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โลหะและเททราเอทิลีนเพนทามีน/เพนทาเอทิลีนเฮกซามีน

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PREPARATION OF RIGID POLYURETHANE FOAMS USING CATALYSTS
PREPARED FROM METAL NITRATES AND TETRAETHYLENEPENTAMINE/
PENTAETHYLENEHEXAMINE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
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ศิริวรรณ จีวีวรรณกร: การเตรียมโฟมพอลิยูรีเทนแบบแข็งโดยใช้ตัวเร่งปฏิกิริยาที่เตรียมได้จากสารประกอบไนเตรตของโลหะ และเททราเอทิลีนเพนทามีน/เพนทาเอทิลีนเฮกซามีน. (PREPARATION OF RIGID POLYURETHANE FOAMS USING CATALYSTS PREPARED FROM METAL NITRATES AND TETRAETHYLENEPENTAMINE/PENTAETHYLENEHEXAMINE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก:
 รศ. ดร. นवलพรรณ จันทศิริ, 103 หน้า.

งานวิจัยนี้มีแนวคิดที่จะพัฒนาตัวเร่งปฏิกิริยาโดยใช้สารประกอบเชิงซ้อนคอปเปอร์-เททราเอทิลีนเพนทามีน และ คอปเปอร์-เพนทาเอทิลีนเฮกซามีน คือ $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ และ $\text{Cu}(\text{Cl})_2(\text{tetraen})$ สำหรับใช้เป็นตัวเร่งปฏิกิริยาการเตรียมพอลิยูรีเทน โฟมแบบแข็ง สารประกอบเชิงซ้อนของคอปเปอร์สังเคราะห์ได้จากปฏิกิริยาระหว่างสารประกอบอนินทรีย์ (คอปเปอร์ ไนเตรต/คอปเปอร์ คลอไรด์) และแอมีน (เททราเอทิลีนเพนทามีน/เพนทาเอทิลีนเฮกซามีน) นำสารประกอบเชิงซ้อนของคอปเปอร์มาพิสูจน์เอกลักษณ์ด้วยเทคนิค ไออาร์สเปกโทรสโกปี ยูวี-วิสทิเบิลสเปกโทรสโกปี และการวิเคราะห์ธาตุ สารประกอบเชิงซ้อนของคอปเปอร์จะใช้ในการเตรียมพอลิยูรีเทน โฟมแบบแข็ง โดยจะทำการศึกษาเวลาในการเกิดปฏิกิริยาของโฟม สมบัติทางกายภาพ และสมบัติเชิงกลของพอลิยูรีเทน โฟมแบบแข็งเปรียบเทียบกับโฟมที่เตรียมโดยใช้ไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA) ซึ่งเป็นตัวเร่งปฏิกิริยาอ้างอิงที่ใช้ในทางการค้า หากการเปลี่ยนแปลงของหมู่ไอโซไซยานาต โดยใช้เทคนิคเอทีอาร์-อินฟราเรดสเปกโทรสโกปี จากการทดลองจะพบว่าตัวเร่ง $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ สามารถเร่งปฏิกิริยาการเกิดพอลิยูรีเทน โฟมได้ดีเมื่อเทียบกับตัวเร่งปฏิกิริยา $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ และ $\text{Cu}(\text{Cl})_2(\text{tetraen})$ นอกจากนี้ยังพบว่าความหนาแน่นโฟมและความทนทานต่อแรงกดอัด ของพอลิยูรีเทน โฟมที่เร่งปฏิกิริยาด้วย $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ และ $\text{Cu}(\text{Cl})_2(\text{tetraen})$ มีค่าสูงกว่าโฟมที่เตรียมขึ้นด้วยตัวเร่งทางการค้าที่ดัชนีไอโซไซยานาต 100 สันฐานวิทยาของพอลิยูรีเทน โฟมที่เตรียมจาก $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ มีลักษณะทางสันฐานวิทยาที่ดี และขนาดของเซลล์เพิ่มขึ้นเมื่อทำการเพิ่มปริมาณของสารฟู

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์. ลายมือชื่อนิติ.....
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SIRIWAN CHAWIWANNAKORN: PREPARATION OF RIGID POLYURETHANE FOAMS USING CATALYSTS PREPARED FROM METAL NITRATES AND TETRAETHYLENEPENTAMINE/PENTAETHYLENEHEXAMINE. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph. D., 103 pp.

The scope of this research was to synthesize copper-tetraethylenepentamine and copper-pentaethylenhexamine complexes, namely $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ and used as catalysts in the preparation of rigid polyurethane foams. These copper complexes were synthesized from the reaction between inorganic compounds (copper nitrate/copper chloride) and amines (tetraethylenepentamine/pentaethylenhexamine). The copper complexes were characterizes by FTIR, UV-visible and elemental analysis. The copper complexes were used as catalysts to prepare rigid polyurethane foams. The reaction time, physical properties, and mechanical properties of rigid polyurethane foams were studied and compares with the foam catalyzed by dimethylcyclohexylamine (DMCHA), which is a reference commercial catalyst. The isocyanate conversion was obtained by ATR-IR. It was found that $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ could accelerate the reaction of polyurethane foam better than $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$. Foam density and compressive strength of polyurethane foams which were catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ showed higher values than the foam catalyzed by DMCHA at NCO index 100. The morphology of RPUR prepared from $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ showed good morphology and the cell size increased when increasing the amount of blowing agent.

Field of Study: Petrochemistry and Polymer Science Student's Signature.....

Academic Year: 2012 Advisor's Signature.....

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LIST OF ABBREVIATIONS

%	percentage
ϵ	molar absorptivity
ATR-IR	Attenuated Total Reflectance-Infrared
AA	Atomic absorption
cm	centimeter
cm^{-1}	unit of wavenumber
$^{\circ}\text{C}$	degree Celsius (centigrade)
DBTDL	dibutyltin dilaurate
DMCHA	N,N-dimethylcyclohexylamine
EA	Elemental Analysis
FTIR	Fourier Transform Infrared Spectrophotometer
g	gram
h	hour
IDT	Initial Decomposition Temperature
kg	kilogram
kV	kilovolt
m^3	cubic meter
MDI	4,4'-methane diphenyl diisocyanate
mA	milliampere
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mmol	millimole
N	newton unit
NCO	isocyanate
OHV	hydroxyl value
pbw	part by weight
PIR	polyisocyanurate

pentaen	pentaethylenehexamine
tetraen	tetraethylenepentamine
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PU	polyurethane
PUR	polyurethane
PS	polystyrene
rpm	round per minute
RPUR	rigid polyurethane
RT	room temperature
ref	reference
s	second
SEM	Scanning Electron Microscope
t	time
TDI	toluene diisocyanate
TGA	Thermogravimetric Analysis
T _{max}	maximum core temperature
UV	ultraviolet

CHAPTER I

INTRODUCTION

Rigid polyurethane foam (RPUR foam) is a widely used material in many applications such as thermal insulation, building construction, refrigeration, transportation and packaging. Because it features are light weight, good mechanical properties and low thermal conductivity [1]. However, the major proportions of RPUR foam are a thermal insulation which has low density at 28 kg/m^3 - 50 kg/m^3 [2].

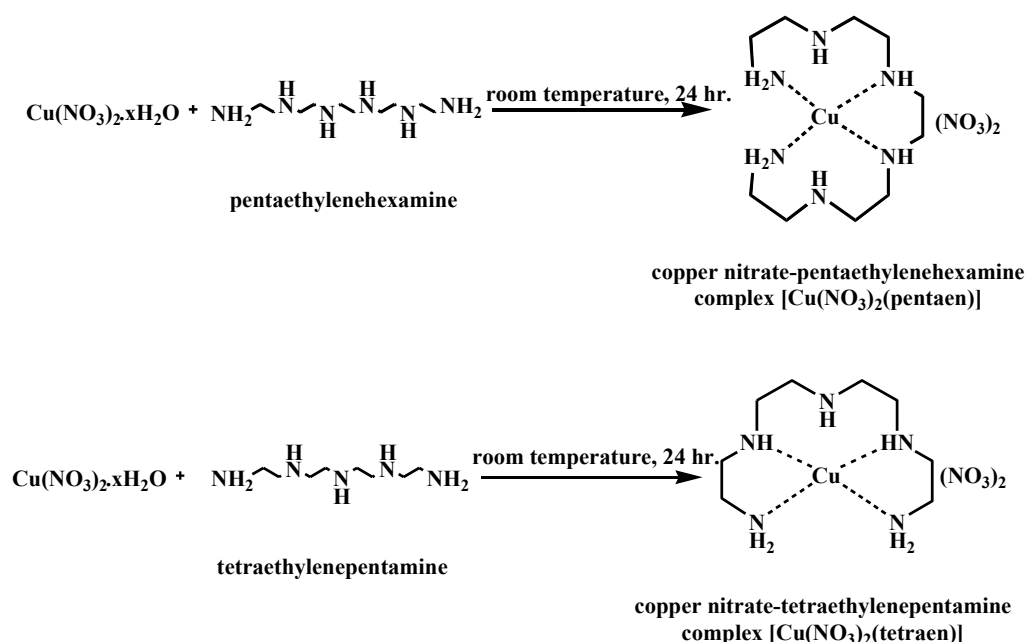
RPUR foam produced by polyaddition polymerization alcohols which contains hydroxyl groups in molecule more than 2 groups and compound isocyanate groups at least 2 groups to a molecule (diisocyanate or polyisocyanate). The production of RPUR foam is an easy process. It can be done by using one shot or two shot. The one shot method is done by mixing all starting material consisting of polyol, isocyanate, catalyst, surfactant, and blowing agent. In two shot method, the isocyanate is added into the mixture of polyol, blowing agent, catalyst and surfactant [3].

In the industrial manufacturing of polyurethane foam, tertiary amines and organometallic compounds are used as catalysts. Examples of catalysts are dibutyltin dilaurate (DBTDL), dibutyltin mercaptide, dimethylcyclohexylamine (DMCHA) and pentamethyldiethylenetriamine (PMDETA). Catalyst is important for control a balancing during polymerization reaction, generates CO_2 gas, and also has impact to the properties of RPUR foams too [4]. The catalyst used in the industry speed up the foam reaction; however, there are some disadvantages due to strong odor and toxicity. So, there comes with a new idea of developing catalyst for preparation of rigid RPUR foam by using metal-amine complexes which can be prepared from inorganic metal compounds and amines because they have no odor and their starting materials are readily available.

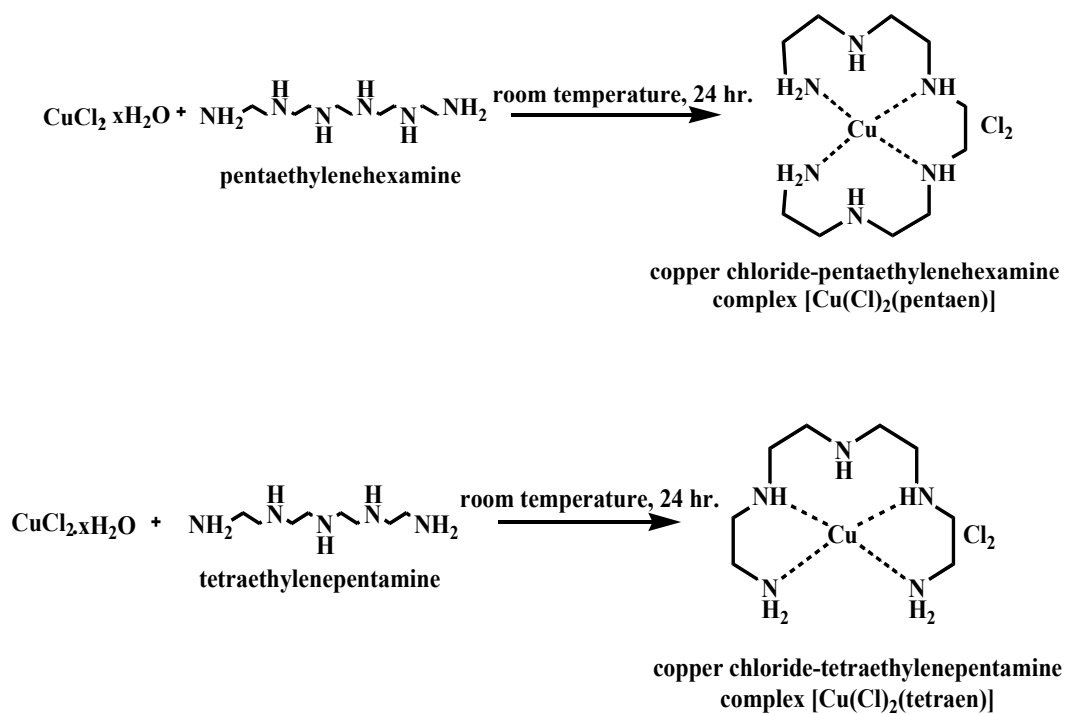
Objective and scope of the research

An objective of this research is to prepare RPUR foam by using copper-amine complexes as catalysts. The experimental was divided into 2 steps. First step was the synthesis of metal-amine complex catalysts from copper nitrate or copper chloride and pentaethylenhexamine (pentaen) or tetraethylenepentamine (tetraen). Metal-amine complex catalysts that would be synthesized were $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ (Schemes 1.1 and 1.2). Copper-amine complexes would be characterized by ultraviolet-visible spectroscopy, elemental analysis, mass spectrometry, atomic absorption spectroscopy and FTIR spectroscopy. It was expected that these catalysts would have good solubility in RPUR foam formulation, good catalytic activity on RPUR foaming reaction and gave good foam appearance.

The second step was the preparation of RPUR foams by focusing on reaction times, physical and mechanical properties of RPUR foams. Conversion of starting material in the foaming reaction, RPUR foam density, morphology and compressive strength would be studied.



Scheme 1.1 Synthesis of copper nitrate-pentaethylenhexamine and copper nitrate-tetraethylenepentamine complexes



Scheme 1.2 Synthesis of copper chloride-pentaethylenhexamine and copper chloride-tetraethylenepentamine complexes

CHAPTER II

THEORY AND LITERATURE REVIEWS

Commercially, polyurethanes (PU) reaction are prepared formed polyaddition polymerization between molecules containing two or more isocyanate groups and polyol that have two or more hydroxyl groups which give polyurethane chain (-NH-COO-). Relatively, few basic isocyanates and a far broader range of polyols of difference molecular weights and functionalities are used to produce of urethane [5].

Polyurethane plays an essential role in many industries. Comfortable, domestic, seating, automotive are produced form flexible foam. Rigid polyurethane (RPUR) foam is one of the most effectible uses in practical thermal insulation materials use in refrigerated container, industrial pipe insulation, protecting packaging and construction. [6]

2.1 Raw Materials

The main reactions involved in the production of RPUR foams are prepared by isocyanates, polyol, surfactant, catalyst, blowing agent and additives such as flame retardants, chain extenders and fillers.

The highly cross-linked homogeneous glassy network structure is important for final properties of rigid polyurethane foams, which have good heat stability, high compressive strength and good barrier properties. The properties of polyurethane foams can be adjusted wide limits depending on starting material used. And properties of polyurethane foams can be modified to suit the requirement of application.

2.1.1 Isocyanate

The most common isocyanate, which account for about 95% of isocyanate usage are 4,4-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI). The number of isocyanate groups per molecule, functionality will effect the properties of polyurethane foams if has higher functionality caused hard, glassy and brittle

polyurethane foams. Aromatic isocyanate groups have better reactivity than aliphatic isocyanate groups because aliphatic isocyanate groups slowly curing with OH groups [7].

2.1.1.1 Toluene diisocyanate (TDI)

Toluene diisocyanate (liquid, boiling point 120 °C) is normally available as pure 2,4 and as 80/20 (2,4-TDI/2,6-TDI) or as a 65/35 (2,4/2,6) mixture. Toluene diisocyanate isomer illustrate in Figure 2.1 [7].

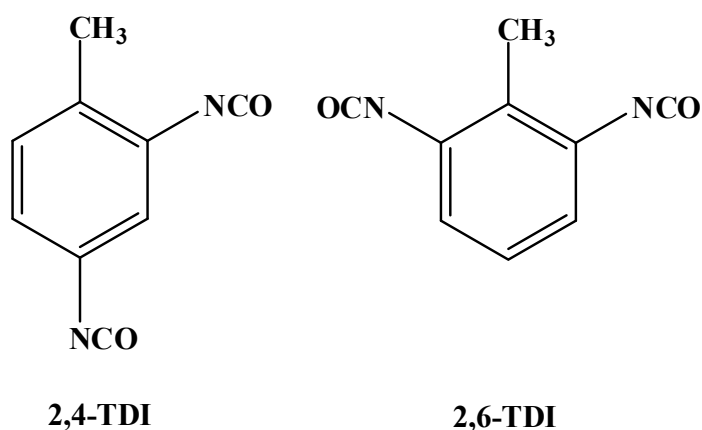


Figure 2.1 Toluene diisocyanate isomer.

TDI has high vapor pressure, contain a risk for skin exposed and respiratory so use MDI instead because ahs a limited favor and lower volatility lower than TDI [8].

2.1.1.2 4,4'-Diphenylmethane diisocyanate

4,4'-Diphenylmethane diisocyanate or Methylene diphenylene diisocyanate (MDI) Pure MDI (Figure 2.2) in commercial contains 4,4'-isomer, 2,4'-isomer about 2% and has hydrolysable chloride lower than 5 ppm. Pure MDI is a white to pale yellow solid of boiling point and melting point about 195 °C and 38 °C, respectively. The lower volatility is a safely TDI. MDI is trend to form more trimmers when stored as a liquid at temperature more than 40 °C.

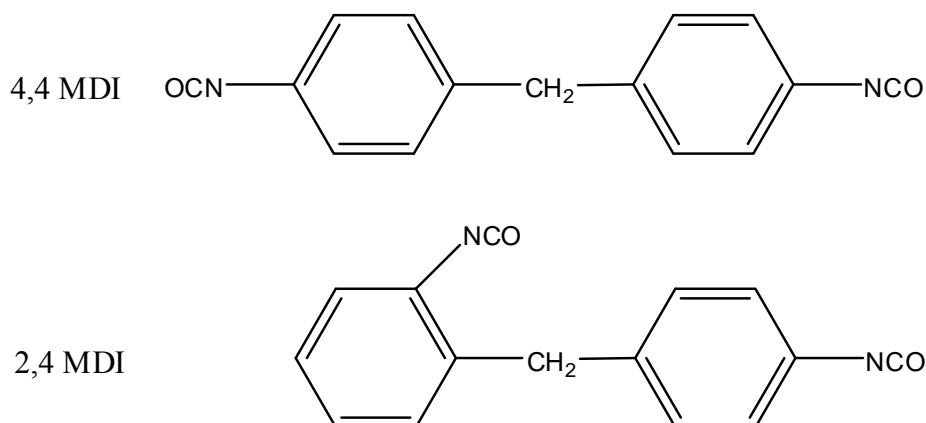


Figure 2.2 Structure of Pure MDI

Polymeric MDI (Figure 2.3) is used for rigid and semi-rigid urethane foams. Polymeric MDI compositions are functionalities from about 2.2 to over 3.0. The viscosity of polymeric MDI increases with increasing molecular weight and polymeric isocyanate content.

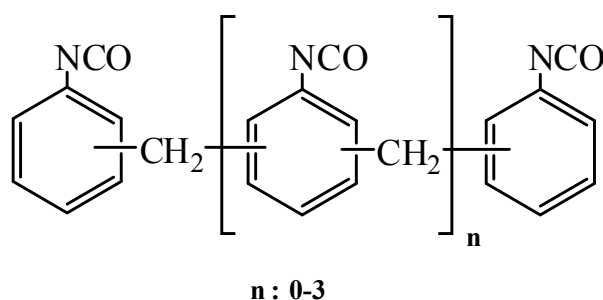


Figure 2.3 The structures of polymeric MDI.

2.1.2 Polyols

Polyol is widely used in the manufacture of polyurethane foams. Mostly polyol is divided into 2 categories; hydroxyl-terminated polyether or hydroxyl-terminated polyester. The structure shows a large influence in determining the properties of final polyurethane foam depend on molecular weight and functionality of polyol. Commonly flexible foam will have molecule weight around 1000-6500 g/mol, functionality 2.0-3.0 and hydroxyl value 28-160 mg.KOHg^{-1} but in a rigid

polyurethane foams has molecular weight around 150-1000 g/mol, functionality 2.5-8.0 and hydroxyl value 250-1000 mg.KOHg⁻¹(Table 2.1) which rigid polyurethane foams need lower and higher functionality polyol by rigidity of rigid polyurethane foams is increasing by decreasing chain segment length or increasing crosslink network. From Table 2.2 shows an example of commercial polyol and hydroxyl value [9].

Table 2.1 Polyol for polyurethane manufacture

Characteristic	Rigid polyurethane foam	Flexible polyurethane foam
Molecular weight range	150 to 1,600	1,000 to 6,500
Functionality range	3.0 to 8.0	2.0 to 3.0
Hydroxy value range (mgKOH/g)	250 to 1,000	28 to 160

Table 2.2 Commercial polyols and functionality values

Alcohol	Chemical Structure	Functionality
Ethylene glycol (EG)	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	2
Diethylene glycol (DEG)	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$	2
Glycerol	$\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{CH}-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$	3
Pentaerythritol	$\begin{array}{c} \text{CH}_2-\text{OH} \\ \\ \text{HO}-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_2-\text{OH} \end{array}$	3
Trimethylol propane (TMP)	$\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{OH} \\ \\ \text{CH}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	4
Sorbitol	$\text{HO}-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2-\text{OH}$	6

2.1.2.1 Polyether polyols

About 90% of polyol which use in manufacture of polyurethane foams especially hydroxyl-terminated polyethers polyol (Figure 2.4) because low cost and low viscosity. Polyether based foams have resistance hydrolysis and resiliene better

than polyester-based foams. During a production will contain ring opening of alkylene oxide by using polyfunctional as initiator. Polyol used for prepare rigid polyurethane foam have molecular weight around 500 gmol^{-1} but flexible polyurethane foams have molecular weight around 3000 to 6000 [10].

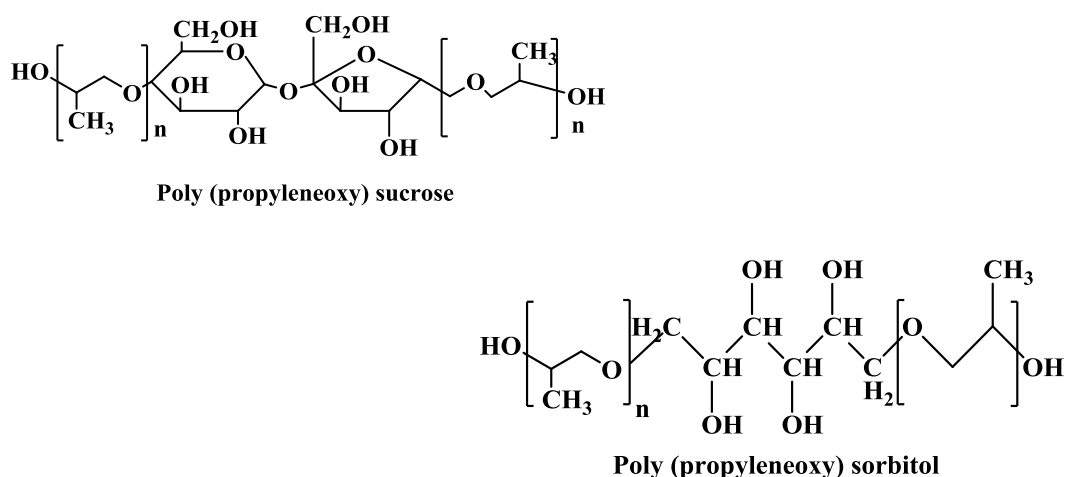


Figure 2.4 Structure of polyether polyol based on sorbitol and sucrose used in the RPUR foams

2.1.2.2 Polyester polyols

Polyester polyols is occurred from condensation reaction between diols or triol and dicarboxylic acid. Polyester polyols has reactive more than polyether polyols in foams production give a better mechanical property because has less soluble in organic solvents. However, polyester polyols is still more and more viscosity, it is difficult to use, mostly will use in flexible foams for shoulder pad or textile interlining because polyester-based foams has high elongation and good resistance to solvents.

2.1.3 Blowing Agents

Blowing agent is a major role in production of polyurethane foam. Chemical are blowing agent and physical blowing agent are used. For example, a chemical blowing agent, water, helps produces CO_2 gas. The reaction with diisocyanate uses typical water concentration are 3-5 parts of water per 100 parts at polyester polyol and

1.8-5 parts per 100 parts of polyester polyol. The Blowing agent impacts to density and cellular morphology of RPUR foams. The reaction between isocyanate and water is exothermic reaction and results in the formation of active area sites [10].

2.1.4 Surfactant

Surfactants are necessary additives using in RPUR foam formulation. Using surfactant in foam will help to control cell size of foam and reduced surface tension. Selected surfactant or mixtures of surfactants help in mixing components of mixture. Most RPUR foams and flexible foams use organosiloxanes or silicone surfactants. Silicone surfactant for RPUR foams have a greater surface activity than those used for flexible foam. Silicone surfactant is typically added in amounts of 0.4 - 2.0% w/w of the polyol formulation. Structure silicone surfactant of silicone used in RPUR foams formals (Figure 2.5) [11].

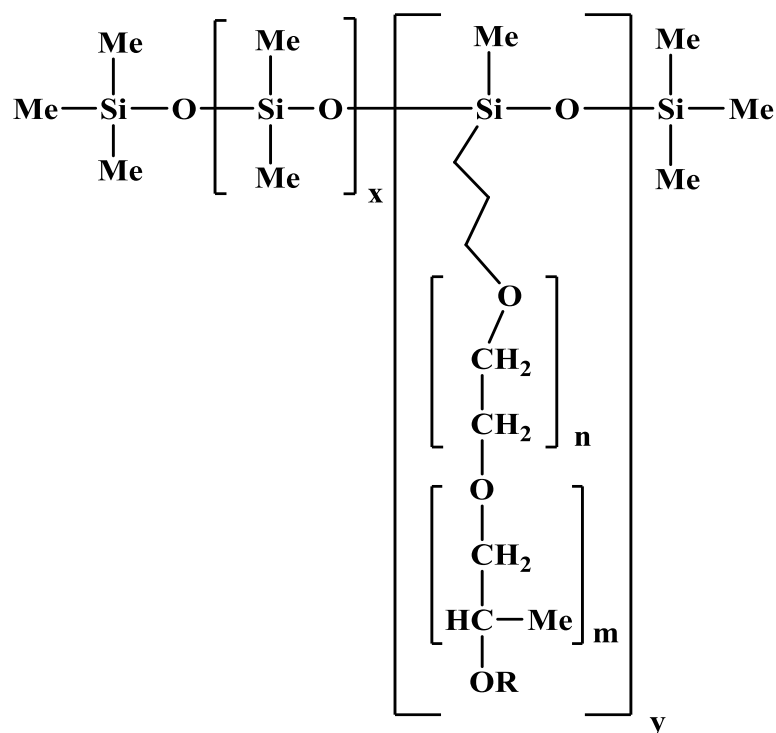


Figure 2.5 Structure of silicone surfactants used in PUR foams manufacture

2.1.5 Catalysts

Catalysts are playing as an important role. The catalysts include a range chemical structure, such as of aromatic tertiary amines, aliphatic tertiary amines, Alkali metal salts of carboxylic acid organometallic compound especially in tin compound (Figure 2.6), each catalyst type is specifies for each chemical reaction. Catalyst mixture normally is an important for controlling balancing of polymerization reaction and gas generation reaction. The catalyst activity of catalysts is depends on basicity, structure (steric hindrance) on the active site [12]. The catalytic effect increase with increasing basicity but is reduced by steric hindrance of the amine nitrogen. Catalysts exert an influence upon the rates of competing reactions and have a major effect on the ultimate properties of the final foam. Tin organometallic catalyst especially tin compound is gelling catalysts which support a reaction between isocyanate and hydroxyl. In the other way, tertiary amine catalyst are generally considered to blowing catalysts will accelerate mainly the reaction of isocyanate and water reaction which generates CO₂ gas [10-13].

The choice of catalysts for making rigid, closed-cell, polyurethane foams from PMDI is usually concerned with obtaining the gelation/blowing reaction and cure rate most suitable for the process application, tertiary amine catalysts are normally used.

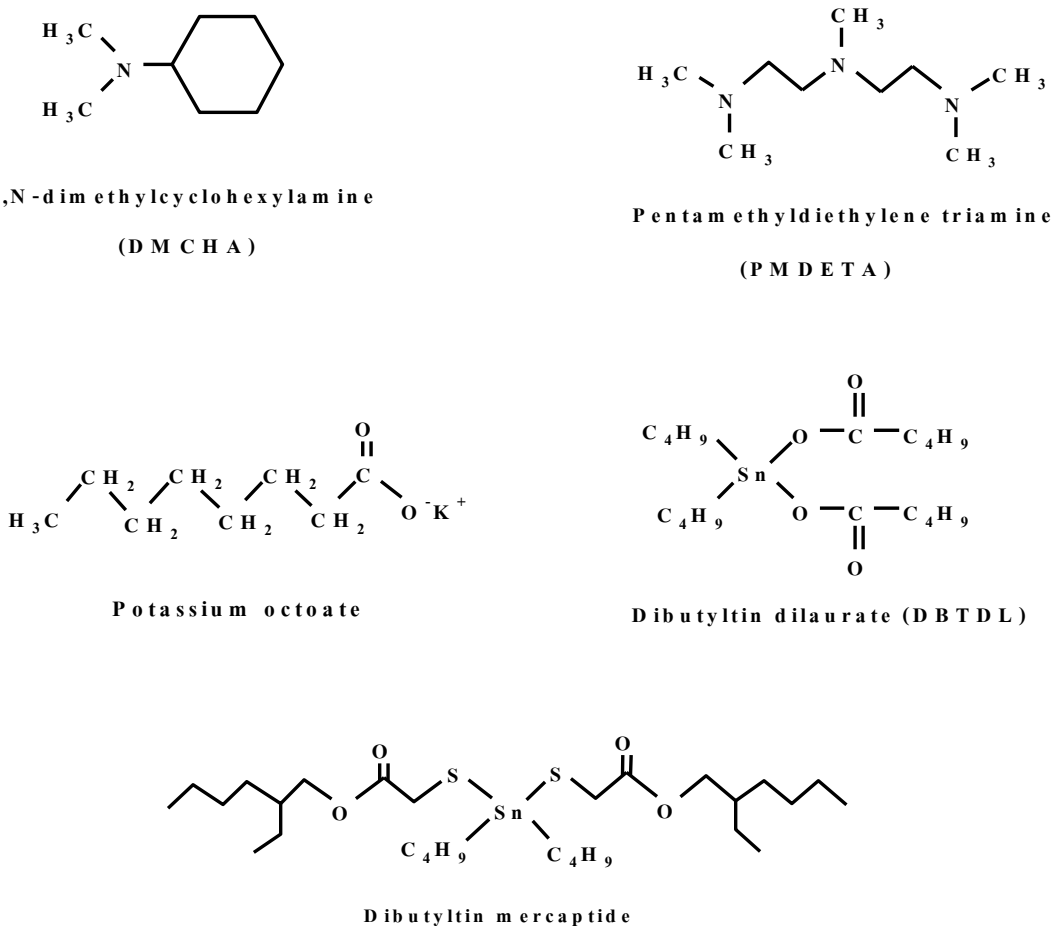
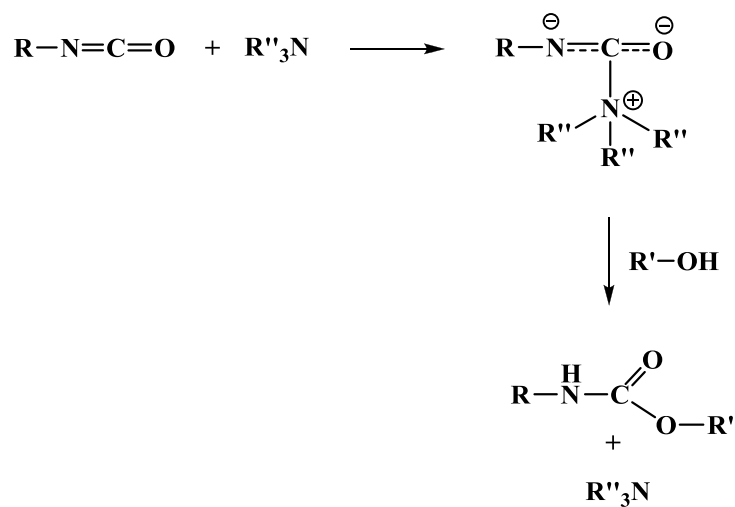


Figure 2.6 Commercial catalysts used in rigid polyurethane foams manufacture.

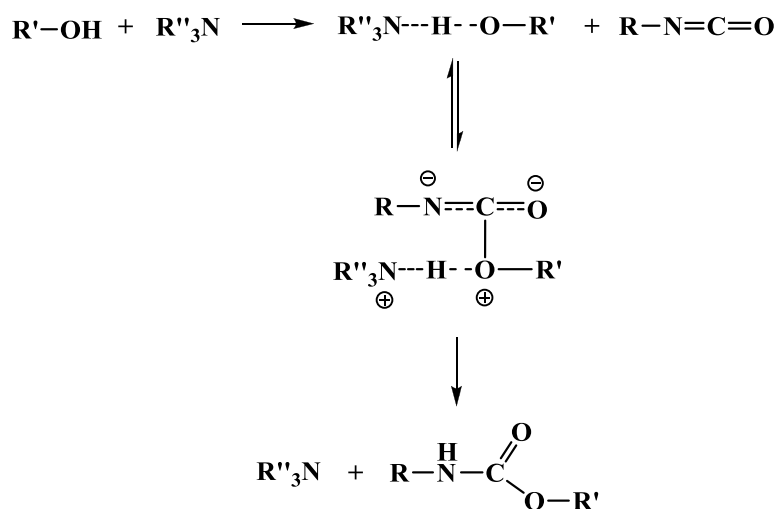
2.2 Reaction mechanisms

2.2.1 Amine catalysts

Tertiary amines are the most widely used polyurethane catalysts. Two mechanisms have been proposed for amine catalysis. In the one proposed by Baker (Scheme 2.1), the activation 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.



Scheme 2.1 Baker mechanism amine catalysts [14].



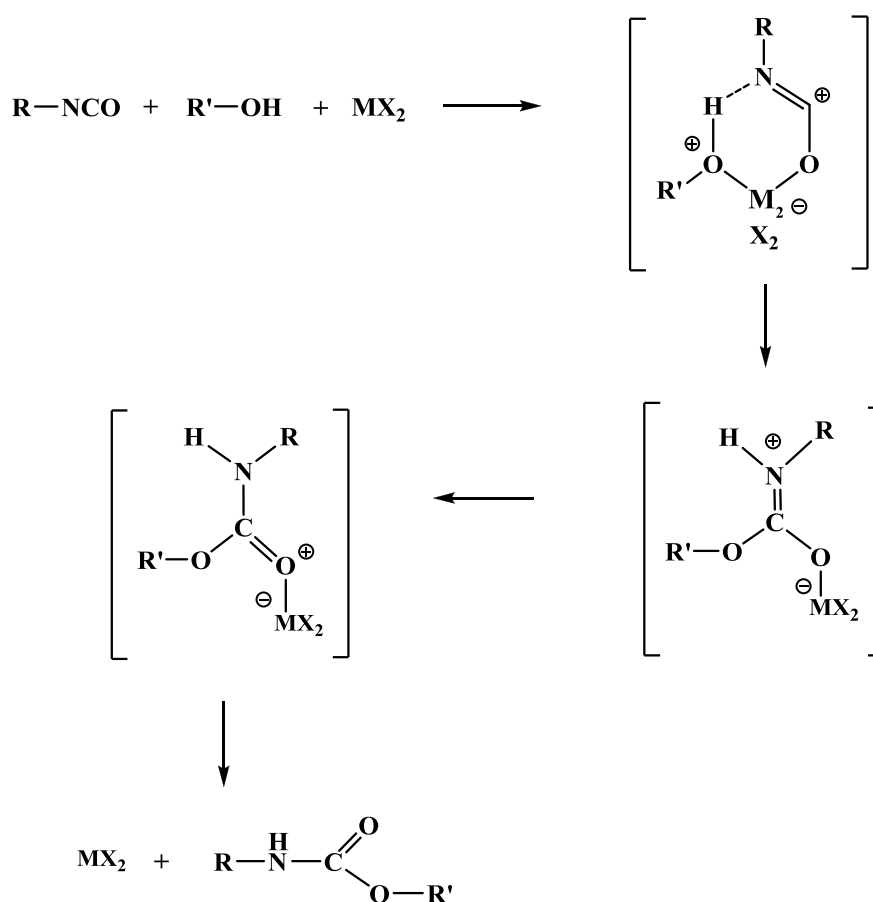
Scheme 2.2 Farka mechanism amine catalysts [14].

In the second mechanism, proposed by Farka (Scheme 2.2), which is supported in the more recent literature, the activation starts by the amine interacting with the proton source (polyol, water, 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 and volatility and end groups. The level of basicity is determined from the pKa value, defined as the pH at

which the concentration of unprotonated and protonated forms, of an ionizable group, are equal

2.2.2 Organotin catalysts

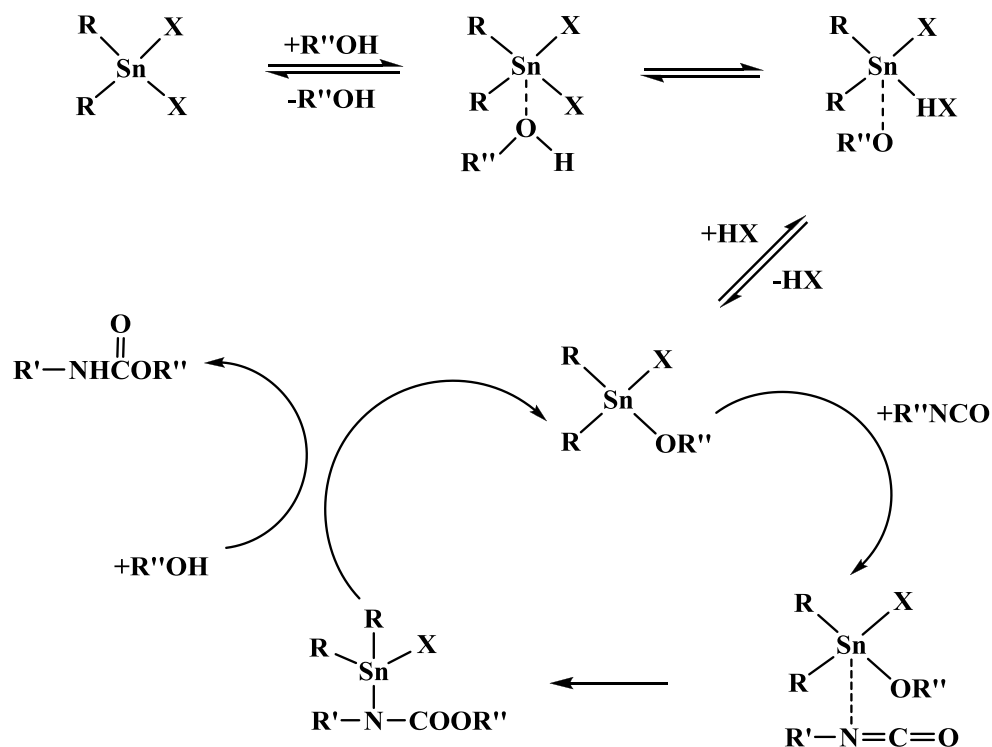


Scheme 2.3 Mechanism of tin(II) salts catalyst

For the tin II salts the following mechanism has been proposed, Scheme 2.3. 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 one the tin first adds to the polyol then the isocyanate. In the second one the tin adds to the oxygen of the isocyanate then reacts with the polyol.

The proposed mechanisms for tin(IV) catalysts, dialkyltin dicarbonates and dialkyltin dialkylthiolates, is the reaction of the tin with a polyol forming a tin

alkoxide, which can then react with the isocyanate to form a complex (Scheme 2.4). Transfer of the alkoxide anion onto the co-ordinated isocyanate affords an N-stannylurethane, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide.



Scheme 2.4 Mechanism of tin(IV) salts catalyst.

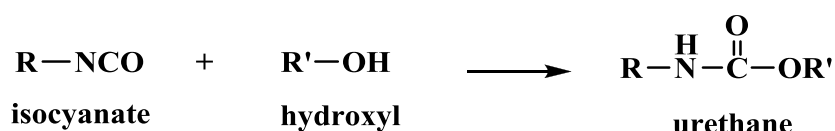
2.3 Chemistry

Polyurethane (PUR) chemistry is based on the high reactivity of the isocyanate group with any compound containing active hydrogen. RPUR foam produced by polyaddition polymerization of alcohols which contain hydroxyl groups in molecules more than 2 groups and compound isocyanate groups at least 2 groups to a molecule (diisocyanate or polyisocyanate) [9]. For simplicity, the basic principle of urethane chemistry is described below using monofunctional reagents.

2.3.1 Primary reaction of isocyanates (very fast reactions)

2.3.1.1 Reaction of isocyanate with hydroxyl compounds

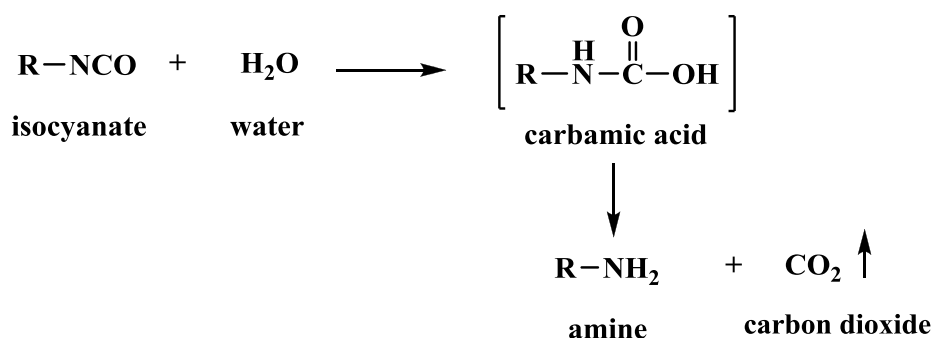
This is an important reaction for production. The reaction between isocyanate and hydroxyl groups produced a carbamate, which is called a urethane in the case of high molecular weight polymers.



This reaction is called the “gelling reaction”. The emission of heat of reaction it must be temperature controlled. The rate of polymerization is affected by the chemical structure of the isocyanate, polyol and catalyst is used to accelerate the reaction rate.

2.3.1.2 Reaction of isocyanate with water

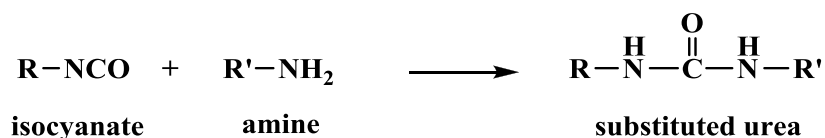
Isocyanates react with water to form produced to form unstable carbamic acid, which immediately decomposes into amine and carbon dioxide.



This reaction is known as the “blowing reaction” because the CO₂ gas produced is used for blowing the foam which, this reaction had an effect to foam density. The CO₂ gas trapped in the closed cell of rigid polyurethane foam [15-16]. The reaction rate is accelerating by suitable choice of catalyst system.

2.3.1.3 Reaction of isocyanate with amines

The reaction of an isocyanate with an amine forms a urea linkage.



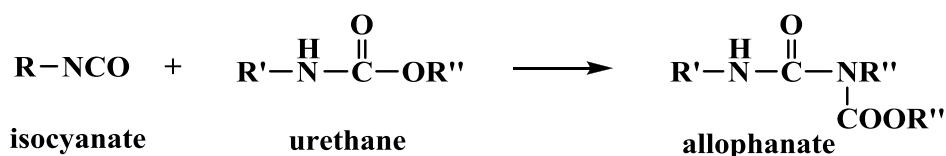
Reactions of unhindered isocyanates with primary amines occur approximately 100-1000 times faster than with primary alcohols [9]. The reactivity of amines increases with the basicity of the amine, and aliphatic amines react much faster than aromatic amines [3].

2.3.2 Secondary reaction of isocyanates

Since isocyanate reacts in the fairly complexes way, produced of different products such as urethane, biuret, urea, allophanate and other.

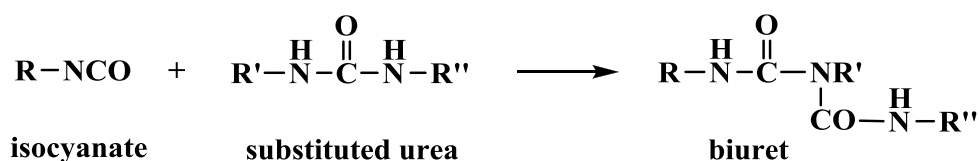
2.3.2.1 Reaction of isocyanate with urethane

The reaction of urethane groups may be considered hydrogen active compounds, the hydrogen action atom linked to the nitrogen atom. The reaction of an isocyanate and generate urethane group an allophanate is formed [17].



2.3.2.2 Reaction with urea

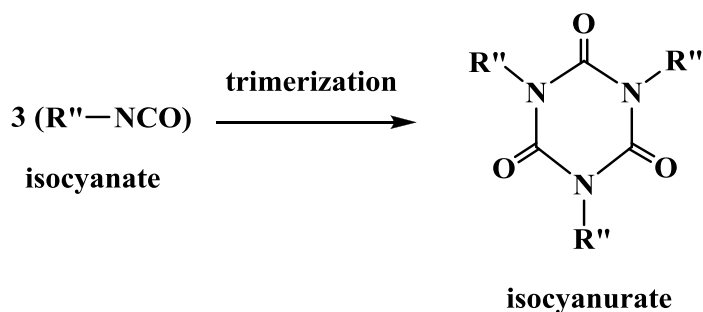
The reaction between isocyanate and the allophanate formation, the -N-H groups of urea react with isocyanates, to generate a biuret.



Formation of allophanates and biurets in polyurethane chemistry, especially when an excess of isocyanate is used, is in fact a supplementary source of crosslinking [17]. In general, reactions of isocyanates with urea groups are significantly faster and occur at lower temperature than that with urethane groups.

2.3.2.3 Trimer formation

Isocyanate trimer can be formed on heating either aliphatic or aromatic isocyanates. The reaction is accelerated by basic catalysts such as sodium and potassium salts of carboxylic acids [17].



2.3 Formulations [5,17]

The amount of isocyanate needed 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 required, ambient conditions and scale of production. The adaptation of amount of isocyanate used is referred to as the “isocyanate index”,

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

The conventional way of calculating the ratio of the components required for polyurethane manufacture is to calculate the number of part by weight of the isocyanate needed to react with 100 parts by weight of polyol and use proportionate amount of additives.

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

-NCO groups:

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

Hydroxyl value (hydroxyl number; OHV)

The hydroxyl value (OHV) sometime is called the hydroxyl number of the polyol, is used as a measurement of the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol and is expressed in mg.KOHg^{-1} 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 g of the compound or polymer.

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

Acid value is also expressed as mg.KOHg^{-1} of polyol and numerically equal to OHV in isocyanate useage.

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

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

Isocyanate conversion (α), isocyanate conversion can be calculated by FTIR method [18], defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0:

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

where;

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

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

2.5 Mechanical properties

2.5.1 Compressive properties

Compressive properties are the most important mechanical properties for RPUR foams. Compressive energy absorption characteristics and deformation characteristics of foam mainly depend on density, type of base polymer and the predominance of either open or closed cells.

In simple terms, close cell foam deformation involves cell walls bending and buckling, gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rupture (Figure 2.7).

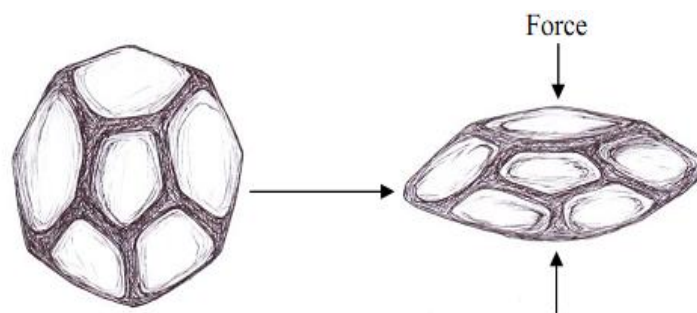


Figure 2.7 Schematic representation of closed cell deformation [9].

Closed cell rigid foams (e.g. PS and PU foams) exhibited from very limited to no yielding behavior. Consequently, gas compression and matrix strength play important roles during the mechanical deformation of rigid foams. In addition, cell rupture often occurs during the energy absorption process. The energy absorption characteristics of foam can be represented in term of compression stress-strain curves. Figure 2.8 show typical compression stress-strain curve of rigid foams.

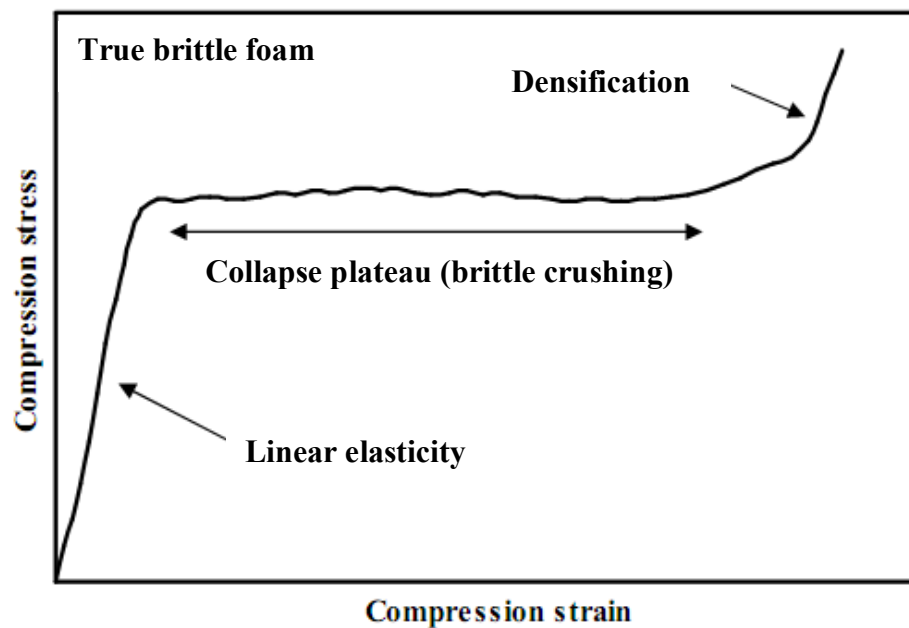


Figure 2.8 Typical compression stress-strain curve for rigid foams [9]

For rigid foams, the compression stress-strain curve is divided into three regions; initial linear elasticity is controlled by cell wall bending and by cell wall stretching due to the contained gas pressure, plateau is due to collapse of cell wall or in brittle foams and densification occur as foam density increases.

The compressive strength of rigid cellular polymers is usually reported at some definite deformation (5 or 10%). The compressive strength of rigid polyurethane foam and densities increased when the foam cell in the direction of rise. The compressive strength perpendicular to rise would be lower than parallel [17].

2.6 Literature reviews

There are many researches studying properties of rigid polyurethane foam both in physical and mechanical. Moreover, many researches also study about the impact of blowing agent, catalyst, surfactant, and isocyanate on polyurethane foam.

Singh and coworkers [18] studied the reactivity of raw materials and the effects of raw materials on the structures and properties of rigid polyurethane foams. In the formulation, they used 4,4-diphenylmethane diisocyanate, polyether polyol, triethylenediamine, 1,4-butane diol, poly(siloxane ether), methylene chloride and water as the blowing agents. This research varied the ratios of ingredients which affects the physical properties, for example; cream time, gel time, tack free time and density of rigid polyurethane foam. The results showed that the percentage of rigid polyurethane foam was increased when the content of catalysts were increased. For the cell morphology and thermal properties of foam investigated by SEM technique, it was found that, when increased the amount of water, cell size was increased, but the density was reduced. Moreover, Han and coworkers [19] studied the impact of silicone surfactant on the cell size and the thermal conductivity of foam, which used four different silicone surfactants. The result indicated that the optimum concentration of silicone surfactant was approximately 1.5 to 2.5 pbw for various surfactants could reduce cell size and thermal conductivity. Lim and coworkers [20] also reported an impact of surfactant ϕ on foam density and reaction times; the density decreased very fast when the small amount of surfactant was added. When the surfactant was decreased, the surface tension and the size of the cell were also decreased, but the cream time, gel time and tack free time increased.

Currently, the blowing agents, trichloroethane (CFC) and HCFC-141b, are used in production of RPUR foams. Moreover, these agents also improve the thermal insulation of the foam. However, CFC and HCFC-141b have impacts on the environment; another blowing agent, which is environment friendly for RPUR synthesis is needed. Water is used to replace CFC and HCFC-141b because it has no harm. However, the excessive use of water causes a negative pressure gradient due to the rapid diffusion of CO₂ through the cell wall causing cell collapse [21-24].

Thirumal and coworkers [25] studied the effects of density on the properties of water blown rigid polyurethane foam for investigating mechanical, morphological, water absorption, thermal conductivity and thermal behavior of rigid poly urethane foam. From experimental data, it was found that when the amount of blowing agent was increased, the density of the foam decreased. Thermal conductivity increased because cell size was reduced and also changed the mechanical properties of foam. Xiaobin and coworkers [26] studied structures and physical properties of rigid polyurethane foam and found that when the amount of water was increased from 3 to 7 pbw, the density and the average size of the cell would be decreased.

Choe and coworkers [27] studied the properties of RPUR foams, which used water as blowing agent and cyclopentane and hydrofluorocarbon (HCF) as physical blowing agents. From an experimental, it could be concluded that the kinetic rate of PUF would increase when increased amount of catalyst. In case of using only water as blowing agent, blowing catalyst had no effects on density and compressive strength. On the other hand, when HCF or cyclopentane was used instead of water, both density and compressive strength also increased. When compare different PUF prepared from different blowing agents, the physical blowing agent provides smaller cell size than the chemical blowing agent. Moreover, PUF prepared from a mixed blowing agent (cyclopentane/water = 7/3) showed lower conductivity than PUF prepared from only cyclopentane or water.

An effective of the isocyanate on aliphatic waterborne polyurethane foam a property was reported by Wang and coworkers [28]. the different proportion of isocyanate affected the structure and the properties of the foam (tensile strength, water resistance and thermal stabilities).

Modesti and coworkers [29] studied the trimerization of isocyanate reaction to isocyanurate. The result showed that when increased the amount of isocyanate, the reaction rate of trimerization could be increased due to the excess amount of isocyanate.

Lee and coworkers [30] studied the effects of polyol and additive on the polyurethane properties by using distilled water as blowing agent. It is concluded that when increased the amount of surfactant, cell size would be changed. However, if the surfactant reaches the maximum point, increasing of surfactant could not affect any

change in cell size. The increasing of the catalysts, water, and/or OH value and functionality were increased in the reaction of reaction of rigid polyurethane foam could increase the density and the compressive strength of the foam.

Sardon and coworkers [31] compared the effectiveness of dibutyltin diacetate (DBTDA) and zirconium acetylacetonate [$\text{Zr}(\text{acac})_4$], which were used as catalyst in the preparation of waterborne polyurethane. The result showed that $\text{Zr}(\text{acac})_4$ was an effective catalyst with low toxicity. Therefore, using of tin complexes as a catalyst in polymerization of isophorone diisocyanate (IPD) could be replaced by using of $\text{Zr}(\text{acac})_4$.

Inoue and coworkers [32] studied the effectiveness of metal transition complexes and tertiary amine as a catalyst used in the synthesis of polyurethane. The metal used in the preparation of catalyst were manganese(II) acetylacetonates [$\text{Mn}(\text{acac})_2$], iron(III) acetylacetonates [$\text{Fe}(\text{acac})_3$], cobalt(II) acetylacetonate [$\text{Co}(\text{acac})_2$], nickel(II) acetylacetonate [$\text{Ni}(\text{acac})_2$], and copper(II) acetylacetonate [$\text{Cu}(\text{acac})_2$]. The result showed that catalyst prepared from metal transition and tertiary amine was more effective than the catalyst prepared from only metal transition.

Pengjam and coworkers [33] studied the effectiveness of catalyst used in the preparation of rigid polyurethane foam. The catalysts were prepared from metal-amine complexes and metal-amine-salicylate. The result showed that the copper complexes was more effective catalyst when compared to the complex of manganese and dimethylcyclohexylamine.

In the preparation of rigid polyurethane foam, the balance between blowing and gelling catalyst is important in accelerate the reaction of isocyanate. While the balance between gelling and blowing reaction commercial catalyst (DMCHA) supported both gelling and blowing reaction. However, the disadvantage of the catalyst is its strong smell.

In this work, copper-amine complexes were used in the preparations of rigid polyurethane foams (Figures 2.9-2.10). The results were compared with commercial catalyst. (Figure 2.11)

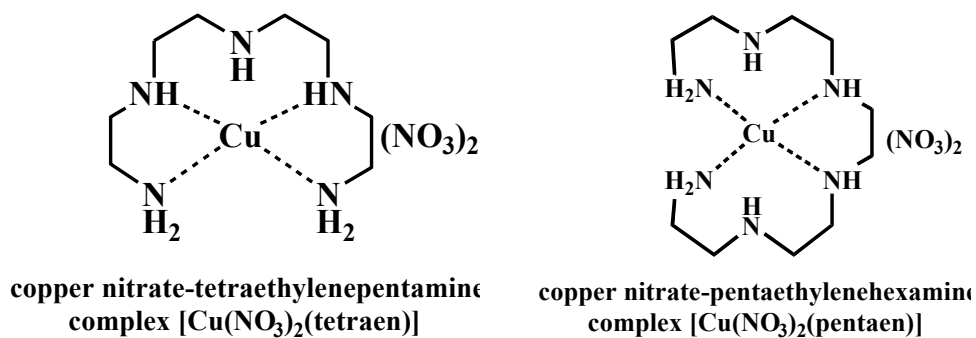


Figure 2.9 Structure of copper nitrate-pentaethylenhexamine and copper nitrate-tetraethylenepentamine complexes.

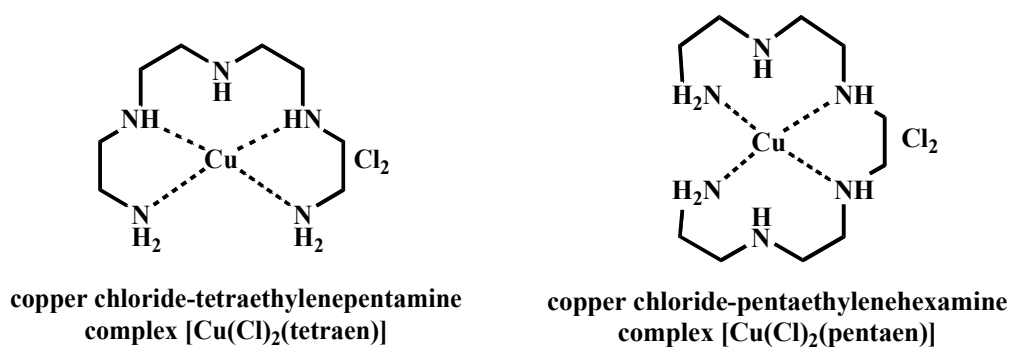


Figure 2.10 Structure of copper chloride-pentaethylenhexamine and copper chloride-tetraethylenepentamine complexes.

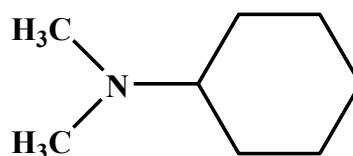


Figure 2.11 N, N-dimethylcyclohexyl amine (DMCHA) [4].

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and raw materials

3.1.1 Metal complexes synthesis

Copper(II) nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$), copper(II) chloride ($\text{Cu}(\text{Cl})_2 \cdot 2\text{H}_2\text{O}$) and pentaethylenehexamine (pentaen)/ tetraethylenepentamine (tetraen) as aliphatic amine were obtained from Fluka and Aldrich Co. Ltd. All compounds were used without purification.

3.1.2 Preparation of Rigid Polyurethane (RPUR) Foams

(a) Isocyanate

Polymeric MDI (4,4'-methane diphenyl diisocyanate; PMDI, Suprasec[®] 5005) was supplied by Huntsman (Thailand) Co., Ltd. (Table 3.1)

Table 3.1 Typical properties of Polymeric MDI (Suprasec[®] 5005)

Typical properties	
NCO content (%w/w)	31.0
Viscosity (mPa.s at 25 °C)	170-270
Specific gravity at 25 °C	1.3
Average functionality	2.7
Appearance	Medium brown

(b) Polyol

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 (Table 3.2).

Table 3.2 Typical properties of polyether polyol (Daltolac[®] R 180)

Typical properties	
Hydroxy Value (mgKOH/g)	440
Viscosity (mPa.s at 25 °C)	5500
Specific gravity at 25 °C	1.1
Functionality	4.3

(c) Surfactant

Polysiloxane (Tegostab[®] B8460) obtained from Huntsman (Thailand) Co., Ltd. are used as a surfactant.

Distilled water was used as a chemical blowing agent.

N,N-dimethylcyclohexylamine (DMCHA), supplied by Huntsman (Thailand) Co., Ltd., was used as a commercial reference catalyst.

3.2 Synthetic procedures

Metal-amine complexes were prepared by using two methods. In the first method, copper nitrate/copper chloride was reacted with pentaethylenehexamine or tetraethylenepentamine to form $\text{Cu}(\text{NO}_3)_2(\text{pentaen})/\text{Cu}(\text{NO}_3)_2(\text{tetraen})/$ and $\text{Cu}(\text{Cl})_2(\text{pentaen})/\text{Cu}(\text{Cl})_2(\text{tetraen})$ complexes. Distilled methanol was used as a solvent for this method. Methanol was removed from the metal-amine complexes before using in the preparation of rigid polyurethane foam.

In the second method, metal-pentaethylenehexamine complexes [M(pentaen)] and metal-tetraethylenepentamine complexes [M(tetraen)] were synthesized from the reaction between metal(II) nitrate, metal(II) chloride or metal(II) sulfate with pentaethylenehexamine (pentaen) or tetraethylenepentamine (tetraen) in water to obtain an aqueous solution containing metal complexes. The metal-amine complexes solution was used in the preparation of rigid polyurethane foam without purification.

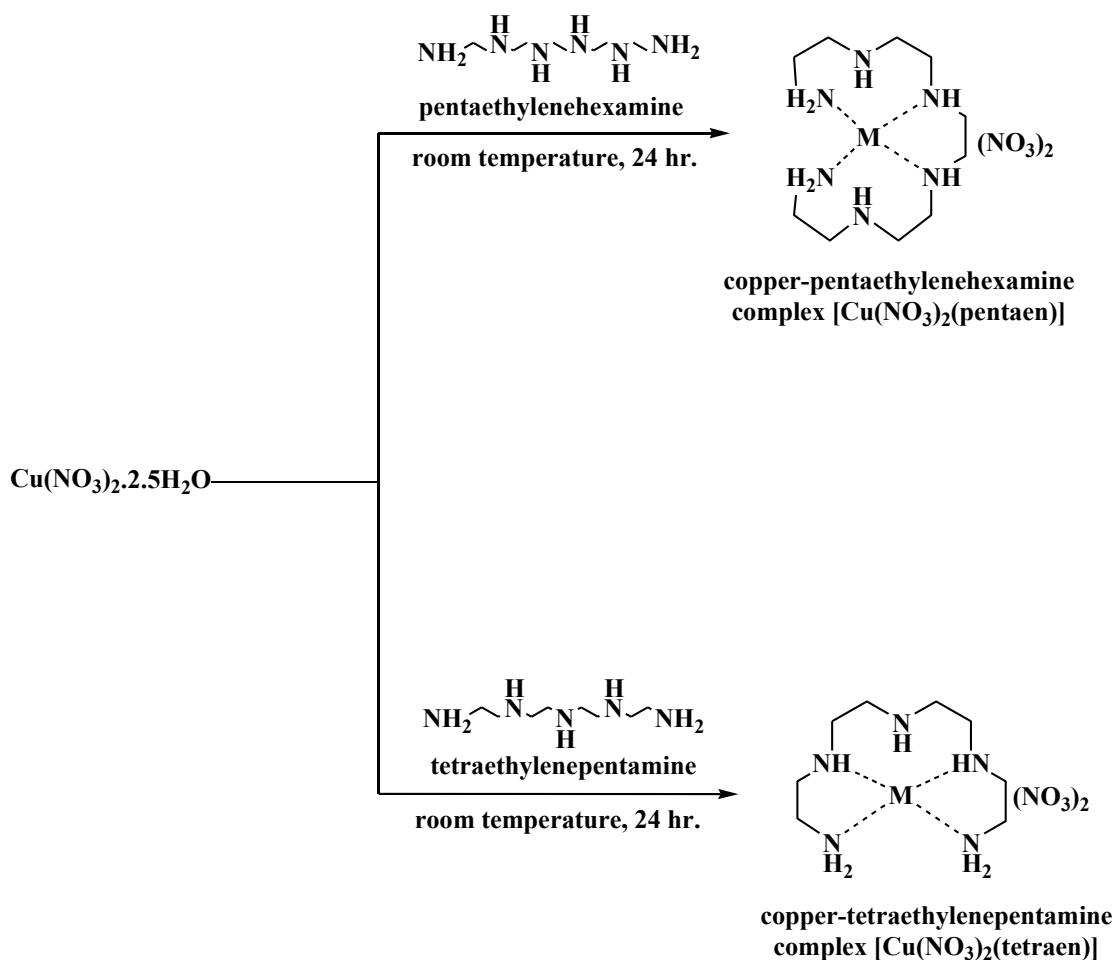
3.2.1 Synthesis of metal-amine complexes in methanol

3.2.1.1 Synthesis of copper-nitrate-pentaethylenhexamine

[Cu(NO₃)₂(pentaen)] and copper nitrate-tetraethylenepentamine [Cu(NO₃)₂(tetraen)] complexes

The preparation of Cu(NO₃)₂(pentaen) was done as follows [34-36]: solution of pentaethylenhexamine (pentaen) (0.55 ml, 2.36 mmol) was stirred in methanol (10 mL) at room temperature for 30 minutes. After that, copper(II) nitrate hemi(pentahydrate) (0.500 g, 2.15 mmol) was added and the reaction mixture was stirred at room temperature for 24 hours (Scheme 3.1). Precipitated of Cu(NO₃)₂(pentaen) complexes was dried under vacuum. Cu(NO₃)₂(pentaen) was obtained as a dark blue viscous liquid (0.73 g, 73%): IR (cm⁻¹); 3239 (N-H), 2931 (C-H), 1463 cm⁻¹ (N-O asymmetric stretching) and 1321 cm⁻¹ (N-O symmetric stretching). UV; λ_{max}(MeOH) = 270 nm, molar absorptivity (ε) = 1,150. Cu(NO₃)₂(pentaen) showed *m/z* = 461.485. Anal. Calcd. For C₁₀H₂₈CuN₆O₆: C 28.60; H 6.72; N 26.68; found C 28.87; H 6.89; N 23.23. AAS. Calcd. For C₁₀H₂₈CuN₆O₆: Cu 15.13; found Cu 15.07.

The preparation of Cu(NO₃)₂(tetraen) was done as follows: tetraethylenepentamine (0.46 mL, 2.41 mmol) was stirred in methanol (10 mL) at room temperature for 30 minutes. After that, copper(II) nitrate hemi(pentahydrate) (0.551 g, 2.28 mmol) was added and the reaction mixture was stirred at room temperature for 24 hour (Scheme 3.1). The reaction mixture was dried under vacuum to remove solvent. Cu(NO₃)₂(tetraen) was obtained as a dark blue power (0.86 g, 86%): IR (cm⁻¹); 3207 (N-H), 2939 (C-H), 1474 cm⁻¹ (asymmetric N-O), and 1329 cm⁻¹ (symmetric N-O). UV; λ_{max}(MeOH) = 265 nm, molar absorptivity (ε) = 8,125. Cu(NO₃)₂(tetraen) showed *m/z* = 433.565. Anal. Calcd. For C₈H₂₃CuN₇O₆: C 25.50; H 6.15; N 26.02; found C 25.88; H 6.22; N 24.27. AAS. Calcd. For C₈H₂₃CuN₇O₆: Cu 16.86; found Cu 16.36.



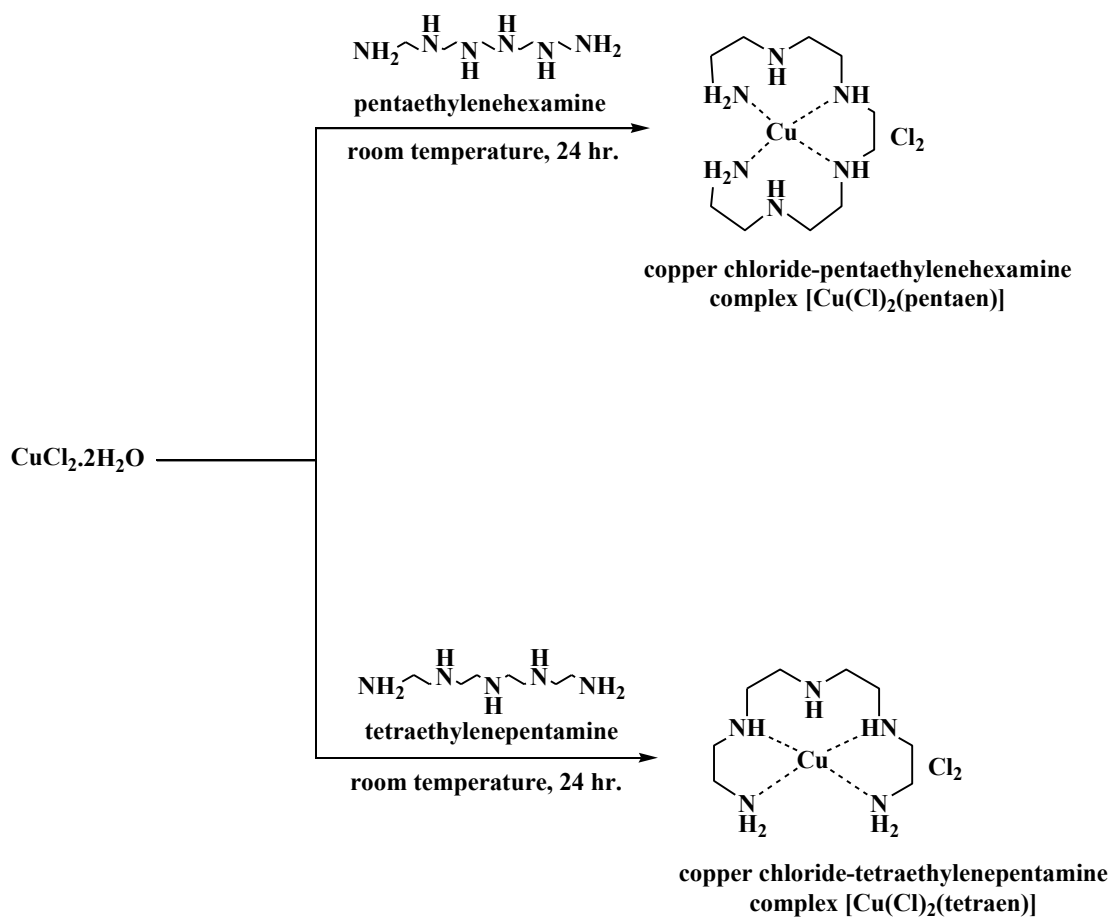
Scheme 3.1 Synthesis of copper nitrate-pentaethylenhexamine and copper nitrate-tetraethylenepentamine complexes

3.2.1.2 Synthesis of copper-nitrate-pentaethylenhexamine [Cu(Cl)₂(pentaen)] and copper chloride-tetraethylenepentamine [Cu(Cl)₂(tetraen)] complexes

The preparation of copper chloride complex was done as described above (Scheme 3.2). Cu(Cl)₂(pentaen) was obtained as blue viscous liquid (0.70 g, 70%): UV; $\lambda_{\max}(\text{MeOH})=268 \text{ nm}$, molar absorptivity (ϵ) = 2,597. Cu(pentaen) showed $m/z = 401.953$.

Cu(Cl)₂(tetraen) was obtained as blue viscous liquid (0.75 g, 75%) : UV; $\lambda_{\max}(\text{MeOH}) = 267 \text{ nm}$, molar absorptivity (ϵ) = 2,673. CuCl₂(tetraen) shown $m/z = 363.486$.

Composition of starting material which used in preparation of copper-amine complexes is shown in Table 3.3.



Scheme 3.2 Synthesis of copper chloride-pentaethylenhexamine and copper chloride-tetraethylenepentamine complexes

Table 3.3 Composition of starting materials in the preparation of copper-amine complexes

Metal complexes	Wt. of Cu(NO₃)₂/CuCl₂ (g)	Weight of composition Pentaen/Tetraen (mL)	Yield (%)	Appearance
metal:pentane/tetraen =1:1				
Cu(NO ₃) ₂ (pentaen)	0.500	0.55	73	Dark blue viscous liquid
Cu(NO ₃) ₂ (tetraen)	0.551	0.46	86	Dark blue powder
Cu(Cl) ₂ (pentaen)	0.577	0.64	70	Blue viscous liquid
Cu(Cl) ₂ (tetraen)	0.474	0.54	75	Blue viscous liquid

3.2.2 Synthesis of metal-amine complexes in water

3.2.2.1 Synthesis of copper nitrate-pentaethylenhexamine complex

Metal(II) salt (Cu(NO₃)₂) were dissolved in deionized water (3 mL). Desired amount of pentaethylenhexamine was added on previous solution with stirring until homogeneous solution was obtained. Silicone surfactant (Tegostab[®] B8460) (2.5 g) was added to reaction mixture and stirred for 24 hours. Cu(NO₃)₂(pentaen) was obtained aqueous solution. Cu(NO₃)₂(pentaen). UV; λ_{\max} = 270 nm, molar absorptivity (ϵ) = 1027. Cu(NO₃)₂(pentaen) was used as catalysts for RPUR foam preparation in the next step without purification.

3.2.2.2 Synthesis of copper nitrate-tetraethylenepentamine complex

$\text{Cu}(\text{NO}_3)_2$ was dissolved in deionized water (3 mL). Desired amount of tetraethylenepentamine was added on previous solution, solution was stirred until homogeneous solution was obtained. Then silicone surfactant (Tegostab[®] B8460) (2.5 g) was added to mixture, the solution was stirred for 24 hours. $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ was obtained aqueous solution. $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$. UV; $\lambda_{\text{max}} = 265 \text{ nm}$, molar absorptivity (ϵ) = 8020.

3.2.2.3 Synthesis of copper chloride-pentaethylenehexamine complex

$\text{Cu}(\text{Cl})_2$ was dissolved in deionized water (3 mL). Desired amount of pentaethylenehexamine was added on previous solution with stirring until homogeneous solution was obtained. Silicone surfactant (Tegostab[®] B8460) (2.5 g) was added to reaction mixture and stirred for 24 hours. $\text{Cu}(\text{Cl})_2(\text{pentaen})$ was obtained as aqueous solution. $\text{Cu}(\text{Cl})_2(\text{pentaen})$: UV; $\lambda_{\text{max}} = 268 \text{ nm}$, molar absorptivity (ϵ) = 1222.

3.2.2.4 Synthesis of copper chloride-tetraethylenepentamine complex

$\text{Cu}(\text{Cl})_2$ was dissolved in deionized water (3 mL). Desired amount of tetraethylenepentamine was added on previous solution with stirring until homogeneous solution was obtained. Silicone surfactant (Tegostab[®] B8460) (2.5 g) was added to reaction mixture and stirred for 24 hours. $\text{Cu}(\text{Cl})_2(\text{tetraen})$ was obtained aqueous solution. $\text{Cu}(\text{Cl})_2(\text{tetraen})$: UV; $\lambda_{\text{max}} = 267 \text{ nm}$, molar absorptivity (ϵ) = 1053.

3.2.3 The preparation of rigid polyurethane (RPUR) foam

The preparation of RPUR foam is divided into 2 step; The first step, was a mixed of polyol, blowing agent (water), surfactant and catalyst (DMCHA or copper-amine complexes) into a paper cup (700 mL) and stirred together for 20 seconds. Then added isocyanate (polymeric MDI) into mixture and stirred by mechanical stirrer at speed 2000 rpm for 20 seconds. This part is illustrated in Figure 3.1.

The time for polymerization reaction of RPUR foam studied were cream time, gel time, rise time, tack free time. And then keep foam at room temperature for 48 hours for physical properties and mechanical properties studies of RPUR foam which prepared from formulation as shown in Table 3.4.

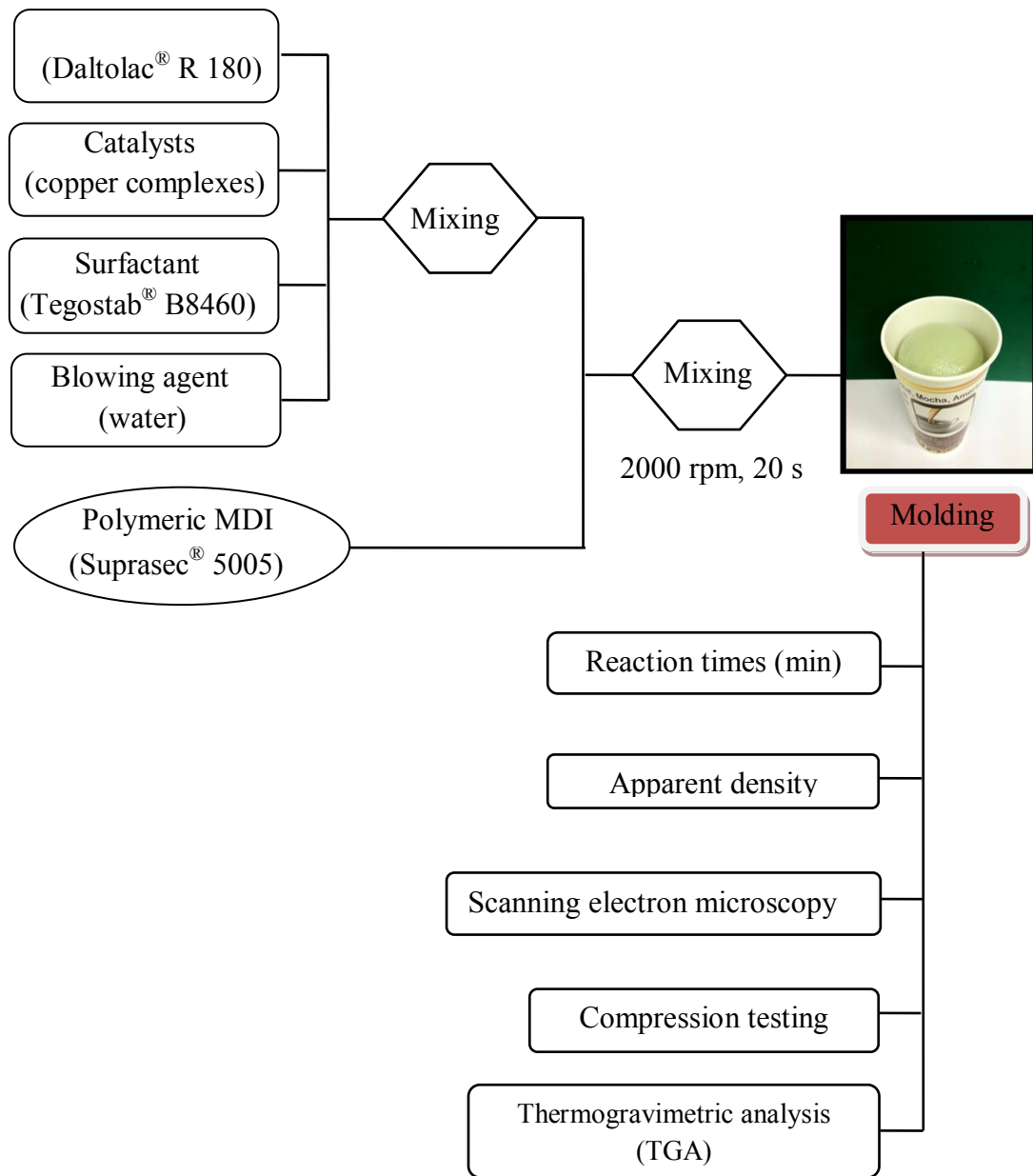


Figure 3.1 RPUR foam processing

Table 3.4 RPUR foam formulations at different NCO indexes (in parts by weight,

Formulations (pbw)	NCO index		
	100	130	150
Polyether polyol (Daltolac [®] R 180)	100	100	100
Catalysts (DMCHA or copper complexes)	1.0	1.0	1.0
Silicone surfactant (TEGOTAB B8460)	2.5	2.5	2.5
Blowing agent (water)	3.0	3.0	3.0
Polymeric MDI (Suprasec [®] 5005)	152	197	227

pbw unit)

3.2.4 The preparation of rigid polyurethane foam by using plastic mold

Polyol and catalyst were put into 700 mL paper cup and stirred together by mechanical stirrer at speed 2000 rpm for 20 seconds. After that, isocyanate (polymeric MDI) was added into mixture and mixed well for 20 seconds. When mixture was homogeneous, it was poured in to plastic mold sized 10×10×10 cm, and allowed to rise independently. Foams were kept for 48 hours at room temperature to polymerization reaction, removed from mold and characterized [24-25]. It was found that RPUR foams from a different catalysts has the same peak IR spectra. Therefore, only the IR peaks of RPUR foams obtained from Cu(NO₃)₂(tetraen) (Figure 3.2) are observed as follows:

IR (cm⁻¹); amine group (NH stretching) at 3321 cm⁻¹, phenyl group (Ar-H) at 1598 cm⁻¹, NH bending was urethane groups at 1511 cm⁻¹, C-N of isocyanurate at 1417 cm⁻¹, C=O stretching of urethane at 1709 cm⁻¹, and C-O of urethane peaks at 1218 cm⁻¹.

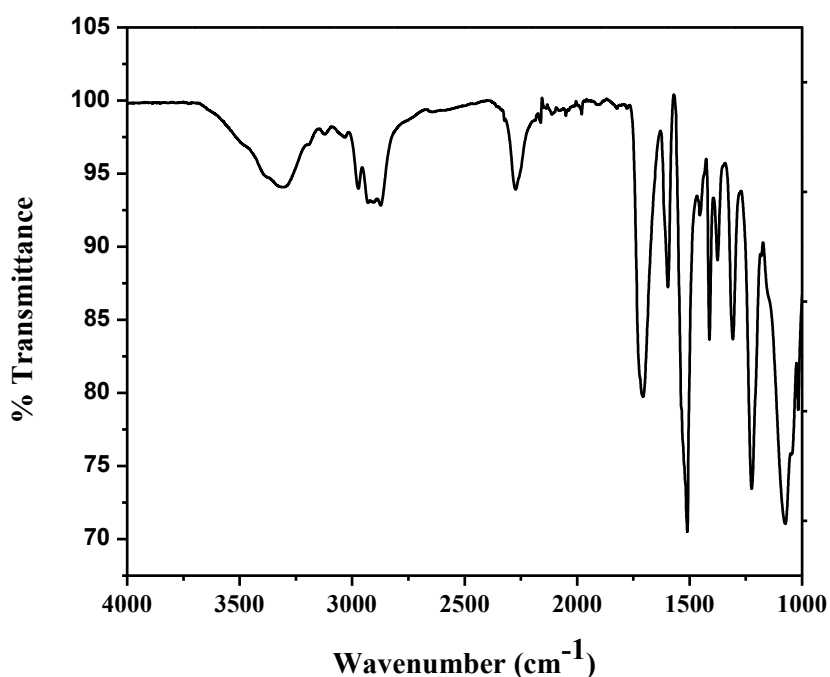


Figure 3.2 IR spectra of RPUR foam catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$

3.4 Instrumentation

3.4.1 Infrared spectroscopy

FTIR spectrometer Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. The aim of IR spectroscopic analysis is to determine the chemical functional groups in the specimen. Different functional groups absorb characteristic frequencies of IR radiation.

FTIR spectroscopy is used to study the functional groups on metal-amine complexes as catalyst and rigid polyurethane foams using a Nicolet at a resolution of 4 cm^{-1} and a total of 64 interferograms were signal averaged. The ATR crystal is integrated into the beam of an ATR-IR spectrometer (Nicolet 6700) in such a way that IR light is passed through. ATR occurs on the measuring surface which in contact with the foam sample. The IR bands given in Table 3.5 are used for the analysis. The measurement was controlled by Omnic software.

Table 3.5 Characteristic IR bands of RPUR foam

Functional group	Vibration mode	IR peak (cm⁻¹)
NCO	NCO antisymm. Str.	2180-2310
CO	CO str.(urethane, urea, isocyanurate, allophanate, Biuret, etc.	1620-1760
Isocyanurate	Ring deformation and CH ₂ -deformation in PMDI	1370-1443
Amide	CN-str. (urethane, urea)	1155-1245
Reference	Non-reaction groups in polyol and isocyanate	935-1050

3.4.2 Ultraviolet-visible spectroscopy (UV-vis)

Ultraviolet-visible spectroscopy involves the ultraviolet/visible light. UV-vis spectroscopy is used in analytical chemistry for quantitative determination of different analyze. Different wavelengths are absorbed different molecules absorb. The sample at a concentration of 10⁻³ mol/L was prepared using DI water as a solvent. The samples were scan over range 200-500 nm.

3.4.3 Mass spectrometry (MS)

Mass spectrometry is an analytical tool used to determine the mass (m) -to-charge (z) ratios (m/z) of a specimen. The type of mass spectrometer used was MALDI-TOF. MALDI-TOF mass spectra were obtained on a Bruker Bifex mass spectrometer using ethanol as a matrix.

3.4.4 Atomic absorption spectroscopy (AAS)

The presences of metals in liquid samples are determines as atomic absorption spectroscopy (Perkin-Elmer: Analyst 100). The sample concentration of solvent is around 1- 5 ppm.

3.4.5 Atomic absorption spectrometry (EA)

For elemental analysis (EA) almost usually refers to C, H and N analysis determination of the mass fractions of carbon, hydrogen and nitrogen of a specimen. Elemental analysis was carried out using a Perkin-Elmer EP 2400 analyzer.

3.4.6 Digital Stopwatch

Using a digital stop watch to measured the chemical reactions which are cream time, gel time, rise time and tack free time in a process of preparing rigid Polyurethane foam.

3.4.7 Thermocouple

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

3.5 Physical and Mechanical properties of RPUR foam

3.5.1 Density

The density of material is defined as its mass per unit volume. For measurement foam-density, using a sample which is specimen was 30×30×30 mm (length×width×thickness) and average of the values of three samples to be reported.

3.5.2 Compressive testing

The compressive testing of foams in perpendicular and parallel to the foam rise direction were performed using universal testing machine (Lloyd). The sample size was 30×30×30 mm (length×width×thickness) dimension, the rate of crosshead movement was fixed at 2.54 mm/min and the preload cell used was 0.100 N. The of stress-strain value was used to plot a graph.

3.5.3 Scanning electron microscope (SEM)

The morphology and cell size's rigid foam samples were measured on a JSM-5800LV scanning electron microscope (SEM). During analysis RPUR foams will prepare foams thickness is at 1.0 mm and coating with gold in order to make electrically conductive surface.

3.5.4 Thermogravimetric analysis (TGA)

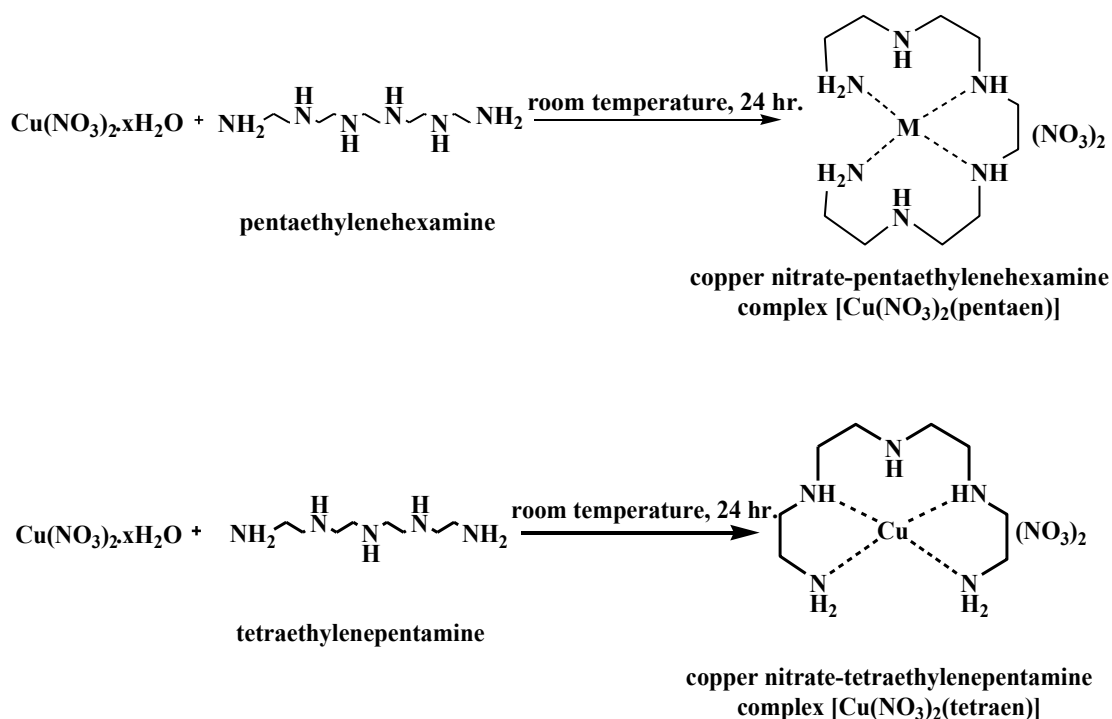
Thermogravimetric Analysis (TGA) measures the amount and rate of change in the material weight. The measurements are used to determine and predict thermal stability of rigid polyurethane foam. TGA determination was performed by Netzsch STA 409C Thermo Gravimetric Analyzer. All specimens were heated from 25 °C to 600 °C at a heating rate of 20 °C/min under N₂ gas. The results were reported 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 copper nitrate-amine complexes [Cu(NO₃)₂(pentaen) and Cu(NO₃)₂(tetraen)]

Metal-amine complexes were synthesized using copper nitrate and amines, namely pentaethylenehexamine (pentaen) and tetraethaylenepentamine (tetraen), by using methanol or water as solvent (Scheme 4.1). When methanol was used as a solvent, after the reaction between copper nitrate and petraen or teraen was completed and metal-amine complex was obtained, methanol was evaporated from metal-amine complex under vacuum. This method gave metal-amine complexes in the form of viscous liquid. Metal-amine was then used to prepare the rigid polyurethane foam.

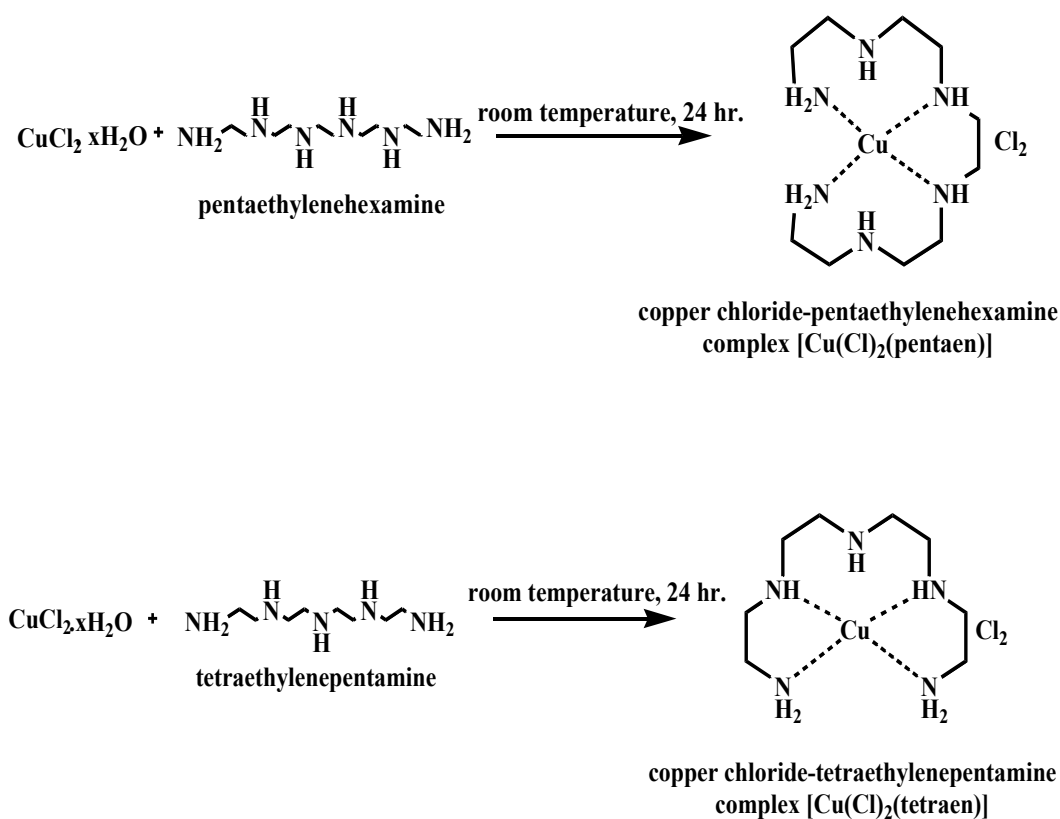


Scheme 4.1 Synthesis of copper nitrate-pentaethylenehexamine and copper nitrate-tetraethylenepentamine complexes.

For the synthesis of metal-amine complexes using water as a solvent, the aqueous solutions metal-amine complexes were obtained and could be used directly without purification to prepare the rigid polyurethane foam.

4.2 Synthesis of copper chloride-amine complexes [Cu(Cl)₂(pentaen) and Cu(Cl)₂(tetraen)]

By following the synthetic method used in the preparation of copper nitrate-amine complexes in section 4.1, methanol and water was also used as solvents in the synthesis of Cu(Cl)₂(pentaen) and Cu(Cl)₂(tetraen) complexes (Scheme 4.2).



Scheme 4.2 Synthesis of copper chloride-pentaethylenhexamine and copper chloride-tetraethylenepentamine complexes.

4.3 Characterization of copper nitrate-pentaethylenehexamine complex

4.3.1 IR spectroscopy of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex

Figure 4.1 shown the IR spectra of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2$ and pentaethylenehexamine which had absorption bands at $3230\text{-}3275\text{ cm}^{-1}$ (N-H stretching), $2933\text{-}2931\text{ cm}^{-1}$ (C-H stretching), $1604\text{-}1596\text{ cm}^{-1}$ (N-H bending). The N-O stretching (nitrate groups) of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ was found at the absorption band of 1321 cm^{-1} (symmetric N-O), and 1463 cm^{-1} (asymmetric N-O), respectively, which was different from the absorption bands of $\text{Cu}(\text{NO}_3)_2$ at 1431 cm^{-1} (symmetric N-O) and 1509 cm^{-1} (asymmetric N-O). The N-H stretching of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ was found at 3239 cm^{-1} , which slightly shifted from the absorption band of pentaethylenehexamine at 3275 cm^{-1} . These IR data confirmed that copper nitrate-pentaethylenehexamine was formed.

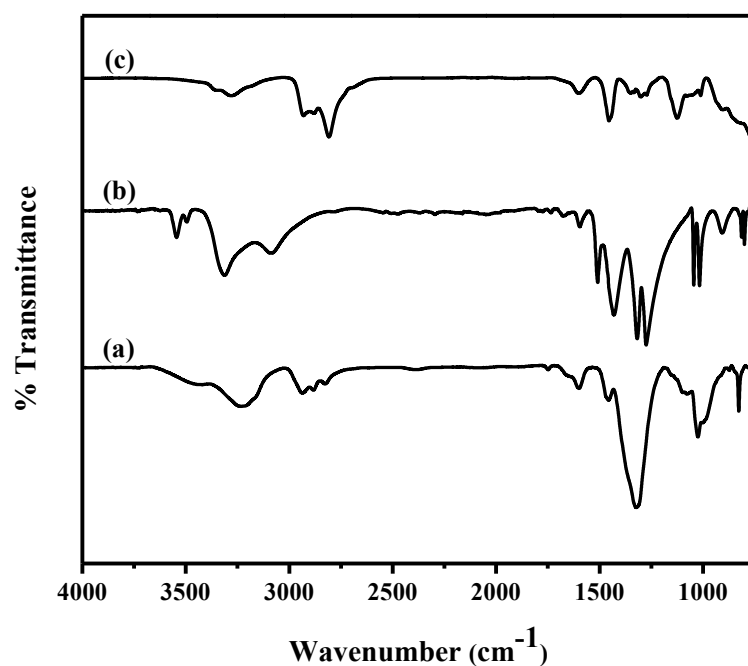


Figure 4.1 IR spectra of (a) $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$; (b) $\text{Cu}(\text{NO}_3)_2$; (c) pentaethylenehexamine.

4.3.2 UV-visible spectroscopy of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex

UV-visible spectra of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{MeOH}}$ (synthesized in methanol) and $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{W}}$ (synthesized in water) are shown in Figure 4.2. There is a consistency between the maximum wavelength of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{W}}$ and $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{MeOH}}$ complexes at 270 nm. Evidently, the maximum wavelength of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{MeOH}}$ and $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{W}}$ complexes shifted from typical maximum wavelength of $\text{Cu}(\text{NO}_3)_2$ at 202 nm, which confirmed the complex formation.

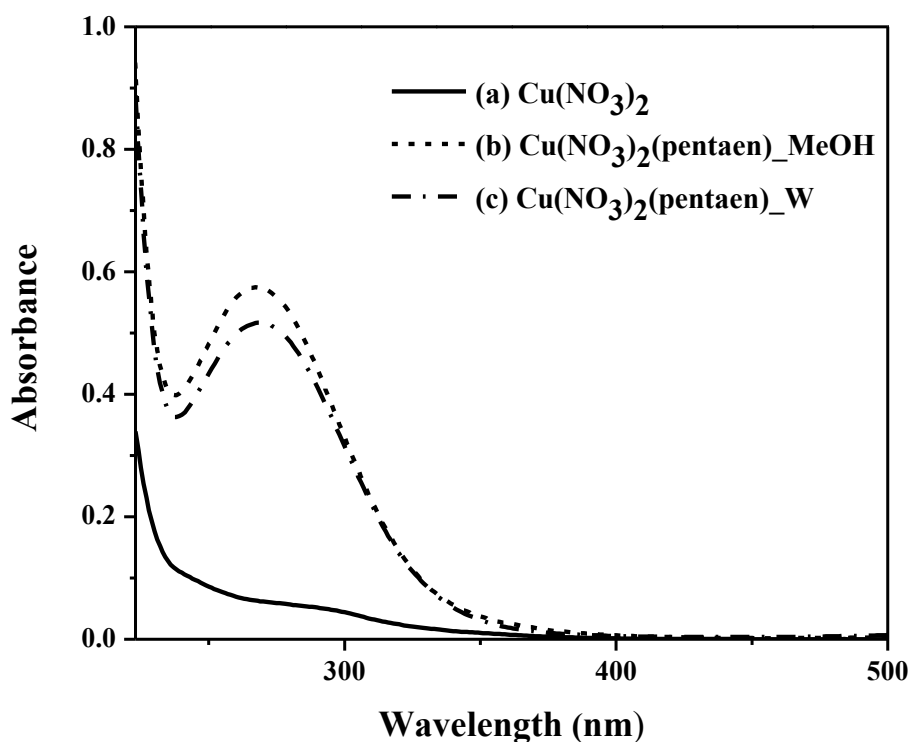


Figure 4.2 UV spectra of (a) $\text{Cu}(\text{NO}_3)_2$; (b) $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{MeOH}}$ and (c) $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{W}}$.

4.3.3 Determination of metal amount in $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex by flame atomic spectrometry (FAAS)

Analytical characteristics of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ are shown in Table 4.1. From Table 4.1, there is the consistency between the experimental value and the calculated value. This result confirmed the structure of metal complex.

Table 4.1 Analytical Characteristics of the FAAS method

Catalyst	Elements determined	Experimental (%)	Calculated (%)
$\text{Cu}(\text{NO}_3)_2(\text{pentaen})$	Cu	15.07	15.13

4.3.4 Elemental analysis of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex

Table 4.2 shown the elemental analysis values of (C, H and N) in $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex. It could be seen that the experimental and calculated value of %C, %H and %N are consistent.

Table 4.2 Elemental analysis (%C, %H, and %N) of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$

Metal complex	Elements determined	Experimental (%)	Calculated (%)
$\text{Cu}(\text{NO}_3)_2(\text{pentaen})$	%C	28.87	28.60
	%H	6.89	6.72
	%N	23.23	26.68

4.3.5 Mass spectrometry of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex

The molecular ion peak of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ at m/z 461.485 corresponding to $[\text{}^{63}\text{Cu}(\text{NO}_3)_2(\text{pentaen})+\text{H}_2\text{O}+\text{Na}^+]$; m/z 461.143 appeared in the MALDI-TOF mass spectrum (Figure 4.3).

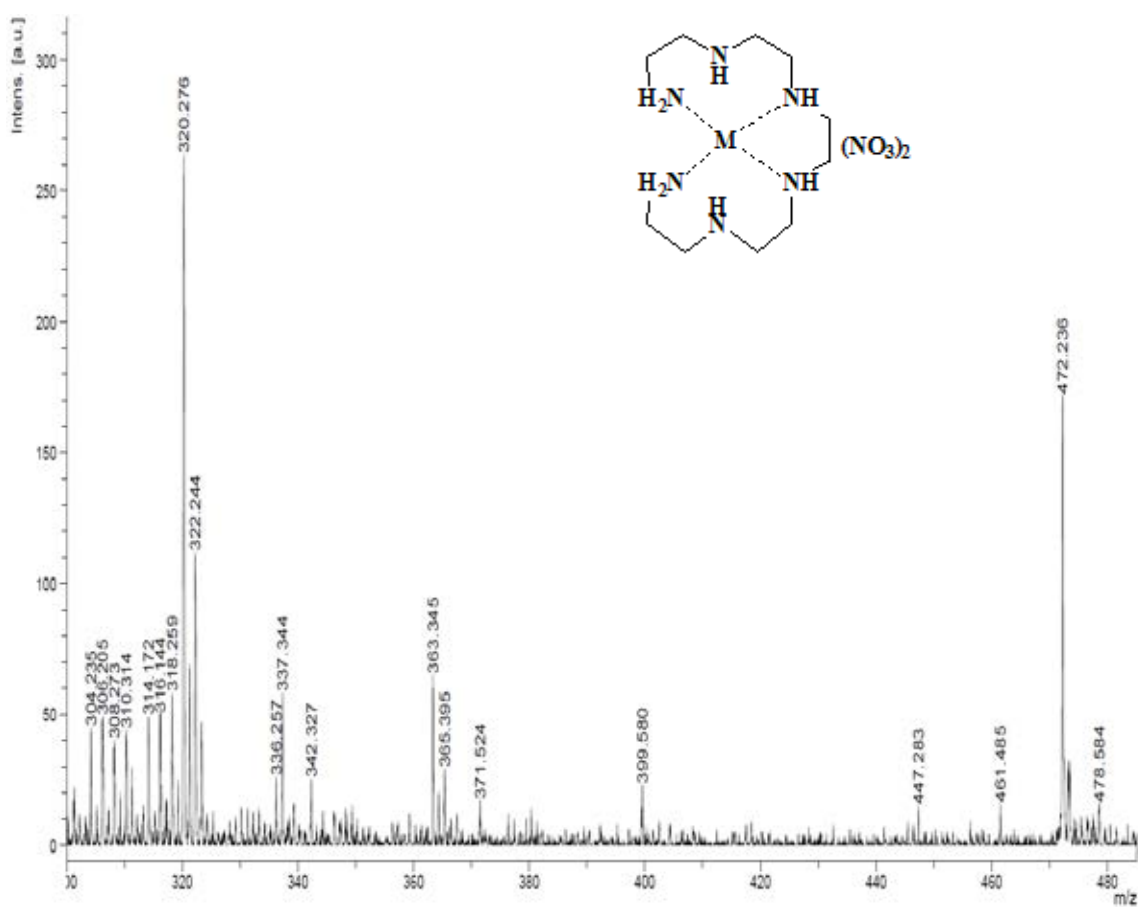


Figure 4.3 Mass spectrum of $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ complex.

4.4 Characterization of copper nitrate-tetraethylenepentamine complex

4.4.1 IR spectroscopy of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ complex

The IR spectra of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{NO}_3)_2$ and tetraethylenepentamine are shown in Figure 4.4. There are absorption bands at $3283\text{-}3207\text{ cm}^{-1}$ (N-H stretching), $2939\text{-}2939\text{ cm}^{-1}$ (C-H stretching), $1603\text{-}1586\text{ cm}^{-1}$ (N-H bending), The N-O stretching (nitrate group) in $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ at absorption band 1474 cm^{-1} (asymmetric N-O), and 1329 cm^{-1} (symmetric N-O) by order. The different that found in experimental is typically different from at absorption band at 1509 cm^{-1} (asymmetric N-O) and 1431 cm^{-1} (symmetric N-O). The absorption bands of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ is a peak of N-H stretching at 3207 cm^{-1} , respectively which shifted from typical absorption band of tetraethylenepentamine at 3283 cm^{-1} . Which can confirm that copper nitrate-tetraethylenepentamine caused a formation complex.

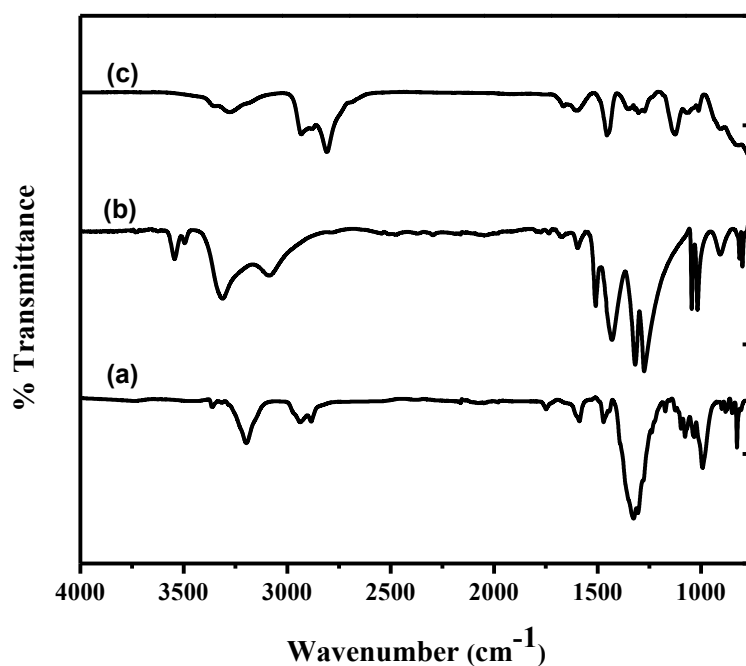


Figure 4.4 IR spectra of (a) $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$; (b) $\text{Cu}(\text{NO}_3)_2$; (c) tetraethylenepentamine

4.4.2 UV-visible spectroscopy of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ complex

UV-visible spectra of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{MeOH}}$ (synthesized in methanol) and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{W}}$ (synthesized in water) are shown in Figure 4.5. There is the consistency experiment between the maximum wavelength of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{W}}$ and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{MeOH}}$ complexes at 265 nm. Evidently, the maximum wavelength of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{MeOH}}$ and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{W}}$ complexes shifted from typical maximum wavelength of $\text{Cu}(\text{NO}_3)_2$ at 202 nm, which confirmed the complex formation.

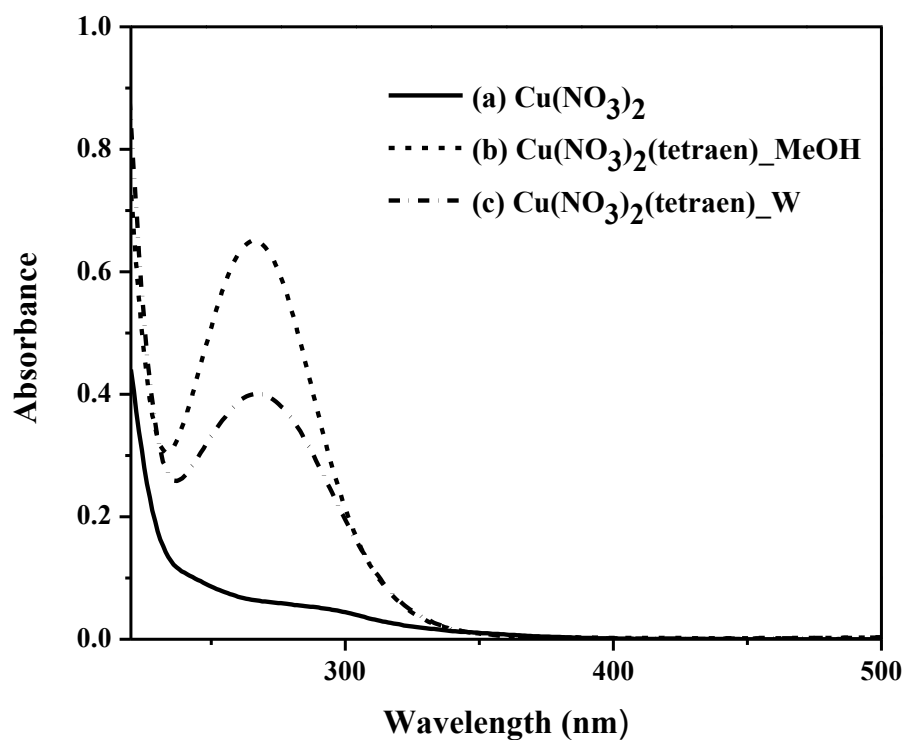


Figure 4.5 UV spectra of (a) $\text{Cu}(\text{NO}_3)_2$; (b) $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{MeOH}}$ and (c) $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{W}}$.

4.4.3 Determination of metal amount in $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ complex by flame atomic spectrometry (FAAS)

Table 4.3 shows the experimental and the calculated value of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$. This result indicates that there is the consistency between the experimental and the calculated value, which is agreeing that the formation of complex has been occurred.

Table 4.3 Analytical Characteristics of the FAAS method

Catalyst	Elements determined	Experimental (%)	Calculated (%)
$\text{Cu}(\text{NO}_3)_2(\text{tetraen})$	Cu	16.36	16.86

4.4.4 Elemental analysis of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ complex

Elemental analysis %C, %H and %N of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ are shown in Table 4.4. This result indicates that there is the consistency between the experimental value and the calculated value.

Table 4.4 Elemental analysis (%C, %H, and %N) of $\text{Cu}(\text{tetraen})$

Metal complex	Elements determined	Experimental (%)	Calculated (%)
$\text{Cu}(\text{NO}_3)_2(\text{tetraen})$	%C	25.88	25.50
	%H	6.22	6.15
	%N	24.27	26.02

4.4.5 Mass spectrometry of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ complex

The molecular ion peak of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ at m/z 433.565 corresponding to $[\text{}^{63}\text{Cu}(\text{NO}_3)_2(\text{pentaen})+\text{H}_2\text{O}+\text{K}^+]$; m/z 433.100 appears in the MALDI-TOF mass spectrum in Figure 4.6.

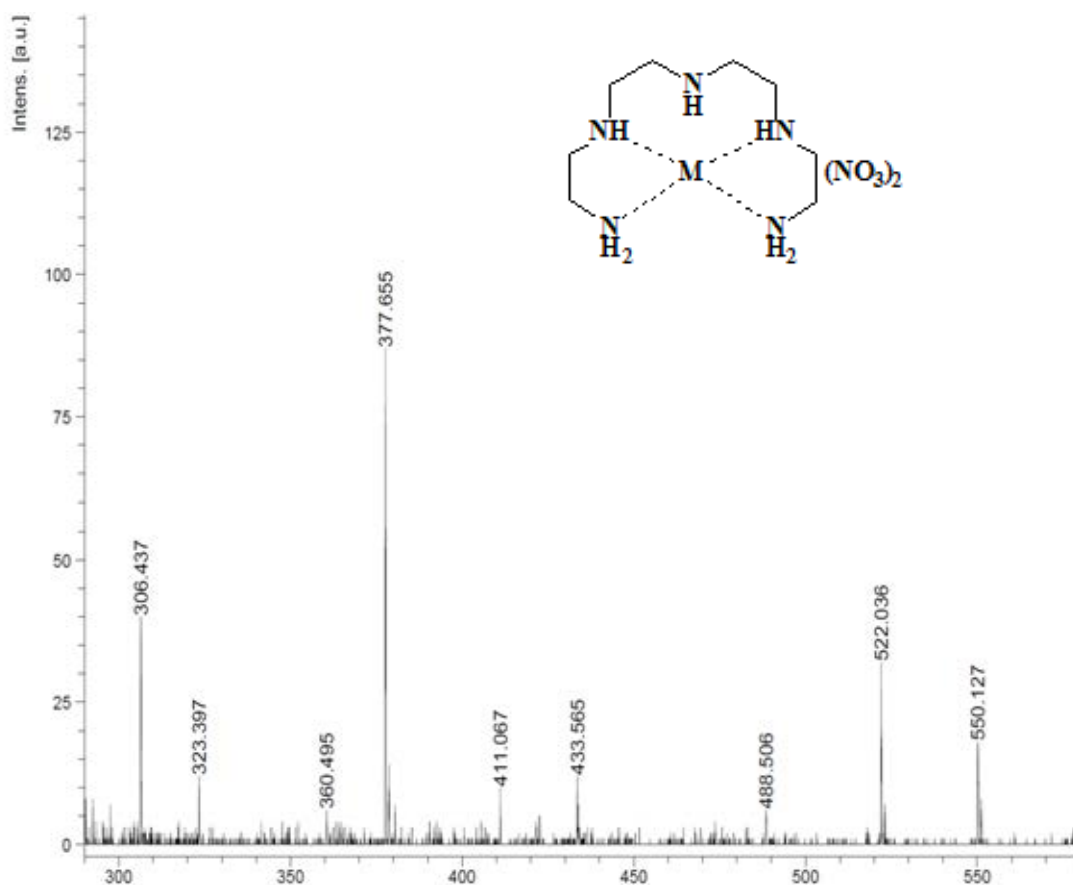


Figure 4.6 Mass spectrum of $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ complex.

4.5 Synthesis of copper chloride-pentaethylenhexamine complex

4.5.1 UV-visible spectroscopy of $\text{Cu}(\text{Cl})_2(\text{pentaen})$ complex

UV-visible spectra of $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{MeOH}}$ (synthesized in methanol) and $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{W}}$ (synthesized in water) are shown in Figure 4.7. There is the consistency experiment between the maximum wavelength of $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{W}}$ and $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{MeOH}}$ complexes at 268 nm. Evidently, the maximum wavelength of $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{MeOH}}$ and $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{W}}$ complexes shifted from typical maximum wavelength of $\text{Cu}(\text{Cl})_2$ at 263 nm, which confirmed the complex formation.

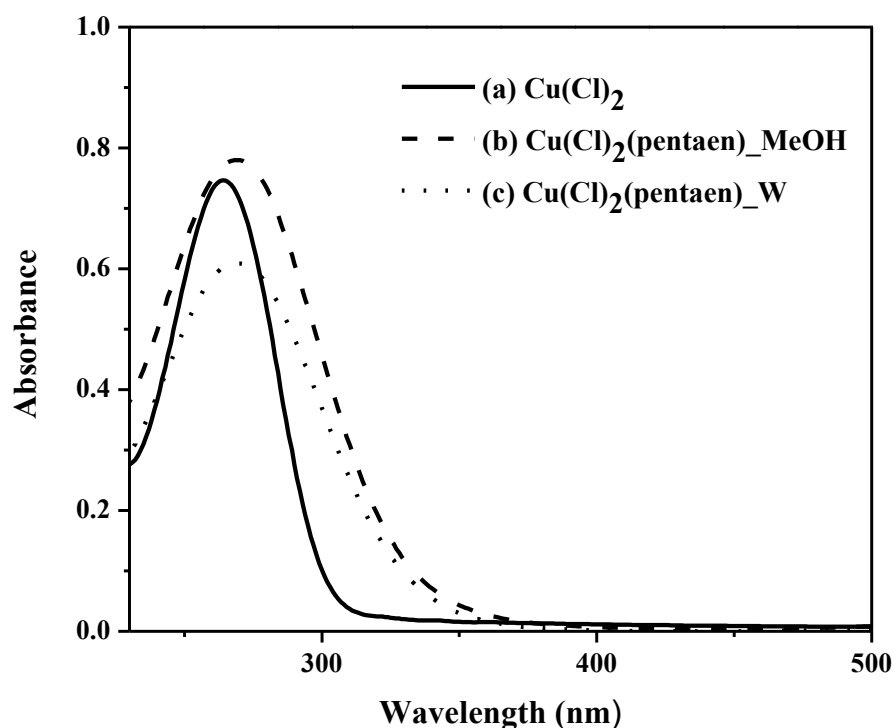


Figure 4.7 UV spectra of (a) $\text{Cu}(\text{Cl})_2$; (b) $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{MeOH}}$ and (c) $\text{Cu}(\text{Cl})_2(\text{pentaen})_{\text{W}}$.

4.5.2 Mass spectrometry of $\text{Cu}(\text{Cl})_2(\text{pentaen})$ complex

The molecular ion peak of $\text{Cu}(\text{Cl})_2(\text{pentaen})$ at m/z 401.953 corresponding to $[\text{}^{63}\text{Cu}(\text{Cl})_2(\text{pentaen})+\text{H}_2\text{O}^+]$; m/z 401.956 appears in the MALDI-TOF mass spectrum (Figure 4.8).

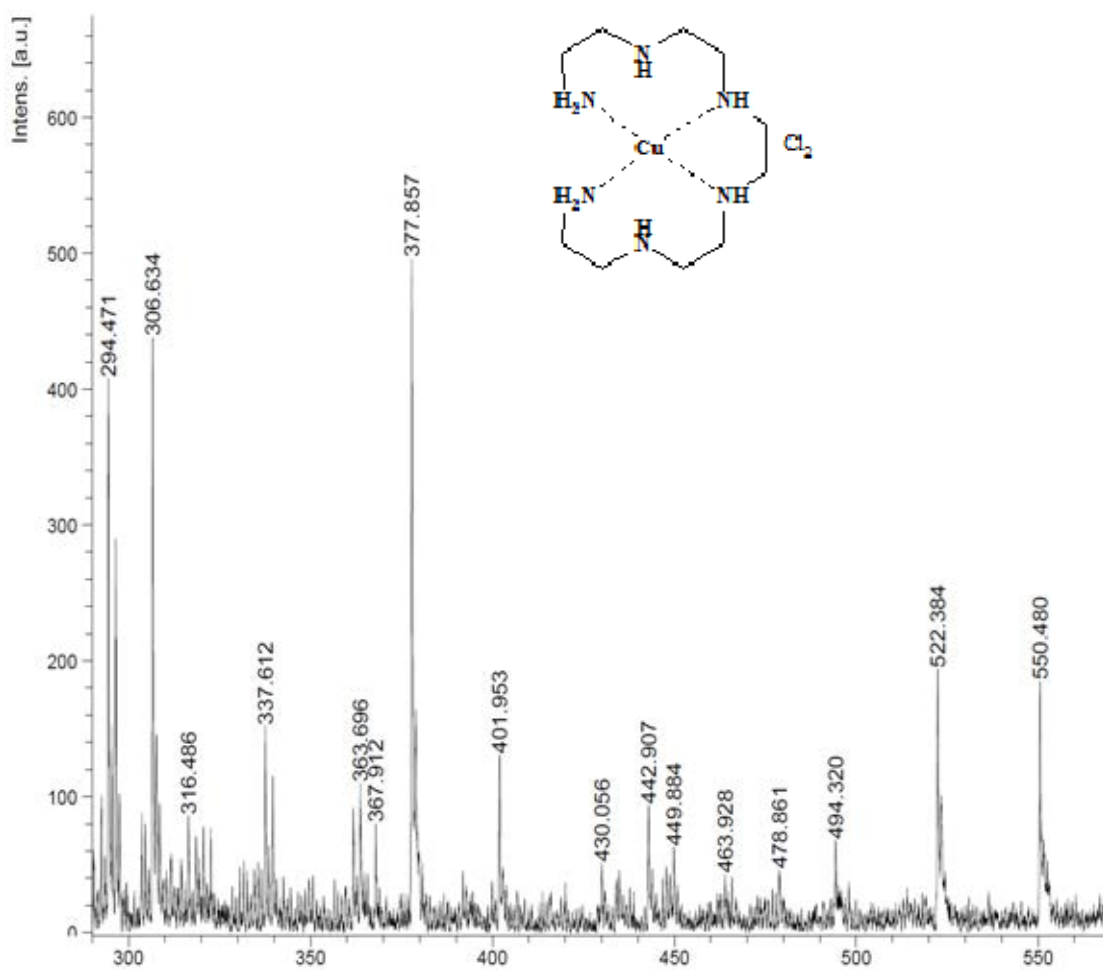


Figure 4.8 Mass spectrum of $\text{Cu}(\text{Cl})_2(\text{pentaen})$ complex.

4.6 Synthesis of copper chloride-tetraethylenepentamine complex

4.6.1 UV-visible spectroscopy of $\text{Cu}(\text{Cl})_2(\text{tetraen})$ complex

UV-visible spectra of $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{MeOH}}$ (synthesized in methanol) and $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{W}}$ (synthesized in water) are shown in Figure 4.9. There is the consistency experiment between the maximum wavelength of $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{W}}$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{MeOH}}$ complexes at 267 nm. Evidently, the maximum wavelength of $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{MeOH}}$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{W}}$ complexes shifted from typical maximum wavelength of $\text{Cu}(\text{Cl})_2$ at 263 nm, which confirmed the complex formation.

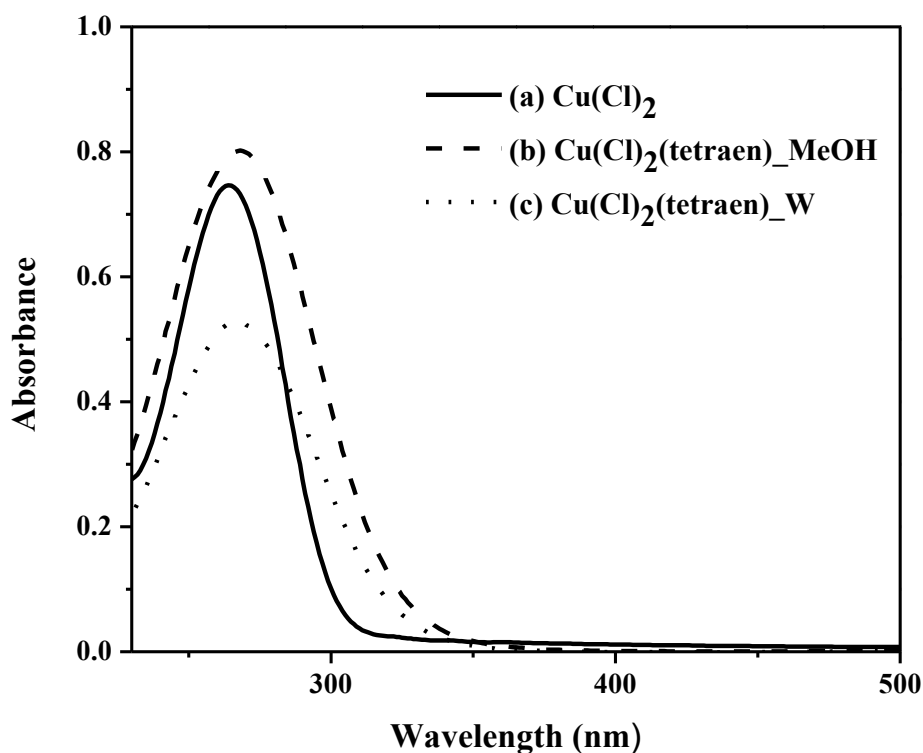


Figure 4.9 UV spectra of (a) $\text{Cu}(\text{Cl})_2$; (b) $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{MeOH}}$ and (c) $\text{Cu}(\text{Cl})_2(\text{tetraen})_{\text{W}}$

4.6.2 Mass spectrometry of $\text{Cu}(\text{Cl})_2(\text{tetraen})$ complex

The molecular ion peak of $\text{Cu}(\text{Cl})_2(\text{tetraen})$ at m/z 363.486 corresponding to $[\text{}^{63}\text{Cu}(\text{Cl})_2(\text{tetraen})+\text{K}^+]$; m/z 363.060 appears in the MALDI-TOF mass spectrum (Figure 4.10).

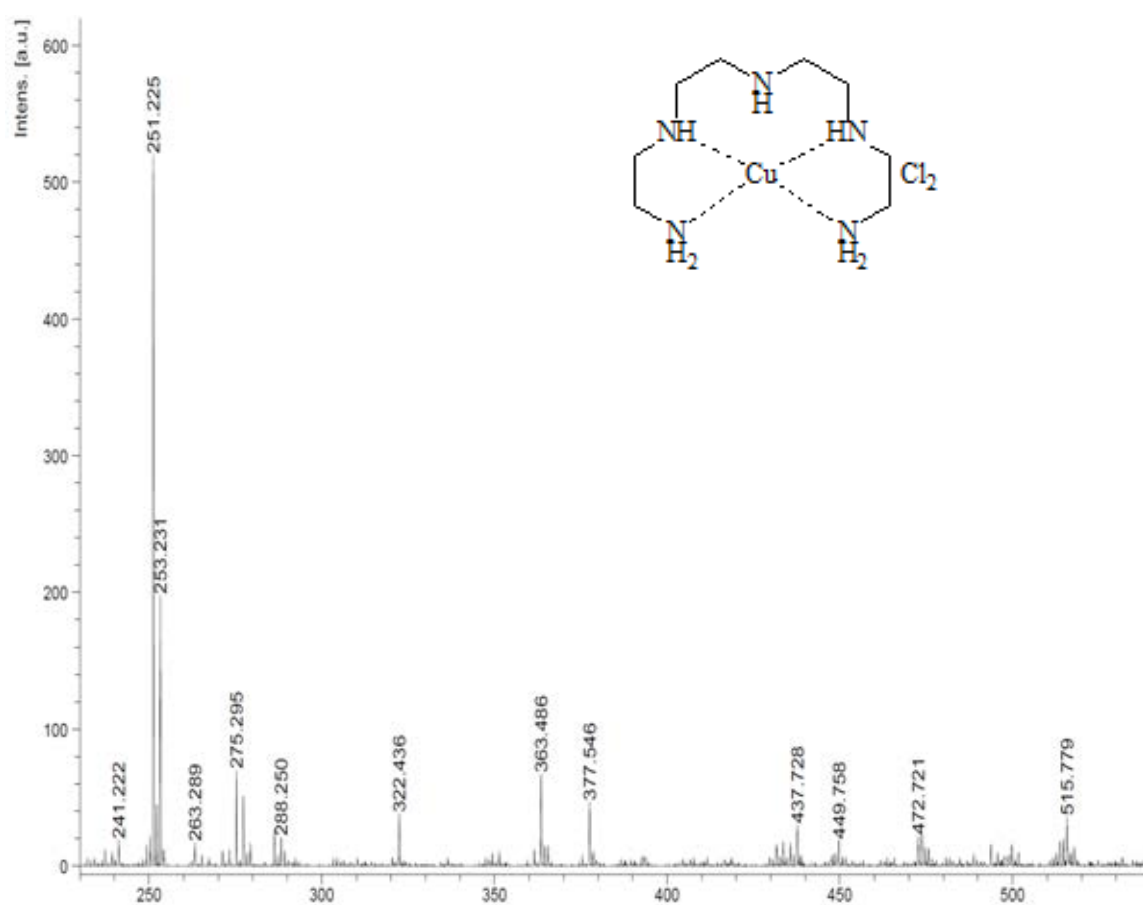


Figure 4.10 Mass spectrum of $\text{Cu}(\text{Cl})_2(\text{tetraen})$ complex

4.7 Preparation of Rigid Polyurethane (RPUR) Foams

4.7.1 RPUR Foams prepared by using copper-amine complexes as catalysts

Copper-amine complexes, namely $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$, were used as catalysts in the preparation of RPUR foams. At the first step, RPUR foams were prepared by mixing polyol, catalysts (DMCHA or copper-amine complexes), blowing agent (water), and surfactant and homogenizing them in a 700 mL paper cup. Then, isocyanate (polymeric MDI) was added to the mixture of the first step (mixed polyol). The mixture was stirred for 20 seconds with a mechanical stirrer to make it homogeneous. The reaction time of foaming reaction, namely cream time, gel time, tack free time, and rise time were recorded. Then, the foams were kept for 48 hours to complete the polymerization reaction. After that, the foams were cut to examine their density and mechanical properties. This research investigated RPUR foam preparations from different types of catalysts, amount in blowing agents and NCO indexes. Table 4.5 shows the formula used in the preparation of the different NCO indexes in the preparation of RPUR foams.

Table 4.5 RPUR foam formulation

Formulations (pbw*)	NCO index		
	100	130	150
Polyether polyol (Daltolac [®] R 180)	100	100	100
Catalyst			
- Copper-amine complexes or DMCHA (commercial catalyst)	1.0	1.0	1.0
Blowing agent (water)	3.0	3.0	3.0
PMDI (Suprasec [®] 5005)	152	197	227

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



Figure 4.11 RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2$ (tetraen) at different NCO indexes (a) 100; (b) 130 and (c) 150

Preparation of RPUR foams by using $\text{Cu}(\text{NO}_3)_2$ (pentaen) and $\text{Cu}(\text{NO}_3)_2$ (tetraen) as catalysts at different NCO indexes showed that the foams prepared at the NCO indexes of 100 to 130 had good quality. However, the foams prepared at the higher NCO indexes of 150 were fragile and not suitable for applications.

4.7.1.1 Preparation of RPUR foams using a plastic mold

Instead of using a paper cup as a mold, preparation of RPUR foams in a plastic mold with the dimension of $10 \times 10 \times 10$ cm was done at the NCO index of 100. In the first step, the reactants were mixed in a paper cup and then poured into the plastic mold. The appearance and density of RPUR foams prepared in paper cup and plastic mold (Figure 4.12) were similar.



Figure 4.12 RPUR foams catalyzed by (a) $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ and (b) $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ prepared in a plastic mold

4.7.2 Reaction times and rise profiles

In the preparation of rigid polyurethane foams, reaction time during the foam formation studied were cream time (the start of bubble rise and hence color of the mixture became cream-like from opaque.), gel time (the time of foam mixture begin to gel or mixture stopped flowing), rise time (the time of the foam stop rising and no CO_2 occurred.) and tack free time (the time of the foam could not tack with other materials).

4.7.2.1 Effect of catalyst content on reaction time of RPUR foams

Tables 4.6 and 4.7 show reaction times of RPUR foams catalyzed by copper-amine complexes. For all catalysts, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$, the results showed that upon increasing

amount of the catalyst, gel time and tack free time decreased while cream time slightly decreased. These data indicated that $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ could catalyzed gelling reaction better than blowing reaction.

Table 4.6 Reaction times of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$

Catalyst type at NCO index 100						
Catalyst Content (pbw)	$\text{Cu}(\text{NO}_3)_2(\text{pentaen})$			$\text{Cu}(\text{NO}_3)_2(\text{tetraen})$		
	Cream Time (min)	Gel Time (min)	Tack free Time (min)	Cream Time (min)	Gel Time (min)	Tack free Time (min)
1.0	0:35	3:37	16:38	0:31	3:21	15:12
2.0	0:33	3:27	15:42	0:30	3:11	14:17
2.5	0:31	3:22	15:19	0:30	3:05	14:10
3.0	0:29	2:51	14:41	0:26	2:32	12:32

Table 4.7 Reaction times of RPUR foams catalyzed by $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$

Catalyst type at NCO index 100						
Catalyst Content (pbw)	$\text{Cu}(\text{Cl})_2(\text{pentaen})$			$\text{Cu}(\text{Cl})_2(\text{tetraen})$		
	Cream Time (min)	Gel Time (min)	Tack free Time (min)	Cream Time (min)	Gel Time (min)	Tack free Time (min)
1.0	0:40	4:03	18:48	0:37	4:55	17:59
2.0	0:34	3:27	18:02	0:35	3:41	17:14
2.5	0:33	3:22	17:35	0:33	3:38	16:58
3.0	0:31	3:21	16:44	0:30	2:59	15:27

Table 4.8 showed reaction times of RPUR foams prepared with commercial catalyst (DMCHA), copper-amine complexes which was synthesized in both water and methanol. In preparation of RPUR foams, it was found that $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_W$ and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_W$ (synthesized in water) gave similar reaction times and foam density as $\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{MeOH}}$ and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{MeOH}}$ (synthesized in methanol). RPUR foams prepared by copper-amine complexes foam had less volume and had higher density than those prepared by DMCHA. This result indicated that copper-amine complexes catalyzed gelling reaction, which was the reaction between isocyanate and alcohol, to form urethane groups. Synthesis of copper-amine complexes in water was a convenient method because RPUR foams formulation used water as a blowing agent. The preparation of copper-amine complexes synthesized in water spent less time than synthesized in methanol because methanol had to be removed from copper-amine complexes before used.

Table 4.8 Reaction times of RPUR foams prepared at NCO indexes of 100 catalyzed by DMCHA and copper-amine complexes

Catalysts types	Cream time (min)	Gel Time (min)	Rise Time (min)	Tack free time (min)	Volume (V)	Density (kg/m^3)
DMCHA (ref.)	0:10	0:13	0:58	1:17	7.5/8V	34.1
$\text{Cu}(\text{NO}_3)_2(\text{pentaen})_{\text{MeOH}}$	0:29	3:15	13:07	15:53	6/8V	47.1
$\text{Cu}(\text{NO}_3)_2(\text{tetraen})_{\text{MeOH}}$	0:30	3:03	11:45	13:40	6/8V	45.8
$\text{Cu}(\text{NO}_3)_2(\text{pentaen})_W$	0:29	2:51	13:07	14:41	6.5/8V	46.0
$\text{Cu}(\text{NO}_3)_2(\text{tetraen})_W$	0:26	2:32	10:15	12:32	6.5/8V	45.1
$\text{CuCl}_2(\text{pentaen})_W$	0:31	3:21	13:42	16:44	6/8V	47.2
$\text{CuCl}_2(\text{tetraen})_W$	0:30	2:59	11:39	15:27	6/8V	46.4

Reaction times of RPUR foams prepared with the use of commercial catalysts (DMCHA) and copper-amine complexes synthesized in water and methanol are shown in Figure 4.13. DMCHA had a better catalytic activity than all synthesized copper-amine complexes. Although copper-amine complexes had a lower catalytic activity than DMCHA, but copper-amine complexes gave RPUR foams with good appearance. In comparison to DMCHA, copper-amine complex catalysts do not have strong smell and had longer gel time which is appropriate for RPUR foam preparation in large mold, which requires longer time to make the starting materials to cover the mold.

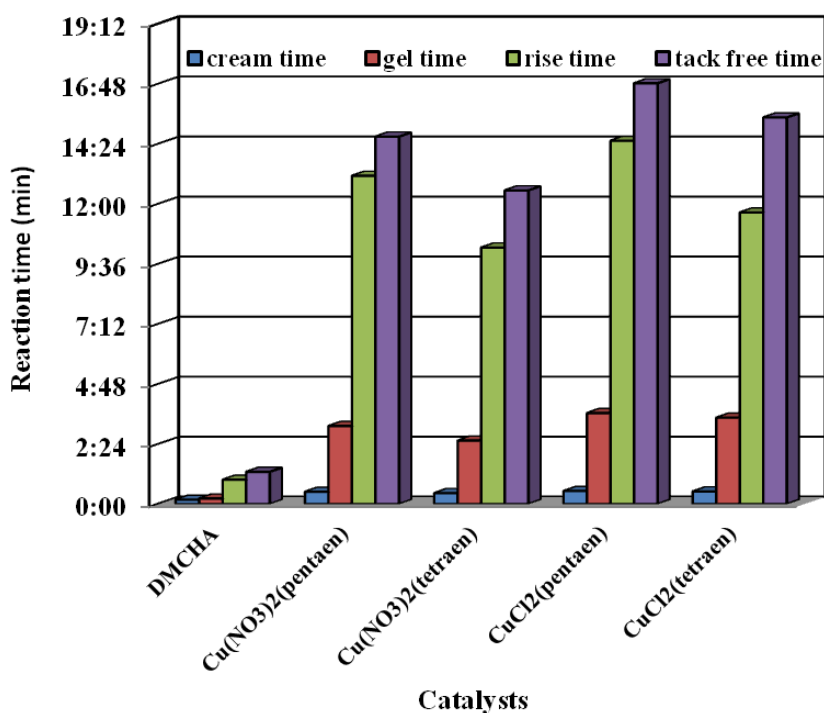


Figure 4.13 Reaction times of RPUR foams catalyzed by DMCHA and copper-amine complexes at the NCO index of 100

Rise profiles of RPUR foams catalyzed by Cu(NO₃)₂(pentaen), Cu(NO₃)₂(tetraen), Cu(Cl)₂(pentaen) and Cu(Cl)₂(tetraen) showed similar trend and foam rising was slower than that catalyzed by DMCHA (Figures 4.14 and 4.15). DMCHA catalyst is a tertiary amine-based catalyst and has strong catalytic activity

towards both blowing and gelling reactions. DMCHA catalyst showed shorter initial time than all copper-amine complexes and exhibited a fast rise curve in the latter stage.

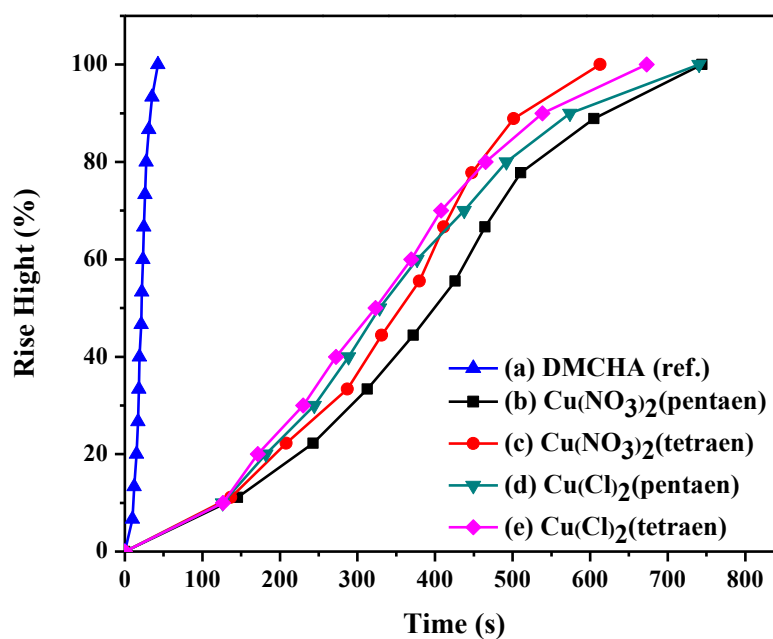


Figure 4.14 Rise profiles of RPUR foams catalyzed by different metal complexes
(a) DMCHA (ref.); (b) Cu(NO₃)₂(pentaen); (c) Cu(NO₃)₂ (tetraen);
(d) Cu(Cl)₂(pentaen); (e) Cu(Cl)₂(tetraen)

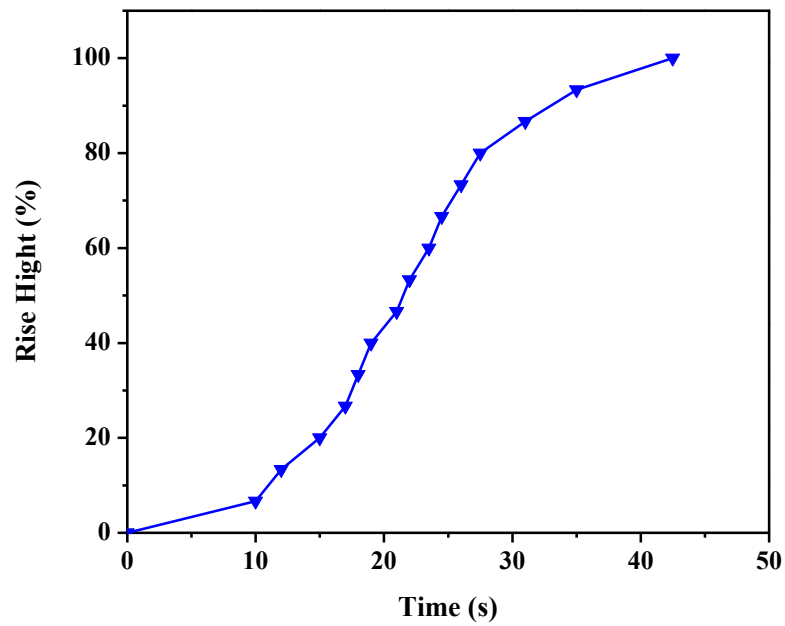


Figure 4.15 Rise profile of RPUR foam catalyzed by DMCHA (ref.)

4.7.3 Apparent density

RPUR foams were kept in a room temperature for 48 hours, then cut into 30 x 30 x 30 mm cubic samples (Figure 4.16) and their density were measured.

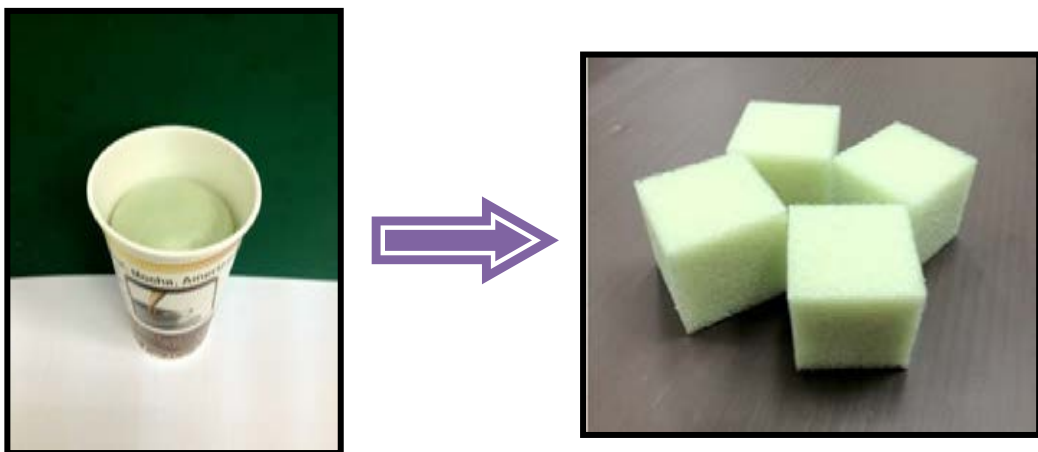


Figure 4.16 RPUR samples for foam density measurements

4.7.3.1 Effect of NCO indexes on foams density

The density of RPUR foams catalyzed by DMCHA, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ was obtained at different isocyanate (NCO) indexes of 100, 130 and 150. It was found that apparent density of RPUR foams increased when increased NCO indexes as shown in Figure 4.17. This was because at the NCO index 130 and 150, there was excess NCO which underwent the reaction to give crosslinked structure in RPUR foam. RPUR foams which prepared at the NCO index of 100 and 130 had good appearance foam. RPUR foams prepared by NCO indexes greater than 150 resulted in fragile materials.

The comparisons of the density of RPUR foams prepared from copper-amine complexes and DMCHA as catalysts, the foam prepared from copper complexes at NCO index of 100 had a higher density value than that prepared from DMCHA. This indicated that copper complexes were not good blowing catalysts which resulted in high foam density. RPUR foams prepared from copper complexes at the NCO indexes 100 to 130 had a density in range 45.1-49.5 kg/m^3 , which was an appropriate density for application.

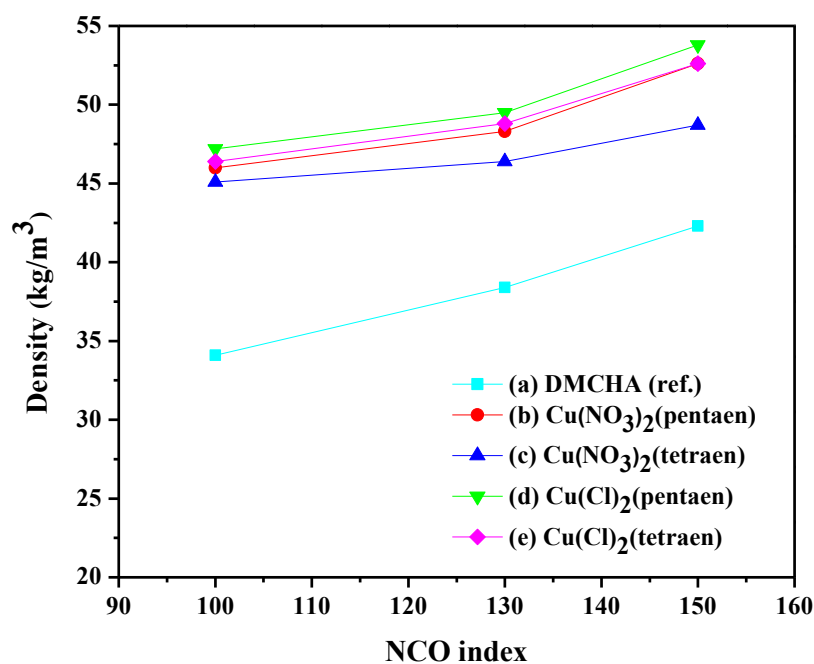


Figure 4.17 Apparent densities of RPUR foams catalyzed by (a) DMCHA (ref.); (b) Cu(NO₃)₂(pentaen); (c) Cu(NO₃)₂(pentaen); (d) Cu(Cl)₂(tetraen); (e) Cu(Cl)₂(tetraen)

4.7.3.2 Effect of blowing agent quantity on foam density

The effect of the blowing agent content on RPUR foams density at the NCO index of 100 is shown in Figure 4.18. RPUR foam density decreased when the blowing agent (water) amount was increased. Water reacted with isocyanate (NCO group) and generated CO₂ which was an exothermic reaction. The result indicated that the RPUR foam prepared at catalyst quantity of 2.0 part by weight (pbw) showed the lowest blowing reaction when compared with prepared from 2.5, 3.0 and 4.0 pbw of blowing agent (Figure 4.19) and the foams were prepared at the NCO index of 100.

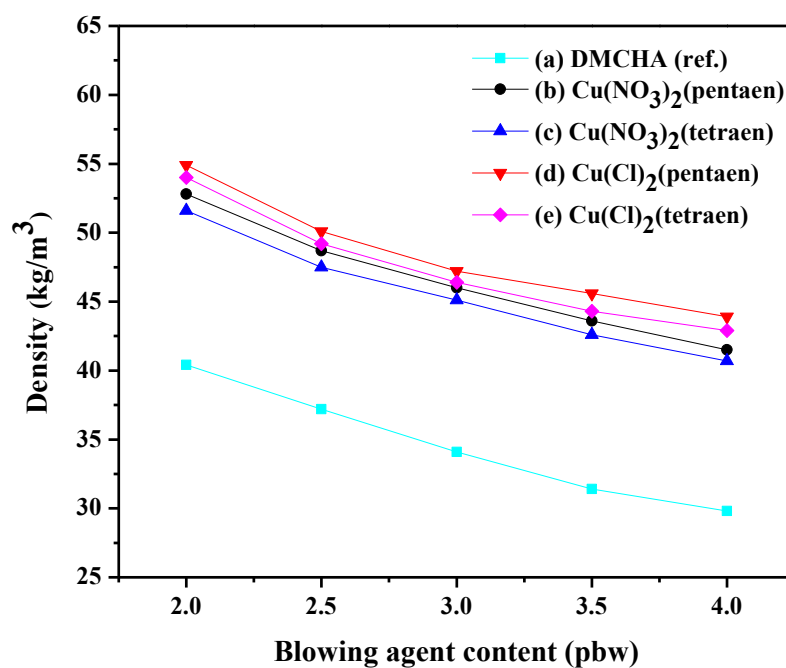


Figure 4.18 Effect of blowing agent quantities on RPUR foam density when catalyzed by (a) DMCHA (ref.); (b) Cu(NO₃)₂(pentaen); (c) Cu(NO₃)₂(tetraen); (d) Cu(Cl)₂(pentaen); (e) Cu(Cl)₂(tetraen) and the foams were prepared at the NCO index of 100

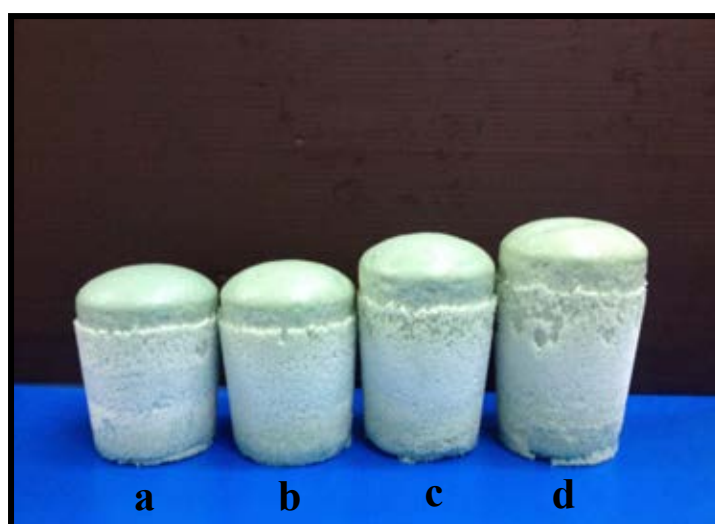


Figure 4.19 Appearance of RPUR foam prepared at the NCO index of 100 and catalyzed by Cu(NO₃)₂(tetraen) when the amount of blowing agent was (a) 2 pbw; (b) 2.5 pbw; (c) 3 pbw; (d) 4 pbw

4.7.3.3 Effect of catalyst quantity on foam density

Figure 4.20 shows the effect of catalyst quantity on RPUR foam density when the foams were catalyzed by DMCHA, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$. It was found that the RPUR foam density decreased when the catalyst amount in the foam formulation was increased. This was because increasing amount of catalyst also increased blowing reaction. Although high catalyst quantity at 4.0 pbw caused a better blowing reaction, but RPUR foams were soft materials having cell size and were not suitable for application.

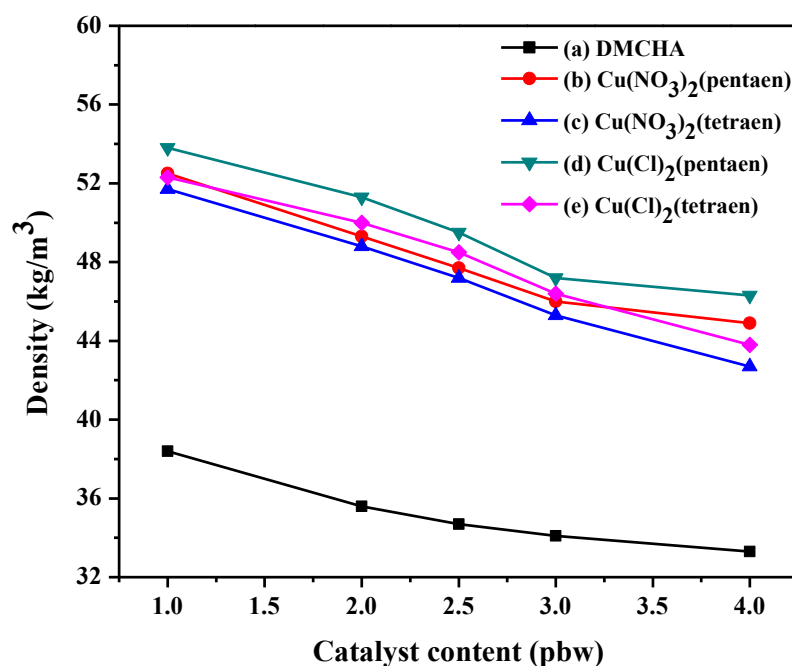


Figure 4.20 Effect of catalyst content on RPUR foam density when the foams were prepared at the NCO index of 100 and catalyzed by (a) DMCHA (ref.); (b) $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$; (c) $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$; (d) $\text{Cu}(\text{Cl})_2(\text{pentaen})$; (e) $\text{Cu}(\text{Cl})_2(\text{tetraen})$

4.7.4 Foaming temperature

The effect of NCO index on foaming temperature of RPUR foams is shown in Table 4.9. Foaming temperature increased when increasing NCO indexes from 100 to 150 since the reactions between isocyanate-polyol and isocyanate-water were exothermic reactions. The maximum core temperature of RPUR foams prepared from DMCHA, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{tetraen})$ was in the range 105-133°C

Table 4.9 Maximum core temperature of RPUR foams catalyzed by DMCHA and copper-amine complexes at different NCO indexes

Catalysts	NCO indexes	Maximum core temperature (°C)	Starting times (min) at T_{max}
DMCHA	100	124	315 (5:15)
	130	129	393 (6:33)
	150	133	411 (6:51)
$\text{Cu}(\text{NO}_3)_2(\text{pentaen})$	100	114	765 (12:45)
	130	119	858 (14:18)
	150	123	940 (15:40)
$\text{Cu}(\text{NO}_3)_2(\text{tetraen})$	100	117	705 (11:45)
	130	122	725 (12:05)
	150	126	786 (13:06)
$\text{Cu}(\text{Cl})_2(\text{pentaen})$	100	105	809 (13:29)
	130	107	860 (14:20)
	150	108	889 (14:49)
$\text{Cu}(\text{Cl})_2(\text{tetraen})$	100	107	735 (12:25)
	130	112	795 (13:15)
	150	113	815 (13:35)

Temperature profiles of RPUR foams prepared at the NCO index of 100 are illustrated in Figures 4.21 and 4.22. The temperature profiles of RPUR foams prepared from copper-amine complexes and DMCHA were similar. DMCHA had a better polymerization reaction profile than copper-amine complexes since the heat was released at a shorter time.

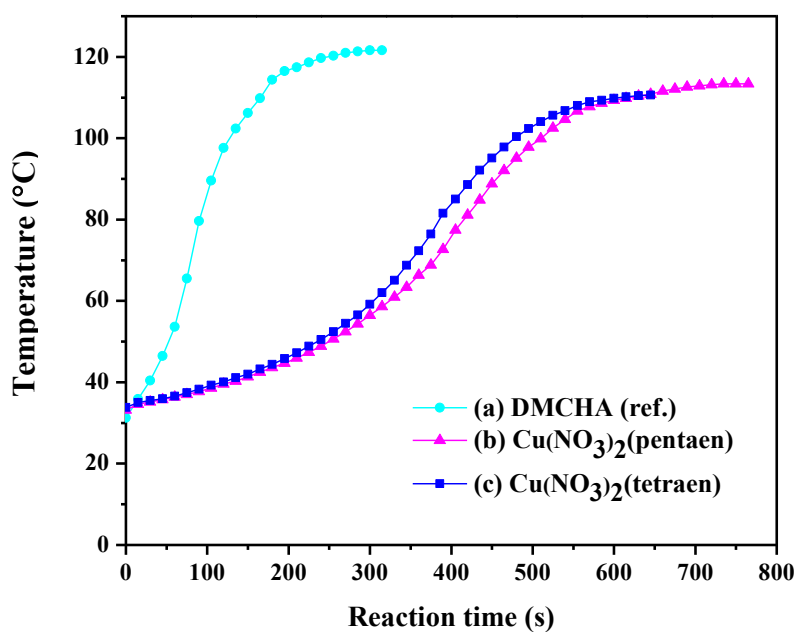


Figure 4.21 Temperature profiles of RPUR foams catalyzed by (a) DMCHA (ref.); (b) Cu(NO₃)₂(pentaen) and (c) Cu(NO₃)₂(tetraen)

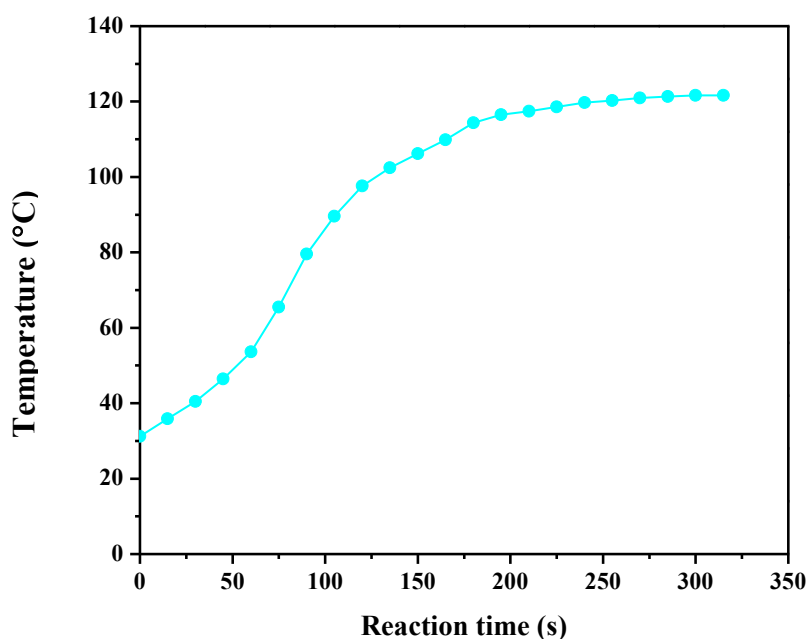


Figure 4.22 Temperature profile of RPUR foam catalyzed by DMCHA (ref.)

4.7.5 Characterization of RPUR foams

Figure 4.23 shows IR spectra of starting materials, polyether polyol, polymeric MDI (PMDI) and catalysts, which were used in preparation of RPUR foams catalyzed by DMCHA, $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$. IR spectra of polyether polyol showed broad peak of hydroxyl groups (OH groups) at 3425 cm^{-1} , and PMDI peak at 2247 cm^{-1} . Therefore, when the reaction between isocyanate and polyether polyol occurred during preparation of RPUR foams, the peaks of isocyanate groups (NCO groups) at 2247 cm^{-1} disappeared. The results indicated that the foaming reaction catalyzed by DMCHA and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ was completed as shown in Figures 4.19 (c) and (d), respectively. All RPUR foams showed absorption as follows: NH stretching of urethane and urea at 3338 cm^{-1} , NH bending of urethane and urea at 1511 cm^{-1} , C=O stretching of urethane and urea at 1709 cm^{-1} and a peak of C-O of urethane at 1218 cm^{-1} .

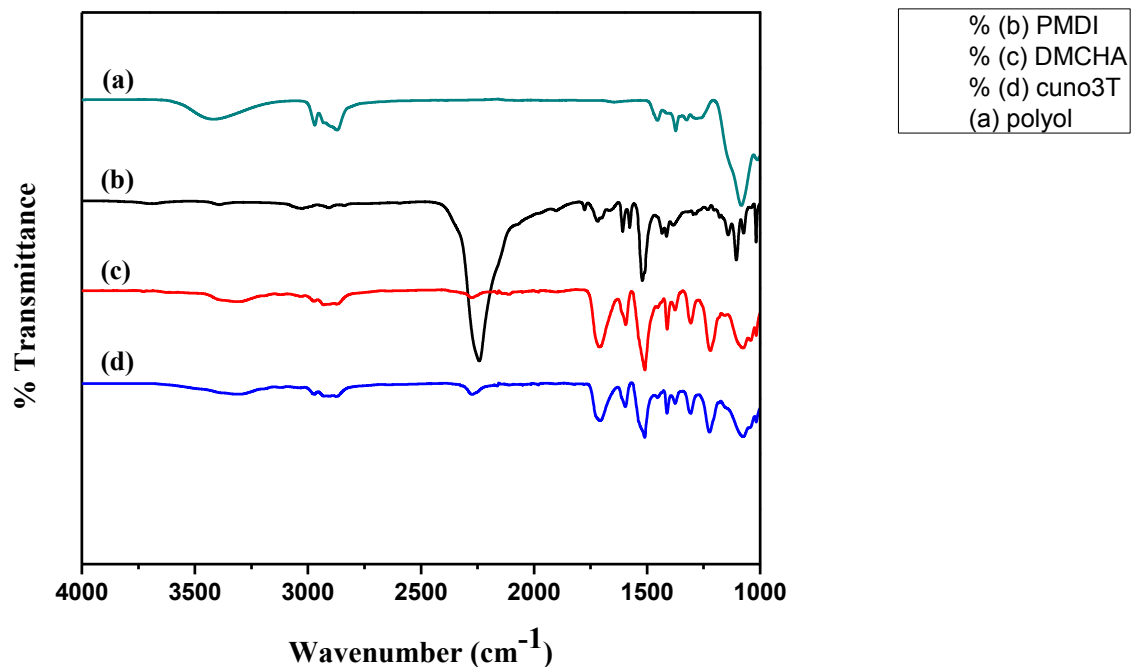


Figure 4.23 IR spectra of (a) polyether polyol; (b) PMDI; (c) DMCHA (ref.); (d)RPUR foam catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$

4.7.6 NCO conversion of RPUR foams

FTIR spectra of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ at different NCO indexes in range 100 to 150 showed absorption band NCO group at 2270-2278 cm^{-1} . When increased amount of NCO index in foam formulation from 100, 130 and 150, it was found the intensity of NCO absorption band was also increased respectively since NCO indexes at 130 and 150 gave incomplete an incomplete reaction, isocyanate was ran off. The intensity of absorption band can be observed from IR spectra of RPUR foam in Figure 4.24.

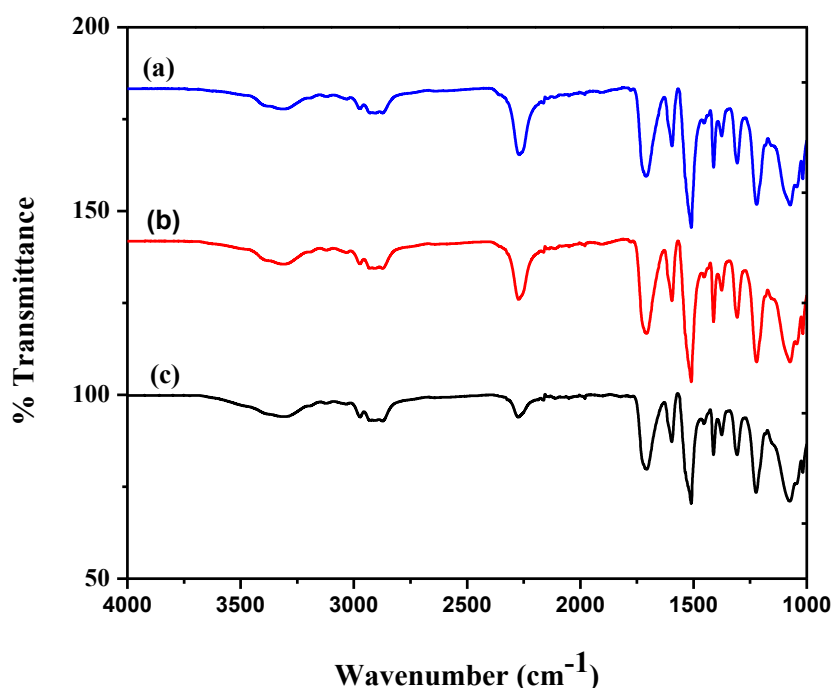


Figure 4.24 IR spectra of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ at different NCO indexes (a) 150; (b) 130; (c) 100

The NCO conversion can be observed from FTIR spectra. The NCO conversion is defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0 as shown in following equation:

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

where;

NCO^f is the area of isocyanate absorbance peak area at time t (spectra (c) and (d) in Figure 4.22)

NCO^i is the area of isocyanate absorbance peak area at initial time 0 (spectra (b) in Figure 4.22)

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 at 1415 and urethane at 1220 cm^{-1} shown in Table 4.10

Table 4.10 Wavenumber of the functional groups used in calculation

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

Figures 4.25 and 4.26 shows NCO conversion of RPUR foams catalyzed by DMCHA, $\text{Cu}(\text{NO}_3)_2$ (pentaen), $\text{Cu}(\text{NO}_3)_2$ (tetraen), $\text{Cu}(\text{Cl})_2$ (pentaen), $\text{Cu}(\text{Cl})_2$ (tetraen) at NCO indexes 100, 130 and 150. From these experiments, when the amount of NCO index was increased, NCO conversion would be decreased and NCO conversion was in the range 96.1-99.1%. In the other hand, if there was excess NCO amount, trimerization of isocyanate group occurred and resulted in isocyanurate group.

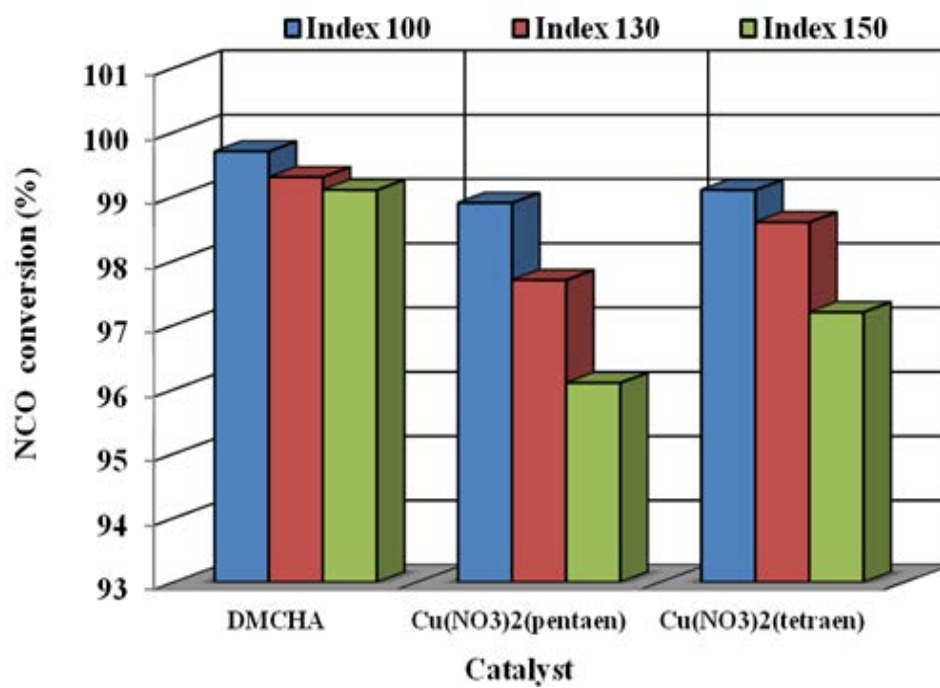


Figure 4.25 NCO conversions of RPUR foams catalyzed by DMCHA, Cu(NO₃)₂(pentaen) and Cu(NO₃)₂(tetraen)

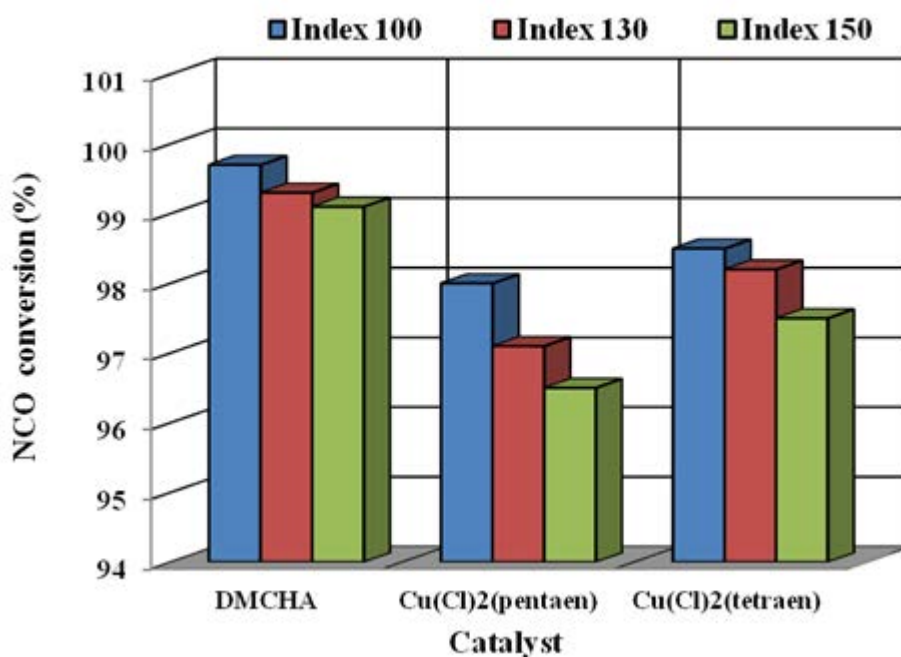


Figure 4.26 NCO conversions of RPUR foams catalyzed by DMCHA, Cu(Cl)₂(pentaen) and Cu(Cl)₂(tetraen)

The ratio between polyisocyanurate : polyurethane (PIR: PUR) of RPUR foams which prepared from different catalysts at NCO indexes of 100, 130 and 150 as shown in Figure 4.27. The result from an experiment showed that the value of PIR/PUR of RPUR foam was increasing when increased amount of NCO indexes. PIR occurred from trimerization reaction and gave isocyanurate instead of urethane. That brings to the conclusion that copper-amine complexes are good catalysts for polyurethane formation but unsuitable for trimerization reaction. Table 4.11 shows NCO conversion and PIR/PUR ratio of RPUR foams catalyzed by DMCHA and copper-amine complexes.

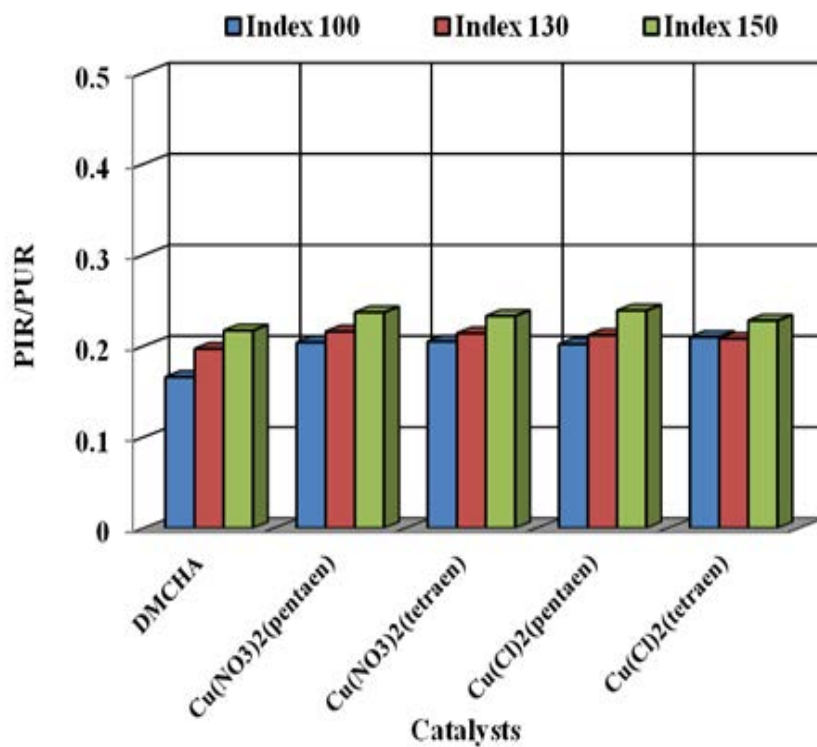


Figure 4.27 PIR/PUR ratios of RPUR foams catalyzed by different metal complexes

Table 4.11 NCO conversions and PIR/PUR ratios of RPUR foams prepared by DMCHA and copper-amine complexes catalyzed at different NCO indexes

Catalysts	NCO indexes	NCO conversion (%)	PIR/PUR
DMCHA (ref.)	100	99.7	0.166
	130	99.3	0.197
	150	99.1	0.217
Cu(NO ₃) ₂ (pentaen)	100	98.9	0.202
	130	97.7	0.217
	150	96.1	0.225
Cu(NO ₃) ₂ (tetraen)	100	99.1	0.189
	130	98.6	0.219
	150	97.2	0.234
Cu(Cl) ₂ (pentaen)	100	98.0	0.202
	130	97.1	0.212
	150	96.5	0.239
Cu(Cl) ₂ (tetraen)	100	98.5	0.211
	130	98.2	0.214
	150	97.5	0.228

4.8 Compressive properties of RPUR foams

Compressive strength of RPUR foams is an important parameter in the foam application. The compressive strength of RPUR foams is the value of maximum compressive force is reported at 10% strain. If the maximum compressive force reported at 10% strain, the compression strength reported as compressive strength. The Parallel/Perpendicular compression stress-strain curves of RPUR foams catalyzed by DMCHA and copper-amine complexes are illustrated in Figures 4.28 and 4.29. The ratio between stress and strain is called compressive modulus of foam.

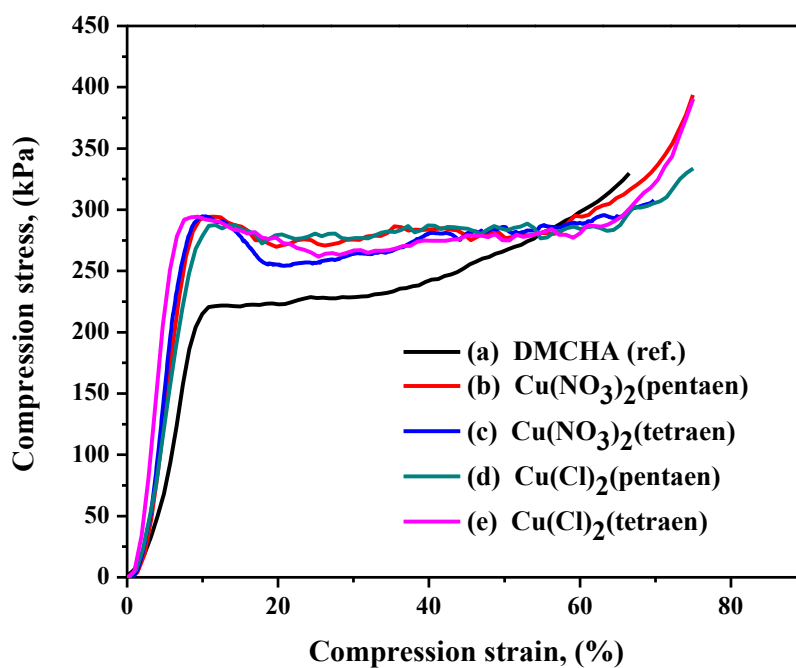


Figure 4.28 Parallel compression stress-strain curve of RPUR foams prepared at NCO index of 100 and catalyzed by different catalysts (a) DMCHA (ref.); (b) Cu(NO₃)₂(pentaen); (c) Cu(NO₃)₂(tetraen); (d) Cu(Cl)₂(pentaen); (e) Cu(Cl)₂(tetraen)

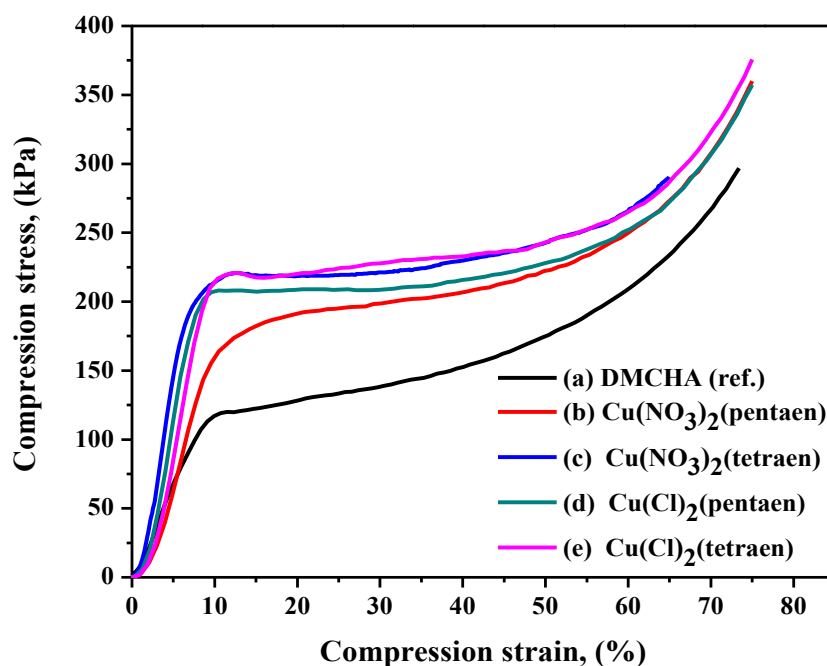


Figure 4.29 Perpendicular compression stress-strain curve of RPUR foams prepared at NCO index of 100 and catalyzed by different catalysts
 (a) DMCHA (ref.); (b) $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$; (c) $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$;
 (d) $\text{Cu}(\text{Cl})_2(\text{pentaen})$; (e) $\text{Cu}(\text{Cl})_2(\text{tetraen})$

According to figures 4.28 and 4.29, the parallel compressive strength and perpendicular compressive strength of RPUR foam at NCO index at 100 shows that all copper-amine complexes show higher compressive strength than the foam prepared from a commercial reference catalyst (DMCHA). And if NCO index was increased from 100 to 130 and up to 150, the compressive strength of RPUR foam was increasing (Figure 4.30). Compressive strength of RPUR foam catalyzed by DMCHA and copper-amine complexes in parallel and perpendicular direction of RPUR foam rise is demonstrated. From Figure 4.31, it was found that the parallel compressive strength of RPUR foam was higher than perpendicular compressive strength. This was because the RPUR foam cells were elongated in the direction of the rise.

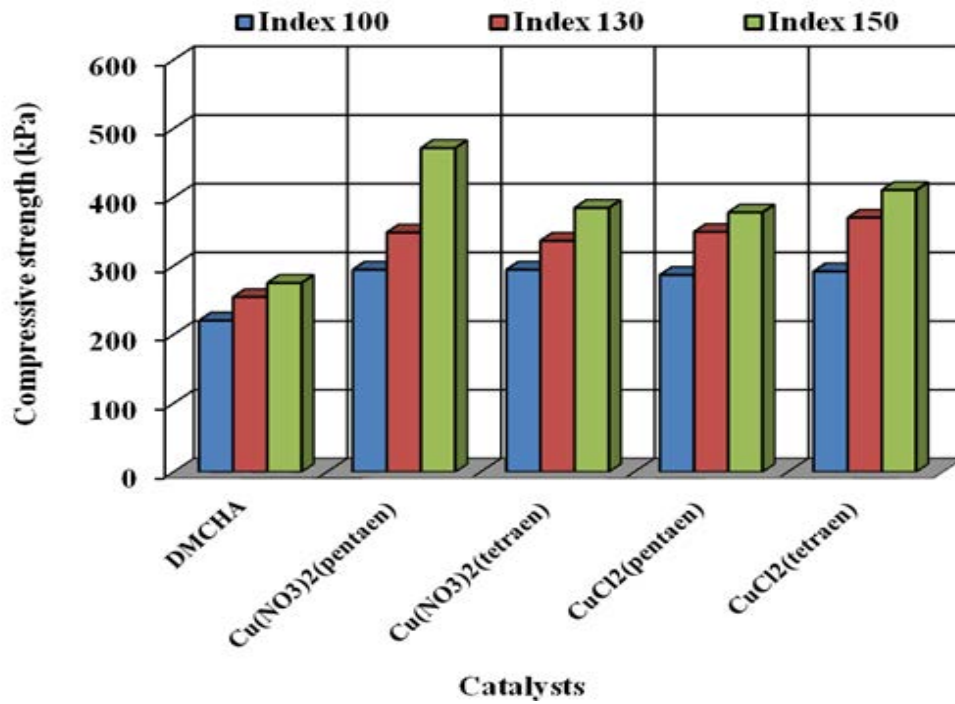


Figure 4.30 Comparison of parallel compressive strength of RPUR foams at NCO indexes of 100, 130 and 150

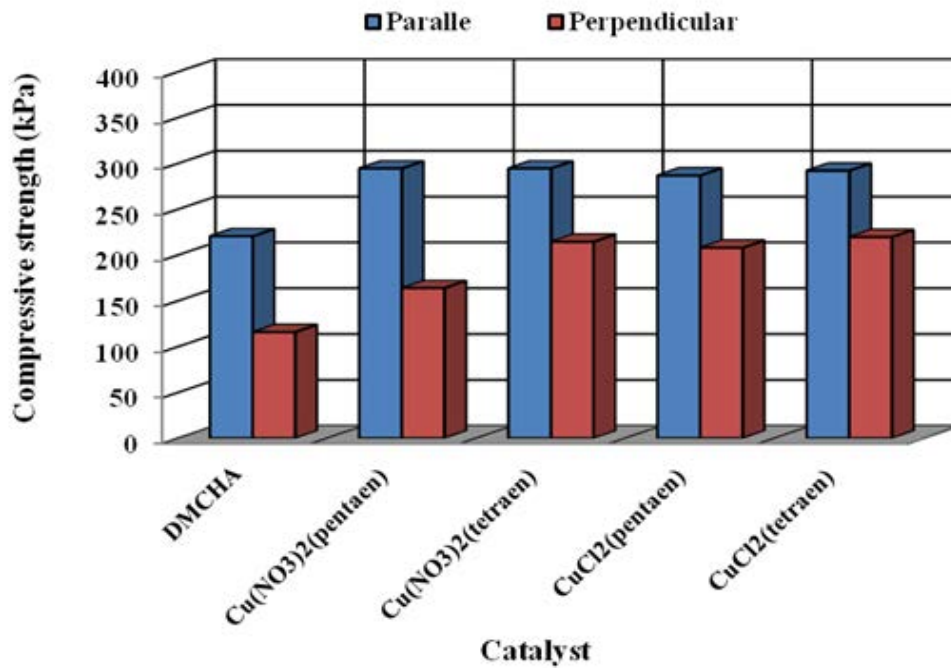


Figure 4.31 Comparison of compressive strength of RPUR foams between parallel and perpendicular direction of foam rising at NCO index of 100

It can be explained that RPUR foams which prepared with higher NCO index normally had higher compressive strength the RPUR foam which prepare from lower NCO index. Figure 4.32 shows that compressive strength of RPUR foam catalyzed by $\text{Cu}(\text{NO}_3)_2$ (tetraen) increases from 294.5 to 384.6 kPa with an increasing density from 45.1 to 48.7 kg/m^3 . Therefore it indicates that the mechanical properties of foams mainly depend on the density.

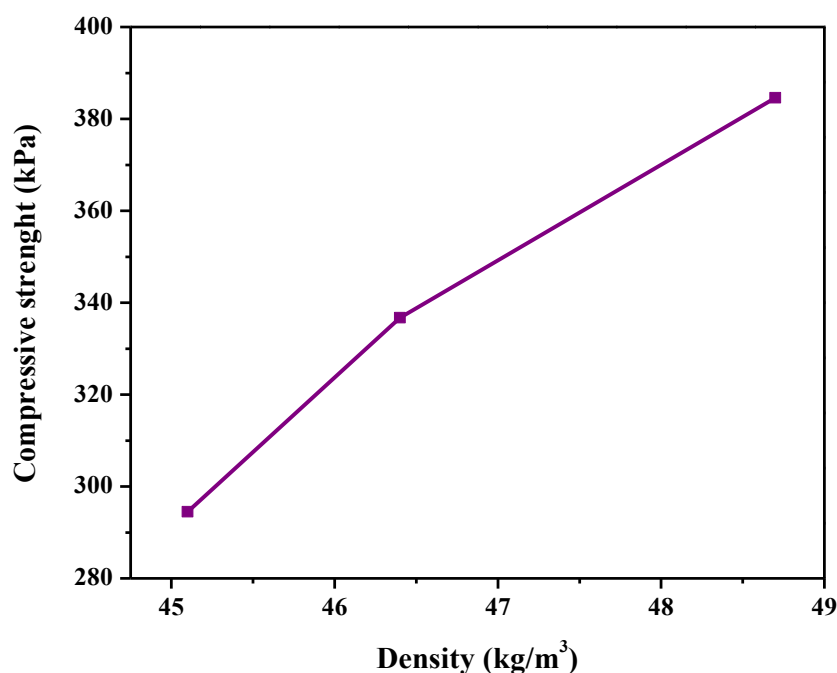


Figure 4.32 Compressive strength of RPUR foam catalyzed by $\text{Cu}(\text{NO}_3)_2$ (tetraen)

4.9 RPUR Foams Morphology

Morphology of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2$ (pentaen) and $\text{Cu}(\text{NO}_3)_2$ (tetraen) in parallel and perpendicular of foam rising is shows in Figures 4.33 and 4.34. The shows the cell morphology showed spherical cell in parallel direction and elongated cell in perpendicular direction.

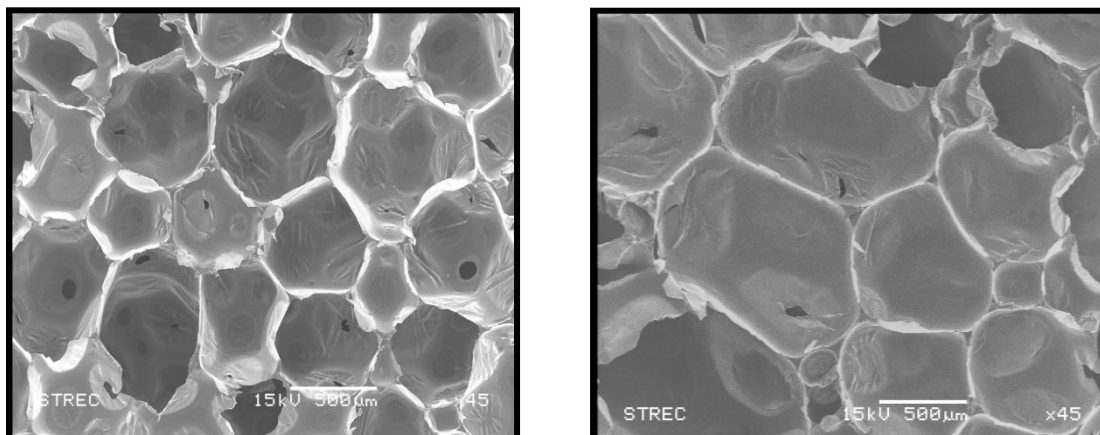


Figure 4.33 SEM of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$ prepared at NCO index 100; (a) top view; (b) side view (45x)

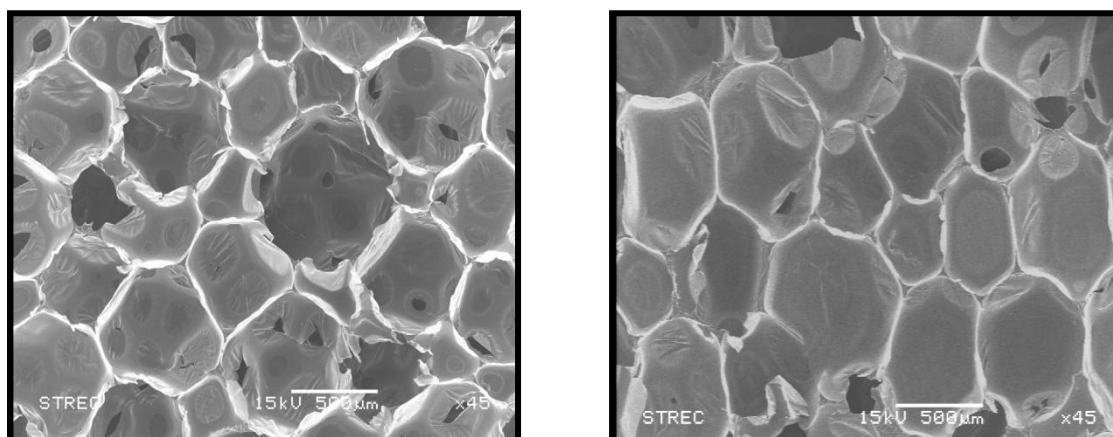


Figure 4.34 SEM of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ prepared at NCO index 100; (a) top view; (b) side view (45x)

SEM micrographs of RPUR foams catalyzed by DMCHA and $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ are shown in Figure 4.35. It illustrates the RPUR foams are observed that closed cell foams. Then RPUR foam catalyzed by DMCHA has smaller cell size than $303.8 \mu\text{m}$ when comparing with RPUR foam catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ (cell size = $459.0 \mu\text{m}$).

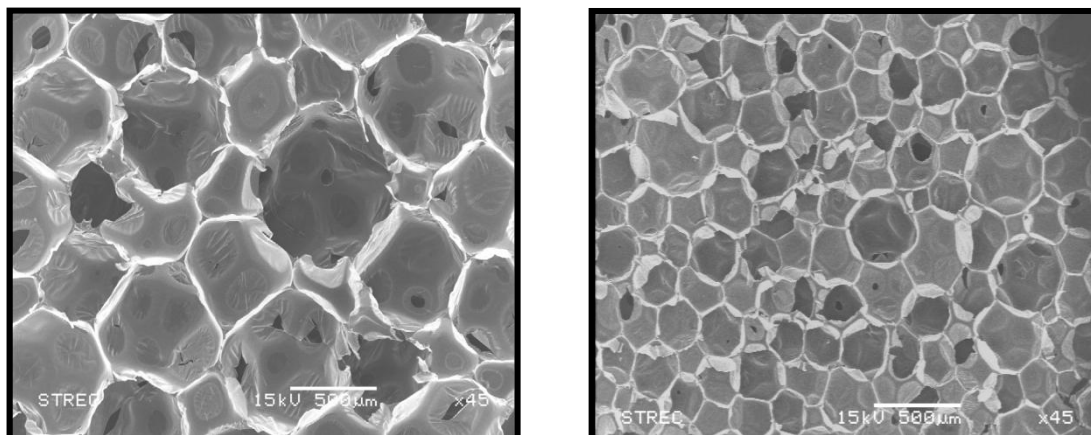


Figure 4.35 SEM of RPUR foams prepared at the NCO index of 100 and catalyzed by (a) $\text{Cu}(\text{NO}_3)_2$ (tetraen); (b) DMCHA (ref.) (top view, 45 \times)

4.9.1 Effect of blowing agent on morphology of RPUR foams

Figure 4.36 shows cell morphology of RPUR foam with different blowing agent content. When increasing blowing agent content from 2.0 to 4.0 pbw, the average cell size of RPUR foam increased from 412.9 to 549.5 μm , respectively (Table 4.12). This is because the increased blowing agent content generated more CO_2 . Therefore, the cell size of foams increased with the increase in the blowing agent content.

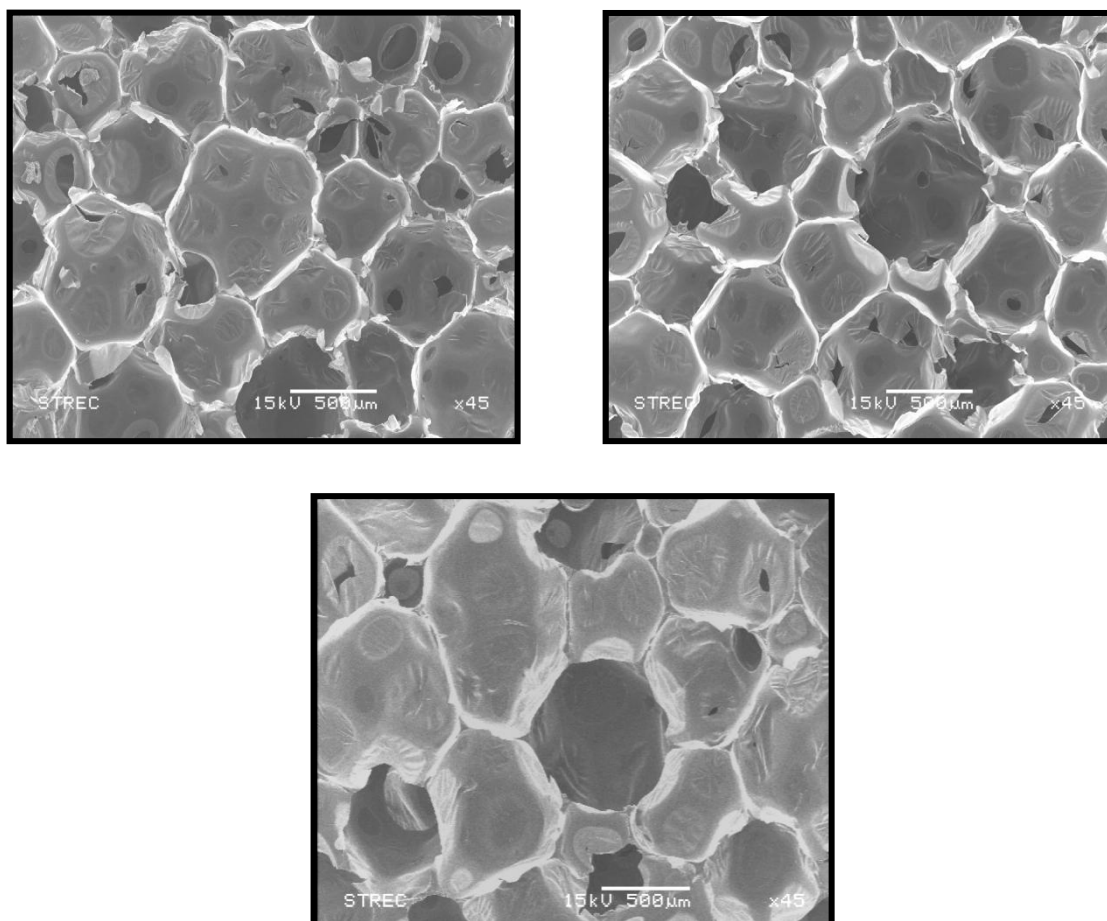


Figure 4.36 SEM of RPUR foams prepared at the NCO index of 100, catalyzed by $\text{Cu}(\text{NO}_3)_2$ (tetraen) and blown by different blowing agent content (a) 2.0 pbw (b) 3.0 pbw (c) 4.0 pbw (top view, 45 \times)

Table 4.12 The cell size of RPUR foam with different blowing agent content

Blowing agent content	Cell size (μm)
2.0 pbw	412.9
3.0 pbw	459.0
4.0 pbw	549.5

4.10 Thermal stability

Figure 4.37 and Table 4.13 show TGA thermograms and TGA data of RPUR foams catalyzed by DMCHA and copper-amine complexes at NCO index of 100. TGA thermograms under nitrogen atmosphere of all RPUR foams showed the decomposition of foams in one step.

The initial composition temperature (IDT), which is the temperature at 5% weight loss was found in the range of 265.2-275.7 °C. The residual weights at 600 °C were in the range of 16.8-24.5%. RPUR foams catalyzed by DMCHA, Cu(NO₃)₂(pentaen), Cu(NO₃)₂(tetraen), Cu(Cl)₂(pentaen) and Cu(Cl)₂(tetraen) showed their maximum decomposition temperature (T_{max}) values in the range of 349.4-354.4 °C. The RPUR foams prepared from copper-amine complexes catalysts showed similar thermal decomposition with that prepared from DMCHA catalyst. This indicated that the metal complexes showed similar catalytic reaction with that of DMCHA.

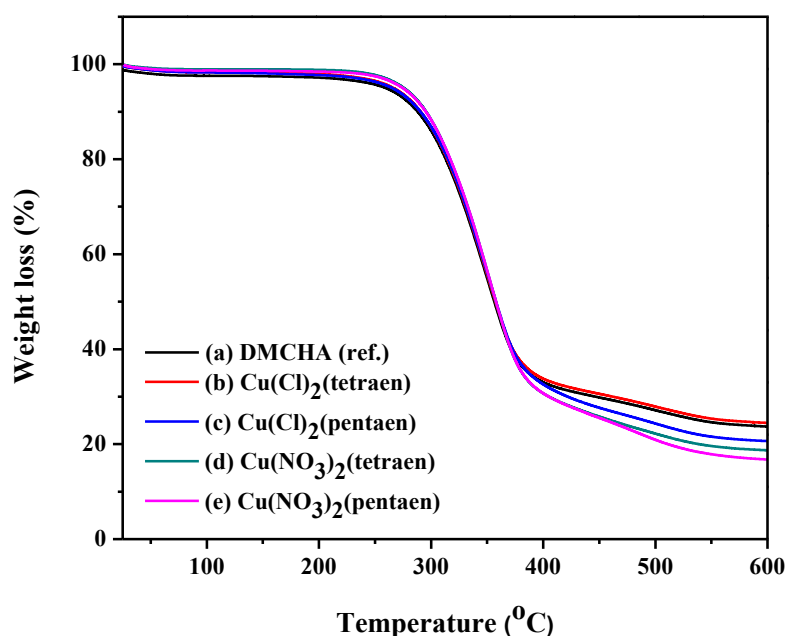
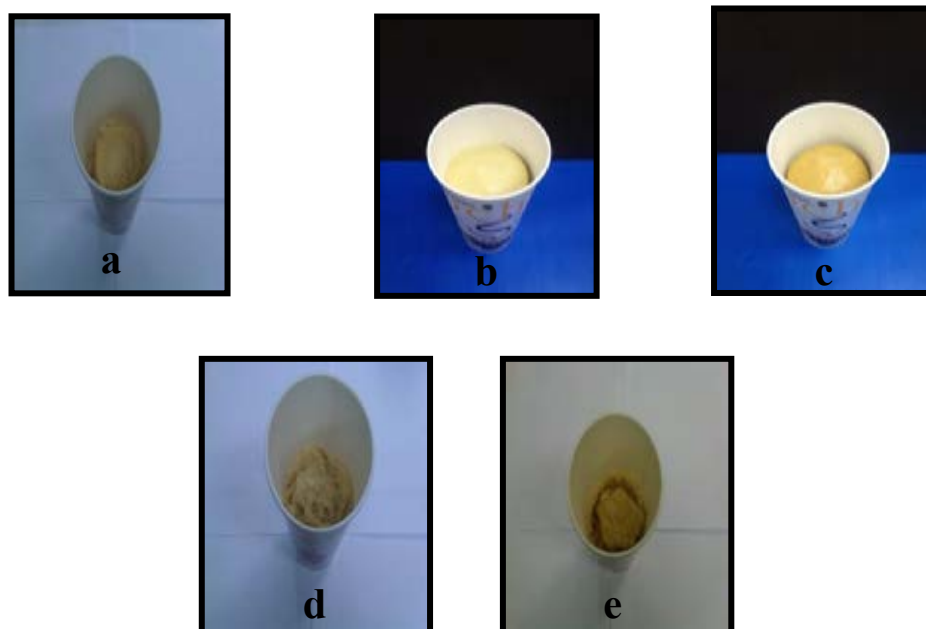


Figure 4.37 TGA thermograms of RPUR foams catalyzed by (a) DMCHA (ref.); (b) Cu(Cl)₂(pentaen); (c) Cu(Cl)₂(tetraen); (d) Cu(NO₃)₂(pentaen); (e) Cu(NO₃)₂(tetraen) at the NCO index of 100

Table 4.13 TGA data of RPUR foam catalyzed by various metal complexes catalysts

RPUR catalyzed by various catalysts	IDT (°C)	Weight residue (%) at different temperatures (°C)					T_{\max} (°C)
		200	300	400	500	600	
		DMCHA (ref.)	265.3	97.2	86.4	33.1	
Cu(NO ₃) ₂ (pentaen)	274.6	98.5	88.3	30.7	21.0	16.8	354.4
Cu(NO ₃) ₂ (tetraen)	275.7	98.8	88.4	30.7	22.2	18.7	353.7
Cu(Cl) ₂ (pentaen)	265.2	97.7	86.9	32.6	24.3	20.7	351.3
Cu(Cl) ₂ (tetraen)	266.4	97.9	86.8	33.7	27.9	24.5	350.2

To prove that the formation of copper-amine complexes was important, RPUR foams catalyzed by starting materials, namely Cu(NO₃)₂, Cu(Cl)₂, pentaen and tetraen, gave brittle foams with poor appearance (Figure 4.38). This indicated that Cu(NO₃)₂, Cu(Cl)₂, pentaen and tetraen are unsuitable catalysts. While RPUR foams catalyzed by DMCHA, Cu(NO₃)₂(pentaen), Cu(NO₃)₂(tetraen), Cu(Cl)₂(pentaen) and Cu(Cl)₂(tetraen) were good foams (Figure 4.38).

**Figure 4.38** External appearances of RPUR foams (a) prepared without catalyst and catalyzed by (b) Cu(NO₃)₂; (c) Cu(Cl)₂; (d) pentaen and (e) tetraen

RPUR foams catalyzed by DMCHA, $\text{Cu}(\text{NO}_3)_2$ (pentaen), $\text{Cu}(\text{NO}_3)_2$ (tetraen), $\text{Cu}(\text{Cl})_2$ (pentaen) and $\text{Cu}(\text{Cl})_2$ (tetraen) (Figure 4.39) showed good foam.

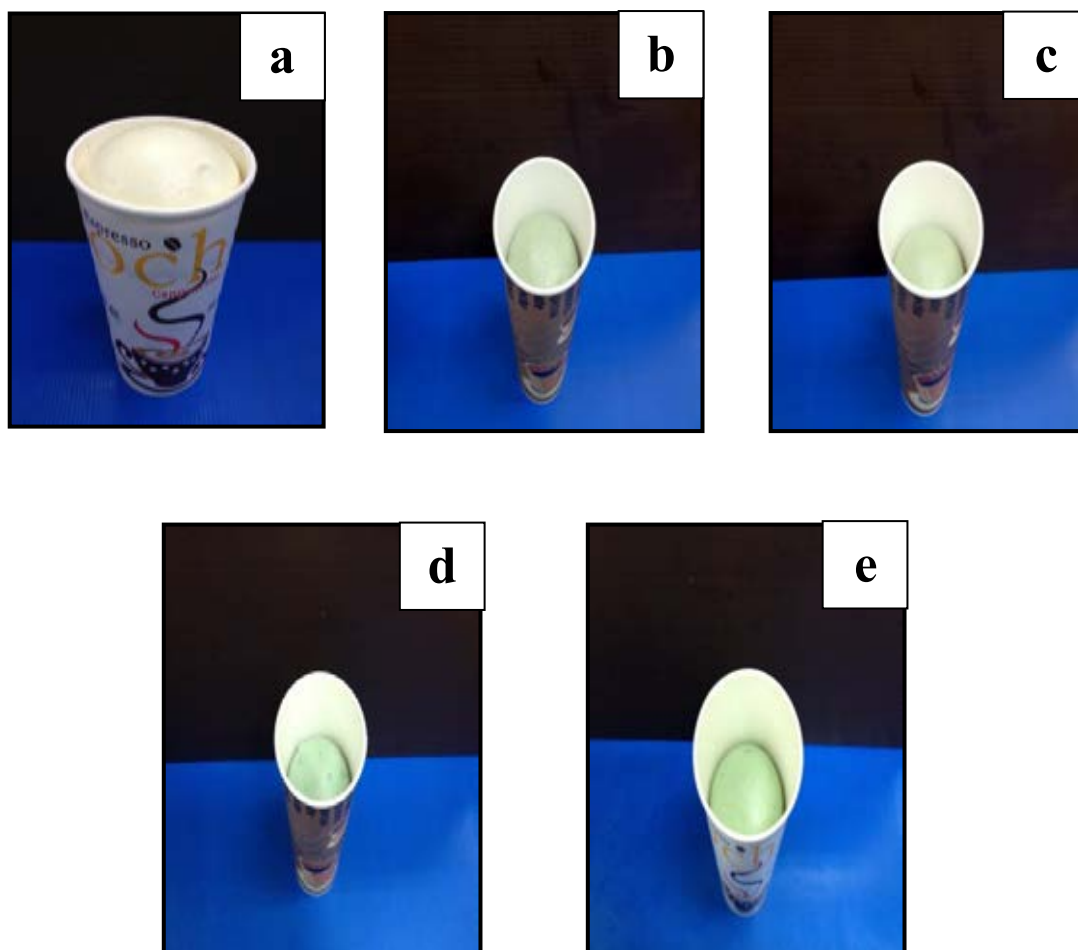


Figure 4.39 External appearance of RPUR foams catalyzed by (a) DMCHA, (b) $\text{Cu}(\text{NO}_3)_2$ (pentaen), (c) $\text{Cu}(\text{NO}_3)_2$ (tetraen), (d) $\text{Cu}(\text{Cl})_2$ (pentaen), (e) $\text{Cu}(\text{Cl})_2$ (tetraen)

CHAPTER V

CONCLUSION

5.1 Conclusion

Copper-amine complexes, namely $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ were synthesized and used as catalysts in the preparation of rigid polyurethane (RPUR) foam. Copper-amine complexes were characterized by FTIR spectroscopy, ultraviolet-visible spectroscopy, mass spectrometry, atomic absorption spectroscopy and elemental analysis.

Copper-amine complexes were odorless and showed good solubility in starting materials of RPUR foam formulation. They showed the catalytic activity of being gelling catalyst more than blowing catalyst when compared to reference commercial catalyst, DMCHA, which were both gelling and blowing catalyst.

Among all copper-amine complexes, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ showed better catalytic activity than $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$. The good catalytic activity could be observed from short tack free time and gel time of foaming reaction. $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ had less catalytic activity than DMCHA. Although $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ had longer tack free time than DMCHA, the foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ had good appearance.

Apparent density of RPUR foams increased when the NCO indexes were increased from 100 to 150. RPUR foam prepared at the NCO index of 100 to 150 had apparent density in the range 45.1-53.8 kg/m^3 . An appropriate NCO index in the RPUR foam formation was the NCO index of 100 since RPUR foam had good appearance, that is, the resulting foams were rigid and not fragile.

ATR-IR spectroscopy was used to determined NCO conversion in the foaming reaction. It was found that NCO conversion decreased when NCO index in the foam formulation was increased.

Compressive strength of RPUR foam depends on the density of prepared RPUR foam. RPUR foams prepared by use of copper-amine complexes as catalysts at the NCO index of 100 had parallel compressive strength in the range 292.1-294.5 kPa. and perpendicular compressive strength in the range 164.0-219.7 kPa. RPUR foam prepared by using DMCHA as catalyst had parallel compressive strength of 254.8 kPa and perpendicular compressive strength of 119.0 kPa.

Scanning electron microscopy (SEM) was used to observe morphology and cell size of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$. It was found that when the amount of blowing agent in the foam formulation was increased from 2 pbw to 4 pbw, the cell size average would increase from 412 to 549 μm .

Thermogravimetric data of RPUR foams catalyzed by $\text{Cu}(\text{NO}_3)_2(\text{pentaen})$, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$, $\text{Cu}(\text{Cl})_2(\text{pentaen})$ and $\text{Cu}(\text{Cl})_2(\text{tetraen})$ at NCO index = 100 showed that the foams had similar thermal stability to RPUR foam that prepared by using DMCHA as a catalyst.

5.2 Suggestion for future work

Although $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ had less catalytic activity than DMCHA, $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ had much less odor as compared to DMCHA. The suggestion for future work is to use $\text{Cu}(\text{NO}_3)_2(\text{tetraen})$ with other commercial catalyst in the foam formulation to improve the reaction time and facilitate better blowing reaction.

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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 and 150 required to react with the following formulation:

Formulation (pbw)	Part by weight (g)
Daltolac [®] R 180 (OHV = 440 mgKOH/ g, functionality = 4.3)	100.0
Catalysts	1.0
Surfactant	2.5
Blowing agent (water, M _w = 18 g/mole, functionality = 2)	3.0
PMDI (Suprasec [®] 5005), NCO indexes of 100, 130 and 150	?

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

$$\text{Equivalent weight of water} = \frac{18}{3} = 6.0$$

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:

$$\begin{aligned} \text{Polyol (Daltolac® R 180)} &= \frac{100}{127.5} = 0.784 \\ \text{Water (blowing agent)} &= \frac{3.0}{9.0} = 0.333 \\ \text{Total equivalent weight} &= 1.117 \end{aligned}$$

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

thus:

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

Note: 151.8 defines the isocyanate quantity at 100 index

where;

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

thus:

Isocyanate index = 100;

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

Isocyanate index = 130;

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

Isocyanate index = 150;

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

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

Formulations (pbw)	NCO index		
	100	130	150
Polyether polyol (Daltolac [®] R 180)	100	100	100
Catalysts (DMCHA or copper complexes)	1.0	1.0	1.0
Silicone surfactant (TEGOTAB B8460)	2.5	2.5	2.5
Blowing agent (water)	3.0	3.0	3.0
Polymeric MDI (Suprasec [®] 5005)	152	197	227

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:

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

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	97.274
Average (NCO ⁱ); ATR-IR	97.9

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

Conversion of isocyanate (%)

Data at **Table A2**

Absorbance peak area of initial NCO = 97.9 = NCOⁱ

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,

$$\begin{aligned} \text{Conversion of isocyanate (\%)} &= \left[1 - \frac{\text{NCO}^f}{\text{NCO}^i} \right] \times 100 \\ &= \left[1 - \frac{1.023}{97.9} \right] \times 100 \end{aligned}$$

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

PIR:PUR

Absorbance peak area of PIR (polyisocyanurate) = 0.944

Absorbance peak area of PUR (polyurethane) = 4.909

$$\text{thus, PIR:PUR} = \frac{0.944}{4.909} = 0.202$$

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	0.664	2.276	1.229	6.749	0.292	99.7	0.166
130	1.526	2.281	1.262	4.674	0.669	99.3	0.197
150	2.122	2.442	1.323	3.799	0.869	99.1	0.217

Table A4 NCO conversion of RPUR foam catalyzed by Cu(NO₃)₂(pentaen) 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	2.039	1.993	0.944	4.909	1.023	98.9	0.202
130	4.938	2.177	1.107	5.111	2.269	97.7	0.217
150	7.537	1.989	1.033	4.343	3.789	96.1	0.238

Table A5 NCO conversion of RPUR foam catalyzed by $\text{Cu}(\text{NO}_3)_2$ (tetraen) 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	1.282	1.473	0.711	3.467	0.870	99.1	0.205
130	4.632	1.906	0.960	4.376	2.430	98.6	0.219
150	5.092	1.837	0.941	3.875	2.772	97.2	0.234

Table A6 NCO conversion of RPUR foam catalyzed by CuCl_2 (pentaen) 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	4.314	2.156	1.043	5.176	2.000	98.0	0.202
130	6.157	2.134	1.039	4.890	2.885	97.1	0.212
150	6.916	1.993	1.035	4.315	3.609	96.5	0.239

Table A7 NCO conversion of RPUR foam catalyzed by CuCl₂(tetraen) 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	0.728	1.862	0.903	4.765	0.391	98.5	0.211
130	0.974	1.443	0.791	3.688	0.675	98.2	0.214
150	2.034	1.827	0.947	4.217	1.113	97.5	0.228

Appendix B

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(Cl) ₂	Cu(NO ₃) ₂	pentaen	tetraen	Non-catalyst
<i>Reaction times</i>					
Cream time (min.)	0:34	0:30	1:10	0:13	0:26
Gel time (min.)	2:01	2:30	2:44	1:14	2:29
Tack free time (min.)	4:12	4:03	14:49	14:24	18.19
Rise time (min.)	4:27	4:20	9:06	10:35	10:51
<i>Density (kg/m³)</i>	-	-	-	-	-
<i>External appearance</i>	Brittle foam	Brittle foam	Brittle foam	Brittle foam	Brittle foam

Table B2 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by different metal complexes

Formulations (pbw)	Catalysts at different NCO indexes											
	DMCHA (Ref.)						Cu(NO ₃) ₂ (pentaen)					
	100		130		150		100		130		150	
Daltolac [®] R 180	100		100		100		100		100		100	
Catalysts	3.0		3.0		3.0		3.0		3.0		3.0	
B8460	2.5		2.5		2.5		2.5		2.5		2.5	
H ₂ O	3.0		3.0		3.0		3.0		3.0		3.0	
Suprasec [®] 5005	152		197		227		152		197		227	
Efficiency parameters	Data	S.D.	Data	S.D.	Data	S.D.	Data	S.D.	Data	S.D.	Data	S.D.
<i>Reaction times</i>												
Cream time (min.)	0:10	0.6	0:23	0.6	0:24	0.5	0:29	0.6	0:32	1.0	0:31	0.6
Gel time (min.)	0:13	0.7	0:36	1.0	0:41	0.5	2:51	1.0	3:49	1.1	4:01	0.9
Tack free time (min.)	1:17	0.9	3:35	1.0	4:02	1.0	14:41	1.0	15:49	1.3	16:23	1.0
Rise time (min.)	0:58	1.3	2:40	1.7	3:05	1.0	13:07	2.2	13:52	2.8	14:55	2.2
<i>Density (kg/m³)</i>	34.1	0.3	38.4	0.8	42.3	0.9	46.0	0.6	48.3	0.9	52.6	1.1
<i>Mechanical properties</i>												
Compressive strength (kPa)	220.5	-	254.8	-	275.3	-	294.1	-	348.7	-	471.6	-

Table B3 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by different metal complexes

Formulations (pbw)	Catalysts at different NCO indexes											
	Cu(NO ₃) ₂ (tetraen)						CuCl ₂ (pentaen)					
	100		130		150		100		130		150	
Daltolac [®] R 180	100		100		100		100		100		100	
Catalysts	3.0		3.0		3.0		3.0		3.0		3.0	
B8460	2.5		2.5		2.5		2.5		2.5		2.5	
H ₂ O	3.0		3.0		3.0		3.0		3.0		3.0	
Suprasec [®] 5005	152		197		227		152		197		227	
Efficiency parameters	Data	S.D.	Data	S.D.	Data	S.D.	Data	S.D.	Data	S.D.	Data	S.D.
<i>Reaction times</i>												
Cream time (min.)	0:26	0.6	0:26	0.7	0:25	0.6	0:31	0.6	0:30	0.6	0:28	0.6
Gel time (min.)	2:32	1.0	2:48	1.0	3:20	1.1	3:21	1.5	4:00	1.0	4:09	1.0
Tack free time (min.)	12:32	1.2	13:26	1.1	14:02	1.5	16:44	1.0	17:21	1.9	18:25	1.1
Rise time (min.)	10:15	2.0	10:38	2.6	11:50	2.5	13:42	2.9	15:32	2.2	16:46	2.5
<i>Density (kg/m³)</i>	45.1	0.5	46.4	0.9	48.7	0.5	47.2	1.1	49.5	1.2	53.8	1.2
<i>Mechanical properties</i>												
Compressive strength (kPa)	294.5	-	336.7	-	384.6	-	286.9	-	349.6	-	378.0	-

Table B4 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by different metal complexes

Formulations (pbw)	Catalysts at different NCO indexes					
	CuCl ₂ (tetraen)					
	100		130		150	
Daltolac [®] R 180	100		100		100	
Catalysts	3.0		3.0		3.0	
B8460	2.5		2.5		2.5	
H ₂ O	3.0		3.0		3.0	
Suprasec [®] 5005	152		197		227	
Efficiency parameters	Data	S.D.	Data	S.D.	Data	S.D.
<i>Reaction times</i>						
Cream time (min.)	0:30	0.2	0:29	0.6	0:27	0.6
Gel time (min.)	2.59	0.6	3:36	1.0	3:42	1.0
Tack free time (min.)	15:27	1.3	16:52	1.7	17:43	1.0
Rise time (min.)	11:39	2.1	15:13	1.9	15:47	2.4
<i>Density (kg/m³)</i>	46.4	0.7	48.8	0.6	52.6	0.6
<i>Mechanical properties</i>						
Compressive strength (kPa)	292.1	-	370.4	-	410.5	-

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