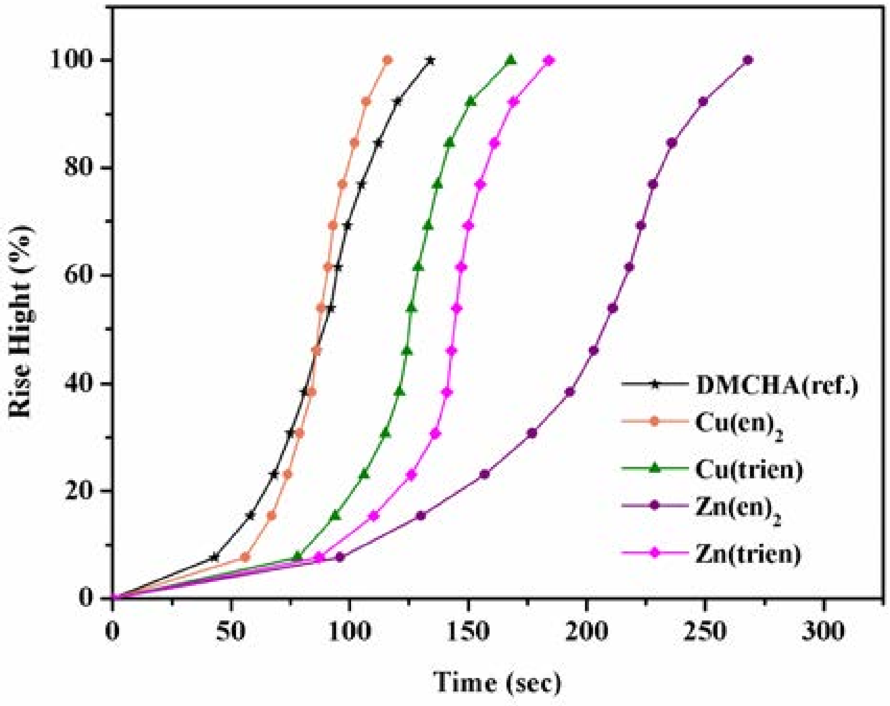


Figure 4.19 Rise profiles of RPUR foams catalyzed by different metal-amine complexes.

4.4.2.1 Effect of catalyst content on reaction time

The effect of catalyst content on the reaction time of RPUR foam is shown in Figures 4.20-4.21. It was found that when the amount of catalyst was decreased, the reaction time had a trend to slow down. It can be seen that when the amount of catalyst was decreased to 0.5 part by weight (pbw) in the foam formulation, the foaming reaction showed longer tack-free time. In contrast, when compared between using 1.0 and 1.5 pbw of catalyst in the foam formulation, both used less time and gave the similar trend, which was confirmed by faster tack-free time. The adjustment of catalyst dosage in the foam formulation to obtain a reactivity of foaming reaction is an industrial requirement. In particular, slow cream time and gel time are needed whereas fast tack-free time should be maintained. Therefore, it could be concluded that the catalyst amount of 1.0 pbw in the formulation should be chosen for the next step of this study.

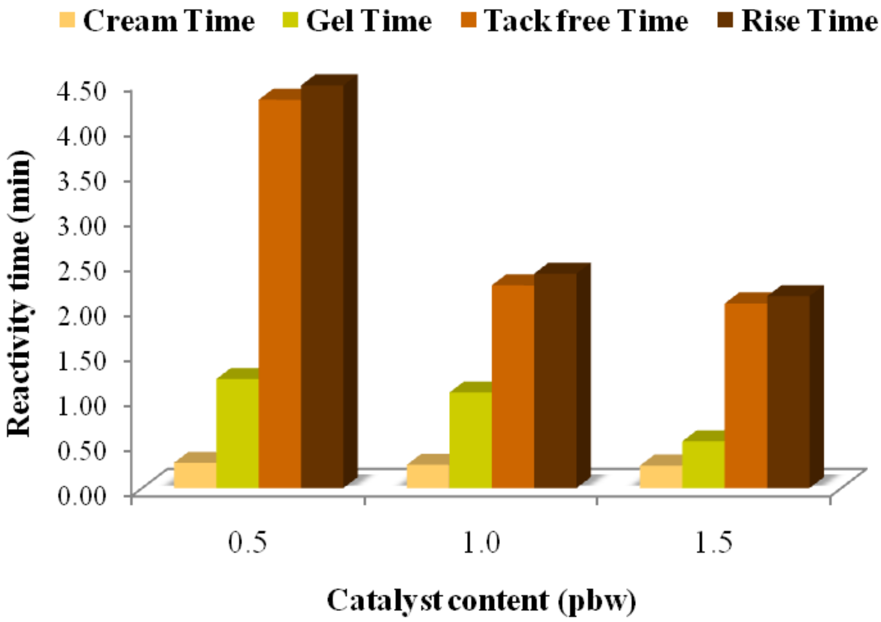


Figure 4.20 Reaction times of RPUR foams catalyzed by Cu(trien) in various amount.

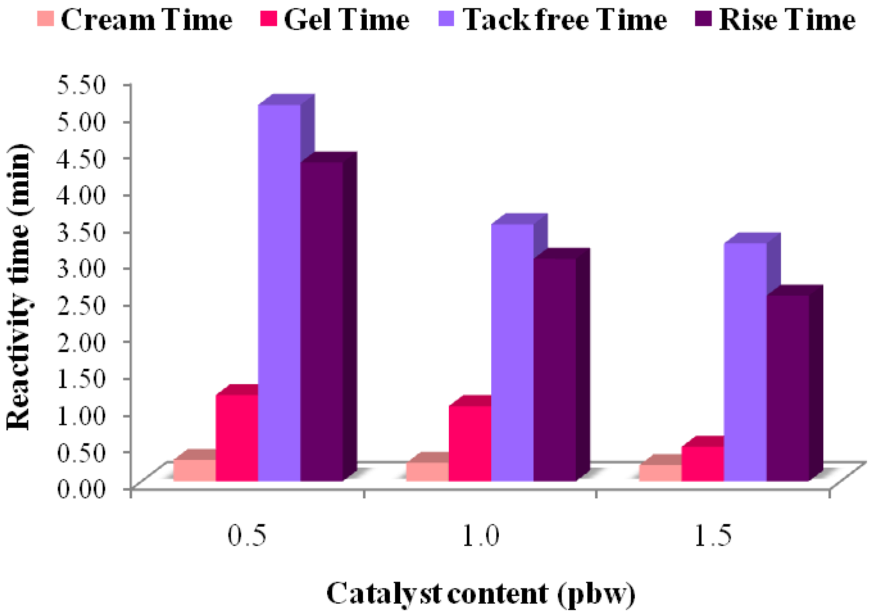
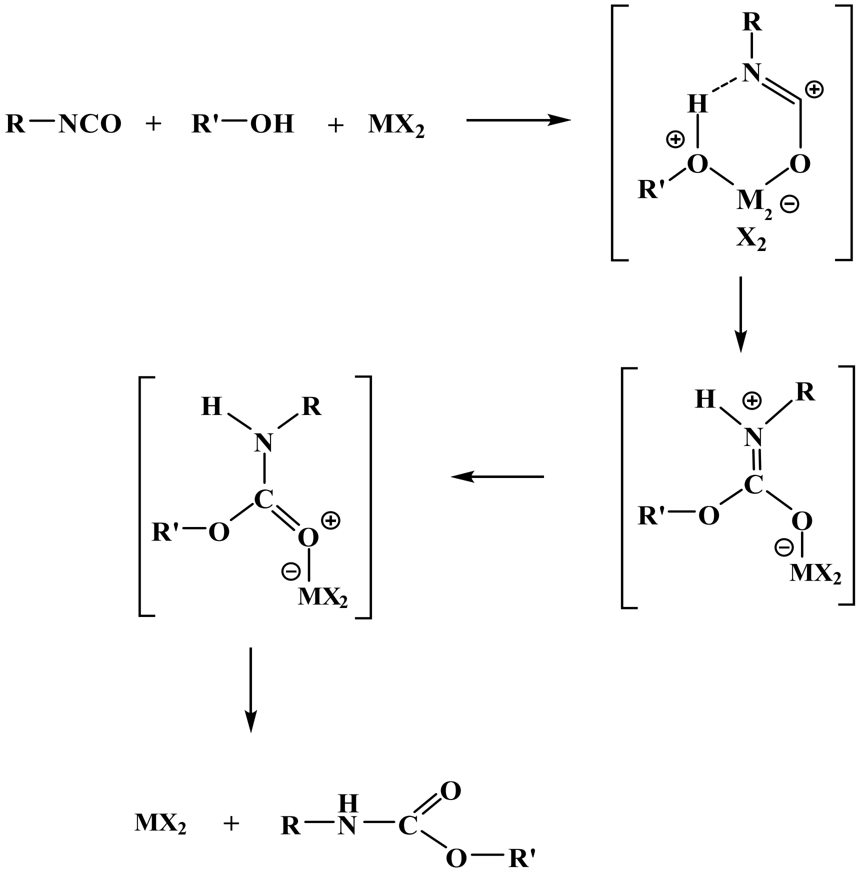


Figure 4.21 Reaction times of RPUR foams catalyzed by Zn(trien) in various amount.

From the reaction mechanism of RPUR foams catalyzed by metal-amine complexes in Schemes 4.5, it is proposed that the metal-amine complexes acted as a Lewis acid. The activation starts by coordinated to the oxygen atom of the NCO group and activated the electrophilic nature of the carbon [19] and amine interacting with the proton of hydroxyl group in polyol, which then reacts with the isocyanate. While, the tertiary amine coordinate to the positive electron charged carbon of the NCO group or hydrogen of the OH group and forms a transition state to activate urethane formation reaction. Tertiary amine can be tuned by maximizing its ability to form a hydrogen bond with alcohol, thereby activating the O–H bond so it can attach to the isocyanate more easily.



Scheme 4.5 Activation mechanism of metal-amine catalyst on urethane formation reaction [19]

4.4.3 Free rise density

The free rise density of RPUR foams were measured according to ASTM D 1622 [51] by cutting into cubic shape with 3.0 cm x 3.0 cm x 3.0 cm dimensions (Figure 4.22). The samples were weighted, then the sample volume and density were calculated.

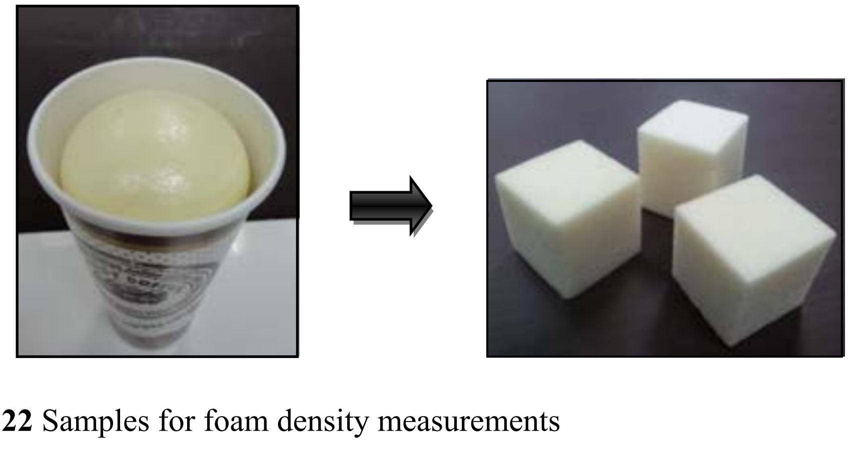


Figure 4.22 Samples for foam density measurements

4.4.3.1 Effect of NCO indexes on foam density

The effect of NCO indexes on the density of RPUR foams is shown in Figure 4.23. When the NCO index was increased, the density of the foams also increased because the excess of isocyanate in polyurethane system could undergo further polymerization to provide crosslinked structure such as isocynurate and allophanate [6]. RPUR foams prepared from metal-amine complexes had suitable density when prepared at the NCO index of 100-150. The foams prepared at an NCO index of 150 had densities in the range around 40–50 kg/m^3, which was the desirable density for foam applications [4, 52]. Additionally, foams prepared from metal-amine complexes showed apparent density similar to those prepared from DMCHA. This result indicated that metal-amine complexes were suitable for industrial application.

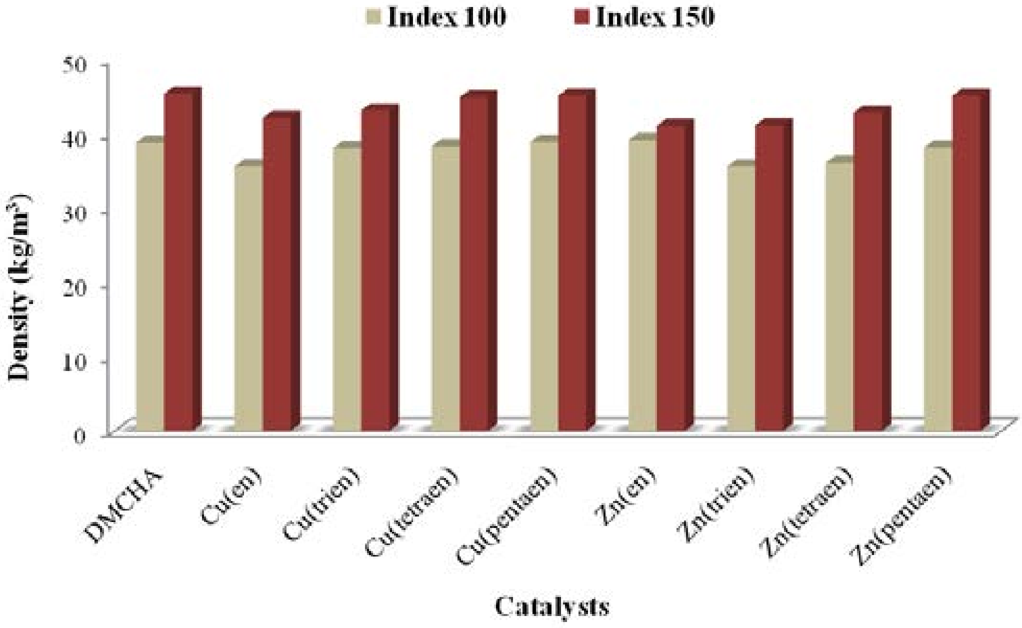


Figure 4.23 Free rise density of RPUR foams catalyzed by DMCHA and metal-amine complexes at different NCO indexes.

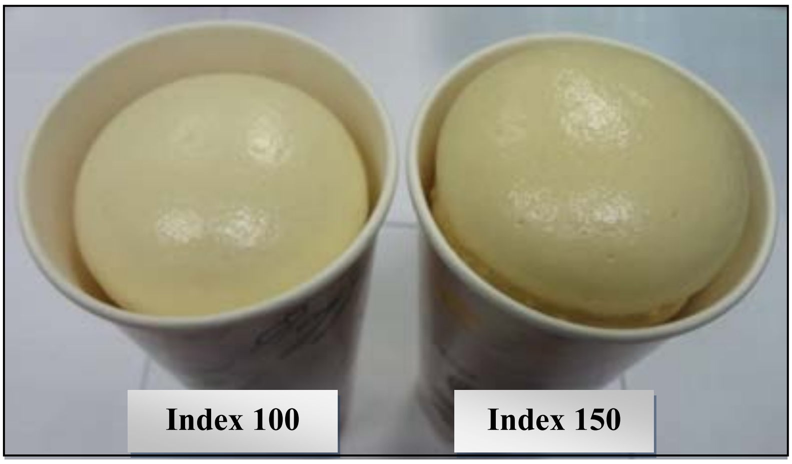


Figure 4.24 Appearance of RPUR foams catalyzed by metal-amine complex at NCO index of 100 and 150.

4.4.3.2 Effect of catalyst quantity on foam density

The effect of catalyst quantity on RPUR foam density is shown in Figure 4.25. It may be concluded that the foam density decreased with increasing the amount of catalyst in foam formulation since more blowing reactions could occur when increasing amount of catalyst. It was observed that the foam prepared at catalyst quantity of 0.5 part by weight (pbw) showed lower blowing reaction than those prepared from 1.0 and 1.5 pbw of catalyst. Furthermore, the foams prepared from 1.0 and 1.5 pbw of catalyst showed similar apparent density. However, the high quantity of catalyst resulted in the decreasing of foam density, which was not suitable for applying in foam manufacturing.

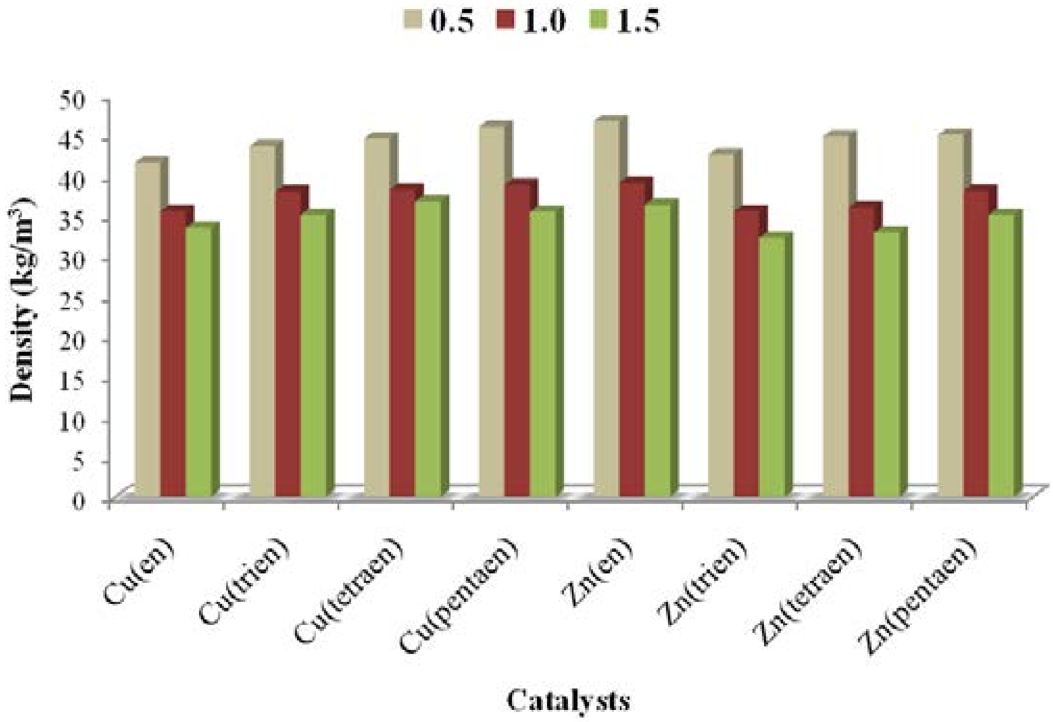


Figure 4.25 Effect of catalyst content on RPUR foam density catalyzed by different catalysts type at NCO index of 100.

4.4.3.3 Effect of blowing agent quantity on foam density

Figure 4.26 showed the effect of the content of blowing agent on RPUR foams density at NCO index 100. From this result, it may be concluded that if the amount of blowing agent (water) was increased, free rise density of the foams would decrease. Since blowing agent could react with isocyanate group to generate CO_2 gas and the temperature of foam was higher due to exothermic reaction, therefore the blowing agent of 4.0 pbw released more CO_2 and made the foam volume increased than that of 3.0 pbw (Figure 4.27). Therefore, the foams prepared at blowing agent of 3.0 pbw showed higher free rise density than those prepared from 4.0 pbw.

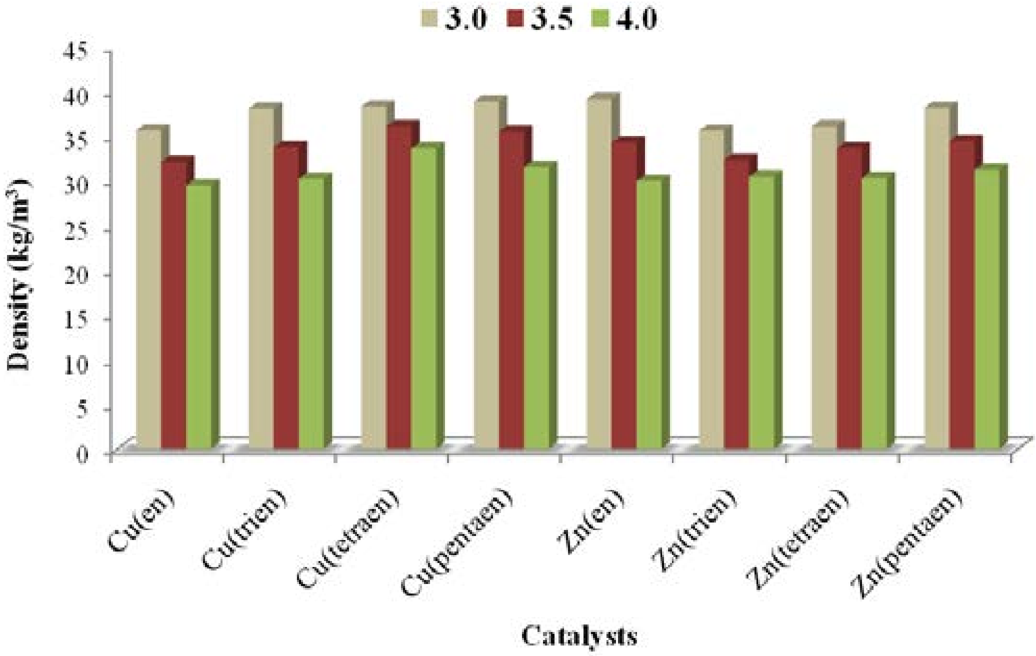


Figure 4.26 Effect of blowing agent quantities on RPUR foam density catalyzed by different catalysts at NCO index of 100.

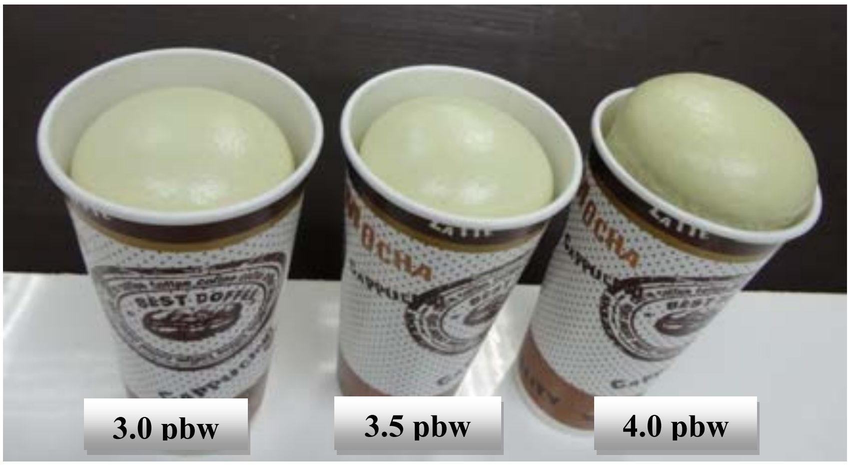


Figure 4.27 Appearance of RPUR foam catalyzed by metal-amine complex in various amounts of blowing agent.

4.4.4 Foaming temperature

The maximum core temperature of RPUR foams catalyzed by various catalysts at different NCO indexes is shown in Table 4.8. It was found that the polymerization reaction is exothermic reaction. The maximum core temperature of foams prepared from metal-amine complexes was in the range of 116-134 ^{o}C. Moreover, the foams prepared at NCO index of 150 showed higher core temperature than those prepared at NCO index of 100. This result suggested that the foaming temperature increased with increasing NCO index due to the released heat from reaction between isocyanate and water. At NCO index less than 150, less isocyanate was present to react with water and thus less heat was released leading to a lower foaming temperature [52, 54-55].

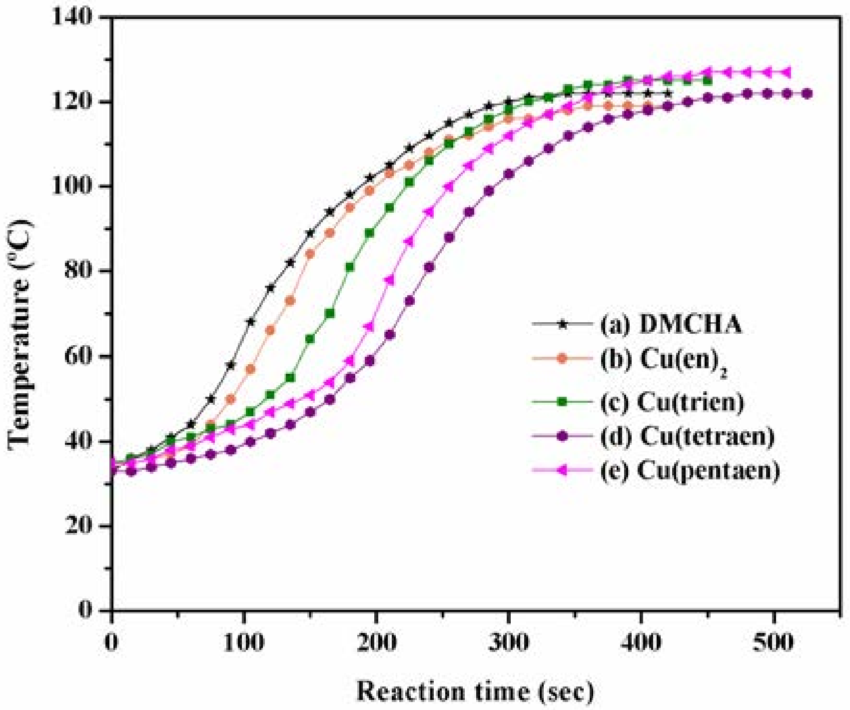


Figure 4.28 Temperature profiles of RPUR foams catalyzed by (a) DMCHA (ref.); (b) Cu(en)$_2$; (c) Cu(trien); (d) Cu(tetraen); (e) Cu(pentaen)

The temperature profiles of RPUR foam prepared from different catalysts at NCO index of 100 were investigated. It was found that the profiles of foams prepared from copper-amine complexes (Figure 4.28) and zinc-amine complexes (Figure 4.29) showed similar trend to that of DMCHA.

Table 4.8 Maximum core temperature of RPUR foam catalyzed by metal-amine complexes at different NCO indexes

Catalysts	**NCO indexes**	**Maximum core temperature (^{o}C)**	**Starting times (min) at T_{max}**
DMCHA	100	122	345 (5:45)
	150	127	390 (6:30)
$Cu(en)_2$	100	119	360 (6:00)
	150	125	420 (7:00)
Cu(trien)	100	125	390 (6:30)
	150	131	435 (7:15)
Cu(tetraen)	100	122	480 (8:00)
	150	129	540 (9:00)
Cu(pentaen)	100	127	450 (7:30)
	150	134	540 (9:00)
$Zn(en)_2$	100	123	390 (6:30)
	150	126	435 (7:15)
Zn(trien)	100	116	420 (7:00)
	150	124	465 (7:45)
Zn(tetraen)	100	121	480 (8:00)
	150	130	540 (9:00)
Zn(pentaen)	100	126	375 (6:15)
	150	133	420 (7:00)

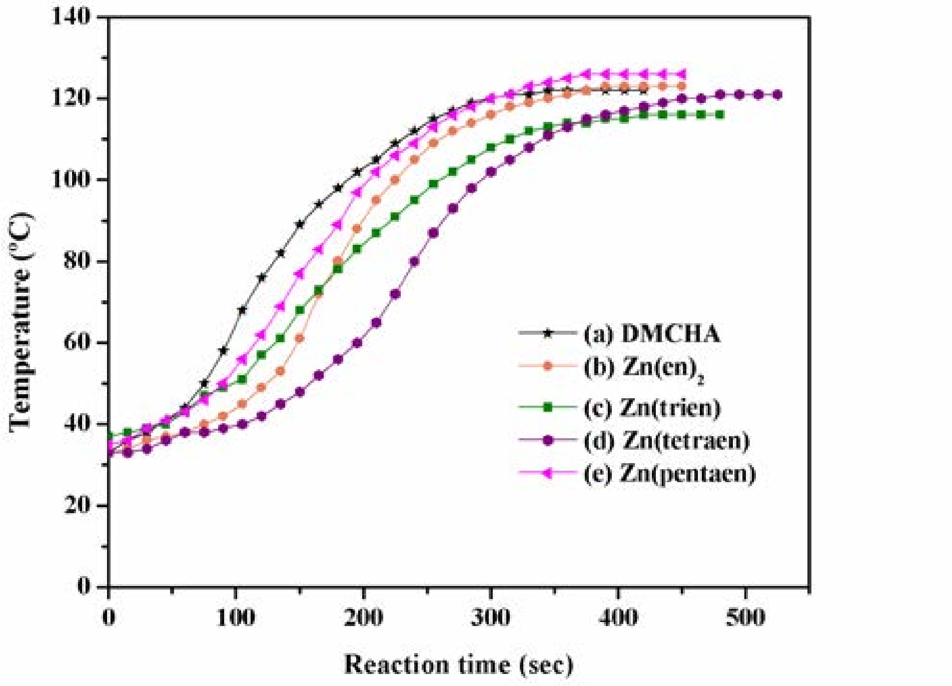


Figure 4.29 Temperature profiles of RPUR foams catalyzed by (a) DMCHA (ref.); (b) Zn(en)$_2$; (c) Zn(trien); (d) Zn(tetraen); (e) Zn(pentaen)

4.4.5 Characterization of RPUR foams

FTIR spectroscopy was employed to investigate the polymerization of RPUR foam system. IR spectra of polymeric MDI, polyether polyol and RPUR foams are shown in Figure 4.30. From the IR spectrum of polyol (Figure 4.30 a), the broad band at about 3400 cm^{-1} was the characteristic stretching vibration of hydroxyl groups. PMDI (Figure 4.30 b) showed high intensity of isocyanate stretching at 2277 cm^{-1}.

From the IR spectra of RPUR foams, it was found that RPUR foams exhibit the characteristic spectrum peaks of urethane and urea linkages occurred from the polymerization of isocyanate groups, hydroxyl groups and water. The bands at 3420 and 1720 cm^{-1}were the characteristic stretching vibrations of amine group (N-H) and carbonyl group (C=O) of urethane and urea linkages, respectively, while the band at 1510 cm^{-1}could be attributed to N-H bending vibration and C-N stretching vibration of urethane and urea groups. The band at 1230 cm^{-1} was associated with the characteristic stretching vibration of C-N-H bond of urethane and urea [53]. Also, isocyanate groups at 2277 cm^{-1} in RPUR foams disappeared, which indicate that isocyanate group were completely consumed by the reactions with hydroxyl groups and water.

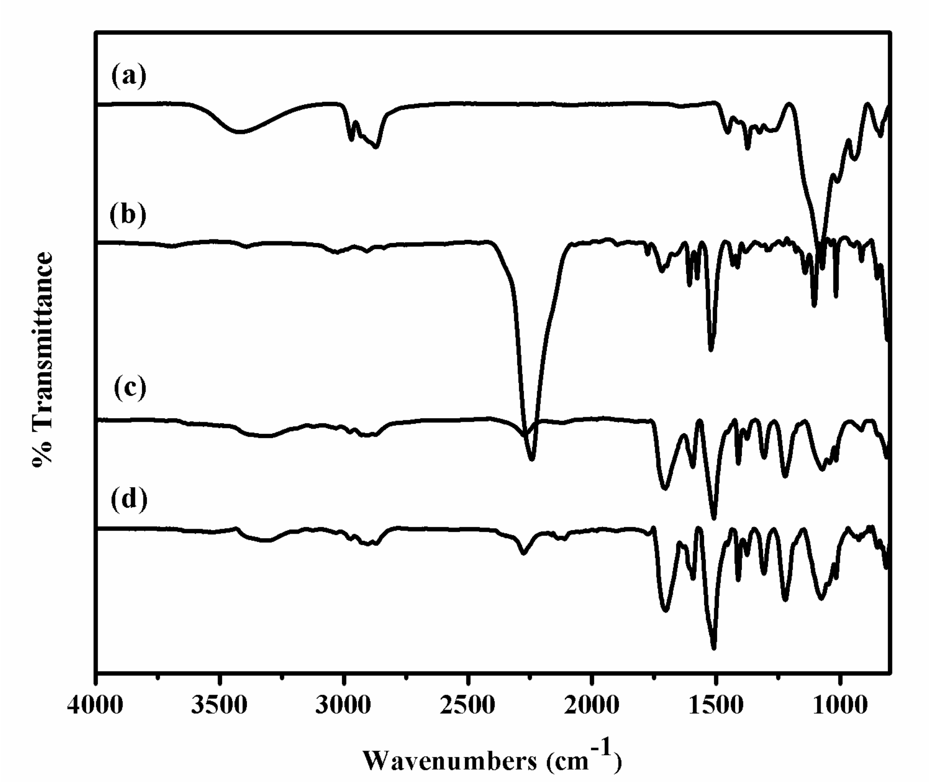


Figure 4.30 IR spectra of starting materials (a) polyether polyol; (b) PMDI and RPUR foams catalyzed by (c) DMCHA; (d) metal-amine complex

4.4.6 NCO conversion of RPUR foams

An example of ATR-FTIR spectrum of PMDI and RPUR foams catalyzed by metal-amine complex at different NCO indexes are shown in Figure 4.31. It indicated that the absorption band of isocyanate could be observed at 2277 cm^{-1}. When higher NCO index was used in the foam formulation, high intensity of NCO absorption band could be observed. The peak areas used in calculation % isocyanate conversion and PIR:PUR ratio were C-O of urethane, C-N of isocyanurate and N=C=O of isocyanate (Table 4.9). It can be seen that all RPUR foams had the isocyanate conversion higher than 95%. This result was similar to the previous work [48]. They also had the polyurethane:polyisocyanurate (PIR:PUR) ratio less than 0.22 since all formulations were prepared with the NCO index of 100. Therefore, the reaction between isocyanate and polyol to give urethane group was the major reaction and trimerization reaction of isocyanate to form isocyanurate group was a minor reaction.

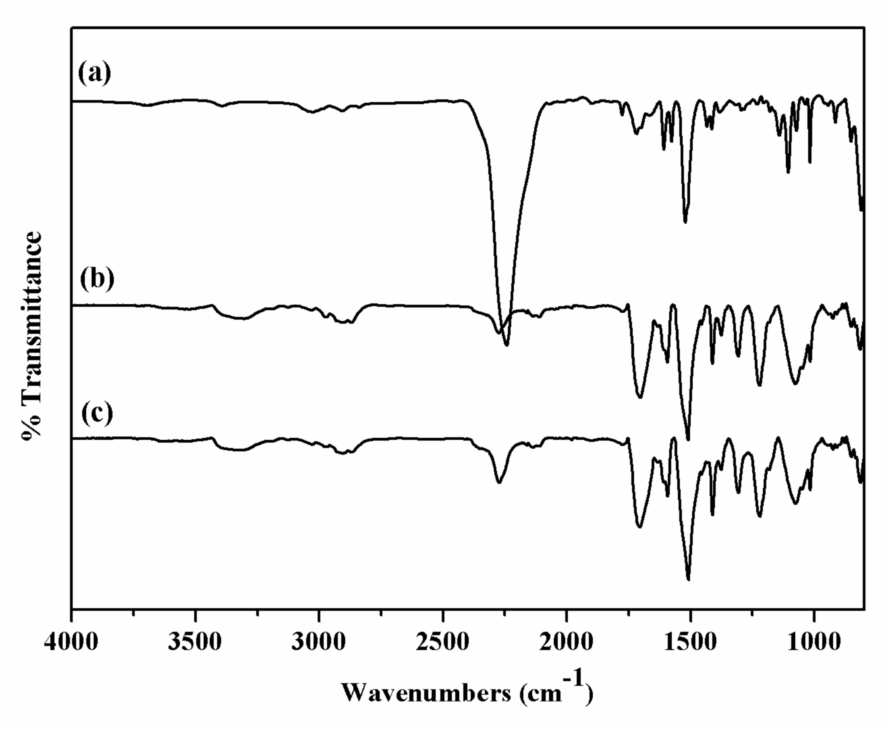


Figure 4.31 IR spectra of starting materials (a) PMDI and RPUR foams catalyzed by metal-amine complexes at different NCO indexes (b) 100; (c) 150

The NCO conversion defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0 as shown in following equation [52, 54-55]:

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

where;

NCO^f is the area of isocyanate absorbance peak area at time t (Figures 4.30 c and d)

NCO^i is the area of isocyanate absorbance peak area at initial time 0 (Figure 4.30 b)

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

Polyisocyanurate:polyurethane (PIR:PUR) ratio was calculated from the peak area of isocyanurate and urethane at 1415 and 1220 cm^{-1}, respectively (Table 4.9).

Table 4.9 Wavenumber of the functional groups used in calculation [50]

Functional groups	Wave number (cm^{-1})	Chemical structure
Isocyanate	2277	N=C=O
Phenyl	1595	Ar-H
Isocyanurate	1415	PIR
Urethane	1220	-C-O-

The results of NCO conversion of RPUR foams catalyzed by metal-amine complexes at NCO indexes 100 and 150 are demonstrated in Figure 4.32. It can be observed that NCO conversion decreased by increasing the content of NCO indexes. The excess isocyanate could not undergo trimerization to provide isocyanurate group. Therefore metal-amine complex catalysts were not specific toward of isocyanurate formation.

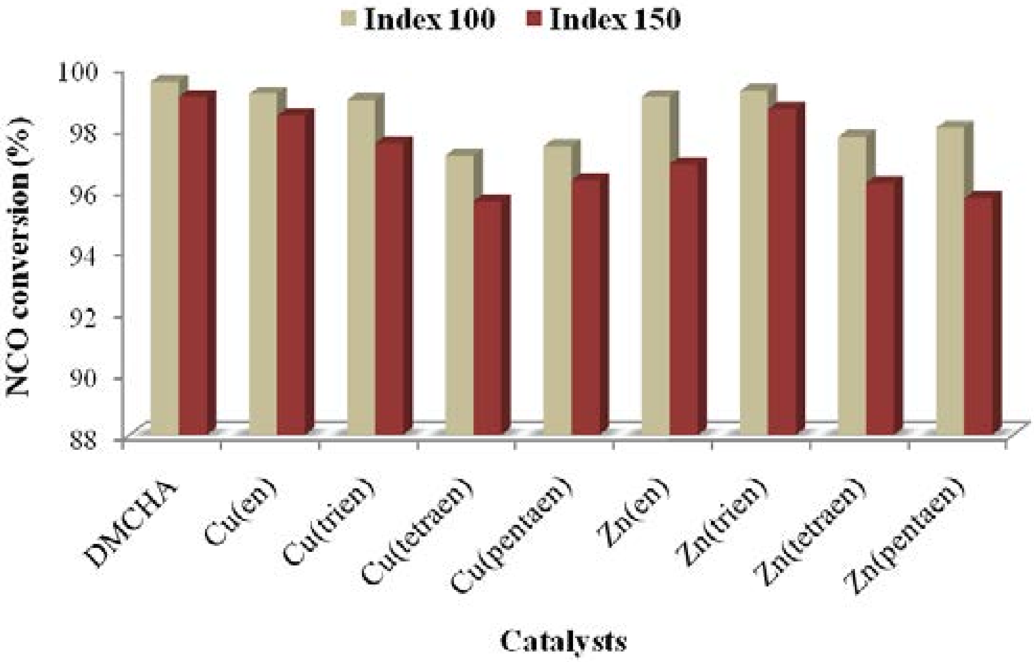


Figure 4.32 NCO conversions of RPUR foams catalyzed by metal-amine complexes at different NCO indexes.

The ratio of polyisocyanurate:polyurethane (PIR:PUR) in RPUR foams prepared from different catalysts is shown in Figure 4.33. From these results, PIR:PUR of all RPUR foam slightly increased with increasing the content of NCO index. This result indicated that metal-amine complexes were not good catalyst for polyisocyanurate formation. It could be concluded that metal complexes were good catalysts for polyurethane formation and blowing reaction but they were not good catalysts for trimerization reaction. Tables 4.10 and 4.11 show the data of NCO conversion and PIR:PUR ratio in RPUR foams catalyzed by metal-amine complexes.

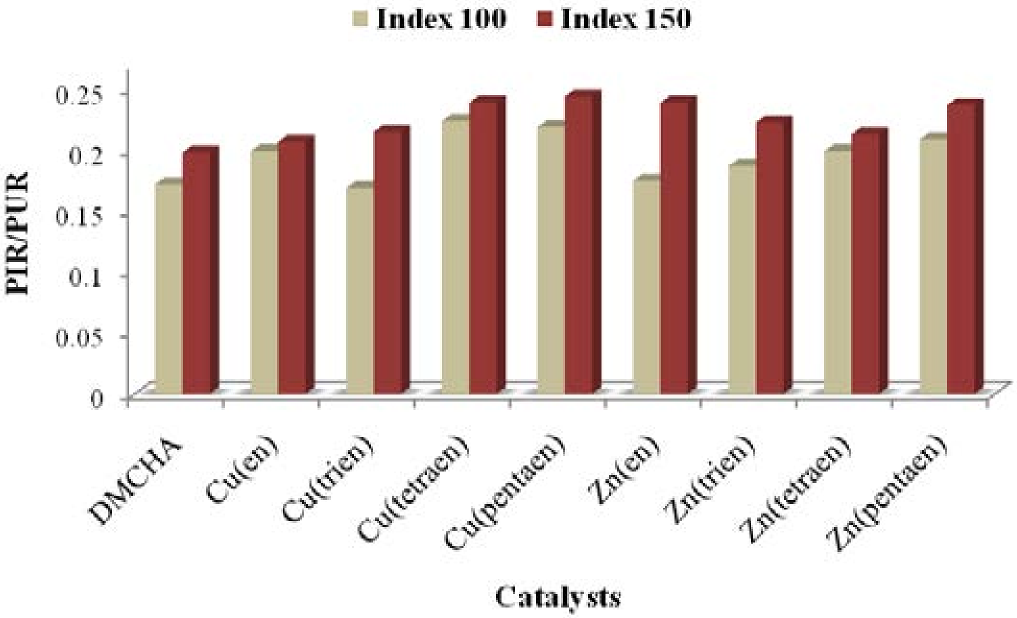


Figure 4.33 PIR:PUR of RPUR foams catalyzed by metal-amine complexes at different NCO indexes.

Table 4.10 NCO conversions and PIR:PUR ratio of RPUR foams prepared by copper-amine complexes at different NCO indexes

Catalysts	NCO indexes	NCO conversion (%)	PIR/PUR
DMCHA (ref.)	100	99.5	0.172
	150	99.0	0.198
$Cu(en)_2$	100	99.1	0.199
	150	98.4	0.207
Cu(trien)	100	98.9	0.169
	150	97.5	0.215
Cu(tetraen)	100	97.1	0.214
	150	95.6	0.239
Cu(pentaen)	100	97.4	0.219
	150	96.3	0.244

Table 4.11 NCO conversions and PIR:PUR ratio of RPUR foams prepared by zinc-amine complexes at different NCO indexes

Catalysts	NCO indexes	NCO conversion (%)	PIR/PUR
DMCHA (ref.)	100	99.5	0.172
	150	99.0	0.198
$Zn(en)_2$	100	99.0	0.175
	150	96.8	0.239
Zn(trien)	100	99.2	0.187
	150	98.6	0.223
Zn(tetraen)	100	97.7	0.199
	150	96.2	0.213
Zn(pentaen)	100	98.0	0.209
	150	95.7	0.237

4.5 Compressive properties of RPUR foams

Compression stress-strain curves of RPUR foams catalyzed by metal-amine complexes in parallel and perpendicular to the foam rising direction are shown in Figures 4.34-4.35. From the compressive strength, it was found that the compressive strength in parallel to the foam rising direction (288.6 kPa) are higher than those in perpendicular to the foam rising direction (205.3 kPa). These data confirm that the cell structures of the foam sample are anisotropic structures [56-57]. This is due to perpendicular, the foam cells were elongated in the direction of the rise [58]. The compressive properties depend on direction of measurement. All foams were anisotropic foams. In general, a high compressive strength in one direction occurred at the expense of the compressive strength in the other directions which were could be explained by the foam cell model as illustrated in Figure 4.36.

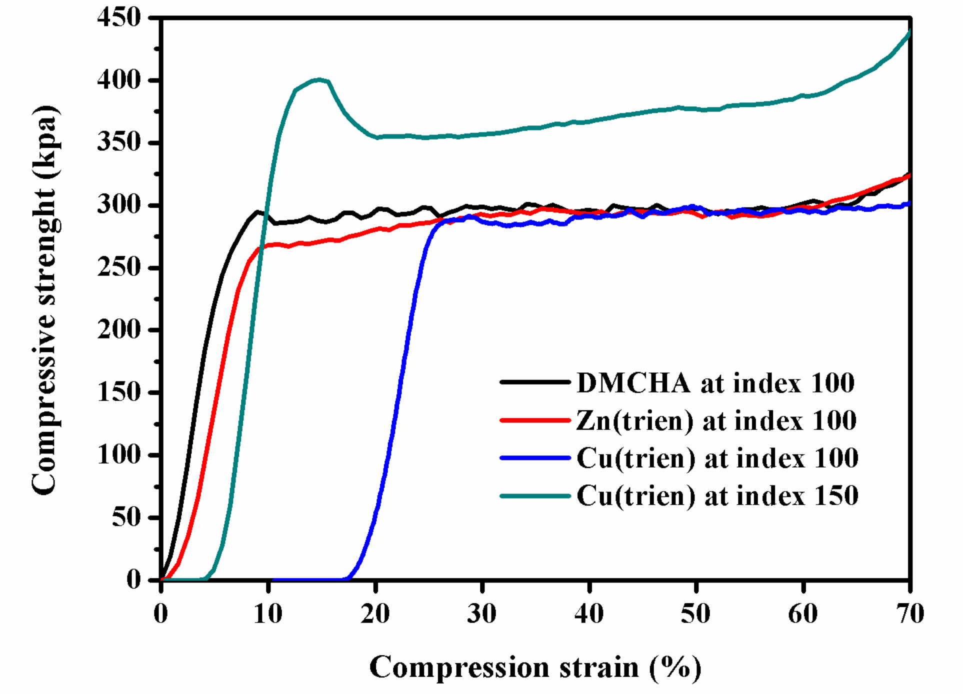


Figure 4.34 Compression stress-strain curve of RPUR foams in parallel to the foam rising direction.

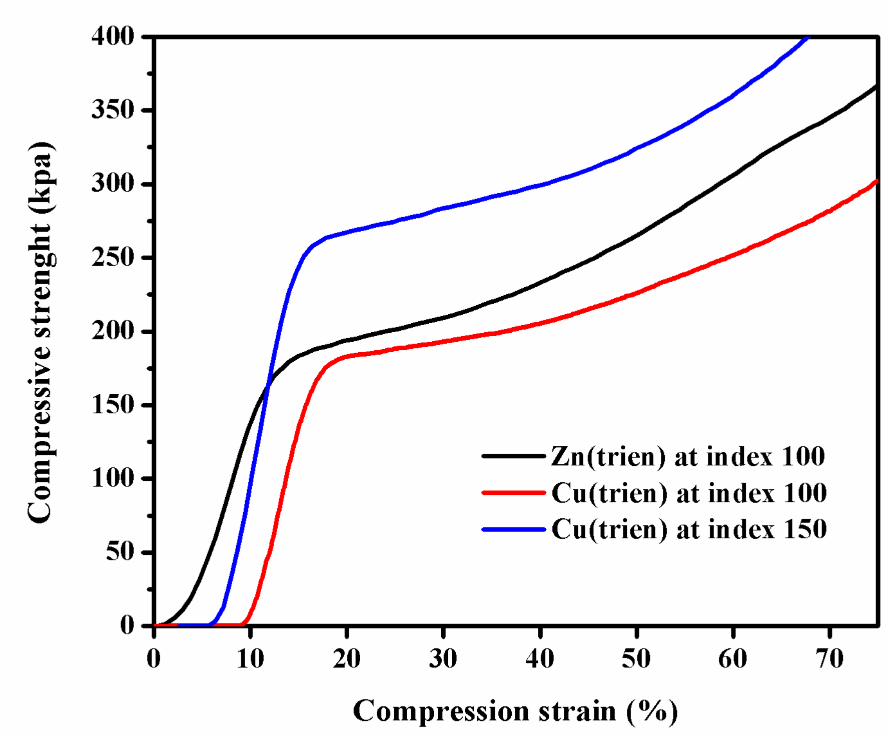


Figure 4.35 Compression stress-strain curve of RPUR foams in perpendicular to the foam rising direction.

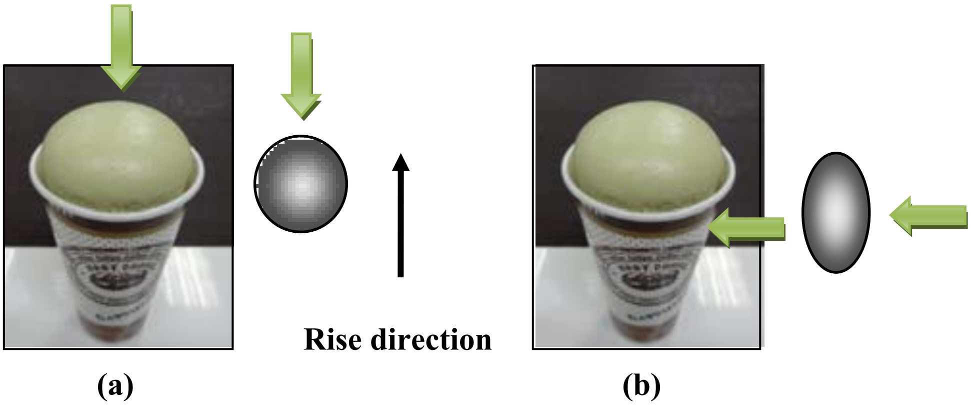
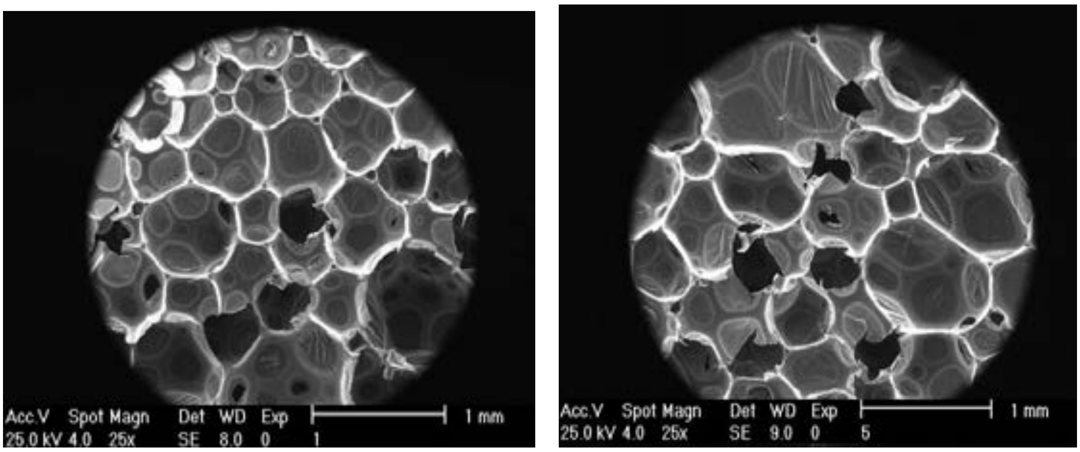


Figure 4.36 Isotropic foam (a): spherical cells, equal properties in all directions; anisotropic foam (b): ellipsoid cells, which properties depend on direction [1]

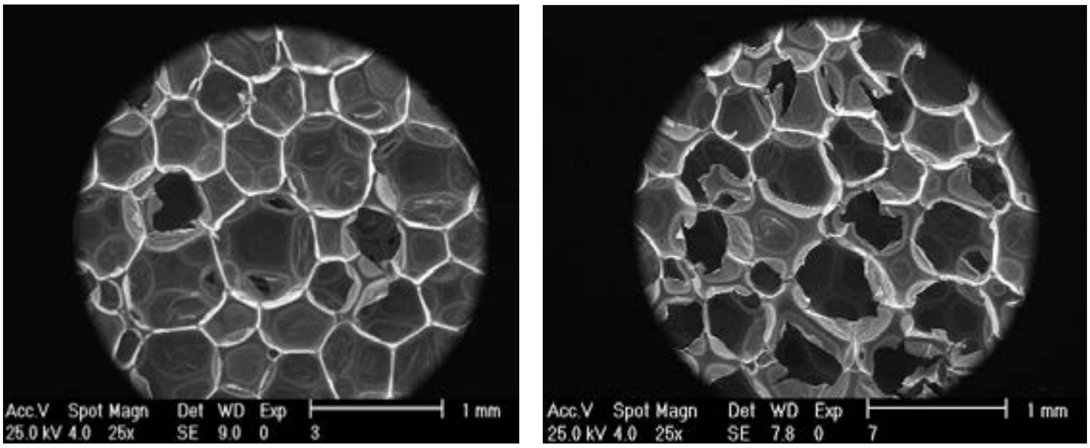
4.6 RPUR Foams Morphology

SEM micrographs of RPUR foams catalyzed by metal-amine complexes are shown in Figures 4.37-4.40. It was observed that cell morphology showed spherical cell and elongated cell in (a) perpendicular and (b) parallel direction, respectively. From the cell morphology results, all the cell structure are anisotropic structure, that is, the cell distance in parallel to the foam rising direction is significant larger than the one in perpendicular to foam rising direction [57].



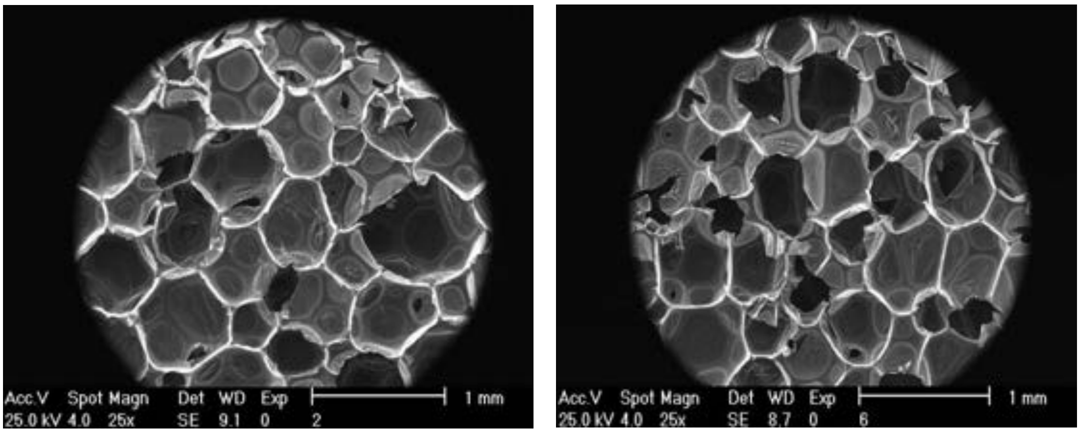
(a) **(b)**

Figure 4.37 SEM of RPUR foams catalyzed by $Cu(en)_2$; (a) top view; (b) side view (25x)



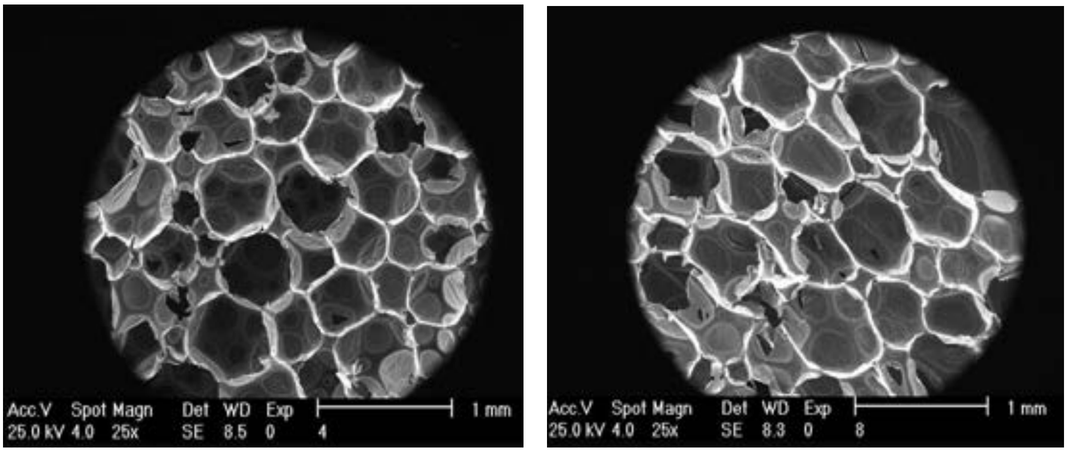
(a) **(b)**

Figure 4.38 SEM of RPUR foams catalyzed by Cu(trien); (a) top view; (b) side view (25x)



(a) **(b)**

Figure 4.39 SEM of RPUR foams catalyzed by $Zn(en)_2$; (a) top view; (b) side view (25x)



(a) **(b)**

Figure 4.40 SEM of RPUR foams catalyzed by Zn(trien); (a) top view; (b) side view (25x)

4.7 Thermal stability

The thermal stability was performed by thermogravimetric analysis (TGA). All samples were heated from 50^{o}C to 750^{o}C at heating rate of 10^{o}C/min under nitrogen atmosphere. An example of decompositon temperature (Td) analysis and it derivative thermogram and weight loss were shown in Figures 4.41 and 4.42, respectively.

The initial composition temperature (IDT), which is the temperature at 10% weight loss was found in the range of 282-296 ^{o}C. This step was attributed to decomposition of urethane [59]. The foams prepared from all metal-amine complexes catalysts showed similar thermal decomposition with that prepared from DMCHA catalyst. This indicated that the metal complexes showed similar catalytic reaction with that of DMCHA.

From the result showed in Figures 4.42, it was found the foams prepared from DMCHA (the reference commercial foam) and metal-amine complexes had the same weight loss pattern, which related to the loss of volatile component (moisture, solvents and or unreacted monomer), polymer decomposition and final residues. In addition, the decomposition temperature of all foams were also in the same range. Therefore, it may be concluded that the thermal stability the foams prepared from all metal-amine complexes catalysts is the same with the commercial one.

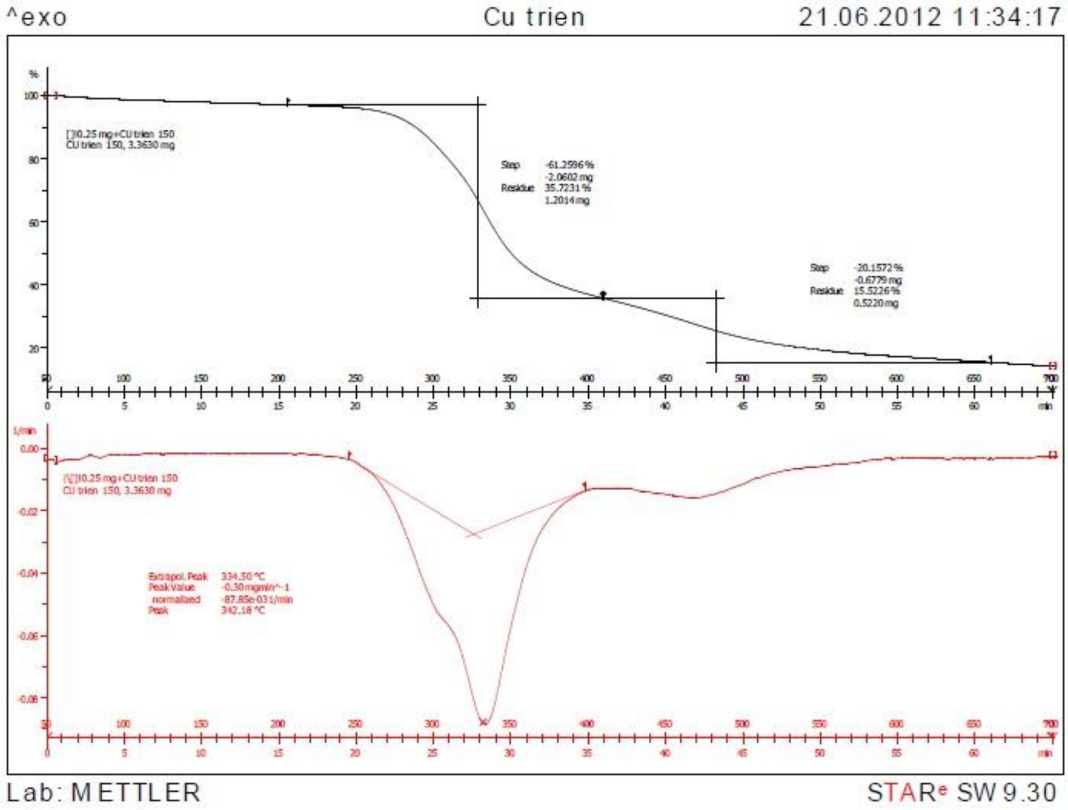


Figure 4.41 TGA and derivative TGA thermograms of RPUR foam catalyzed by Cu(trien).

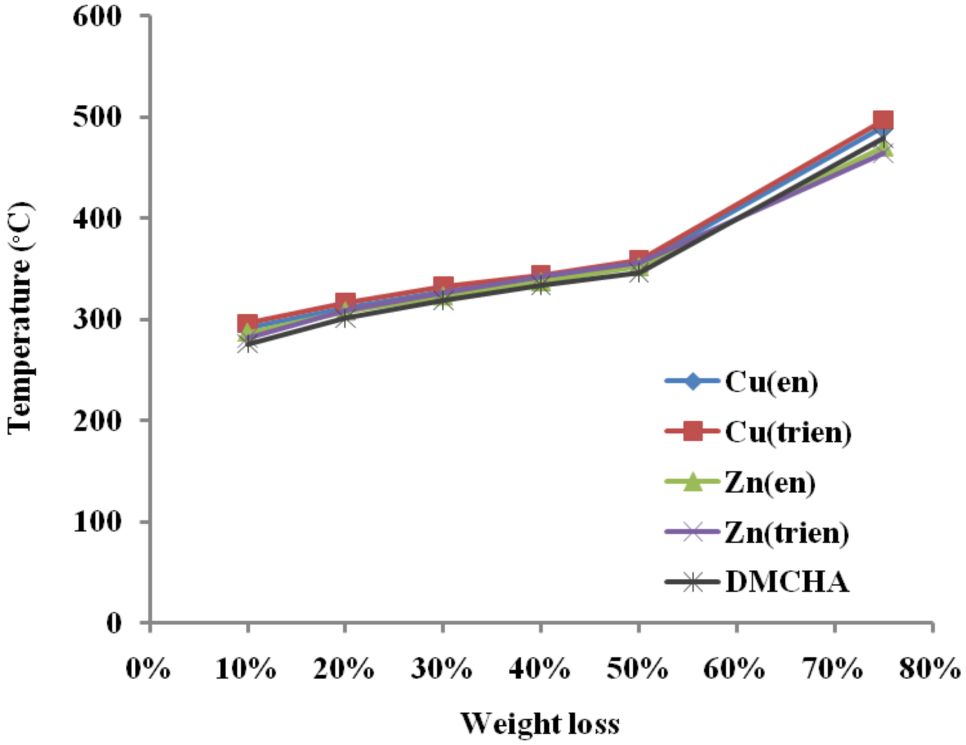


Figure 4.42 %Weight loss at different temperature of RPUR foams catalyzed by metal-amine complexes.

CHAPTER V

CONCLUSION

5.1 Conclusion

A novel series of metal-amine catalysts was synthesized with a simple procedure using metal acetylacetonate by changing the type of amine and utilized for the rigid polyurethane (RPUR) foam preparation. The metal-amine complexes were odorless and could be easily dissolved in the raw materials of RPUR foam formulation. The spectroscopic analyses, namely FTIR spectroscopy, UV-vis spectroscopy, flame atomic spectroscopy, mass spectrometry and elemental analysis of the metal-amine complexes show that the amine is coordinated to metal, which confirmed the complex formation.

The catalytic activity of the metal-amine complexes for RPUR foam preparation has been evaluated. From the reaction times, the metal-amine complexes showed comparable catalytic activity to commercial catalyst (DMCHA). Thus, these complexes are suitable to be used as the catalyst in preparing RPUR foams. Both complexes synthesized in methanol and water gave the similar reactivity results. Therefore, the preparation of metal complexes in water had advantage because foam formulation had water which was blowing agent. The preparation of metal-amine complexes in water without organic solvent is an environmentally friendly method.

By varying the catalyst content, it could be concluded that the catalyst amount of 1.0 pbw in the formulation should be chosen for foam preparation. RPUR foams prepared from metal-amine complexes had suitable density when prepared at the NCO index of 100-150. Free rise density of RPUR foams increased with increasing of the NCO index. The foams prepared at an NCO index of 150 had densities in the range around 40–50 kg/m^3, which was the desirable density for foam applications. When the amount of catalyst was increased, the free rise density decreased.

Investigation of free rise density of RPUR foams by varying the content of blowing agent showed that this was an important factor. It may be concluded that if the amount of blowing agent (water) was increased, free rise density of the foams would decrease. Analysis of foaming temperature showed that the polymerization reaction is exothermic reaction. The maximum core temperature of foams prepared from metal-amine complexes was in the range of 116-134 ^{o}C.

Increasing the content of NCO indexes leads to a decreased of NCO conversion, as confirmed by ATR-FTIR spectroscopy. It can be seen that all RPUR foams had the NCO conversion higher than 95%. They also had the polyurethane:polyisocyanurate (PIR:PUR) ratio less than 0.22. Therefore, the reaction between isocyanate and polyol to give urethane group was the major reaction and trimerization reaction of isocyanate to form isocyanurate group was a minor reaction. These data indicates that metal-amine complexes have good catalytic reactivity in the reaction between isocyanate and polyol to give urethane group.

On the basis of the compressive strength data, it was found that the compressive strength in parallel to the foam rising direction are higher than those in perpendicular to the foam rising direction. These data confirm that the cell structures of the foam sample are anisotropic structures.

From the cell morphology results, all the cell structure are anisotropic structure, that is, the cell distance in parallel to the foam rising direction is significant larger than the one in perpendicular to foam rising direction.

From the TGA results, it could be seen that the foams prepared from DMCHA and metal-amine complexes had the same weight loss pattern. It may be concluded that the thermal stability the foams prepared from all metal-amine complexes catalysts is the same with the commercial one.

5.2 Suggestion for future work

This research presents a beginning work for exploring the new metal-amine complexes with good catalytic activity. Further study in this direction that will provide useful data is the preparation of metal complexes in the solvent that is used in the commercial foam formulation, such as ethylene glycol.

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APPENDICES

Appendix A

NCO index and NCO conversion Calculations

NCO index calculation

#Example Calculate the parts by weight (pbw) of pure PMDI (Suprasec® 5005), molar mass = 366.99, functionality = 2.7 at an isocyanate indexes of 100 and 150 required to react with the following formulation:

Formulation (pbw)	**Part by weight (g)**
Polyol (Daltolac® R180), OHV = 440 mg KOH/ g, functionality = 4.3)	100.0
Catalysts (metal-amine complexes or DMCHA)	1.0
Surfactant (Tegostab® B8460)	2.5
Blowing agent (water, M_w = 18 g/mole, functionality = 2)	3.0
PMDI (Suprasec® 5005), NCO indexes of 100 and 150	?

$$\text{Equivalent weight of Daltolac R180} = \frac{56.1}{440} \times 1000 = 127.5$$

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

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

Equivalent in the above formulation:

$$\text{Polyol (Daltolac R180)} = \frac{100}{127.5} = 0.784$$

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

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

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

thus:

$$\text{PMDI (pbw)} = 1.117 \text{ x } \frac{\text{PMDI molar mass}}{\text{functionality}} = 1.117 \text{ x } \frac{366.99}{2.7} = 151.8$$

Note: 151.8 defines the isocyanate quantity at 100 index

where;

thus:

Isocyanate index = 100;

$$\text{Isocyanate actual} = \frac{151.8}{100} \text{ x } 100 = 151.8 \text{ pbw}$$

Isocyanate index = 150;

$$\text{Isocyanate actual} = \frac{151.8}{100} \text{ x } 150 = 227.7 \text{ pbw}$$

Table A1 Isocyanate quantity at different NCO indexes in the above formulations

Formulations (pbw)	**NCO index**	
	100	**150**
Polyol (Daltolac® R180)	100	100
Catalysts	1.0	1.0
Surfactant	2.5	2.5
Blowing agent	3.0	3.0
PMDI (Suprasec® 5005)	**151**	**227**

NCO conversion calculation

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

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

where;

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

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

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

Table A2 Free NCO absorbance peak area in PMDI (Suprasec® 5005) from ATR-IR

PMDI (Suprasec® 5005) spectra	NCO Absorbance peak area Normalized @ 1.0 Ar-H peak area
1	98.024
2	97.950
3	98.106
Average (NCO^i); ATR-IR	98.0

 # *Example* Calculate the conversion of isocyanate (α) and PIR:PUR of rigid polyurethane foams catalyzed by $Cu(en)_2$ catalyst at NCO index 100

Conversion of isocyanate (%)

Data at **Table A2**

Absorbance peak area of initial NCO = 98.0 = NCO^i

The data from **Table A4** at NCO index 100, absorbance peak area of free NCO was normalized by aromatic ring quantity:

Absorbance peak area of final NCO = 0.888 = NCO^f

thus,

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

$$= \left[1 - \frac{0.888}{98.0}\right] \times 100$$

% NCO conversion = 99.1

PIR:PUR

Absorbance peak area of PIR (polyisocyanurate) = 0.996

Absorbance peak area of PUR (polyurethane) = 5.011

$$\text{thus, PIR:PUR} = \frac{0.996}{5.011} = 0.199$$

Table A3 NCO conversion of RPUR foam catalyzed by DMCHA

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO $2277\ cm^{-1}$	Ar-H $1595\ cm^{-1}$	PIR $1415\ cm^{-1}$	PUR $1220\ cm^{-1}$	NCO^f (Ar-H=1.0)		
100	0.934	1.772	1.076	6.256	0.527	99.5	0.1720
150	2.791	2.944	0.996	5.028	0.948	99.0	0.1981

Table A4 NCO conversion of RPUR foam catalyzed by $Cu(en)_2$

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO $2277\ cm^{-1}$	Ar-H $1595\ cm^{-1}$	PIR $1415\ cm^{-1}$	PUR $1220\ cm^{-1}$	NCO^f (Ar-H=1.0)		
100	2.445	2.755	0.996	5.011	0.8875	99.1	0.1988
150	3.003	1.955	0.989	4.772	1.5361	98.4	0.2072

Table A5 NCO conversion of RPUR foam catalyzed by Cu(trien)

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	2.239	2.118	1.013	6.012	1.0571	98.9	0.1685
150	5.002	2.024	0.938	4.363	2.4713	97.5	0.2150

Table A6 NCO conversion of RPUR foam catalyzed by Cu(tetraen)

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	5.804	2.034	0.942	4.401	2.8535	97.1	0.2140
150	9.011	2.078	0.967	4.046	4.3364	95.6	0.2390

Table A7 NCO conversion of RPUR foam catalyzed by Cu(pentaen)

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595cm^{-1}	PIR 1415cm^{-1}	PUR 1220cm^{-1}	NCO^f (Ar-H=1.0)		
100	5.205	2.048	0.969	4.423	2.5415	97.4	0.2191
150	8.057	2.209	0.986	4.042	3.6474	96.3	0.2439

Table A8 NCO conversion of RPUR foam catalyzed by Zn(en)$_2$

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	2.058	2.202	0.993	5.662	0.9346	99.0	0.1754
150	8.757	2.784	1.202	5.026	3.1455	96.8	0.2392

Table A9 NCO conversion of RPUR foam catalyzed by Zn(trien)

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	1.679	2.158	1.168	6.242	0.7780	99.2	0.1871
150	3.086	2.182	1.039	4.653	1.4143	98.6	0.2233

Table A10 NCO conversion of RPUR foam catalyzed by Zn(tetraen)

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	4.778	2.116	0.985	4.963	2.2580	97.7	0.1985
150	7.274	1.966	0.932	4.379	3.6999	96.2	0.2128

Table A11 NCO conversion of RPUR foam catalyzed by Zn(pentaen)

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	4.021	2.088	0.996	4.758	1.9258	98.0	0.2093
150	8.544	2.034	1.095	4.629	4.2006	95.7	0.2366

Appendix B

Compressive strength property and Data

Table B1 Full result of compressive strength analysis of RPUR foams

Catalyst	**Index**	**Sample**	**Stiffness (N/m)**	**Young's Modulus (kPa)**	**Stress at Yield (kPa)**	**Percentage Strain at Yield**	**Work to Yield (J)**	**Stress at Offset Yield (kPa)**
Zn(trien)	100	Parallel	150233.18	5007.77	269.16	10.88	0.43	268.64
		Perpendicular	69619.04	2320.63	-	-	-	188.53
Cu(trien)	100	Parallel	166865.42	5382.76	288.57	27.32	0.46	287.88
		Perpendicular	94236.08	3039.87	205.29	39.79	1.49	184.44
Cu(trien)	150	Parallel	231730.68	7724.36	400.87	15.12	0.71	393.78
		Perpendicular	110472.69	3682.42	307.76	43.98	2.49	266.61

Table B2 Formulations, reaction times and physical properties of RPUR foams catalyzed by different copper-amine complexes

Formulations (pbw)	**Catalysts at different NCO indexes**											
	DMCHA (Ref.)				**Cu(en)$_2$**				**Cu(trien)**			
	100		**150**		**100**		**150**		**100**		**150**	
Daltolac® R180	100		100		100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0		1.0		1.0	
B8460	2.5		2.5		2.5		2.5		2.5		2.5	
H_2O	3.0		3.0		3.0		3.0		3.0		3.0	
Suprasec® 5005	151		227		151		227		151		227	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times												
Cream time (min.)	0:22	0.03	0:23	0.04	0:24	0.05	0:28	0.05	0:26	0.03	0:28	0.02
Gel time (min.)	0.32	0.01	0:37	0.02	0:46	0.03	0:50	0.04	1:06	0.01	1:29	0.04
Tack free time (min.)	3:07	0.05	3:19	0.05	1:40	0.06	1:39	0.05	2:25	0.06	3:03	0.07
Rise time (min.)	2:21	0.04	2:37	0.06	1:54	0.11	1:59	0.06	2:38	0.05	3:24	0.08
Density												
Density (kg/m^3)	39.7	0.6	45.3	0.5	35.5	0.7	42.0	0.6	38.0	0.5	43.0	0.4

Table B3 Formulations, reaction times and physical properties of RPUR foams catalyzed by different copper-amine complexes

Formulations (pbw)	**Catalysts at different NCO indexes**							
	Cu(tetraen)				**Cu(pentaen)**			
	100		**150**		**100**		**150**	
Daltolac® R180	100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0	
B8460	2.5		2.5		2.5		2.5	
H_2O	3.0		3.0		3.0		3.0	
Suprasec® 5005	151		227		151		227	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times								
Cream time (min.)	0:26	0.03	0:28	0.02	0:24	0.03	0:27	0.04
Gel time (min.)	1:20	0.04	1:51	0.02	1:15	0.05	1:35	0.06
Tack free time (min.)	2:51	0.03	4:44	0.05	2:42	0.12	3:34	0.14
Rise time (min.)	3:14	0.06	4:52	0.04	3:03	0.05	4:04	0.08
Density								
Density (kg/m^3)	38.2	0.4	44.8	0.9	38.8	0.5	45.0	0.8

Table B4 Formulations, reaction times and physical properties of RPUR foams catalyzed by different zinc-amine complexes

Formulations (pbw)	**Catalysts at different NCO indexes**							
	Zn(en)				**Zn(trien)**			
	100		**150**		**100**		**150**	
Daltolac® R180	100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0	
B8460	2.5		2.5		2.5		2.5	
H_2O	3.0		3.0		3.0		3.0	
Suprasec® 5005	151		227		151		227	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times								
Cream time (min.)	0:30	0.03	0:32	0.04	0:25	0.02	0:29	0.02
Gel time (min.)	1:33	0.02	1:52	0.02	1:02	0.01	1:14	0.02
Tack free time (min.)	6:06	0.03	7:02	0.05	3:49	0.04	4:29	0.04
Rise time (min.)	5:01	0.04	6:36	0.05	3:02	0.03	4:04	0.05
Density								
Density (kg/m^3)	39.0	0.7	40.9	1.1	35.5	0.5	41.0	0.8

Table B5 Formulations, reaction times and physical properties of RPUR foams catalyzed by different zinc-amine complexes

Formulations (pbw)	**Catalysts at different NCO indexes**							
	Zn(tetraen)				**Zn(pentaen)**			
	100		**150**		**100**		**150**	
Daltolac® R180	100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0	
B8460	2.5		2.5		2.5		2.5	
H_2O	3.0		3.0		3.0		3.0	
Suprasec® 5005	151		227		151		227	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times								
Cream time (min.)	0:29	0.03	0:31	0.02	0:28	0.03	0:32	0.04
Gel time (min.)	1:10	0.02	1:25	0.04	1:08	0.03	1:23	0.05
Tack free time (min.)	5:25	0.06	5:50	0.07	5:29	0.05	5:50	0.10
Rise time (min.)	4:49	0.12	5:17	0.03	4:34	0.11	5:10	0.07
Density								
Density (kg/m^3)	36.0	0.3	42.7	0.5	38.1	0.4	45.0	0.9

VITAE

Name : Miss Alisa Limsirinawa

Date of birth : November 27, 1987

Nationality : Thai

Address : 42/440 Kingkaew Road, Rachathewa,
Bangplee, Samutprakarn 10540

University Education : Bachelor's Degree from Department of Chemistry, Faculty of Science, Chulalongkorn University, 2007-2010

Master's Degree from Department of Chemistry, Faculty of Science, Chulalongkorn University, 2010-2012

Conference attendance: Poster presentation "Preparation of Rigid Polyurethane Foams using Catalysts prepared from Metal acetylacetonate and Tetraethylenepentamine" at Pure and Applied Chemistry International Conference 2012 (PACCON 2012) in Chiang Mai, Thailand, January 11-13, 2012