POLYISOCYANURATE FOAMS PREPARATION CATALYZED BY MIXTURES OF COPPER-AMINE COMPLEXES/POTASSIUM 2-ETHYLHEXANOATE

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จุฬาลงกรณ์มหาวิทยาลัย
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การเตรียมโฟมพอลิไอโซไซยานูเรตเร่งปฏิกิริยาด้วยสารผสมของสารประกอบเชิงซ้อนคอปเปอร์-แอมีน/โพแทสเซียม 2-เอทิลเฮกซาโนเอต

น.ส.ธีรพร สุวรรณเวช

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ธีรพร สุวรรณเวช : การเตรียมโฟมพอลิไอโซไซยานูเรตเร่งปฏิกิริยาด้วยสารผสมของสารประกอบเชิงซ้อนคอปเปอร์-แอมีน/โพแทสเซียม 2-เอทิลเฮกซาโนเอต. (POLYISOCYANURATE FOAMS PREPARATION CATALYZED BY MIXTURES OF COPPER-AMINE COMPLEXES/POTASSIUM 2-ETHYLHEXANOATE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร.นวลพรรณ จันทรศิริ

งานวิจัยนี้มีแนวคิดที่จะพัฒนาตัวเร่งปฏิกิริยาชนิดใหม่สำหรับเตรียมโฟมพอลิไอโซไซยานูเรต ตัวเร่งปฏิกิริยาที่พัฒนาเป็นสารผสมของประกอบเชิงซ้อนคอปเปอร์-แอมีน:โพแทสเซียม 2-เอทิลเฮกซาโนเอต (K-15) และสารประกอบเชิงซ้อนโลหะ-เอทานอลามีน:K-15 โดยสารประกอบเชิงซ้อนคอปเปอร์-แอมีน 2 ชนิด และ สารประกอบเชิงซ้อนโลหะ-เอทานอลามีน 2 ชนิด คือ $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$ (trien), $Cu(OAc)_2(EA)_2$ และ $Zn(OAc)_2(EA)_2$ เมื่อ en คือ เอทิลีนไดแอมีน trien คือ ไตรเอทิลีนเตตรามีน EA คือ เอทานอลามีน ถูกนำมาใช้เป็นเป็นตัวเร่งปฏิกิริยาเร่งปฏิกิริยาการเกิดเจลและปฏิกิริยาการฟู K-15 เป็นตัวเร่งปฏิกิริยาไตรเมอไรเซชันที่นิยมใช้ในอุตสาหกรรม โดยตัวเร่งปฏิกิริยาสามารถนำไปใช้ในการเตรียมโฟมพอลิไอโซไซยานูเรตโดยไม่ต้องทำให้บริสุทธิ์ พิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาด้วยยูวี-วิซิเบิลสเปกโทรสโกปี ศึกษาสมบัติของโฟมพอลิไอโซไซยานูเรตจากเวลาที่ใช้ในการทำปฏิกิริยาพอลิเมอไรเซชัน ความหนาแน่นของโฟม การเปลี่ยนแปลงไอไซไซยาเนต ความเร็วในการฟู อุณหภูมิในการเกิดปฏิกิริยาพอลิเมอไรเซชัน สมบัติการต้านทานแรงกดอัดของโฟมและศึกษาสัณฐานวิทยาของโฟม เทียบกับโฟมพอลิไอโซไซยานูเรตที่เร่งปฏิกิริยาด้วยสารผสมของไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA):K-15 ซึ่งเป็นตัวเร่งปฏิกิริยาทางการค้า จากการทดลองพบว่า $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 และ $Zn(OAc)_2(EA)_2$:K-15 มีความว่องไวในการเร่งปฏิกิริยาการเกิดเจลดีกว่า DMCHA:K-15 โดยอัตราส่วนของตัวเร่งปฏิกิริยา:K-15ที่เหมาะสมสำหรับโฟมพอลิไอโซไซยานูเรตคือ 0.5:3.0 และปริมาณน้ำที่ 5 pbw

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POLYISOCYANURATE FOAMS PREPARATION CATALYZED BY MIXTURES OF COPPER-AMINE COMPLEXES/POTASSIUM 2-ETHYLHEXANOATE. ADVISOR: Assoc. Prof. Nuanphun Chantarasiri, Ph.D.

In this research, a new catalyst system for the preparation of polyisocyanurate (PIR) foam was developed. The mixture of copper-amine complex:potassium 2-ethylhexanoate (K-15) and metal-ethanolamine complex:K-15 were used as catalysts. Two copper-amine complexes and two metal-ethanolamine complexes, namely $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$, respectively; where en = ethylene diamine, trien = triethylenetetramine and EA = ethanolamine, were used as catalyst for blowing and gelling reactions. K-15 was used as a catalyst for trimerization reaction. These catalysts could be further used in the preparation of PIR forms without purification. Characterization of catalysts were done by using UV-visible spectroscopy. The factors investigated in the preparation of PIR foams were reaction times, foam density, NCO conversion, rise profile, temperature profile, compressive strength and morphology. PIR foams catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15 were compared with those prepared from a commercial catalyst system, *N,N´*-dimethylcyclohexylamine (DMCHA):K-15. The experimental results showed that $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 had better gelling catalytic activity than DMCHA:K-15. The ratio of catalyst:K-15 = 0.5:3 and the amount of water = 5 pbw are suitable for preparation of PIR foam.

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LIST OF ABBREVIATIONS

%	percentage
ε	molar absorptivity
°C	degree Celsius
μm	micrometre
ASTM	American Society for Testing and Material
cm	centimeter
cm^{-1}	unit of wavenumber
CO_2	carbondioxide
DBTDL	dibutyltin dilaurate
DEG	diethylene glycol
DMCHA	*N, N´*-dimethyl cyclohexylamine
EA	ethanolamine
EG	Ethylene glycol
en	ethylenediamine
EO	ethyleneoxide
e.g.	example
FTIR	Fourier transform infrared spectrophotometer
g	gram
GWP	ozone-depleting potential
h	hour
HCFC-141b	1,1-dichloro-1-fluoroethane
K-15	potassium 2-ethylhexanoate
KOAc	potassium acetate
kg	kilogram
KOH	potassium hydroxide
kPa	kilopascal

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kV	kilovolt
m^3	cubic meter
MDI	methylene diphenyl diisocyanate
mg	milligram
mL	milliliter
mm	millimeter
NCO	isocyanate group
nm	nanometer
OAc	acetate
ODP	ozone-depleting potential
OH	hydroxyl group
OHV	hydroxyl value
pbw	parts by weight
PDMS	polydimethyl-siloxane
PMDETA	pentamethyldiethylenetriamine
PMDI	polymeric diphenyl methane diisocyanate
PIR	polyisocyanurate
PUR	polyurethane
Ref	reference
rpm	round per minute
RT	room temperature
sec	second
SEM	scanning electron microscopy
Si	silicon
T_{max}	maximum core temperature
TDI	toluene diisocyanate
TEDA	triethylenediamine
Temp	Temperature

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TMP	trimetylol propane
TMR	1-propanaminium 2-hydroxy-N,N,N-trimertyl 2-ethylhexanoate
TMR-2	1-propanaminium 2-hydroxy-N,N,N-trimertyl formate
trien	triethylenetetramine
UV-vis	ultraviolet visible
Vol.	volume
Wt.	weight
λ_{max}	maximum absorption peak
$Zn(OAc)_2$	zinc acetate

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CHAPTER I

INTRODUCTION

Polyisocyanurate (PIR) foam is a thermosetting polymer used in heat insulating materials and building panels. An important property of PIR foam is the better thermal stability than polyurethane foam due to isocyanurate group. PIR foam provides good heat insulating properties, flame retardancy, highly effective, low thermal conductivity, lightweight, low density and good mechanical properties[1, 2].

PIR foam is produced by the one-shot technique, which is produced from excessive isocyanate and polyol. PIR foam preparation is described in three reactions, namely blowing reaction, gelling reactions and trimerization reaction. Blowing reaction is the reaction between isocyanate and water to produce unstable carbamic acid, which immediately decomposes into amine and carbon dioxide. Gelling reaction is reaction between isocyanate and polyol to generate polyurethane. Trimerization reaction produced the key structure of PIR foam which is isocyanurate rings from the excessive isocyanate. However, the rate three reactions are slow. Therefore, the catalysts are required for preparation of PIR foam[3].

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Two types of catalysts are needed in the preparation of PIR foam, namely blowing/gelling catalyst and trimerization catalyst. Tertiary amines, such as *N,N´*-dimethylcyclohexylamine (DMCHA) and organometallic compounds, such as dibutyltin dilaurate (DBTDL)[4] are widely used as a commercial catalyst in gelling and blowing reactions. For trimerization reaction, potassium salts of carboxylic acids are used as commercial catalysts, such as potassium 2-ethylhexanoate (K-15) and potassium acetate[5]. However, the tertiary amine catalysts have strong odor and organometallic catalyst which are toxic. These cause important problem in the preparation PIR foam in large scale.

In PIR foam preparation, blowing agent is used to react with isocyanate group which are physical and chemical blowing agent. 1,1-dichloro-1-fluoroethane (HCFC-141b)[5] and pentane are the physical blowing agent, whereas, the chemical blowing agent is water which is commonly used for PIR foam preparation. Although the physical blowing agents have better mechanical properties than the chemical blowing agent, HCFC-141b and pentane are ozone layer destroyer and highly flammable liquid, respectively. In addition, water is environmentally-friendly blowing agent.

In our previous researches, copper-amine complexes were used as gelling and blowing catalysts for preparation of rigid polyurethane (RPUR) foams. These catalysts were copper-ethylenediamine [$Cu(OAc)_2(en)_2$], copper-triethylenetetramine [$Cu(OAc)_2$ (trien)], copper-ethanolamine [$Cu(OAc)_2(EA)_2$] and zinc-ethanolamine [$Zn(OAc)_2(EA)_2$] complexes which are odorless. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) complexes were prepared in the form of solution in water (aqueous solution)[6]. $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ complexes were prepared in the reaction between copper acetate [$Cu(OAc)_2$] or zinc acetate[$Zn(OAc)_2$] and ethanolamine by using ethylene glycol as the solvent[7]. These catalysts can be used in the preparation of rigid polyurethane foams without purification which has very weak odor as compared to DMCHA which is a reference commercial catalyst.

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Objective

In this work, PIR foam will be prepared by using $Cu(OAc)_2(en)_2$:K-15 , $Cu(OAc)_2$ (trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 (where OAc = acetate, en = ethylenediamine, trien = triethylenetetramine and EA = ethanolamine) as the catalysts which compared with PIR foam prepared from the commercial catalysts, DMCHA:K-15. The objectives are described as follows:

1.To synthesize $Cu(OAc)_2(en)_2$:K-15 , $Cu(OAc)_2$ (trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 following the methods reported in the literature [6, 7]

2. To optimize the PIR foam formulation

3. To investigate reaction time, physical and mechanical properties of PIR foam

Scope of the research

For the scopes of this work, PIR foams were prepared by using the mixture of copper-amine complex:K-15 and metal-ethanolamine complex:K-15 as catalysts. The experiment consists of two parts. In the first part, blowing and gelling catalyst were prepared as previous research works [6, 7]. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) were prepared in the form of aqueous solution, $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ complexes were prepared by the reaction between $Cu(OAc)_2$ or $Zn(OAc)_2$ and ethanolamine using ethylene glycol as the solvent. These catalysts were characterized by UV-visible spectroscopy.

In the second part, PIR foams were prepared by using mixture of copper-amine complex:K-15 and metal-ethanolamine complex:K-15 as catalysts. The variation in mole ratios of complex to K-15 (at 0.5:2.0, 0.5:2.5 and 0.5:3.0), blowing agent contents (water in 3, 4 and 5 parts by weight) and NCO indexes (at 160, 200 and 250) were employed. The reaction times, free rise density, rise profile, temperature profile, foam morphology and compressive strength were investigated. The reaction time, free rise density and compressive strength of PIR foam prepared by mixture of copper-amine complex:K-15 and metal-ethanolamine complex:K-15 were measured according to ASTM D7487-13, ASTM D1622-10 and ASTM D695, respectively. All properties of the results will be compared with PIR foam prepared from the commercial catalysts, DMCHA:K-15.

CHAPTER II

THEORY AND LITERATURE REVIEW

PIR foam is prepared with the one-shot technique by exothermic reaction which has been widely employed in heat insulating materials and building panels. Isocyanate and polyol are main component. Surfactant, blowing agent and catalyst are other components which employed to regulate the properties of foams because pure PIR foam are very friable. PIR foam has good heat insulating properties, flame retardancy, highly effective, low thermal conductivity, lightweight, low density and good mechanical properties.

2.1 Raw materials

PIR foam is prepared from the reaction between polyol and isocyanate to form urethane linkages and the reaction between excessive isocyanate that produces isocyanurate group. Surfactant, blowing agent and catalyst are added to help processing the foams or to change the properties of foams.

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2.1.1 Isocyanate

The diisocyanate is generally used within the group of isocyanates in PIR foam preparation which are methylene diphenyl diisocyanate (MDI) and toluene diisocya nate (TDI)[1]. These have high reactivity in foaming reaction.

TDI is produced by phosgenation of diaminotoluene. Commercial TDI is mixtures of 2,4- and 2,6-isomers in the weight ratio of 80:20 or 65:35. TDI with 80:20 isomer ratio is mainly used for flexible foam preparation, but it is not suited for PIR foam and TDI-based foam does not show an increase of fire resistance with

increasing NCO/OH ratios. Moreover, TDI has relatively high vapor pressure and more toxic than MDI.

MDI is produced by the phosgenation of the condensation product of aniline with formaldehyde. Monomeric MDI (4,4′-diphenylmethane diisocyanate) is not suitable because it is a solid form at room temperature and more expensive than polymeric MDI which is a liquid form at room temperature. Polymeric MDI are mainly 4,4′-isomer based functionality is 2.3 to 3.0 range. Therefore, only polymeric MDI can be used for PIR foams. The examples of isocyanate are TDI isomer, monomeric MDI and polymeric MDI as shown in Figures 2.1-2.3, respectively.

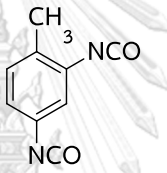

Figure 2.1 Structure of 2,4 TDI

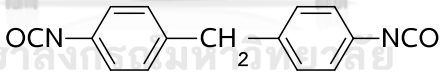

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Figure 2.2 Structure of 4,4′ MDI

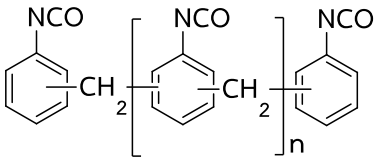

Figure 2.3 Structure of PMDI

2.1.2 Polyol

Polyol is an important factor in PIR foam preparation that are highly flame-resistant but still low friability. The general polyols used for the preparation of PIR foam can be classified into two types, polyether polyols and polyester polyols[8].

2.1.2.1 Polyester polyol

Polyester polyol is more reactive than polyether polyol and produces foams with better mechanical properties which is produced by condensation reactions between diols (and triols) and dicarboxylic acid. However, polyester polyols have high viscosity and low functionality than polyether. Examples of aliphatic and aromatic dicarboxylic are used in the production of polyester polyols shown in Figure 2.4

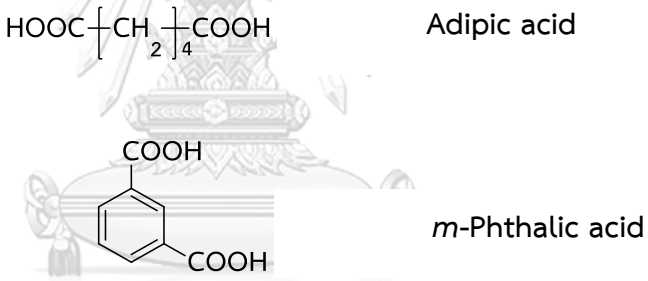

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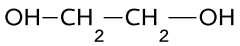
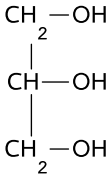
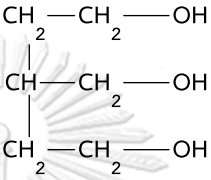
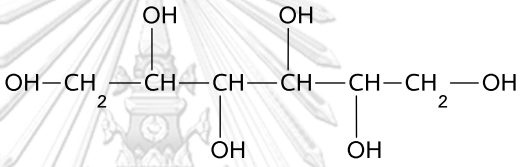
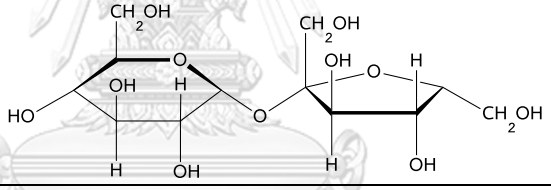
Figure 2.4 Examples of aliphatic and aromatic dicarboxylic used in the production of polyester polyols

2.1.2.2 Polyether polyol

Polyether polyol has low molecular weight, wide range of functionality, lower viscosity, equivalent weight which can be widely changed and lower costs than polyester polyol, however, the disadvantage is lower oxidation resistance than those of polyester foams. Polyether polyol for PIR foam has hydroxy number in the range of 350-600 and 40-75 is used for flexible foam. Example of polyether polyol is shown in Table 2.1.

Table 2.1 Example of polyether polyol[9]

Alcohol	Chemical structure	Functionality
Ethylene glycol (EG)		2
Glycerol		3
Trimetylol propane (TMP)		3
Sorbitol		6
Sucrose		8

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2.1.3 Surfactant

In the preparation of PIR foam, surfactant was added into this process which can improve foam processing and play a key role in optimizing PIR foam properties. Surfactant used in PIR foams has two type of silicone which are ionic and nonionic. Structural parameters of silicone surfactants such as the ratios of ethyleneoxide (EO)/(EO + PO), and (EO + PO)/Si are major factors of silicone surfactants. The chosen surfactant provides the optimum result with the different foam system. The mostly used surfactants are polydimethyl-siloxane (PDMS)[4] backbone and polyethylene oxide-co-propylene oxide (PEO-PPO). These are lower surface tension between two liquids or between a liquid and a solid so that is easy to be emulsified. Surfactants have the cell window stabilization steps in the foam process and significant effect on bubble generation. Surfactant is normally added in the amount of 0.4-2.0% w/w in the polyol formulation. An example of silicone surfactant is shown in Figure 2.5.

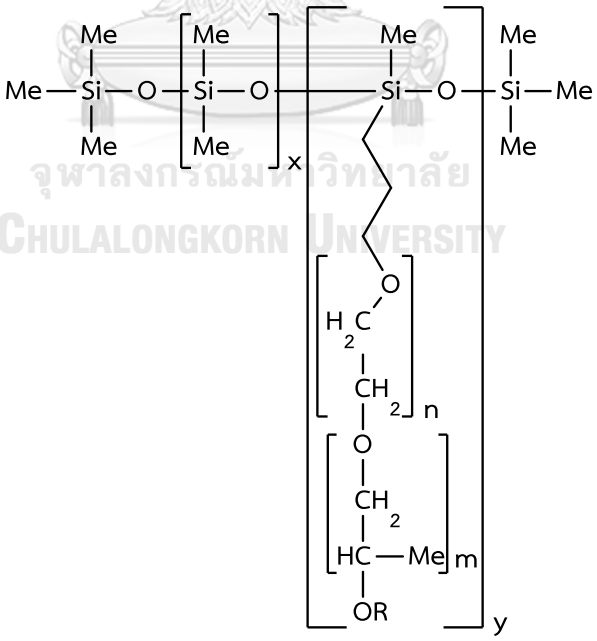

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Figure 2.5 Structure of silicone surfactant[4]

2.1.4 Blowing agent

Blowing agent is used to react with isocyanate groups for generation of air bubbles which is entrapped inside PIR foam mixture. The blowing agents are divided into two types as physical and chemical blowing agents.

Physical blowing agent is inert liquid or gas which have a lower boiling point around room temperature, low molecular weight compound and nonreactivity to isocyanate group which generate gas by vaporizing the exotherm of foaming reaction. In early history, a major blowing agent is CFC-11 and HCFC-141b[5], but they must be phased out because of its high ozone-depleting potential (ODP) and high global warming (GWP) which are serious problems. Nowadays, the most widely used physical blowing agent is C_5-hydrocarbon such as pentane, cyclopentane and isoprene because they provide lower foam density and have zero ODP, near zero ODP and inexpensive[1].

Chemical blowing agent is chemical compound which generate gas by the reaction with isocyanate groups. A typical chemical blowing agent is water which reacts with isocyanate groups to generate carbon dioxide (CO_2) gas. The use of water, as a single- or co- blowing agent for PIR foam decreases flame retardation and temperature resistance of obtained foam, because the urea linkage increases and isocyanurate linkage decreases. Other chemical blowing agents are nitroalkane, aldoxime, nitrourea, acid amide and active methylene[1].

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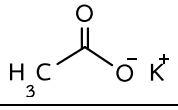
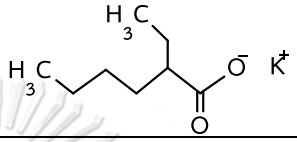
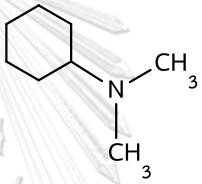
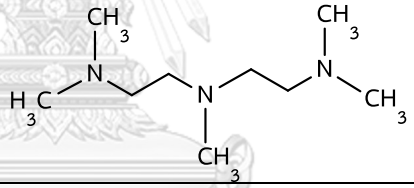
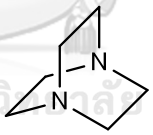
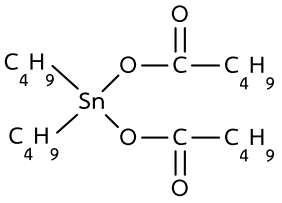
2.1.5 Catalyst

Catalyst is an important component for PIR foam preparation. Catalysts for PIR foam are trimerization catalyst, gelling catalyst and blowing catalyst. The important of catalyst affects not only the rate of reaction, but also influences the final properties of PIR foams. The common catalysts for prepared PIR foam are tertiary amine, organometallic compound and alkali metal carboxylate.

Table 2.2 Catalyst for prepared PIR foam[5]

Types of catalyst	Structures	Types of reaction
Alkali metal carboxylates		
Potassium acetate (KOAc)		Trimerization
Potassium 2-ethylhexanoate (KOct or K-15)		Trimerization
Tertiary amines		
N,N´-dimethylcyclohexylamine (DMCHA)		Gelling/blowing
Pentamethyldiethylenetriamine (PMDETA)		Blowing
Triethylenediamine (TEDA)		Gelling
Organotin compounds		
Dibutyltin dilaurate (DBTDL)		Gelling

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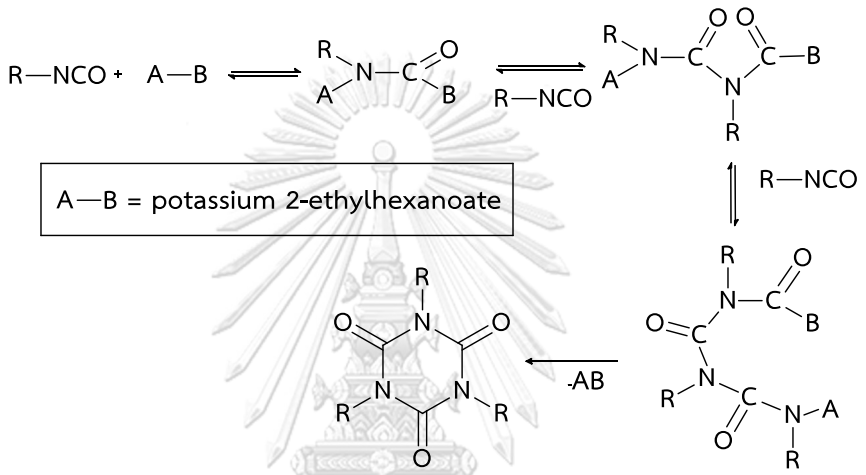
2.1.5.1 Alkali metal carboxylates catalysts

The catalyst for PIR foam preparation that shows in history is alkali metal carboxylate such as potassium acetate and potassium 2-ethylhexanoate. The proposed catalytic mechanism of potassium 2-ethylhexanoate is shown in Scheme 2.1. Potassium 2-ethylhexanoate react with the isocyanate to generate isocyanurate ring due to nucleophilic attraction.



Scheme 2.1 Catalytic mechanism of potassium 2-ethylhexanoate[10]

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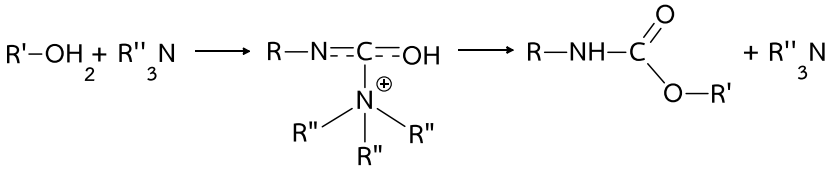
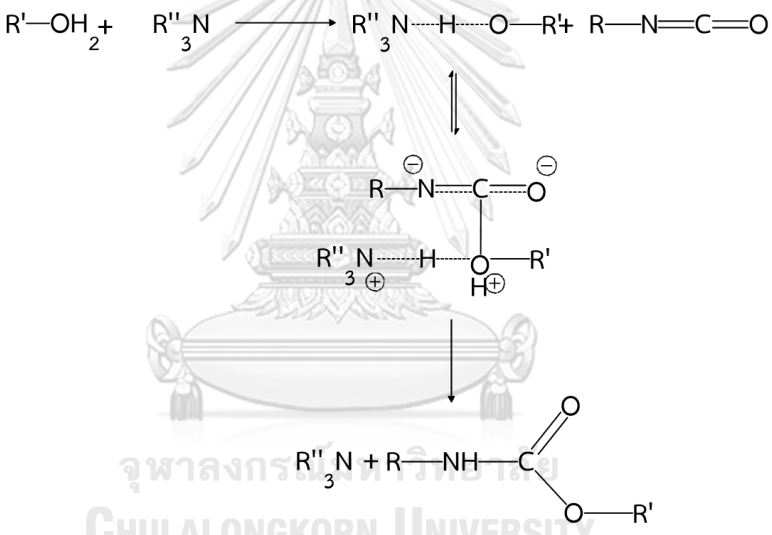
2.1.5.2 Tertiary amines catalysts

Tertiary amine is mainly catalyst for PIR foam preparation in gelling reaction which has two catalytic mechanisms for PIR foam preparation. The catalytic of amine is due to free electron pair present on the nitrogen atom and is dependent upon the availability of electron pair for complex. The first mechanism is Baker[11] mechanism which shown in Scheme 2.2. The reaction starts by nitrogen of amine using its lone pair of electrons to coordinate with carbonyl carbon of the isocyanate group, afterwards complex intermediate is formed. This intermediate then reacts with active hydrogen from alcohol of polyol to generate a urethane group. The second mechanism is Farka[12] mechanism as shown in Scheme 2.3 which start by nitrogen

of amine using its lone pair of electrons to coordinate with hydrogen atom of hydroxyl group. Afterwards, it forms a transition state with isocyanate to generate a urethane group. But, tertiary amine catalyst has strong odor which is an important problem in the preparation PIR foam in large scale.



Scheme 2.2 Baker mechanism[11]



Scheme 2.3 Farka mechanism[12]

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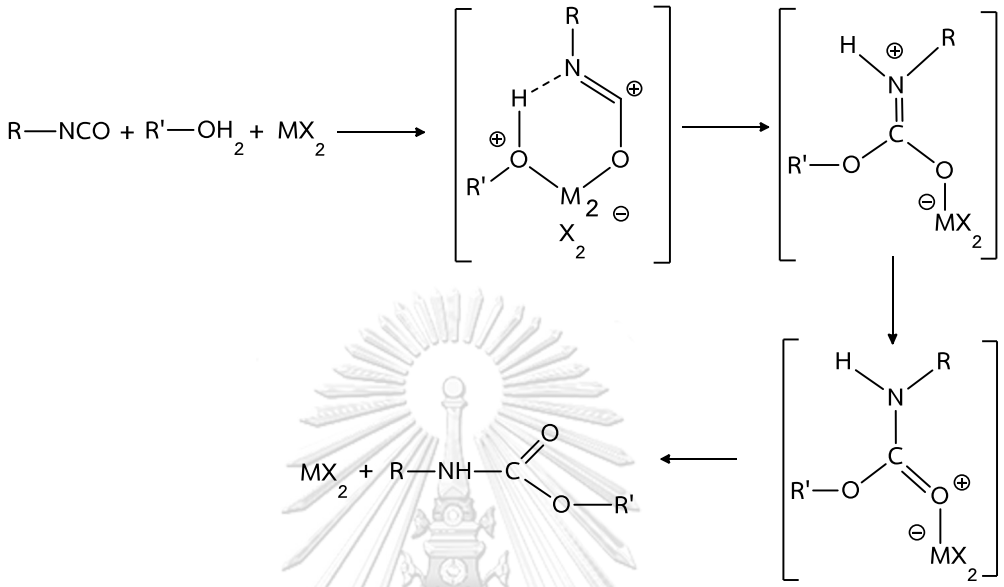
2.1.5.3 Organometallic catalysts

The mainly organometallic compound for PIR foam preparation is organotin such as dibutyltin dilaurate (DBTDL) which remains in PIR foam permanently. Tin catalysts improve reaction between isocyanate and hydroxyl which are gelling catalyst. The mechanism of tin (II) salt catalysts is shown in Scheme 2.4. The reaction starts by reaction between tin (II) and polyol to form tin alkoxide and react with isocyanate to form a complex. The OH group of the tin catalyst react with

isocyanate groups in order to, eliminate the odor problem. However, an important problem of organotin in the preparation PIR foam is its toxicity.



Scheme 2.4 Catalytic mechanism of tin (II) salt catalyst[11]

2.1.6 Additive

2.1.6.1 Chain Extender and Crosslinker

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Chain Extender and crosslinker are reactive cross-linking agents that can be used to modify the structure. Chain extender is low-molecular-weight diol such as ethylene glycol, diethylene glycol and 1,3-propylene glycol. Crosslinker is low-molecular weight triols and more functionalities such as glycerol, trimethylol propane, and aminoalcohol are called crosslinkers[1].

2.1.6.2 Flame Retardant

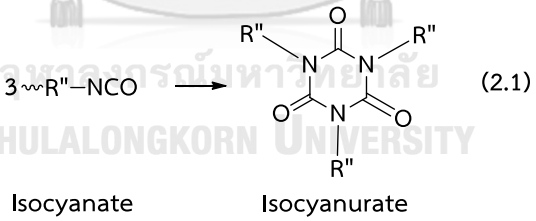
Flame retardant is chemical which is added to PIR foam for slowing down or prevent the start/growth of fire and consequently materials have high strength such as alumina trihydrate, ammonium sulfate and clay[1].

2.2 Basic chemistry

PIR foam is prepared by exothermic reaction between polyfunctional isocyanate and polyfunctional hydroxyl groups[9].

2.2.1 Reaction of excessive isocyanate

This reaction is known as trimerization which is very important for PIR foam preparation to form isocyanurate linkage (equation 2.1). This reaction could be formed by excessive polymerization of isocyanate oligomers with basic catalysts such as potassium acetate and potassium 2-ethylhexanoate. The isocyanurate linkage is thermally stable and contribute to fire resistance of PIR foams.



(2.1)

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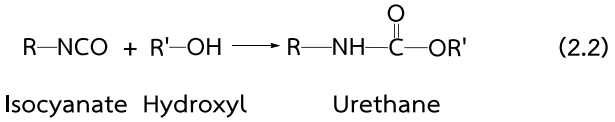
2.2.2 Reaction of isocyanate with polyol

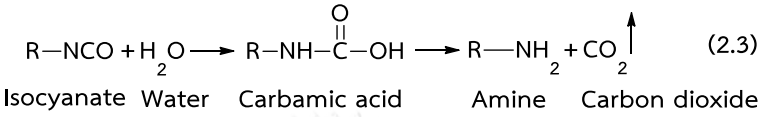
Reaction between isocyanate and polyol is called gelling reaction. The gelling reaction affects the rate of polymerization to form urethane linkage. Reaction rate is slow which can be accelerated by catalyst. The reaction is shown in equation 2.2.



(2.2)

2.2.3 Reaction of isocyanate with water

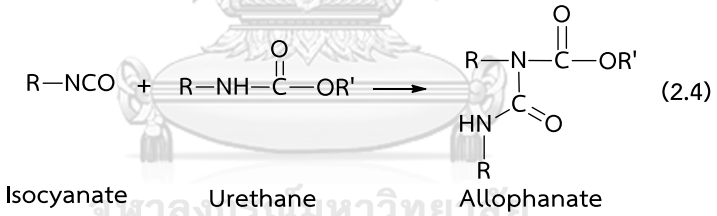
This reaction is known as blowing reaction (equation 2.3). Blowing reaction is reaction between isocyanate and water to form unstable carbamic acid which give amine and generates CO_2 gas. CO_2 gas from this reaction is used for blowing PIR foam and influencing density of foam.



(2.3)

2.2.4 Reaction of isocyanate with urethane

This reaction is reaction between isocyanate and hydrogen atom on nitrogen atom of the urethane linkages to form branched allophanates (equation 2.4) which is reversible reaction.



(2.4)

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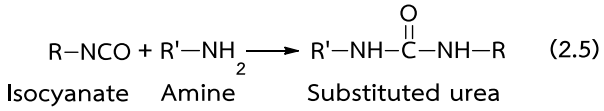
2.2.5 Reaction of isocyanate with amine

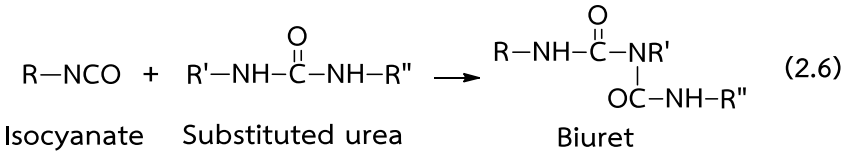
The reaction between isocyanate and amine to produce the urea linkage (equation 2.5). Commonly, the reactions of unhindered isocyanate with primary amines approximately 100-1000 times faster than primary alcohols with the result that amine which is used as chain extender and curing agent in polyurethane foams manufacture.



(2.5)

2.2.6 Reaction of isocyanate with urea

This reaction is reaction between isocyanate with the nitrogen atom of substituted urea to produce a biuret structure which is shown in equation 2.6.



(2.6)

2.3 Formulation[13]

The amount of isocyanate needed to react with polyol and other reactive hydroxyl components could be calculated to obtain chemically stoichiometric equivalents. This theoretical amount is called NCO index. The required NCO index depends on the RPUR system, properties required, conditions and scale of production.

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

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The calculation of the component ratio for PIR foam is to calculate number of part by weight of the isocyanate react with 100 parts by weight of polyol and hydroxyl additives. The analytical data needed for the calculation are isocyanate value, hydroxyl value and equivalent weight.

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

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

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

Hydroxyl value (hydroxyl number; OHV) is defined as milligram of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound. It is used as measurement of the isocyanate amount to reactive hydroxyl groups per unit weight of the polyols and is expressed in mg KOH/g of polyols.

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

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

*Functionality = number of hydroxy group in raw materials

Water content reacts with two isocyanate groups and the equivalent weight of water is:

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

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Isocyanate conversion (NCO conversion) can be calculated by FTIR method which is defined as the ratio between isocyanate peak area at final time and isocyanate peak area at initial time[14]:

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

Where;

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

NCO^i (Initial isocyanate) = the area of isocyanate absorbance peak area at time 0

2.4 Foam properties [1, 15]

In this section, surface flammability, flame resistance, smoke generation, HCN generation and compressive properties is discussed

Surface flammability of PIR foam is affected by the OH/NCO equivalent ratio. An increase of the OH/NCO ratio results in low friability because of the reduction of trimer content. PIR foam friability is also influenced to some extent by other factors, kind of catalyst, functionality and equivalent weight of polyol.

PIR foam is good flame resistance due to a high trimer content which can be investigated by flame penetration test. PIR foam at high trimer content or high NCO/OH equivalent ratio shows a flame penetration time around 30-60 minutes.

Smoke generation is another problem in PIR foam. The hazards of smoke generated from building materials have become one of the most serious problems. The smoke hazards include smoke hindering of occupants. Therefore, the smoke suppression problem of polyurethane and polyisocyanurate foam becomes one of the most important problems to be solved with two methods of smoke suppression. One method is the smoke scavenger method, and the other method is the specific silicone-modification method.

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HCN generation from PIR foam is a serious fire problem. Some of the literature discusses HCN generating from PIR foams in nitrogen or air atmosphere. The temperature of maximum HCN generating was found around 500-600 °C, while at high temperature the amount of HCN decrease because of oxidation. PIR foam was found to generate higher amount of HCN than TDI-based foam.

Compressive property is the most important mechanical property for PIR foam which are used to characterize both types of foam therefore differ, as do their

application areas. This property depends on density, type of foams and type of cell foams including opened cell and closed cell structure as shown in Figures 2.6-2.7.

From Figures 2.6-2.7, closed cell structure has thin cell wall on the cell surfaces, it important for PIR foams. Closed cell structure deformation is cell wall bending and bucking (reversible), gas compression and cell wall stretching/yielding (nonreversible). Severe compression causes cell rapture. Moreover, closed cell structure has a high strength and help the pressure durability increase. For open cell structure, the cell surface does not have thin cell wall. Therefore, it is flexible when compressed and relies on cell walls bucking and bending, which is an essentially reversible process.

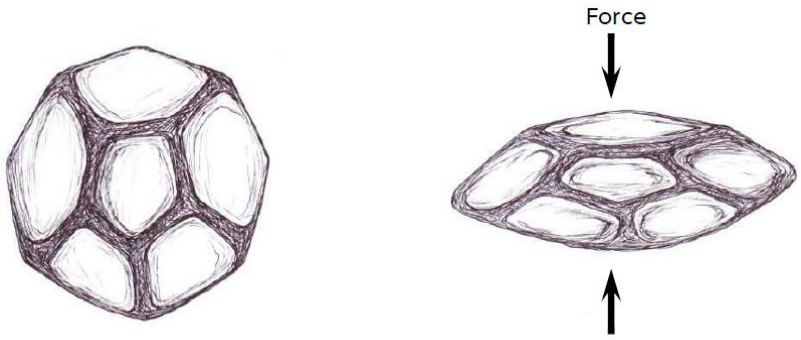

Figure 2.6 Schematic representation of closed cell deformation[15]

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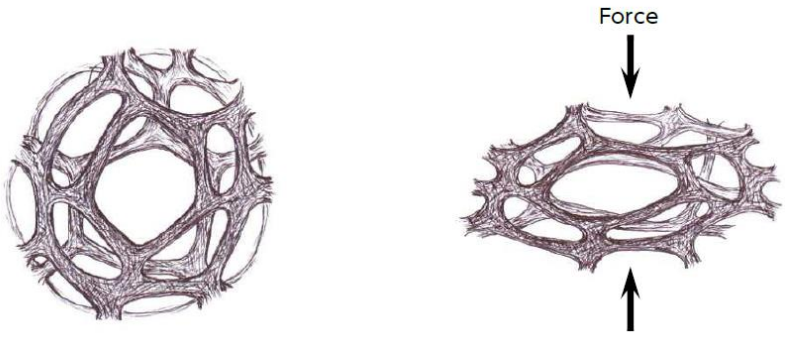

Figure 2.7 Schematic representation of open cell deformation[15]

2.5 Literature reviews

PIR foams are made from reaction between isocyanate and polyol, however, reaction is slow. Therefore, the catalysts are required for PIR foam preparation. Catalysts which are blowing, gelling and trimerization catalyst are important component in preparation of PIR foams to complete the reaction. There are several researches study about the catalysts used in PIR foam preparation.

In 1994, Clift and coworkers [5] studied the investigating reactivity of trimerization catalyst which used potassium salts and quaternary ammonium salts (TMR; 1-propanaminum 2-hydroxy-*N,N,N*-trimertyl 2-ethylhexanoate and TMR-2) as the catalysts. Blowing agent in this work are HCFC and water. The result showed that the decrease of polyol functionality has negative effects on foam dimensional stability and flame resistance. Moreover, water delays the reaction with significantly longer rise times at higher NCO index.

In 2000, Modesti and Lorenzetti [16] studied experimental method for evaluating conversion and trimerization in PIR-foam which used pentamethyl diethylenetriamine and potassium 2-ethylhexanoate as the catalysts. The results showed that NCO index increased with increasing trimer content resulting in improvement of mechanical properties. On the other hand, an increase of the NCO index leaded to decrease NCO conversion. Two years later, they[17, 18] studied halogen-free flame retardants for polymeric foams which was blown with n-pentane or water, pentamethyl diethylenetriamine and potassium 2-ethylhexanoate as catalyst. The thermal stability and mechanical properties result showed that blowing with pentane showed physical-mechanical properties were decreased with increased amount of expandable graphite. The result of physical-mechanical characterization showed that blowing with water shows the decrease of compressive strength and thermal conductivity with increasing amount of expandable graphite. In the same year, they[19] studied different charring agents of flame retardancy PIR foam which

used pentamethyl diethylenetriamine, potassium 2-ethylhexanoate as catalyst and n-pentane as blowing agent. The results showed that compressive strength decreased with increasing filler content.

In 2005, Romeo and coworkers [20] studied the reaction kinetic of PIR foam formulation using real-time FTIR. Potassium 2-ethylhexanoate and tertiary amine such as bis-(2-dimethylaminoethyl)ether, pentamethyldiethylenetriamine were used as catalyst and blown by water and cyclopentane which had been shown to produce the greatest amount of isocyanurate.

In 2006, Lovenich and Raffel [14] investigated the effect of recipe on trimer-yield in PIR foam which used water as a blowing agent, potassium acetate and potassium 2-ethylhexanoate as trimerization catalyst. The effect of index on PIR reaction could be studied quantitatively. Isocyanurate yield was decreased with the presence of water and potassium 2-ethylhexanoate had higher isocyanurate yield than potassium acetate.

In 2007, Eilbracht and coworkers[21] studied factor in PIR surfactant and used blowing agent are CFC/HCFC blends, HCFCs, cyclopentane, cyclo-/isopentane, iso-/n-pentane and n- pentane. Surfactant effects on flowability if liquid reaction mixture and volume flow of expending polymer. Moreover, surfactant can improve PIR foam processing and final PIR foam properties.

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In 2012, Park and coworkers [22] prepared PIR foams and investigated with respect to NCO index and blowing agent. In this work, potassium 2-ethylhexanoate was used as trimerization catalyst and they used cyclopentane, water and water/cyclopentane (50:50, wt%) as the blowing agent. The FTIR results showed that isocyanurate ring increased with increasing NCO index. When isocyanurate ring content in PIR foam increased, cell size slightly decreased. Form the result of TGA, thermal stability of PIR foam increased with increasing NCO index. Thermal stability of

PIR foam blown by water was higher than that PIR foam blown by pentane because water-blown give urea formation in PIR foam. But, compressive strength of PIR foam blown by cyclopentane was higher than PIR foam blown by water. However, maximum compressive strength of PIR foam was at NCO index 200.

In 2014, Gao and coworkers [23] studied halogen free-retarded rosin-based rigid PIR foam nanocomposites which prepared by in-situ polymerization. *N, N*-dimetylcyclo hexylamine (DMCHA), potassium 2-ethylhexanoate (K-15), cyclopentane and water were used as a gelling/blowing catalyst, trimerization catalyst and blowing agent, respectively. From the result, the flammability and compressive strength tests showed that PIR foam nanocomposites significantly improved flame retardancy and slightly enhanced mechanical property compared with PIR foam.

In 2017, Zhang and coworkers [24] studied an intermeshing corotating twin-screw extruder which used dibutyltin dilaurate (DBTDL) and potassium salts as catalyst. From the result, the analysis of reactively extruded foam processed at 75–150 ℃ and 90–165 ℃ has showed, the trimer content is slightly decreased with increasing temperature, while the urethane and allophanate/biuret increased in the structure.

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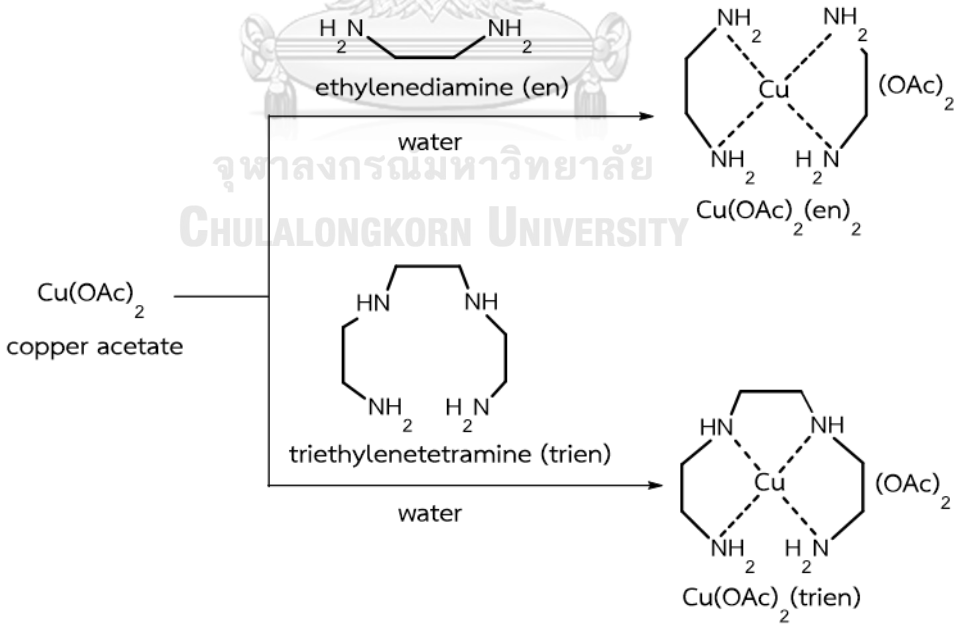
In 2018, Xu and coworkers [25] were used quaternary ammonium (TMR-2, 1-propanaminum, 2-hydroxy-*N,N,N*-trimertyl formate), potassium 2-ethylhexanoate (K-15) and potassium acetate (PU-1792) as the trimerization catalyst. Water and HCFC-141b were used as blowing agents. From FTIR result, K-15 had higher catalytic efficiency than TMR-2, however, PU-1792 was highest catalytic efficiency. Moreover, PIR foam illustrated more excellent fire resistant than polyurethane foam.

In 2018, Feng and coworkers[26] studied rigid polyisocyanurate-waterglass foam (PIWGRF) which was blown by water and used 2,4,6-tris(dimethylaminomethyl)phenol as catalyst and without polyol. PIWGRF was prepared by polyaryl poly(methyene

isocyanate) and waterglass (WG). WG is inorganic silicone material which was inexpensive, easily obtained, can be used in polyurethane adhesive and can be used alone in the reaction with polyaryl poly(methylene isocyanate). PIWGRF increased with increasing density but the thermal conductivity and closed-cell content slightly decreased.

In 2012, Pengjam and coworkers [27] synthesized new catalysts for polyurethane foam preparation which was copper-amine complexes, namely $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ [OAc = acetate; en = ethylenediamine; trien = triethylenetetramine]. The synthesis of copper-amine complexes used acetone as a solvent. In 2016, Noiasa [6] developed the method for synthesis of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ in the form of solution (Scheme 2.5). Polyurethane foams catalyzed by $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ showed similar catalytic activity as DMCHA and gave low density foams as compared with DMCHA.



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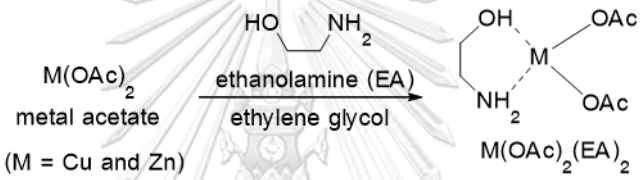
Scheme 2.5 Synthesis of copper-amine complexes using water as a solvent[6]

In 2016, Sridaeng [28] and coworkers synthesized new catalysts for polyurethane foam preparation which were metal-alkanolamine complexes, namely $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ [EA = ethanolamine], using acetone as the solvent. In 2017, Jongjitsatitmun [7] developed the method for synthesis of $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ by using ethylene glycol as the solvent (Scheme 2.6). Comparing with RPUR foam prepared by DMCHA catalyst, they found that RPUR foams prepared from $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ had longer gel time than the DMCHA. Thus, RPUR foams prepared by using metal-alkanolamine complexes as the catalyst had longer time availability in the foam molding process.



Scheme 2.6 Synthesis of metal-ethanolamine complex[7]

Therefore, the objective of this this research was development of new catalyst system for preparation of PIR foam. The mixture of copper-amine complex and potassium 2-ethylhexanoate will be used as catalysts in the preparation of PIR foams without purification. Various mole ratios of copper-amine complex to K-15 and NCO indexes will be employed. The reaction times, rise profile and amount of isocyanurate group in PIR foam will be investigated. The results will be compared with PIR foam prepared by the commercial catalysts, DMCHA:K-15.

CHAPTER III
EXPERIMENTAL

3.1 Chemicals

Copper (II) acetate monohydrate [$Cu(OAc)_2.H_2O$], zinc (II) acetate dihydrate [$Zn(OAc)_2{\cdot}2H_2O$], ethylenediamine (en), triethylenetetramine (trien), ethanolamine (EA) and ethylene glycol (EG) were obtained from Aldrich and used without further purification. Polyether polyol (Polimaxx® 4221; OH-number = 440 mgKOH/g; functiona-lity = 4.3, viscosity at 25 °C = 5500 cP), silicone surfactant (polysiloxane, Tegostab® B8460), polymeric diphenyl methane diisocyanate (PMDI, Raycore® B9001; % NCO = 31.0; functionality = 2.7), N,N-dimethyl cyclohexylamine (DMCHA, a commercial reference gelling and blowing catalyst) and potassium 2-ethylhexanoate (K-15, Dabco® K-15; K-15:DEG = 70:30, a commercial trimerization catalyst) were supplied by IRPC Public Company Limited. Distilled water was used as a chemical blowing agent.

3.2 Synthetic procedures

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3.2.1 Synthesis of copper-amine complexes in aqueous solutions

The synthesis of copper-amine complexes was performed according to the method reported in our previous work[6]. Copper-amine complexes were synthesized by using water as a solvent which are copper-ethylenediamine [$Cu(OAc)_2(en)_2$] and copper-triethylenetetramine [$Cu(OAc)_2(trien)$]. Composition of starting materials in the synthesis of copper-amine complexes in water solution as shown in Table 3.1.

Table 3.1 Composition of starting materials in the synthesis of copper-amine complexes in water solution

Copper-amine complexes	Mole ratios of $Cu(OAc)_2.H_2O$:amine	Wt. of $Cu(OAc)_2.H_2O$ (g)	Vol. of amine (ml)		Appearance
			en	trien	
$Cu(OAc)_2(en)_2$	1:2	0.661	0.44	-	dark purple solution
$Cu(OAc)_2(trien)$	1:1	0.609	-	0.45	dark blue solution

3.2.1.1 Synthesis of copper-ethylenediamine complex

The synthesis of $Cu(OAc)_2(en)_2$ had the mole ratio of $Cu(OAc)_2$ to ethylenediamine was 1:2 which was synthesized to the method as follows: a solution of ethylenediamine (0.44 ml, 6.63 mmol) in water (4 and 5 ml) was stirred at room temperature for 15 minutes. After that, $Cu(OAc)_2.H_2O$ (0.661 g, 3.31 mmol) was added into the solution. The solution mixture was stirred at room temperature for 24 hours (Scheme 3.1). The aqueous solution of $Cu(OAc)_2(en)_2$ was obtained as an odorless dark purple solution.

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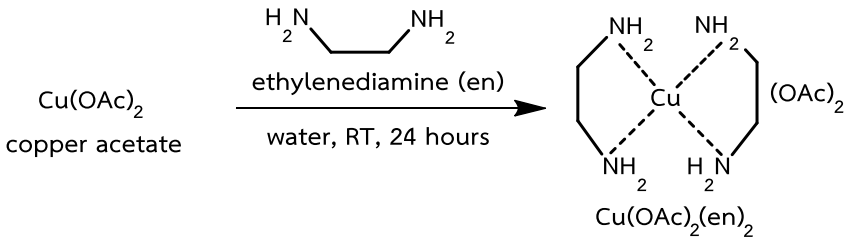
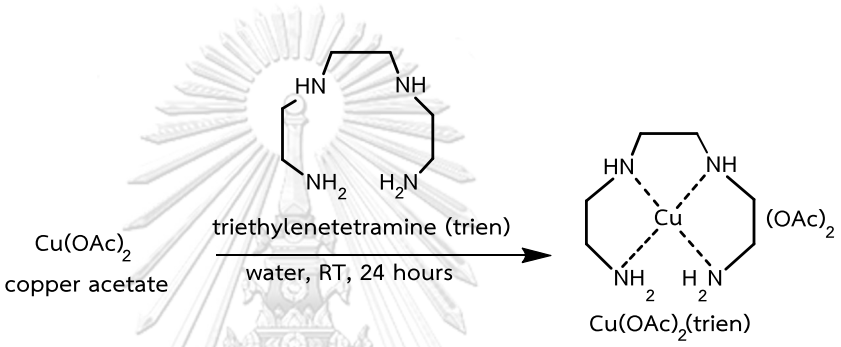


Scheme 3.1 Synthesis of copper-ethylenediamine complex [6]

3.2.1.2 Synthesis of copper-triethylenetetramine complex

The synthesis of $Cu(OAc)_2$(trien) had the mole ratio of $Cu(OAc)_2$ to triethylenetetramine was 1:1. The synthesis of $Cu(OAc)_2$(trien) aqueous solution was done by using the same procedure as $Cu(OAc)_2(en)_2$. Triethylenetetramine (0.45 ml, 3.05 mmol), $Cu(OAc)_2.H_2O$ (0.609 g, 3.05mmol) and water (4 and 5 ml) were used in the synthesis (Scheme 3.2). The aqueous solution of $Cu(OAc)_2$(trien) was obtained as an odorless dark blue solution.



Scheme 3.2 Synthesis of copper-triethylenetetramine complex [6]

3.2.2 Synthesis of metal-ethanolamine complexes in ethylene glycol

The synthesizes of metal-ethanolamine complexes in ethylene glycol are copper-ethanolamine complex $[Cu(OAc)_2(EA)_2]$ and zinc-ethanolamine complex $[Zn(OAc)_2\ (EA)_2]$ which are performed according to the method reported in our previous work and using ethylene glycol as a solvent[7]. Composition of starting materials in the synthesis of $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ complexes in ethylene glycol are shown in Table 3.2.

Table 3.2 The synthesis of copper-ethanolamine and zinc-ethanolamine complexes in ethylene glycol

Metal complexes	Mole ratios of $M(OAc)_2$:EA	Wt. of $Cu(OAc)_2.H_2O$ (g)	Vol. of Reactant (ml)		Appearance
			EA	EG	
$Cu(OAc)_2(EA)_2$	1:4	0.268	0.328	0.404	dark blue solution
$Zn(OAc)_2(EA)_2$	1:1	0.313	0.087	0.600	light yellow solution

3.2.2.1 Synthesis of copper-ethanolamine complex in ethylene glycol

The synthesis of $Cu(OAc)_2(EA)_2$ had the mole ratio of $Cu(OAc)_2$ to ethanolamine was 1:4 which was synthesized as follows: a solution of ethanolamine (0.328 ml) in ethylene glycol (EG; 0.404 ml) was stirred at room temperature for 20 minutes. After that, $Cu(OAc)_2.H_2O$ (0.268 g) was added into the solution. The solution mixture was stirred at room temperature for 2 hours (Scheme 3.3). The solution of $Cu(OAc)_2(EA)_2$ in ethylene glycol was obtained as an odorless viscous dark blue solution.

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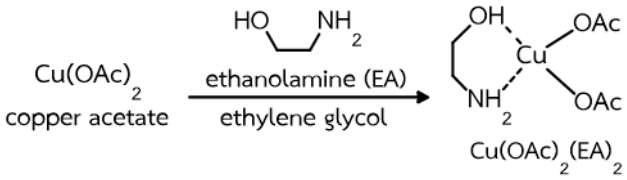
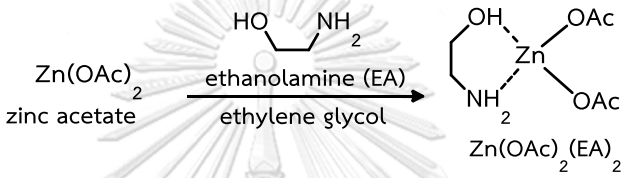


Scheme 3.3 Synthesis of copper-ethanolamine complex [7]

3.2.2.2 Synthesis of zinc-ethanolamine complex in ethylene glycol

The synthesis of $Zn(OAc)_2(EA)_2$ had the mole ratio of $Zn(OAc)_2$ to ethanolamine was 1:1. The synthesis of $Zn(OAc)_2(EA)_2$ aqueous solution was done by using the same procedure as $Zn(OAc)_2(EA)_2$. Ethanolamine (0.087 ml), ethylene glycol (EG; 0.600 ml) and $Cu(OAc)_2.H_2O$ (0.313 g) were used in the synthesis (Scheme 3.4). The solution of $Zn(OAc)_2(EA)_2$ in ethylene glycol was obtained as an odorless viscous light-yellow solution.



Scheme 3.4 Synthesis of zinc-ethanolamine complex [7]

3.3 Preparation of polyisocyanurate (PIR) foam

PIR foam is produced with the one-shot technique which was done both in cup-test and molded methods. In cup-test method, PIR foam was used for investigation of the reaction time, free rise density, rise profile, temperature profile, NCO conversion and morphology. In molded method, PIR foam was used for investigation of compression properties and thermal stability.

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The reaction time in the preparation of PIR foams were investigated, namely cream time (the time when polyol and isocyanate mixture begins to change from the liquid state to a creamy appearance and foam expansion subsequently starts), gel time (the time when polymerization occurs and the foam start to stiffen), rise time (the time when the foam reach its maximum height), tack free time (the time when the outer skin of the foam loses its stickiness or polymerization is completed).

3.3.1 Preparation of PIR foams by cup test method

The preparation of PIR foams using cup test method was done by following ASTM D7487-13 [29]. In the first step, polyol, surfactant, catalyst for gelling and blowing reaction (DMCHA or copper-amine complexes or copper-ethanolamine or zinc-ethanolamine), catalyst for trimerization reaction (K-15) and blowing agent (water) were mixed in a paper cup (700 ml) by hand mixing for 20 seconds to obtain homogeneous mixture and were stirred by mechanical stirrer at 2000 rpm for 20 seconds. In the second step, PMDI was added into the mixture and mixed by mechanical stirrer at 2,000 rpm for 20 seconds. PIR foam was allowed to rise freely at room temperature. Reaction times for polymerization of PIR foam were studied, namely cream time, gel time, rise time and tack free time. After that, PIR foam was kept for 48 hours at room temperature to complete the polymerization reactions and then carrying out physical and mechanical characterization.

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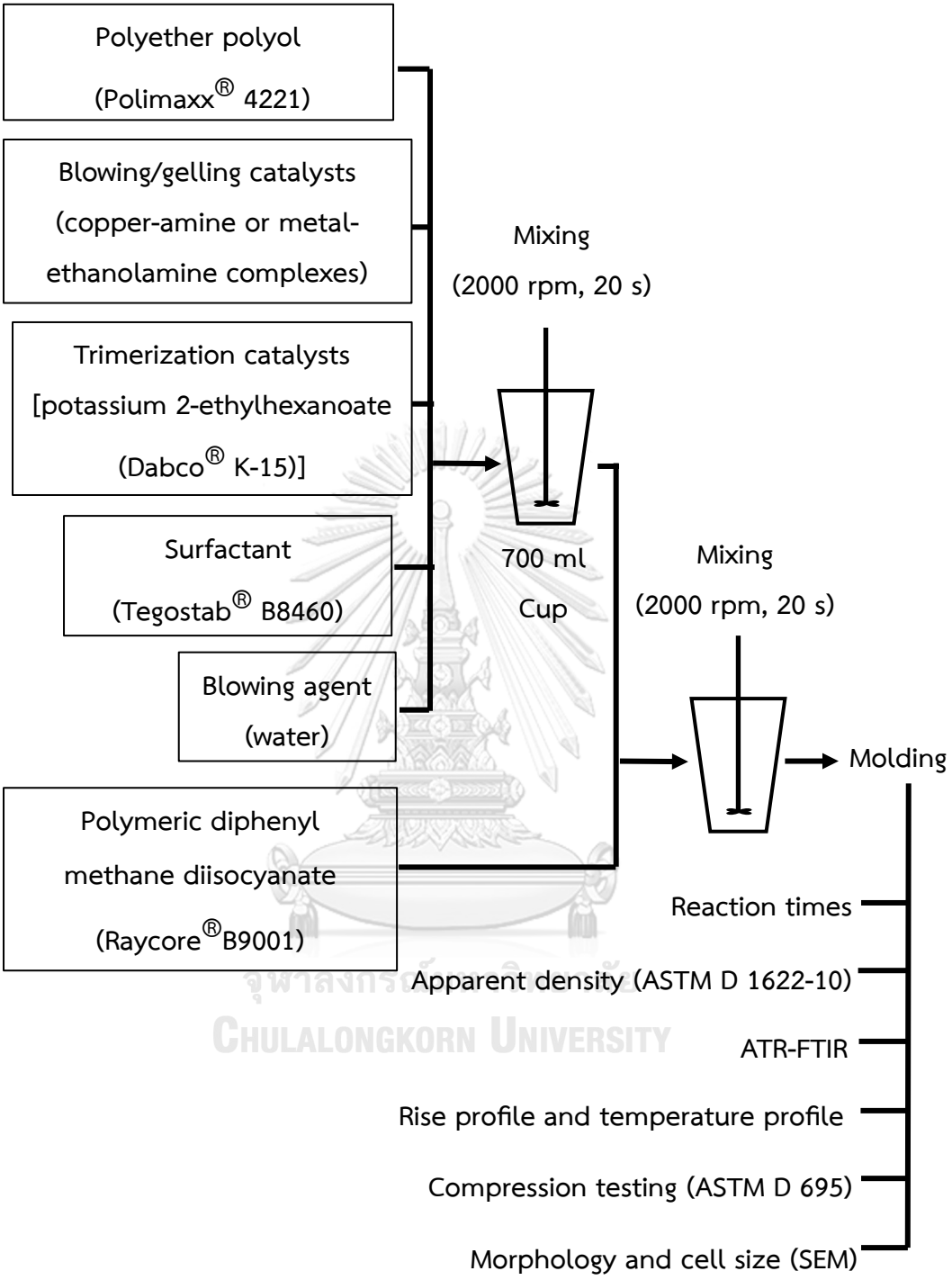

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Figure 3.1 Process for the preparation of PIR foam

3.3.1.1 Preparation of PIR foams catalyzed by DMCHA:K-15

In the first step, the optimum foam formulation was investigated in DMCHA:K-15 catalyst system at NCO index of 160, 200 and 250. Three mole ratios of DMCHA:K-15; 0.5:2, 0.5:2.5 and 0.5:3.0 were employed. The amount of blowing agent (water) was varied at 3, 4 and 5 pbw (Tables 3.3-3.5).

Table 3.3 PIR foam formulations catalyzed by DMCHA:K-15 = 0.5:2.0

Starting Materials	Formulation (pbw)[a]		
Polyether polyol (Polimaxx® 4221)	100	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5	2.5
Catalyst (DMCHA)	0.5	0.5	0.5
Catalyst (K-15)	2.0	2.0	2.0
Blowing agent (H_2O)	3[b]	4[b]	5[b]
Polymeric MDI (Raycore® B9001)	244.7[c] 305.9[d] 382.4[e]	268.8[c] 336.0[d] 420.0[e]	292.9[c] 366.1[d] 457.6[e]

[a]Parts by weight (pbw) is 1 g in 100 g of polyol

[b]Water was added to the polyol blend for RPUR foam catalyzed by DMCHA

[c]NCO index =160

[d]NCO index =200

[e]NCO index =250

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Table 3. 4 PIR foam formulations catalyzed by DMCHA:K-15 = 0.5:2.5

Starting Materials	Formulation (pbw)[a]		
Polyether polyol (Polimaxx® 4221)	100	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5	2.5
Catalyst (DMCHA)	0.5	0.5	0.5
Catalyst (K-15)	2.5	2.5	2.5
Blowing agent (H_2O)	3[b]	4[b]	5[b]
Polymeric MDI (Raycore® B9001)	245.3[c] 306.7[d] 383.3[e]	269.4[c] 336.8[d] 421.0[e]	293.5[c] 366.9[d] 458.6[e]

[a]Parts by weight (pbw) is 1 g in 100 g of polyol

[b]Water was added to the polyol blend for RPUR foam catalyzed by DMCHA

[c]NCO index =160

[d]NCO index =200

[e]NCO index =250

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Table 3.5 PIR foam formulations catalyzed by DMCHA:K-15 = 0.5:3.0

Starting Materials	Formulation (pbw)[a]		
Polyether polyol (Polimaxx® 4221)	100	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5	2.5
Catalyst (DMCHA)	0.5	0.5	0.5
Catalyst (K-15)	3.0	3.0	3.0
Blowing agent (H_2O)	3[b]	4[b]	5[b]
Polymeric MDI (Raycore® B9001)	245.9[c] 307.4[d] 384.3[e]	270.0[c] 337.5[d] 421.9[e]	294.1[c] 367.7[d] 459.6[e]

[a]Parts by weight (pbw) is 1 g in 100 g of polyol

[b]Water was added to the polyol blend for RPUR foam catalyzed by DMCHA

[c]NCO index =160

[d]NCO index =200

[e]NCO index =250

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3.3.1.2 Preparation of PIR foams catalyzed by copper-amine complex :K-15

In the first step, the optimum foam formulation was investigated in copper-amine complex:K-15 catalyst system at the mole ratios of copper-amine complex:K-15 = 0.5:3.0. The NCO index of 200 and 250 were employed. The amount of blowing agent (water) was investigated at 4 and 5 pbw. (Table 3.6).

Table 3.6 PIR foam formulations catalyzed by copper-amine complex:K-15

Starting Materials	Parts by weight (pbw)[a]		
	200	**250**	**250**
Polyether polyol (Polimaxx® 4221)	100	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5	2.5
Catalysts [$Cu(OAc)_2(en)_2$ or $Cu(OAc)_2(trien)$]	0.5[b]	0.5[b]	0.5[b]
Catalyst (K-15)	3.0	3.0	3.0
Blowing agent (H_2O)	5[c]	4[c]	5[c]
Polymeric MDI (Raycore® B9001)	367.7	421.9	459.6

[a]Parts by weight (pbw) is 1 g in 100 g of polyol

[b]Calculated from the weight of copper-amine complexes in aqueous solution of copper-amine complexes

[c]Calculated from the weight of water in aqueous solution of copper-amine complexes

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3.3.1.3 Preparation of PIR foams catalyzed by copper-ethanolamine complex:K-15

In the first step, the optimum foam formulation was investigated in copper-ethanolamine complex:K-15 catalyst system at the mole ratios of copper-amine complex:K-15 = 0.5:3.0. The NCO index of 200 and 250 were employed. The amount of blowing agent (water) was investigated at 5 pbw. (Table 3.7).

Table 3.7 PIR foam formulations catalyzed by copper-ethanolamine complex:K-15

Starting Materials	Parts by weight (pbw)[a]	
	200	**250**
Polyether polyol (Polimaxx® 4221)	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5
Catalysts [$Cu(OAc)_2(EA)_2$]	0.5[b]	0.5[b]
Catalyst (K-15)	3.0	3.0
Blowing agent (H_2O)	5	5
Polymeric MDI (Raycore® B9001)	373.6	467.0

[a]Parts by weight (pbw) is 1 g in 100 g of polyol

[b]Calculated from the weight of copper-ethanolamine complex in solution of metal-ethanolamine complex in ethylene glycol

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3.3.1.4 Preparation of PIR foams catalyzed by zinc-ethanolamine complex:K-15

In the first step, the optimum foam formulation was investigated in zinc-ethanolamine complex:K-15 catalyst system at the mole ratios of copper-amine complex:K-15 = 0.5:3.0. The NCO index of 200 and 250 were employed. The amount of blowing agent (water) was investigated at 5 pbw. (Table 3.8).

Table 3.8 PIR foam formulations catalyzed by zinc-ethanolamine complex:K-15

Starting Materials	Parts by weight (pbw)[a]	
	200	**250**
Polyether polyol (Polimaxx® 4221)	100	100
Silicone surfactant (polysiloxane, Tegostab® B8460)	2.5	2.5
Catalysts [$Zn(OAc)_2(EA)_2$]	0.5[b]	0.5[b]
Catalyst (K-15)	3.0	3.0
Blowing agent (H_2O)	5	5
Polymeric MDI (Raycore® B9001)	374.2	467.7

[a]Parts by weight (pbw) is 1 g in 100 g of polyol

[b]Calculated from the weight of zinc-ethanolamine complex in solution of metal-ethanolamine complex in ethylene glycol

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3.3.2 Preparation of PIR foams by molded method

Preparation of PIR foams by molded method was done by using the same procedure as cup test method but the amount of all starting materials was increased to 3-4 folds. After PMDI was added into the mixture and mixed by mechanical stirrer at 2,000 rpm for 20 seconds, the mixture was poured into a 10 × 10 × 10 cm^3 (width x length x thickness) plastic bag and allowed to free rise at room temperature. PIR foam was kept for 48 hours at room temperature to complete the polymerization reactions and then carrying out physical and mechanical characterization.

3.4 Instrumentation

3.4.1 Ultraviolet-visible spectroscopy

UV-visible spectroscopy was used in the quantitative different analyses for characterize catalysts [$Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$]. UV-visible spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer at room temperature. Absorption spectra were obtained, and the samples were scan over range 200-800 nm at a medium speed. Water was used as solvent for $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien). The solvent used was ethylene glycol for $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$.

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3.4.2 Digital stopwatch

The reaction times namely, cream time, gel time tack free time and rise time were investigated by using a digital stopwatch in accordance with ASTM D7487-13[29].

3.4.3 Density measurement

The density of PIR foam was determine by averaging the ratio of mass to volume measurement result of three examples per sample following the procedure in ASTM D 1622-09[30] standard. The shape of the sample was cube (size: 30 mm x 30 mm x 30 mm).

3.4.5 Thermocouple

The thermocouple Digicon DP-71 was used as a temperatures sensor for detect the foaming temperatures of PIR foams which presented temperature profiles.

3.4.6 ATR-FTIR spectroscopy

The ATR-FTIR analysis of PIR foam was performed on a Nicolet 6700 FTIR spectrometer with 16 scans at the range of 4000-800 cm^{-1} which used for characterizing the functional groups and study about NCO conversion of PIR foam. The IR bands shown in the Table 3.9 were used for the analysis. The measurement was controlled by the Omnic software.

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Table 3.9 Characteristic IR bands of PIR foam

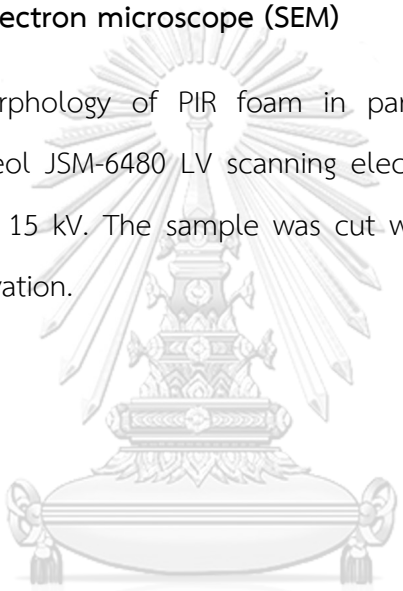
Chemical bond	Wavenumber (cm^{-1})	Chemical structure
Isocyanate (NCO)	2272	N=C=O
Phenyl	1595	Ar-H
Isocyanulate (PIR)	1413	PIR
Urethane	1221	-C-O

3.4.7 Compressive strength

Compressive strength measurements of different of PIR foam in parallel and perpendicular were performed with universal testing machine (Lloyd/LRX) according to ASTM D 695[31]. The size of the specimen was cube (size: 50 mm x 50 mm x 50 mm). The speed of crosshead movement was fixed at 50 mm/min and the preload cell used was 0.100 N.

3.4.8 Scanning electron microscope (SEM)

The cellular morphology of PIR foam in parallel and perpendicular was characterized with a Jeol JSM-6480 LV scanning electron microscope (SEM) at the accelerating voltage of 15 kV. The sample was cut with a razor blade and coated with gold before observation.



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CHAPTER IV
RESULTS AND DISCUSSION

4.1 Synthesis of copper-amine complexes

4.1.1 Synthesis of copper-amine complexes in aqueous solutions

$Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) were synthesized following by the synthetic route described in the literature reviews[6]. The reactions between $Cu(OAc)_2$ and amine derivative [ethylenediamine, (en) or triethylenetetramine, (trien)] in water are shown in Scheme 2.5. $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) had a good solubility in water and were obtained as an odorless dark purple solution and odorless dark blue solution, respectively (Figure 4.1). Subsequently, they were used cooperated with K-15 for preparation of PIR foams without purification.

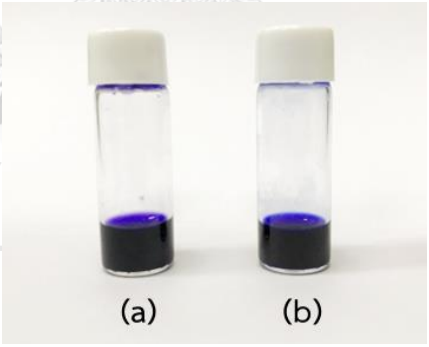

Figure 4.1 Copper-amine complexes in water (a) $Cu(OAc)_2(en)_2$ and (b) $Cu(OAc)_2$ (trien)

4.1.2 Synthesis of metal-ethanolamine complexes in ethylene glycol

The metal-ethanolamine complexes of $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ were synthesized following by the synthetic route described in the literature review[7]. The reaction between $Cu(OAc)_2$ or $Zn(OAc)_2$ and ethanolamine in ethylene glycol are shown in Scheme 2.6. $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ were obtained homogeneous

solution in ethylene glycol as odorless viscous dark-blue solution and odorless viscous light-yellow solution, respectively (Figure 4.2). Subsequently, they were used cooperated with K-15 for preparation of PIR foams without purification.

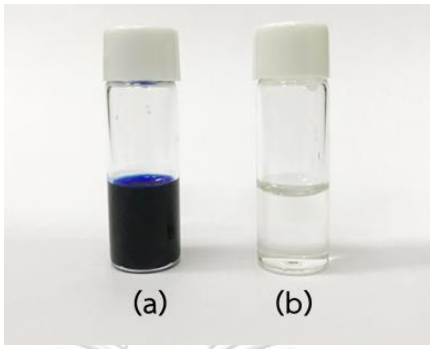

Figure 4.2 Metal-ethanolamine complexes in ethylene glycol: (a) $Cu(OAc)_2(EA)_2$ and (b) $Zn(OAc)_2(EA)_2$

4.2 Characterization of copper-amine complexes

4.2.1 The optical property of copper-amine complexes in aqueous solutions by using UV-visible spectroscopy

The optical property UV-visible spectra of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) were studied by using UV-visible spectroscopy. The UV-visible spectrum of $Cu(OAc)_2$ was obtained in methanolic solution because $Cu(OAc)_2$ had a poor solubility in water. However, $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) was obtained in water. As shown in the Figure 4.3, the absorption spectra of $Cu(OAc)_2$, $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) exhibited the maximum absorption band (λ_{max}) at 245, 231 and 259 nm, respectively. Comparing to $Cu(OAc)_2$, the absorption peak of $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) were significantly shift to 231 nm and 259 nm, respectively. Consequently, these results suggested the successful complex formation corresponding to Noiasa work [6].

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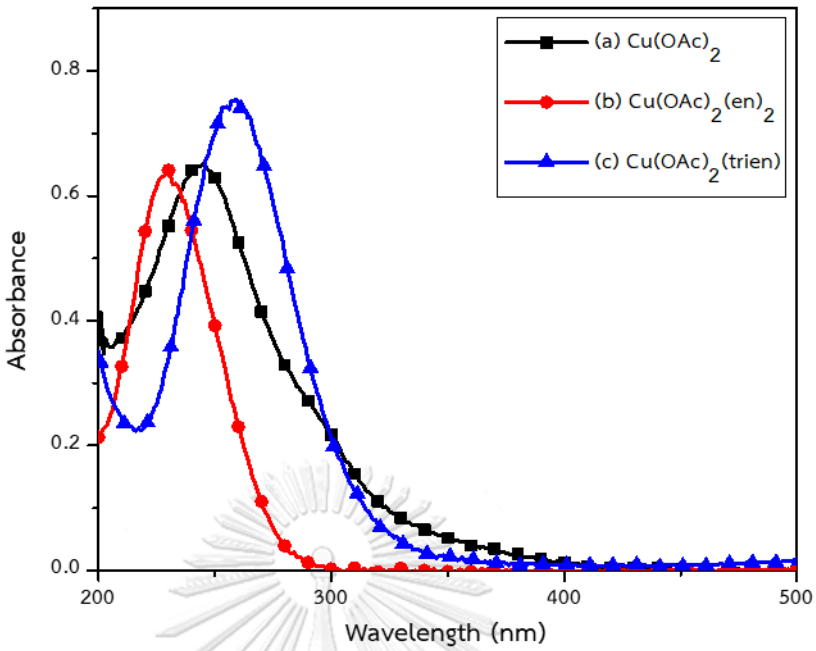

Figure 4.3 UV-visible spectra of (a) $Cu(OAc)_2$, (b) $Cu(OAc)_2(en)_2$ and (c) $Cu(OAc)_2$(trien)

4.2.2 The optical property of metal-ethanolamine complexes in ethylene glycol by using UV-visible spectroscopy

The optical property of $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ were investigated by using UV-visible spectroscopy, as shown in Figures 4.4 and 4.5, respectively. In case of complexation of $Cu(OAc)_2$ and $Zn(OAc)_2$ were prepared by dissolving in methanolic solution because $Cu(OAc)_2$ and $Zn(OAc)_2$ had a poor solubility in water. The absorption peak of $Cu(OAc)_2$ and $Cu(OAc)_2(EA)_2$ were observed at a wavelength of 245 and 273 nm, respectively. The absorption of $Zn(OAc)_2$ and $Zn(OAc)_2(EA)_2$ were close to each other. These results suggested the complex formation corresponding to Jongjitsatitmun work [7].

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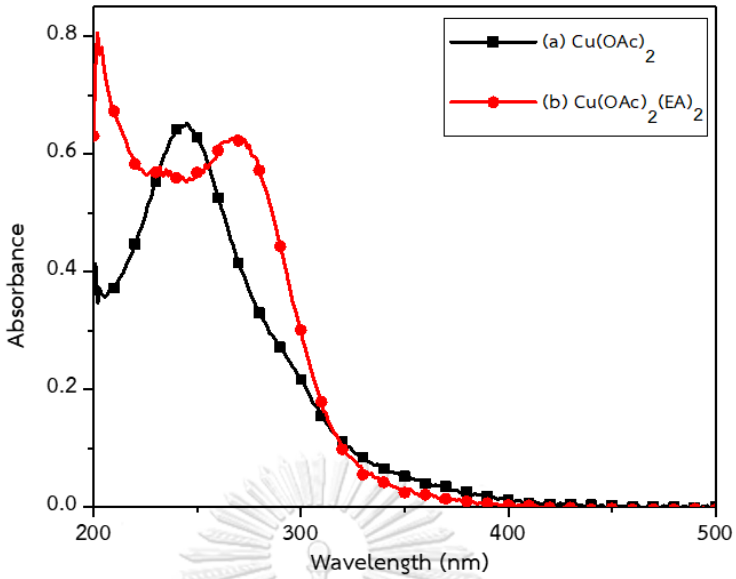

Figure 4.4 UV-visible spectra of (a) $Cu(OAc)_2$ and (b) $Cu(OAc)_2(EA)_2$

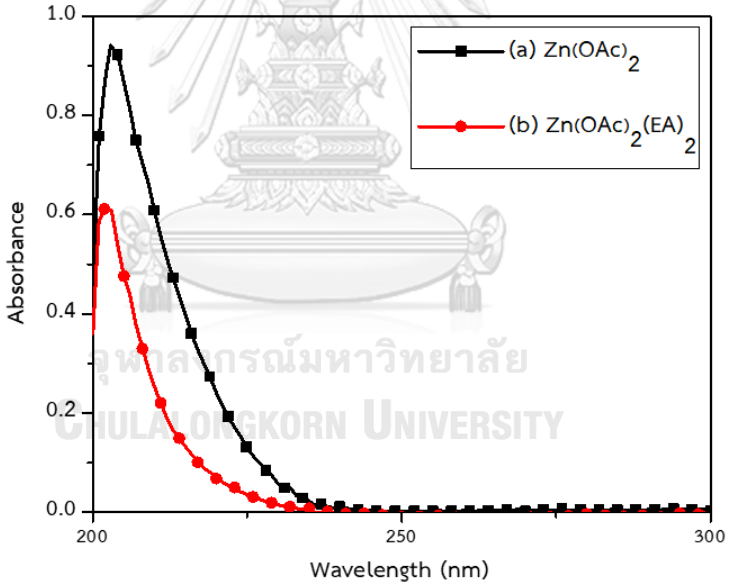

Figure 4.5 UV-visible spectra of (a) $Zn(OAc)_2$ and (b) $Zn(OAc)_2(EA)_2$

4.3 Preparation of polyisocyanurate (PIR) foams

4.3.1 Preparation of PIR foams by using cup test method

In cup-test method, PIR foam was used to investigate the reaction time, free rise density, rise profile, temperature profile, NCO conversion and morphology.

4.3.1.1 Reaction times and density of PIR foams

The reaction times for preparation of PIR foams were investigated know as a cream time, gel time, rise time and tack free time. The PIR foams catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15, compared to commercially catalyst as DMCHA:K-15.

4.3.1.1.1 Preparation of PIR foams catalyzed by DMCHA:K-15

The optimal foam formulation was investigated in the three mole ratios of DMCHA:K-15; 0.5:2, 0.5:2.5 and 0.5:3.0. DMCHA:K-15 at NCO index = 160, 200 and 250. The amount of water was varied by 3, 4 and 5 pbw to investigate the change of PIR foam density. Sequentially, all PIR foams were catalyzed by DMCHA:K-15 (Figures 4.6-4.32), formed foams have no large hole at the bottom of the mold resulting in a good property of foams. The foams were cut to measure density. As show in Table 4.1, these results suggested that the PIR foams prepared in these different three mole ratios had similar the cream time and the gel time. However, rise time and tack free time showed that the time decreased with an increasing amount of K-15. As the results mentioned above, the mole ratio = 0.5:3.0 had a better catalytic activity in gelling and blowing reaction than the mole ratio = 0.5:2.0 and 0.5:2.5. Moreover, the amount of water level and height of PIR foam were increased, whereas density of the foam was also decreased due to the generation of carbon dioxide (CO_2) gas in the system. However, when the NCO index was increased from 160 to 250. The PIR foams prepared at NCO index = 250 provided the longest reaction times and highest density over other NCO index values, because the excess of isocyanate in PIR foam preparation could undergo the further trimerization to give isocyanurate. Therefore, the important parameter including a ratio of DMCHA:K-15 = 0.5:3.0, the amount of water = 5 pbw and NCO index =200 and 250 were employed as the proper parameter for further experiment.

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Table 4.1 Reaction times, density and height of PIR foams were catalyzed by DMCHA:K-15

Mole ratios of DMCHA: K-15	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free (sec)	Rise time (sec)	Density (kg/m^3)	Height (cm)
0.5:2.0	3	160	26	39	109	81	43.5	16.0
		200	30	43	125	95	54.1	15.4
		250	36	58	160	125	61.4	15.5
	4	160	25	39	130	103	38.5	18.9
		200	29	45	148	118	45.0	18.5
		250	33	52	190	130	53.1	18.9
	5	160	24	37	133	99	35.0	21.1
		200	30	46	151	120	40.6	21.1
		250	34	55	181	144	48.6	21.4
0.5:2.5	3	160	23	37	106	79	45.9	15.2
		200	29	43	111	89	53.0	15.1
		250	32	49	140	103	62.6	15.5
	4	160	23	38	114	82	37.6	18.8
		200	27	42	132	98	43.1	19.3
		250	32	43	143	111	50.2	19.9
	5	160	23	34	117	88	33.2	21.5
		200	28	45	142	103	39.0	21.8
		250	33	53	175	129	48.8	21.5

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Table 4.1 (Continued)

Mole ratios of DMCHA: K-15	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free (sec)	Rise time (sec)	Density (kg/m^3)	Height (cm)
0.5:3.0	3	160	23	33	88	67	43.6	15.5
		200	26	38	101	80	51.2	15.7
		250	29	41	110	87	61.3	15.7
	4	160	25	33	101	74	36.4	19.5
		200	28	40	119	92	41.0	20.1
		250	32	49	132	103	51.6	19.6
	5	160	23	30	101	73	32.9	21.4
		200	26	42	130	93	38.9	22.6
		250	29	45	154	113	43.2	23.7

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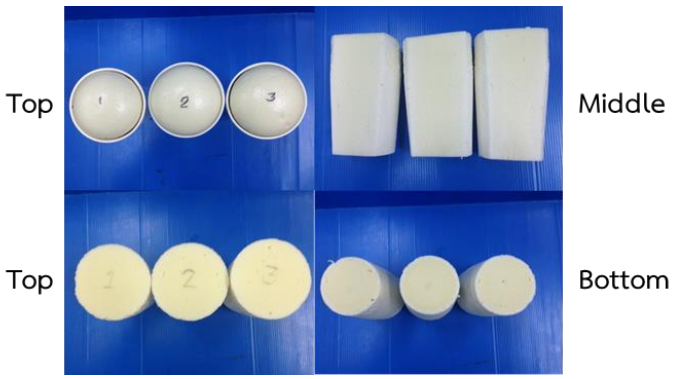

Figure 4.6 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 3 pbw and NCO index =160

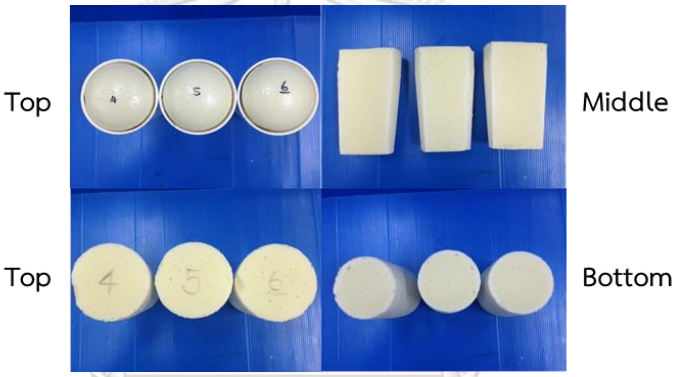

Figure 4.7 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 3 pbw and NCO index =200

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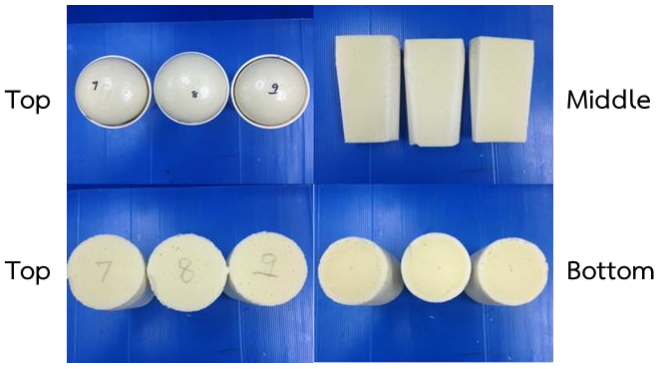

Figure 4.8 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 3 pbw and NCO index =250

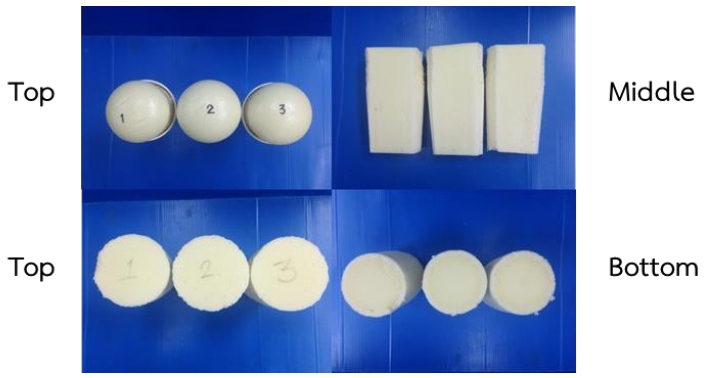

Figure 4.9 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 4 pbw and NCO index =160

Figure 4.10 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 4 pbw and NCO index =200

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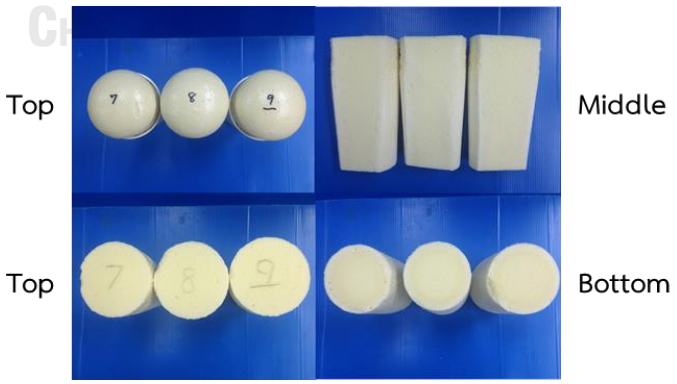

Figure 4.11 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 4 pbw and NCO index =250

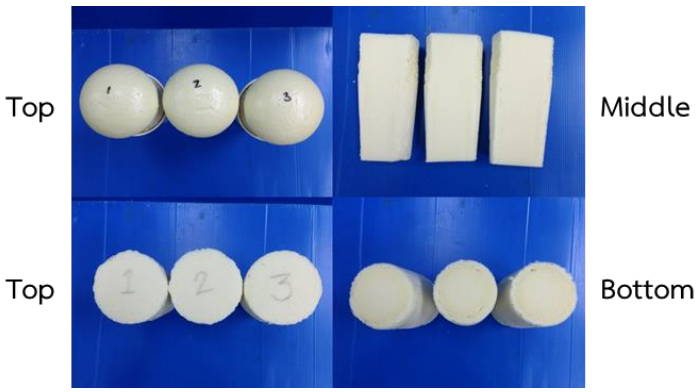

Figure 4.12 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 5 pbw and NCO index =160

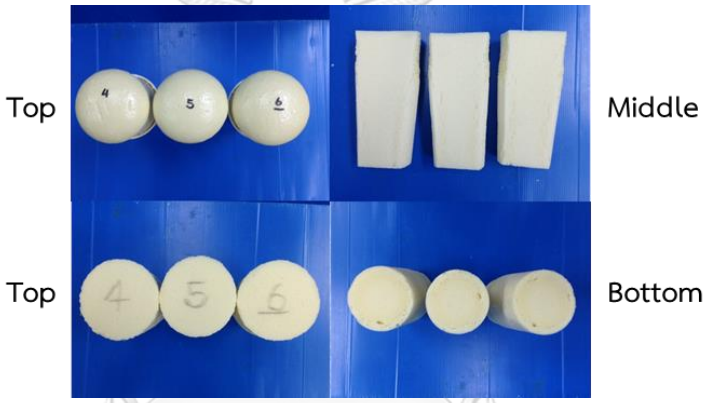

Figure 4.13 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 5 pbw and NCO index =200

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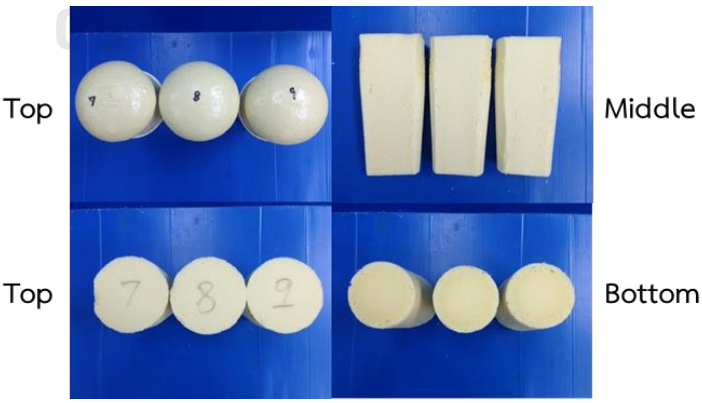

Figure 4.14 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.0, water 5 pbw and NCO index =250

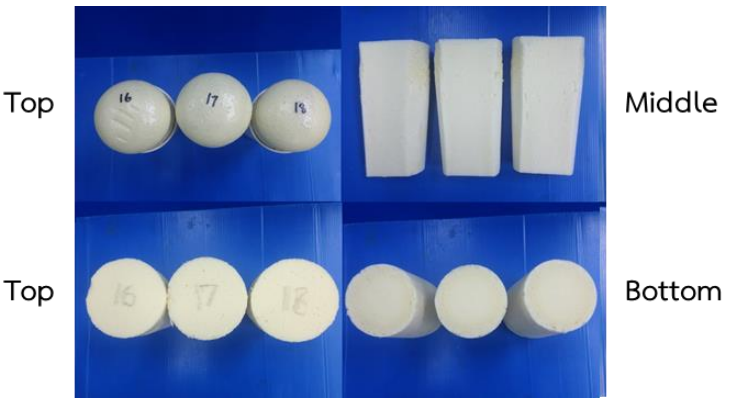

Figure 4.15 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 3 pbw and NCO index =160

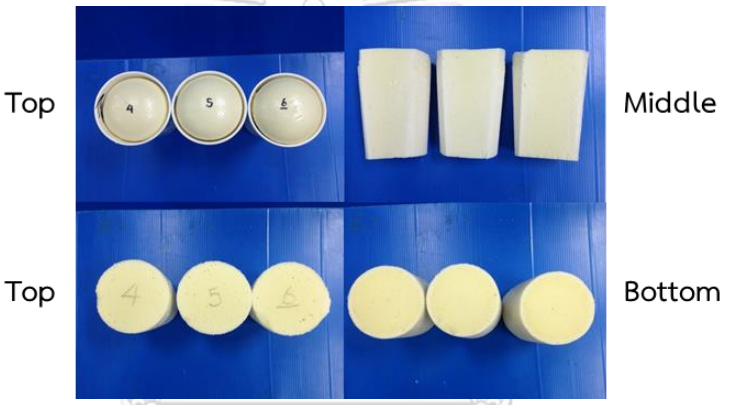

Figure 4.16 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 3 pbw and NCO index =200

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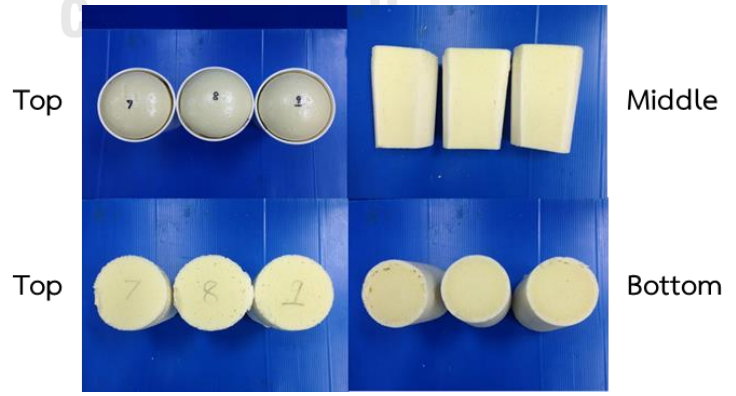

Figure 4.17 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 3 pbw and NCO index =250

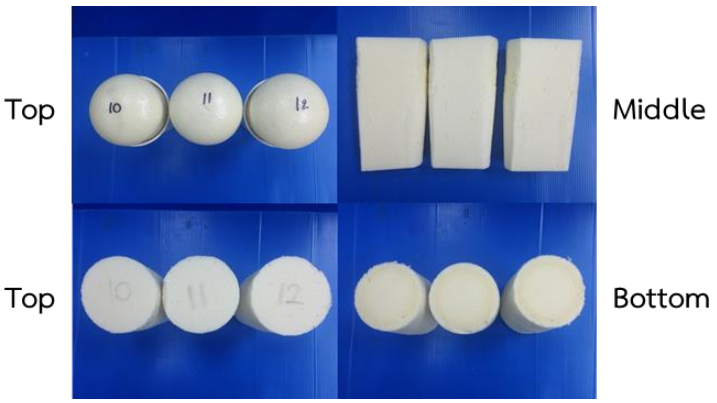

Figure 4.18 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 4 pbw and NCO index =160

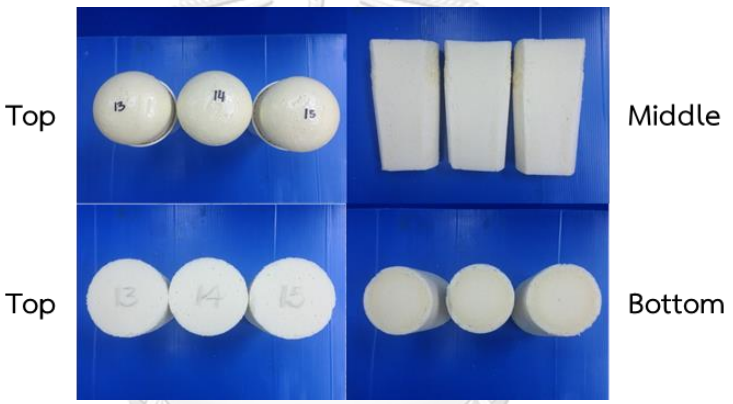

Figure 4.19 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 4 pbw and NCO index =200

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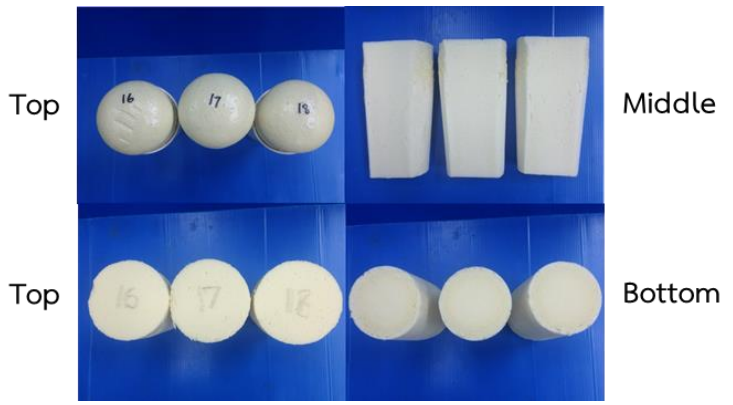

Figure 4.20 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 4 pbw and NCO index =250

Figure 4.21 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 5 pbw and NCO index =160

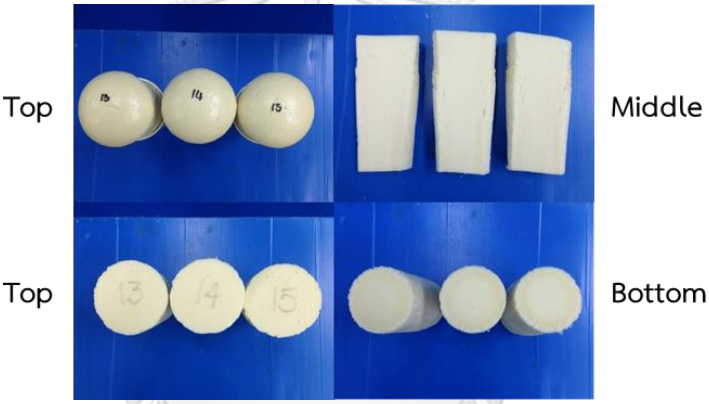

Figure 4.22 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 5 pbw and NCO index =200

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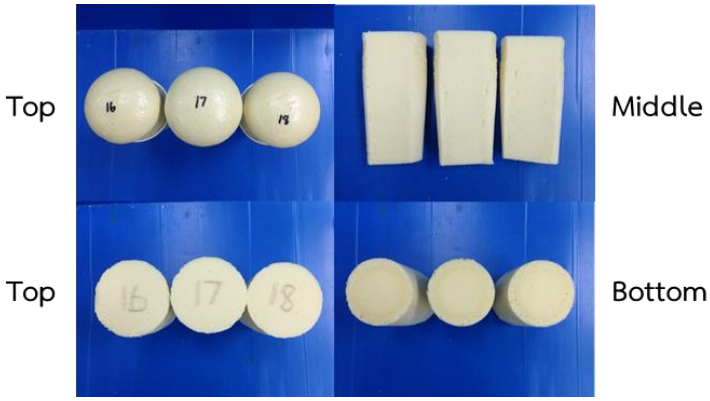

Figure 4.23 PIR foam catalyzed by DMCHA:K-15 = 0.5:2.5, water 5 pbw and NCO index =250

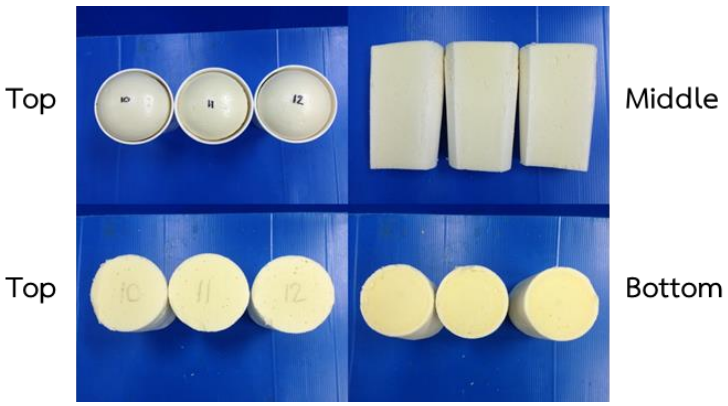

Figure 4.24 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 3 pbw and NCO index =160

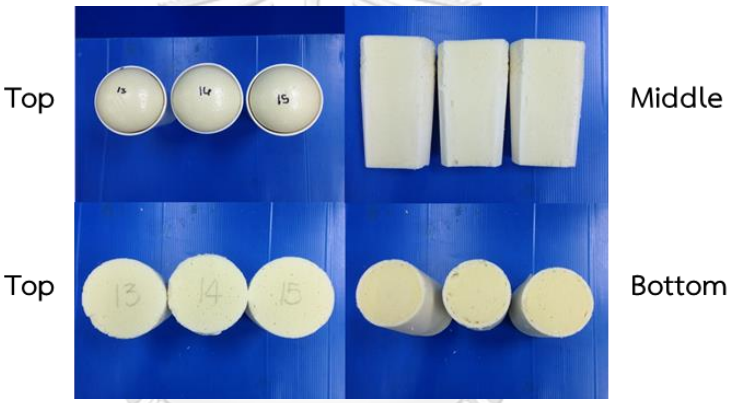

Figure 4.25 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 3 pbw and NCO index =200

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Figure 4.26 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 3 pbw and NCO index =250

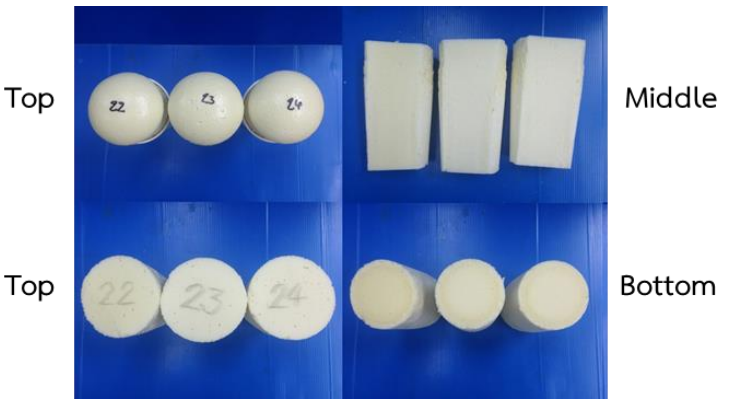

Figure 4.27 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 4 pbw and NCO index =160

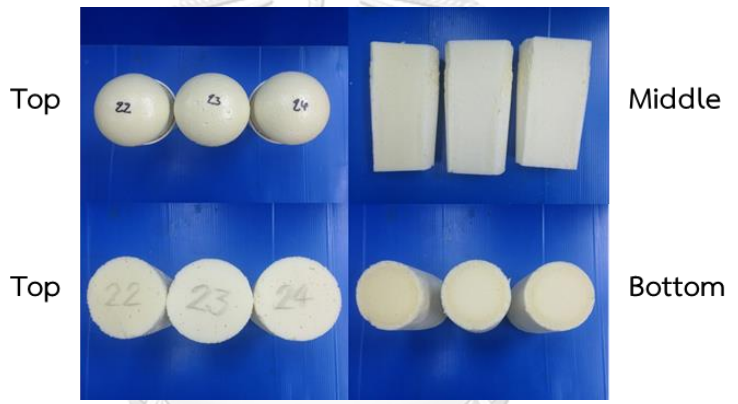

Figure 4.28 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 4 pbw and NCO index =200

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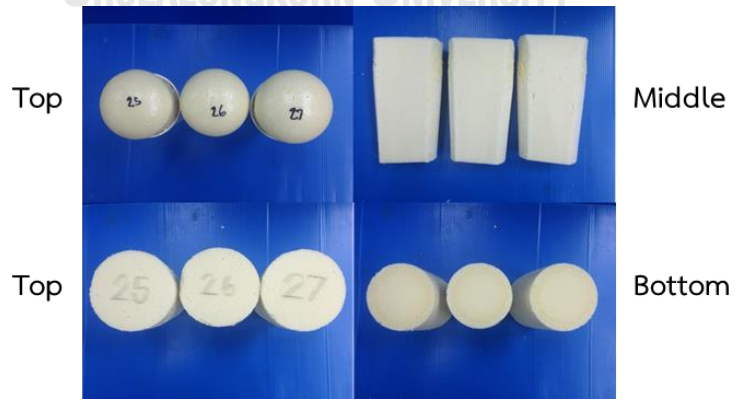

Figure 4.29 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 4 pbw and NCO index =250

Figure 4.30 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 5 pbw and NCO index =160

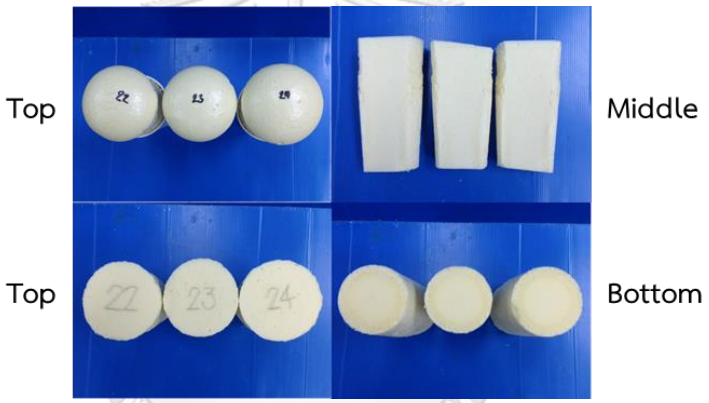

Figure 4.31 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 5 pbw and NCO index =200

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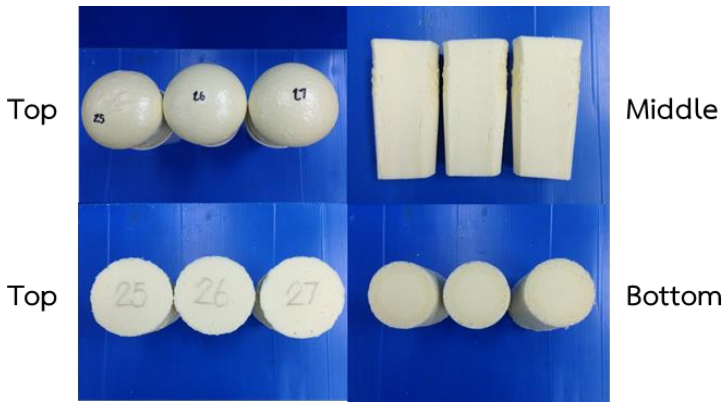

Figure 4.32 PIR foam catalyzed by DMCHA:K-15 = 0.5:3.0, water 5 pbw and NCO index =250

4.3.1.1.2 Preparation of PIR foams catalyzed by copper-amine complex:K-15

Considering the PIR foams prepared from copper-amine complex:K-15 at the mole ratio of 0.5:3.0, the amount of water = 4 pbw at NCO index = 200 and the amount of water = 5 pbw at NCO index = 200 and 250 (Table 4.2). Both $Cu(OAc)_2(en)_2$:K-15 and $Cu(OAc)_2$(trien):K-15 gave shorter tack free time than DMCHA:K-15 because they have more gelling catalytic activity than DMCHA:K-15. Moreover, $Cu(OAc)_2(en)_2$:K-15 and $Cu(OAc)_2$(trien):K-15 gave shorter rise time as DMCHA:K-15 because of blowing catalytic activity. In addition, $Cu(OAc)_2(en)_2$:K-15 has shorter rise time than $Cu(OAc)_2$(trien) because of rigid of the amines. PIR foams catalyzed by copper-amine complex:K-15 had higher density than that catalyzed by DMCHA:K-15. Because copper-amine complex:K-15 give more crosslinked structure than DMCHA:K-15. The amount of water = 4 pbw had shorter reaction time, shorter height and higher density than amount of water = 5 pbw because of CO_2 increasing. When the NCO index increased from 200 to 250, the PIR foams prepared at NCO index = 250 had longer reaction times and higher density than those prepared at NCO index = 200 because of crosslinked structure. From Figures 4.33-4.38, PIR foams catalyzed by copper-amine complex:K-15 were darker than PIR foam catalyzed by DMCHA:K-15 because $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) are darker solution than DMCHA. However, they still had no large hole at the top, the middle and the bottom of the mold resulting in a good property of foams.

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Table 4.2 Reaction times, density and height of PIR foams catalyzed by copper-amine complex:K-15 at mole ratio = 0.5:3.0

catalysts	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free (sec)	Rise time (sec)	Density (kg/m^3)	height (cm)
$Cu(OAc)_2(en)_2$:K-15	4	250	29	45	80	100	62.9	16.8
	5	200	30	45	60	75	47.8	17.0
		250	32	45	85	93	53.5	19.9
$Cu(OAc)_2$ (trien): K-15	4	250	36	55	94	101	60.7	17.1
	5	200	35	52	84	91	48.2	17.9
		250	36	55	98	107	54.2	20.0

Figure 4.33 PIR foam catalyzed by $Cu(OAc)_2(en)_2$:K-15 = 0.5:3.0, water 4 pbw and NCO index =250

Figure 4.34 PIR foam catalyzed by $Cu(OAc)_2(en)_2$:K-15 = 0.5:3.0, water 5 pbw and NCO index =200

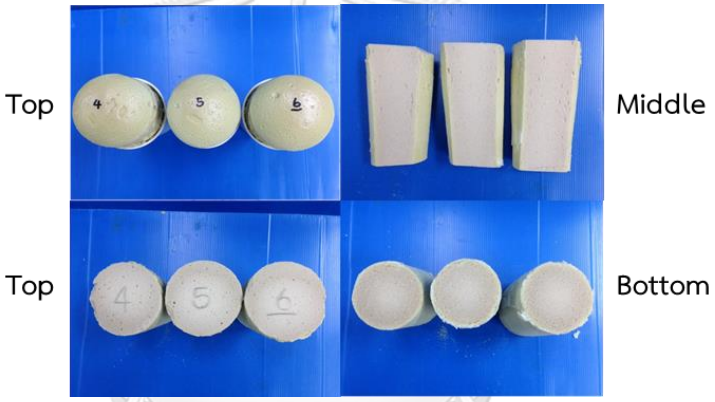

Figure 4.35 PIR foam catalyzed by $Cu(OAc)_2(en)_2$:K-15 = 0.5:3.0, water 5 pbw and NCO index =250

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Figure 4.36 PIR foam catalyzed by $Cu(OAc)_2$(trien):K-15 = 0.5:3.0, water 4 pbw and NCO index =250

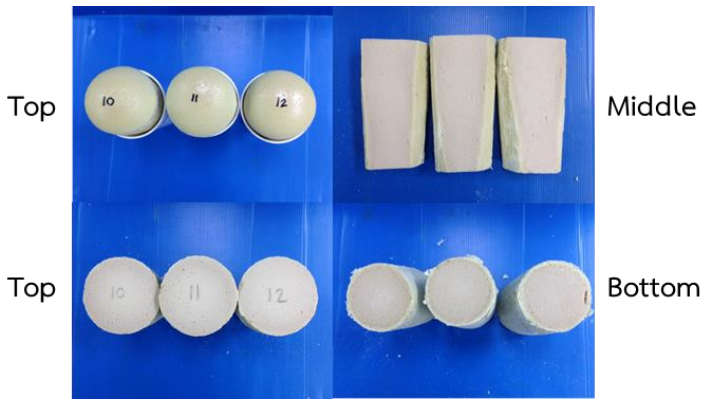

Figure 4.37 PIR foam catalyzed by $Cu(OAc)_2$(trien):K-15 = 0.5:3.0, water 5 pbw and NCO index =200

Figure 4.38 PIR foam catalyzed by $Cu(OAc)_2$(trien):K-15 = 0.5:3.0, water 5 pbw and NCO index =250

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4.3.1.1.3 Preparation of PIR foams catalyzed by metal-ethanol amine complex:K-15

Considering the PIR foams prepared from $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 catalyst at the mole ratio of 0.5:3.0, the amount of water = 5 pbw at NCO index = 200 and 250 (Table 4.3). Both $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 provided shorter rise time and tack free time than DMCHA:K-15 because they have more blowing and gelling catalytic activity than DMCHA:K-15. In addition, $Cu(OAc)_2(EA)_2$ has shorter rise time and tack free time than $Zn(OAc)_2(EA)_2$:K-15 because $Cu(OAc)_2(EA)_2$ has more coordination number than $Zn(OAc)_2(EA)_2$:K-15. PIR foams catalyzed by $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 had higher density than DMCHA:K-15 at NCO index = 200 and 250 because more crosslink of structure. From Figures 4.39-4.42, All PIR foams have no large hole at the top, the middle and the bottom of the mold resulting in a good property of foams. PIR foams catalyzed by $Cu(OAc)_2(EA)_2$:K-15 is darker than PIR foam catalyzed by DMCHA:K-15 because $Cu(OAc)_2(EA)_2$ is dark blue solution but PIR foam catalyzed by $Zn(OAc)_2(EA)_2$:K-15 is the same color as DMCHA:K-15 because it is light-yellow solution.

Table 4.3 Reaction times, density and height of PIR foams catalyzed by metal-ethanolamine complex:K-15 at mole ratio = 0.5:3.0

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catalysts	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free (sec)	Rise time (sec)	Density (kg/m^3)	Height (cm)
$Cu(OAc)_2(EA)_2$:K-15	5	200	27	39	58	80	41.2	21.9
		250	31	43	82	95	49.8	21.5
$Zn(OAc)_2(EA)_2$:K-15	5	200	25	43	72	93	42.4	20.6
		250	30	50	83	107	53.1	20.3

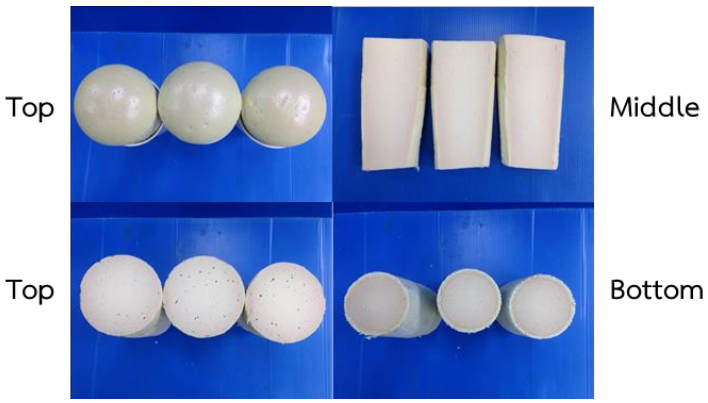

Figure 4.39 PIR foam catalyzed by $Cu(OAc)_2(EA)_2$:K-15 = 0.5:3.0, water 5 pbw and NCO index =200

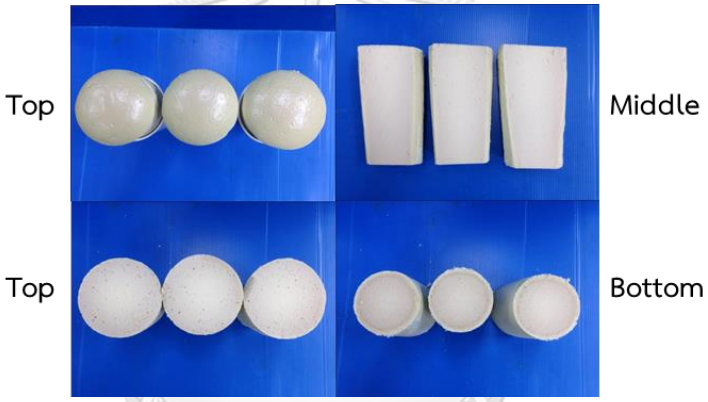

Figure 4.40 PIR foam catalyzed by $Cu(OAc)_2(EA)_2$:K-15 = 0.5:3.0, water 5 pbw and NCO index =250

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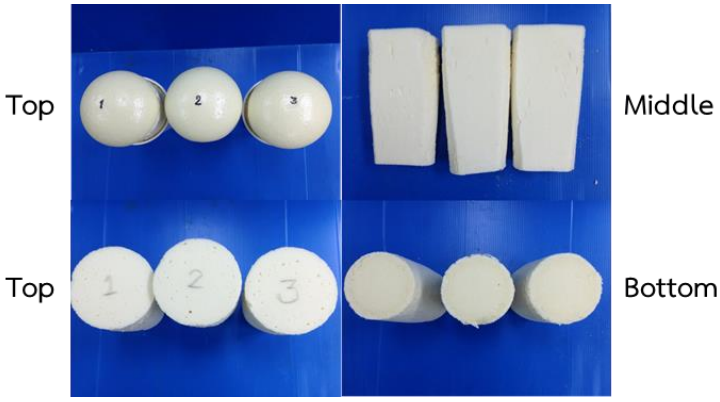

Figure 4.41 PIR foam catalyzed by $Zn(OAc)_2(EA)_2$:K-15 = 0.5:3.0, water 5 pbw and NCO index =200

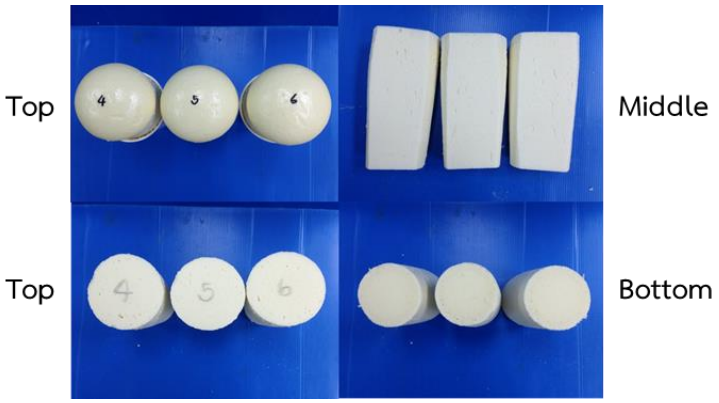

Figure 4.42 PIR foam catalyzed by $Zn(OAc)_2(EA)_2$:K-15 = 0.5:3.0, water 5 pbw and NCO index =250

4.3.1.2 NCO conversion of PIR foams

NCO conversion of PIR foam was determined from the IR absorption band of the NCO group at 2277 cm^{-1} (Figure 4.43-4.47) as shown in the following equation[14].

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

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Where NCO^t is the area of isocyanate peak at time t, which is the time after the foam was kept at room temperature for 48 hours to complete the polymerization reaction and NCO^i is the area of the isocyanate peak at initial time. The isocyanate peak area was normalized by the aromatic ring peak at 1595 cm^{-1}. PIR:PUR ratio was calculated from the peak area of isocyanurate and urethane at 1415 and 1220 cm^{-1}, respectively.

4.3.1.2.1 NCO conversion of PIR foam catalyzed by DMCHA:K-15

NCO conversion of PIR foams catalyzed by DMCHA:K-15 in three mole ratios at NCO index of 160, 200 and 250 was investigated as shown in Table 4.4 and Figures 4.45-4.47. It was found that three mole ratios of DMCHA:K-15 (0.5:2.0, 0.5:2.5 and 0.5:3.0) at NCO index 160 and 200 showed approximately 99% of NCO conversion which showed that the polymerization reactions were completed. However, NCO index 250 showed approximately >95% of NCO conversion. All of PIR foams have PIR:PUR ratio > 1. Therefore, trimerization reaction which form isocyanate group was the major reaction and gelling reaction which form urethane group is a minor reaction. The mole ratio of DMCHA:K-15 = 0.5:3.0 showed the highest PIR:PUR ratio. The amount of water = 3 pbw provides higher PIR:PUR ratio than the amount of water = 4 and 5 pbw. Because PIR bonds from trimerization reaction would had less likely through parallel reactions of NCO with water to form urea and CO_2 [14]. As NCO index increased, the PIR:PUR ratio also increased. Therefore, the ratio at 0.5:3.0, the amount of water = 5 pbw and NCO index = 200 and 250 were used in the next step.

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Table 4.4 NCO conversion of PIR foams catalyzed by DMCHA:K-15

Mole ratios of DMCHA:K-15	H_2O (pbw)	NCO index	NCO conversion (%)	PIR:PUR
0.5:2.0	3	160	99.7	0.90
		200	99.7	1.24
		250	95.9	1.69
	4	160	99.2	0.81
		200	99.4	1.20
		250	98.2	1.70
	5	160	99.1	0.75
		200	99.3	1.17
		250	97.5	1.72
0.5:2.5	3	160	99.8	0.95
		200	99.7	1.27
		250	99.5	1.90
	4	160	99.7	0.87
		200	99.6	1.23
		250	99.3	1.77
	5	160	99.6	0.93
		200	99.3	1.39
		250	99.2	1.91

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Table 4.4 (Continued)

Mole ratios of DMCHA:K-15	H_2O (pbw)	NCO index	NCO conversion (%)	PIR:PUR
0.5:3.0	3	160	99.9	0.99
		200	99.7	1.43
		250	99.4	2.01
	4	160	99.5	1.02
		200	99.5	1.29
		250	98.5	1.94
	5	160	99.1	1.05
		200	99.5	1.47
		250	98.2	2.11

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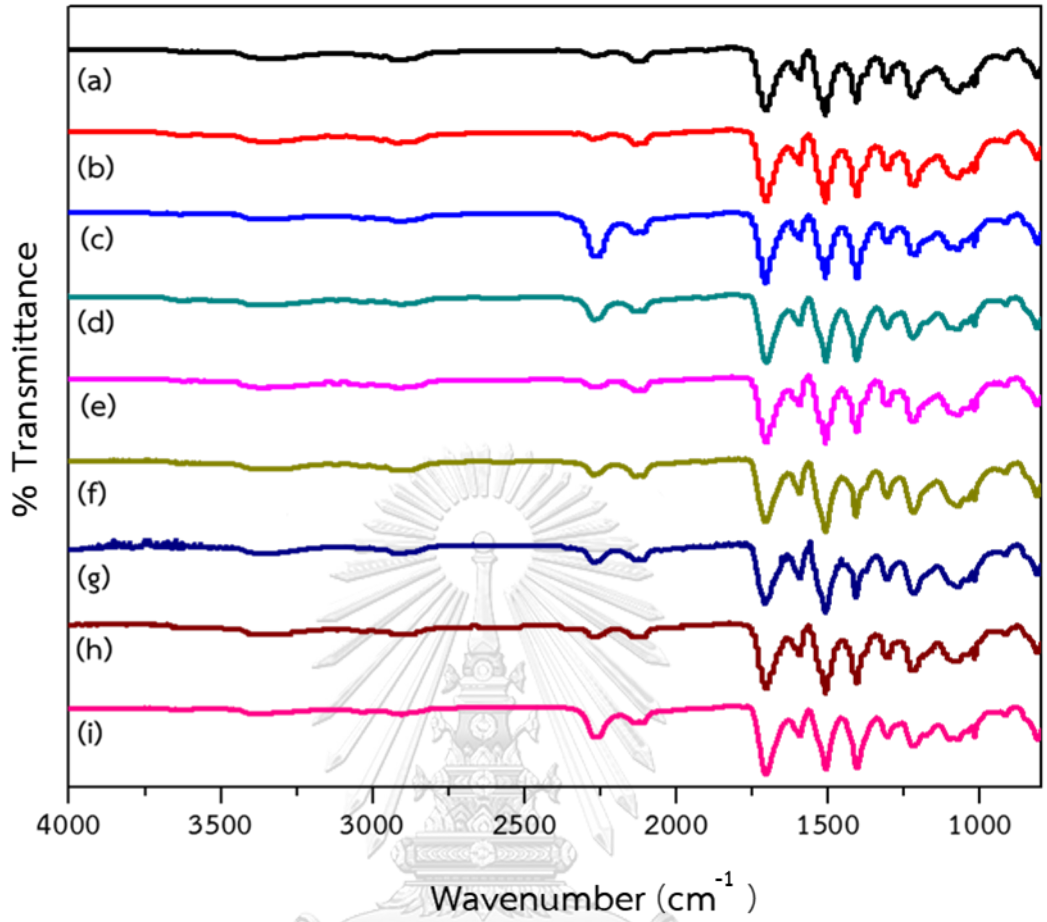

Figure 4.43 FTIR spectra of PIR foams catalyzed by DMCH:K-15 at mole ratio = 0.5:2.0: (a) water = 3 pbw and NCO index = 160, (b) water = 3 pbw and NCO index = 200, (c) water = 3 pbw and NCO index = 250, (d) water = 4 pbw and NCO index = 160, (e) water = 4 pbw and NCO index = 200, (f) water = 3 pbw and NCO index = 250, (g) water = 5 pbw and NCO index =160, (h) water = 5 pbw and NCO index = 200 and (i) water = 5 pbw and NCO index = 250

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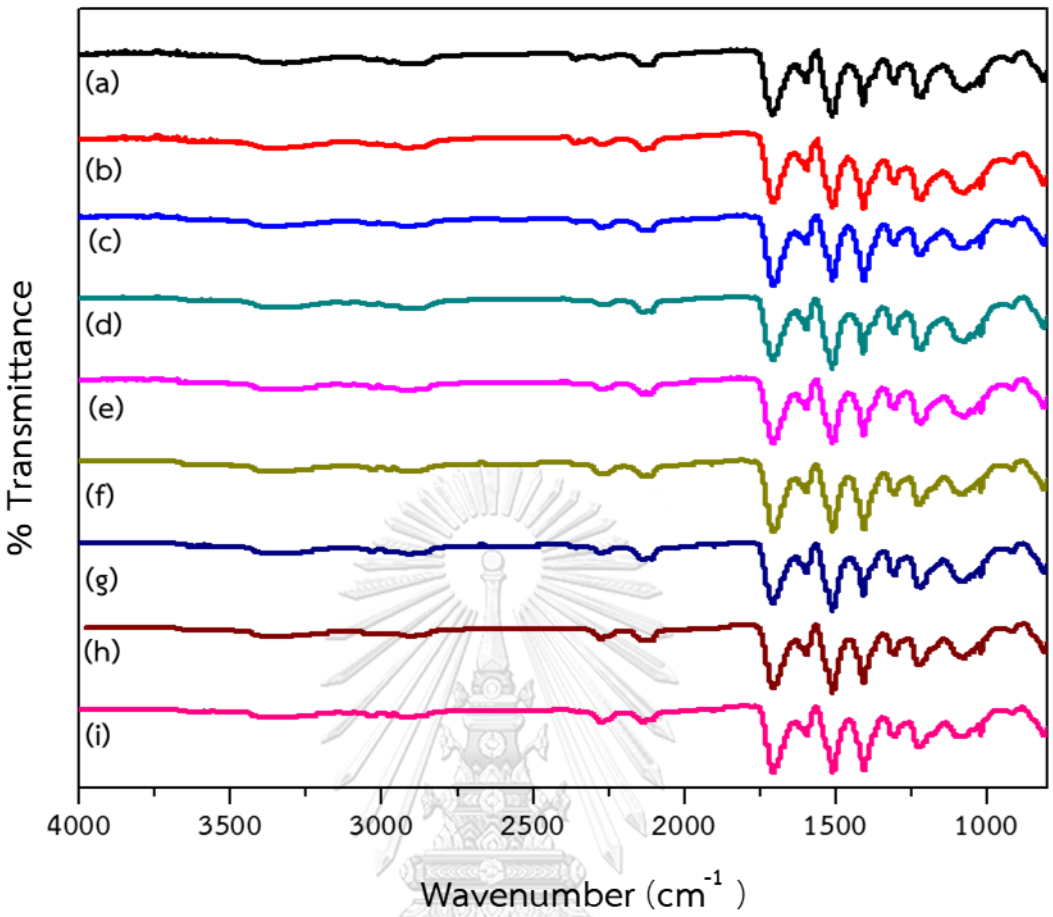

Figure 4.44 FTIR spectra of PIR foams catalyzed by DMCHA:K-15 at mole ratio = 0.5:2.5: (a) water = 3 pbw and NCO index = 160, (b) water = 3 pbw and NCO index = 200, (c) water = 3 pbw and NCO index = 250, (d) water = 4 pbw and NCO index = 160, (e) water = 4 pbw and NCO index = 200, (f) water = 3 pbw and NCO index = 250, (g) water = 5 pbw and NCO index =160, (h) water = 5 pbw and NCO index = 200 and (i) water = 5 pbw and NCO index = 250

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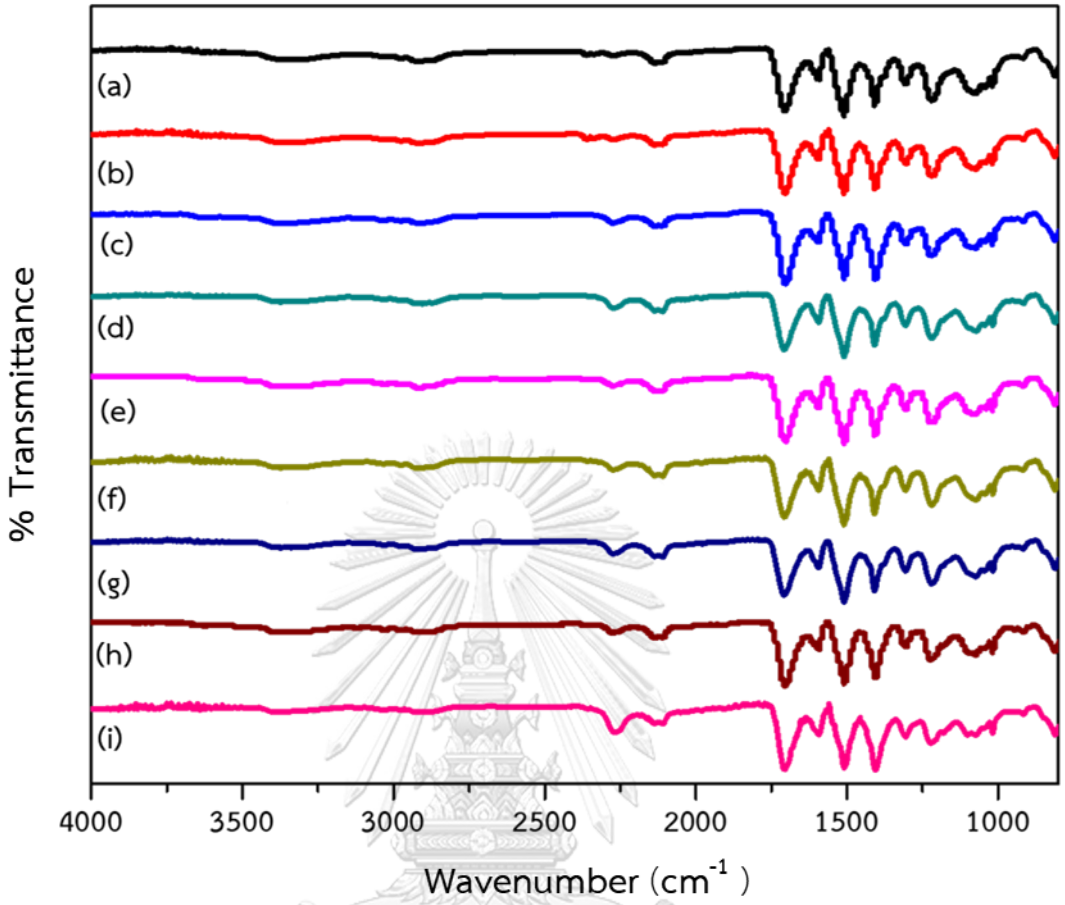

Figure 4.45 FTIR spectra of PIR foams catalyzed by DMCHA:K-15 at mole ratio = 0.5:3.0 (a) water = 3 pbw and NCO index = 160, (b) water = 3 pbw and NCO index = 200, (c) water = 3 pbw and NCO index = 250, (d) water = 4 pbw and NCO index = 160, (e) water = 4 pbw and NCO index =200, (f) water = 3 pbw and NCO index = 250, (g) water = 5 pbw and NCO index =160, (h) water = 5 pbw and NCO index = 200 and (i) water = 5 pbw and NCO index = 250

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4.3.1.2.3 NCO conversion of PIR foams catalyzed by copper-amine complex:K-15

From Table 4.5 and Figure 4.46, It was found that PIR foams catalyzed by copper-amine complex:K-15 showed approximately 97-98% of NCO conversion which showed that the polymerization reactions were completed. The amount of water = 4 pbw provides higher foam density than the amount of water = 5 pbw because of the increasing in CO_2 amount. Moreover, The amount of water = 4 pbw provides higher PIR:PUR ratio than the amount of water = 5 pbw. PIR foams catalyzed by metal complex:K-15 showed the order of PIR:PUR ratio as follow: $Cu(OAc)_2$(trien):K-15 > $Cu(OAc)_2$ $(en)_2$:K-15 > DMCHA:K-15. Moreover, as NCO index increased, the PIR:PUR ratio also increased. All of PIR foams have PIR:PUR ratio > 1. Therefore, this result indicates that copper-amine complex:K-15 is a suitable catalyst for PIR foam preparation.

Table 4.5 NCO conversion of PIR foams catalyzed by copper-amine complex:K-15 at mole ratio = 0.5:3.0

catalysts	H_2O (pbw)	NCO index	NCO conversion (%)	PIR:PUR
$Cu(OAc)_2(en)_2$:K-15	4	250	97.8	2.31
	5	200	97.0	1.78
		250	97.7	2.21
$Cu(OAc)_2$(trien):K-15	4	250	97.4	2.44
	5	200	97.3	2.02
		250	97.4	2.25

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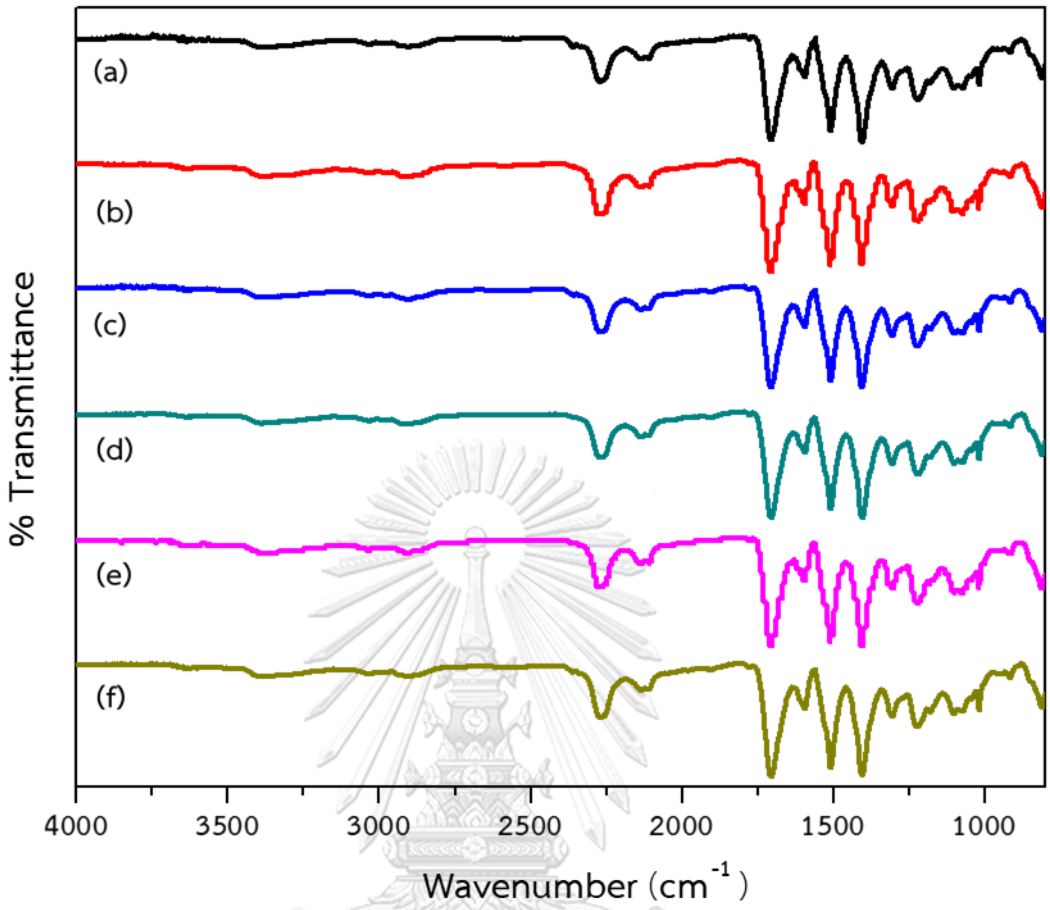

Figure 4.46 FTIR spectra of PIR foams catalyzed by copper-amine complex:K-15 at mole ratio = 0.5:3.0: (a) $Cu(OAc)_2(en)_2$:K-15 (water = 4 pbw and NCO index = 250), (b) $Cu(OAc)_2(en)_2$:K-15 (water = 5 pbw and NCO index = 200), (c) $Cu(OAc)_2(en)_2$:K-15 (water = 5 pbw and NCO index = 250), (d) $Cu(OAc)_2$ trien):K-15 (water = 4 pbw and NCO index = 250), (e) $Cu(OAc)_2$(trien):K-15 (water = 5 pbw and NCO index = 200) and (f) $Cu(OAc)_2$(trien):K-15 (water = 5 pbw and NCO index = 250)

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4.3.1.2.4 NCO conversion of PIR foams catalyzed by metal-ethanolamine complex

From Table 4.6 and Figure 4.47, it is found that PIR foams catalyzed by metal-ethanolamine complex:K-15 gave approximately 96-98% of NCO conversion which showed the polymerization reactions were completed. When NCO index was increased, the PIR:PUR ratio also increased. The order of PIR:PUR ratio is $Zn(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2(EA)_2$:K-15 > DMCHA:K-15 Because, DMCHA gave more urethane bond than $Zn(OAc)_2$ $(EA)_2$ and $Cu(OAc)_2(EA)_2$ while K-15 gave similar isocyanurate bond. All of PIR foams have PIR:PUR ratio > 1. Therefore, this result indicates that copper-amine complex:K-15 is a suitable catalyst for PIR foam preparation.

Table 4.6 NCO conversion of PIR foams catalyzed by metal-ethanolamine complex at mole ratio = 0.5:3.0

catalysts	H_2O (pbw)	NCO index	NCO conversion (%)	PIR:PUR
$Cu(OAc)_2(EA)_2$:K-15	5	200	97.5	1.52
		250	96.6	2.12
$Zn(OAc)_2(EA)_2$:K-15	5	200	98.0	1.59
		250	97.2	2.23

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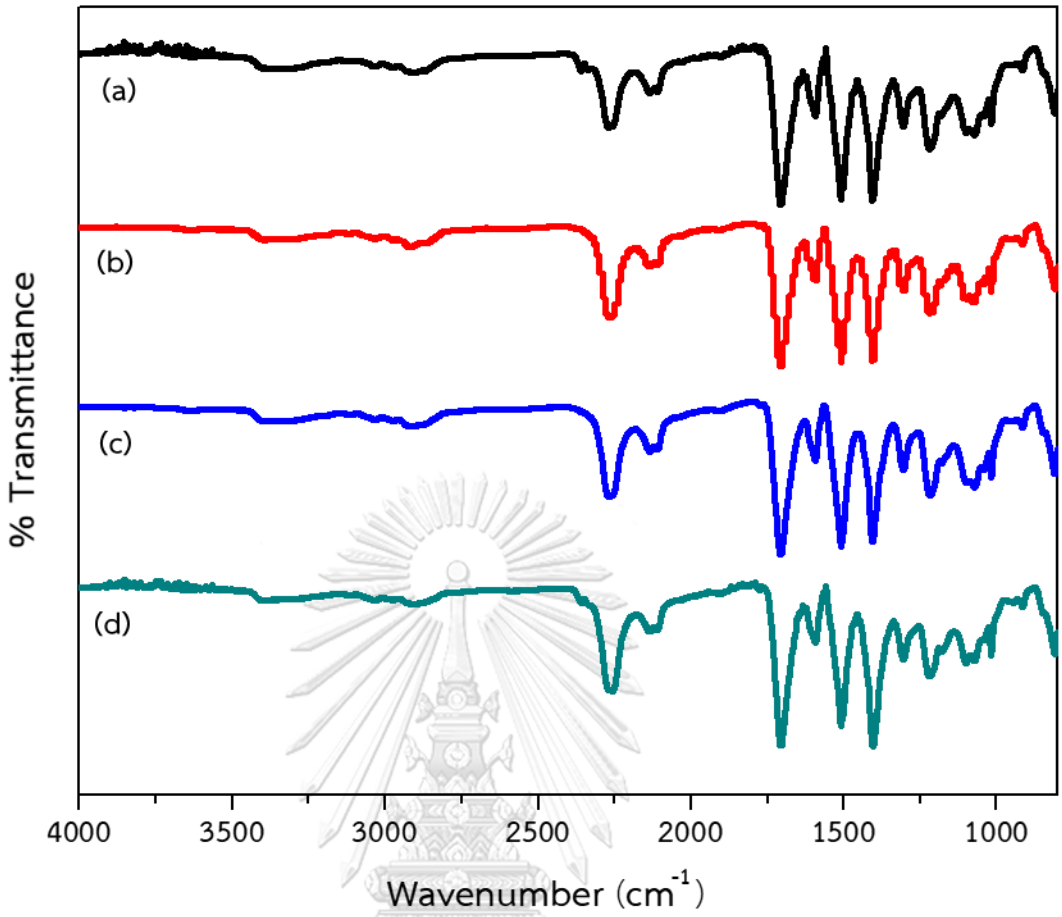

Figure 4.47 FTIR spectra of PIR foams catalyzed by metal-ethanolamine complex:K-15 at mole ratio = 0.5:3.0: (a) $Cu(OAc)_2(EA)_2$:K-15 (water = 5 pbw and NCO index = 200), (b) $Cu(OAc)_2(EA)_2$:K-15 (water = 5 pbw and NCO index = 250), (c) $Zn(OAc)_2(EA)_2$:K-15 (water = 5 pbw and NCO index = 200) and (d) $Zn(OAc)_2(EA)_2$:K-15 (water = 5 pbw and NCO index = 250)

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4.3.1.3 Rise profile

From Figures 4.48-4.49, rise profile of PIR foams at NCO index = 200 and 250 show that the order of catalyst activity in blowing reaction is DMCHA:K-15 > $Zn(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2$(trien):K-15 > $Cu(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2(en)_2$:K-15. This result agrees with the rise time (Tables 4.1-4.3). However, the order of foam height is DMCHA:K-15 > $Zn(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2$(trien):K-15 > $Cu(OAc)_2(en)_2$:K-15. This can be indicated that $Zn(OAc)_2(EA)_2$:K-15 had higher activity in blowing reaction than $Cu(OAc)_2(EA)_2$:K-15 and copper-amine complex:K-15. Because $Zn(OAc)_2(EA)_2$ has similar foam height and shorter rise time than DMCHA:K-15.

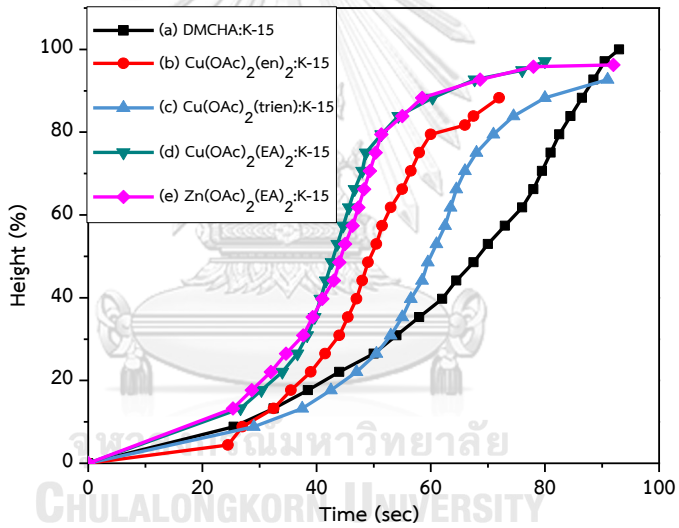

Figure 4.48 Rise profiles of PIR foams prepared at the mole ratio of 0.5:3.0, NCO index = 200, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15 (100% height), (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

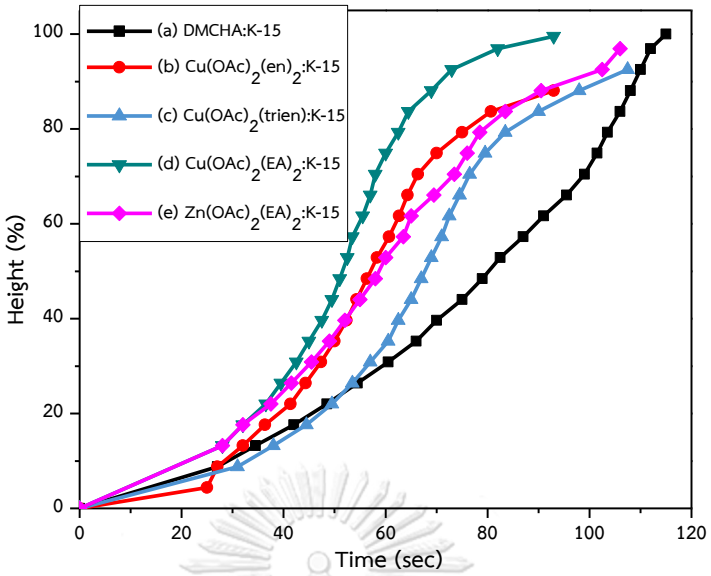

Figure 4.49 Rise profiles of PIR foams prepared at the mole ratio of 0.5:3.0, NCO index = 250, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15 (100% height), (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

4.3.1.4 Temperature profile

From Figures 4.50-4.51, temperature profile of PIR foams catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15 are investigated and compared with the PIR foam catalyzed by DMCHA:K-15 at NCO index = 200 and 250, respectively. The results show that all PIR foams were carried out under exothermic foaming reaction. PIR foam at NCO index = 200 and 250 had similar trend of temperature profiles. Therefore, the increasing of core temperature indicated a good catalytic activity. The order of maximum reaction temperature was DMCHA:K-15 > $Cu(OAc)_2(EA)_2$:K-15 > $Zn(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2(en)_2$:K-15 = $Cu(OAc)_2$(trien):K-15. The maximum core temperature was in the range of 126-142 °C. This value was suitable for polymerization of PIR foam because the foam did not decompose at this temperature rang.

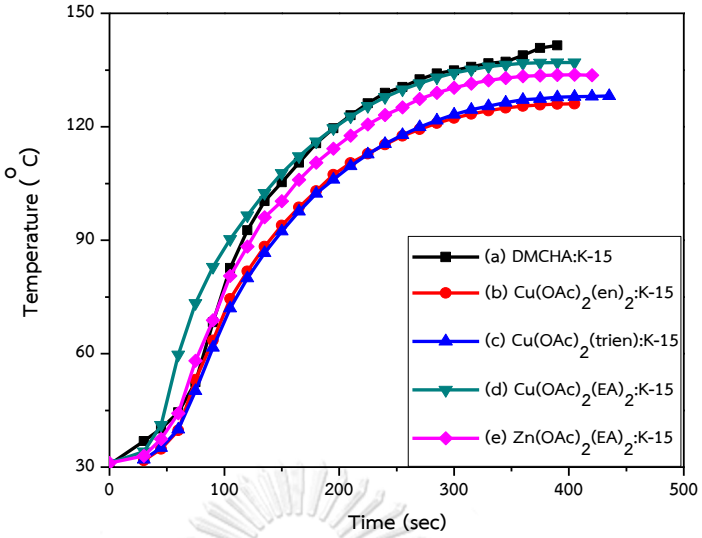

Figure 4.50 Temperature profiles of PIR foams prepared at the mole ratio of 0.5:3.0, NCO index = 200, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15, (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

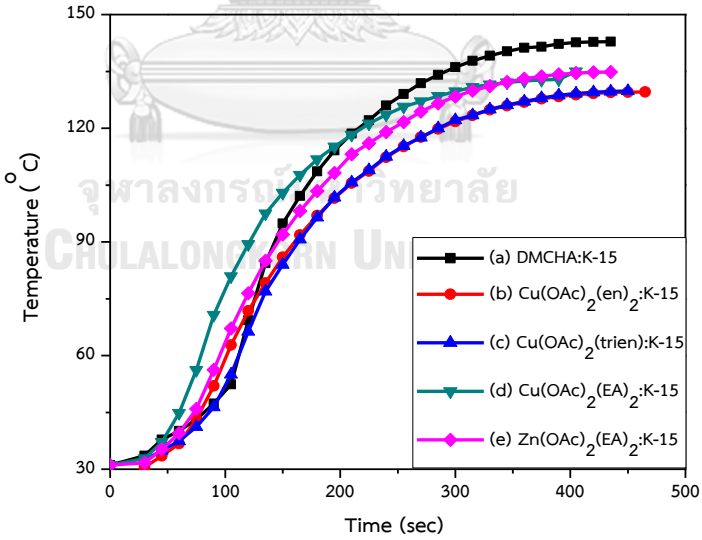

Figure 4.51 Temperature profiles of PIR foams prepared at the mole ratio of 0.5:3.0, NCO index = 200, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15, (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

4.3.1.5 PIR foam morphology

Morphology of PIR foams catalyzed by $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien) :K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 at NCO index = 200 and 250 in parallel and perpendicular direction to the foam rising direction are shown in Figures 4.60-4.67 which were investigated and compared with PIR foam catalyzed by DMCHA:K-15 (Figures 4.58-4.59). It was found that all PIR foams was mainly closed cell foam structure. The cell morphology showed the spherical shape in parallel direction and ellipsoidal shape in perpendicular direction. The cell in perpendicular direction has ellipsoidal shape because of the CO_2 rise and expansion along with the foam rising direction. The average cell sizes of PIR foams catalyzed by DMCHA:K-15, $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 are shown in Tables 4.7 and 4.8 which were determined by the image analysis as shown Figure 4.68. The cell size of spherical cell and ellipsoidal cell were measured from cell-w and cell-h.

From the SEM micrographs in top view, it was found that cell size of PIR foams catalyzed by $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 was smaller than PIR foam catalyzed by DMCHA:K-15. However, the cell size of PIR foam catalyzed by $Cu(OAc)_2(en)_2$:K-15 was larger than PIR foam catalyzed by DMCHA:K-15 at NCO index = 250 which might be affected by some error. From the SEM micrographs in side view, it was found that cell size of PIR foams catalyzed by $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 was smaller than PIR foam catalyzed by DMCHA:K-15. However, PIR foams (Cell size-h) size at NCO index = 250 was larger than cell size of PIR foam catalyzed by DMCHA:K-15. PIR foam at NCO index = 200 was smaller than NCO index =250.

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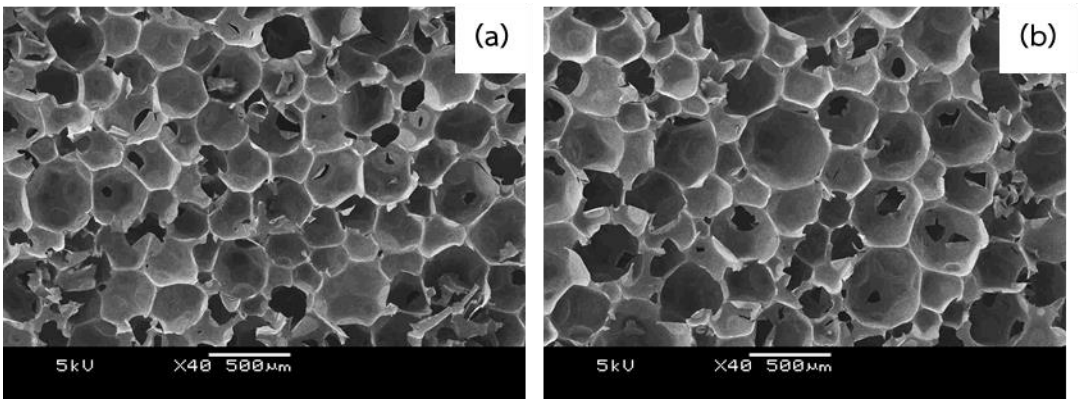

Figure 4.52 SEM of PIR foam catalyzed by DMCHA:K-15 at NCO = 200 (a) top view, and (b) side view (40x)

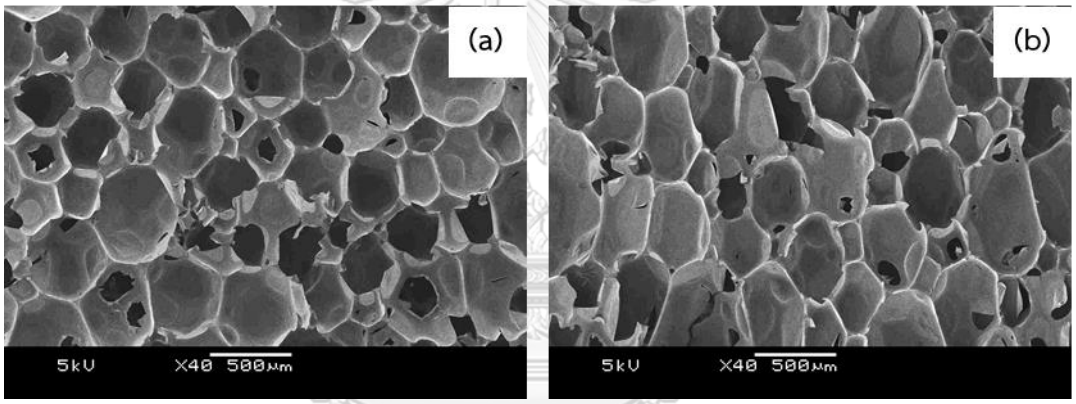

Figure 4.53 SEM of PIR foam catalyzed by DMCHA:K-15 at NCO = 250 (a) top view and (b) side view (40x)

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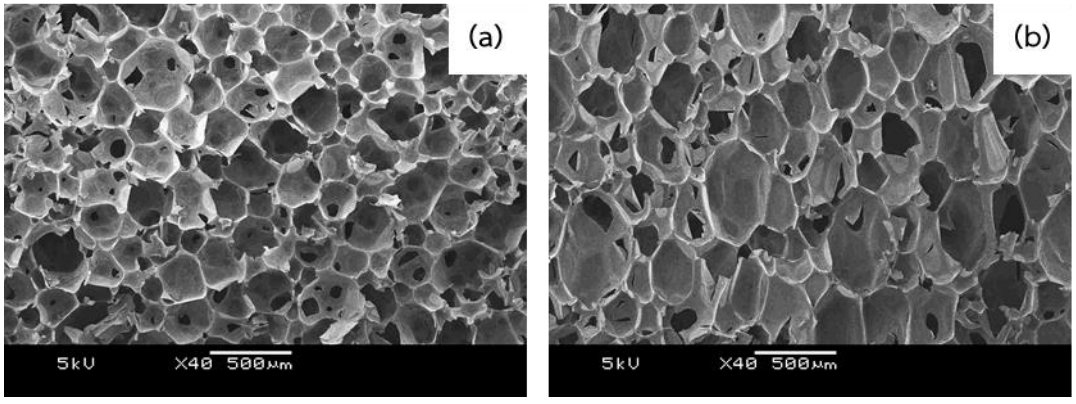

Figure 4.54 SEM of PIR foam catalyzed by $Cu(OAc)_2(en)_2$:K-15 at NCO = 200 (a) top view and (b) side view (40x)

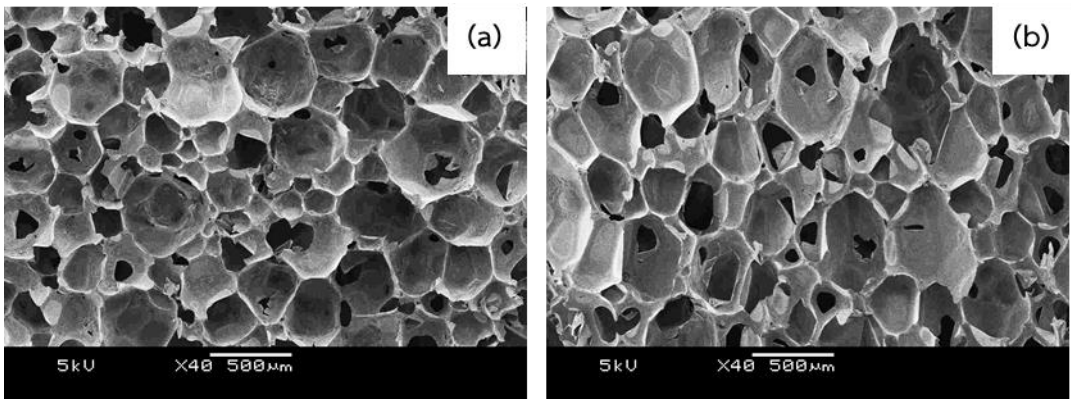

Figure 4.55 SEM of PIR foam catalyzed by $Cu(OAc)_2(en)_2$:K-15 at NCO = 250 (a) top view and (b) side view (40x)

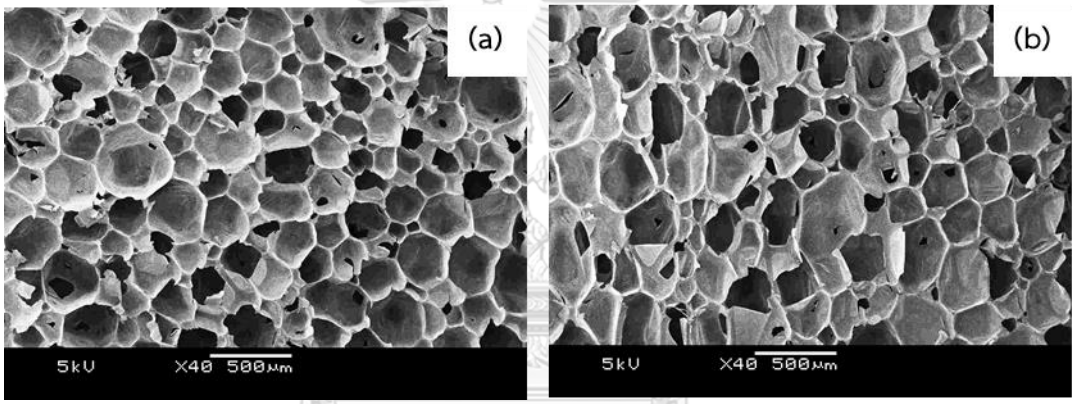

Figure 4.56 SEM of PIR foam catalyzed by $Cu(OAc)_2$(trien):K-15 at NCO = 200 (a) top view and (b) side view (40x)

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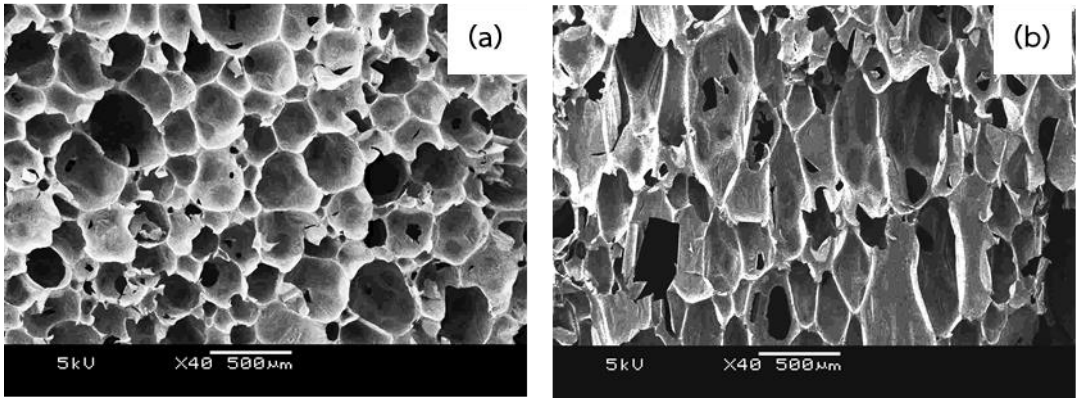

Figure 4.57 SEM of PIR foam catalyzed by $Cu(OAc)_2$(trien):K-15 at NCO = 250 (a) top view and (b) side view (40x)

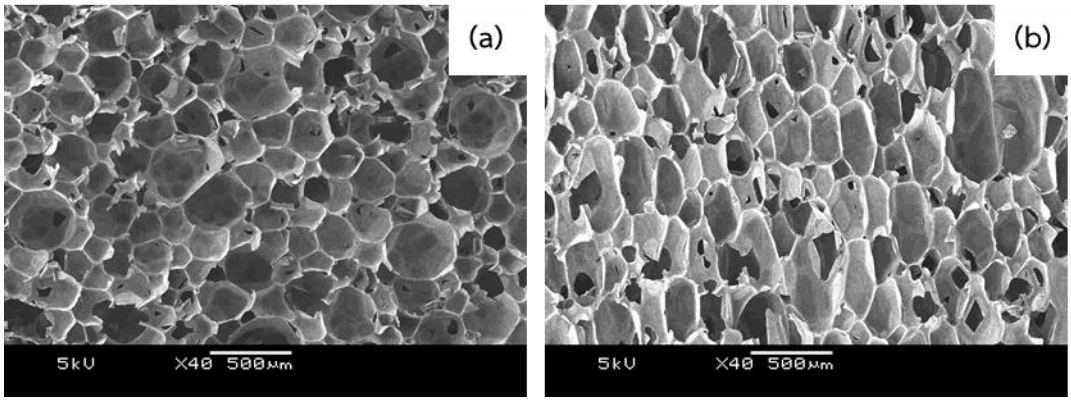

Figure 4.58 SEM of PIR foam catalyzed by $Cu(OAc)_2(EA)_2$:K-15 at NCO = 200 (a) top view and (b) side view (40x)

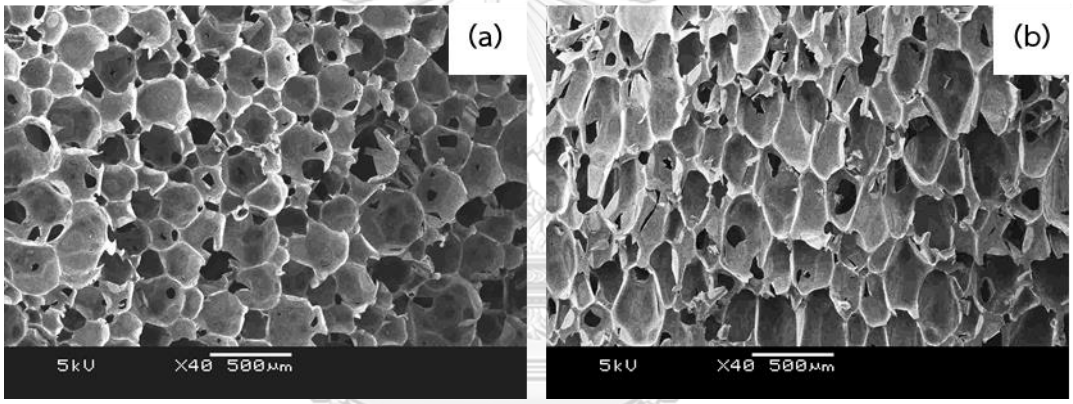

Figure 4.59 SEM of PIR foam catalyzed by $Cu(OAc)_2(EA)_2$:K-15 at NCO = 250 (a) top view and (b) side view (40x)

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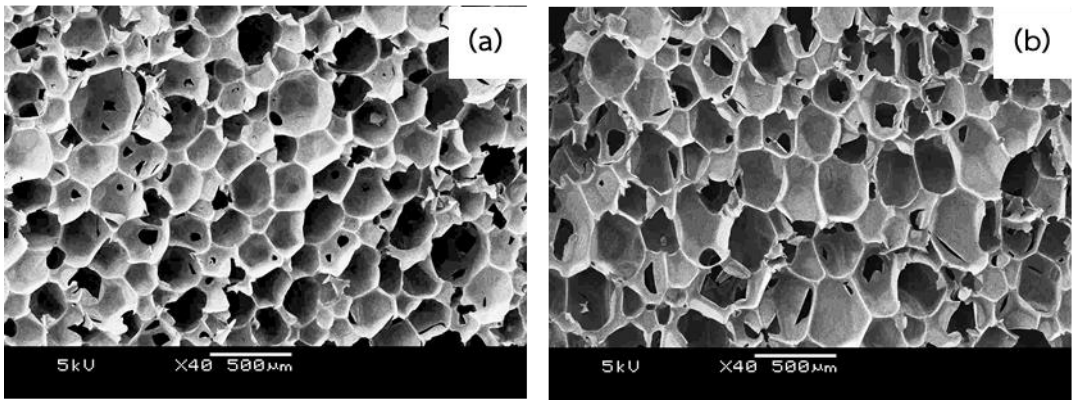

Figure 4.60 SEM of PIR foam catalyzed by $Zn(OAc)_2(EA)_2$:K-15 at NCO = 200 (a) top view and (b) side view (40x)

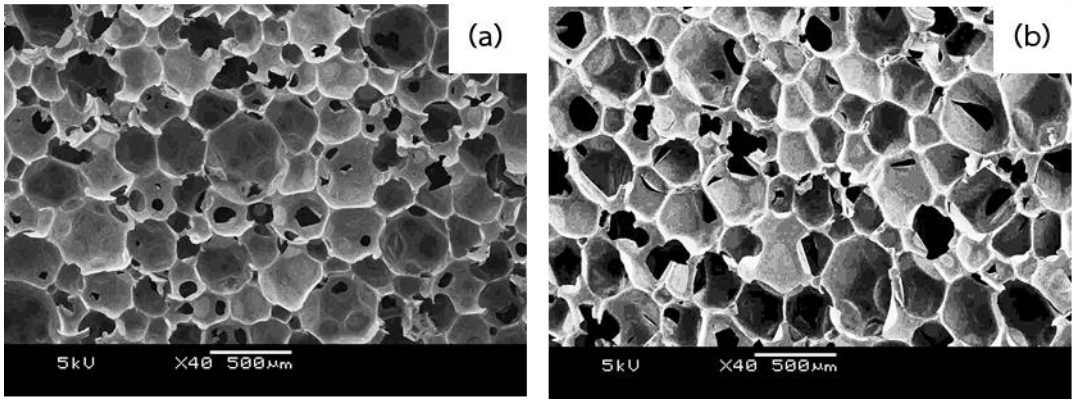

Figure 4.61 SEM of PIR foam catalyzed by $Zn(OAc)_2(EA)_2$:K-15 at NCO = 250 (a) top view and (b) side view (40x)

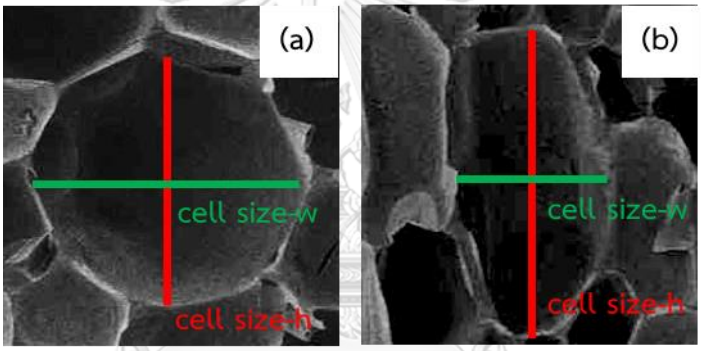

Figure 4.62 Measurement of cell size of PIR foam (a) Top view and (b) side view

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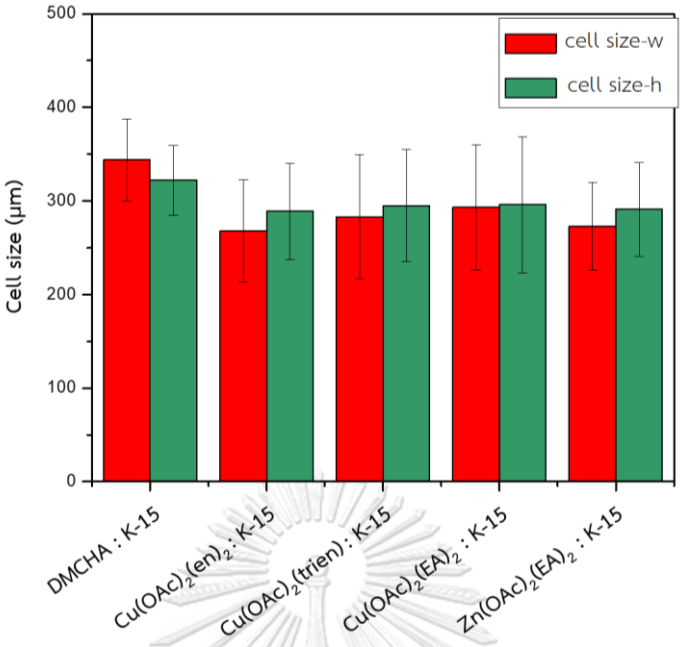

Figure 4.63 The cell size of PIR foams catalyzed by DMCHA:K-15, $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 at NCO index =200

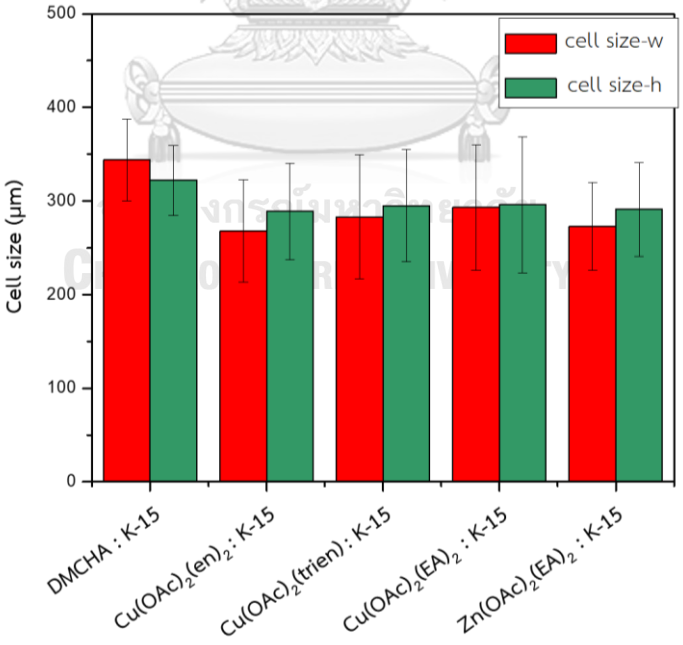

Figure 4.64 The cell size of PIR foams catalyzed by DMCHA:K-15, $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 at NCO index =200

4.3.2 Preparation of PIR foams by molded method

In molded method, PIR foam was used to investigate the compressive properties.

4.3.2.1 Compressive strength testing

The compression stress-strain curves of PIR foams in perpendicular and parallel direction was studied the foam rising direction, were catalyzed by DMCHA:K-15, $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 at NCO index = 200 and 250, as shown in Figures 4.52-4.57. The results supposed that compressive strength was decreased with increasing of NCO index. PIR foams in perpendicular direction had higher compressive strength than PIR foams in parallel direction. In addition, the compressive strength was affected by density and reaction time. The order of compressive strength of PIR foams prepared by different catalysts was DMCHA:K-15 > $Cu(OAc)_2(en)_2$:K-15 > $Cu(OAc)_2$(trien):K-15 > $Zn(OAc)_2(EA)_2$:K-15 > $Cu(OAc)_2(EA)_2$:K-15. Because, $Cu(OAc)_2(en)_2$:K-15 and $Cu(OAc)_2$ (trien):K-15 have higher density than $Zn(OAc)_2$ $(EA)_2$:K-15 and $Cu(OAc)_2(EA)_2$:K-15. Moreover, DMCHA:K-15 has the slowest reaction time might provide more crosslinking than other catalysts. However, at NCO index = 250, the data of $Cu(OAc)_2$(trien):K-15 in perpendicular direction and $Cu(OAc)_2$(trien):K-15 in parallel direction might be affected by some error.

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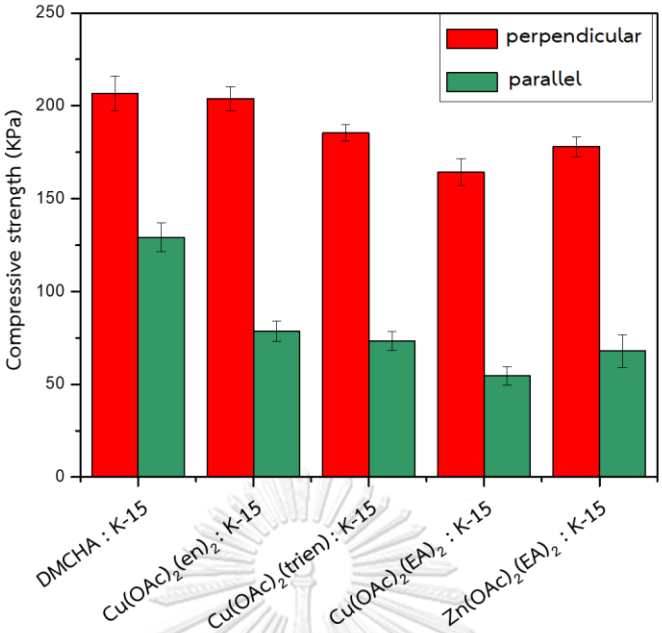

Figure 4.65 Comparison of compressive strength of PIR foams in perpendicular and parallel direction of foam rising at NCO index = 200

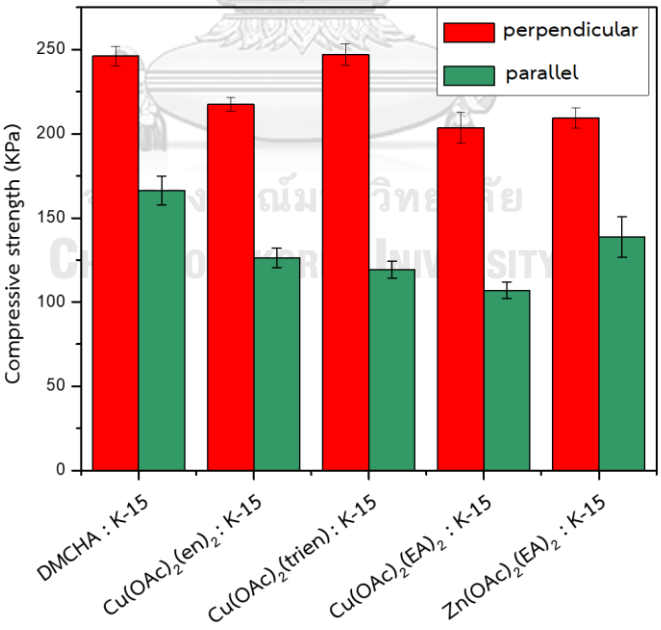

Figure 4.66 Comparison of compressive strength of PIR foams in perpendicular and parallel direction of foam rising at NCO index = 250

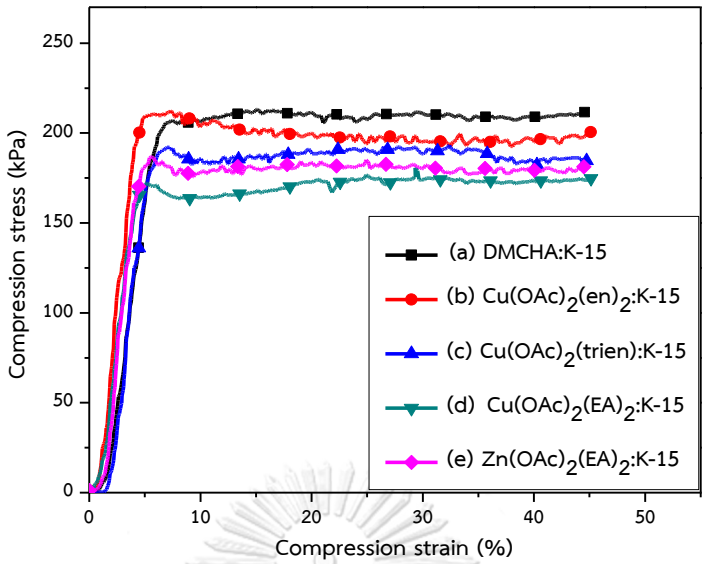

Figure 4.67 Compression stress-strain curves of PIR foams in perpendicular to the foam rising direction at the mole ratio of 0.5:3.0, NCO index = 200, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15, (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

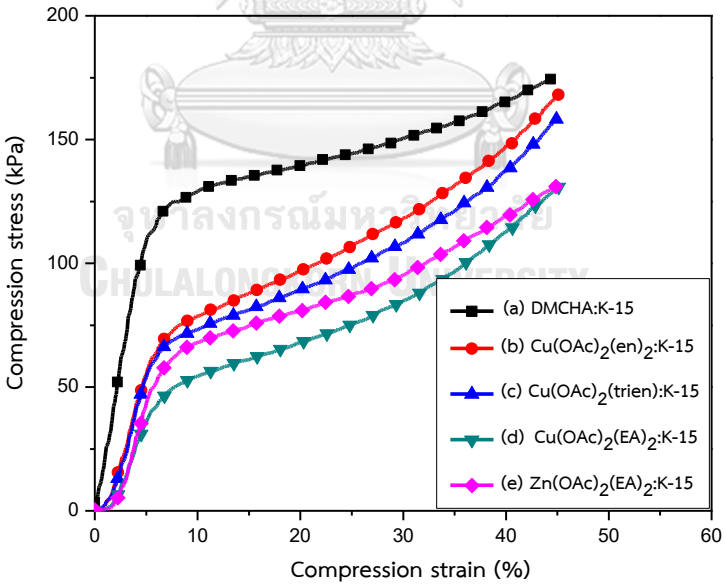

Figure 4.68 Compression stress-strain curves of PIR foams in parallel to the foam rising direction at the mole ratio of 0.5:3.0, NCO index = 200, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15, (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$ (trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

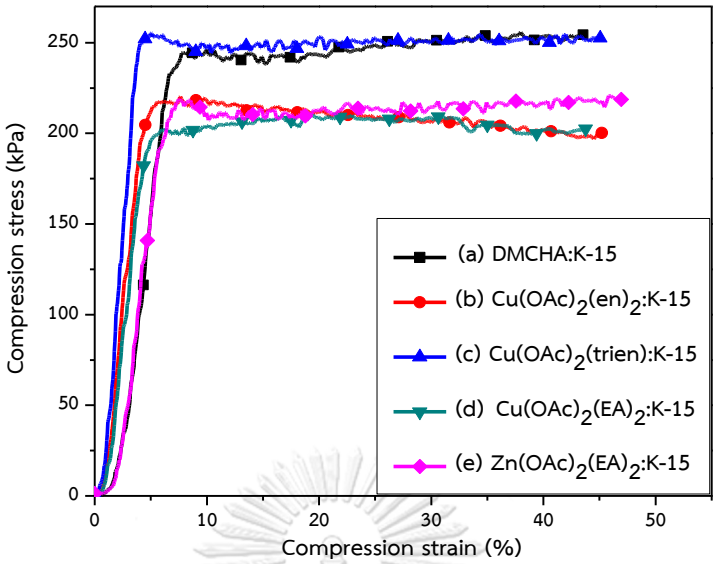

Figure 4.69 Compression stress-strain curves of PIR foams in perpendicular to the foam rising direction at the mole ratio of 0.5:3.0, NCO index = 250, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15, (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien):K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

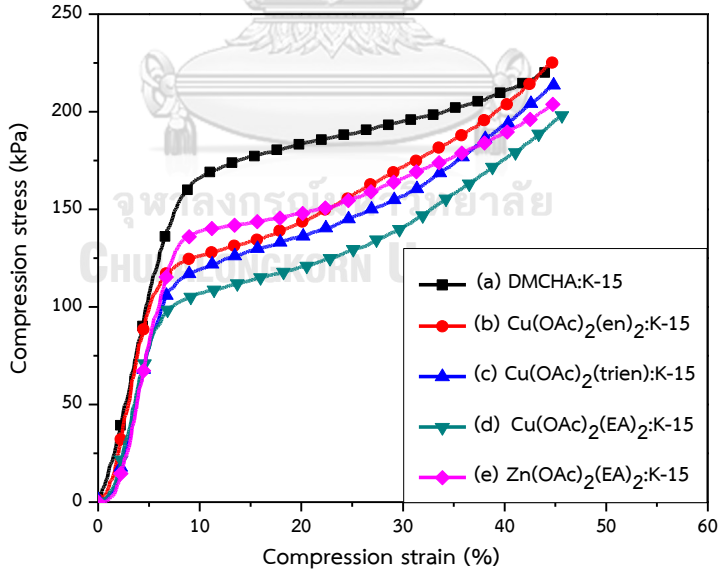

Figure 4.70 Compression stress-strain curves of PIR foams in parallel to the foam rising direction at the mole ratio of 0.5:3.0, NCO index = 250, H_2O = 5 pbw and catalyzed by (a) DMCHA:K-15, (b) $Cu(OAc)_2(en)_2$:K-15, (c) $Cu(OAc)_2$(trien) :K-15, (d) $Cu(OAc)_2(EA)_2$:K-15 and (e) $Zn(OAc)_2(EA)_2$:K-15

CHAPTER V

CONCLUSION

5.1 Conclusion

Copper-amine complexes, known as $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2$(trien) have been successfully synthesized in an aqueous solution. Whereas metal-ethanolamine complexes, $Cu(OAc)_2(EA)_2$ and $Zn(OAc)_2(EA)_2$ have been synthesized in ethylene glycol. Both copper-amine complexes and metal-ethanolamine complexes could be performed as catalyst with K-15. PIR foam catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15 were compared with those prepared by a commercial catalyst system, DMCHA:K-15. The results of absorption spectra confirmed the complex formation of copper-amine complexes and metal-ethanolamine complexes.

5.1.1 Effect of mole ratio of catalyst

In case of the mole ratios of commercial catalyst (DMCHA:K-15), it was found that the reaction times and foam density decreased with increasing the mole ratio of DMCHA:K-15. Base on the amount of blowing agent, it could be the amount of water level increased, density also decreased and the height of PIR foam increased because the amount of blowing agent = 5 pbw released more CO_2 than the amount of blowing agent at 3 pbw. Therefore, the ratio of DMCHA:K-15 = 0.5:3.0 and the amount of water = 5 were optimal ratio for preparation of PIR foam.

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5.1.2 Effect of metal complexes

In the reaction times, catalytic activity of copper-amine complex:K-15 and metal-ethanolamine complex:K-15 at mole ratio = 0.5:3.0 for preparation of PIR foam has been investigated. $Cu(OAc)_2(en)_2$:K-15 showed shorter reaction time than $Cu(OAc)_2$(trien):K-15 because $Cu(OAc)_2$(trien) has more steric hindrance than

$Cu(OAc)_2(en)_2$. Moreover, $Cu(OAc)_2(EA)_2$:K-15 showed shorter reaction time than $Zn(OAc)_2(EA)_2$:K-15 because $Cu(OAc)_2(EA)_2$ has a promising property of Lewis acid more than $Zn(OAc)_2(EA)_2$.

5.1.3 NCO conversion and PIR:PUR ratio

The NCO conversions were investigated by using FTIR spectroscopy. The PIR foams were catalyzed by DMCHA:K-15 provided in approximately 98-99% of NCO conversion improvement which are higher than PIR foams catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15. The mole ratio of DMCHA:K-15 = 0.5:3 gave the highest PIR:PUR ratio. Moreover, the NCO index values was proportional to the PIR:PUR ratio. PIR foams were catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15 showed the higher PIR:PUR ratio than PIR foams catalyzed by DMCHA:K-15. These PIR foam at PIR:PUR ratio of 1.47 (NCO index =200) and 2.11 (NCO index = 250). Therefore, the trimerization reaction including as isocyanurate group as a major reaction and blowing/gelling reaction which form urethane group as minor reaction. It could be suggested that copper-amine complex:K-15 and metal-ethanolamine complex:K-15 were served as promising catalysts for preparation of PIR foams.

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5.1.4 Rise profile

The rise profile of PIR foaming reaction catalyzed by $Zn(OAc)_2(EA)_2$:K-15 show the shorter rise time than $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and DMCHA:K-15. Moreover, it had a similar height as DMCHA:K-15. However, $Cu(OAc)_2(en)_2$:K-15 also had the shortest rise time because of steric hindrance effect.

5.1.5 Temperature profile

The reaction of PIR foam is exothermic. The temperature profile of PIR foam catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15 had similar trend to PIR foam catalyzed by DMCHA:K-15. The maximum core temperature during foaming reaction was exhibited in the range of 126.1-141.5 ^{o}C at NCO index = 200 and 129.6-142.5 ^{o}C at NCO index = 250. This value was suitable for polymerization of PIR foam because the foam did not decompose at this temperature range.

5.1.6 Morphology of PIR foams

The morphology of PIR foams indicated that the cell structure of PIR foams had main structure of closed cell foam. The size of PIR foam at NCO index = 200 was smaller than NCO index =250. PIR foams were catalyzed by DMCHA:K-15 had larger cell size than that catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15. The shapes of foam cells in perpendicular (top view) to the foam rising direction and parallel (side view) to the foam rising direction showed the spherical and ellipsoidal morphology, respectively.

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5.1.7 Compressive properties of PIR foams

The compressive properties of PIR foams catalyzed by copper-amine complex:K-15 and metal-ethanolamine complex:K-15 showed compressive strength value lower than that catalyzed by DMCHA:K-15 and PIR foam at NCO index = 250 show higher compressive strength than PIR foam at NCO index =200. The compressive strength in parallel to the foam rising direction are higher than that in perpendicular to the foam rising direction which show that PIR foams were anisotropic materials and had an ellipsoid cell shape.

According to the good behavior of catalysts, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 could be used for further application stead of commercial catalyst

as (DMCHA:K-15) under the condition of mole ratio = 0.5:3.0, the amount of water = 0.5 pbw at NCO index = 250

5.2 Suggestion for future work

The suggestion for future work is to apply this methodology to PIR foam. $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15 will be used as catalyst. Starch will be added to PIR foams to enhance their mechanical property.

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APPENDIX

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APPENDIX A

NCO index and NCO conversion calculations

NCO index calculation

For example Calculate the parts by weight (pbw) of PMDI (Raycore® B9001), molar mass = 365.8, functionality = 2.7 at NCO index = 200 and 250, the amount of H_2O = 5 pbw required to react with the following formulation:

Starting materials	Formulation (parts by weights, pbw)[a]	
	NCO index = 200	NCO index =250
Polyol (Polymaxx® 4221)	100.0	100
Surfactant (Tegostab® B8460)	2.5	2.5
Catalysts (DMCHA or copper-amine complex or metal-ethanolamine complex)	0.5	0.5
Catalyst (K-15)	0.3	0.3
Blowing agent (distilled water)	5.0	5.0
PMDI (Raycore® B9001)	?	?

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

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

Equivalent weight of diethylene glycol = $\frac{106.12}{2}$ = 53.06

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

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

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

Equivalent in the above formulation:

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

Water (blowing agent) = $\frac{5.0}{9.0}$ = 0.555

Diethylene glycol (solvent of K-15) = $\frac{0.9}{53.06}$ = 0.017

Ethylene glycol (solvent of metal-ethanolamine) = $\frac{0.4848}{31}$ = 0.016

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Ethanolamine (excessive solvent of copper-ethanolamine) = $\frac{0.1968}{30.5}$ = 0.006

Total equivalent weight (DMCHA or copper-amine complex:K-15) = 1.356

Total equivalent weight (copper-ethanolamine complex:K-15) = 1.378

Total equivalent weight (zinc-ethanolamine complex:K-15) = 1.380

For stoichiometric equivalence, PMDI pbw is total equivalent × equivalent weight because PMDI reacts with polyol, water, diethylene glycol, ethylene glycol and ethanolamine

$$\text{PMDI (pbw)} = \frac{\text{Total of equivalent} \times \text{molar mass}}{\text{functionality}}$$

PMDI of PIR foams catalyzed by DMCHA or copper-amine complex:K-15

$$= \frac{1.356 \times 365.8}{2.7} = 183.8$$

PMDI of PIR foams catalyzed by copper-ethanolamine complex:K-15

$$= \frac{1.378 \times 365.8}{2.7} = 186.8$$

PMDI of PIR foams catalyzed by copper-ethanolamine complex:K-15

$$= \frac{1.380 \times 365.8}{2.7} = 187.1$$

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Where;

$$\text{NCO index} = \frac{\text{Actual amount of isocyanate}}{\text{Theoretical amount of isocyanate}} \times 100$$

Therefore:

at Isocyanate index = 200;

Isocyanate actual (DMCHA or copper-amine complex:K-15)

$$= \frac{183.8}{100} \times 200 = 367.7 \text{ pbw}$$

Isocyanate actual (copper-ethanolamine complex:K-15)

$$= \frac{186.8}{100} \times 200 = 373.6 \text{ pbw}$$

Isocyanate actual (zinc-ethanolamine complex:K-15)

$$= \frac{187.1}{100} \times 200 = 374.2 \text{ pbw}$$

at Isocyanate index = 250;

Isocyanate actual (DMCHA or copper-amine complex:K-15)

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$$= \frac{183.8}{100} \times 250 = 459.6 \text{ pbw}$$

Isocyanate actual (copper-ethanolamine complex:K-15)

$$= \frac{186.8}{100} \times 250 = 467.0 \text{ pbw}$$

Isocyanate actual (zinc-ethanolamine complex:K-15)

$$= \frac{187.1}{100} \times 250 = 467.8 \text{ pbw}$$

Table A2 Foam formulation

Starting materials	Formulation (parts by weight, pbw)	
	NCO index = 200	NCO index = 250
Polyol (Polymaxx® 4221)	100.0	100
Surfactant (Tegostab® B8460)	2.5	2.5
Catalysts (DMCHA or copper-amine complex or metal-ethanolamine complex)	0.5	0.5
Catalyst (K-15)	0.3	0.3
Blowing agent (distilled water)	5.0	5.0
PMDI (Raycore® B9001)	367.7[a], 373.6[b], 374.2[c]	459.6[a], 467.0[b], 467.8[c]

[a]PIR foam catalyzed by DMCHA or copper-amine complex:K-15

[b]PIR foam catalyzed by copper-ethanolamine complex:K-15

[c]PIR foam catalyzed by zinc-ethanolamine complex:K-15

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NCO conversion calculation

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

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

where;

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

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

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

Table A3 Free NCO absorbance peak area in PMDI (Raycore® B9001) from IR-ATR

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

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Conversion of isocyanate (%)

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

NCO^i = 98.0

NCO^f = 0.1067

$$\alpha = [1 - (\frac{0.1067}{98.0})] \times 100 = 99.9$$

Table A4 NCO conversion of PIR foams catalyzed by DMCHA:K-15

Mole ratios of DMCHA: K-15	H_2O (pbw)	NCO index	Peak area				NCO conversion (%)	PIR / PUR
			NCO 2272 cm^{-1}	ArH 1595 cm^{-1}	PIR 1413 cm^{-1}	PUR 1221 cm^{-1}		
0.5:2.0	3	160	0.583	2.362	4.721	5.231	99.7	0.90
		200	0.678	2.027	6.618	5.337	99.7	1.24
		250	6.854	1.700	6.997	4.137	95.9	1.69
	4	160	1.531	2.020	4.409	5.465	99.2	0.81
		200	0.969	1.771	5.689	4.757	99.4	1.20
		250	3.227	1.781	7.365	4.321	98.2	1.70
	5	160	1.791	2.000	3.804	5.051	99.1	0.75
		200	1.383	1.938	5.805	4.958	99.3	1.17
		250	4.555	1.842	7.185	4.176	97.5	1.72
0.5:2.5	3	160	0.403	2.394	4.723	4.961	99.8	0.95
		200	0.376	1.175	5.594	4.415	99.7	1.27
		250	0.888	1.987	8.076	4.242	99.5	1.90
	4	160	0.632	2.059	4.793	5.505	99.7	0.87
		200	0.699	1.928	5.782	4.691	99.6	1.23
		250	1.317	1.895	6.678	3.780	99.3	1.77
	5	160	0.765	1.846	4.195	4.519	99.6	0.93
		200	1.215	1.906	6.022	4.342	99.3	1.39
		250	1.431	1.857	7.503	3.920	99.2	1.91

Table A4 (Continued)

Mole ratios of DMCHA: K-15	H_2O (pbw)	NCO index	Peak area				NCO conversion (%)	PIR:PUR
			NCO 2272 cm^{-1}	ArH 1595 cm^{-1}	PIR 1413 cm^{-1}	PUR 1221 cm^{-1}		
0.5:3.0	3	160	0.282	2.040	5.146	5.186	99.9	0.99
		200	0.555	1.870	6.310	4.418	99.7	1.43
		250	1.045	1.775	8.199	4.070	99.4	2.01
	4	160	1.020	1.938	4.980	4.868	99.5	1.02
		200	0.647	1.886	5.752	4.463	99.6	1.29
		250	2.691	1.813	8.363	4.321	98.5	1.94
	5	160	1.254	1.461	4.959	4.737	99.1	1.05
		200	0.926	1.741	6.374	4.341	99.5	1.47
		250	3.556	1.913	7.953	3.772	98.1	2.11

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Table A5 NCO conversion of of PIR foams catalyzed by various types of catalysts:K-15 at mole ratio = 0.5:3.0

Catalyst	H_2O (pbw)	NCO index	Peak area				NCO conversion (%)	PIR:PUR
			NCO 2272 cm^{-1}	ArH 1595 cm^{-1}	PIR 1413 cm^{-1}	PUR 1221 cm^{-1}		
$Cu(OAc)_2(en)_2$:K-15	4	250	3.719	1.763	8.172	3.532	97.8	2.31
	5	200	5.255	1.812	7.295	4.108	97.0	1.78
		250	3.858	1.673	7.601	3.446	97.6	2.21
$Cu(OAc)_2(trien)$:K-15	4	250	4.864	1.894	8.693	3.572	97.4	2.43
	5	200	4.386	1.654	7.672	3.799	97.3	2.02
		250	4.924	1.922	8.602	3.815	97.4	2.25
$Cu(OAc)_2(EA)_2$:K-15	5	200	4.063	1.684	6.167	4.0	97.5	1.52
		250	6.064	1.796	8.254	3.895	96.6	2.12
$Zn(OAc)_2(EA)_2$:K-15	5	200	3.468	1.736	6.606	4.165	98.0	1.59
		250	4.136	1.506	6.805	3.045	97.2	2.23

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APPENDIX B

Reaction time

Table B1 Reaction time of PIR foams catalyzed by DMCHA:K-15

Mole ratios of DMCHA: K-15	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free time (sec)	Rise time (sec)	Density (kg/m^3)	Height (cm)
0.5:2.0	3	160	26±0	39±0	109±2	81±2	43.5±0.1	16.0±0.2
		200	30±0	43±1	125±2	95±1	54.1±0.7	15.4±0.1
		250	36±0	58±1	160±2	125±2	61.4±1.4	15.5±0.1
	4	160	25±0	39±0	130±3	103±2	38.5±0.5	18.9±0.1
		200	29±0	45±1	148±1	118±3	45.0±0.5	18.5±0.0
		250	33±0	52±1	190±2	130±2	53.1±0.4	18.9±0.1
	5	160	24±0	37±1	133±2	99±2	35.0±0.2	21.1±0.1
		200	30±0	46±1	151±2	120±3	40.6±0.3	21.1±0.1
		250	34±1	55±1	181±3	144±3	48.6±0.5	21.4±0.1
0.5:2.5	3	160	23±1	37±0	106±1	79±3	45.9±0.5	15.2±0.1
		200	29±0	43±1	111±2	89±2	53.0±0.4	15.1±0.1
		250	32±1	49±1	140±2	103±2	62.6±1.0	15.5±0.1
	4	160	23±0	38±1	114±2	82±2	37.6±0.6	18.8±0.1
		200	27±0	42±1	132±3	98±1	43.1±0.4	19.3±0.1
		250	32±0	43±0	143±2	111±3	50.2±0.2	19.9±0.2

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Table B1 (Continued)

Mole ratios of DMCHA: K-15	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free time (sec)	Rise time (sec)	Density (kg/m^3)	Height (cm)
0.5:2.5	5	160	23±0	34±0	117±2	88±3	33.2±0.2	21.5±0.1
		200	28±1	45±1	142±3	103±2	39.0±0.2	21.8±0.1
		250	33±1	53±0	175±3	129±3	48.8±0.2	21.5±0.2
0.5:3.0	3	160	23±0	33±1	88±2	67±3	43.6±1.6	15.5±0.1
		200	26±0	38±2	101±4	80±2	51.2±0.8	15.7±0.1
		250	29±0	41±0	110±3	87±2	61.3±0.8	15.7±0.1
	4	160	25±0	33±1	101±3	74±3	36.4±0.2	19.5±0.2
		200	28±0	40±0	119±4	92±3	41.0±0.2	20.1±0.2
		250	32±1	49±1	132±3	103±1	51.6±0.4	19.6±0.2
	5	160	23±0	30±2	101±3	73±2	32.9±0.2	21.4±0.1
		200	26±0	42±2	130±1	93±3	39.0±0.0	22.0±0.2
		250	29±1	45±0	154±2	113±2	43.2±0.2	23.7±0.6

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Table B2 Reaction time of PIR foams catalyzed by various types of catalysts:K-15 at mole ratio = 0.5 :3.0

catalyst	H_2O (pbw)	NCO index	Cream time (sec)	Gel time (sec)	Tack free (sec)	Rise time (sec)	Density (kg/m^3)	Height (cm)
$Cu(OAc)_2(en)_2$:K-15	4	250	29±1	45±0	80±3	100±4	62.9±0.3	16.8±0.1
	5	200	30±0	45±2	60±2	75±3	47.8±0.3	17±0.1
		250	32±0	45±1	85±3	93±2	53.5±0.3	19.9±.2
$Cu(OAc)_2$(trien):K-15	4	250	36±1	55±1	94±5	101±4	62.9±0.3	17.1±0.1
	5	200	35±0	52±1	84±3	91±4	47.8±0.3	17.9±0.1
		250	36±0	55±1	98±3	107±3	53.5±0.3	20.0±0.1
$Cu(OAc)_2(EA)_2$:K-15	5	200	27±1	39±3	58±3	80±3	60.7±0.7	21.9±0.2
		250	31±1	43±2	82±4	95±2	48.2±0.4	21.5±0.1
$Zn(OAc)_2(EA)_2$:K-15	5	200	25±0	43±0	72±2	93±3	54.2±0.3	20.6±0.1
		250	30±0	50±1	83±4	107±4	60.7±0.7	20.3±0.2

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APPENDIX C

Rise profiles

Table C1 Rise profiles of PIR foams catalyzed by various types of catalysts:K-15 at mole ratio = 0.5 :3.0 , water = 5 pbw and NCO index =200

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)
0	0.0	0	0.0	0	0.0	0.0	0.0	0.0	0.0
26	8.8	25	4.4	29	8.8	27	13.2	25	13.2
32	13.2	27	8.8	38	13.2	31	17.7	29	17.7
38	17.7	32	13.2	43	17.7	34	22.1	32	22.1
44	22.1	35	17.7	47	22.1	37	26.5	35	26.5
50	26.5	39	22.1	51	26.5	38	30.9	38	30.9
54	30.9	42	26.5	53	30.9	40	35.3	39	35.3
58	35.3	44	30.9	55	35.3	41	39.7	41	39.7
62	39.7	46	35.3	57	39.7	42	44.2	43	44.2
64	44.2	47	39.7	58	44.2	43	48.6	44	48.6
68	48.6	48	44.2	60	48.6	44	53.0	45	53.0
70	53.0	49	48.6	61	53.0	45	57.4	46	57.4
73	57.4	50	53.0	62	57.4	46	61.8	47	61.8
76	61.8	51	57.4	64	61.8	47	66.2	48	66.2
78	66.2	53	61.8	64	66.2	48	70.6	49	70.6

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Table C1 (continued)

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)
80	70.6	55	66.2	66	70.6	49	75.1	50	75.1
81	75.1	57	70.6	68	75.1	51	79.5	51	79.5
83	79.5	58	75.1	71	79.5	54	83.9	55	83.9
85	83.9	60	79.5	75	83.9	60	88.3	59	88.3
87	88.3	66	81.7	80	88.3	68	92.7	69	92.7
89	92.7	68	83.9	91	92.7	76	94.9	78	95.8
91	97.1	72	88.3	-	-	80	97.1	88	96.2
93	100.0	-	-	-	-	-	-	-	-

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Table C2 Rise profiles of PIR foams catalyzed by various types of catalysts:K-15 at mole ratio = 0.5 :3.0 , water = 5 pbw and NCO index =250

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)
0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
27	8.8	25	4.4	31	8.8	28	13.2	28	13.2
35	13.2	27	8.8	38	13.2	32	17.6	32	17.6
42	17.6	32	13.2	45	17.6	37	22.0	38	22.0
49	22.0	36	17.6	50	22.0	40	26.4	42	26.4
55	26.4	41	22.0	54	26.4	43	30.8	46	30.8
61	30.8	44	26.4	57	30.8	45	35.2	49	35.2
66	35.2	47	30.8	61	35.2	48	39.6	52	39.6
70	39.6	50	35.2	63	39.6	50	44.1	55	44.1
75	44.1	52	39.6	65	44.1	51	48.5	58	48.5
79	48.5	54	44.1	67	48.5	53	52.9	60	52.9
83	52.9	56	48.5	69	52.9	54	57.3	64	57.3
87	57.3	58	52.9	71	57.3	56	61.7	65	61.7
91	61.7	61	57.3	73	61.7	57	66.1	70	66.1
96	66.1	63	61.7	75	66.1	58	70.5	74	70.5
99	70.5	64	66.1	77	70.5	60	74.9	76	74.9
102	74.9	66	70.5	80	74.9	63	79.3	79	79.3

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Table C2 (continued)

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)	Time (sec)	Height (%)
104	79.3	70	74.9	84	79.3	65	83.7	84	83.7
106	83.7	75	79.3	90	83.7	69	88.1	91	88.1
108	88.1	81	83.7	98	88.1	73	92.5	103	92.5
110	92.5	93	88.1	109	92.5	82	96.9	106	96.9
112	96.9	-	-	-	-	93	99.6	-	-
115	100.0	-	-	-	-	-	-	-	-

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APPENDIX D

Temperature profiles

Table D1 Temperature profiles of PIR foams catalyzed by various types of catalysts :K-15 at mole ratio = 0.5 :3.0 , water = 5 pbw and NCO index =200

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)
30	36.9	30	31.8	30	32.0	30	34.1	30	33.0
45	40.2	45	34.8	45	35.1	45	41.1	45	37.4
60	44.5	60	39.7	60	40.0	60	59.7	60	44.2
75	52.4	75	53.1	75	50.1	75	73.3	75	58.1
90	68.3	90	63.5	90	61.6	90	82.9	90	68.8
105	82.6	105	74.5	105	72.0	105	90.3	105	80.5
120	92.6	120	81.8	120	80.0	120	96.6	120	88.3
135	100.3	135	88.3	135	86.6	135	102.5	135	96.1
150	105.3	150	93.9	150	92.4	150	107.7	150	100.3
165	110.5	165	98.7	165	97.6	165	112.2	165	106.0
180	115.6	180	103.0	180	102.3	180	116.1	180	110.5
195	119.6	195	107.3	195	106.1	195	119.6	195	114.2
210	123.1	210	110.4	210	109.6	210	122.7	210	117.7
225	126.2	225	112.8	225	112.7	225	125.4	225	120.6
240	128.9	240	115.3	240	115.5	240	127.8	240	123.1

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Table D1 (continued)

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)
255	130.6	255	117.6	255	117.9	255	129.9	255	125.1
270	132.6	270	119.3	270	119.9	270	131.5	270	127.4
285	134.1	285	120.9	285	121.7	285	133.0	285	129.0
300	134.9	300	122.3	300	123.3	300	134.2	300	130.3
315	135.9	315	123.4	315	124.5	315	135.1	315	131.4
330	136.8	330	124.2	330	125.5	330	135.9	330	132.3
345	137.2	345	125.0	345	126.4	345	136.4	345	132.9
360	138.9	360	125.5	360	127.1	360	136.8	360	133.3
375	140.8	375	125.8	375	127.4	375	136.9	375	133.5
390	141.5	390	126.0	390	127.8	390	137.0	390	133.7
-	-	405	126.1	405	128.0	405	137.0	405	133.7
-	-	-	-	420	128.0	-	-	420	133.6
-	-	-	-	435	128.2	-	-	-	-

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Table D2 Temperature profiles of PIR foams catalyzed by various types of catalysts :K-15 at mole ratio = 0.5 :3.0 , water = 5 pbw and NCO index =250

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)
30	33.6	30	30.5	30	32.4	0	31.1	0	31.1
45	37.8	45	33.5	45	34.9	30	32.8	30	31.7
60	40.1	60	36.8	60	37.4	45	37.1	45	35.2
75	43.2	75	43.2	75	41.2	60	44.8	60	39.5
90	47.3	90	52.0	90	46.4	75	56.1	75	45.9
105	52.4	105	62.8	105	55.0	90	70.7	90	56.2
120	69.3	120	71.8	120	66.4	105	80.9	105	67.1
135	84.4	135	79.1	135	76.9	120	89.4	120	76.4
150	94.8	150	86.0	150	84.0	135	97.5	135	85.0
165	102.1	165	91.8	165	90.7	150	103.0	150	91.9
180	108.6	180	96.9	180	96.5	165	107.6	165	98.2
195	114.1	195	101.5	195	101.7	180	111.8	180	103.4
210	118.6	210	105.5	210	105.7	195	115.1	195	108.2
225	122.1	225	108.7	225	108.9	210	118.3	210	113.1
240	126.0	240	112.3	240	112.5	225	121.2	225	116.0
255	129.0	255	115.2	255	115.4	240	123.6	240	119.0
270	131.8	270	117.6	270	117.6	270	127.1	270	124.4

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Table D2 (continued)

DMCHA:K-15		$Cu(OAc)_2(en)_2$:K-15		$Cu(OAc)_2$(trien) :K-15		$Cu(OAc)_2(EA)_2$:K-15		$Zn(OAc)_2(EA)_2$:K-15	
Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)
285	134.1	285	119.8	285	120.0	285	128.5	285	126.5
300	136.1	300	121.8	300	122.2	300	129.7	300	128.3
315	137.8	315	123.4	315	123.4	315	130.8	315	129.9
330	139.2	330	124.9	330	125.0	330	131.5	330	131.1
345	140.3	345	125.9	345	126.2	345	132.1	345	132.2
360	141.2	360	126.9	360	127.1	360	132.5	360	133.1
375	141.5	375	127.7	375	127.9	375	132.7	375	133.7
390	142.3	390	128.4	390	128.7	390	132.9	390	134.2
405	142.7	405	128.8	405	129.2	405	135.0	405	134.5
420	142.8	420	129.2	420	129.5	-	-	420	134.7
435	142.9	435	129.4	435	129.7	-	-	435	134.8
-	-	450	129.5	450	129.8	-	-	-	-
-	-	465	129.6	-	-	-	-	-	-

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APPENDIX E

PIR foam morphology

Table E1 The cell size (top view) of PIR foams catalyzed by DMCHA:K-15, $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15

Catalyst Types	NCO index	Top view	
		Cell size-w (μm)	Cell size-h (μm)
DMCHA:K-15	200	344±43.56	322±37.33
	250	385±79.63	390±75.96
$Cu(OAc)_2(en)_2$:K-15	200	268±54.64	289±51.67
	250	436±77.41	445±72.33
$Cu(OAc)_2$(trien) :K-15	200	283±66.32	295±59.98
	250	307±71.05	333±62.16
$Cu(OAc)_2(EA)_2$:K-15	200	293±76.00	296±72.69
	250	277±51.43	305±48.20
$Zn(OAc)_2(EA)_2$:K-15	200	273±46.85	291±49.95
	250	341±65.70	346±66.27

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Table E2 The cell size (side view) of RPUR foams catalyzed by DMCHA:K-15, $Cu(OAc)_2(en)_2$:K-15, $Cu(OAc)_2$(trien):K-15, $Cu(OAc)_2(EA)_2$:K-15 and $Zn(OAc)_2(EA)_2$:K-15

Catalyst Types	NCO index	Side view	
		Cell size-w (μm)	Cell size-h (μm)
DMCHA:K-15	200	323±45.23	477±75.93
	250	348±67.69	398±70.34
$Cu(OAc)_2(en)_2$:K-15	200	243±51.15	387±74.29
	250	287±48.57	444±88.50
$Cu(OAc)_2$(trien): K-15	200	249±60.19	356±66.69
	250	224±55.67	569±177.28
$Cu(OAc)_2(EA)_2$:K-15	200	191±30.39	374±62.67
	250	228±45.10	466±84.91
$Zn(OAc)_2(EA)_2$:K-15	200	281±46.07	402±51.59
	250	314±72.27	414±80.89

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APPENDIX F

Compressive strength testing

Table F1 Comparison of compressive strength of PIR foams in perpendicular and parallel direction of foam rising at compression strain = 10% and NCO index = 200

Catalysts	Perpendicular (kPa)	Parallel (kPa)
DMCHA:K-15	206.65±9.33	129.16±7.69
$Cu(OAc)_2(en)_2$:K-15	203.89±6.55	78.59±5.36
$Cu(OAc)_2$(trien):K-15	185.49±4.53	73.24±5.12
$Cu(OAc)_2(EA)_2$:K-15	164.17±7.30	54.51±4.89
$Zn(OAc)_2(EA)_2$:K-15	177.92±5.43	67.91±8.77

Table F2 Comparison of compressive strength of PIR foams in perpendicular and parallel direction of foam rising at compression strain = 10% and NCO index = 250

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Catalysts	Perpendicular (kPa)	Parallel (kPa)
DMCHA:K-15	246.14±5.87	166.20±4.86
$Cu(OAc)_2(en)_2$:K-15	217.62±4.09	126.32±5.76
$Cu(OAc)_2$(trien):K-15	247.03±6.32	119.27±5.04
$Cu(OAc)_2(EA)_2$:K-15	203.45±8.96	107.02±4.98
$Zn(OAc)_2(EA)_2$:K-15	209.40±5.87	138.68±12.23

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