การเตรียมโฟมพอลิยูรีเทนแบบแข็งโดยใช้ตัวเร่งปฏิกิริยาที่เตรียมจากสารประกอบไนเทรตของโลหะและเอทิลีนไดแอมีน/ไตรเอทิลีนเททรามีน

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PREPARATION OF RIGID POLYURETHANE FOAMS USING CATALYSTS PRREPARED FROM METAL NITRATES AND ETHYLENEDIAMINE/TRIETHYLENETETRAMINE

Miss Piyachat Sirojpornphasut

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By	Miss Piyachat Sirojpornphasut
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Nuanphun Chantarasiri, Ph. D.

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

…………………………………………..… Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

…………………………………….…… Chairman
(Assistance Professor Tharapong Vitidsant, Ph. D.)

…………………………………………..… Thesis Advisor
(Associate Professor Nuanphun Chantarasiri, Ph. D.)

…………………………………………..… Examiner
(Associate Professor Mongkol Sukwattanasinitt, Ph. D.)

………………………………………….. External Examiner
(Duangruthai Sridaeng, Ph.D.)

ปิยฉัตร ศิโรตม์พรพศุตม์: การเตรียมโฟมพอลิยูรีเทนแบบแข็งโดยตัวเร่งปฏิกิริยา ที่เตรียมจากสารประกอบไนเทรตของโลหะและเอทิลีนไดแอมีน/ไตรเอทิลีนเตตระมีน (PREPARATION OF RIGID POLYURETHANE FOAMS USING CATALYSTS PREPARED FROM METAL NITRATES AND ETHYLENEDIAMINE/ TRIETHYLENETETRAMINE)
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ในงานวิจัยนี้ได้ทำการพัฒนาตัวเร่งปฏิกิริยา สำหรับเตรียมพอลิยูรีเทนโฟมแบบแข็ง โดยใช้สารประกอบเชิงซ้อนของโลหะชนิดต่างๆ [M(X)(en)$_2$ และ M(X)(trien) เมื่อ M = Cu, Ni, Co, Fe and Zn; X = $(NO_3)_2$, SO_4, $(Cl)_2$, CO_3; en = ethylenediamine and trien = triethylenetetramine), (M = Cu, Ni, Fe, Co และ Zn)] กับเอทิลีนไดแอมีนหรือไตรเอทิลีนเททรามีน เป็นตัวเร่งปฏิกิริยา โดยศึกษาเวลาในการเกิดปฏิกิริยาและลักษณะของโฟม พบว่า $Cu(NO_3)_2(en)_2$ และ $Cu(NO_3)_2$(trien) เป็นตัวเร่งปฏิกิริยาที่ดีกว่าตัวเร่งปฏิกิริยาที่เตรียมจากโลหะชนิดอื่นๆ ตัวเร่งปฏิกิริยาที่เตรียมขึ้นจะนำมาพิสูจน์เอกลักษณ์ด้วยเทคนิค อินฟราเรดสเปกโทรสโกปี อัลตราไวโอเลตและวิสิเบิลเปกโทรสโกปี แมสสเปกโทรเมตรี อะตอมมิกแอบซอร์พชันสเปกโทรสโกปี และการวิเคราะห์ธาตุ

ประสิทธิภาพของตัวเร่งปฏิกิริยาที่เตรียมจากสารประกอบเชิงซ้อนของโลหะกับเอมีนและสมบัติของพอลิยูรีเทนโฟมได้ถูกศึกษาและเปรียบเทียบกับไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA) ซึ่งเป็นตัวเร่งปฏิกิริยาอ้างอิงที่ใช้ทางการค้า โดยความหนาแน่นและความสามารถทนทานต่อแรงกดอัดของพอลิยูรีเทนโฟมที่เตรียมได้ขึ้นอยู่กับปริมาณของตัวเร่งปฏิกิริยาและปริมาณน้ำที่ใช้เป็นสารฟู พบว่าปริมาณของตัวเร่งปฏิกิริยาและปริมาณน้ำที่เหมาะสมคือ 1 และ 3 ส่วนโดยน้ำหนัก ตามลำดับ

ความสามารถทนทานต่อแรงกดอัดของพอลิยูรีเทนโฟมขึ้นกับความหนาแน่นของโฟม โดยความสามารถทนทานต่อแรงกดอัดของโฟมที่เร่งปฏิกิริยา โดย $Cu(NO_3)_2$(trien) มีค่าสูงกว่าโฟมที่เร่งปฏิกิริยาโดย $Cu(NO_3)_2(en)_2$ เนื่องจากโฟมที่เร่งปฏิกิริยาโดย $Cu(NO_3)_2$(trien) มีความหนาแน่นที่สูงกว่า

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
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PIYACHAT SIROJPORNPHASUT: PREPARATION OF RIGID POLYURETHANE FOAMS USING CATALYSTS PREPARED FROM METAL NITRATES AND ETHYLENEDIAMINE/ TRIETHYLENETETRAMINE. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph. D., 103 pp.

The development of catalysts for rigid polyurethane (RPUR) foam were investigated. Metal-amine complexes, [M(X)(en)$_2$ and M(X)(trien) where M = Cu, Ni, Co, Fe and Zn; X = $(NO_3)_2$, SO_4, $(Cl)_2$, CO_3; en = ethylenediamine and trien = triethylenetetramine], were synthesized and used as catalysts for preparation of RPUR foam. FTIR, UV-Vis spectroscopy, mass spectrometry, atomic absorption spectroscopy and elemental analysis were used to characterize these catalysts.

The reaction times of RPUR foams formation and foam appearance were investigated. The results indicated that $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2$(trien) had good catalytic activity when compare with other metal complexes. The catalytic activity of metal-amine complexes and properties of RPUR foams were investigated and compared to those prepared by commercial catalyst, N,N-dimethylcyclohexylamine (DMCHA). RPUR foams with different densities and compressive strength were prepared by varying the amount of catalysts and water which acted as a blowing agent. The optimum formulation of catalyst content and water content were 1 pbw and 3 pbw, respectively.

The compressive strength of RPUR foams varying with the density. The higher compressive strength of foam which catalyzed by $Cu(NO_3)_2$(trien) was due to higher foam density when compared with foam that catalyzed by $Cu(NO_3)_2(en)_2$.

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LIST OF ABBREVIATIONS

%	percentage
ε	molar absorptivity
AAS	Atomic Absorption Spectrophotometer
ATR-IR	Attenuated Total Reflectance-Infrared
APP	ammonium polyphosphate
cm	centimeter
cm^{-1}	unit of wavenumber
^{o}C	degree Celsius (centrigrade)

CO_2	carbon dioxide
DABCO	Diazabicyclooctane
DEEP	Diethylethylphosphonate
DMCHA	N,N-dimethylcyclohexylamine
DBTDL	Dibutyltin dilaurate
DMAEMA	N,N-bis(2-dimethylamine ethyl)methylamine
EA	Elemental Analysis
en	Ethylenediamine
FR	flame retardant
FTIR	Fourier Transform Infrared Spectrophotometer
g	gram
h	hour
IDT	Initial Decomposition Temperature
IPDI	Isophorone diisocyanate
K Ac	Potassium acetate
K Oct	Potassium octoate
KOH	potassium hydroxide
kg	kilogram
M	metal
$M(NO_3)_2$	metal nitrate
m^3	cubic meter
MDI	4,4'-methane diphenyl diisocyanate
MEO	2-morpholinoethanol
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mmol	millimole
MS	Mass spectrometer
N	newton unit
NMR	nuclear magnetic resonance
NCO	isocyanate

OHV	hydroxyl value
pbw	part by weight
PIR	polyisocyanurate
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PU	polyurethane
PUD	polyurea dispersion
PUR	polyurethane
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
ref	reference
s	second
SEM	Scanning Electron Microscope
t	time
TDI	toluene diisocyanate
TEA	Triethylamine
TEDA	Triethylenediamine
TGA	Thermogravimetric Analysis
T_{max}	maximum core temperature
trien	Triethylenetetramine
UV	ultraviolet

CHAPTER I

INTRODUCTION

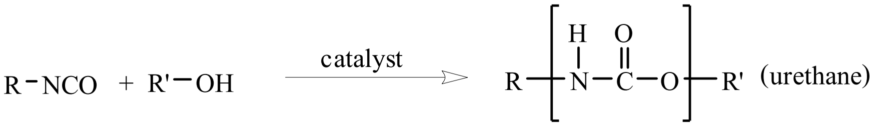
Rigid Polyurethane (RPUR) foams are recognized as an engineering material for different applications. It has many desirable properties such as low thermal conductivity, high compression strength, low density, high strength-to-weight ratio, low moisture permeability and low water absorption [1, 2]. Consequently, RPURs find such applications as transportation, household refrigerators, construction, automotive industry, packaging and industrial insulation [2, 3].

Polyurethanes are made by the addition reaction of polyisocyanates and polyol. The way to form polyurethanes is done by reacting molecules containing two or more isocyanate groups with polyol molecules containing two or more hydroxyl groups [3]. The functionality of the isocyanate or the polyol can be adjusted for controlling the physical and mechanical properties of foams.

The foaming reaction can be done in one shot and two shot methods. For one shot method, all materials consisting of polyol, catalyst, surfactant, blowing agent and isocyanate are put into a mixing cup and mixed homogeneously before they are poured into a mold. For two shot method, all materials except the isocyanate are mixed before the isocyanate is added [1, 4]. The rigid polyurethane foam processing can be carried out with a physical blowing agent, chemical blowing agent, or the mixture of both blowing agents [5]. For system that used physical blowing agents, reactions between isocyanate and polyol produce polyurethane linkages with releasing heat of reaction. After that the blowing agent vaporizes and gas is trapped in the closed cell of foam [1]. This method gives small closed cell structure and low thermal conductivity foam. Water is the most widely used as the chemical blowing agent. Water can react with isocyanate to form unstable carbamic acid which immediately decomposes into carbon dioxide and amine [6].

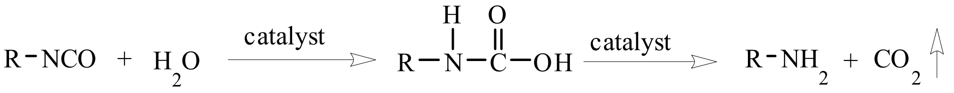
There are three main reactions which happen during polyurethane formation as follows [7, 8]:

1. Reaction between isocyanate (-NCO) and hydroxyl (-OH) groups results in urethane formations.



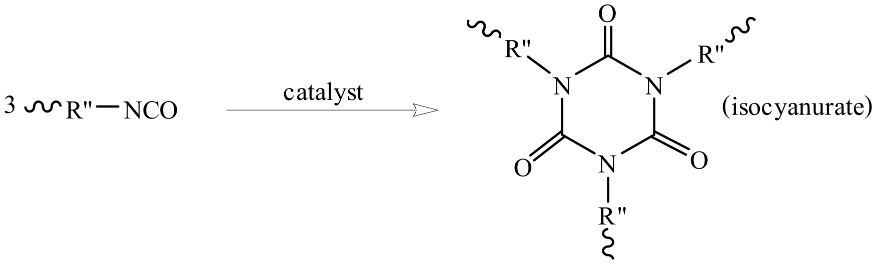
$$R{-}NCO + R'{-}OH \xrightarrow{\text{catalyst}} R\left[\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\right]R' \quad \text{(urethane)}$$

2. Reaction between isocyanate groups (-NCO) and blowing agent (water) releases carbon dioxide gas.



$$R{-}NCO + H_2O \xrightarrow{\text{catalyst}} R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{catalyst}} R{-}NH_2 + CO_2\uparrow$$

3. Reaction of three isocyanate groups in polymer chain produces isocyanurate.



Since the reaction between isocyanate with hydroxyl group is slow [9], catalyst is needed for catalyzed polyurethane formation. The common catalysts which used for catalyzed this reaction are tertiary amines, quaternary ammonium salts, alkali metal carboxylates and tin complexes [10, 11]. It is therefore interesting to develop new catalysts synthesize from metal and amine complexes which less toxic and lower cost in synthesis.

Objective and scope of the research

The present research aimed to prepare rigid polyurethane (RPUR) foams catalyzed by metal-amine complexes; [M(X)(en)$_2$ and M(X)(trien)]. It was expected that the synthesized metal complexes showed good solubility and good catalytic activity, which should provide the desirable physical and mechanical properties of RPUR foams. In addition, the study focused on the effect of catalyst types, content of catalyst and blowing agent, NCO index on the physical and mechanical properties of foams.

The first part was the investigation of metal complex synthesis from the reaction between different types of metal (II) salts with ethylenediamine (en) or triethylenetetramine (trien) in water or methanol media. The obtained metal complexes were characterized by Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible spectroscopy, elemental analysis and mass spectrometry.

In the second part, the work was focused on the preparation and characterization of the rigid polyurethane foams which were catalyzed by metal complexes prepared in the first part. Two shot method for foam preparation was used for this study. Reaction times, namely cream time, gel time, rise time, tack free time were recorded. FTIR was used to determine the completeness of foaming reaction. Physical and mechanical properties of prepared foams investigated were density, compressive strength and morphology. In addition, the results from synthesized catalysts were compared with the commercial catalyst, N,N-dimethylcyclohexylamine (DMCHA), which is used as the reference catalyst.

CHAPTER II

THEORY AND LITERATURE REVIEWS

The synthesis of polyurethane is usually presented as proceeding via the formation of urethane linkages by the reaction between alcohols with two or more reactive hydroxyl groups per molecules (diols or polyols) and isocyanates that have two or more reactive isocyanate groups per molecule (diisocyanate or polyisocyanate). The ratio of the two compounds will in part dictate both the physical and mechanical properties of PU foams. As a general rule, the polyols are soft segments whereas the isocyanates are hard segments that impart rigidity to the polymer [4].

The wide variations possible in synthesis give rise to a wide range of polyurethane products including flexible and rigid foams, because specific chemical structure and the degree of crosslinking can be introduced. The type of PUR foams can vary from flexible, commonly used in many applications such as cushioning, packaging and textile industry through semi-rigid, used in automotive industry and protective packaging to rigid PUR foam, mainly used in insulation and structural applications [3, 12].

2.1 Raw materials

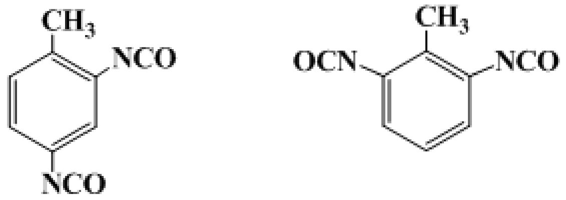
In manufacturing rigid polyurethane (RPUR) foams, isocyanate and polyol are main reactants for polymerization. Other chemicals such as catalysts, surfactants, blowing agents and fillers are also added to mixture for controlling and modification the reaction process and properties of RPUR foams. The properties of RPUR foams depend on concentration of raw materials and final chemical structures of foams.

2.1.1 Isocyanates

Several aromatic and aliphatic isocyanates are commercially used for preparing PU foams, the most common aromatic isocyanate used are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) [4, 5]. Their chemical structures are displayed in Figures 2.1 and 2.2. Aromatic isocyanates have been used for the preparation of isocyanate based foams. Aliphatic isocyanates were not used because foaming reactions require high reactivity and aliphatic polyisocyanates react slowly with hydroxyl groups. Variation of polyurethane properties can be achieved by variation of the types of isocyanate used [13].

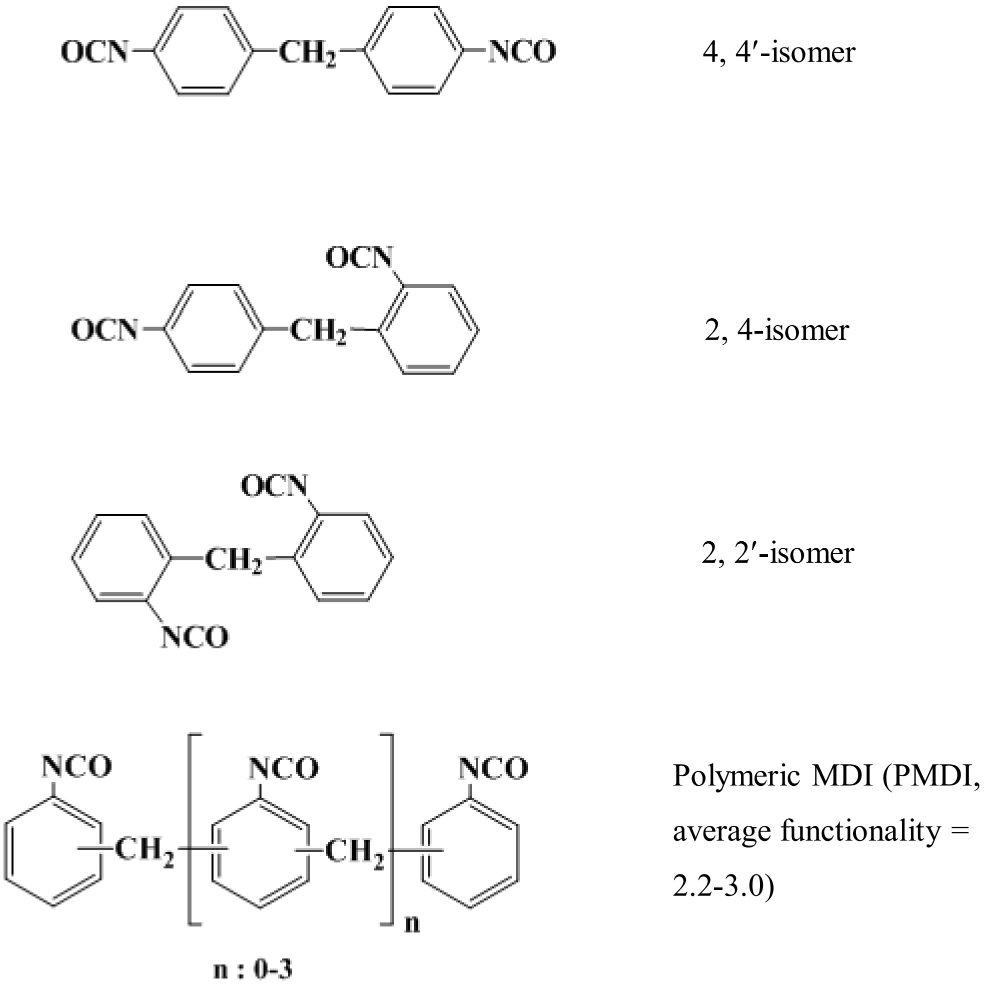
TDI (toluene diisocyanate) is obtained by phosgenation of diaminotoluene, which is obtained by the reduction of nitrotoluene. Commercial products of TDI are mixtures of 2,4- and 2,6-isomers in the weight ratio of 80:20 or 65:35. TDI with a 80:20 isomer ratio is used mainly for flexible foams. Modified TDI and undistilled TDI are mostly used for rigid polyurethane foams.

MDI (methylene diphenyl diisocyanate) is manufactured by phosgenation of the condensation product of aniline with formaldehyde. Polymeric and oligomeric MDI is in liquid form. They are mainly 4, 4′-isomer based and have small quantities of 2, 2′-isomer and up to 10% of the 2, 4′-isomer. The average functionality is in a range of 2.3 to 3.0. MDI offers a number of advantages, because it is safe to use based on its much lower vapor pressure and is available in convenient forms. Pure MDI (or monomeric MDI) is recovered by distillation of a crude reaction product and is used for elastomer and coating. Polymeric MDI (PMDI) that sold commercially is used for preparation rigid and semi-rigid PU foams. Polymeric MDI are usually characterized by their NCO content, acidity and viscosity. Functionality, structure and composition of polymeric MDI are affected to properties of PU foams.



2, 4-isomer 2, 6-isomer

Figure 2.1 Chemical structure of TDI [5].



4, 4′-isomer

2, 4-isomer

2, 2′-isomer

Polymeric MDI (PMDI, average functionality = 2.2-3.0)

Figure 2.2 Chemical structure of MDI and PMDI [5].

2.1.2 Polyols

Polyols are viscous liquid. Isocyanates react with any molecules which have active hydrogens, such as hydroxyl, carboxylic and amine groups. For polyurethane foams, hydroxyl group terminated polyether polyols and polyester polyols are most important. Molecular weight and functionality of the polyols are the main factor that will affect to properties of PU foams, structure of polyol is also important. The characteristics of the polyol used to make the two main classes of flexible and rigid polyurethane foam are displayed in Table 2.1 [9].

Table 2.1 Polyols used to make flexible and rigid polyurethane foams

Characteristic	**Flexible polyurethane foam**	**Rigid polyurethane foam**
Molecular weight range	1,000 to 6,500	150 to1,600
Functionality range	2.0 to 3.0	3.0 to 8.0
Hydroxyl value range (mgKOH/g)	28 to160	250 to 1,000

The functionality of a polyol indicates the number of hydroxyl groups per molecule. If the polyol is a mixture of components with different functionalities, the average functionality is given. Parts of the molecule which can undergo reactions, such as the hydroxyl groups, are called functional groups. A measurement of the hydroxyl group content is the hydroxyl value. To select a polyol, information on the hydroxyl value, viscosity and water content is necessary in addition to the chemical nature. From Table 2.1, flexible PU foams need higher molecular weight and lower functionality polyols. On the contrary, lower molecular weight and higher functionality polyols are used in the production of rigid polyurethane (RPUR) foams. This was due to higher degree of crosslinking which contributes to the stiffness of foam. Thus amount of polyol that added to produce PU foam will affect to properties of obtained foam.

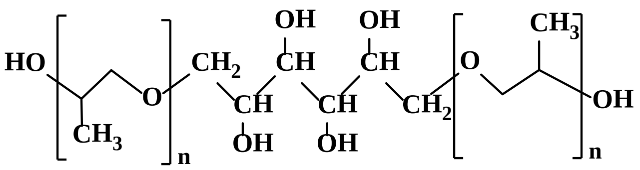
2.1.2.1 Polyether polyols

Conventional polyether polyols are representative polyols for PU foams. They are classified into four groups: polyoxyalkylene polyols, graft polyols (polymer polyols), polyurea dispersion (PUD) polyols and polytetramethylene ether glycol (PTMEG). Sorbitol- and sucrose-based polyether polyols are commonly used for produce PU foams. Their chemical structures are shown in Figure 2.3.

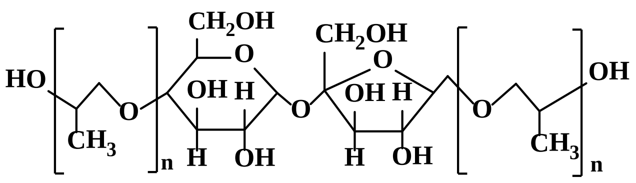
Polyether polyols are widely used for producing various PU foams such as flexible, semi-flexible and rigid foams, elastomers, coatings, adhesives, sealants and resin due to they have many advantages over polyester polyols as below [5]:

- Polyether polyols have various functionalities (from 2 to 8).
- Equivalent weight can be widely changed.
- Viscosities of polyether polyols are lower than those of polyester polyols.
- Production costs are cheaper than those of aliphatic polyesters.
- Resulting foams have better resilience and resistance to hydrolysis.

However, the polyether polyols have lower oxidation resistance than that of polyester foams.



Poly (propyleneoxy) sorbitol



Poly (propyleneoxy) sucrose

Figure 2.3 Structure of sorbitol- and sucrose-based polyether polyols

2.1.2.2 Polyester polyols

Polyester polyols for PU foams include aliphatic and aromatic polyesters. Castor oil is one type of natural polyester polyol that used to produce semi-rigid foams but it is not used to produce commercial foam. When polyether and polyester polyols are compared, the foams that prepared from polyester polyols have better mechanical properties due to their more reaction and are less soluble in organic solvents. But they are more expensive, higher viscosity and therefore not easy to handle. As a consequence, they are only used in applications that require their superior properties.

2.1.3 Blowing agents

Blowing agent plays a very important role in both the manufacturing and performance of polyurethane foam. The blowing agents should dissolve well in the reaction components. The blowing agent is the dominant factor controlling density of the foam. It also affects to the cellular microstructure and morphology of the foam, which in turn define the end-use performance [14].

The desirable characteristics of blowing agents for RPUR foams are well understood, they should have low boiling point, good solubility in the foam precursors, poor solubility in foam, low thermal conductivity of gas, low diffusion rate of gas through the polymer, low flammability both as liquid and gas and chemically inert [11].

In RPUR foams preparation, two kinds of gas generation methods are used: chemical gas generation and physical gas generation, as well as their combinations. Chemical blowing agents are chemical compounds that react with isocyanate groups to form unstable carbamic acid which immediately decomposes into an amine and carbon dioxide gas. A typical chemical blowing agent is water. Physical blowing agents are inert liquids with low boiling points. They evaporate by the exothermal of foaming reaction. Physical blowing agents include various fluorine-containing compounds such as C5-hydrocarbons, azeotropes with or without halogen and liquefied carbon dioxide [5].

Water has been used as a chemical blowing agent. It reacts with isocyanate to produce carbon dioxide gas. The reaction of water with isocyanate is exothermic and results in the formation of active urea sites which form crosslink via hydrogen bonding. Small amount of water (3-5 parts of water per 100 parts of polyol) is added. This is due to the increasing amount of water results in higher exothermic reaction, which is the cause of scorching or fire. In addition, higher amount of isocyanate groups are consumed to react with higher amount of water, production cost is higher.

To reduce the high crosslink density, auxiliary blowing agents are used to produce low density foams with a softer feel than water-blown foams and to produce closed cell flexible foams.

Pentanes has been used as a physical blowing agent. The great advantage of pentanes is their low price. The n-pentane is used predominantly for the production of rigid polyurethane foam for the building industry. When they used as blowing agents, certain safety precautions have to be taken because pentanes are highly flammable liquids, the vapors can form mixtures with air and explosive.

2.1.4 Surfactants

By reducing the surface tension of polyols, surfactants can perform several useful functions in foam manufacture. The surfactants are added to raw material for two purposes in polyurethane foaming. First, they stabilize the foam immediately after mixing polyol and isocyanate by lowering the surface tension of the emerging gas-liquid interface, and presumably also by emulsifying the polyol-isocyanate interface. Mechanistically, this effect arises from a preferred accumulation of surfactant molecules at interfaces. A second, surfactants is used to stabilize the polymerizing liquid-gas interface during the roughly 30 to 50 fold volume increase of rising foam. The mechanism is rather dynamic: the expanding foam continuously generates new surface area of high tension that needs to be stabilized by fast migration of surfactant towards the interface (the Marangoni effect) [10].

Rigid foam surfactants are designed to produce very fine cells and a very high closed cell content. Flexible foam surfactants are designed to stabilize the reaction mass while at the same time maximizing open cell content to prevent the foam from shrinking. The need for surfactant can be affected by choice of isocyanate, polyol, component compatibility, system reactivity, process conditions and equipment. Without surfactants the foaming system will experience catastrophic coalescence and eventually cause foam collapse.

Silicone surfactants are normally added in concentrations of 0.4–2.0% w/w of the polyol formulation. The chemical structure is displayed in Figure 2.4. To meet specific processing needs of different foam systems, the chemical structure may be changed by varying the length and the composition of the polydimethylsiloxane backbone or the number, length, and composition of the pendant polyether chains [10].

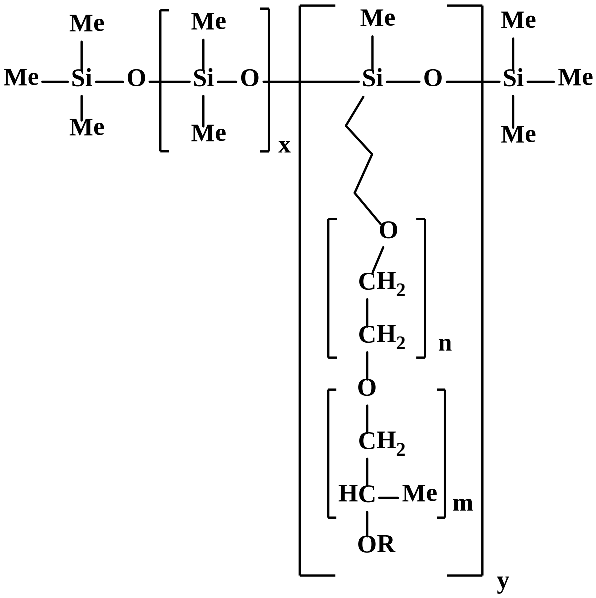


Figure 2.4 Structure of silicone surfactant used in PUR foams manufacture [10]

2.1.5 Catalysts

The catalysts for isocyanate-based polymeric foams include gelling catalysts, blowing catalysts, cyclotrimerization catalysts, oxazolidone catalysts and carbodiimide catalysts. Foam catalysts have a very substantial influence on process rheology, dimension stability and physical properties. Examples of catalysts that used in RPUR foams manufacture are shown in Table 2.2 and Figure 2.5. Aliphatic and aromatic tertiary amines, quaternary ammonium salts, alkali metal carboxylates, and organo-tin compounds are commonly used for RPUR foam preparation.

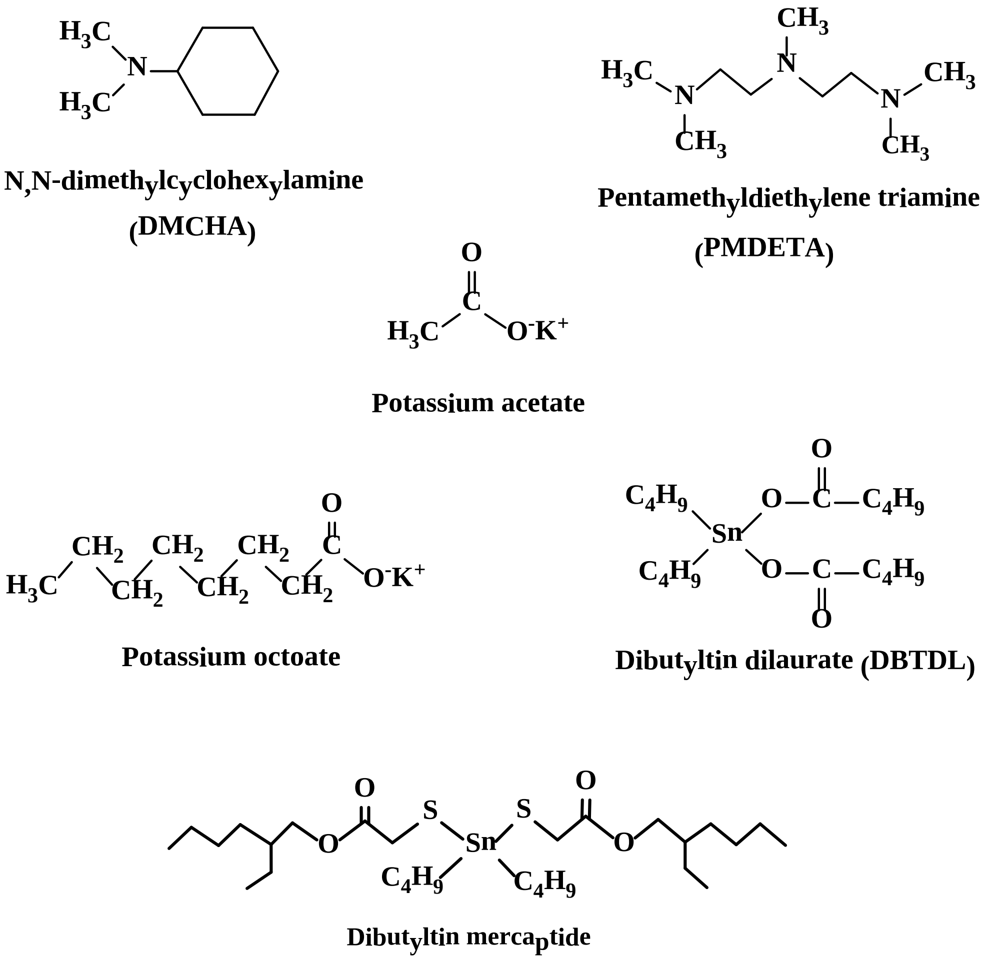
Their catalyst activity is dependent on their basicity, with steric hindrance on the active site playing a secondary role [15]. Catalysts are affected to rates of competing reactions and have a major effect on the ultimate properties of the final foam. Each catalyst type is specific for a particular chemical reaction. Catalyst mixtures are generally necessary to control the balance of the polymerization and the gas generation reactions which both are exothermic reactions. Getting the correct balance of polymerization and foaming is a major importance in the production of closed cell foam. A typical catalyst system would consist of a mixture of a tertiary amine and organometallic compounds. For tin compounds, the most important one is stannous octoate.

Table 2.2 Catalysts for use in rigid polyurethane foams manufacture [10, 11]

- **Tertiary amines**
  Dimethylcyclohexylamine (DMCHA)
  Pentamethyldiethylene triamine (PMDETA)
  Triethylenediamine (TEDA)
  Triethylamine (TEA)
- **Tin compounds**
  Stannous octoate (Sn Oct)
  Dibutyltin dilaurate (DBTDL)
  Dibutyltin mercaptide
- **Quaternary ammonium salts**
  2-hydroxy propyl trimethyl ammonium (TMR)
- **Alkaline metal carboxylates**
  Potassium acetate (K Ac)
  Potassium octoate (K Oct)
  Sodium N-2-hydroxy, 5-nonylphenol methyl N-methyl glicinate (Curithane 52)

For rigid polyurethane foam formation, two kinds of reactions, which are an isocyanate-hydroxyl reaction and an isocyanate-water reaction, are employed. Thus two types of catalyst are necessary to balance and accelerate between gelling and blowing reaction.

Tin catalysts mainly promote the reaction between isocyanate and hydroxyl groups and they are considered “gelling catalysts”, whereas tertiary amines accelerate both this and the water-isocyanate reaction. The reaction between water and isocyanate generates CO_2 gas and they are considered “blowing catalysts”. These reactions are shown in Scheme 2.1. Potassium salts catalyzed the trimerization of isocyanates to form isocyanurates.



N,N-dimethylcyclohexylamine (DMCHA)

Pentamethyldiethylene triamine (PMDETA)

Potassium acetate

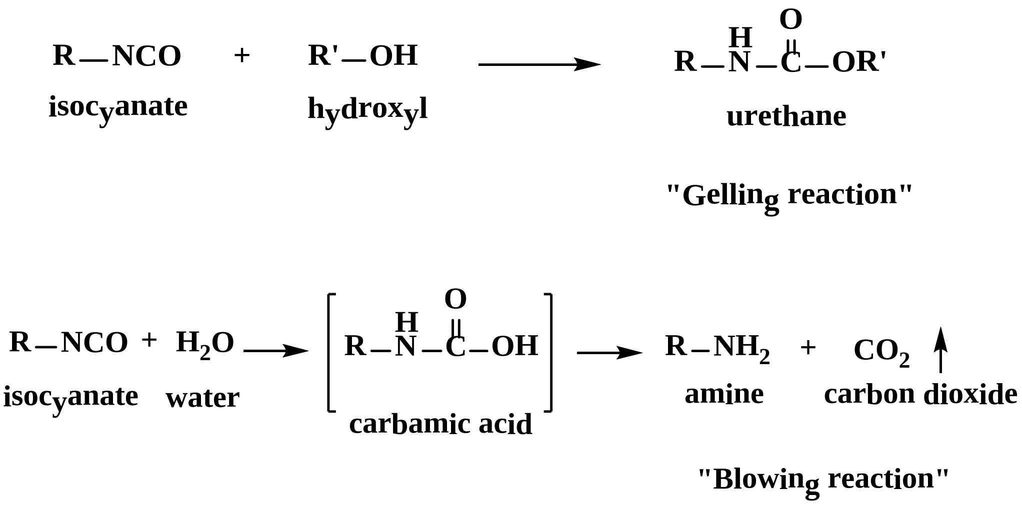
Potassium octoate

Dibutyltin dilaurate (DBTDL)

Dibutyltin mercaptide

Figure 2.5 Commercial catalysts used in rigid polyurethane foams manufacture

For preparation of PU foams for specific processing and application, catalysts are thought to balance these reactions and synergistic effects of certain catalyst combinations are known as well. If the polymerization is completed before sufficient gas has been generated. High density foam will result, i.e. virtually a solid product containing few gas cells. Thus blends of catalysts are required to balance the relative chemical reaction rates.



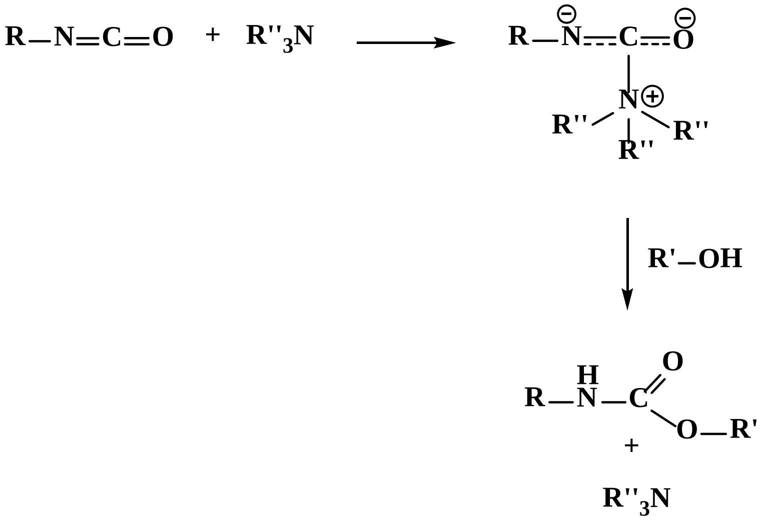
Scheme 2.1 Gelling and blowing reaction that occurred during produce PUR foam [8]

2.1.5.1 Reaction mechanisms

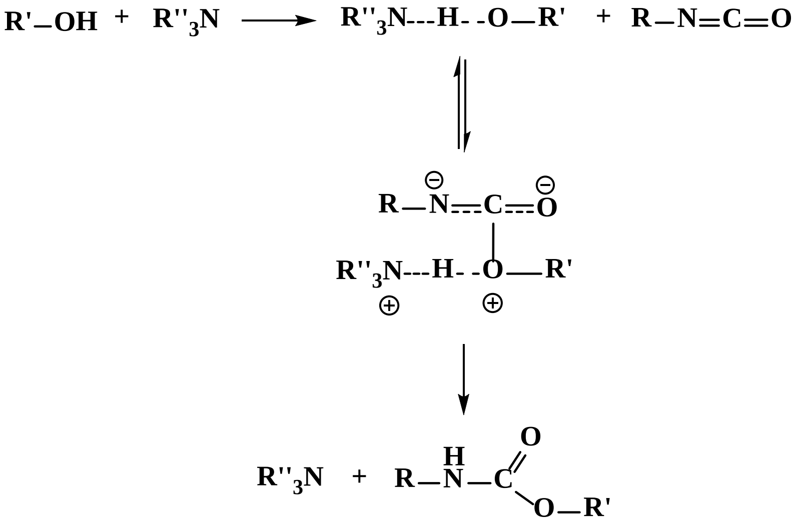
2.1.5.1.1 Tertiary amine catalysts

Tertiary amines are the most widely used catalysts for preparation polyurethane foams. Two mechanisms have been proposed for amine catalysis. The first mechanism which proposed by Baker is shown in Scheme 2.2. The activation is starts by the amine using its lone pair of electrons to coordinate with the carbon of the isocyanate group. This intermediate then reacts with active hydrogen from an alcohol to produce a urethane group.

The second mechanism proposed by Farka is shown in Scheme 2.3, which is supported in the more recent literature. The activation starts by the amine interacting with the proton source (polyol, water or amine) to form a complex, which then reacts with the isocyanate. Factors that affect the catalytic activity of an amine are nitrogen atom basicity, steric hindrance, spacing of heteroatoms, molecular weight, volatility and end groups.



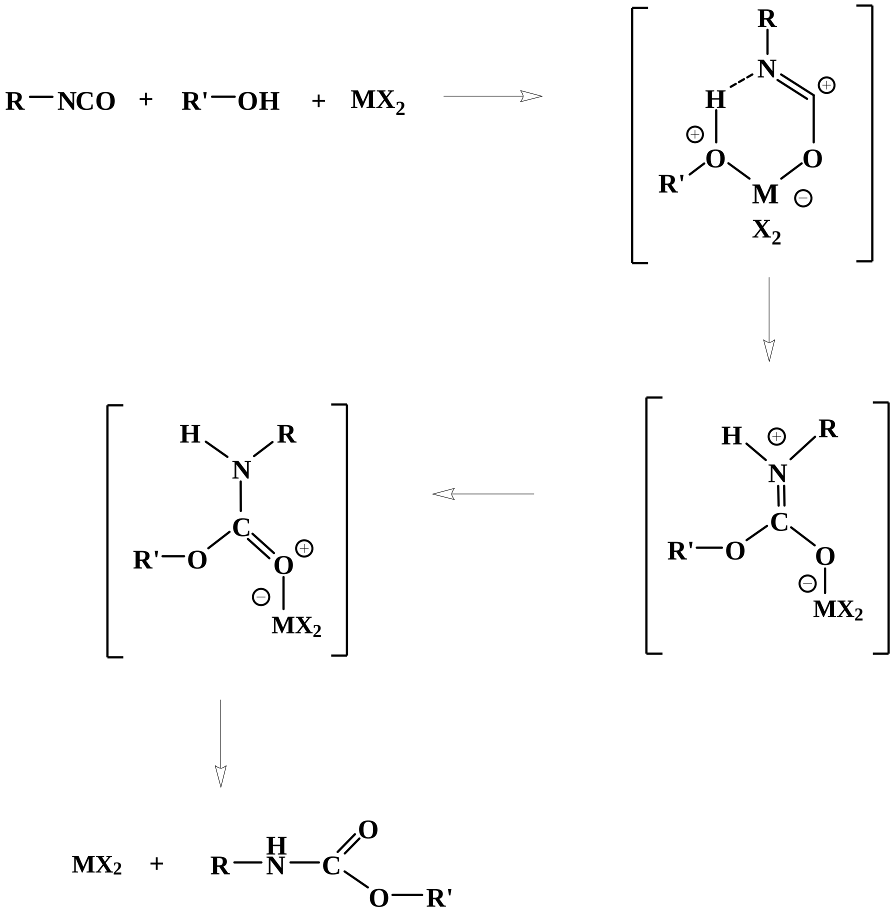
Scheme 2.2 Baker mechanism amine catalysts [16]



Scheme 2.3 Farka mechanism amine catalysts [16]

2.2.5.1.2 Organotin catalysts

The reaction mechanism of PU preparation by used organotin as a catalyst is shown in Scheme 2.4. The isocyanate, polyol and tin catalyst form a ternary complex, which then gives the urethane product. Two routes, not shown, to the complex have been proposed. In the first route, the tin first adds to the polyol then the isocyanate. In the second route, the tin adds to the oxygen of the isocyanate then reacts with the polyol.



Scheme 2.4 Mechanism of tin (II) salts catalyst [16]

2.1.6 Other additives

Other additives such as flame retardant, antioxidant, colorant and mold releasing agent are also added during produce PU foams for improve some properties.

2.1.6.1 Activators

Activators are added to the reaction mixture. These are usually tertiary amines, organo-tin compounds or alkali salts of aliphatic carboxylic acids which particulary promote isocyanurate formation. The best known activators are triethylamine, dimethylcyclohexylamine, dibutyltin dilaurate and potassium acetate. Some of the individual compounds from the large number of activators have very different effects on the reactions described. This can be used to control the progress of the reaction and foaming according to requirements.

2.1.6.2 Foam stabilizers

The foam which forms as a results of the developing or evaporating blowing agent is usually unstable and would collapse if the reaction continued without the addition of foam stabilizers. Organo-silicon compounds (polyether polysiloxanes) which have a surface-active effect are used almost exclusively as foam stabilizers, but also function as emulsifiers. Foam stabilizers regulate the foam structure, cell character and the cell size.

2.1.6.3 Flame retardants

Polyurethane are organic compounds which are flammable material. In order to delay their ignition and reduce the spread of the flames, an appropriate chemical structure and the addition of flame retarding components are required. Rigid polyurethane foams used as building insulants resulted in some serious fire hazards. Flame retardant will add to solve this problem. Triethyl phosphate, tris-chlorisopropyl phosphate and diphenylcresyl phosphate are typical examples.

2.2 Chemistry

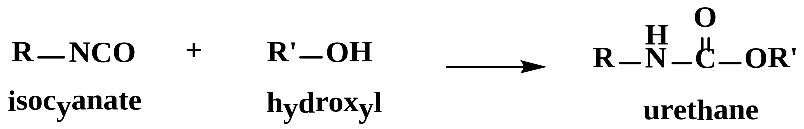
Polyurethane chemistry is based on the high reactivity of the isocyanate group with any compound containing active hydrogen; polyether polyol or polyester polyol. Most polyurethane is formed by exothermic reaction between di- or polyfunctional isocyanates and di- or polyfunctional hydroxyl species. For simplicity, the basic principle of urethane chemistry is described below using monofunctional reagents.

2.2.1 Primary reaction of isocyanates

Primary isocyanate reactions produce urethane, amines, and substituted ureas, all of which still contain active hydrogen atom. In the presence of suitable catalysts at elevated temperatures, controlled secondary reactions occur which strongly influence the physical properties of the foam by introducing chain branching and crosslinking.

2.2.1.1 Reaction of isocyanate with polyol

The most important reaction in the manufacture of polyurethanes is between isocyanate and hydroxyl groups. The reaction product has urethane linkage in their chemical structure. The reaction is exothermic and reversible going back to the isocyanate and alcohol.



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

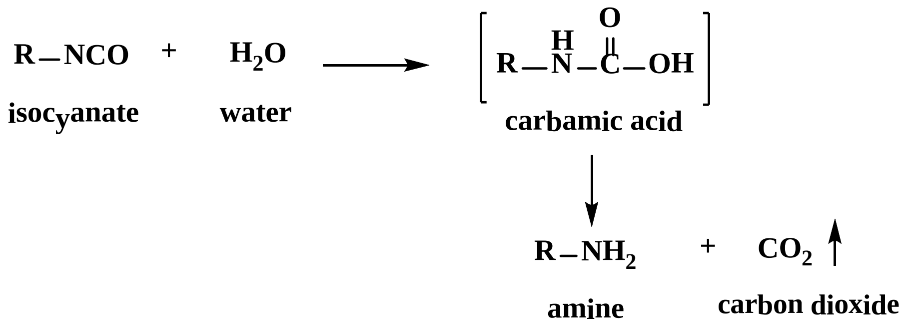
Scheme 2.5 Reaction between isocyanate with hydroxyl group

This reaction is known as the “gelling reaction” as shown in Scheme 2.5. Since it is an exothermic reaction, it must be temperature controlled. The rate of polymerization is affected by the chemical structure of the isocyanate and polyol. A catalyst is used to accelerate the reaction rate.

2.2.1.2 Reaction of isocyanate with water

The reaction of isocyanates with water to produce an amine and carbon dioxide is highly exothermic. Carbamic acid is an intermediate for this reaction, which breaks down into carbon dioxide and a primary amine. The reaction was shown in Scheme 2.6.

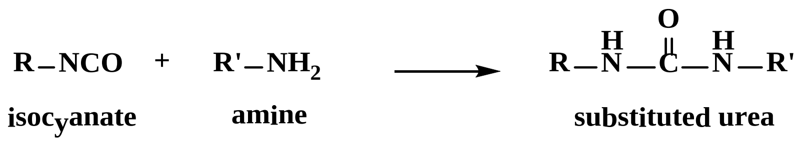
This reaction is known as the “blowing reaction” because the CO_2 gas produced is used for blowing the foam which, this reaction had an effect to foam density. The reaction rate is accelerating by suitable choice of catalyst system.



Scheme 2.6 Reaction between isocyanate with water

2.2.1.3 Reaction of isocyanate with amines

The reaction of an isocyanate with an amine forms an urea linkage as displayed in Scheme 2.7. Reactions of unhindered isocyanates with primary amines occur approximately 100-1000 times faster than with primary alcohols [17]. The reactivity of amines increases with the basicity of the amine, and reactivity of aliphatic amines was higher than that of aromatic amines [16].



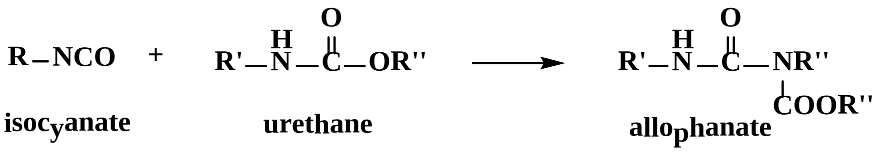
Scheme 2.7 Reaction between isocyanate with amine group

2.2.2 Secondary reaction of isocyanates [18]

Isocyanate may react with the active hydrogen atoms of urethane and urea linkages from the primary reactions under suitable conditions, the detail is shown below:

2.2.2.1 Reaction of isocyanate with urethane

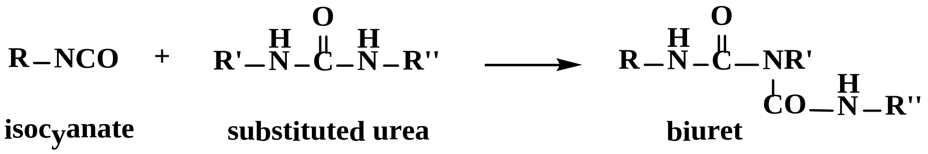
Urethane groups which have active hydrogen atoms, due to the hydrogen atom linked to the nitrogen atom. By the reaction of an isocyanate with an urethane group an allophanate is formed, as shown in Scheme 2.8.



Scheme 2.8 Reaction between isocyanate with urethane

2.2.2.2 Reaction of isocyanate with urea

Reaction between isocyanate with urea is similar to previous reaction, the -N-H groups of urea react with isocyanates to generate a biuret.

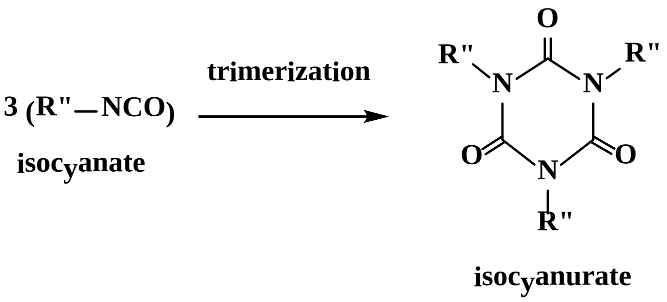


Scheme 2.9 Reaction between isocyanate with substituted urea

Formation of allophanates and biurets in polyurethane chemistry, especially when an excess of isocyanate is used, is in fact a supplementary source of crosslinking [18]. In general, reactions of isocyanates with urea groups are significantly faster and occur at lower temperature than that with urethane groups.

2.2.2.3 Trimer formation

Isocyanurate ring can be formed on heating either aliphatic or aromatic isocyanates, the reaction was shown in Scheme 2.10. The reaction is accelerated by basic catalysts such as sodium and potassium salts of carboxylic acids [17].



Scheme 2.10 Trimerization of isocyanate

2.3 Chemical calculation [9, 17]

The amount of isocyanate required to react with polyol and other reactive components can be calculated to obtain chemically stoichiometric equivalents. This theoretical amount may be adjusted up or down dependent on the polyurethane system, properties of products, ambient conditions and scale of production. The amount of isocyanate used relative to the theoretical equivalent quantity, is known as the "isocyanate index". An isocyanate index of 130 means that there is thirty percent excess of isocyanate.

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

The conventional method for calculation the ratio of the components required for PUR manufacture is to calculate the number of part by weight of any components needed to react with 100 parts by weight of polyol. The isocyanate value is the weight percentage of reactive isocyanate (NCO) groups, that is given by the following equation. The molecular weight of isocyanate group is 42.

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

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

The hydroxyl value (OHV) of a polyol, sometime called the hydroxyl number is defined as the concentration of isocyanate reactive hydroxyl groups per unit weight of the polyol, expressed in mg KOH/g of polyol. The hydroxyl value is also defined as the number of milligrams of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 gram of the polymer.

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

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

The acid value of polyol, sometimes called the acid number, is determined by measuring the different between titration of blank and polyol with a standard potassium hydroxide solution. The acid value is also expressed as mg KOH/g of polyol and numerically equal to hydroxyl value.

Water content is defined as water reacts with two isocyanate groups and the equivalent weight of water as equation below:

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

Isocyanate conversion (α) can be calculated by FTIR technique, defined as the ratio between isocyanate peak area at time t and isocyanate peak area at starting time.

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

where;

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

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

2.4 Properties of rigid polyurethane foams

2.4.1 Morphology

The cell structure has a very significant influence on many properties. Morphology of PU foams in parallel and perpendicular direction of foam rising are analyzed by scanning electron microscope. The cell morphology is spherical and elongated shape in parallel and perpendicular direction of foam rising, respectively. Aspect ratio is one parameter that calculated as the ratio of the diameters of the major and minor ellipse axes. The ellipsoid cells usually have aspect ratio more than 1. A spherical cell structure is most likely to occur when the foam system reacts slowly and uniformly and if there are no influence from surrounding surface. The cell deviates from spherical shape is observed when the reaction become faster and as the influence of the surfaces or mold wall increases. Spherical cells show the same properties in all directions. The cell morphology in two directions are shown in Figure 2.6.

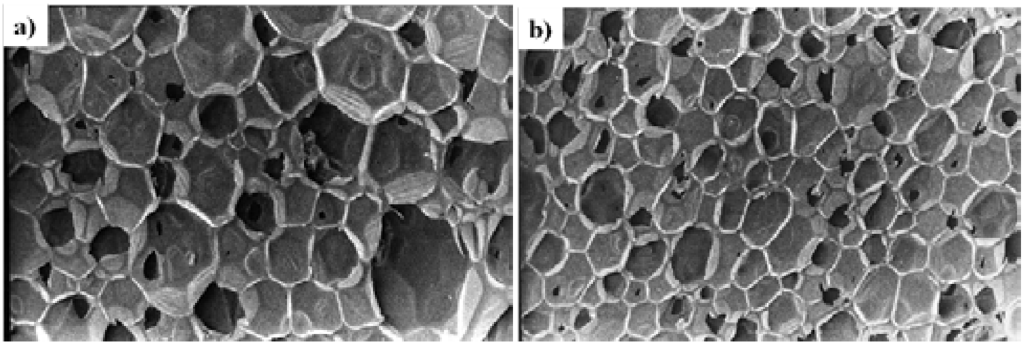


Figure 2.6 Cell structure of PU foams (a) spherical cell in the parallel of foam rise and (b) elongated cells in the perpendicular of foam rise [19]

2.4.2 Compressive strength

The mechanical properties response of RPUR foams under compression in the rise and transverse direction and found that the direction deformation responses in different directions are attributed to anisotropy in the internal cellular structure. Apparent density of PU foams is also related to compressive strength. The compressive strength increases with the increasing of apparent density. The compressive strength of foam in parallel of foam rise is higher than that in perpendicular direction of foam rise. Figure 2.7 shows the compressive stress-strain curve that may be divide into three regions; linear elasticity, collapse plateau and densification. In the first region, stress is dramatically increased when increased strain. The linear elastic behavior in this region is controlled by cell wall bending and cell wall stretching due to the contained gas pressure. In the second region, the cell collapse through cell wall bucking, or in brittle foams, by cell crushing and cell wall fracture. Densification occurs in the third region. As foam density increases, modulus increases as shown in Figure 2.8.

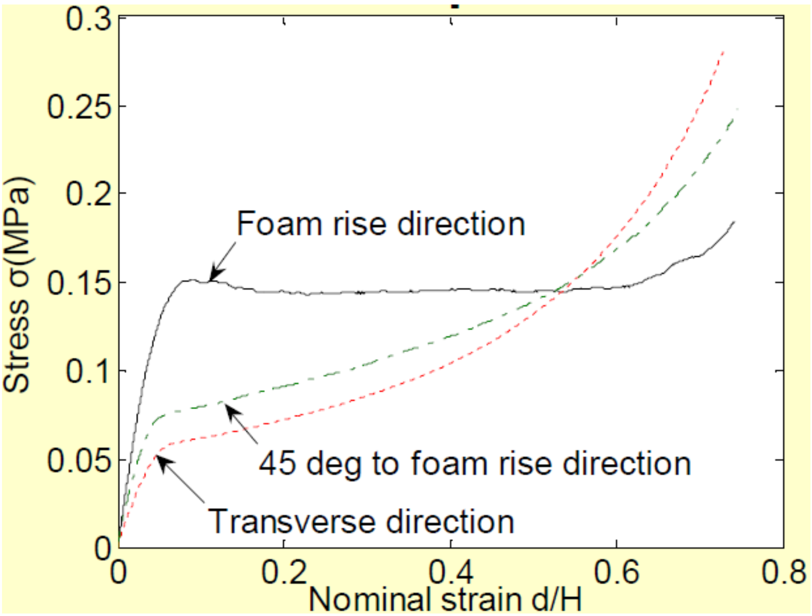


Figure 2.7 Compressive stress-strain curve of RPUR in different foam direction [19]

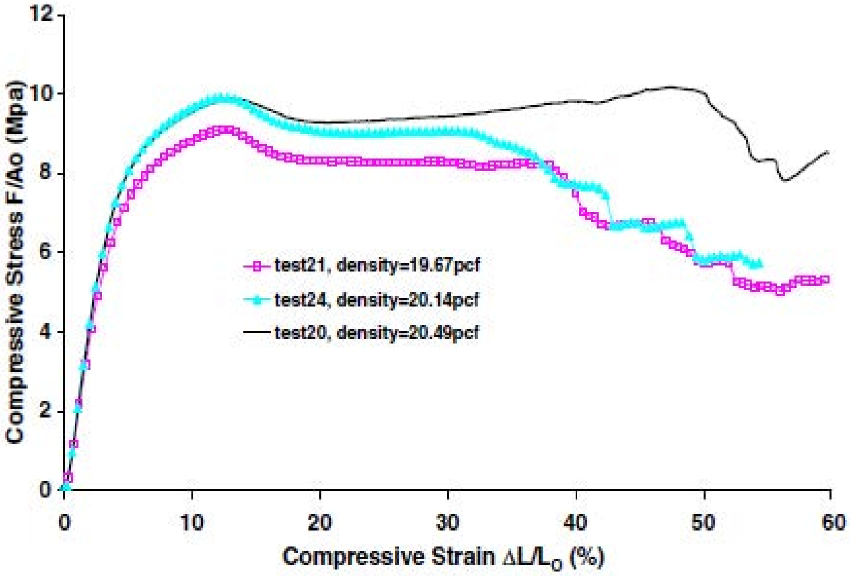


Figure 2.8 Compressive stress-strain curve of RPUR in different foam density [20]

2.4.3 Thermal stability

Thermogravimetric analysis is one type of testing that use for determine changes in weight with related to temperature change in a controlled atmosphere. From TGA thermogram, the weight loss curve may be interpreted and derivative weight loss curve is also used to identify the point where weight loss is most apparent. This technique uses to determine composition and purity of material. Thermogravimetric analysis is the act of heating sample to high enough temperature so that one of the components decomposes into a gas, which dissociates into the air. So this technique is interested in the model of the weight losses of rigid polyurethane foam under linear heating rates in an inert atmosphere .

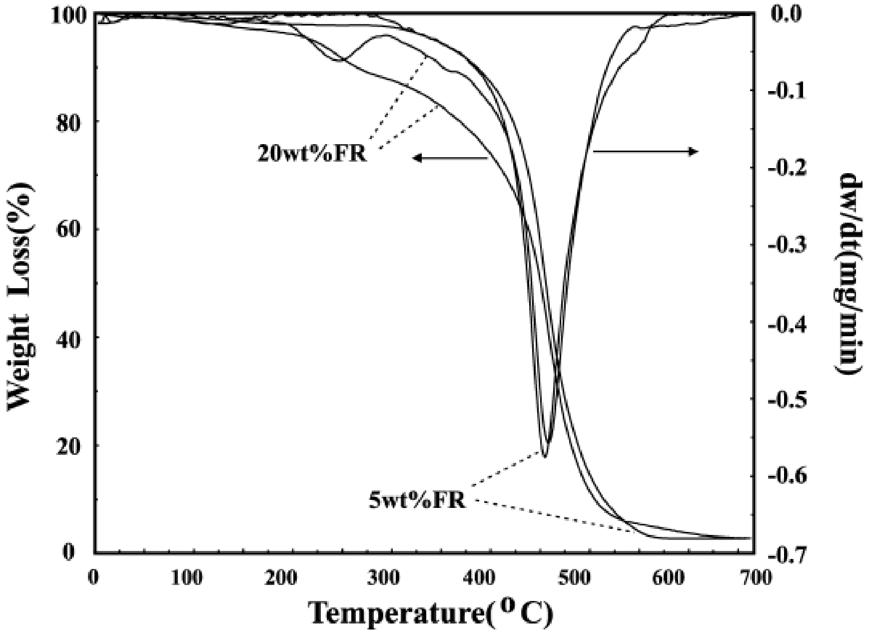


Figure 2.9 TGA/DTG curves of HCFC-141b series chars with flame retardant (FR) [21]

Tang and coworker [21] used TGA technique for study thermal degradation behavior of RPUR foams with different flame retardant concentration. From Figure 2.9, the maximum degradation reactivity of the char increases with increasing flame retardant concentration in the foams. These results indicate that the flame retardant can preserve the chemical structure of the polyurethane foam. The best known flame retardants are aluminium phosphinate (IPA), diethylethylphosphonate (DEEP), triethylphosphate (TEP) and ammonium polyphosphate (APP).

2.5 Literature reviews

Rigid polyurethanes are prepared through the mixing of polyol with isocyanate, surfactant, blowing agent and other additives. Quantities of raw materials which affected to either physical or mechanical properties are reported. Singh and coworkers [22] prepared rigid PU foams based on crude 4, 4'-diphenylmethane diisocyanate, polyether polyol, triethylenediamine, 1, 4-butanediol, poly(siloxane ether), methylene chloride and water. They found that the rate of PU formation increased with increased the catalyst and water content. The density of RPUR foams blown with water, methylene chloride and mixture of water and methylene chloride decreased with an increase blowing agent content. In contrast, the density of PU foam increased with increasing content of 1, 4-butanediol. Thermal behavior study indicated that the foam samples decomposed in nitrogen and degraded in air through two and three weight loss stages, respectively. It can be concluded that PU foams were more stable in nitrogen than in air.

Effect of silicone surfactant in rigid polyurethane foams was studied by Lim and coworkers [23]. Cream time, gel time and tack free time increased with increased surfactant content. It was due to increase surfactant content, increased stability of reaction mixture and rising bubbles. Foam density decreased rapidly to a minimum at 0.5 pphp surfactant due to the increased blowing efficiency with surfactant.

Water is a low cost blowing agent, easy handling and low global warming effect. Many research works have been accomplished to incorporate water as blowing agent for polyurethane formation. Seo [24] studied the properties of water-blown rigid polyurethane foams with reactivity of raw material. They found that kinetic rate of reaction increased with increased catalyst and water content. In addition, the density, compressive strength and glass transition temperature of PU foams increased, as the OH value and the functionality of polyols are higher.

Li and coworkers [25] were also studied the structures and physical properties of RPUR foams with water as blowing agent. They compared reaction times of RPUR foams which used water or cyclopentane as blowing agent. Cream time and gel time of water blown RPUR samples were shorter than cyclopentane blown RPUR foams. This was due to exothermic reaction heat when water was used as chemical blowing agent. When increased water level in formulation, density and compressive strength of foams decreased but the cell size increased. At the same time, poor dimensional stability was encountered with increase cell size due to fast diffusion rate of carbon dioxide gas out of foam. In addition, effect of foam density on the properties of water blown RPUR foams was investigated by Thirumal and coworkers [2]. The results were similar to the results that reported by Li. They also found that when decreased density of foam, cell size and glass transition temperature increased but cell wall thickness and thermal stability decreased.

Many studies utilizing the natural materials such as sugar-cane bagasse, soybean oil and seed oil to prepare degradability of PU foam have been carried out [26, 27, 28]. Hakim and coworkers [26] studied liquefied of sugar-cane bagasse as the polyol for preparation RPUR foam in the presence of DMCHA as a catalyst, water as chemical blowing agent and silicon oil as surfactant. They found that the partial replacement of polyethylene glycol polyol by liquefied sugar-cane bagasse polyol had significant effect on physical, mechanical and thermal properties of PRUR foam. Cream time and tack free time of biopolyol shifted to longer side. Furthermore, density and compressive strength of foam increased with increasing biopolymer content. But the compressive strength decreased when biopolyol was more than 30%. Thermal conductivity decreased but the glass transition temperature increased with increasing biopolyol content.

Tan and coworkers [27] used soybean oil-based polyol (SBOP) replacing a polypropylene-based polyol for preparation PU foam. Foams that prepared from SBOP had comparable foaming kinetic, density, cellular morphology and initial thermal conductivity (K value). But the glass transition temperature and compressive strength of SBOP based PU foams were higher than those of petroleum-based foam. This was possibly due to smaller cell size. Dutta and Karak [28] had been synthesized

PU from seed oil and 2, 4-toluenediisocyanate in the presence of dibutyltin dilaurate as the catalyst with varying NCO/OH ratios. These ratios affected to curing characteristic, physical properties and thermal properties of foam. They found that higher NCO/OH ratios led to shorter curing times, harder obtained foam and higher adhesive strengths.

The catalysis of reaction between isocyanate with hydroxyl groups has been studied by many researchers. They found that the reaction of isocyanates with hydroxyl groups is catalyzed by many metal carboxylates and organotin compounds. Blank and coworkers [29] found that zirconium chelates can catalyze the isocyanate-hydroxyl reaction by insertion mechanism with high reaction rate. This reaction was selective and preferred over the isocyanate-water reaction.

Strachota and coworkers [30] prepared PU foams by using various types of catalysts; selective commercial morpholine-based catalysts, tin (II) 2-ethyl-hexanoate, as well as combinations of these catalysts. Their activity and selectivity were evaluated compared with DMCHA, DABCO (Diazabicyclooctane), DBTDL (Dibutyltindilaurate) and DMAEMA (N,N-bis(2-dimethylamine ethyl)methylamine). They found that DMCHA was the best catalyst, followed by DMAEMA for the single catalyst system. But MEO (2-morpholinoethanol) was not acted as a good catalyst, due to its low gelation activity. All prepared foams were non-collapsed foam with large V/Vo. For catalyst mixture system, the mixtures of DABCO-SnOct-DMAEMA produced the best foam, followed by the mixture of DMCHA-SnOct.

Sardon and coworkers [31] studied the catalytic activity of tin and zirconium based catalysts for synthesized polyurethane based isophorone diisocyanate (IPDI). Zirconium acetyl acetonate has a lower toxicity that tin compound about 10 to 20 times. But it is deactivated in the presence of acid function. Thus acid groups of functionalized diol must be neutralized to avoid hydrolysis of zirconium complex before further reaction. From FTIR and ^{13}C-NMR results, it can be concluded that zirconium catalyst is a good catalyst to replace tin compounds used in synthesis polyurethane dispersion by acetone process.

Catalyst is one component has played an important role in catalytic system of PU synthesis since it controlled and balance between the gelling and blowing reactions. In addition, the reaction between isocyanate with hydroxyl group of polyol is slow. Therefore, catalyst is necessary to add for synthesize PU foams. Many articles reported that amine catalyst was used for producing PU foams [32-35]. Maris and coworkers [33] studied relationship between molecular catalyst structure and PU properties. They found that the tertiary amine catalytic activities have a strong relationship with rise profile, blowing efficiency, moldability, productivity and foam properties. From the results, triethylenediamine (TEDA) is strong gelling catalyst whereas pentamethyldiethylenetriamine (DT) is strong blowing catalyst. Tetramethylenediamine (TE) and tetramethylhexamethylenediamine (MR) show the moderate activity between the gelling and blowing reaction. The balances between both types of catalysts used in flexible foam and rigid foam applications.

Pengjam and coworkers [34] synthesized copper-amine complexes as catalysts for the reaction of RPUR foams. Copper acetate and nickel acetate were reacted with ethylenediamine (en) or triethylenetetramine (trien) to form metal complex catalysts. The obtained catalysts were used in preparation of RPUR foams. The results indicated that catalytic activities of $Cu(en)_2$ and Cu(trien) were comparable to that of DMCHA. The density of foams prepared by using copper complexes as catalysts was closed to those prepared by using DMCHA catalyst. In addition, the compressive strength of foams catalyzed by copper complexes was higher than those prepared from DMCHA. However, nickel complexes were not good catalysts since they gave longer reaction time and brittle foam.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Inorganic metal salts used in this study were copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), copper (II) carbonate ($CuCO_3 \cdot Cu(OH)_2$), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), zinc (II) sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), nickle (II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$). Two types of aliphatic amine; ethylenediamine (en) and triethylenetetramine (trien) were used as received from Fluka and Aldrich. Methanol was used as solvent.

In this work, polyol (Daltolac® R180, sucrose-based polyether polyol) supplied from Huntsman (Thailand) Co., Ltd., was used to prepare polyurethane foam. The polyether polyol has functionality of 4.3 and hydroxyl value (OHV) is 440 mgKOH/g.

Polymeric MDI (4,4'-methane diphenyl diisocyanate; PMDI, Suprasec® 5005) was supplied by Huntsman (Thailand) Co., Ltd. %NCO of PMDI was 31.0 %wt., the average functionality was 2.7.

Polysiloxane (Tegostab® B8460) which was obtained from Huntsman (Thailand) Co., Ltd. was used as a surfactant. Distilled water was used as a chemical blowing agent. Metal complexes were prepared and used as catalysts. N,N-dimethylcyclohexylamine (DMCHA), supplied by Huntsman (Thailand) Co., Ltd., was used as a commercial reference catalyst.

3.2 Instrumentation

The instruments used in the present study are shown in Table 3.1

Table 3.1 Instruments

Instruments	Model
Fourier Transformed Infrared Spectrometer	Nicolet 6700
UV-Visible Spectrophotometer	Varian Cary 50
Mass Spectrometer	Micromass Quattro micro^{TM} API spectrometer and Bruker Bifex spectrometer
Atomic Absorption Spectrophotometer	Varian AA 28OFS
Elemental Analyzer	Perkin Elmer EP2400 Analyzer
Thermocouple	Digicon DP-71
Scanning Electron Microscope	Jeol 5800LV
Compressive Strength Tester	Lloyd/LRX
Thermogravimetric Analyzer	Netzsch STA 409C

3.3 Synthesis of metal-amine complexes [$M(X)(en)_2$ and $M(X)(trien)$]

Metal-amine complexes were prepared by using two methods. In the first method, metal-ethylenediamine complexes [$M(X)(en)_2$] and metal-triethylene tetramine complexes [M(X)(trien)] were synthesized from the reaction between metal (II) nitrate, metal (II) chloride, metal (II) sulfate or metal (II) carbonate with ethylenediamine (en) or triethylenetetramine (trien) in water to obtain an aqueous solution containing metal complexes. The metal complex solution was used in the preparation of rigid polyurethane foam without purification.

In the second method, copper nitrate was reacted with ethylenediamine or triethylenetetramine to form $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ complexes. Distilled methanol was used as a solvent for this method [36]. Methanol was removed from the metal complex before using in the preparation of rigid polyurethane foam.

3.3.1 Synthesis copper nitrate-amine complexes in methanol

3.3.1.1 Synthesis of copper nitrate-ethylenediamine complex [$Cu(NO_3)_2(en)_2$] in methanol

The preparation of $Cu(NO_3)_2(en)_2$ was performed according to the method reported in the literature [37] as follows: a solution of ethylenediamine (en) (0.19 mL, 2.85 mmol) was stirred in methanol (10 mL) at room temperature for 30 minutes. After that, copper (II) nitrate trihydrate (0.33 g, 1.38 mmol) was added and the reaction mixture was stirred at room temperature for 12 hours. Precipitated of $Cu(NO_3)_2(en)_2$ complexes was dried under vacuum. $Cu(NO_3)_2(en)_2$ was obtained as a purple powder (0.49 g, 93%): IR (cm^{-1}); 3156 (N-H stretch), 2886 (C-H stretch), 1454 (asymmetric N-O, nitrate), 1336 (symmetric N-O, nitrate), 1605 (N-H bend), $Cu(NO_3)_2(en)_2$ shown $m/z = 308.06$, UV; λ_{max}(MeOH) = 207 nm, molar absorptivity (ε) = 4,890.

3.3.1.2 Synthesis of copper nitrate-triethylenetetramine complex [$Cu(NO_3)_2(trien)$] in methanol

The preparation of $Cu(NO_3)_2(trien)$ was done as follow: triethylenetetramine (0.19 mL, 1.27 mmol) was stirred in methanol (10 mL) at room temperature for 30 minutes. Afterthat, copper (II) nitrate trihydrate (0.31 g, 1.28 mmol) was added and the reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was dried under vacuum to remove solvent. $Cu(NO_3)_2(trien)$ was obtained as a blue viscous liquid (0.41 g, 82%): IR (cm^{-1}); 3233 (N-H stretch), 2881 (C-H stretch), 1454 (asymmetric N-O, nitrate), 1304 (symmetric N-O, nitrate), 1590 (N-H bend),

$Cu(NO_3)_2$(trien) shown *m/z* = 334.288, UV; λ_{max}(MeOH) = 261 nm, molar absorptivity (ε) = 3,540.

3.3.2 Synthesis metal-amine complexes in water

3.3.2.1 Synthesis of metal-ethylenediamine complex [M(X)(en)$_2$_W] in water

Various types of metal (II) salts ($Cu(NO_3)_2$, $Cu(SO_4)$, $Cu(CO_3)$, $Cu(Cl_2)$, $Co(NO_3)_2$, $Co(Cl_2)$, $Ni(SO_4)$, $Fe(SO_4)$ or $Zn(SO_4)$) were dissolved in deionized water (1.5 mL). Desired amount of ethylenediamine was added on previous solution by pipette, solution was stirred until homogeneous solution was obtained. Mole ratio between inorganic metal compound and ethylenediamine was fixed at 1:2. Then surfactant (Tegostab® B8460) (1.25 g) was added to mixture, the solution was stirred for 12 hours. The obtained complexes were used as catalysts for RPUR foam preparation without purification. Composition of starting materials in the preparation of metal-ethylenediamine complexes in water are shown in Table 3.2.

3.3.2.2 Synthesis of metal-triethylenetetramine complex [M(X)(trien)_W] in water

Metal (II) salts ($Cu(NO_3)_2$, $Cu(SO_4)$, $Cu(CO_3)$, $Cu(Cl_2)$, $Co(NO_3)_2$, $Co(Cl_2)$, $Ni(SO_4)$, $Fe(SO_4)$ or $Zn(SO_4)$) were dissolved in deionized water (1.5 mL). Desired amount of triethylenetetramine was added on previous solution with stirring until homogeneous solution was obtained. Mole ratio between inorganic metal compound and triethylenetetramine was fixed at 1:1. Silicone surfactant (Tegostab® B8460) (1.25 g) was added to reaction mixture and stirred for 12 hours. The obtained complexes were used as catalysts for RPUR foam preparation in the next step without purification. Composition of starting materials in the preparation of metal-triethylenetetramine complexes in water are shown in Table 3.3.

Table 3.2 Composition of starting materials in the preparation of metal-ethylenediamine complexes in water [M(X)(en)$_2$_W] at the mole ratio of M(X):en = 1:2

Metal complexes	**Amount of Metal (II) salts [M(X)] (g)**	**Amount of en (mL)**	**Appearance**
Cu(NO$_3$)$_2$(en)$_2$_W	0.33	0.19	Purple solution
Cu(CO$_3$)(en)$_2$_W	0.32	0.20	Purple solution
Cu(SO$_4$)(en)$_2$_W	0.34	0.18	Purple solution
Cu(Cl)$_2$(en)$_2$_W	0.30	0.23	Purple solution
Co(NO$_3$)$_2$(en)$_2$_W	0.36	0.16	Brown solution
Co(Cl)$_2$(en)$_2$_W	0.33	0.19	Red solution
Ni(SO$_4$)(en)$_2$_W	0.35	0.18	Purple solution
Fe(SO$_4$)(en)$_2$_W	0.35	0.17	Brown solution
Zn(SO$_4$)(en)$_2$_W	0.36	0.17	White solution

Table 3.3 Composition of starting materials in the preparation of metal-triethylenetetramine complexes in water [M(X)(trien)_W] at the mole ratio of M(X):trien = 1:1

Metal complexes	Amount of Metal (II) salts [M(X)] (g)	Amount of trien (mL)	Appearance
$Cu(NO_3)_2$(trien)_W	0.31	0.19	Blue solution
$Cu(CO_3)$(trien)_W	0.30	0.20	Blue solution
$Cu(SO_4)$(trien)_W	0.32	0.19	Blue solution
$Cu(Cl)_2$(trien)_W	0.27	0.24	Blue solution
$Co(NO_3)_2$(trien)_W	0.33	0.17	Red solution
$Co(Cl)_2$(trien)_W	0.31	0.19	Red solution
$Ni(SO_4)$(trien)_W	0.32	0.18	Purple solution
$Fe(SO_4)$(trien)_W	0.33	0.18	Orange solution
$Zn(SO_4)$(trien)_W	0.33	0.17	White solution

3.3.3 Synthesis of metal-amine complexes from different copper nitrate:amine mole ratio

Copper nitrate-amine complexes with variable mole ratios of copper nitrate:amine = 1:2, 1:1 and 1:0.5 were prepared using similar procedure as describe above. Compositions of starting materials are shown in Table 3.4.

Table 3.4 Composition of starting materials in the preparation of metal-amine complexes from different copper nitrate:amine mole ratio

Metal complexes	**$Cu(NO_3)_2$:amine ratio**	**Weight of $Cu(NO_3)_2$ (g)**	**Weight of en (mL)**	**Weight of trien (mL)**
$Cu(NO_3)_2(en)_2$_W	1:2	0.33	0.19	-
	1:1	0.40	0.11	-
	1:0.5	0.45	0.06	-
$Cu(NO_3)_2(trien)$_W	1:2	0.23	-	0.28
	1:1	0.31	-	0.19
	1:0.5	0.38	-	0.12

3.4 Preparation of rigid polyurethane foams

3.4.1 Preparation of RPUR Foam in Paper Cup Test

RPUR foams were prepared with two step methods at room temperature (30 °C). The foams were prepared by mechanical mixing technique. In the first mixing step, polyol, catalysts (metal-amine complexes or DMCHA), surfactant and blowing agent were mixed into a paper cup. For catalysts that prepared in methanol media, catalyst (1 pbw) was dissolved in deionized water (3 pbw) before addition of polyol and surfactant in the first step.

In the second mixing step, an isocyanate was added to the mixed polyol from the first mixing then the mixture were mixed by mechanical stirrer at 2000 rpm for 20 seconds. The homogeneous mixture was obtained. The foam formulations are shown in Table 3.5.

The polymerization times investigated in the synthesis of rigid polyurethane foam were cream time, gel time, rise time and tack free time. The reaction times of the prepared foams were investigated and compared to those catalyzed with commercial catalyst (DMCHA). After that, the foams were kept at room temperature for 48 hours and then carrying out physical and mechanical characterization.

Table 3.5 RPUR foam formulations at different NCO indexes (in parts by weight unit, pbw*)

Formulations (pbw)	**NCO index**			
	100	**130**	**150**	**170**
Polyol (Daltolac® R180)	100	100	100	100
Catalysts (metal complexes or DMCHA)	1.0	1.0	1.0	1.0
Blowing agent (H_2O)	3.0	3.0	3.0	3.0
Surfactant (Tegostab® B8460)	2.5	2.5	2.5	2.5
Polymeric MDI (PMDI, Suprasec® 5005)	151.8	197.3	227.7	258.1

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

3.4.2 Preparation of RPUR foam in plastic mold

Polyol, blowing agent, surfactant and catalysts [$Cu(NO_3)_2(en)_2$_W or $Cu(NO_3)_2$(trien)_W] were mixed into a paper cup. Then, PMDI was added and immediately stirred at 2000 rpm for 20 seconds. The mixture was poured into an open plastic mold (10 x 10 x 10 cm). After that, RPUR foams were kept at room temperature for 48 hours before being removing from plastic mold.

3.5 Characterization of metal-amine complexes catalysts

3.5.1 Infrared spectroscopy

An Attenuated Total Reflectance Fourier Transformed Infrared Spectrometer (ATR-FTIR) was used to compare the functional groups between $Cu(NO_3)_2$ and copper-amine complexes. FTIR spectrum was recorded on a Nicolet 6700 FTIR spectrometer with 64 interferograms at resolution of 4 cm^{-1} in the range of 4000-800 cm^{-1}.

3.5.2 UV-Visible spectroscopy

UV-visible spectroscopy was used to measure the absorbance of copper-amine complexes. UV-Vis spectra were recorded on Varian Cary 50 UV-Vis spectrophotometer in the range of 200-500 nm.

3.5.3 Mass spectrometry (MS)

Metal-amine complexes were also analyzed by mass spectrometry (micromass Quattro micro^{TM} API spectrometer). Electrospray ionization (ESI) is used to analyze complexes by separating ions by their unique mass (mass-to-charge ratio). This method relies on the fact that every compound has a unique fragmentation pattern in the mass spectrum. The sample is ionized, then sample ions are separated based on their differing masses and relative abundance.

3.5.4 Flame Atomic absorption spectrometry (FAAS)

A Varian AA 28OFS Atomic absorption spectrometer equipped with air/nitrogen burner was used for measurement of Cu amount in metal complexes. The suitable wavelength for copper amount determination in samples is 327.4 nm, the lamp current is 5.0 mA. All of the measurements were carried out in using air/acetylene flame at flow rates of 13.5 and 2.0 L/min.

3.5.5 Elemental analysis (EA)

Elemental analysis was obtained with Perkin-Elmer EP 2400 analyzer. The percentage weight of carbon, hydrogen and nitrogen in copper-amine complexes were determined.

3.6 Characterization of RPUR foams

3.6.1 Reaction times and reaction temperatures

The reaction times namely, cream time, gel time, tack free time and rise time were investigated by using a digital stopwatch. Thermocouple (Digicon DP-71) was used to determine the temperature profile of foaming reaction.

3.6.2 Density

Density of RPUR foams was measured according to ASTM D1622-09, the dimension of specimen was 3.0 x 3.0 x 3.0 cm. The average values of three samples were reported.

3.6.3 Infrared Spectroscopy

ATR-FTIR Nicolet 6700 was also used to analyze functional groups on RPUR foams at a resolution of 4 cm^{-1} and a total of 64 interferograms. The main peaks of isocyanurate C-N stretching (at 1405-1451 cm^{-1}), urethane C=O stretching (at 1725-1735 cm^{-1}) and isocyanate asymmetric stretching (at 2265-2278 cm^{-1}) were investigated.

3.6.4 Compressive strength

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise direction were performed using universal testing machine (Lloyd/LRX) according to ASTM D 1621-09, the specimen size was 3.0 x 3.0 x 3.0 cm, the rate of crosshead movement was fixed at 2.54 mm/min and the preload cell used was 0.100 N. The compression stress at 10% strain deformation was calculated.

3.6.5 Scanning electron microscope (SEM)

The morphology and cell size of rigid foam samples were measured on a Jeol 5800LV scanning electron microscope (SEM). A slice of foam about 1.0 mm in thickness was prepared for SEM analysis by coating with gold before analyze in order to provide an electrically conductive on the surface. The slice was done at an accelerating voltage of 20 kV and magnification of 50X.

3.6.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of RPUR foam. TGA determination was perform by Netzsch STA 409C thermogravimetric analyzer. All samples were heated from 25 ^{o}C to 600 ^{o}C at heating rate of 20 ^{o}C/min under nitrogen gas. The result of thermal stability was report in percentage weight residue of foams. Initial decomposition temperature (IDT) was taken at the temperature where 5 wt% loss of foam occurred.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of metal-amine complexes [M(X)(en)$_2$ and M(X)(trien)]

Metal-amine complexes were synthesized using two methods. In the first method, metal (II) salts [MX, where M = Cu, Co, Ni, Fe, Zn; X = $(NO_3)_2$, SO_4, $(Cl)_2$, CO_3], namely metal (II) nitrate, metal (II) sulfate, metal (II) chloride or metal (II) carbonate was stirred in water. Then, a solution of ethylenediamine (en) or triethylenetetramine (trien) was added dropwise followed by addition of polysiloxane surfactant [38]. As an example, the synthesis of $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2$(trien) are shown in Scheme 4.1. The complex formation was obtained in aqueous solution. The metal (II) salts:en and metal (II) salts:trien mole ratios employed were 1:2, 1:1 and 1:0.5. The aqueous solution containing metal complexes could be further used in the preparation of rigid polyurethane foam without purification.

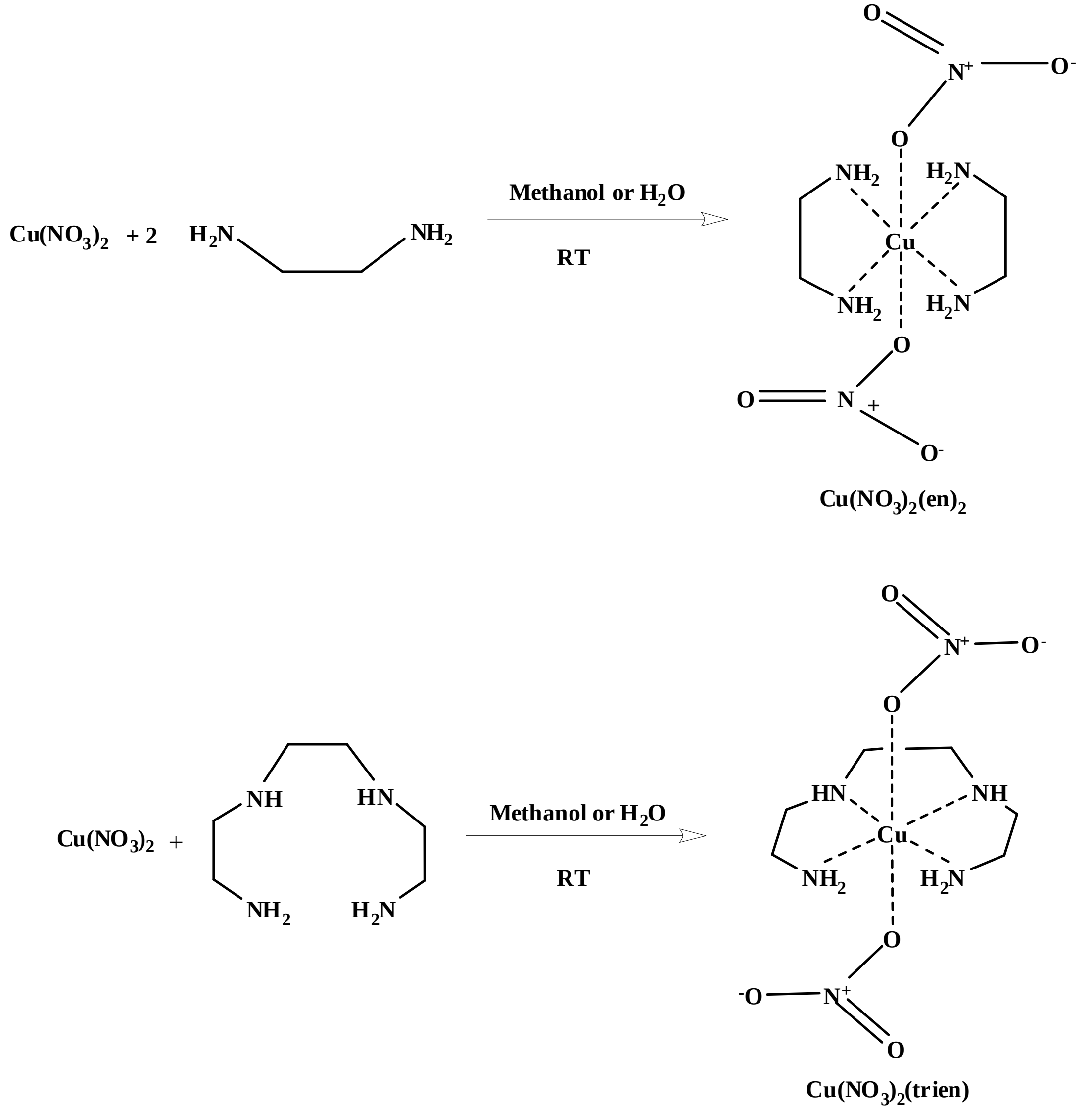
In the second method, metal-ethylenediamine complexes [M(X)(en)$_2$] and metal-triethylenetetramine complexes [M(X)(trien)] were synthesized from the reaction between metal (II) nitrate, ethylenediamine (en) or triethylenetetramine (trien) using methanol as a solvent. M(X)(en)$_2$ was obtained as a solid whereas M(X)(trien) was obtained as a viscous liquid. Methanol was removed from the metal complexes under vacuum before using in the preparation of rigid polyurethane foam.

4.2 Characterization of copper nitrate-ethylenediamine complex [$Cu(NO_3)_2(en)_2$] synthesized at the mole ratio of $Cu(NO_3)_2$:en = 1:2

4.2.1 IR spectroscopy of $Cu(NO_3)_2(en)_2$ complex

IR spectrum of $Cu(NO_3)_2(en)_2$ (Figure 4.1) exhibited absorption bands at 3156 cm^{-1} (N-H stretching), 2886 cm^{-1} (C-H stretching), 1605 cm^{-1} (N-H bending), 1454 cm^{-1} (N-O asymmetric stretching) and 1336 cm^{-1} (N-O symmetric stretching). The N-O stretching of nitro group in $Cu(NO_3)_2(en)_2$ appeared as absorption band at

1454 cm^{-1} (asymmetric N-O) and 1336 cm^{-1} (symmetric N-O), which were different from those of $Cu(NO_3)_2$ absorption bands around at 1507 cm^{-1} (asymmetric N-O) and 1432 cm^{-1} (symmetric N-O). It was found that the IR peak of $Cu(NO_3)_2(en)_2$ complex shifted from that of $Cu(NO_3)_2$ to lower energy, which suggested that the complex was formed. The lower stretching frequency of nitrate can be thought as the decrease of bond strength of N-O, due to the interaction between oxygen of nitro group and N-H of amine.



Scheme 4.1 Synthesis of $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$

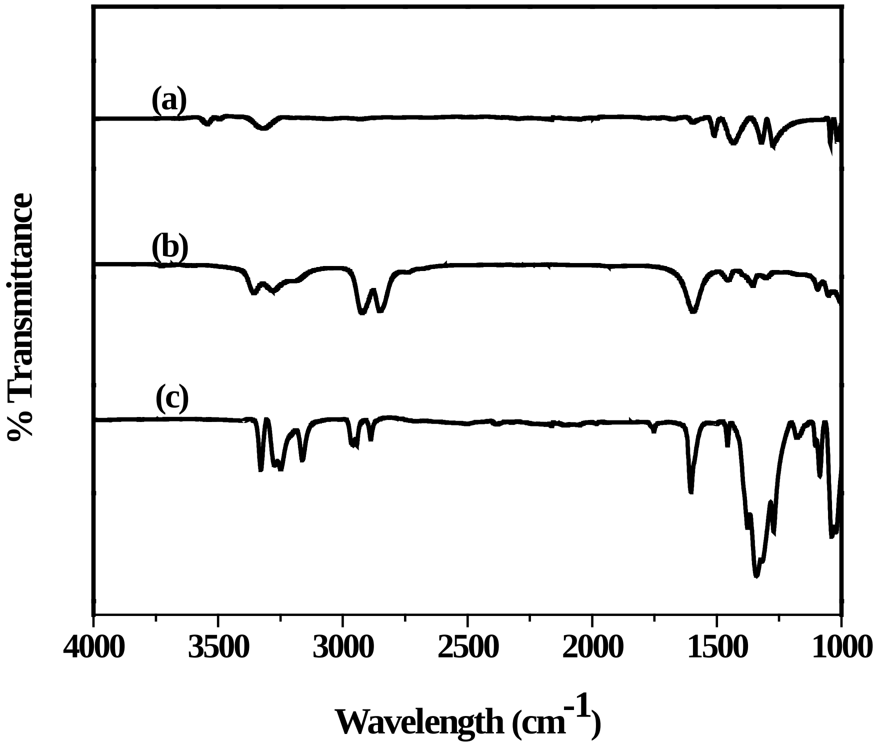


Figure 4.1 IR spectra of (a) $Cu(NO_3)_2$; (b) ethylenediamine and (c) $Cu(NO_3)_2(en)_2$ synthesized at the mole ratio of $Cu(NO_3)_2$:en = 1:2

4.2.2 UV-visible spectroscopy of $Cu(NO_3)_2(en)_2$ complex

UV-visible spectrum of $Cu(NO_3)_2$ was compared to that of $Cu(NO_3)_2(en)_2$_W, which is synthesized in water, and $Cu(NO_3)_2(en)_2$, which is synthesized in methanol as illustrated in Figure 4.2. The maximum wavelength of $Cu(NO_3)_2(en)_2$ which appeared at 207 nm shifted from the maximum wavelength of $Cu(NO_3)_2$ which showed at 205 nm, which confirmed the complex formation. In addition, $Cu(NO_3)_2(en)_2$_W and $Cu(NO_3)_2(en)_2$ had peak shoulder at 235 and 245 nm, respectively.

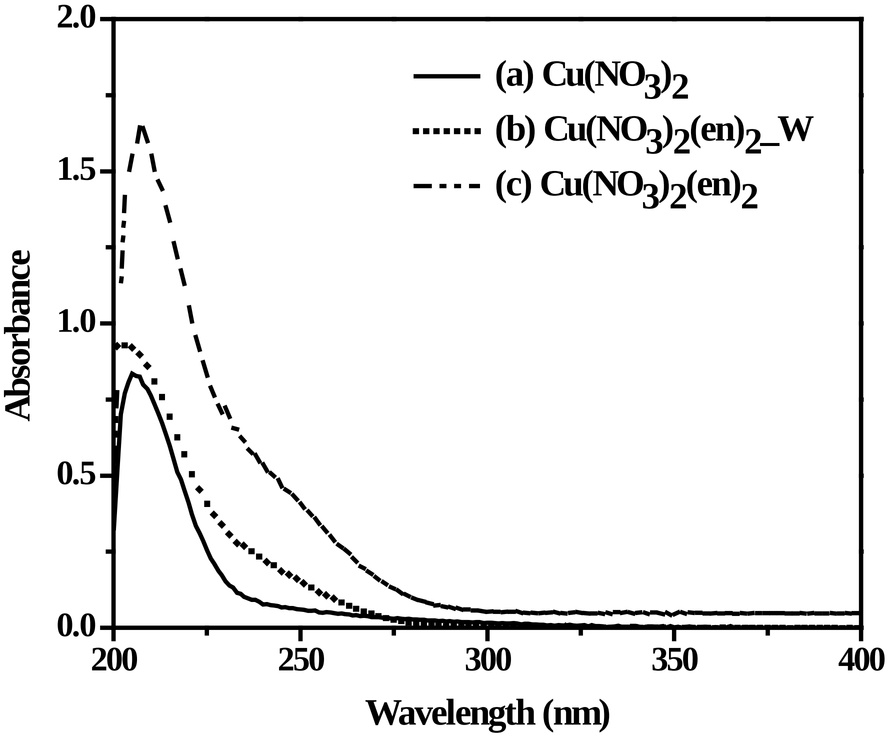


Figure 4.2 UV spectra of (a) $Cu(NO_3)_2$; (b) $Cu(NO_3)_2(en)_2$_W and (c) $Cu(NO_3)_2(en)_2$ synthesized at the mole ratio of $Cu(NO_3)_2$:en = 1:2

4.2.3 Determination of metal amount in $Cu(NO_3)_2(en)_2$ complex by flame atomic spectrometry (FAAS)

For analytical characteristics of $Cu(NO_3)_2(en)_2$ illustrated in Table 4.1 This result indicates that the experimental value and the calculated value were different.

Table 4.1 Analytical Characteristics of the FAAS method

Catalyst	**Elements determined**	**Experimental (%)**	**Calculated (%)**
$Cu(NO_3)_2(en)_2$	Cu	14.54	20.65

4.2.4 Elemental analysis of $Cu(NO_3)_2(en)_2$ complex

Elemental analysis (%C, %H and %N) of $Cu(NO_3)_2(en)_2$ is shown in Table 4.2. This result indicates that there is the consistency between the experimental value and the calculated value. It confirmed the structure of metal complex (Scheme 4.1).

Table 4.2 Elemental analysis (%C, %H, and %N) of $Cu(NO_3)_2(en)_2$

Catalyst	Elements determine	Experimental (%)	Calculate (%)
$Cu(NO_3)_2(en)_2$	%C	16.05	15.61
	%H	5.87	5.24
	%N	27.57	27.31

4.2.5 Mass spectrometry of $Cu(NO_3)_2(en)_2$ complex

The molecular ion peak of $Cu(NO_3)_2(en)_2$ at *m/z* = 307.75 corresponding to $[^{63}Cu(NO_3)_2(en)_2]^+$; *m/z* = 308.06 is observed in the ESI mass spectrum (Figure 4.3).

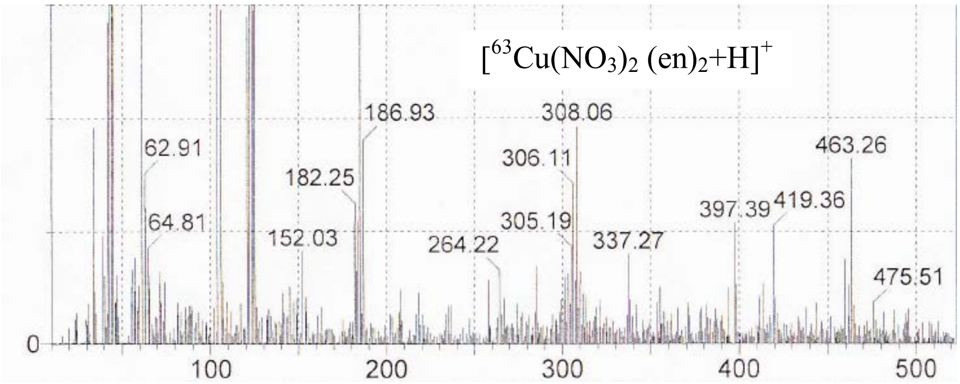


Figure 4.3 Mass spectrum of $Cu(NO_3)_2(en)_2$ synthesized at the mole ratio of $Cu(NO_3)_2$:en = 1:2

4.3 Characterization of copper nitrate-triethylenetetramine complex synthesized at the mole ratio of $Cu(NO_3)_2$:trien = 1:1

4.3.1 IR spectroscopy of $Cu(NO_3)_2$(trien) complex

IR spectrum of $Cu(NO_3)_2$(trien) (Figure 4.4) exhibited absorption bands at 3233 cm^{-1} (N-H stretching), 2881 cm^{-1} (C-H stretching), 1590 cm^{-1} (N-H bending), 1454 cm^{-1} (N-O asymmetric stretching) and 1304 cm^{-1} (N-O symmetric stretching). The N-O stretching of nitro group in $Cu(NO_3)_2$(trien) appeared as absorption band at 1454 cm^{-1} (asymmetric N-O) and 1304 cm^{-1} (symmetric N-O), which were different from the $Cu(NO_3)_2$ absorption band around at 1507 cm^{-1} (asymmetric N-O) and 1432 cm^{-1} (symmetric N-O). It was found that the IR peak of $Cu(NO_3)_2$(trien) complex shifted from $Cu(NO_3)_2$, which indicated that the complex was formed.

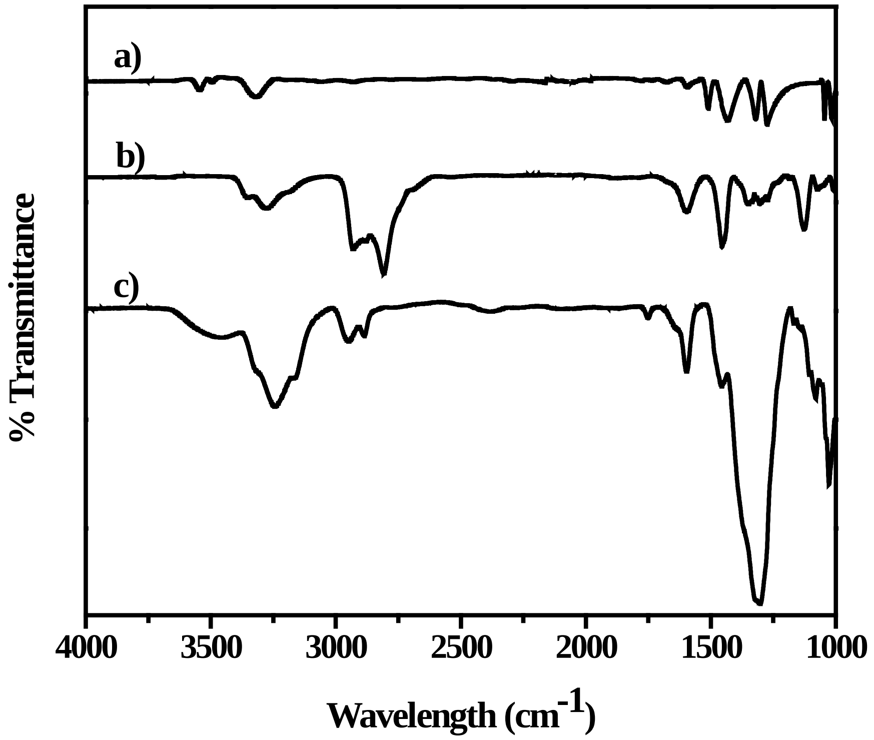


Figure 4.4 IR spectra of (a) $Cu(NO_3)_2$; (b) triethylenetetramine and (c) $Cu(NO_3)_2$(trien) synthesized at the mole ratio of $Cu(NO_3)_2$:trien = 1:1

4.3.2 UV-visible spectroscopy of $Cu(NO_3)_2$(trien) complex

UV-visible spectra of $Cu(NO_3)_2$(trien) (synthesized in methanol) was compared to that of $Cu(NO_3)_2$(trien)_W (synthesized in water) as shown in Figure 4.5. The maximum wavelength $Cu(NO_3)_2$(trien) and $Cu(NO_3)_2$(trien)_W appeared at 210 and 207 nm, respectively. Their maximum wavelengths slightly shifted from typical maximum wavelength of $Cu(NO_3)_2$ at 205 nm, which confirmed the complex formation. On the other hand, $Cu(NO_3)_2$(trien)_W and $Cu(NO_3)_2$(trien) had peak shoulder at 257 and 261 nm, respectively.

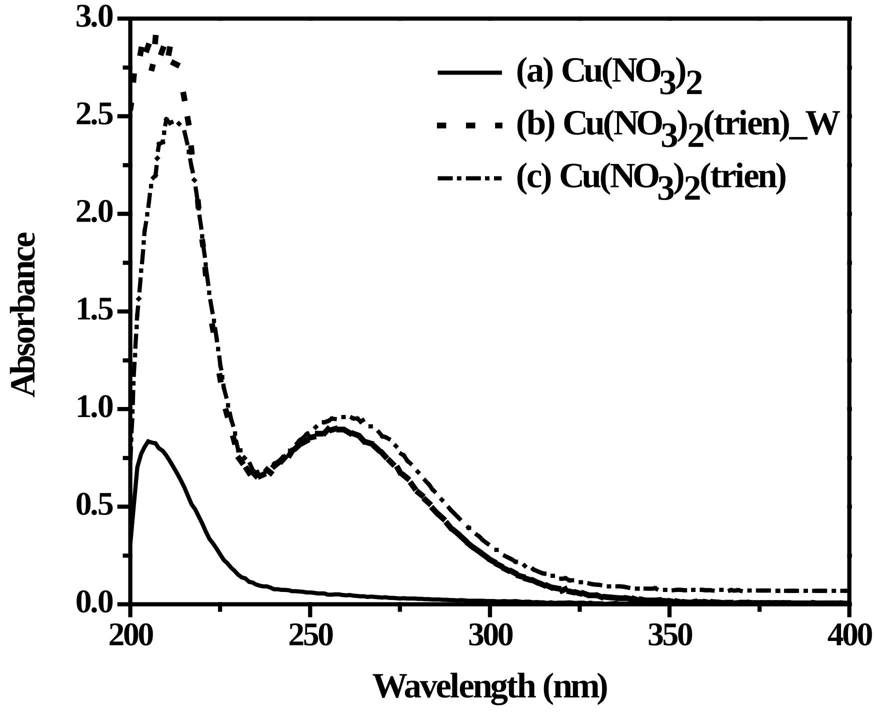


Figure 4.5 UV spectra of (a) $Cu(NO_3)_2$; (b) $Cu(NO_3)_2$(trien)_W and (c) $Cu(NO_3)_2$(trien) synthesized at the mole ratio of $Cu(NO_3)_2$:trien = 1:1

4.3.3 Determination of metal amount in $Cu(NO_3)_2$(trien) complex by flame atomic spectrometry (FAAS)

For analytical characteristics of $Cu(NO_3)_2$(trien) illustrated in Table 4.3. This result indicates that the experimental value and the calculated value were different.

Table 4.3 Analytical Characteristics of the FAAS method

Catalyst	**Elements determined**	**Experimental (%)**	**Calculated (%)**
$Cu(NO_3)_2$(trien)	Cu	15.48	19.04

4.3.4 Elemental analysis of $Cu(NO_3)_2$(trien) complex

Elemental analysis (%C, %H and %N) of $Cu(NO_3)_2$(trien) shown in Table 4.4. This result indicates that there is the consistency between the experimental value and the calculated value. It confirmed the structure of metal complex.

Table 4.4 Elemental analysis (%C, %H, and %N) of $Cu(NO_3)_2$(trien)

Catalyst	**Elements determine**	**Experimental (%)**	**Calculate (%)**
$Cu(NO_3)_2$(trien)	%C	19.78	21.58
	%H	6.64	5.44
	%N	20.39	25.17

4.3.5 Mass spectrometry of $Cu(NO_3)_2$(trien) complex

The molecular ion peak of $Cu(NO_3)_2$(trien) at *m/z* = 333.786 corresponding to $[^{63}Cu(NO_3)_2(trien)]^+$; *m/z* = 334.288 is observed in the mass spectrum (MALDI-TOF) (Figure 4.6).

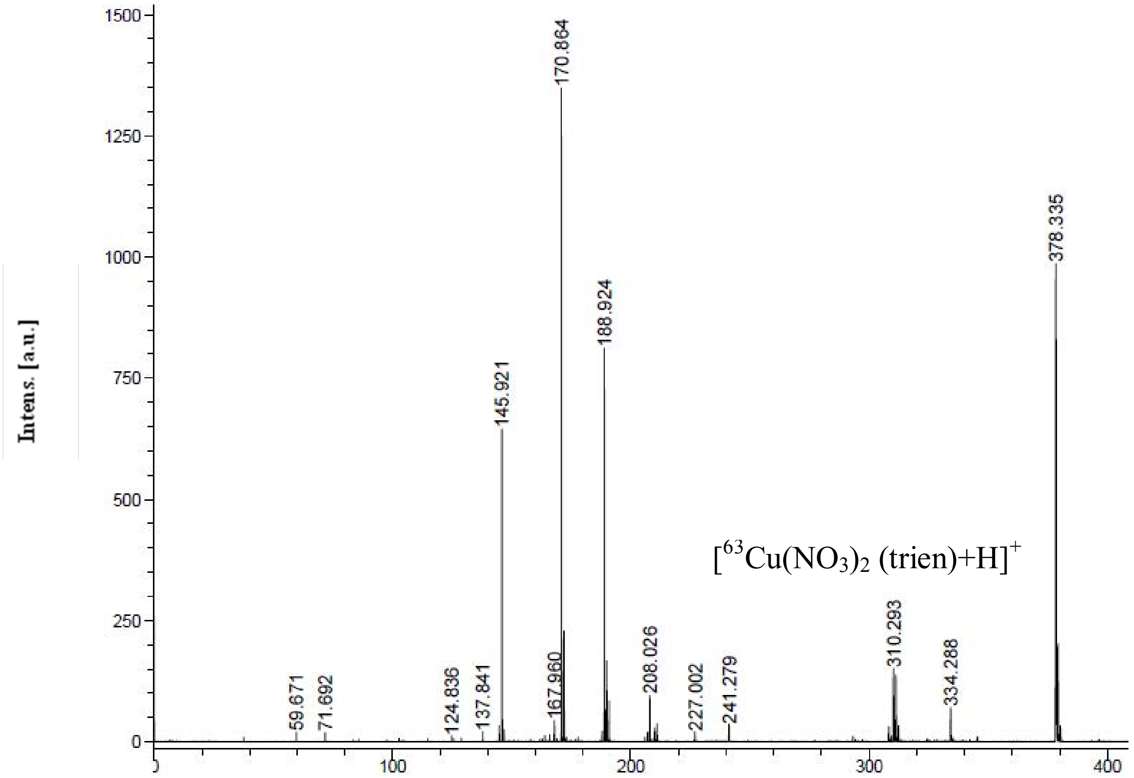


Figure 4.6 Mass spectrum of $Cu(NO_3)_2$(trien) synthesized at the mole ratio of $Cu(NO_3)_2$:trien = 1:1

4.4 Preparation of rigid polyurethane (RPUR) foams

4.4.1 Preparation of RPUR catalyzed by different metal (II) salts-ethylenediamine (en) complexes

In this section, various types of inorganic metal (II) salts were used to form complexes with ethylenediamine. Inorganic metal compounds that used in this experiment were copper (II) nitrate ($Cu(NO_3)_2$), copper (II) sulfate ($Cu(SO_4)_2$), copper (II) chloride ($CuCl_2$), copper (II) carbonate ($CuCO_3$), cobalt (II) nitrate ($Co(NO_3)_2$), cobalt (II) chloride ($CoCl_2$), nickel (II) sulfate ($NiSO_4$), zinc (II) sulfate ($ZnSO_4$) and iron (II) sulfate ($FeSO_4$).

Rigid polyurethane foams catalyzed by metal-ethylenediamine complexes were prepared by mechanical mixing technique in two steps. In the first step, polyol was mixed with catalysts, which have surfactant and water as a blowing agent. In the second step, isocyanate (polymeric MDI) was added to the mixed polyol from the first mixing, then the mixture were mixed to obtained homogeneous mixture by mechanical stirrer at 2000 rpm for 20 seconds. DMCHA was used as a commercial reference catalyst.

Cream time, gel time, rise time and tack free time were investigated during the reaction. After that, the foams were kept at room temperature for 48 hours before physical and mechanical properties characterization. In this part, content of polyol, catalyst, silicone surfactant, blowing agent (water) and NCO index of polymeric MDI were fixed as shown in Table 4.5.

Table 4.5 RPUR foam formulation catalyzed by metal complexes at the NCO index = 100

Formulations	Content (pbw*)
Daltolac® R180	100
Catalyst (metal complexes or DMCHA)	1.0
Surfactant (Tegostab® B8460)	2.5
Blowing agent (Water)	3.0
Polymeric MDI (PMDI, Suprasec® 5005)	151.8

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

The influence of types of metal salts used to form complexes with with ethylenediamine on the reaction times is presented in Table 4.6. From Table 4.6, it was found that copper nitrate-ethylenediamine complex, $Cu(NO_3)_2(en)_2$, acted as a good catalyst when compared with the other metal salts. The reaction time of foaming reaction was shorter and the foam external appearance was better than the foams prepared from other metal complexes. The appearances of RPUR foams catalyzed by different types of metal complexes are shown in Figure 4.7.

Table 4.6 Reaction times of RPUR foams prepared by different types of metal complexes prepared from different inorganic metal (II) salts and ethylenediamine at the mole ratio of metal (II) salts:en = 1:2

Catalyst	**Cream time (min:sec)**	**Gel time (min:sec)**	**Rise time (min:sec)**	**Tack free time (min:sec)**	**Volume (V)**
$Cu(NO_3)_2(en)_2$	1:34	2:39	4:29	4:41	6/8V
$Cu(CO_3)(en)_2$	0:37	0:53	3:20	4:57	7/8V
$Cu(SO_4)(en)_2$	0:45	2:20	9:30	14:11	5/8V
$Cu(Cl)_2(en)_2$	0:40	1:54	8:36	12:47	5/8V
$Co(NO_3)_2(en)_2$	0:37	1:59	6:50	14:08	4/8V
$Co(Cl)_2(en)_2$	0:37	2:15	7:57	16:35	4/8V
$Ni(SO_4)(en)_2$	0:44	2:22	10:50	16:10	5/8V
$Fe(SO_4)(en)_2$	0:42	1:20	4:28	7:44	4/8V
$Zn(SO_4)(en)_2$	0:36	2:10	7:29	17:45	4/8V

$Cu(NO_3)_2(en)_2$ $Cu(CO_3)(en)_2$ $Co(NO_3)_2(en)_2$

$Cu(Cl_2)(en)_2$ $Ni(SO_4)(en)_2$ $Cu(SO_4)(en)_2$

$Zn(SO_4)(en)_2$ $Co(Cl)_2(en)_2$ $Fe(SO_4)(en)_2$

Figure 4.7 External appearance of RPUR foams catalyzed by different types of metal (II) salts-ethylenediamine complexes

The reactions catalyzed by $Co(NO_3)_2(en)_2$, $Cu(Cl)_2(en)_2$, $Ni(SO_4)(en)_2$, $Cu(SO_4)(en)_2$, $Zn(SO_4)(en)_2$, $Co(Cl)_2(en)_2$ and $Fe(SO_4)(en)_2$ had long reaction times and the foam collapsed after reaction completed. These metal complexes catalysts were unsuitable catalysts for the RPUR foam formation. But RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ showed good foam and short reaction time. RPUR foam that prepared from $Cu(NO_3)_2(en)_2$ had fine surface, whereas foam prepared from $Cu(CO_3)(en)_2$ had rough surface. After cutting foam that prepared by used $Cu(CO_3)(en)_2$ as catalyst, friable appearance was observed. Also, $Cu(CO_3)(en)_2$ had poor solubility in polyol. In addition, the longer gel time and shorter tack free time were observed in $Cu(NO_3)_2(en)_2$ system, these results will affected to good processing of foam. Thus, $Cu(NO_3)_2(en)_2$ was selected as a catalyst for further detail study.

4.4.2 Preparation of RPUR catalyzed different metal (II) salts-triethylenetetramine (trien) complexes.

The effect of types of metal (II) salts that form different metal complex catalysts with triethylenetetramine on the time of foaming reaction is shown in Table 4.7.

Table 4.7 Reaction times of RPUR foams prepared by different types of metal complexes prepared from different inorganic metal (II) salts and triethylenetetramine at the mole ratio of metal (II) salts:trien = 1:1

Catalyst	**Cream time (min:sec)**	**Gel time (min:sec)**	**Rise time (min:sec)**	**Tack free time (min:sec)**	**Volume (V)**
$Cu(NO_3)_2$(trien)	0:40	2:25	7:04	8:33	5/8V
$Cu(SO_4)$(trien)	0:52	3:02	9:48	16:20	4/8V
$Cu(CO_3)$(trien)	0:48	1:12	3:31	5:45	7/8V
$Cu(Cl)_2$(trien)	0:53	3:09	8:21	13:33	6/8V
$Co(NO_3)_2$(trien)	0:47	3:04	9:56	16:26	5/8V
$Co(Cl)_2$(trien)	0:51	3:11	10:13	16:47	4/8V
$Ni(SO_4)$(trien)	1:23	2:35	6:48	10:22	4/8V
$Fe(SO_4)$(trien)	1:03	3:05	8:38	15:27	5/8V

$Zn(SO_4)$(trien)	0:57	3:02	9:15	17:42	4/8V

It can be seen from Table 4.7 that in the case of metal complex catalysts prepared from triethylenetetramine, the results was similar those prepared from ethylenediamine. $Cu(NO_3)_2$(trien) and $Cu(CO_3)$(trien) gave good foam and shorter reaction time as compared to the other metal complexes. Copper nitrate-triethylenetetramine gave the best results and was selected for further study in details in the next step. Appearances of RPUR foams which prepared by different types of inorganic metal compounds with triethylenetetramine complexes are displayed in Figure 4.8.

$Cu(NO_3)_2$(trien)

$Cu(CO_3)$(trien)

$Zn(SO_4)$(trien)

$Cu(Cl)_2$(trien)

$Ni(SO_4)$(trien)

$Co(Cl)_2$(trien)

$Fe(SO_4)$(trien)

$Co(NO_3)_2$(trien)

$Cu(SO_4)$(trien)

Figure 4.8 External appearance of RPUR foams catalyzed by different types of metal (II) salts-triethylenetetramine complexes.

4.4.3 Catalytic activity of metal complexes prepared from different copper nitrate:amine mole ratio

Copper nitrate-amine complex was used as a catalyst in the formulation of rigid polyurethane foams for this study. The reaction time, namely cream time, gel time, rise time and tack free time were investigated.

4.4.3.1 Catalytic activity of metal complexes prepared from different copper nitrate:ethylenediamine mole ratio

RPUR foams were prepared from copper nitrate-ethylenediamine complex prepared with variable mole ratios of $Cu(NO_3)_2$:en = 1:2, 1:1 and 1:0.5. At the mole ratios of $Cu(NO_3)_2$:en = 1:1 and 1:0.5, it was expected that there would be a mixture of excess $Cu(NO_3)_2$ and $Cu(NO_3)_2(en)_2$ that would also catalyze the foaming reaction. Metal complexes were synthesized in water and methanol. The reaction times and volume of RPUR foams synthesized in water and methanol were studied.

The data in Table 4.8 showed that by decreasing the amount of ethylenediamine in copper nitrate:ethylenediamine ratio from 1:2 to 1:1 and the metal complex was prepared in water media, the reaction time slightly decreased and foam appearance changed to brittle material. This might be because there was not enough $Cu(NO_3)_2(en)_2$ to catalyze gelling reaction and $Cu(NO_3)_2$ was not a good catalyst. In addition, when reduced the mole ratio of copper nitrate:ethylenediamine to 1:0.5 in water media, the reaction times were not different and foam appearance was also brittle material.

The influence of mole ratio $Cu(NO_3)_2$:en on reaction times when the metal complex was prepared in methanol system was also investigated. The results of reaction times and volume obtained at various mole ratios are shown in Table 4.8. It can be seen that the reaction times were not changed when ethylenediamine content in $Cu(NO_3)_2(en)_2$ was reduced. However, when mole ratio of $Cu(NO_3)_2$:en was 1:0.5, the excess $Cu(NO_3)_2$ was not completely soluble in polyol and therefore, the experimental result could not be obtained.

As the results, it could be concluded that the foam appearance which catalyzed with $Cu(NO_3)_2$:en prepared at the mole ratio of 1:2 gave better foam than those prepared with the mole ratios of 1:1 and 1:0.5. Thus, $Cu(NO_3)_2(en)_2$ prepared at the mole ratio of 1:2 was selected for study in the further step.

Table 4.8 Reaction times of RPUR foams prepared at NCO index of 100 catalyzed by copper nitrate-ethylenediamine complex prepared at different $Cu(NO_3)_2$:en mole ratios

$Cu(NO_3)_2$:en Mole ratio	**Solvent used in synthesis**	**Cream time (min:sec)**	**Gel time (min:sec)**	**Rise time (min:sec)**	**Tack free time (min:sec)**	**Volume (V)**
1:2	water	1:10	1:47	4:04	4:42	6/8V
1:1	water	0:53	1:36	3:15	3:18	6.5/8V
1:0.5	water	0:59	1:47	3:45	3:52	6.5/8V
1:2	methanol	1:13	2:22	3:56	4:19	6/8V
1:1	methanol	0:57	2:28	3:57	4:29	6/8V

4.4.3.2 Catalytic activity of metal complexes prepared from different copper nitrate: triethylenetetramine mole ratio

Copper nitrate-triethylenetetramine complex prepared in water and methanol at different mole ratios of $Cu(NO_3)_2$:trien were also used to catalyzed polyurethane foaming reaction. The reaction times and volume of RPUR foams were investigated (Table 4.9). It was found that metal complex prepared at $Cu(NO_3)_2$:trien mole ratio of 1:2 had long reaction times and gave brittle foam when $Cu(NO_3)_2$(trien) complex was prepared in water and methanol. The foam catalyzed by $Cu(NO_3)_2$(trien) complex prepared at the mole ratio of $Cu(NO_3)_2$:trien = 1:1 had good appearance. Therefore, $Cu(NO_3)_2$(trien) complex prepared at the mole ratio of $Cu(NO_3)_2$:trien = 1:1 was used to prepare RPUR foam in order to study the effect of catalyst quantity on their reaction times and density.

Table 4.9 Reaction times of RPUR foams prepared at NCO indexes of 100 catalyzed by metal complexes prepared at different $Cu(NO_3)_2$:trien mole ratios

$Cu(NO_3)_2$:trien Mole ratio	**Solvent used in synthesis**	**Cream time (min:sec)**	**Gel time (min:sec)**	**Rise time (min:sec)**	**Tack free time (min:sec)**	**Volume (V)**	**Density (kg/m^3)**
1:2	water	1:25	2:26	7:31	11:13	4/8V	43.13
1:1	water	0:51	2:12	5:51	8:32	5/8V	44.09
1:0.5	water	0:45	2:09	6:03	7:37	5/8V	40.76
1:2	methanol	0:55	3:36	7:52	14:21	4/8V	45.38
1:1	methanol	0:53	3:20	6:18	8:48	5/8V	46.62

4.4.4 Effect of catalyst quantity on reaction time of RPUR foams

Catalysts promote the blowing and gelling reactions in polyurethane foam formulation. Catalyst quantity was adjusted for the appropriate foam formulation. The optimum catalyst quantity affected reaction times, density and appearance of RPUR foam.

4.4.4.1 Effect of $Cu(NO_3)_2(en)_2$ quantity

The effect of $Cu(NO_3)_2(en)_2$ catalyst content on the reaction times and density of RPUR foams are shown in Table 4.10. It can be observed that density of RPUR foams decreased with increasing of catalyst content due to promotion of the blowing reaction. The increasing of generated blowing gas conducted to low density [39]. In addition, the increasing of catalyst content promoted the gelling reaction, which was confirmed by faster gel time and tack free time. $Cu(NO_3)_2(en)_2$ complex prepared in water and methanol gave similar foaming reaction time. This data suggested that $Cu(NO_3)_2(en)_2$ is a blowing and gelling catalyst having less catalytic reactivity than the reference commercial amine catalyst (DMCHA).

Table 4.10 Reaction times of RPUR foams prepared at the NCO index of 100 catalyzed by different amount of $Cu(NO_3)_2(en)_2$ in the foam formulation

Catalyst content (pbw)	**Media**	**Cream time (min:sec)**	**Gel time (min:sec)**	**Rise time (min:sec)**	**Tack free time (min:sec)**	**Volume (V)**	**Density (kg/m^3)**
1.0	water	1:10	1:47	4:04	4:42	6/8V	43.73
2.0	water	1:02	1:38	4:02	4:39	6.5/8V	42.52
3.0	water	0:58	1:30	4:00	4:27	6.5/8V	42.32
1.0	methanol	1:23	2:52	4:42	4:55	6/8V	44.91
2.0	methanol	1:26	2:50	4:32	4:47	6/8V	42.49
3.0	methanol	1:30	2:45	4:26	4:44	6.5/8V	42.37

4.4.4.2 Effect of $Cu(NO_3)_2(trien)$ quantity

The influence of $Cu(NO_3)_2(trien)$ content on reaction times and density was also investigated. The results shown in Table 4.11 indicated that gel time and tack free time decreased when increased catalyst for both systems. These results were similar to the works carried out with system that used $Cu(NO_3)_2(en)_2$ catalyst as shown in the previous section. In addition, when the amount of catalyst was increased to 3.0 pbw in methanol system, catalyst was partially dissolved in polyol starting material. Thus, the result at 3.0 pbw was not reported in Table 4.11.

Table 4.11 Reaction times of RPUR foams prepared at the NCO index of 100 catalyzed by different amount of $Cu(NO_3)_2(trien)$ in the foam formulation

Catalyst content (pbw)	**Media**	**Cream time (min:sec)**	**Gel time (min:sec)**	**Rise time (min:sec)**	**Tack free time (min:sec)**	**Volume (V)**	**Density (kg/m^3)**
1.0	water	0:51	2:12	5:51	8:32	5/8V	44.09
2.0	water	0:52	2:06	6:16	8:21	5.5/8V	43.45
3.0	water	0:50	2:02	6:09	8:15	5.5/8V	43.26
1.0	methanol	0:53	3:20	6:18	8:48	5/8V	46.62
2.0	methanol	0:50	2:55	7:04	8:37	5.5/8V	45.53

From the above results, it can be summarized that when the amount of $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ catalysts increased, the gel time and tack free time decreased. The catalyst content at 1.0 pbw in the foam formulation was chosen to study the effect of blowing on foam density in the next section.

4.4.5 Effect of NCO indexes on density of RPUR foams

By increasing amount of polymeric MDI in the foam formulation, various NCO indexes at 100, 130, 150 and 170 was investigated for RPUR formation and using $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ as catalysts. The plots of foam density against various NCO indexes catalyzed by $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ prepared in water and methanol are shown in Figure 4.9. It can be seen that density of RPUR foams increased with increasing the content of NCO indexes. This was due to the excess of isocyanate in RPUR system could undergo further polymerization to provide crosslink structure.

When increasing NCO index, the foam appearance was more brittle. Density of foams catalyzed by both $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ at the NCO index of 100 was in the range of 40-50 kg/m^3, which was the desirable density for foam applications [40]. Thus, the optimum NCO index at 100 was used for study in the next step.

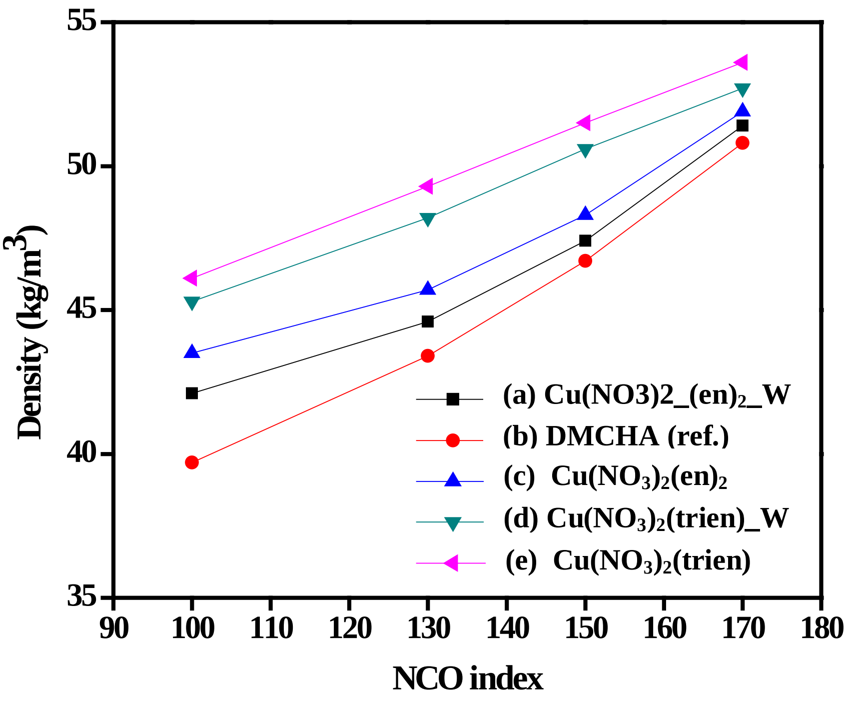


Figure 4.9 Effect of NCO indexes on density of RPUR foams catalyzed by different catalysts (a) $Cu(NO_3)_2(en)_2$_W; (b) DMCHA (ref.); (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2$(trien) _W and (e) $Cu(NO_3)_2$(trien)

Additionally, Figure 4.9 also showed the density of foams which prepared from commercial catalyst (DMCHA). It also indicated that the increased of NCO indexes of DMCHA resulted in an increase of foam density. Furthermore, it was also demonstrated that the density of foams prepared from DMCHA catalyst showed lower density than those prepared from $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2$(trien). This indicated that DMCHA is a better blowing catalyst than $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2$(trien).

4.4.6 Effect of blowing agent quantity on density of RPUR foams

The effect of blowing agent (water) content on density of RPUR foams is shown in Figure 4.10. It was found that density of RPUR foams decreased with increasing blowing agent content from 3 to 4 parts by weight (pbw). Blowing reaction resulted from the reaction of water with isocyanate groups to generate carbon dioxide gas. Therefore, the increase of blowing agent generated more gas bubbles [9]. Moreover, RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2$(trien) synthesized in water and methanol systems showed the similar trend of density.

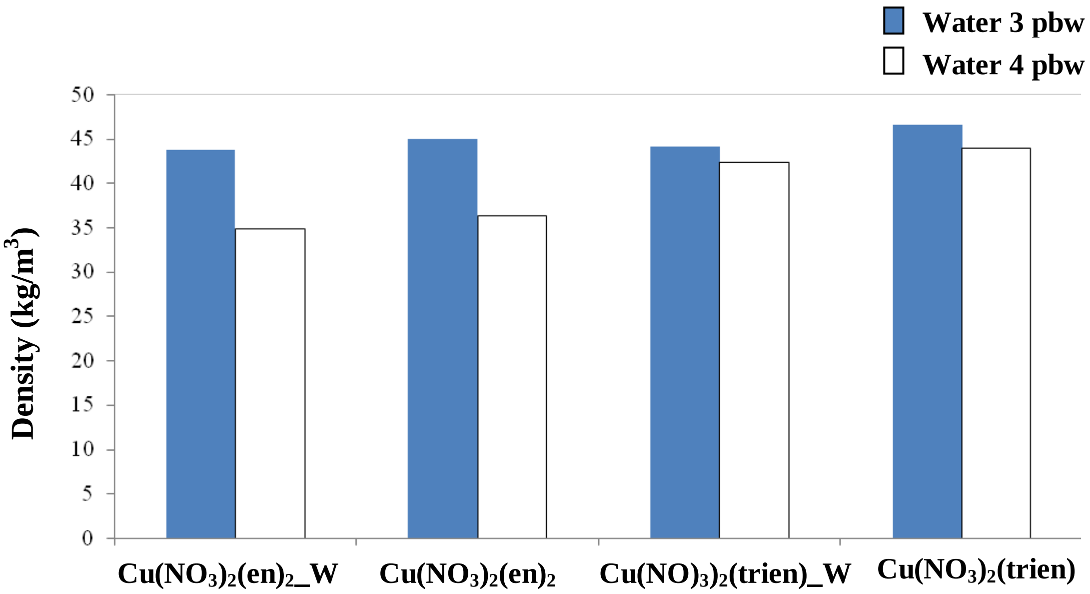


Figure 4.10 Effect of blowing agent content on density of RPUR foams prepared at the NCO index of 100

Therefore, the optimum blowing agent was 3 part by weight. The suitable formulations are listed in Table 4.12 used for preparing and testing RPUR foams.

Table 4.12 The optimum formulation for preparing RPUR foams

Formulation	**Concentration (pbw)**	
	Cu(NO$_3$)$_2$:en	**Cu(NO$_3$)$_2$:trien**
Cu(NO$_3$)$_2$:amine mole ratio	1:2	1:1
Daltolac® R180	100	100
Catalyst (metal complexes or DMCHA)	1.0	1.0

Surfactant (Tegostab® B8460)	2.5	2.5
Blowing agent (Water)	3.0	3.0
Polymeric MDI (PMDI, Suprasec® 5005)	151.8	151.8
NCO index	100	100

4.4.7 Rise profiles of RPUR foams

Rise profiles of RPUR foams catalyzed by DMCHA and copper nitrate-amine complexes are shown in Figure 4.11. RPUR foams catalyzed by DMCHA had faster rise time than those catalyzed by $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$. DMCHA is a tertiary amine-based catalyst and has strong catalytic activity towards both blowing and gelling reaction [30].

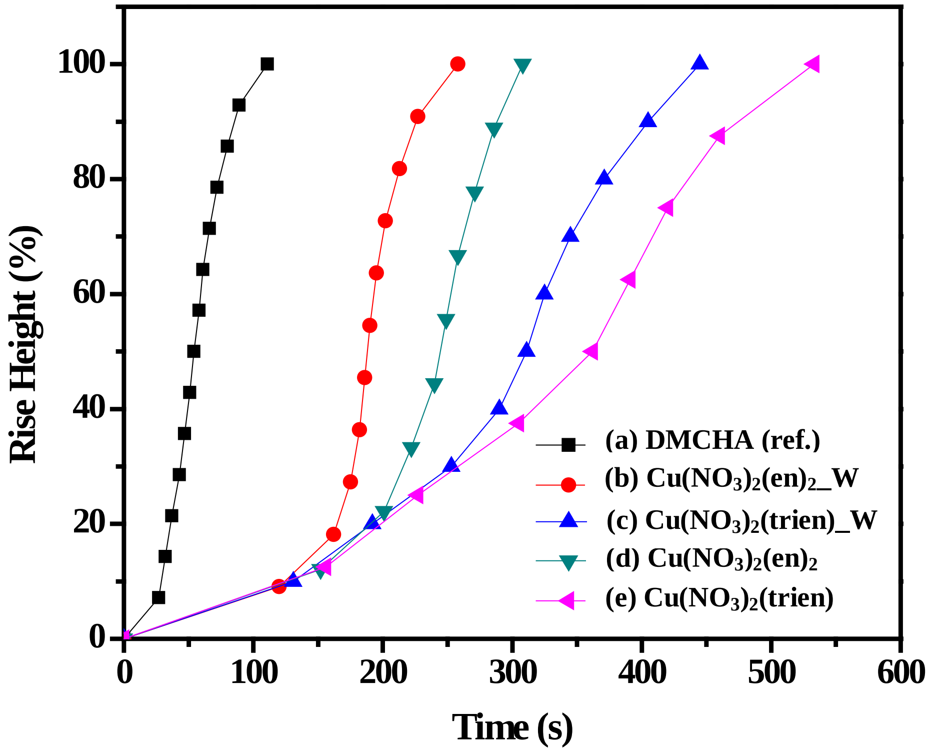


Figure 4.11 Rise profiles of RPUR foams catalyzed by different metal complexes (a) DMCHA (ref.); (b) $Cu(NO_3)_2(en)_2$_W; (c) $Cu(NO_3)_2(trien)$_W; (d) $Cu(NO_3)_2(en)_2$ and (e) $Cu(NO_3)_2(trien)$

Rise profiles of RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ had similar trend. The maximum rise rate can be calculated from maximum slope of graph between reaction time and rise height. RPUR foams prepared from DMCHA had higher maximum rise rate than those prepared from $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ (Figure 4.12).

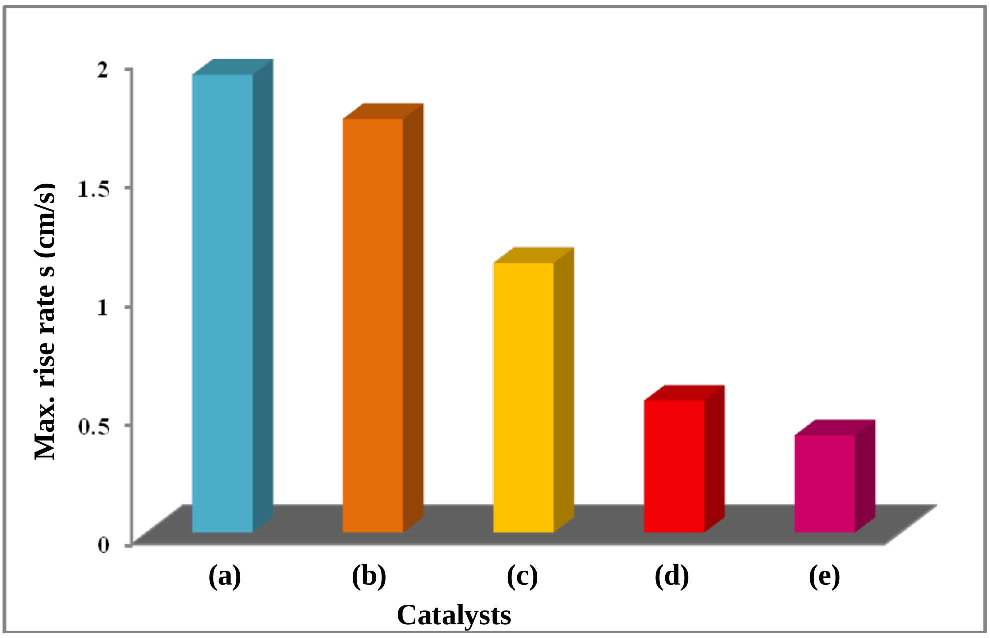


Figure 4.12 Maximum rise rates of RPUR foams catalyzed by different metal complexes at NCO index of 100 (a) DMCHA; (b) $Cu(NO_3)_2$ $(en)_2$_W; (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2$(trien)_W and (e) $Cu(NO_3)_2$ (trien)

4.4.8 Foaming Temperature

Foaming temperature profiles of RPUR foams at the NCO index of 100 are shown in Figure 4.13. It was found that DMCHA and copper nitrate-amine complexes showed similar temperature profiles. The foaming temperature gradually increased after starting reaction between isocyanate and water. The results indicated that polymerization reaction is exothermic reaction. The maximum core temperature (T_{max}) of RPUR foams is shown in Table 4.13. T_{max} of RPUR foams catalyzed by DMCHA and metal-amine complexes were 132°C and 107-119°C, respectively.

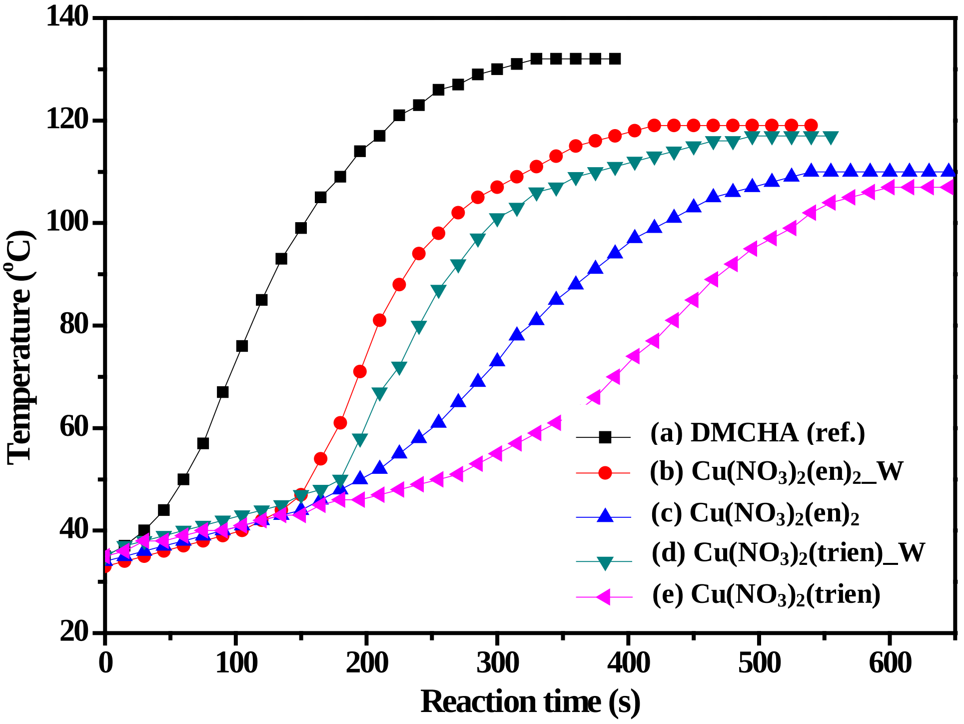


Figure 4.13 Temperature profiles of RPUR foams catalyzed by various catalysts at NCO index of 100 (a) DMCHA (ref.); (b) $Cu(NO_3)_2(en)_2$_W; (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2(trien)$_W and (e) $Cu(NO_3)_2(trien)$

Table 4.13 Maximum core temperature of RPUR foams catalyzed by DMCHA and copper nitrate-amine complexes at NCO index of 100

Catalysts	**Maximum core temperature (°C)**	**Starting time at T_{max} (sec(min))**
DMCHA	132	330 (5:30)
$Cu(NO_3)_2(en)_2$_W	119	420 (7:00)
$Cu(NO_3)_2(en)_2$	117	495 (8:15)
$Cu(NO_3)_2(trien)$_W	110	540 (9:00)
$Cu(NO_3)_2(trien)$	107	600 (10:00)

4.4.9 NCO conversion of RPUR foams

FTIR spectroscopy has been widely use for investigate the polymerization of RPUR foam system. The FTIR spectra in 4000-1000 cm^{-1} regions for starting materials, namely polyol, polymeric MDI and their corresponding RPUR foams are shown in Figure 4.14. Figure 4.14 (a) showed significant signals of O-H stretching at 3400 cm^{-1}. Figure 4.14 (b) indicated absorption signal at 2275 cm^{-1}, which can be assign to NCO stretching. The absorption peak of NCO stretching at 2277 cm^{-1} was obviously decreased as shown in Figures 4.14 (c) and (d).

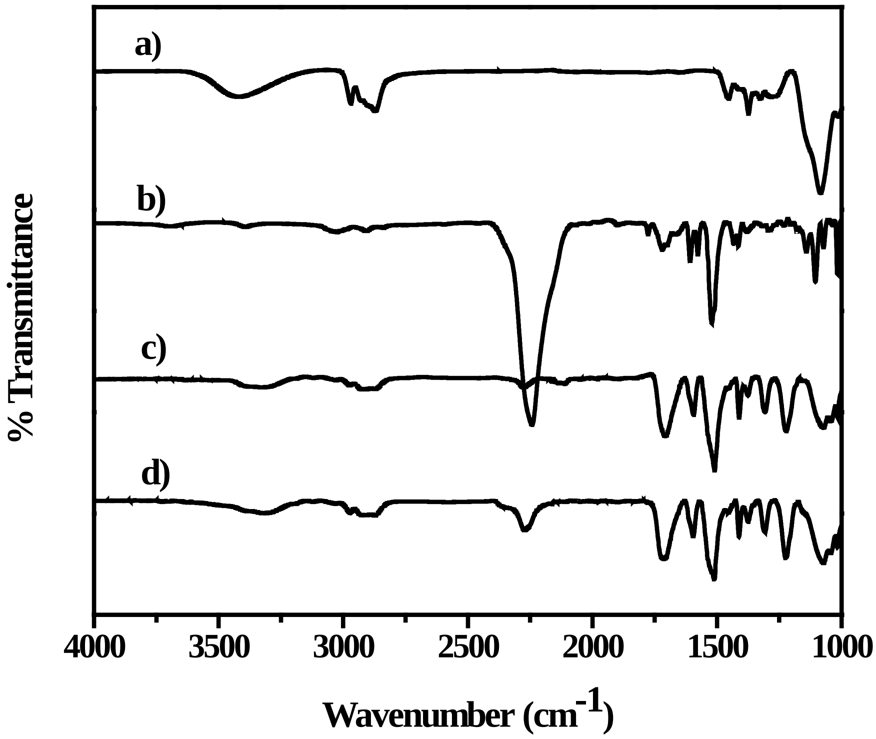


Figure 4.14 FTIR spectra of starting materials and RPUR foams catalyzed by mixed metal complexes (a) polyether polyol; (b) PMDI; (c) RPUR foams catalyzed by DMCHA (ref.) and (d) RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$

In addition, from FTIR spectra of RPUR foams as shown in Figure 4.15, the absorption bands at 3390, 1715, 1520, 1220 cm^{-1} showed the urethane and urea linkages that were formed through the polymerization of isocyanate groups, hydroxyl groups and water. The absorption signals of N-H stretching of amine group and C=O stretching of urethane and urea linkage were also observed at 3390 and 1715 cm^{-1}, respectively. The N-H bending vibration and C-N stretching vibration of urethane and urea groups at 1520 cm^{-1} was observed. The absorption band at 1220 cm^{-1} of C-N-H stretching vibration of urethane and urea groups was also detected [41].

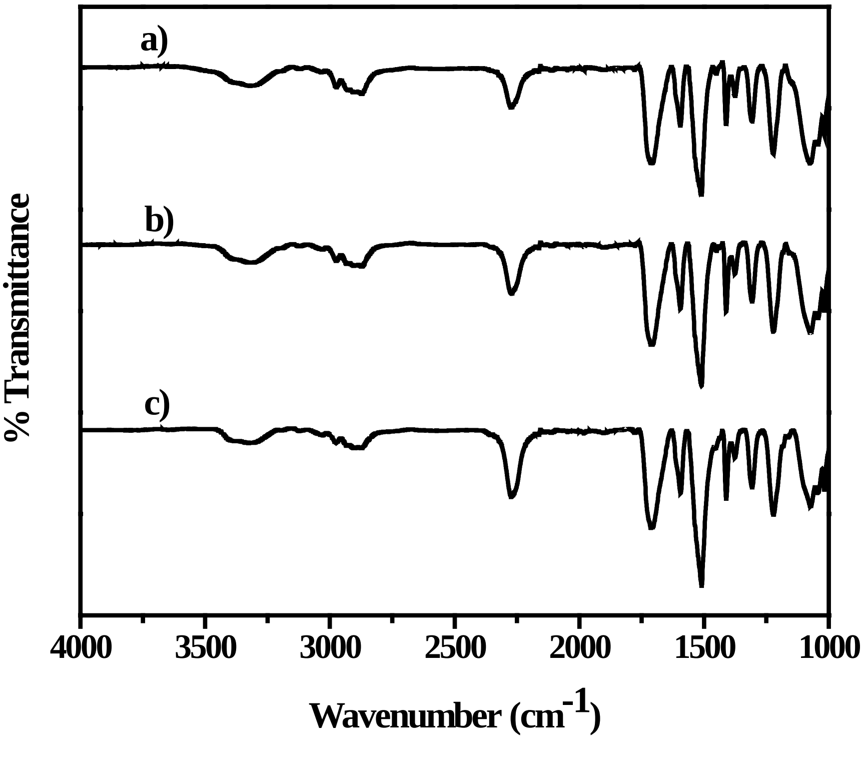


Figure 4.15 IR spectra of RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ at different NCO indexes (a) 100; (b) 130 and (c) 150

NCO conversion of RPUR foams was determined from FTIR spectra. When higher NCO index was used in the foam formulation, higher intensity of free NCO absorption band could be found in RPUR foam as shown in Figure 4.15. The NCO conversion defined as the ratio between isocyanate peak area at time t and isocyanate peak area at initial time as shown in following equation [42-47]:

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

where;

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

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

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

Polyisocyanurate:polyurethane (PIR:PUR) ratio was calculated from the peak area of isocyanurate and urethane at 1415 and 1220 cm^{-1}, respectively (Table 4.14).

Table 4.14 Assignment of IR absorption bands of RPUR foams used for calculation

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

NCO conversion of RPUR foams catalyzed by metal-amine complexes at NCO indexes 100, 130 and 150 are reported in Figure 4.16. It can be observed that NCO conversion decreased with increasing the content of NCO indexes. The excess isocyanate could not undergo trimerization to provide isocyanurate group. Therefore copper-amine complex catalysts were not specific toward of isocyanurate formation. The NCO conversion decreased with increasing the content of NCO index, the conversion was 97-99 %.

The ratio of polyisocyanurate:polyurethane (PIR:PUR) in RPUR foams prepared from different catalysts is shown in Figure 4.17. It can be seen that PIR:PUR of all RPUR foams slightly increased with increasing the content of NCO index. Therefore, this result indicated that $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ were not good catalyst for polyisocyanurate formation. It could be summarized that $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ were good catalysts for polyurethane formation and blowing reaction but they were not good catalysts for trimerization reaction. NCO conversion and PIR:PUR ratio of RPUR foams catalyzed by copper-amine complexes is illustrated in Table 4.15.

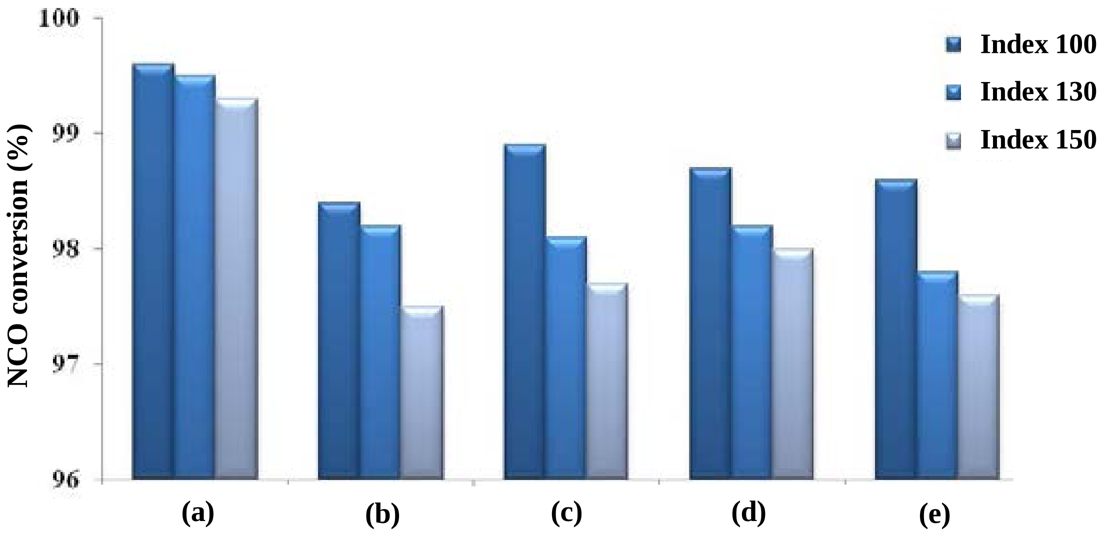


Figure 4.16 NCO conversions of RPUR foams catalyzed by different catalysts at different NCO indexes (a) DMCHA (ref.); (b) $Cu(NO_3)_2(en)_2$_W; (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2(trien)$_W and (e) $Cu(NO_3)_2(trien)$

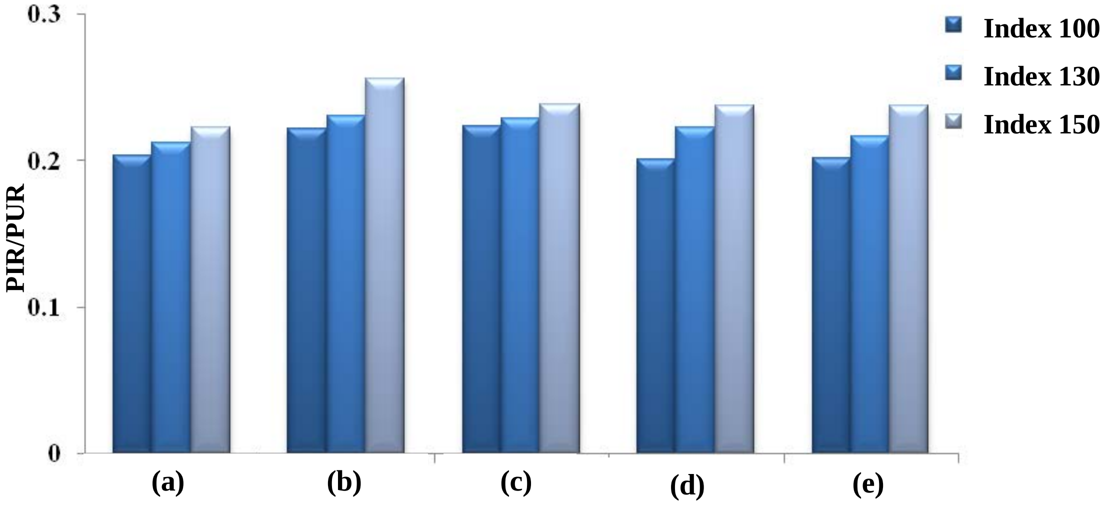


Figure 4.17 PIR:PUR of RPUR foams catalyzed by different catalysts at different NCO indexes (a) DMCHA (ref.); (b) $Cu(NO_3)_2(en)_2$_W; (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2$(trien)_W and (e) $Cu(NO_3)_2$(trien)

Therefore, this result indicated that copper-amine complexes were not good catalyst for polyisocyanurate formation. It could be summarized that metal complexes were good catalysts for polyurethane formation and blowing reaction but they were not good catalysts for trimerization reaction. NCO conversion and PIR:PUR ratio of RPUR foams catalyzed by copper-amine complexes is illustrated in Table 4.15.

Table 4.15 NCO conversions and PIR:PUR ratio of RPUR foams prepared by DMCHA; $Cu(NO_3)_2(en)_2$_W; $Cu(NO_3)_2(en)_2$; $Cu(NO_3)_2$(trien)_W and $Cu(NO_3)_2$(trien) at different NCO indexes

Catalysts	NCO indexes	NCO conversion (%)	PIR/PUR
DMCHA (ref.)	100	99.6	0.204
	130	99.5	0.212
	150	99.3	0.223
$Cu(NO_3)_2(en)_2$_W	100	98.4	0.222
	130	98.2	0.231
	150	97.5	0.256
$Cu(NO_3)_2(en)_2$	100	98.9	0.224
	130	98.1	0.229
	150	97.7	0.239
$Cu(NO_3)_2$(trien)_W	100	98.7	0.201
	130	98.2	0.223
	150	98.0	0.238
$Cu(NO_3)_2$(trien)	100	98.6	0.202
	130	97.8	0.217
	150	97.6	0.238

4.4.10 Compressive properties of RPUR foams

Compressive strength of RPUR foams is an important mechanical properties for foam application. RPUR foams subjected to compressive stress at 10% strain. The compression stress-strain curves of RPUR foams catalyzed by copper-amine complexes and DMCHA are shown in Figure 4.18 and Figure 4.19. The curves showed three stages of deformation; initial linear behavior, linear plateau region and finally, densification. The compressive modulus of foam was determined from initial slope whereas the compressive strength was calculated from intersection point between the initial slope and plateau slope [48]. It was observed that slope of the initial linear are the same for all RPUR foams. The shape of plateau region depends on the cell morphology of RPUR foam. For linear plateau, cell deformation occurs as combination of cell bending and collapse.

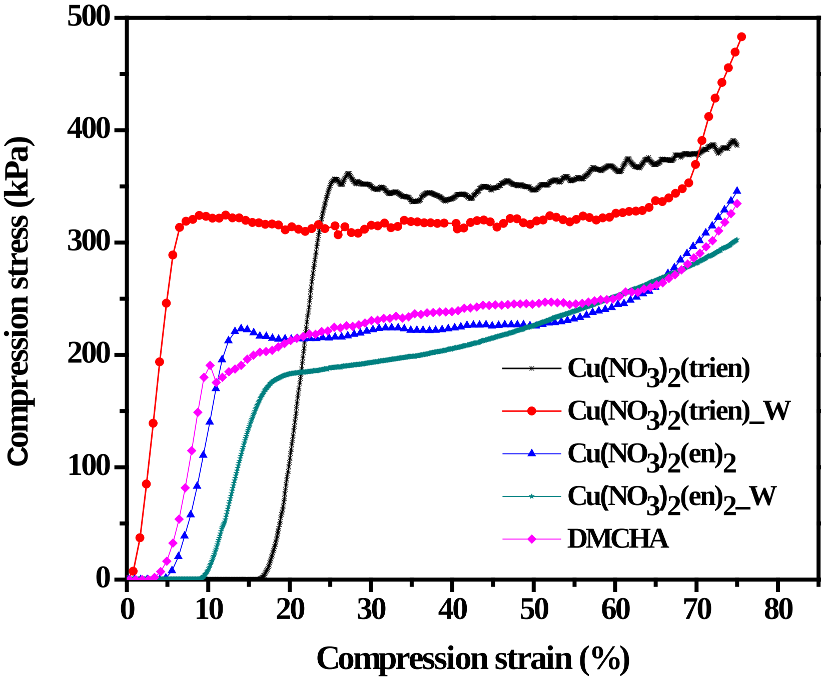


Figure 4.18 Parallel Compression stress-strain curve of RPUR foams catalyzed by (a) $Cu(NO_3)_2$(trien); (b) $Cu(NO_3)_2$(trien)_W; (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2(en)_2$_W and (e) DMCHA at NCO index of 100

From Figure 4.18, compressive strengths of RPUR foam catalyzed by $Cu(NO_3)_2$(trien), $Cu(NO_3)_2$(trien)_W, $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(en)_2$_W in parallel direction of foam rising are compared with those catalyzed by DMCHA. It can be observed that the parallel compressive strength of foams which catalyzed by $Cu(NO_3)_2$(trien) was higher than those catalyzed by $Cu(NO_3)_2(en)_2$ or DMCHA. This was due to higher foam density, which resulted in the higher compressive strength. In addition, compressive strength of foam that catalyzed by $Cu(NO_3)_2$(trien) was higher than that catalyzed by $Cu(NO_3)_2$(trien)_W and compressive strength of foam that catalyzed by $Cu(NO_3)_2(en)_2$ was higher than that catalyzed by

$Cu(NO_3)_2(en)_2$_W. This was because the foams catalyzed by copper complexes synthesized in methanol media had higher density.

The compressive strengths in perpendicular direction of foam rising are shown in Figure 4.19. They had similar trend as in parallel direction, higher density of foam give higher compressive strength. Moreover, it can be observed that the parallel compressive strength of foam was higher than perpendicular compressive strength. This is because the foam cells were elongated in the direction of foam rising [49]. The compressive properties depend on direction of measurement and therefore all foams were anisotropic materials. In general, a high compressive strength in one direction occurred at the expense of the compressive strength in the other direction, which could be explained by the foam cell model as illustrated in Figure 4.20.

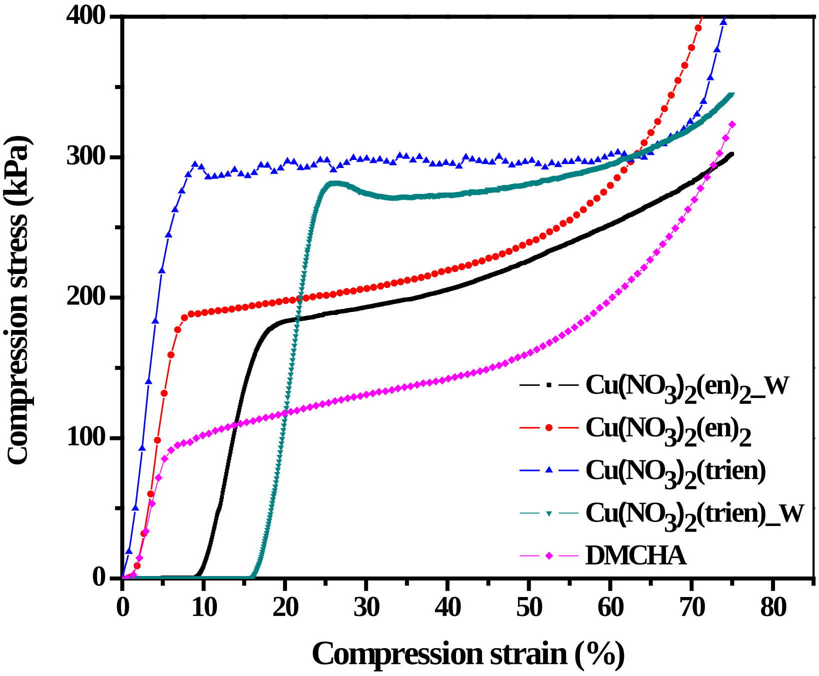
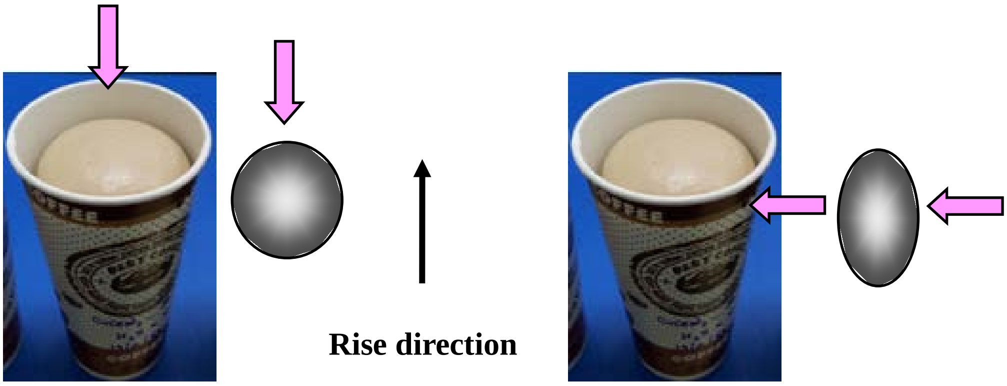


Figure 4.19 Perpendicular Compression stress-strain curve of RPUR foams catalyzed by (a) $Cu(NO_3)_2(en)_2$_W; (b) $Cu(NO_3)_2(en)_2$; (c) $Cu(NO_3)_2$(trien); (d) $Cu(NO_3)_2$(trien)_W and (e) DMCHA at NCO index of 100

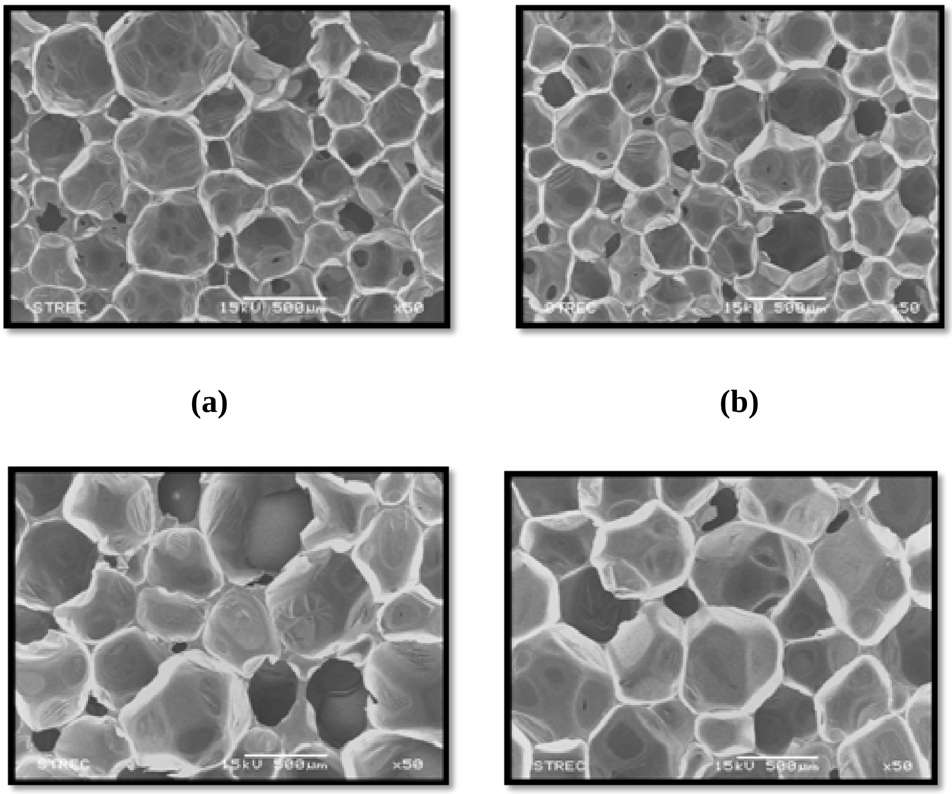


(a) (b)

Figure 4.20 Isotropic foam (a): spherical cells, equal properties in all directions; anisotropic foam (b): ellipsoid cells, which properties depend on direction [6]

4.4.11 RPUR foams morphology

SEM micrographs of RPUR foams synthesized by different copper nitrate-amine complexes in parallel and perpendicular direction were presented in Figures 4.21 and 4.22. The closed-cell foams were observed. From Figure 4.21, the foams catalyzed by $Cu(NO_3)_2(en)_2$_W and $Cu(NO_3)_2(en)_2$ showed the similar morphology and cell size. In addition, morphology and cell size of foams catalyzed by $Cu(NO_3)_2(trien)$_W and $Cu(NO_3)_2(trien)$ were also similar.

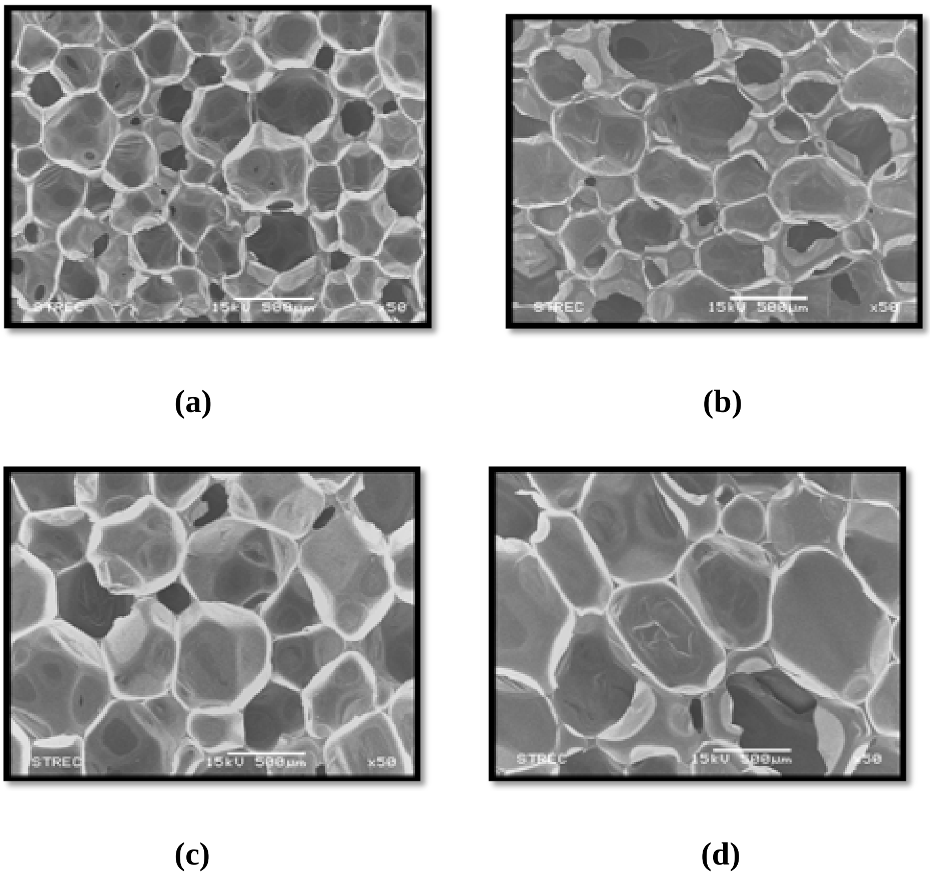


(a) (b)

(c) (d)

Figure 4.21 SEM of RPUR foams catalyzed by (a) $Cu(NO_3)_2(en)_2$_W; (b) $Cu(NO_3)_2(en)_2$; (c) $Cu(NO_3)_2(trien)$_W and (d) $Cu(NO_3)_2(trien)$ (50x)

From Figure 4.22, it was found that cell morphology showed spherical cell and elongated cell in parallel and perpendicular direction of foam rising, respectively. This indicated that the foams were anisotropic materials which were confirmed by compressive strength and cell morphology results.



(a) (b)

(c) (d)

Figure 4.22 SEM of RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$_W (a) top view; (b) side view and $Cu(NO_3)_2(trien)$_W (c) top view; (d) side view (50x)

4.4.12 Thermal stability

Thermal stability of RPUR foams catalyzed by DMCHA, $Cu(NO_3)_2(en)_2$_W, $Cu(NO_3)_2(en)_2$, $Cu(NO_3)_2(trien)$_W and $Cu(NO_3)_2(trien)$ at NCO index of 100 were investigated by thermogravimetric analysis under nitrogen atmosphere. Their thermograms are shown in Figures 4.23 and 4.24. TGA thermograms of all RPUR foams showed the decomposition of foams in one step.

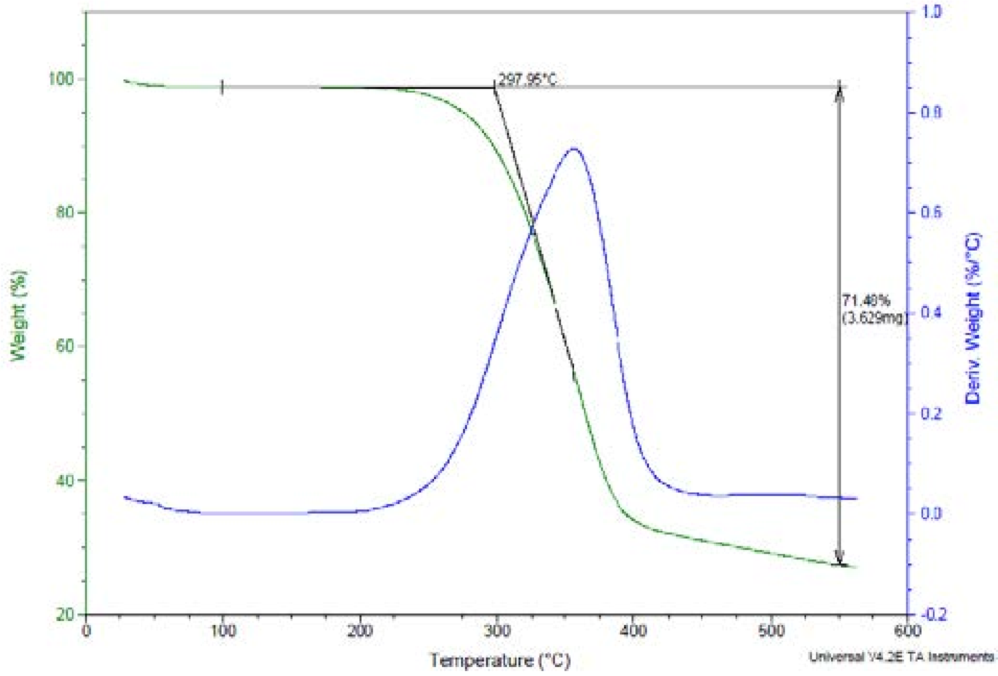


Figure 4.23 TGA and derivative TGA thermograms of RPUR foam catalyzed by $Cu(NO_3)_2(en)_2$_W at the NCO index of 100

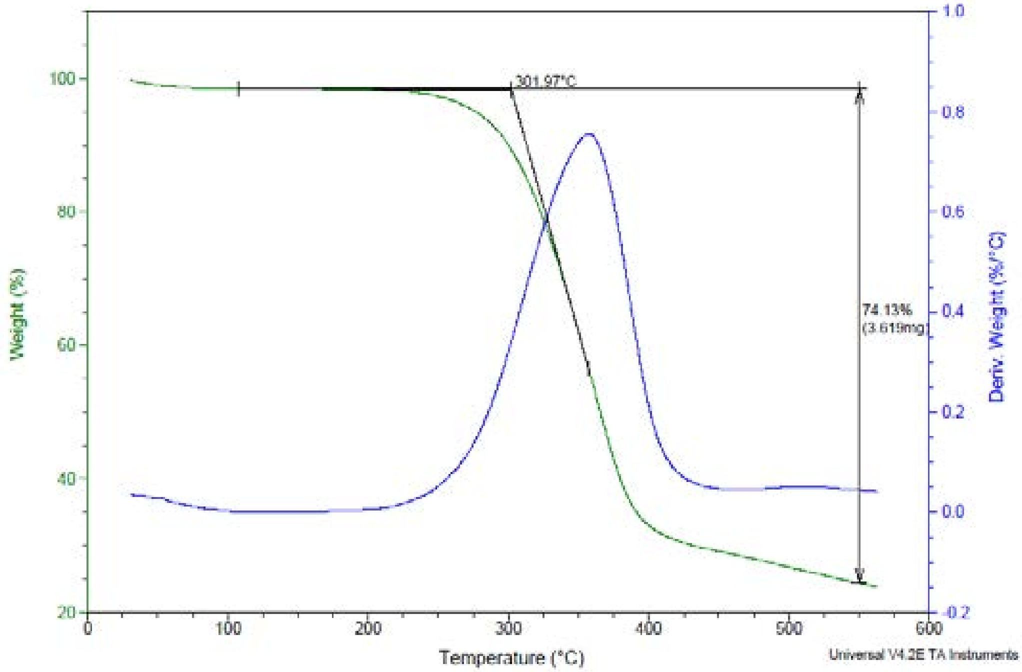


Figure 4.24 TGA and derivative TGA thermograms of RPUR foam catalyzed by $Cu(NO_3)_2$(trien)_W at the NCO index of 100

The initial composition temperature (IDT), which is the temperature at 5% weight loss, was observed at 275.1°C. This step was attributed to decomposition of urethane [51]. The residual weights at 600 °C were in the range of 24.5-27.5%. RPUR foams catalyzed by DMCHA, $Cu(NO_3)_2(en)_2$_W, $Cu(NO_3)_2(en)_2$, $Cu(NO_3)_2$(trien)_W and $Cu(NO_3)_2$(trien) had the maximum decomposition temperature (T_{max}) values in the range of 337.1-361.4°C. Thermal properties of all foams were summarized as shown in Figure 4.25. Weight loss patterns of foams catalyzed by copper-amine complexes were similar to that catalyzed by DMCHA. The thermal stability of foams catalyzed by copper-amine complex were similar that catalyzed by DMCHA.

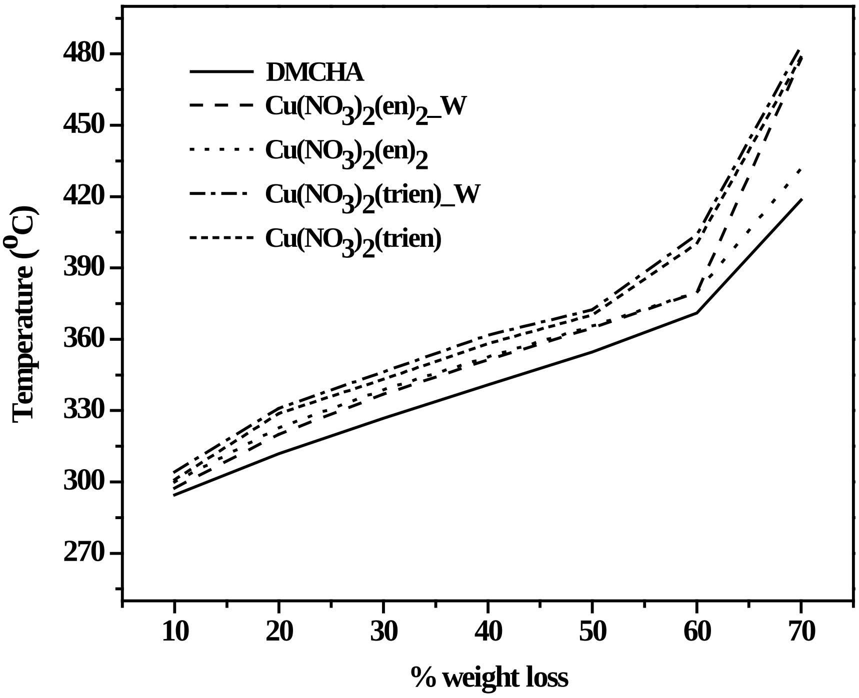


Figure 4.25 % Weight loss at different temperature of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(NO_3)_2(en)_2$_W; (c) $Cu(NO_3)_2(en)_2$; (d) $Cu(NO_3)_2$(trien)_W and (e) $Cu(NO_3)_2$(trien)

4.4.13 Preparation of RPUR foams using a plastic mold

In order to test the foam processing ability, RPUR foams were prepared at index 100 using 10x10x10 cm plastic mold (Figure 4.26) instead of a paper cup. The starting materials were mixed in a paper cup and then poured into the mold. It was found that an RPUR foam appearance was the same as that prepared in a paper cup.

Figure 4.26 RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ and prepared in a plastic mold

CHAPTER V

CONCLUSION

5.1 Conclusion

Metal-amine complexes, namely $M(X)_2(en)_2$ and $M(X)_2(trien)$, were synthesized from the reaction of metal (II) salts (MX, where X = $(NO_3)_2$, SO_4, $(Cl)_2$, CO_3) with ethylenediamine (en) or triethylenetetramine (trien). These complexes were used as catalysts for rigid polyurethane (RPUR) foam preparation. Metal-amine complexes were characterized by FTIR spectroscopy, UV-Vis spectroscopy, mass spectrometry, elemental analysis and atomic absorption spectroscopy.

RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ complexes synthesized in either water or methanol media showed good reaction times and foam appearance. Foams that prepared by use of these complex catalysts would not collapse after reaction was completed. The optimum formulation of catalyst content and blowing agent (water) content was 1 pbw and 3 pbw, respectively. These formulations resulted in the desirable density, which was in the range of 43.7 to 46.6 kg/m^3 at NCO index of 100. In addition, RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ complexes gave higher density and compressive strength than those catalyzed by commercial catalyst (DMCHA). But the reaction times of foams prepared from both $Cu(NO_3)_2(en)_2$ and $Cu(NO_3)_2(trien)$ were longer than that prepared by DMCHA catalyst.

Compressive strength of RPUR foams depends on foam density and rising direction. The compressive strength of foams increased when increased the foam density. Moreover, the compressive strength of foams in parallel direction of foam rising was higher than that in perpendicular direction. This indicated that RPUR foams were anisotropic material, it showed elongated cells and spherical cells in parallel and perpendicular of foam rising direction, respectively.

Reaction times of RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ were shorter than that catalyzed by $Cu(NO_3)_2(trien)$. But the foam that catalyzed by $Cu(NO_3)_2(trien)$ had smaller cell size when compared with foam that catalyzed by $Cu(NO_3)_2(en)_2$. This resulted in higher density and higher compressive strength for foams that catalyzed by $Cu(NO_3)_2$(trien). From TGA results, RPUR foams catalyzed by both catalysts showed similar thermal stability.

5.2 Suggestion for future work

In this work, the preparation of metal-amine complex catalyst could be done in water, which could be used only for the water-blown RPUR foams. The suggestion for future work is to develop the catalyst synthesis in other solvent such as ethylene glycol and propylene glycol for preparation RPUR foams blown with other blowing agents, such as pentane.

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APPENDICES

Appendix A

NCO index and NCO conversion Calculations

NCO index calculation

#Example Calculate the parts by weight (pbw) of pure PMDI (Suprasec® 5005), molar mass = 366.99, functionality = 2.7 at an isocyanate indexes of 100, 130, 150 and 170 required to react with the following formulation:

Formulation (pbw)	Part by weight (g)
Daltolac® R180 (OHV = 440 mgKOH/ g, functionality = 4.3)	100.0
Catalysts	1.0
Surfactant (Tegostab® B8460)	2.5
Blowing agent (water, M_w = 18 g/mole, functionality = 2)	3.0
PMDI (Suprasec® 5005), NCO indexes of 100, 130, 150 and 170	?

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

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

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

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

Equivalent in the above formulation:

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

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

Total equivalent weight = 1.117

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

thus:

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

Note: 151.8 defines the isocyanate quantity at 100 index

where;

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

thus:

Isocyanate index = 100;

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

Isocyanate index = 130;

$$\text{Isocyanate actual} = \frac{151.8}{100} \text{ x } 130 = 197.3 \text{ pbw}$$

Isocyanate index = 150;

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

Isocyanate index = 170;

$$\text{Isocyanate actual} = \frac{151.8}{100} \text{ x } 170 = 258.1 \text{ pbw}$$

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

Formulations (pbw)	**NCO index**			
	100	**130**	**150**	**170**
Polyol (Daltolac® R180)	100	100	100	100
Catalysts	1.0	1.0	1.0	1.0
Surfactant	2.5	2.5	2.5	2.5
Blowing agent	3.0	3.0	3.0	3.0
PMDI (Suprasec® 5005)	**152**	**197**	**228**	**258**

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, following equation:

Isocyanate conversion (%) =

$$\left[1 - \frac{NCO^{f}}{NCO^{i}}\right] \times 100$$

where;

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

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

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

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

PMDI (MR-200) spectra	**NCO Absorbance peak area Normalized @ 1.0 Ar-H peak area**
1	98.886
2	97.547
3	97.755
Average (NCO^i); ATR-IR	98.1

Example Calculate the conversion of isocyanate (α) and PIR:PUR of rigid polyurethane foams catalyzed by $Cu(NO_3)_2(en)_2$ catalyst at NCO index 100

Conversion of isocyanate (%)

Data at **Table A2**

Absorbance peak area of initial NCO = 98.1 = NCO^i

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

Absorbance peak area of final NCO = 0.330 = NCO^f

thus,

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

$$= \left[1 - \frac{1.584}{98.1}\right] \times 100$$

$$\text{\% NCO conversion} = 98.9$$

PIR:PUR

Absorbance peak area of PIR (polyisocyanurate) = 0.869

Absorbance peak area of PUR (polyurethane) = 3.923

$$\text{thus, PIR:PUR} = \frac{0.869}{3.923} = 0.223$$

Table A3 NCO conversion of RPUR foam catalyzed by DMCHA at different NCO indexes

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	0.651	1.809	0.873	4.261	0.359	99.6	0.204
130	0.954	2.102	1.126	5.311	0.452	99.5	0.212
150	1.562	2.305	1.133	5.081	0.687	99.3	0.223

Table A4 NCO conversion of RPUR foam catalyzed by $Cu(NO_3)_2(en)_2$ at different NCO indexes

NCO indexes	**Peak Area**					**NCO conversion (%)**	**PIR/PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
100	2.817	1.778	0.869	3.923	1.584	98.9	0.223
130	3.805	2.048	0.962	4.196	1.858	98.1	0.229
150	4.681	2.111	1.013	4.239	2.218	97.7	0.239

Table A5 NCO conversion of RPUR foam catalyzed by $Cu(NO_3)_2(en)_2$_W at different NCO indexes

NCO indexes	**Peak Area**					**NCO conversion (%)**	**PIR/PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
100	2.817	1.778	0.869	3.923	1.584	98.4	0.222
130	3.427	1.931	0.959	4.147	1.775	98.2	0.231
150	4.675	1.908	0.958	3.747	2.451	97.5	0.256

Table A6 NCO conversion of RPUR foam catalyzed by $Cu(NO_3)_2(trien)$ at different NCO indexes

NCO indexes	**Peak Area**					**NCO conversion (%)**	**PIR/PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
100	2.409	1.818	0.848	4.201	1.325	98.6	0.202
130	3.958	1.859	0.897	4.133	2.129	97.8	0.217
150	4.658	1.988	0.942	4.224	2.343	97.6	0.238

Table A7 NCO conversion of RPUR foam catalyzed by $Cu(NO_3)_2$(trien)_W at different NCO indexes

NCO indexes	**Peak Area**					**NCO conversion (%)**	**PIR/PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595cm^{-1}**	**PIR 1415cm^{-1}**	**PUR 1220cm^{-1}**	**NCO^{f} (Ar-H=1.0)**		
100	2.372	1.846	0.867	4.321	1.285	98.7	0.201
130	3.153	1.777	0.871	3.902	1.774	98.2	0.223
150	3.719	1.871	0.885	3.715	1.988	98.0	0.238

Appendix B

Reaction Time and Compression Data

Table B1 Reaction times and physical properties of RPUR foams catalyzed by copper nitrate and amine

Formulations (pbw)	**Starting materials at NCO index of 100**			
	$Cu(NO_3)_2$	**en**	**trien**	**Non-catalyst**
Reaction times				
Cream time (min.)	1:45	-	-	1:12
Gel time (min.)	3:48	-	-	2:57
Tack free time (min.)	26:34	-	-	27:21
Rise time (min.)	20:37	-	-	17:03
Density (kg/m^3)	60.2	-	-	-
External appearance	Low blowing	Brittle foam	Brittle foam	Brittle foam

Table B2 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by DMCHA at different NCO indexes

Formulations (pbw)	**Catalyst at different NCO indexes**					
	DMCHA					
	100		**130**		**150**	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		197		228	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:22	0.6	0:26	0.6	0:31	0.6
Gel time (min.)	0.40	0.6	0:42	1.0	0:47	0.6
Tack free time (min.)	3:09	1.0	3:55	1.0	4:45	1.0
Rise time (min.)	2:08	1.5	2:47	1.5	2:55	1.0
Density						
Density (kg/m^3)	38.9	0.8	42.6	0.8	44.5	0.6
Mechanical properties						
// Compressive strength (kPa)	198.2	-	250.4	-	285.8	-
// Compressive modulus (kPa)	-	-	-	-	217.5	-

Table B3 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$_W at different NCO indexes

Formulations (pbw)	**Catalyst at different NCO indexes**					
	$Cu(NO_3)_2(en)_2$_W					
	100		**130**		**150**	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		197		228	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	1:34	0.6	1:08	0.6	1:02	0.6
Gel time (min.)	2:39	1.0	3:14	0.6	3:22	1.5
Tack free time (min.)	4:29	1.0	4:57	1.0	5:20	1.0
Rise time (min.)	4:41	1.5	4:45	1.0	5:07	0.6
Density						
Density (kg/m^3)	43.7	0.8	44.3	0.8	45.8	0.6
Mechanical properties						
// Compressive strength (kPa)	226.9	-	-	-	-	-
// Compressive modulus (kPa)	195.5	-	-	-	-	-

Table B4 Formulations, reaction times and physical properties of RPUR foams catalyzed by $Cu(NO_3)_2(en)_2$ at different NCO indexes

Formulations (pbw)	**Catalyst at different NCO indexes**					
	$Cu(NO_3)_2(en)_2$					
	100		**130**		**150**	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		197		228	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	1:34	0.6	1:08	0.6	1:02	0.6
Gel time (min.)	2:39	1.0	3:14	0.6	3:22	1.5
Tack free time (min.)	4:29	1.0	4:57	1.0	5:20	1.0
Rise time (min.)	4:41	1.5	4:45	1.0	5:07	0.6
Density						
Density (kg/m^3)	44.9	0.8	45.5	0.6	46.4	0.8

Table B5 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by $Cu(NO_3)_2$(trien)_W at different NCO indexes

Formulations (pbw)	**Catalyst at different NCO indexes**					
	$Cu(NO_3)_2$(trien)_W					
	100		**130**		**150**	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		197		228	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:51	0.6	0:46	0.6	0:49	0.6
Gel time (min.)	2:12	1.5	3:30	1.0	3:45	1.0
Tack free time (min.)	8:32	1.0	8:26	1.5	8:53	1.5
Rise time (min.)	5:51	1.5	7:07	1.0	7:40	1.5
Density						
Density (kg/m^3)	44.1	0.8	47.2	0.8	49.4	0.6
Mechanical properties						
// Compressive strength (kPa)	361.6	-	-	-	-	-
// Compressive modulus (kPa)	285.5	-	-	-	-	-

Table B6 Formulations, reaction times and physical properties of RPUR foams catalyzed by $Cu(NO_3)_2$(trien) at different NCO indexes

Formulations (pbw)	**Catalyst at different NCO indexes**					
	$Cu(NO_3)_2$(trien)					
	100		**130**		**150**	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		197		228	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:53	0.6	0:44	0.6	0:40	0.6
Gel time (min.)	3:20	1.5	3:30	1.0	3:26	1.0
Tack free time (min.)	8:48	1.0	9:34	1.5	10:35	1.5
Rise time (min.)	6:18	1.0	8:45	1.0	8:57	1.0
Density						
Density (kg/m^3)	46.6	0.8	49.6	0.8	51.1	0.6

Table B7 Formulations and reaction times of RPUR foams catalyzed by different complexes

Formulations (pbw)	**Catalyst at NCO indexes 100**					
	Added Ethylenediamine (en)					
	$Cu(CO_3)_2(en)_2$		**$Cu(SO_4)(en)_2$**		**$Cu(Cl)_2(en)_2$**	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		152		152	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:37	0.6	0:45	0.6	0:40	0.6
Gel time (min.)	0:53	1.0	2:20	1.5	1:54	1.5
Tack free time (min.)	4:57	1.5	14:11	1.5	12:47	1.5
Rise time (min.)	3:20	1.0	9:30	1.0	8:36	1.5

Table B8 Reaction times of RPUR foams catalyzed by different complexes

Formulations (pbw)	**Catalyst at NCO indexes 100**					
	Added Ethylenediamine (en)					
	$Co(NO_3)_2(en)_2$		**$Co(Cl)_2(en)_2$**		**$Ni(SO)_4(en)_2$**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:37	0.6	0:37	1.0	0:44	1.0
Gel time (min.)	1:59	1.5	2:15	1.0	2:22	1.0
Tack free time (min.)	14:08	1.0	16:35	1.5	16:10	1.5
Rise time (min.)	6:50	1.5	7:57	1.0	10:50	1.5

Table B9 Formulations and reaction times of RPUR foams catalyzed by different complexes

Formulations (pbw)	**Catalyst at NCO indexes 100**			
	Added ethylenediamine (en)			
	$Fe(SO_4)(en)_2$		**$Zn(SO_4)(en)_2$**	
Daltolac® R180	100		100	
Catalysts	1.0		1.0	
B8460	2.5		2.5	
H_2O	3.0		3.0	
Suprasec® 5005	152		152	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times				
Cream time (min.)	0:42	0.6	0:36	1.0
Gel time (min.)	1:20	1.0	2:10	1.5
Tack free time (min.)	7:44	1.5	17:45	1.5
Rise time (min.)	4:28	1.5	7:29	1.0

Table B10 Reaction times of RPUR foams catalyzed by different complexes

Formulations (pbw)	**Catalyst at NCO indexes 100**					
	Added Triethylenetetramine (trien)					
	$Cu(CO_3)_2(trien)$		**$Cu(SO_4)(trien)$**		**$Cu(Cl)_2(trien)$**	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:48	0.6	0:52	1.0	0:53	1.0
Gel time (min.)	1:12	1.0	3:02	1.5	3:09	1.5
Tack free time (min.)	5:45	1.5	16:20	1.0	13:33	1.0
Rise time (min.)	3:31	1.0	9:48	1.0	8:21	1.5

Table B11 Formulations and reaction times of RPUR foams catalyzed by different complexes

Formulations (pbw)	Catalyst at NCO indexes 100					
	Added Triethylenetetramine (trien)					
	$Co(NO_3)_2$(trien)		$Co(Cl)_2$(trien)		$Ni(SO)_4$(trien)	
Daltolac® R180	100		100		100	
Catalysts	1.0		1.0		1.0	
B8460	2.5		2.5		2.5	
H_2O	3.0		3.0		3.0	
Suprasec® 5005	152		152		152	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:47	1.0	0:51	1.0	1:23	0.6
Gel time (min.)	3:04	1.5	3:11	1.5	2:35	1.0
Tack free time (min.)	16:26	1.0	16:47	1.5	10:22	1.5
Rise time (min.)	9:56	1.5	10:13	1.0	6:48	1.0

Table B12 Reaction times of RPUR foams catalyzed by different complexes

Formulations (pbw)	Catalyst at NCO indexes 100			
	Added Triethylenetetramine (trien)			
	$Fe(SO_4)$(trien)		$Zn(SO_4)$(trien)	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times				
Cream time (min.)	1:03	1.0	0:57	1.0
Gel time (min.)	3:05	1.0	3:02	1.5
Tack free time (min.)	15:27	1.5	17:42	1.0
Rise time (min.)	8:38	1.5	9:15	1.0

VITAE

Name : Miss Piyachat Sirojpornphasut

Date of birth : June 8, 1987

Nationality : Thai

Address : 217/1, Moo 3, Boekprai, Banpong, Ratchaburi, 70110

University Education : Bachelor’s Degree from Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, 2007-2010

Master’s Degree from Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, 2010-2012

Conference attendance: Poster presentation “Preparation of rigid polyurethane Foam catalyzed by copper nitrate-ethylenediamine complexes” at The 4th Science Research Conference: Naresuan University, Pitsanulok, Thailand