การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนคอปเปอร์-แอมีนในเอทิลีนไกลคอล

นางสาวเบญจธรรม สุขณีวัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY COPPER-AMINE COMPLEXES IN ETHYLENE GLYCOL

Miss Benjatham Sukkaneewat

A Thesis Submitted in Partial Fulfillment of the Requirements
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เบญจธรรม สุขณีวัฒน์: การเตรียมโฟมพอลิยูรีเทนแบบแข็งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนคอปเปอร์-แอมีนในเอทิลีนไกลคอล (PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED BY COPPER-AMINE COMPLEXES IN ETHYLENE GLYCOL)
อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. นวลพรรณ จันทรศิริ, 133 หน้า.

งานวิจัยนี้ได้พัฒนาตัวเร่งปฏิกิริยาในรูปแบบสารละลายสำหรับใช้เตรียมโฟมพอลิยูรีเทนแบบแข็งเพื่อปรับปรุงสมบัติในการละลายของตัวเร่งปฏิกิริยา โดยตัวเร่งปฏิกิริยาดังกล่าวเป็นสารประกอบเชิงซ้อน ระหว่าง โลหะคอปเปอร์ และแอมีน ได้แก่ $\mathrm{Cu(X)_2(en)_2}$, $\mathrm{Cu(X)_2(trien)}$, $\mathrm{Cu(X)_2(tetraen)}$ และ $\mathrm{Cu(X)_2(pentaen)}$ (เมื่อ X= OAc, acac, $\mathrm{NO_3}$, Cl และ en = ethylenediamine, trien = triethylenetetramine, tetraen = tetraethylenepentaime และ pentaen = pentaethylenehexamine) ที่สังเคราะห์ขึ้นโดยใช้เอทิลีนไกลคอลเป็นตัวทำละลาย การพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาใช้เทคนิคยูวี-วิสสิเบิลสเปกโทรสโกปี และแมสสเปกโทรเมตรี โฟมพอลิยูรีเทนแบบแข็ง ถูกเตรียมขึ้นโดยใช้ ปฏิกิริยาระหว่างพอลิเมอริก 4,4′ มีเทนไดฟีนิลไดไอโซไซยาเนตและพอลิอีเทอร์พอลิออล โดยใช้สารประกอบเชิงซ้อนของโลหะคอปเปอร์-แอมีนที่สังเคราะห์ขึ้น เป็นตัวเร่งปฏิกิริยา จากนั้นเปรียบเทียบ ประสิทธิภาพ กับตัวเร่งปฏิกิริยาทางการค้า คือ *เอ็น,เอ็น*-ไดเมทิลไซโคลเฮกซิลแอมีน (DMCHA) ศึกษาผลทางด้านเวลาการเกิดปฏิกิริยา สมบัติทางกายภาพ และสมบัติเชิงกลของโฟม เทคนิคเอทีอาร์-อินฟราเรดสเปกโทรสโกปีถูกนำมาใช้เพื่อหาการเปลี่ยนแปลงของหมู่ไอโซไซยาเนต (NCO conversion) ในการเตรียมโฟมที่ค่าดัชนีไอโซไซยาเนต (NCO index) ต่างกัน คือ 100, 130 และ 150 จากผลการทดลองพบว่าการเตรียมตัวเร่งปฏิกิริยาในรูปแบบสารละลายทำให้สามารถช่วยปรับปรุงสมบัติในการละลายของตัวเร่งปฏิกิริยาในสารตั้งต้นของโฟมให้ดีขึ้น โดยความเข้มข้นของตัวเร่งปฏิกิริยาที่เหมาะสมสำหรับใช้ในการสังเคราะห์ คือ 30%wt ในเอทิลีนไกลคอล จากสารประกอบเชิงซ้อนของโลหะคอปเปอร์-แอมีนทั้งหมดพบว่าตัวเร่งปฏิกิริยาที่มีประสิทธิภาพในการเร่งปฏิกิริยาเทียบเท่าได้กับตัวเร่งปฏิกิริยาทางการค้า DMCHA คือ $\mathrm{Cu(OAc)_2(en)_2}$, $\mathrm{Cu(OAc)_2(trien)}$, $\mathrm{Cu(OAc)_2(tetraen)}$, $\mathrm{Cu(OAc)_2(pentaen)}$ และ $\mathrm{Cu(acac)_2(en)_2}$ แต่ตัวเร่งปฏิกิริยาที่มีประสิทธิภาพมากที่สุด คือ $\mathrm{Cu(OAc)_2(trien)}$ เนื่องจากเร่งปฏิกิริยาการเกิดโฟมได้เร็ว และทำให้ได้โฟมที่มีคุณสมบัติเหมาะสม

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
ปีการศึกษา 2555 ลายมือชื่อ อ. ที่ปรึกษาวิทยานิพนธ์หลัก..................

5372494923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : COPPER-AMINE COMPLEX/ ETHYLENE GLYCOL/ RIGID POLYURETHANE FOAM/ CATALYST

BENJATHAM SUKKANEEWAT: PREPARATION OF RIGID POLYURETHANE FOAMS CATALYZED COPPER-AMINE COMPLEXES IN ETHYLENE GLYCOL. ADVISOR: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph. D., 133 pp.

Copper-amine complex catalysts for rigid polyurethane (RPUR) foam preparation were synthesized , when used, the catalysts were dissolved in ethylene glycol in order to improve its solubility in foam formulation. Copper-amine complex catalysts, namely $Cu(X)_2(en)_2$, $Cu(X)_2$(trien), $Cu(X)_2$(tetraen) and $Cu(X)_2$(pentaen) (where X= OAc, acac, NO_3, Cl; en = ethylenediamine, trien = triethylenetetramine, tetraen = tetraethylenepentamine and pentaen = pentaethylenehexamine) were synthesized using ethylene glycol as a solvent. The synthesized complexes were characterized by UV-visible spectroscopy and mass spectrometry. RPUR foams were prepared from the reaction between polymeric 4,4′ methane diphenyl diisocyanate and polyether polyol. The catalytic activity was compared with a commercial catalyst, N,N-dimethylcyclohexylamine (DMCHA), by investigation of reaction times, physical and mechanical properties of foams. ATR-IR spectroscopy was used to determine isocyanate (NCO) conversion of foams. It was found that the suitable catalyst concentration was 30%wt in ethylene glycol. Among all complexes, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen), $Cu(OAc)_2$(pentaen) and $Cu(acac)_2(en)_2$ showed comparable catalytic activity to DMCHA. $Cu(OAc)_2$(trien) was the best catalyst because it showed high catalytic activity and gave appropriate foam appearance.

Field of Study: Petrochemistry and Polymer Science Student's Signature....................
Academic Year: 2012 Advisor's Signature....................

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In addition, I also thank my friends and all members of Supramolecular Chemistry Research Unit for their encouragement and generous helps. Forthermore, I would like to give a special thanks to Mr. Wittaya Pengjam who give me an invaluable advice throughout the course of this research. My special thanks go to Dr. Preecha Thiampanya for analyzing the metal complex samples by mass spectrometry.

Finally, I would like to express my highest gratitude to my lovely family, especially my father, my mother and my sister, who give their love, care and encouragement to me and always stand beside me.

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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
^{o}C	degree Celsius (centrigrade)
DBTDL	dibutyltin dilaurate
DMCHA	N,N-dimethylcyclohexylamine
EA	Elemental Analysis
FTIR	Fourier Transform Infrared Spectrophotometer
g	gram
h	hour
IDT	initial decomposition temperature
KOH	potassium hydroxide
kg	kilogram
kV	kilovolt
M	metal
$M(OAc)_2$	metal acetate
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
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
TEDA	triethylenediamine
TDI	toluene diisocyanate
TGA	thermogravimetric analysis
T_{max}	maximum core temperature
UV	ultraviolet

CHAPTER I

INTRODUCTION

Polyurethane has been widely produced in polymer industry. This is because polyurethane can be manufactured in an extremely wide range of grades from very flexible elastomers to rigid hard plastics [1]. Polyurethane can be used in many applications such as adhesive, foams, crash, padding for vehicles and reinforced structures in boat and aircraft. Rigid polyurethane (RPUR) foam is defined as a unique insulation material. It has many desirable properties such as low thermal conductivity, low density, excellent dimensional stability, high strength-to-weight ratio, low moisture permeability and low water absorption [2]. Therefore, it is suitable for the application in household refrigerators, construction and industrial insulations.

The specific properties of RPUR foam can be adjusted by the choice of starting materials, namely isocyanates, polyols, blowing agents, catalysts and other additives. The preparation of RPUR foam can be performed by one shot or two shot methods. In one shot method, all of starting materials such as polyol, catalyst, surfactant, blowing agent and isocyanate are put into a mixing cup and mixed homogeneously. In two shot method, the starting materials except isocyanate are first blended and then isocyanate is added to the mixture in the second stage. Polyurethane foam is formed by two main reactions. Firstly, the addition polymerization between isocyanate (-NCO) and hydroxyl (-OH) groups results in urethane formations. Secondly, the reaction between isocyanate groups and chemical blowing agent (water) releases carbon dioxide gas [3]. The foam structure can be formed by either physical blowing agent or chemical blowing agent. Physical blowing agents, such as cyclopentane and HFC, expand the foam by vaporization, and this reaction is endothermic. On the other hand, the chemical blowing agent, such as water, expands RPUR foam by carbon dioxide generation, and this reaction is exothermic [4].

Unfortunately, all above reactions can not be completed without using catalysts because the reaction between the isocyanate and hydroxyl group is slow. In polyurethane technology, catalysts are used to accelerate and give desired balance of reaction rate between different compounds. The important role of catalyst does not only effect the rate of chemical reaction, chain propagation, extension and crosslinking, but also influence the ultimate properties of the final polymer. Catalysts for rigid polyurethane foam include a range of chemical structures, such as tertiary amines, aromatic amines, quaternary ammonium salts, alkali metal carboxylates and organo-tin compounds. The examples of commercial catalysts are dibutyltin mercaptide, N,N-dimethylcyclohexylamine (DMCHA) and dibutyltindilaurate (DBTDL). Although, the conventional catalysts having excellent catalytic activity, but they are toxic to human beings and have strong smell [5]. Accordingly, new catalytic systems are necessary to replace those commercial catalysts.

Objective of the research

The objective of this research was to synthesize copper-amine complexes; $Cu(X)_2(en)_2$, $Cu(X)_2(trien)$, $Cu(X)_2(tetraen)$ and $Cu(X)_2(pentaen)$ (where X= OAc, acac, NO_3 and Cl), as solutions, in ethylene glycol. These copper-amine complex solutions were used as catalysts in the preparation of RPUR foams. It was expected that the synthesized copper-amine complexes had good solubility in RPUR foam ingredients and showed effective catalytic activity, which should provide the desirable physical and mechanical properties of prepared foams. The optimum ethylene glycol content for synthesizing copper-amine complexes was investigated. Moreover, the reaction times during foam preparation, the physical and mechanical properties of foams were studied by varying catalyst types, catalysts content, blowing agent contents, and NCO indexes.

Scope of the research

This research consists of three parts as illustrated in Figure 1.1. In the first part, the experiment was done to determine the optimum copper-amine complex concentration in ethylene glycol for synthesizing copper-amine complexes catalysts. The series of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$ and $Cu(OAc)_2(pentaen)$ complexes were chosen to study and the catalyst concentrations were varied at 15, 30 and 60%wt in ethylene glycol, respectively.

The second part was copper-amine complexes synthesis. $Cu(X)_2(en)_2$, $Cu(X)_2(trien)$, $Cu(X)_2(tetraen)$ and $Cu(X)_2(pentaen)$ were prepared by the reaction between copper salts and aliphatic amines, namely copper(II) acetate [$Cu(OAc)_2$], copper(II) acetylacetonate [$Cu(acac)_2$], copper(II) nitrate [$Cu(NO_3)_2$] and copper(II) chloride [$Cu(Cl)_2$], ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pentaethylenehexamine (pentaen). Copper-amine complexes catalysts were characterized by ultraviolet-visible spectroscopy and mass spectrometry.

The last part was preparation and characterization of rigid polyurethane foams. The RPUR foams were prepared by two shot method using synthesized copper-amine complexes as catalysts. During preparation, reaction times included cream time, gel time, tack free time and rise time were recorded. In order to evaluate the efficiency of developed catalysts, the result experimental data of synthesized catalysts were compared with the commercial catalyst, N,N-dicyclohexylamine (DMCHA), which was used as the reference catalyst. In addition, physical and mechanical properties of RPUR foams at various catalyst types, catalysts contents, blowing agent contents and NCO indexes were also determined.

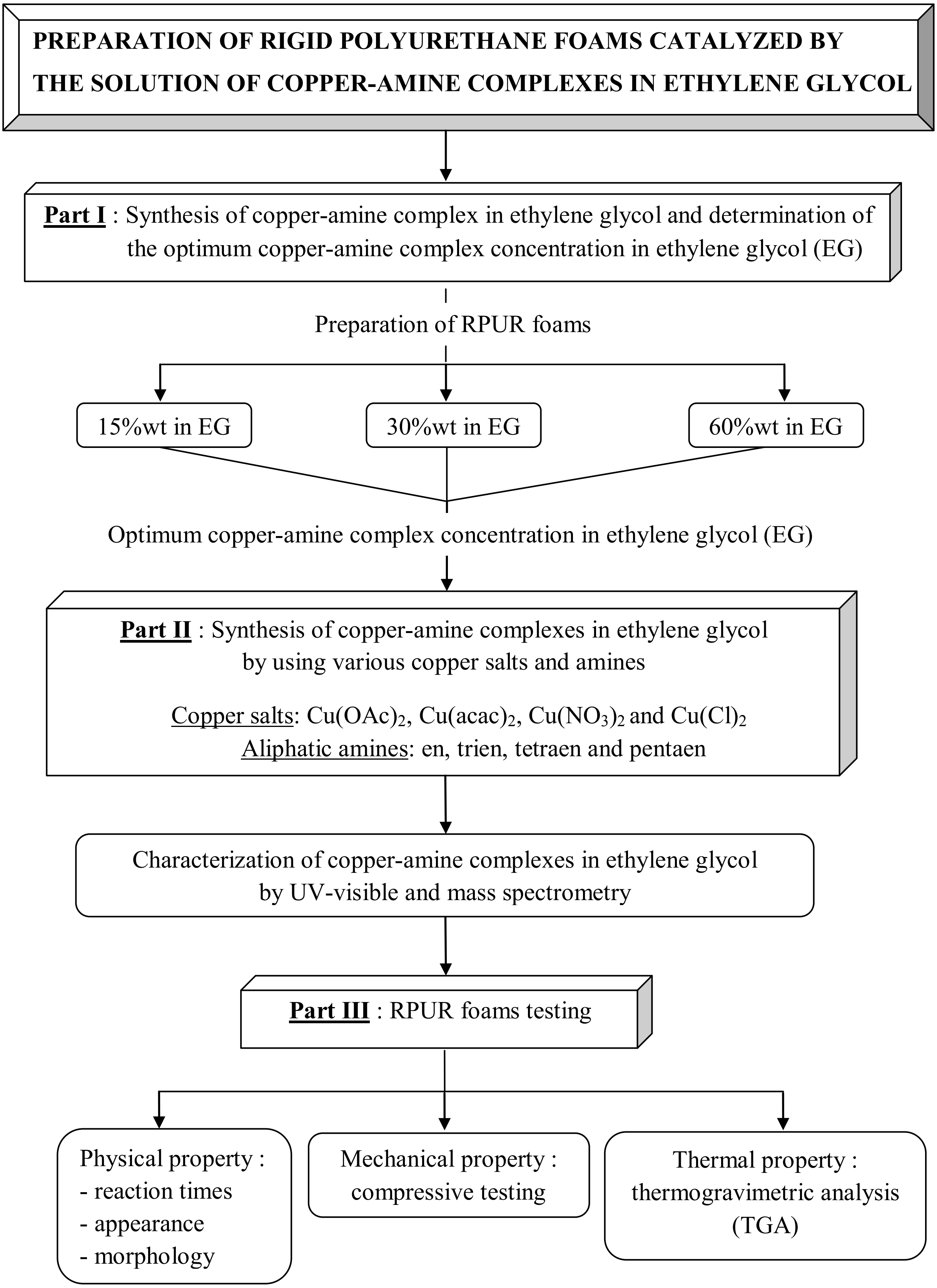


Figure 1.1 Diagram of experiments

CHAPTER II

THEORY AND LITERATURE REVIEWS

The original discovery leading to the world-wide interested in all class of polyurethane was made by Otto-Bayer and his co-worker of I.G. Farbenindustric at Levergusen, Germany in 1937 that commercial potential of polyurethane as fibres, adhesives, coating and foams began to be recognized. In fact, most polyurethane applications have been developed during the past 30 years [1]. Table 2.1 shows the development of polyurethanes. Since that time, they have been finding use in the increasing number of applications and polyurethanes are now all around us, playing a important role in many industries - from furniture to footwear, construction to cars. Polyurethanes appear in an astonishing variety of forms, making them the most versatile of any family of plastic materials.

Polyurethanes can be manufactured in an extremely wide range of grades, in densities from 6 to 1,220 kg/m^3 and polymer stiffness from flexible elastomers to rigid, hard plastics. Although an over simplification, the following chart, Figure 2.1, shows the broad range of polyurethanes, with reference to density and stiffness [6].

2.1 **Chemistry** [1,6]

Polyurethanes (PUR) are obtained by the reaction between isocyanate compounds which have more than one reactive isocyanate groups per molecule (diisocyanate or polyisocyanates) and alcohol compounds which have two or more reactive hydroxyl groups per molecule (diols or polyols). All polyurethanes are based on exothermic reaction. The rate of reaction is influenced by the structure and functionality of both isocyanate and polyol compounds. For simplicity, the basic principle of urethane chemistry is described below in section 2.1.1 using monofunctional reagents.

Table 2.1 Highlights in the development of polyurethanes [1]

1937-40	Otto Bayer and co-worker made polymer by polyaddition processes from various diisocyanates with glycols and/or diamines.
1940-45	Development of millable polyurethane elastomers and adhesives in Germany (I.G. Farben), U.K. (ICI) and the U.S.A. (Du Pont). Polyurethane coatings for barrage balloon (ICI), synthetic polyurethane bristles (I.G. Farben).
1945-47	Manufacture of millable polyurethane elastomers, coatings and adhesives
1950	Cast elastomers from polyester diols, diisocyanate prepolymers and chain-extenders
1953	First flexible polyurethane foam manufacture with a Bayer system using a high pressure machine, a polyester polyol and TDI.
1956	First manufacture of polyether-based flexible polyurethane foam in the U.S.A. using a two stage or 'pre-polymer' process.
1957	ICI introduces the first commercially available polymeric MDI composition for rigid polyurethane foam manufacture.
1959	ICI introduces the first rigid foam system based on polymeric MDI and a polyether polyol.
1959	'One-shot' system for flexible polyether-based foam introduced in U.S.A.
1960	ICI introduces the first polymeric MDI-based semi-rigid energy absorbing foam for vehicles.
1960-65	Rigid foam blowing by chlorofluoromethanes.
1962	First production line molded 'deep seat' flexible polyurethane car cushions at Austin-Morris (U.K.).
1963	ICI demonstrates production line manufacture of refrigerators using MDI-based polyurethane foam.
1963	First cold-store built entirely from metal-faced polyurethane rigid foam laminate mad continuously (Australia).
1964	ICI inverse- and floating- platen systems for the continuous manufacture for rigid polyurethane foam-cored build boards in production.
1965	First commercial production of self-skinning flexible foam (Soc. Quillery, France).
1968	ICI introduces isocyanurate rigid foams.
1968	General Motors make the first polyurethane microcellular bumper for the Pontiac G.T.O.
1973	MDI based 'soft-face' bumpers made by RIM system for Chevrolet taxis.
1979	ICI introduces wholly-MDI-based systems for flexible foam molding.
1983	ICI introduces system to make dual-hardness, molded seating from MDI-based, flexible foam.

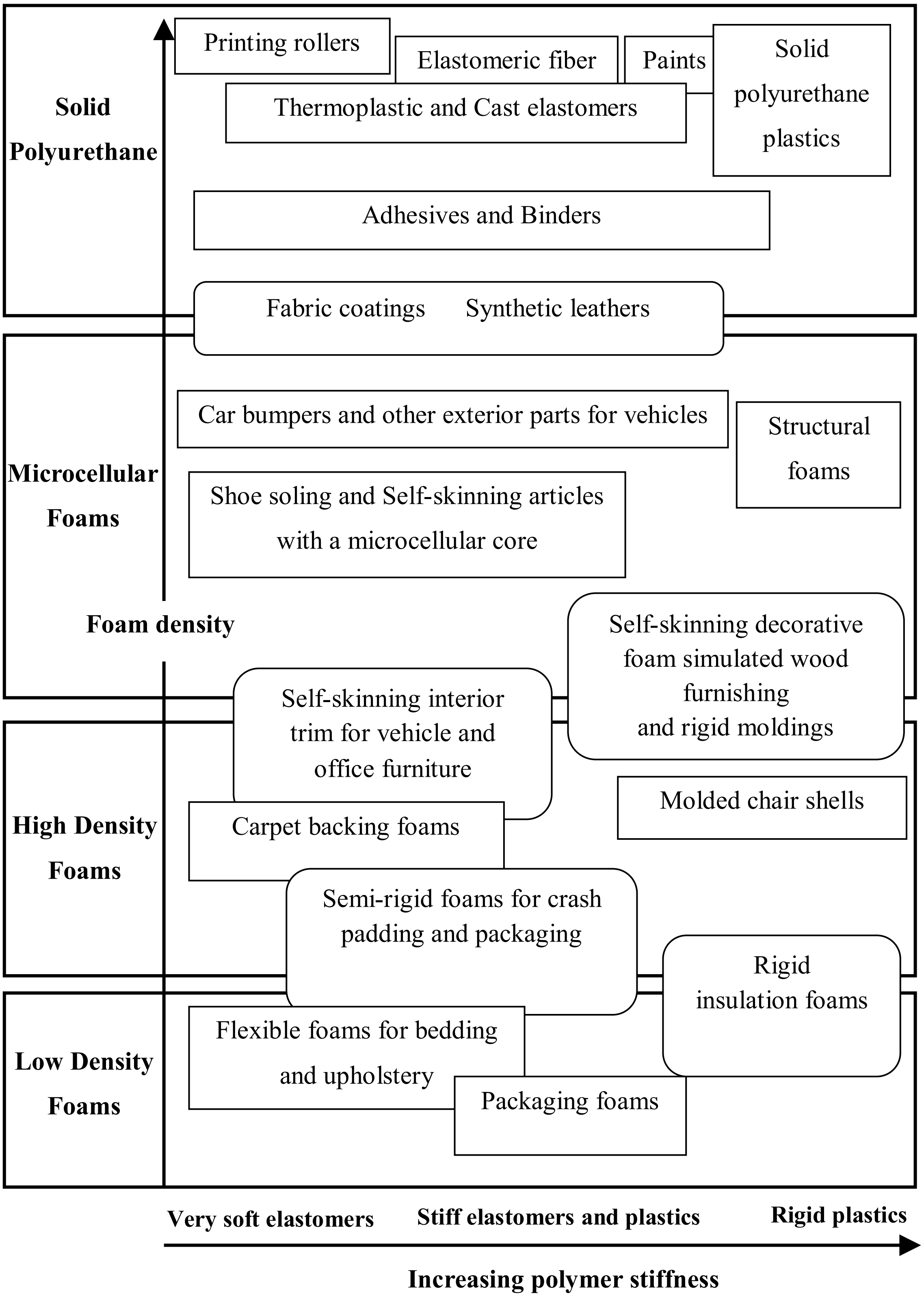


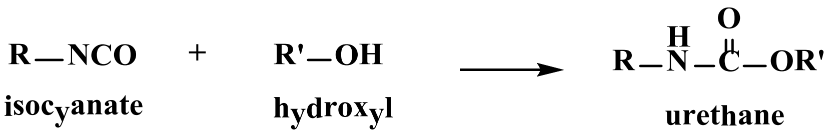
Figure 2.1 Properties of polyurethanes [6]

2.1.1 Primary reaction of isocyanates

Primary reactions of isocyanate with compounds containing active hydrogen atoms give urethane, amines, and substituted ureas. In the presence of suitable catalysts at elevated temperatures, controlled secondary reactions occur which strongly influence the physical properties of the foam by introducing chain branching and crosslinking.

2.1.1.1 Reaction of isocyanate with polyol

The most important reaction in the manufacture of polyurethanes is the reaction between isocyanate and hydroxyl groups. The reaction product is a carbamate, which is called a urethane in the case of high molecular weight polymers. The reaction is exothermic and reversible going back to the isocyanate and alcohol.

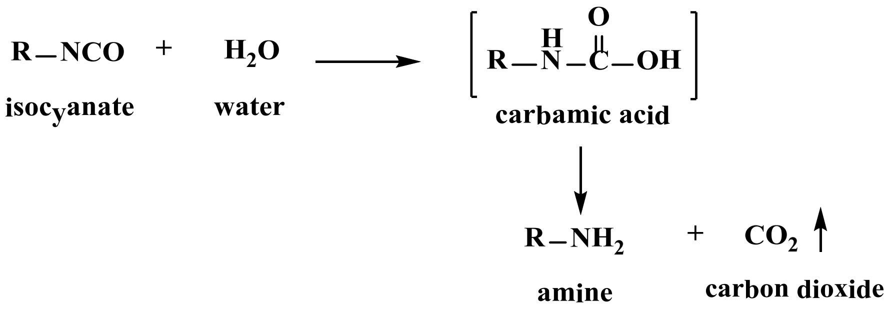


$$\underset{\text{isocyanate}}{R{-}NCO} + \underset{\text{hydroxyl}}{R'{-}OH} \longrightarrow \underset{\text{urethane}}{R{-}\overset{H}{N}{-}\overset{\overset{O}{\|}}{C}{-}OR'}$$

This reaction is known as the “gelling reaction”. Because it is an exothermic reaction, it must be temperature controlled. The rate of polymerization is affected by the chemical structure of both isocyanate and polyol compounds, including the steric hindrance of isocyanate group and the nature of the hydroxyl group (primary or secondary). A catalyst is used to accelerate the reaction rate.

2.1.1.2 Reaction of isocyanate with water

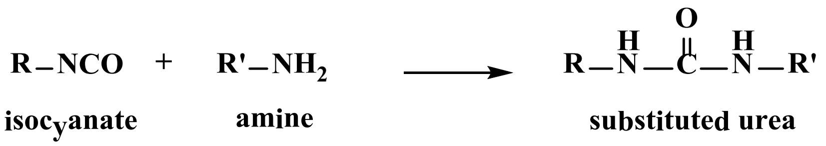
The reaction of isocyanates and water leads to produce substituted carbamic acid (an unstable intermediate product) which decomposed to give primary amine and carbon dioxide gas. This gas acts as the blowing agent in the manufacturing of polyurethane foams.



This reaction is known as the “blowing reaction” because the CO_2 gas, which has an effect on density of foam. The reaction rate is accelerating by suitable choice of catalyst system.

2.1.1.3 Reaction of isocyanate with amines

The reaction of isocyanate and amine give a urea linkage. It can increase both primary and secondary hydrogen-bonding. Thus, amines are usually used as chain-extenders and curing agents in order to produce the crosslink of polyurethane system.



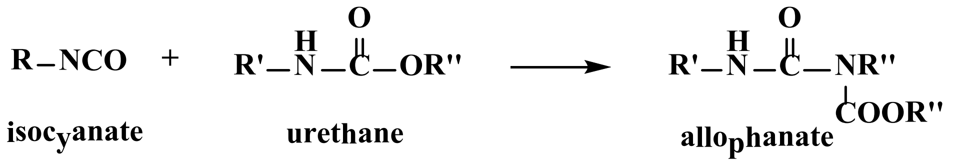
Reactions of unhindered isocyanates with primary amines occur approximately 100-1000 times faster than with primary alcohols [7]. The reactivity of amines increases with the basicity of the amine, and aliphatic amines can react much faster than aromatic amines.

2.1.2 Secondary reaction of isocyanates

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

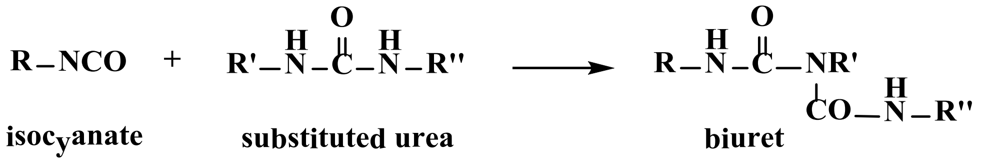
2.1.2.1 Reaction of isocyanate with urethane

isocyanate can react with the active hydrogen atoms of urethane linkages to form branched allophanates.



2.1.2.2 Reaction with urea

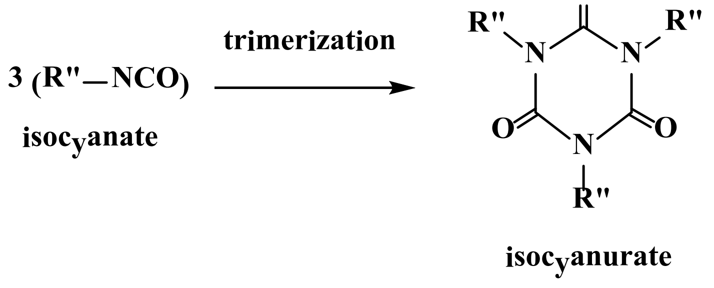
Similarly to the allophanate formation, isocyanate can also react with the active hydrogen atoms of substituted ureas to form branched biuret structures.



Both reactions are crosslinking reactions. The reaction of isocyanate with urea groups is significantly faster and occurs at the lower temperature than that with urethane groups.

2.1.2.3 Trimer formation

Isocyanurate trimers can be formed by further polymerization of isocyanate oligomers at higher temperature, especially in the presence of basic catalysts such as sodium and potassium salts of carboxylic acids. Those trimers are thermally stable and contribute to fire resistance of polyurethane foams.



2.2 Raw materials

The starting materials for produce polyurethane are the two main participants, namely isocyanate and polyol. In additive to the isocyanate and polyol, auxiliary additives such as catalysts, surfactants, blowing agents and chain extenders are added to control the process of reaction and to obtain particular characteristics of final polyurethane [8].

2.2.1 Isocyanates

Several aromatic and aliphatic isocyanates are available, but about 95% of all polyurethanes are based on toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate. Both of them are derived from petrochemical intermediates.

2.2.1.1 Toluene diisocyanate (TDI)

TDI (liquid, b.p. 120°C) is prepared by direct nitration of toluene to give 80:20 of 2,4 and 2,6-dinitroderivatives, followed by hydrogenation to diaminotouenes. The chemical structures of TDI are shown in Figure 2.2. TDI mixture can occurred a serious toxic hazard in used, having a marked effect on the respiratory system and the skin [1]. On the other hand, the diisocyanate of MDI based on diaminodiphenylmethane is considerable safer to use, having as much lower volatile than that of TDI.

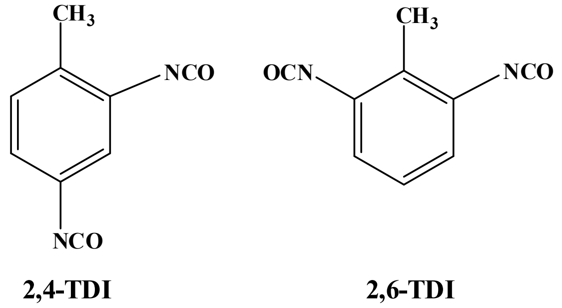


Figure 2.2 Toluene diisocyanate isomers used for PU foam manufacture [1]

2.2.1.2 4,4'-Diphenylmethane diisocyanate (MDI)

4,4′-Diphenylmethane diisocyanate (solid, m.p. 38°C, b.p. 195°C). Pure MDI is a crystalline solid at room temperature, so it must be heated slightly in order to convert it into a more manageable form, i.e. a fairly high viscosity liquid. Molecular structure of MDI is shown in Figure 2.3.

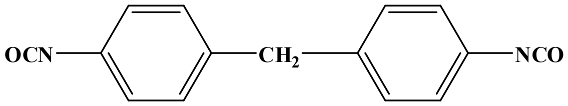
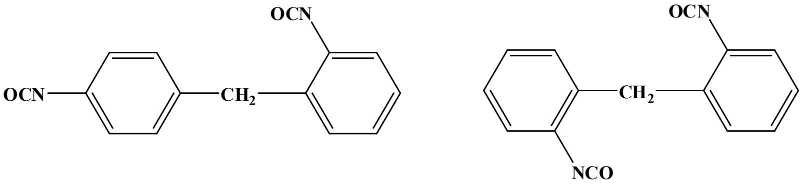
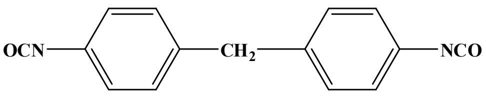


Figure 2.3 Molecular structure of MDI [1]

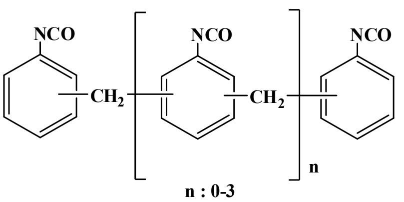
MDI is available in two types, monomeric MDI (pure MDI) and polymeric MDI. Polymeric MDI may contain 55% of 4,4'- and 2,4'-diisocyanate, 20-25% of triisocyanate and small quantities of the 2,2′-diisocyanate. Another form of MDI is pure MDI, which is produced by distillation from a polymeric MDI. It is mainly 4,4′-isomer based and usually contains a small amount of 2,4' isomer. The chemical structures of polymeric MDI and each MDI isomer are shown in Figure 2.4



2,4'-isomer **2,2'-isomer**



4,4'-isomer



Polymeric MDI

Figure 2.4 The chemical structure of MDI isomers and PMDI [1]

Because of different of functionality, structures and composition, the selection of MDI may obtain the various types of polyurethane. Table 2.2 show the suitable applications of MDI which are effect on polyurethane properties.

Table 2.2 Range of MDI variants [1]

Product description	**Average functionality**	**Polyurethane types**
Pure MDI	2.0	High performance elastomer.
Modified, liquid pure MDI	2.01-2.1	High performance elastomer. Microcellular elastomers.
Liquid, low functionality polyisocyanates	2.1-2.3	Flexible, semi-rigid and rigid (structural) foams. One-component froth.
Low viscosity liquid polyisocyanates	2.5	High density flexible foams. Structural foams.
Low viscosity polymeric MDI	2.7	Low density rigid foams. Semi-rigid foams Isocyanurate foams. Particle binders.
High functionality polymeric MDI	2.8-3.1	Rigid polyurethane and isocyanurate foams.

2.2.2 Polyols

Most of the polyols used in making polyurethane foams are classified in two types: hydroxyl-terminated polyether polyol and hydroxyl-terminated polyester polyol. They are ‘prepolymers’ whose structure influences on the final polurethane foam properties with a large dependence being on their functionality and molecular weight. The lower functionality and higher molecular weight polyols are used to produce flexible polyurethane foams. On the other hand, rigid polyurethane foams need the higher functionality and lower molecular weight polyols in order to get the high degree of crosslink which promotes to the stiffness of polymer. Generally, polyol for rigid polyurethane foam has molecular weight of 150-1000 g/mol, functionality 2.5-8.0 and hydroxyl value 250-1000 mgKOH/g. The rigidity of the foam can be increased by decreasing the chain segment length between junction points this effectively produces more tightly crosslinked networks [8].

2.2.2.1 Polyether polyols

Polyether polyols are high molecular weight polyols that range from viscous liquid to waxy solid, depending on structure and molecular weight. They are produced by the ring opening reaction of ethylene or propylene oxides using a polyfunctional initiator. Polyether polyols are widely used in polyurethane foam production due to their low cost and low viscosity. In addition, polyether-based foams have better resilience and resistance to hydrolysis than polyester-based foams. The molecular weight of polyether polyols used for producing rigid polyurethane foams the is approximately 500 g/mol in order to reduce the distance between crosslinks [9]. The structures of polyether polyol are shown in the Figure 2.5

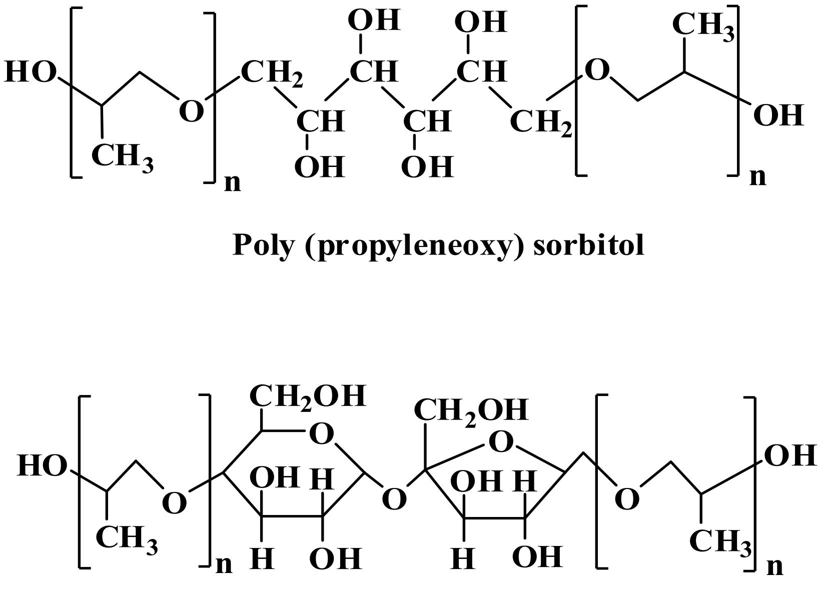


Figure 2.5 Structure of polyether polyol based on sorbitol and sucrose [9]

2.2.2.2 Polyester polyols

In comparison of polyether and polyester polyols, the polyester polyols tend to be more reactive, produce foams with better mechanical properties and resist in organic solvents. However, they are more expensive, more viscous and therefore not easy to handle. As this reason, they are only used in applications that need their superior properties. Polyester polyols are made by condensation reactions between diols (and triol) and dicarboxylic acid such as adipic acid, sebacic acid and m-phthalic acid.

2.2.3 Blowing agents

Polyurethane foams are manufactured by using blowing agents to form gas bubbles in the polymerizing reaction mixture. Blowing agents may be considered in two types as physical and chemical blowing agent. The properties of polyurethane foam are considerably influenced by the type and amount of the blowing agents. Water are the chemical blowing agent, which can react with isocyanate to generate CO_2 gas bubbles and give cellular structure of foams. In addition to generating CO_2 gas, the blowing reaction produces not only polyureas, an essential part of polyurethane hard segment, but also the exothermic heat required to complete the other reactions. Physical blowing agents have no effect upon the hard segment of polyurethane chain but tend to reduce the stiffness of polymer. On the other hand, chemical blowing agents strengthen polymer by increasing the polyurea content and degree of secondary bonding between polymer chain [10].

Recently, production of many of the physical blowing agents such as monofluorotrichloromethane and difluorodichloromethane increases the depletion of ozone layer. Consequently, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane foam. Water has replaced such environmentally hazardous blowing agents [11].

2.2.4 Surfactants

Surface-active materials or surfactants are important ingredients in the production of polyurethane foams. The presence of surfactants helps in mixing incompatible components of reaction mixture. They are very useful in foaming process where help to control the size of the foam cells by stabilizing the gas bubbles formed during nucleation. In addition, they may stabilize the rising foam by reducing stress-concentrations in the thinning cell-walls [12].

The surfactants most widely used in the polyurethane manufacturing are polydimethyl siloxane-polyether copolymers. Since the late 1950s, these so called "silicone surfactants" almost completely replaced other organic, nonionic surfactants which were previously used. The structure of silicone surfactants are illustrated in Figure 2.6, where x and y represent to the average number of dimethylsiloxy and methylpolyethersiloxy groups per molecule, respectively. Similarly, m and n correspond to the average number of polyethylene oxide and polypropylene oxide units, respectively. R is polyether capping group. Silicone surfactants are usually added in content of 0.4–2.0%wt of the polyol formulation. To get specific processing needs of different foam systems, the molecular structure may be adjusted by varying the composition and the length of the polydimethylsiloxane backbone or the number, length, and composition of the pendant polyether chains [13]. Rigid foam Surfactants normally contain 10 to 50 Si-units per molecule while the average molecular weight of a polyether chain ranges from 400 to 1500 g/mol. The ethylene oxide content normally varies from 50 to 100% and the polysiloxane/polyether ratio is in the range of 3/1 to 10/1. The total molecular weight of the surfactant amounts to 1,500 to 15,000 g/mol.

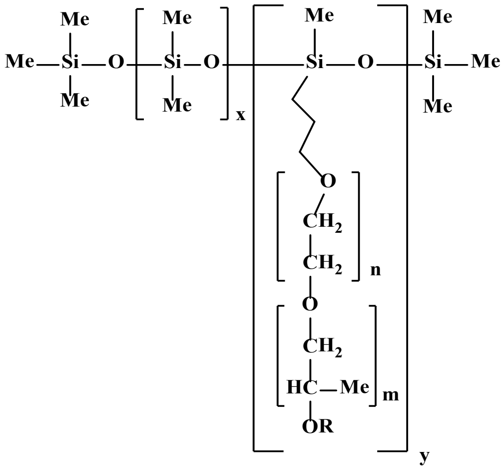


Figure 2.6 Structure of silicone surfactants used in PUR foams manufacture [6]

2.2.5 Catalysts

In polyurethane technology catalysts are widely used to give desired balance of reaction rate between compounds of differing active hydrogen activity. The important role of catalyst is not only affects the rate of chemical reaction, responsible for chain propagation, extension and crosslinking but also influence the ultimate properties of the final polymer. Catalyst for rigid polyurethane foam include a range of chemical structures, such as tertiary amines, aromatic amine, quaternary ammonium salts, alkali metal carboxylates, and organotin compounds as shown in Table 2.3. Their catalyst activity is dependent on their basicity, with steric hindrance on the active site playing a secondary role [14]. Choice of catalysts depends on catalytic activity, odor, vapor pressure, toxicity, solubility, cost and etc. The commonly used catalyst can be devided into two categories as blowing and gelling catalysts. The model diagram in Figure 2.7 shows the relationship between the catalytic activity of gelling/blowing catalysts and the properties of foam. In general, the strong gelling catalysts provide high adhesive strength and due to give the small cell size, but the reacting mixture has poor flowability and the obtained foam shows poor dimensional stability and isotropy cell structure. On the other hand, strong blowing catalysts give the low density foam with better dimensional stability because of the excellent flowability and isotropy cell structure; however, it has worse adhesive strength [14].

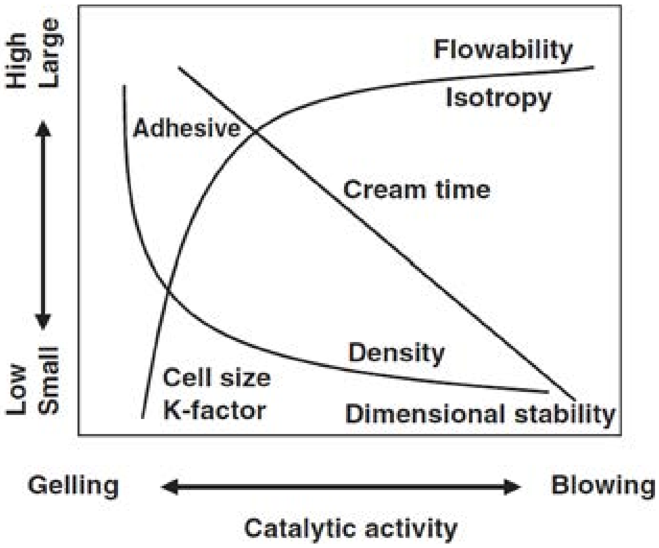


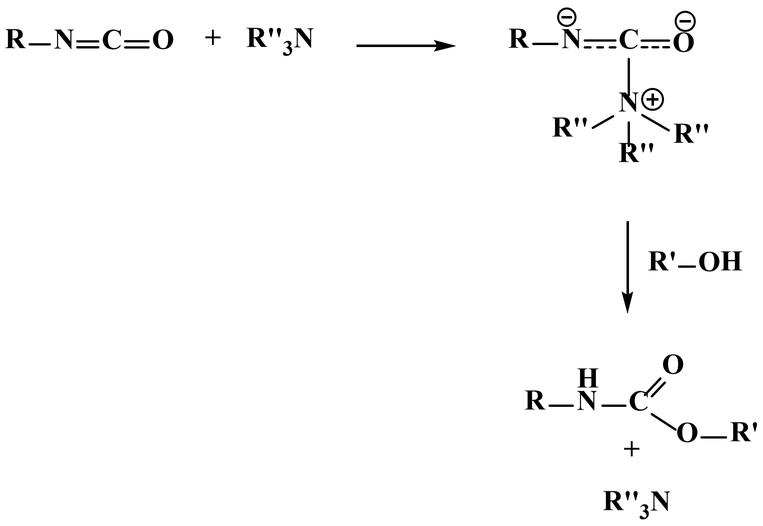
Figure2.7 Relationship between gelling/blowing activity and foam properties [14]

Table 2.3 Overview of frequently used catalysts in rigid polyurethane foams [8]

Catalyst	**Code**	**Catalytic activity**
Tertiary amines		
Pentamethyldiethylene triamine	PMDETA	Blowing
Triethylenediamine	TEDA	gelling
Dimethylcyclohexylamine	DMCHA	blowing/gelling
Quaternary ammonium salts		
2-hydroxy propyl trimethyl ammonium salt	TMR-2	delayed action/ trimer formation
Alkali metal carboxilates		
Potassium acetate	KAc	gelling/ trimer formation
Potassium octoate	KOct	gelling/ trimer formation
Tin complexes		
Stannous octate	SnOct	gelling
Dibutyltin dilaurate	DBTCL	gelling

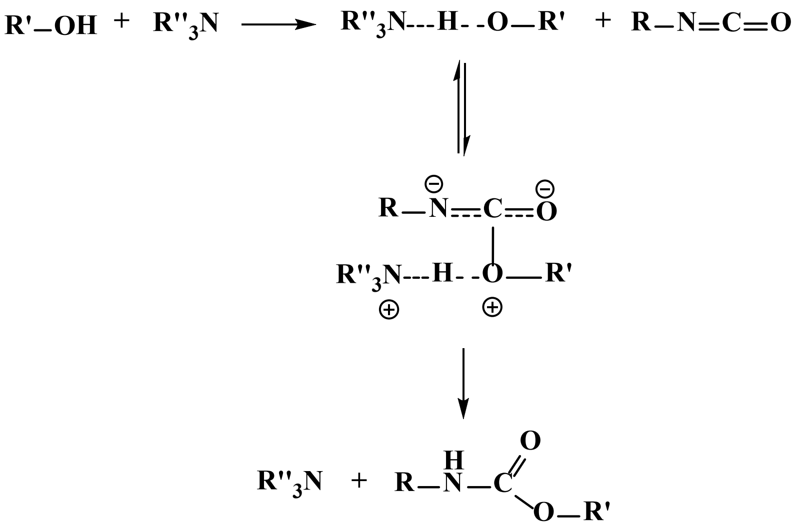
2.2.5.1 Amine Catalysts

Amine catalysts are normally considered to be predominantly blowing catalysts because they can promote the isocyanate-water reaction better than the isocyanate-polyol reaction. Tertiary amines are the most widely used polyurethane catalysts. Two mechanisms have been proposed for amine catalysis. The first is proposed by Baker (Scheme 2.1), the mechanism is started by the tertiary nitrogen of amine using its lone pair of electrons to coordinate with the carbonyl carbon of the isocyanate group, then complex intermediate is formed . This intermediate further reacts with the active hydrogen from an alcohol to produce a urethane group [6].



Scheme 2.1 Baker mechanism amine catalysts [6]

The second mechanism is proposed by Farka (Scheme 2.2), which is supported in the more recent literature, the activation starts by the tertiary nitrogen of amine interacting with the proton source (polyol, water, amine) to form a complex intermediate and then reacts with the isocyanate to produce a urethane group [6].



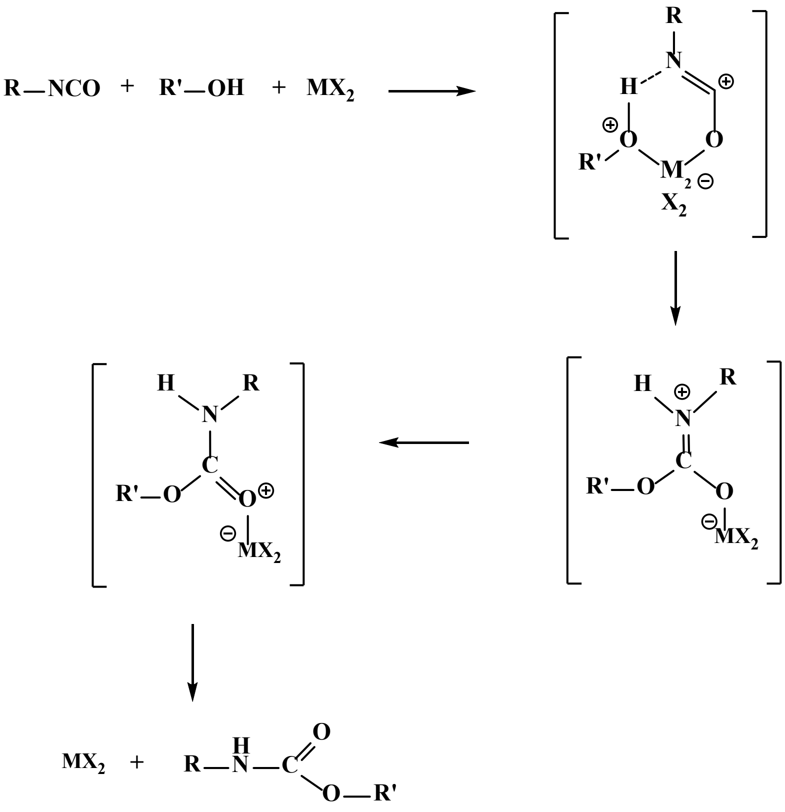
Scheme 2.2 Farka mechanism amine catalysts [6]

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

2.2.5.2 Organometallic Catalysts

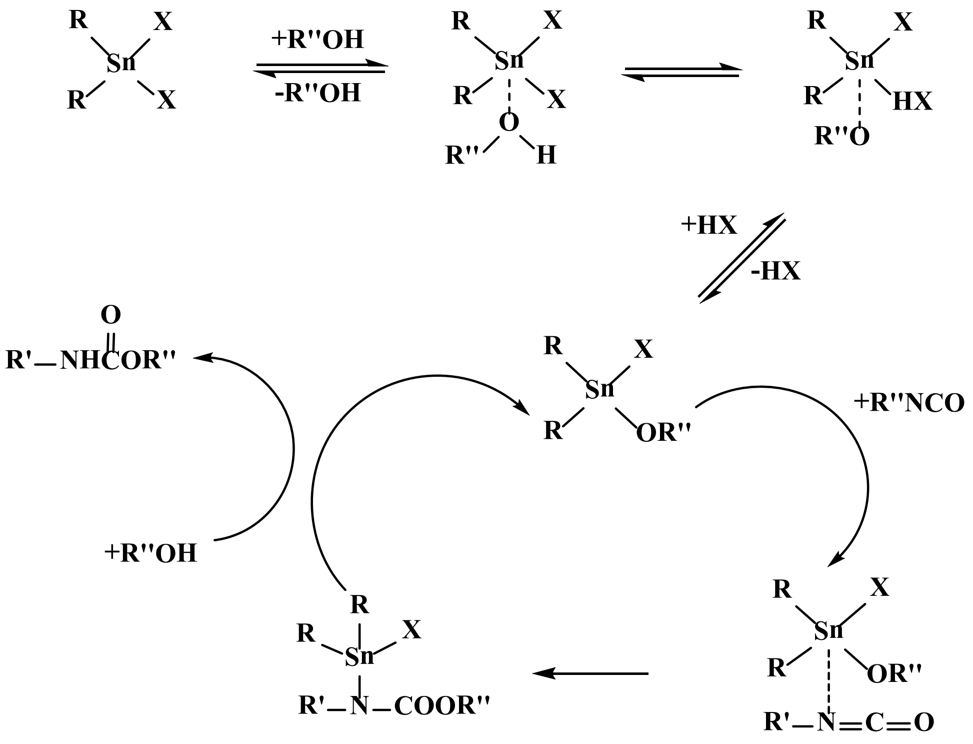
Organometallic compounds are mainly considered to be the gelling catalysts although they can affect the isocyanate-water blowing reaction. Organotins are the most widely used, but organomercury and organolead catalysts are also used in other applications. The mercury catalysts are very good for polyurethane elastomers because they give a long working time with a rapid cure and very good selectivity towards the gelation. The lead catalysts are often used in rigid spray foams. However, both mercury and lead catalysts have unfavorable hazard properties so alternatives are always being sought.

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 [6].



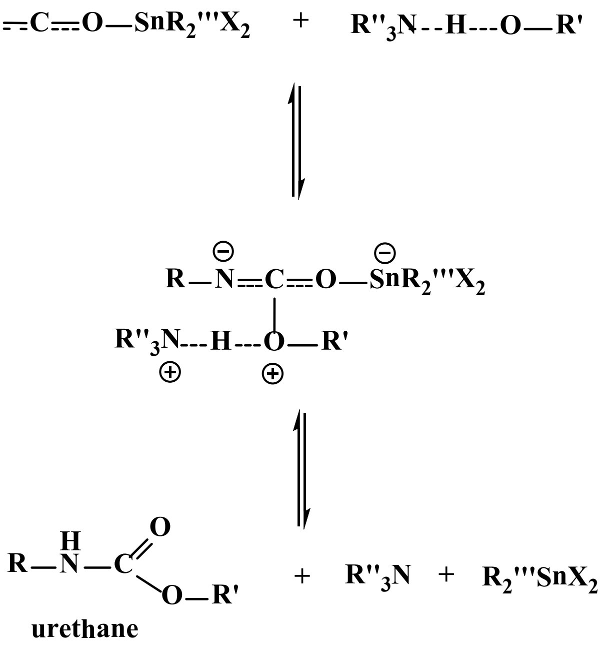
Scheme 2.3 Mechanism of tin (II) salts catalyst [6]

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 [6].



Scheme 2.4 Mechanism of tin (IV) salts catalyst [6]

Each catalyst type is specific for a particular chemical reaction. Catalyst mixtures are necessary to control the balance of gelling (polymerization) and blowing (gas generation) reactions. A typical catalyst system would consist of the mixture of a tertiary amine and organometallic compounds, especially tin compound [6]. This catalyst gives synergism in catalytic activity between tin and amine compound as shown in Scheme 2.5.



Scheme 2.5 Mechanism of tin-amine synergism [6]

2.2.6. Flame retardants

Polyurethane will burn given the sufficient heat in the presence of oxygen. Flame retardants are added to reduce flammability, ignitability and burning rate of polyurethane. The most widely used flame retardants in both flexible and rigid foam systems are chlorinated phosphate ester [1,7].

2.2.7 Fillers

Particulate and fibrous fillers may be used in most kinds of polyurethanes. Particulate fillers are used in flexible foams to reduce flammability and increase stiffness and they increase the range of operating temperature of rigid foams. Mineral fillers are sometimes used to reduce cost and to increase the compressive strength of rigid foams[1,7].

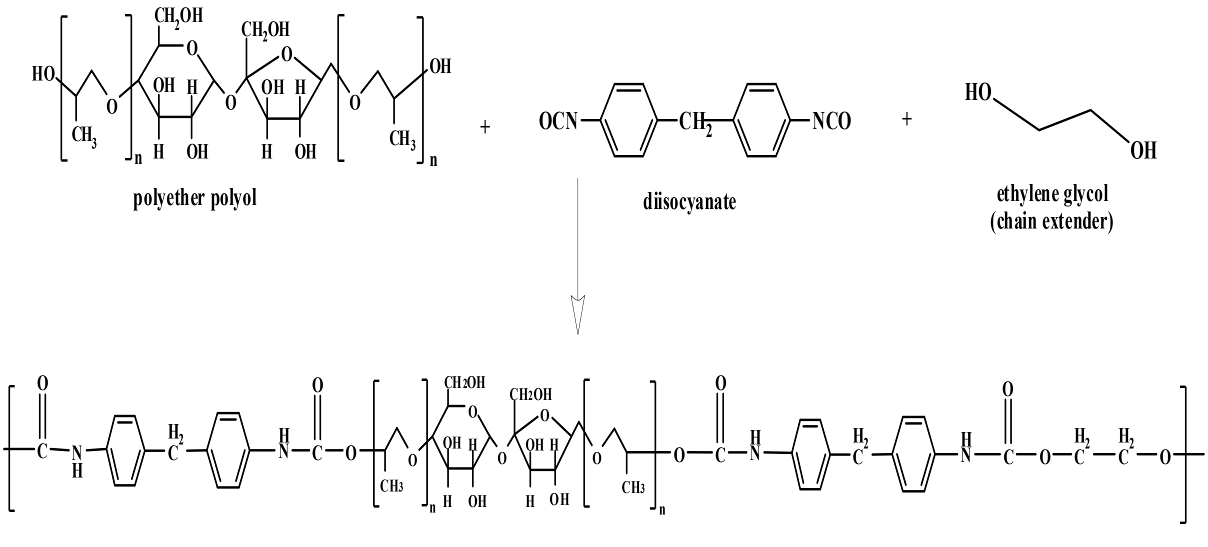
2.6.8 Colorants

Pigments are also used in polyurethane manufacturing, the characteristic of pigment used must not react with isocyanate and must be stable at the high temperature. Carbon black is usually used in order to give some protection against surface discoloration of foam cause by UV-light [1,7].

2.3 Ethylene glycol

Ethylene glycol is a compound with two hydroxyl groups attached to separate carbon atoms in an aliphatic carbon chain [15] as shown in Figure 2.8. Since this compound has low viscosity and able to blend well with many organic substances, it is widely used as a compatibilizing agents in many industries such as cosmetic, food, petroleum, pharmaceutical, surface coating, textile and etc [16]. In polyurethane manufacturing, ethylene glycol is generally used as chain extenders in order to improve the properties of polyurethane [17,18].

Chain extenders are difunctional substances, glycols, diamines or hydroxy amines [1] as shown in Table 2.4, which can react with an isocyanate to form a polyurethane or polyurea segment. Those segments are usually added in sufficient amount to premit hard segment segregation that results in an increased intermolecular association or bonding of polymer chains [17]. Scheme 2.6 shows the chemical reaction of isocyanate, polyether polyol and chain extender (ethylene glycol).



Scheme 2.6 Reaction of isocyanate, polyether polyol and ethylene glycol

Table 2.4 Chain extender and their properties [1]

Chain extender	**Funtio-nality**	**Mw.**	**OH value (mgKOH/g)**	**Weight of diisocyanate (g/100g of chain extender)**	
				TDI	**MDI**
Ethylene glycol $C_2H_4(OH)_2$	2	62.07	1801	280	401
Diethylene glycol $O(C_2H_4OH)_2$	2	106.12	1057	164	235
Propylene glycol $C_3H_6(OH)_2$	2	76.11	1474	229	329
Dipropylene glycol $O(C_3H_6OH)_2$	2	134.18	836	130	168
1,4-Butane diol $C_4H_8(OH)_2$	2	90.12	1245	193	278
Polypropylene glycol	2	400	280	43.5	62
m-Phenylene diamine $C_6H_4(NH_2)_2$	2	108.15	1037	161	231
Diethyl toluene diamine $C_6HCH_3(C_2H_5)(NH_2)_2$	2	178.27	629	97.7	140
Dimethylthio toluene diamine $C_6HCH_3(SCH_3)(NH_2)_2$	2	214.34	523	81.2	116
Water H_2O	2	18.01	6230	968	1389
Diethanolamine $HN(CH_2CH_2OH)_2$	3	105.14	1601	248	357
Triethanolamine $N(CH_2CH_2OH)_3$	3	149.19	1128	175	252
Glycerol $CH_2OHCHOHCH_2OH$	3	92.11	1827	284	407
'Daltolac' C4	3	168	1000	155	223
'Daltolac' C5	3	150	1125	175	251
'Daltolac' 50	4	468	480	75	107
'Uropol' G790	4	280	800	124	178

2.4 **Formulations** [1,7]

The content of isocyanate needed to react with polyol and other reactive ingredients can be calculated to obtain chemically stoichiometric equivalents. This theoretical amount may be adjusted up or down dependent on the PUR system, properties required, ambient conditions and production scale. The adjusted amount of isocyanate used is referred to as the "isocyanate index",

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

The conventional means to calculating the ratio of the components required for PUR manufacture is to calculate the the number of part by weight of the isocyanate required to react with 100 parts by weight of polyol and use proportionate amount of additives. The analytical data require for the calculation are the isocyanate value of the isocyanate and hydroxyl value, residual acid value and water content of the polyol and other reactive additives.

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

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

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

Hydroxyl value (hydroxyl number; OHV)

The hydroxyl value (OHV) sometime 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 KOH/g of polyol. The hydroxyl value is also defined as the number of milligrams of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound or polymer.

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

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

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

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

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

Isocyanate conversion (α), isocyanate conversion can be calculated by FTIR method [19], defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0:

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

where;

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

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

2.5 Mechanical properties

The mechanical properties of rigid foams differ markedly from those of flexible foams. The tests used to characterize both types of foam therefore differ, as do their application areas.

Compression load deflection is used to determine the compressive stress-strain behavior, i.e. it is a measure of the load-bearing properties of the material. The test method is somewhat similar to that developed for noncellular plastics. Test on rigid and flexible foams can be determined according to ASTM D 1621-04. A universal testing machine fitted with a compression rig (cage) consisting of two parallel flat plates (Figure 2.8) is used for the tests.

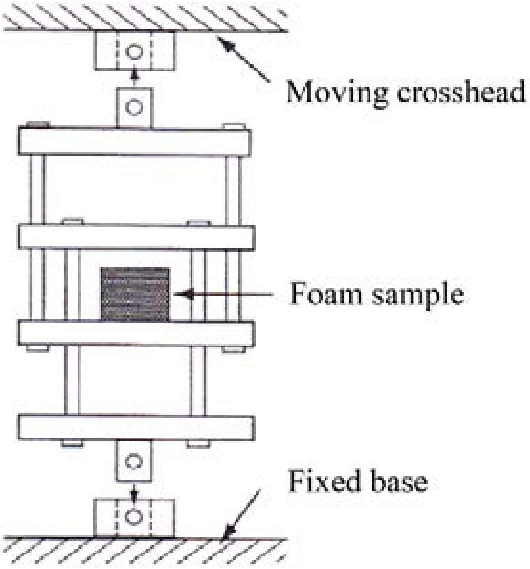


Figure 2.8 Compression load deflection test rig [7]

Compressive properties are perhaps the most important mechanical properties for cellular polymers. Compressive energy absorption characteristics and deformation characteristics of foam depend mainly on density, type of base polymer and the predominance of either open or closed cells. In simple terms, open cell foam (invariably flexible) relies on cell walls bending and bucking, which is essentially a reversible process (Figure 2.9).

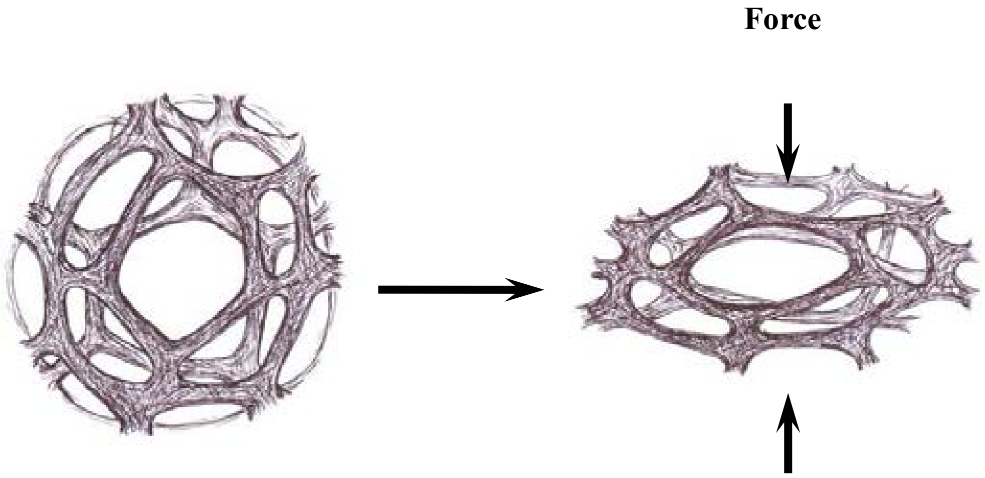


Figure 2.9 Schematic representation of open cell deformation [7]

In addition, as the cell become more compacted during compression, the escape of air through and out of the foam will become increasingly more difficult. The entrapped air will therefore offer some resistance to foam deformation during the final stages of compression. On the other hand, air flow is not a consideration with closed cell foams. In this case (Figure 2.10) deformation involves cell wall bending/bucking (reversible), gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rapture.

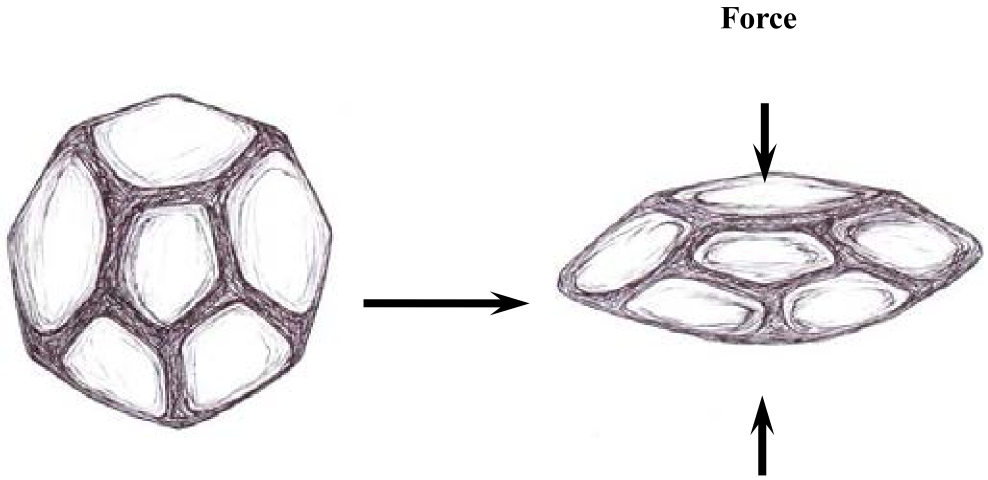


Figure 2.10 Schematic representation of closed cell deformation [7]

Closed cell rigid foams (e.g. PUR foams) exhibit 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 2.11 show typical compression stress-strain curve of rigid cellular polymers.

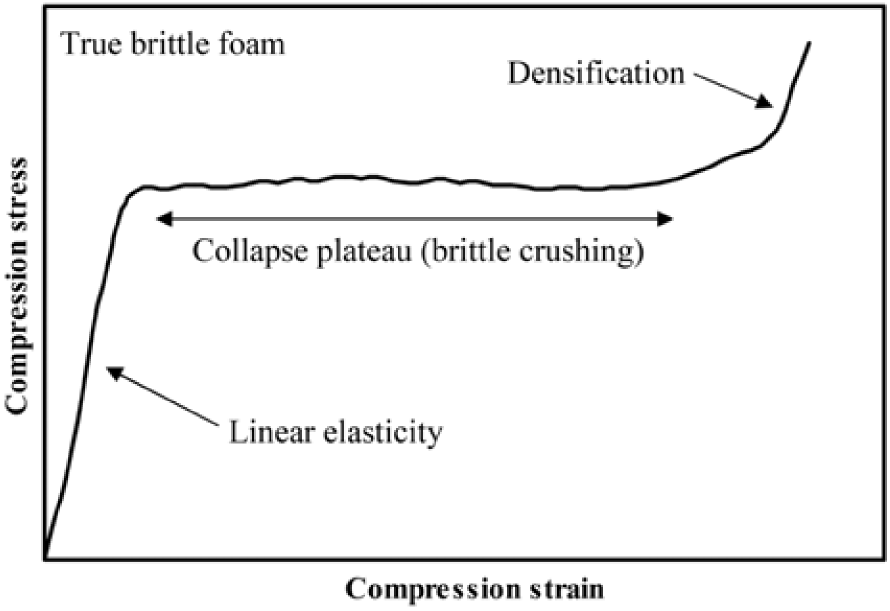


Figure 2.11 Typical compression stress-strain curve for rigid foams [9]

For rigid foams, elements of true brittle crushing are superimposed on the elastic/plastic response. The erratic nature of the collapse plateau corresponds to intermittent rupturing of individual cells. Due to cell rupture in rigid foams, resilience is dramatically affected. Foams can generally withstand only single impacts, for example the liners used inside riding or cycle helmets.

The compressive strength of rigid cellular polymers is usually reported at some definite deformation (5 or 10%). The modulus is then extrapolated to 0% deformation unless otherwise stated. Structural variables that affect the compressive strength and modulus of this foam are, in order of decreasing importance, plastic phase composition, density, cell structure, and gas composition.

Literature reviews

The investigation of structure-property relationships in polyurethanes has gained importance due to their various applications. The properties of polyurethanes can be manipulated by variation of their chemical ingredient. Recent researches concerned about the effect of chemical ingredients in the formulation, i.e. polyols, isocyanate compounds, blowing agents, surfactants and catalysts, on the polyurethane properties as described below:

Deanin *et al* [20] studied the effect of variation of polyol funtional groups, polyol molecular weight and NCO/OH equivalent ratio. Polyurethanes were prepared from 125-M® MDI isocyanate and three polyester polyols of Mw = 1000, 2000 and 3000 or three polyether polyol of Mw = 650, 1000 and 2000. The results of this work were concluded that the increase in NCO/OH ratio also increased mechanical properties such as hardness, tensile modulus, ultimate tensile strength, tear strength, ultimate elongation. In addition, types of polyol also influenced polyurethane properties. Polyether polyols gave higher hardness, tensile modulus, ulimate tensile strength, tear strength and rebond than polyester polyols. Lower molecular weight polyols gave higher hardness, tensile modulus, ulimate tensile strength and tear strength. On the other hand, higher molecular weight polyols gave higher ultimate elongation.

Harris *et al* [21] investigated the effect of variation of isocyanate index in the chemical composition of the reaction between 4,4′-diphenylmethane diisocyanate and 1,4-butanediol on the properties of polyurethanes. The results indicated that the properties such as solvent resistance, melting point, hardness, tensile strength were improved with increasing isocyanate index, which was increase in the amount of 4,4′-diphenylmethane diisocyanate.

Petrovic and Simendic [22] studied the effect of variation of three series of polyurethanes based on 4,4′-diphenylmethane diisocyanate, 1,4-butanediol and three polytetramethylene oxide diols of Mw = 650, 1000 and 2000. It was found that the maximum tensile strength obtained when the soft segment concentration, which was the concentration of polytetramethylene oxide diol, was 40-50%. The elongation at break increased linearly with polytetramethylene oxide diol concentration. On the other hand, hardness, modulus and tear strength are mainly affected by hard segment, which increased linearly with 4,4′-diphenylmethane diisocyanate and1,4-butanediol concentration

Han *et al* [12] studied the effects of silicone surfactant on cell size and thermal conductivity of rigid polyurethane foams. The results showed that the optimum content of the silicone surfactant at 1.5 to 2.5 pbw for various surfactants could reduce the cell size and lower the thermal conductivity. From the relationship between the cell size and the thermal conductivity, the smaller cell size could promote the thermal insulation property of the rigid polyurethane foams.

Lim *et al* [23] reported the effects of silicone surfactant in rigid polyurethane foams. They found that cream time, gel time and tack free time increased with the content of surfactant increasing due to the increased in stability of reaction mixture and rising bubbles. Foam density has a tendency to decrease with increasing surfactant concentration due to the increased blowing efficiency in the presence of surfactant.

Lim *et al* [24] studied the effects of blowing agent types on the properties of rigid polyurethane foams. Three types of environmental friendly blowing agents, namely HFC 365mfc, HFC 245fa and water were used. The results of this work were concluded that among three blowing agents, water gave the highest reactivity to induce the earliest bubble, temperature and pressure rises. The high efficiency in blowing of water leaded to the lowest foam density and compression strength as well as largest cell size. However, water was the chemical blowing agent, which gave the urea linkages through the reaction between water and isocyanate. Those linkages effected on foam properties, water blown foams showed the highest glass transition temperature (T_g) and had dimensional stability at high temperature.

In polyurethane foam manufacturing, catalyst is one component has played important role in catalytic system. Catalyst is necessary for the production of polyurethane foams because the reaction between hydroxyl group and diisocyanate is slow. There are many researches concerning about the catalyst for polyurethane (PUR) and polyisocyanurate (PIR) foams production as follows:

Maris *et al* [14] studied polyurethane catalyzed by tertiary amines. The results found that tertiary amines played an important role in polyurethane production. With a good selection of catalyst, the desired profile in reaction, foaming, flow ability and foam properties could be obtained. The selection of catalyst was based on its activity as well as performance on physical properties of foam. Depending on chemical structure of catalyst, the catalytic activity would be different. This activity related to catalyze not only gelling and blowing reaction but also allophanate, biuret and trimerization reaction.

Strachota *et al* [25] reported the comparison of environmentally friendly, selective polyurethane catalysts. Selected commercially available amines, including N-substituted morpholines, were used as single catalyst and catalyst mixtures for the polyurethane foam preparation. The objective of this research was the search for environmentally attractive replacements of classical catalyst such as dibutyltin dilaurate (DBTDT), diazbicyclooctane and N,N-bis(2-dimethylaminoethyl)methylamine. the results showed that the functionalized morpholine (MEO) showed a poor gelling activity even in comparison to other morpholines. Its reduced mobility due to the desired incorporation into the polyurethane, as well as H-bridging is the probable reasons. Higher amounts of MEO in combination with an analogously OH-functionalized good gel catalyst should lead to better results

Inoue *et al* [5] studied the catalytic activity of M(acac)$_n$-amine catalysts, which were co-catalysts of metal acetylacetonate [M(acac)$_n$, where M= Cu, Mn, Fe, Co and Ni] and tertiary amines, as a new catalytic system. The activity of these catalysts was compared with a commercial catalyst, dibutyltin dilaurate (DBTDL). The results indicated that instead of DBTDT, the tertiary amine-M(acac)$_n$ catalysts could be used to accelerate addition polymerization between hexamethylene diisocyanate (HDI) and diethylene glycol (DEG). The obtained results in Table 2.5

showed that the catalytic activity of $Mn(acac)_n$-TEDA (TEDA = triethylenediamine) catalysts was comparable to commercial catalyst (DBTDL).

Table 2.5 Polyaddition reaction rate between HDI and DEG* [5]

catalyst	reaction rate k/L $mol^{-1}h^{-1}$	catalytic constant (Kc) $Kc \times 10^4/L^2eq^{-1}\ mol^{-1}h^{-1}$
None	0.2	-
DBTDL	139.6	3.8
$Mn(acac)_2$	52.3	1.4
TEDA-$Mn(acac)_2$	102.2	2.8

*[catalyst] = 0.0036 mol L^{-1}, [HDI] = [DEG] = 0.073 mol L^{-1}, temperature = 30 °C

Kurnoskin [26] synthesized metaliferous epoxy chelate polymers (MECPs) by hardening of the diglycidyl ether of bisphenol A (DGEBA) with chelates of metal complexes between transition metal cations (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{4+} and Fe^{3+}) and aliphatic amines (ethylenediamine,diethylenetriamine, triethylenetetramine and cycloethylated diethylenetriamine). The structures of chelates as hardeners are shown in Figure 2.12. They found that the reaction rate of complex formation depended on both metal cation and ligand and decreased in the following order: ligand : trien ~ cydien > dien > en and Metal : Cu^{2+} > Co^{2+} > Fe^{3+} > Ni^{2+} > Zn^{2+}

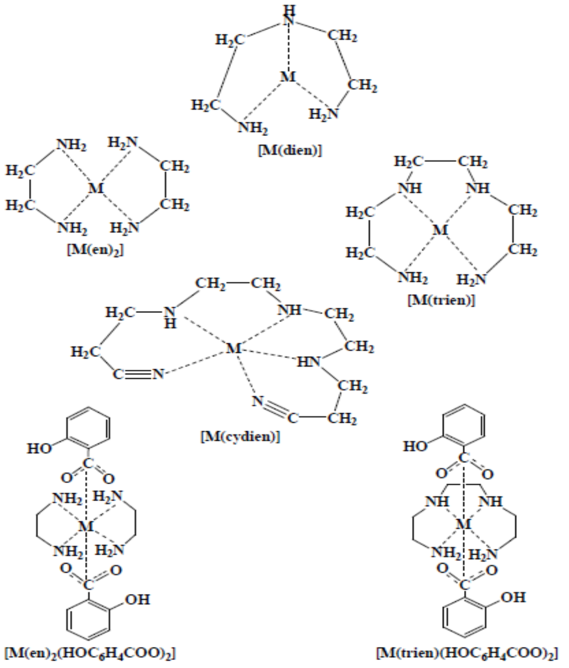


Figure 2.12 Structures of metal complexes and metal salt complexes [26]

The researchers in our group, Pengjam *et al* [9], synthesized new catalysts for rigid polyurethane (RPUR) foams. These catalysts were metal(II)-amine complexes, [$M(OAc)_2(en)_2$ and $M(OAc)_2(trien)$, where M = Cu, Mn, Ni, Co; en = ethylenediamine and trien = triethylenetetramine] synthesized from various metal acetates [$M(OAc)_2$] and amines using acetone or methanol as a solvent. The catalytic activity of metal(II)-amine complexes and properties of RPUR foams were investigated and compared to those prepared by N,N dimethylcyclohexylamine (DMCHA), which is a common commercial tertiary amine catalyst used in the preparation of RPUR foams. They found that $Cu(OAc)_2(en)_2$, had comparable catalytic activity to a reference commercial catalyst (DMCHA).

Although these metal-amine complexes had good catalytic activity, but the organic solvents, namely acetone and methanol, had to be removed from metal complexes before using and this purification took a long time. Moreover, the metal complexes were obtained in powder or viscous liquid forms, which were difficult to obtain homogeneous mixing with the other components in RPUR foam preparation. This non-uniform mixing of starting materials may deteriorate the final properties of RPUR foams.

Ethylene glycol is known to be a good solvent used to blend the ingredients in polyurethane formulation to obtain good mixing. This is because ethylene glycol has low viscosity and able to blend well with both polyol and isocyanate compound. There are reports about using ethylene glycol in polyurethane foams production as listed below:

The research studied about using ethylene glycol as a compatibilizing agent in polyurethane foam reported by Cunningham *et al* [16]. In the experiment, they mixed a dry starch-oil composite (Fantesk$^{®}$) with three compatibilizing glycols (ethylene, polyethylene and propylene glycol) and then added it into polyurethane foam formulation in order to improve the biodegradable property of foam. The result indicated that ethylene glycol allowed the dry composite to blend well with the other ingredients in foam formulation and the presence of dry starch-oil composite would make the foams more susceptible to biodegradation.

There are other researches [17,18] reported about using ethylene glycol as a chain extender in polyurethane foam preparation. They found that addition of chain extender (ethylene glycol) effected on both final properties and morphology of polyurethane foams.

Therefore, we were interested to develop the synthesis of metal-amine complexes, $[M(OAc)_2(en)_2$ and $M(OAc)_2(trien)$, from Pengjam's work [9] to obtain the solution of metal(II)-amine complexes in ethylene glycol. Metal-amine complexes would be synthesized using ethylene glycol as a solvent. After the complex formation was completed and the solution of metal-amine complexes in ethylene glycol was obtained, it could be used as catalysts in the preparation of rigid polyurethane foam without purification. Besides metal acetates, metal-amine complexes would be prepared using other metal salts, namely copper(II) acetylacetonate, copper(II) nitrate and copper(II) chloride. It was expected that the solution of metal-amine complexes in ethylene glycol would mix very well with other ingredients in the foam formulation and the obtained rigid polyurethane foams would have good properties.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and starting materials

3.1.1 Chemicals for copper-amine complexes synthesis

Ethylene glycol was obtained from Carlo Erba. Copper(II) acetate monohydrate [$Cu(OAc)_2.H_2O$] was obtained from TCI Tokyo Kasei, The other chemicals, namely Copper(II) acetylacetonate [$Cu(acac)_2$], copper(II) nitrate trihydrate ($Cu(NO_3)_2\cdot 3H_2O$), copper(II) chloride dihydrate ($CuCl_2\cdot 2H_2O$), zinc acetate

dihydrate [$Zn(OAc)_2.2H_2O$], ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentaime (tetraen) and pentaethylenehexamine (pentaen) were obtained from Fluka and Aldrich.

3.1.2 Starting materials for foam preparation

Sucrose-based polyether polyol [Daltolac® R180; functionality = 4.3 and hydroxyl value (OHV) = 440 mgKOH/g], 4,4'-methane diphenyl diisocyanate (Polymeric MDI; PMDI) [Suprasec® 5005; %NCO of PMDI = 31.0 %wt., average functionality = 2.7], polysiloxane surfactant (Tegostab® B8460) and N,N-dimethylcyclohexylamine (DMCHA; reference commercial catalyst) were supplied from Huntsman (Thailand) Co., Ltd. Distilled water was used as a chemical blowing agent. Copper-amine complexes were synthesized and used as catalysts.

3.2 Synthetic procedures

Synthesis of copper-amine and mixed metal-amine complexes were carried out using ethylene glycol as a solvent to obtain a homogeneous solution containing copper-amine or mixed metal-amine complexes. The procedure was adapted from the synthetic method reported in the literature [9]. The catalyst solution could be further used in the preparation of RPUR foam without purification.

3.2.1 The optimum catalyst (copper-amine complex) content in ethylene glycol

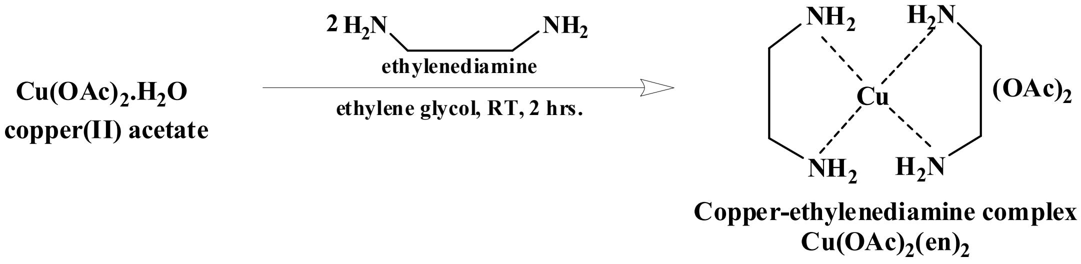
The series of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) were chosen to study about the optimum ethylene glycol content for using as a solvent in synthesizing copper-amine complexes catalysts. In the experiment, ethylene glycol content was represented in the term of catalyst concentration. The catalyst concentrations were varied at 15, 30 and 60%wt in ethylene glycol as shown in Table 3.1

Table 3.1 Composition of chemicals in the synthesizing of copper-amine complexes at different concentrations in ethylene glycol (EG)

Catalysts (copper-amine complexes)	Wt. of copper compound (g)	Vol. of amine (ml)	Vol. of EG (ml)
15%wt of catalyst in EG			
$Cu(OAc)_2(en)_2$	0.624	0.42	5.7
$Cu(OAc)_2$(trien)	0.578	0.43	5.7
$Cu(OAc)_2$(tetraen)	0.514	0.49	5.7
$Cu(OAc)_2$(pentaen)	0.462	0.59	5.7
30%wt of catalyst in EG			
$Cu(OAc)_2(en)_2$	0.624	0.42	2.4
$Cu(OAc)_2$(trien)	0.578	0.43	2.4
$Cu(OAc)_2$(tetraen)	0.514	0.49	2.4
$Cu(OAc)_2$(pentaen)	0.462	0.59	2.4
60%wt of catalyst in EG			
$Cu(OAc)_2(en)_2$	0.624	0.42	0.7
$Cu(OAc)_2$(trien)	0.578	0.43	0.7
$Cu(OAc)_2$(tetraen)	0.514	0.49	0.7

$Cu(OAc)_2$(pentaen)	0.462	0.59	0.7

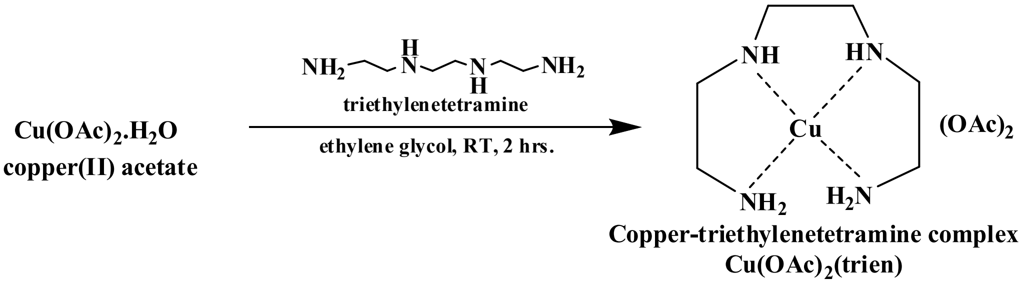
3.2.2 Synthesis of copper-ethylenediamine complex $[Cu(OAc)_2(en)_2]$ from copper(II) acetate



Scheme 3.1 Synthesis of copper-ethylenediamine complex $[Cu(OAc)_2(en)_2]$ from copper(II) acetate

$Cu(OAc)_2(en)_2$ was prepared by modification of the method reported in the literature [9]. The mole ratio of copper(II) acetate monohydrate to ethylenediamine was 1:2. A solution of 30%wt of $Cu(OAc)_2(en)_2$ in ethylene glycol was prepared using the following procedure: a solution of ethylenediamine (0.42 ml, 6.28 mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetate monohydrate (0.624 g, 3.12 mmol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 30%wt of $Cu(OAc)_2(en)_2$ in ethylene glycol was obtained as an odorless purple solution with low viscosity: m/z = 303.05, UV; λ_{max} (MeOH) = 232 nm, molar absorptivity (ε) = 5,667.

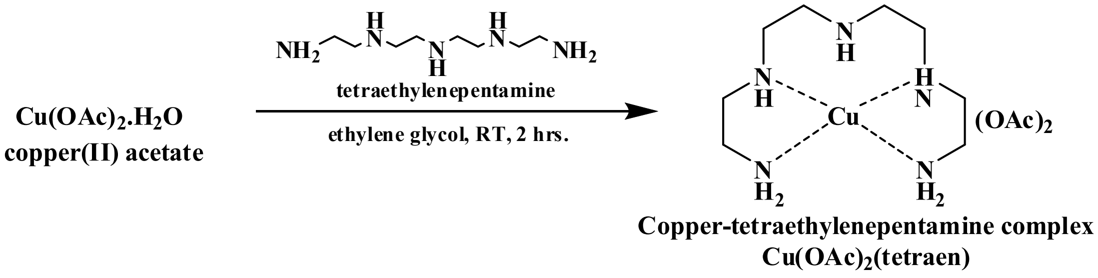
3.2.3 Synthesis of copper-triethylenetetramine complex $[Cu(OAc)_2(trien)]$ from copper(II) acetate



Scheme 3.2 Synthesis of copper-triethylenetetramine complex [Cu(OAc)$_2$(trien)] from copper(II) acetate

The mole ratio of copper(II) acetate monohydrate to triethylenetetramine was 1:1. A solution of 30%wt of Cu(OAc)$_2$(trien) in ethylene glycol was prepared using the following procedure: a solution of triethylenetetramine (0.43 ml, 2.89 mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetate monohydrate (0.578 g, 2.89 mmol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 30%wt of Cu(OAc)$_2$(trien) in ethylene glycol was obtained as an odorless blue solution and low viscosity: *m/z* = 389.22, UV; $\lambda_{\max}$ (MeOH) = 258 nm, molar absorptivity (ε) = 4,322.

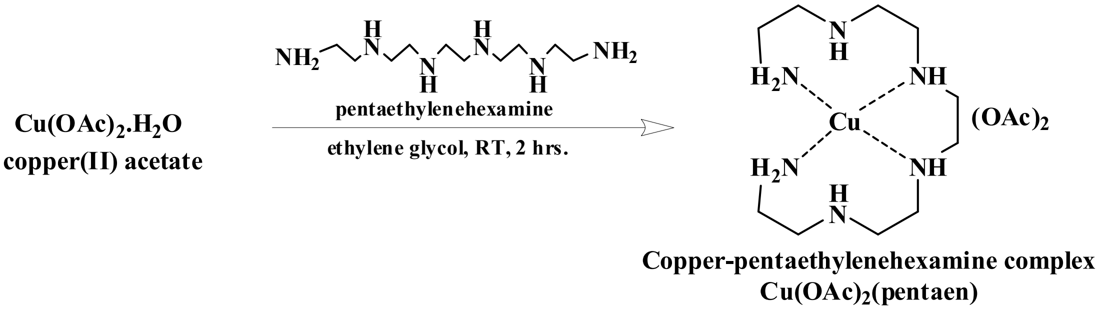
3.2.4 Synthesis of copper-tetraethylenepentamine complex [Cu(OAc)$_2$(tetraen)] from copper(II) acetate



Scheme 3.3 Synthesis of copper-tetraethylenepentamine complex [Cu(OAc)$_2$(tetraen)] from copper(II) acetate

The mole ratio of copper(II) acetate monohydrate to tetraethylenepentamine was 1:1. A solution of 30%wt of Cu(OAc)$_2$(tetraen) in ethylene glycol was prepared using the following procedure: a solution of tetraethylenepentamine (0.49 ml, 2.58 mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetate monohydrate (0.514 g, 2.57 mmol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 30%wt of Cu(OAc)$_2$(tetraen) in ethylene glycol was obtained as an odorless blue solution and low viscosity: *m/z* = 372.21, UV; λ_{max} (MeOH) = 268 nm, molar absorptivity (ε) = 4,226.

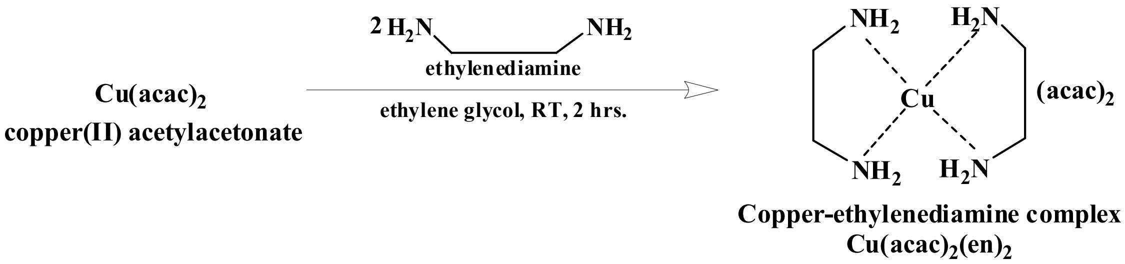
3.2.5 Synthesis of copper-pentaethylenehexamine complex [Cu(OAc)$_2$(pentaen)] from copper(II) acetate



Scheme 3.4 Synthesis of copper-pentaethylenehexaamine complex [Cu(OAc)$_2$(pentaen)] from copper(II) acetate

The mole ratio of copper(II) acetate monohydrate to pentaethylenehexamine was 1:1. A solution of 30%wt of Cu(OAc)$_2$(pentaen) in ethylene glycol was prepared using the following procedure: a solution of pentaethylenehexamine (0.59 ml, 2.31 mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetate monohydrate (0.462 g, 2.31 mmol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 30%wt of Cu(OAc)$_2$(pentaen) in ethylene glycol was obtained as an odorless green-blue solution and low viscosity: *m/z* = 415.30, UV; λ_{max} (MeOH) = 265 nm, molar absorptivity (ε) = 4,725.

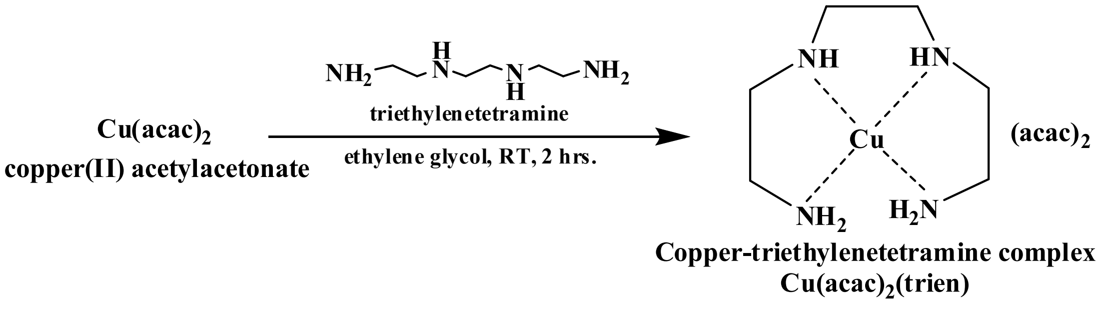
3.2.6 Synthesis of copper-ethylenediamine complex [Cu(acac)$_2$(en)$_2$] from copper(II) acetylacetonate



Scheme 3.5 Synthesis of copper-ethylenediamine complex [$Cu(acac)_2(en)_2$] from copper(II) acetylacetonate

The mole ratio of copper(II) acetylacetonate to ethylenediamine was 1:2. A solution of 30%wt of $Cu(acac)_2(en)_2$ in ethylene glycol was prepared using the following procedure: a solution of ethylenediamine (0.36 ml, 5.24 mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetylacetonate (0.685 g, 2.62 mmol) was added and the reaction mixture was stirred continuously at room temperature for 24 hours. Solution of 30%wt of $Cu(acac)_2(en)_2$ in ethylene glycol was obtained as an odorless dark-brown solution and low viscosity: *m/z* = 382.99, UV; λ_{max} (MeOH) = 295 nm, molar absorptivity (ε) = 6,571.

3.2.7 Synthesis of copper-triethylenetetramine complex [$Cu(acac)_2(trien)$] from copper(II) acetylacetonate

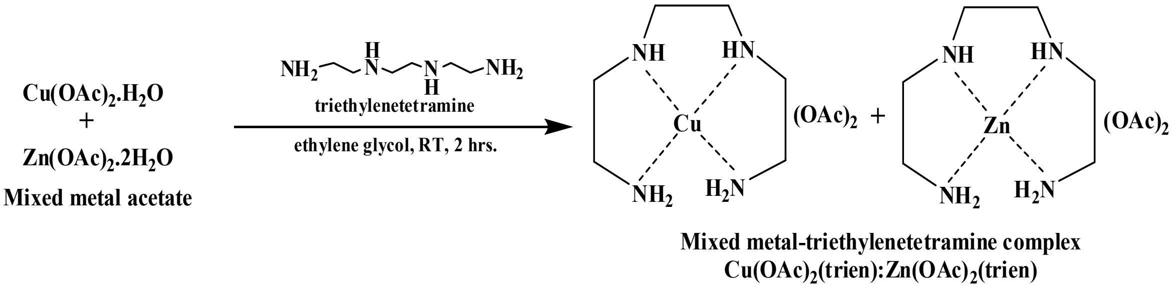


Scheme 3.6 Synthesis of copper-triethylenetetramine complex [$Cu(acac)_2(trien)$] from copper(II) acetylacetonate

The mole ratio of copper(II) acetylacetonate to triethylenetetramine was 1:1. A solution of 30%wt of $Cu(acac)_2(trien)$ in ethylene glycol was prepared using the following procedure: a solution of triethylenetetramine (0.37 ml, 2.45

mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetylacetonate (0.642 g, 2.45 mmol) was added and the reaction mixture was stirred continuously at room temperature for 24 hours. Solution of 30%wt of Cu(acac)$_2$(trien) in ethylene glycol was obtained as an odorless dark-green solution and low viscosity: *m/z* = 469.07, UV; λ_{max} (MeOH) = 273 nm, molar absorptivity (ε) = 5,129.

3.2.8 Synthesis of mixed metal-triethylenetetramine complex [Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien)]



Scheme 3.7 Synthesis of mixed metal- triethylenetetramine complex [Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien)]

The mole ratio of copper(II) acetate monohydrate to Zinc(II) acetate dihydrate and triethylenetetramine was 0.5:0.5:1. A solution of 30%wt of Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) in ethylene glycol was prepared using the following procedure: a solution of triethylenetetramine (0.42 ml, 2.81 mmol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 15 minutes. After that, copper(II) acetate monohydrate (0.280 g, 1.40 mmol) and zinc(II) acetate dihydrate (0.308 g, 1.40 mmol) were added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 30%wt of Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) in ethylene glycol was obtained as an odorless blue solution with low viscosity: UV; λ_{max} (MeOH) = 259 nm, molar absorptivity (ε) = 4,100.

Other copper-amine complexes and mixed metal-amine complexes were prepared using the same procedure as described above. The compositions of chemicals in the synthesizing of all copper-amine and mixed metal-amine complexes in ethylene glycol are shown in Tables 3.2 and 3.3.

Table 3.2 Composition of chemicals in the synthesis of copper-amine complexes at the concentration of 30%wt of copper-amine complexes in ethylene glycol (EG)

Copper-amine complexes	Wt. of copper compound (g)	Vol. of amine (ml)	Vol. of EG (ml)	Appearance
$Cu(X)_2$:en =1:2				
$Cu(OAc)_2(en)_2$	0.624	0.42	2.4	Non-viscous purple solution
$Cu(acac)_2(en)_2$	0.685	0.36	2.4	Non-viscous dark brown solution
$Cu(NO_3)_2(en)_2$	0.668	0.37	2.4	Non-viscous purple solution with precipitated solid
$Cu(Cl)_2(en)_2$	0.587	0.46	2.4	Non-viscous purple solution
$Cu(X)_2$:trien =1:1				
$Cu(OAc)_2(trien)$	0.578	0.43	2.4	Non-viscous blue solution
$Cu(acac)_2(trien)$	0.642	0.37	2.4	Non-viscous dark green solution
$Cu(NO_3)_2(trien)$	0.623	0.39	2.4	Non-viscous blue solution
$Cu(Cl)_2(trien)$	0.539	0.47	2.4	Non-viscous blue solution
$Cu(X)_2$:tetraen =1:1				
$Cu(OAc)_2(tetraen)$	0.514	0.49	2.4	Non-viscous blue solution
$Cu(acac)_2(tetraen)$	0.580	0.43	2.4	Non-viscous green blue solution
$Cu(NO_3)_2(tetraen)$	0.561	0.44	2.4	Non-viscous blue solution
$Cu(Cl)_2(tetraen)$	0.474	0.53	2.4	Non-viscous blue solution
$Cu(X)_2$:pentaen =1:1				
$Cu(OAc)_2(pentaen)$	0.462	0.59	2.4	Non-viscous green blue solution
$Cu(acac)_2(pentaen)$	0.530	0.52	2.4	Non-viscous dark green solution

$Cu(NO_3)_2$(pentaen)	0.510	0.54	2.4	Non-viscous green blue solution
$Cu(Cl)_2$(pentaen)	0.423	0.64	2.4	Non-viscous green blue solution

Table 3.3 Composition of chemicals in the synthesis of mixed metal-amine at the concentration of 30%wt of mixed metal -amine complexes in ethylene glycol (EG)

Mixed metal-amine complexes	**Wt. of Metal compound (g)**		**Vol. of amine (ml)**		**Vol. of EG (ml)**	**Appearance**
	$Cu(OAc)_2$	**$Zn(OAc)_2$**	**en**	**trien**		
$Cu(OAc)_2$(en): $Zn(OAc)_2$(en)	0.303	0.333	0.41	-	2.4	Non-viscous purple solution
$Cu(OAc)_2$(trien): $Zn(OAc)_2$(trien)	0.280	0.308	-	0.42	2.4	Non-viscous blue solution

[*] Mole ratio of $Cu(OAc)_2$:$Zn(OAc)_2$:en and $Cu(OAc)_2$:$Zn(OAc)_2$:(trien) is 0.5:0.5:2 and 0.5:0.5:1, respectively.

3.3 Rigid polyurethane (RPUR) foam preparations

The step of rigid polyurethane foams preparation catalyzed by copper-amine complexes, mixed metal-amine complexes or reference commercial catalyst (DMCHA) is illustrated in Figure 3.1. The RPUR foams were prepared by two steps of mixing using mechanical mixing technique. The first step, polyol, surfactant, catalysts (copper-amine complexes, mixed metal-amine complexes or DMCHA) and blowing agent (distilled water) were mixed into a 700 ml paper cup. In the next step, Polymeric MDI was added to mix with the other ingredients from first. Then, the mixture were mixed again by mechanical stirrer at 2000 rpm for 20 s to obtained the homogeneous mixture. During the reaction, cream time (which is the time of the beginning of reaction or blowing reaction), gel time (which is the time of gel point of foam mixture or gelling reaction),tack free time (which is the time of the foam could not tack with other materials or crosslink reaction) and rise time (which is the time of the foam stop rising) were investigated. After that, the foams were kept at room temperature for 48 hrs in order to complete all of the polymerization reactions. After 48 hrs, the foams were cut to investigated physical and mechanical properties.

Tables 3.4 and 3.5. demonstrated the foam formulations with different NCO indexes

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

Formulations (pbw[*])	**NCO index[**]**		
	100	**130**	**150**
Polyol (Daltolac® R180)	100	100	100
Catalysts (metal complexes in EG)	1.0	1.0	1.0
Surfactant (Tegostab® B8460)	2.5	2.5	2.5
Blowing agent (distilled water)	3.0	3.0	3.0
Polymeric MDI (Suprasec® 5005)	160	208	240

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

Table 3.5 RPUR foam formulations at different NCO indexes (in gram unit, cup test)

Formulations (pbw)	**NCO index[**]**		
	100	**130**	**150**
Polyol (Daltolac® R180)	10.0	10.0	10.0
Catalysts (metal complexes in EG)	0.1	0.1	0.1
Surfactant (Tegostab® B8460)	0.25	0.25	0.25
Blowing agent (distilled water)	0.30	0.30	0.30
Polymeric MDI (Suprasec® 5005)	16.0	20.8	24.0

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

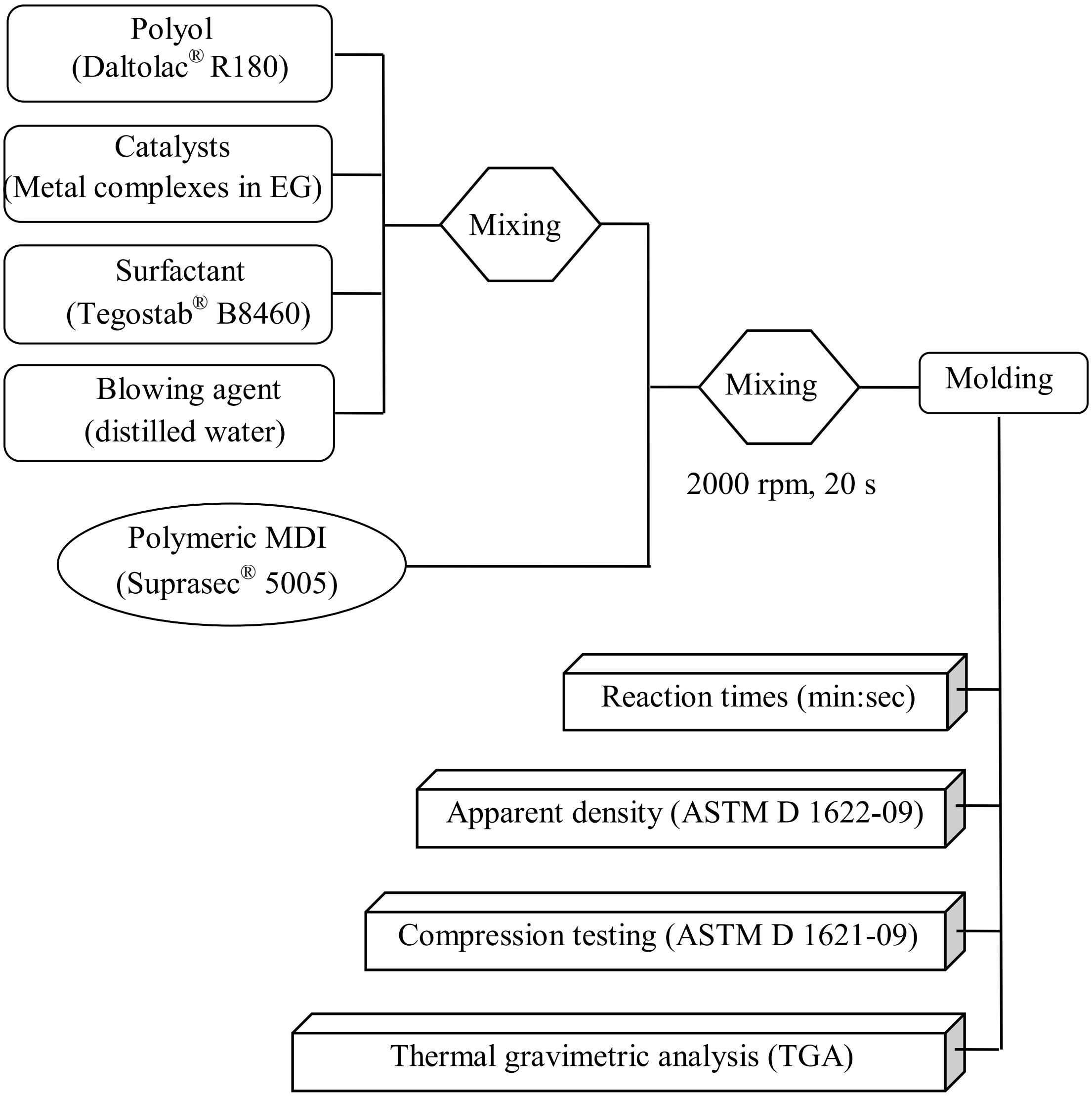


Figure 3.1 RPUR foams processing

3.4 Characterization of copper-amine complexes

3.4.1 Ultraviolet-visible spectroscopy

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

3.4.2 Mass spectrometry (MS)

Electrospray ionization (ESI) mass spectrometry was used to confirmed the complex formations by their unique mass (mass-to-charge ratio). This method relies on the fact that every compound has a unique fragmentation pattern in the mass spectrum. The sample is ionized, then sample ions are separated based on their differing masses and relative abundance. Methanol (analytical grade) is a solvent using in this characterization.

3.5 Characterization of RPUR foams

3.5.1 Infrared spectroscopy

The IR spectroscopy was used to characterize of functional groups and study about NCO conversions of RPUR foams at room temperature. Attenuated total reflectance fourier transformed infrared spectroscopy (ATR-FTIR) were recorded on a Nicolet 6700 FTIR spectrometer, over the range 500-4000 cm^{-1} at a resolution of 4 cm^{-1}. It is important that the samples are pressed, reproducibly and with a constant pressure, against the IR-transmitting ATR crystal. The ATR crystal is integrated into the beam of an ATR-IR spectrometer in such a way that IR light is passed through the crystal by means of total reflection. ATR occurs on the measuring surface that is in contact with the foam sample. The IR bands given in Table 3.6 are used for the analysis. The main peaks of isocyanurate C-N stretching (at 1405-1451 cm^{-1}), urethane C=O stretching (at 1725-1735 cm^{-1}) and isocyanate asymmetric stretching (at 2265-2278 cm^{-1}) were investigated.

3.5.3 Foaming temperature

Dual thermocouple, Digicon DP-71, is a widely used to detected foaming temperatures of RPUR foams. Those foaming temperature is represented by temperature profiles and maximum core temperature.

3.5.2 Kinetic of foaming

The kinetic of RPUR foaming is studied through reaction times such as cream time, gel time tack free time and rise time by using a digital stopwatch.

3.5.4 Density

The apparent density of RPUR foams was measured according to ASTM D 1622-09, the size of specimen was 3.0 x 3.0 x 3.0 cm (length×width×thickness) and the average values of three samples were reported.

3.5.5 Scanning electron microscope (SEM)

The morphology and cell size of RPUR foams were measured on a Hitachi/S-4800 scanning electron microscope (SEM). A thickness of foam sample about 1.0 mm was prepared for SEM analysis by coating with gold before scanning in order to provide an electrically conductive surface. The sample was done at an accelerating of 20kV. The sample was observed in the free-rise direction.

3.5.6 Compressive testing

The compressive testing of RPUR foams in parallel and perpendicular to the foam rise direction were performed in order to study mechanical property of foams using universal testing machine (Lloyd/LRX) according to ASTM D 1621-09, the specimen size was 3.0 x 3.0 x 3.0 cm (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.

3.5.7 Thermalgravimetric analysis (TGA)

Thermalgravimetric analysis (TGA) was used to study the thermal stability of RPUR foam. TGA determination was done by Netzsch STA 409C thermogravimetric analyzer. The foam samples were heated under N_2 gas from 25 ^{o}C to 600 ^{o}C at heating rate of 20 ^{o}C/min. The results of thermal stability were reported in initial decomposition temperature (IDT) at 5 wt% loss of foam, maximum decomposition temperature and percentage weight residue of RPUR foams.

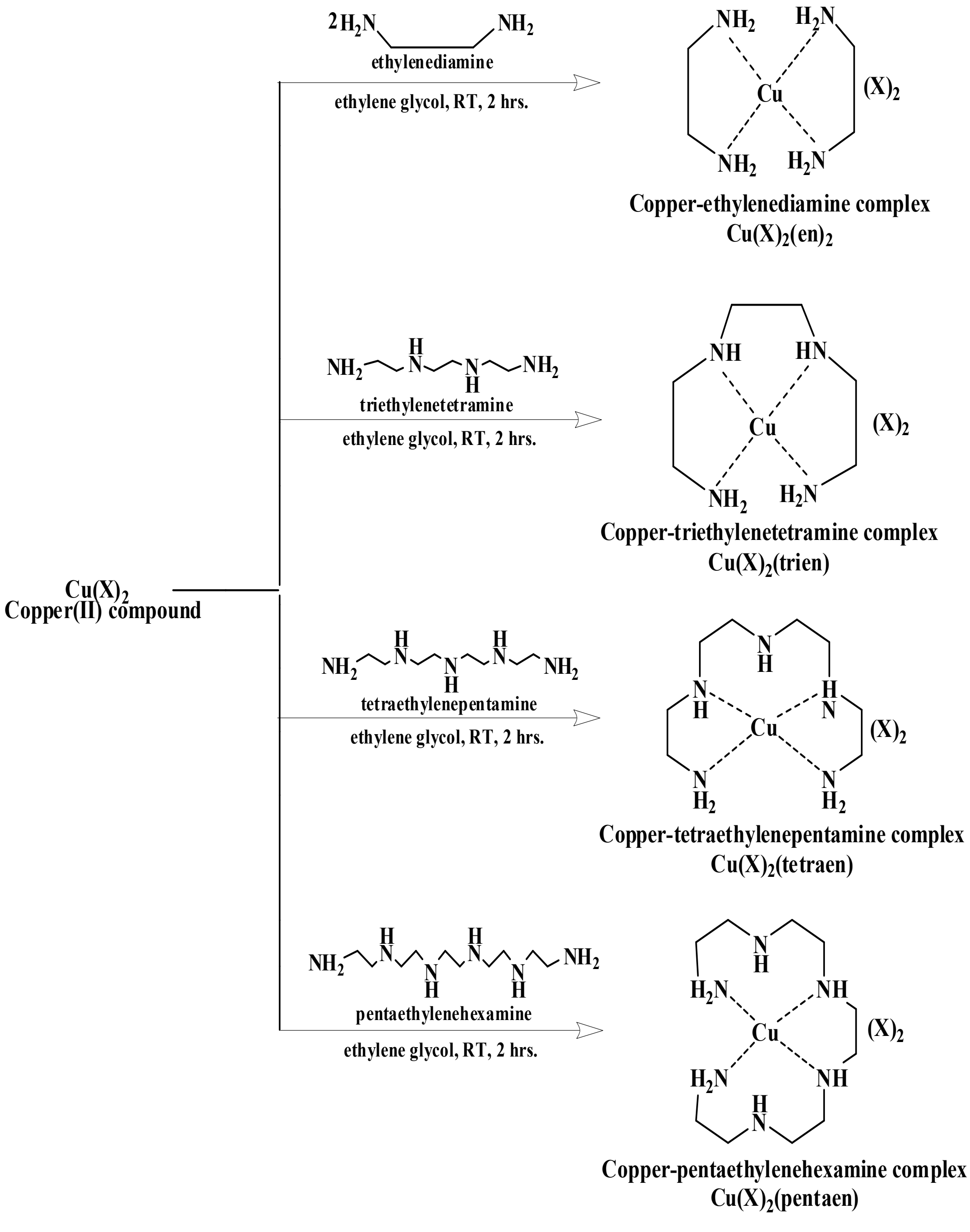
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of copper-amine complexes [$Cu(X)_2(en)_2$, $Cu(X)_2$(trien), $Cu(X)_2$(tetraen) and $Cu(X)_2$(pentaen)] in ethylene glycol

Synthesis of copper-amine complexes were carried out using ethylene glycol as a solvent. Aliphatic amines, namely ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pentaethylenehexamine (pentaen) were dissolved in ethylene glycol. After that, the series of copper compounds, namely copper(II) acetate [$Cu(OAc)_2$], copper(II) acetylacetonate [$Cu(acac)_2$], copper(II) nitrate [$Cu(NO_3)_2$] and copper(II) chloride [$Cu(Cl)_2$] were added to the amine solution to form copper-amine complexes. Mole ratios of copper(II) compound to en, trien, tetraen and pentaen were 1:2, 1:1, 1:1 and 1:1, respectively. The reactions between copper(II) compounds and aliphatic amines gave $Cu(X)_2(en)_2$, $Cu(X)_2$(trien), $Cu(X)_2$(tetraen) and $Cu(X)_2$(pentaen) (where X= OAc, acac, NO_3 and Cl) as shown in Scheme 4.1

It was found that $Cu(OAc)_2$, $Cu(NO_3)_2$ and $Cu(Cl)_2$ were easily soluble in the mixture of ethylene glycol and amine, whereas $Cu(acac)_2$ had poor solubility. Copper-amine complexes were obtained as odorless solution in ethylene glycol and having low viscosity. Furthermore, all of copper-amine complexes had colors which could be visually observed for the solubility of complexes in the ethylene glycol and RPUR foam's raw materials. The solution containing copper-amine complexes could be further used in the preparation of RPUR foam without purification. For the preparation of copper-amine complexes using organic solvents, namely acetone and methanol, the solvents have to be removed from metal complexes before using in RPUR foam preparation. The advantage of preparation copper-amine complexes in ethylene glycol are the process does not use organic solvent that needed to be removed. The solution of copper-amine complexes in ethylene glycol can be obtained in a short time and can be used in foam preparation without purification. The mixing between the solution of copper-amine complexes in ethylene glycol and other starting materials in RPUR foam formulation is also easy.



Scheme 4.1 Synthesis of $Cu(X)_2(en)_2$, $Cu(X)_2(trien)$, $Cu(X)_2(tetraen)$ and $Cu(X)_2(pentaen)$ Where; X= OAc, acac, NO_3 and Cl

4.2 Characterization copper-amine complexes synthesized in ethylene glycol

The solution of copper-amine complexes in ethylene glycol were characterized using UV-visible spectroscopy and mass spectrometry. To confirm the complex formation in ethylene glycol, UV-visible spectra of copper-amine complexes solution in ethylene glycol were compared with copper-amine complexes synthesized in acetone and methanol. It was found that copper-amine complexes synthesized using different methods gave the same maximum wavelength which shifted from the typical maximum wavelength of $Cu(OAc)_2$ or $Cu(acac)_2$. These results indicated that the complexes could be formed in ethylene glycol, acetone and methanol. Electrospray ionization (ESI) mass spectroscopy was also used to identified copper-amine complexes. The peak of mass spectra corresponded to the molecular weight of copper-amine complexes, which could use to identify the copper-amines complexes structures and confirmed the complexes formation. The positive-ion ESI of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen), $Cu(OAc)_2$(pentaen), $Cu(acac)_2(en)_2$ and $Cu(acac)_2$(trien) are shown in Figures 4.2, 4.4, 4.6, 4.8 4.10 and 4.12, respectively. The data of molecular ion peaks corresponding and *m/z* ratio are described in Table 4.1.

Table 4.1. Molecular ion peak corresponding and *m/z* ratio of copper-amine complexes

Molecular ion peak	***m/z* (Calculated)**	***m/z* (Found)**
$[Cu(OAc)_2(en)_2+H^+]^+$	302.86	303.05
$[Cu(OAc)_2(en)_2+ EG]^+$	363.85	363.15
$[Cu(OAc)_2(trien)+ EG]^+$	389.89	389.22
$[Cu(OAc)_2(tetraen)+H^+]^+$	371.96	372.21
$[Cu(OAc)_2(teraen)+ EG]^+$	432.95	432.28
$[Cu(OAc)_2(pentaen)+H^+]^+$	415.04	415.30
$[Cu(OAc)_2(pentaen)+ EG]^+$	476.03	475.33
$[Cu(acac)_2(en)_2+H^+]^+$	382.97	382.90
$[Cu(acac)_2(trien)+EG]^+$	469.74	469.07

* EG = ethylene glycol

4.2.1 Characterization of $Cu(OAc)_2(en)_2$ synthesized in ethylene glycol

4.2.1.1 UV-visible spectroscopy of $Cu(OAc)_2(en)_2$

UV-visible spectra of $Cu(OAc)_2$ and $Cu(OAc)_2(en)_2$ synthesized in ethylene glycol and acetone are illustrared in Figure 4.1. The maximum wavelength of $Cu(OAc)_2$ appeared at 245 nm. It was found that the maximum wavelength of $Cu(OAc)_2(en)_2$ in both solvents appeared at 232 nm and shifted from the typical maximum wavelength of $Cu(OAc)_2$ which indicated that $Cu(OAc)_2(en)_2$ was formed in ethylene glycol.

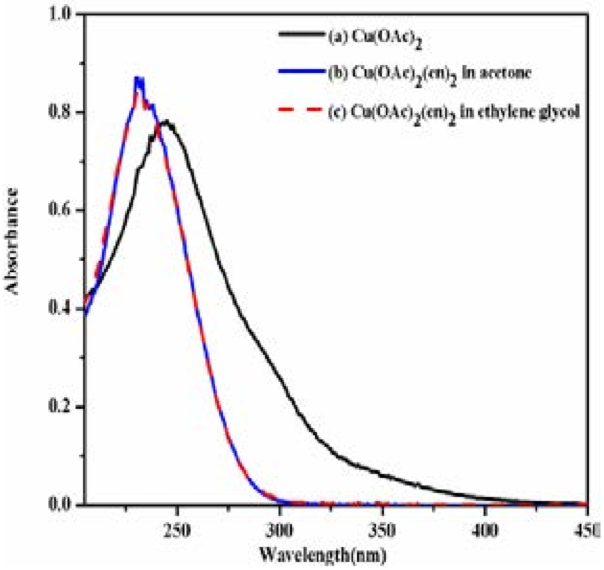


Figure 4.1 UV spectra of (a) $Cu(OAc)_2$; (b) $Cu(OAc)_2$ $(en)_2$ synthesized in acetone and (c) $Cu(OAc)_2$ $(en)_2$ synthesized in ethylene glycol

4.2.1.2 ESI mass spectroscopy of $Cu(OAc)_2(en)_2$

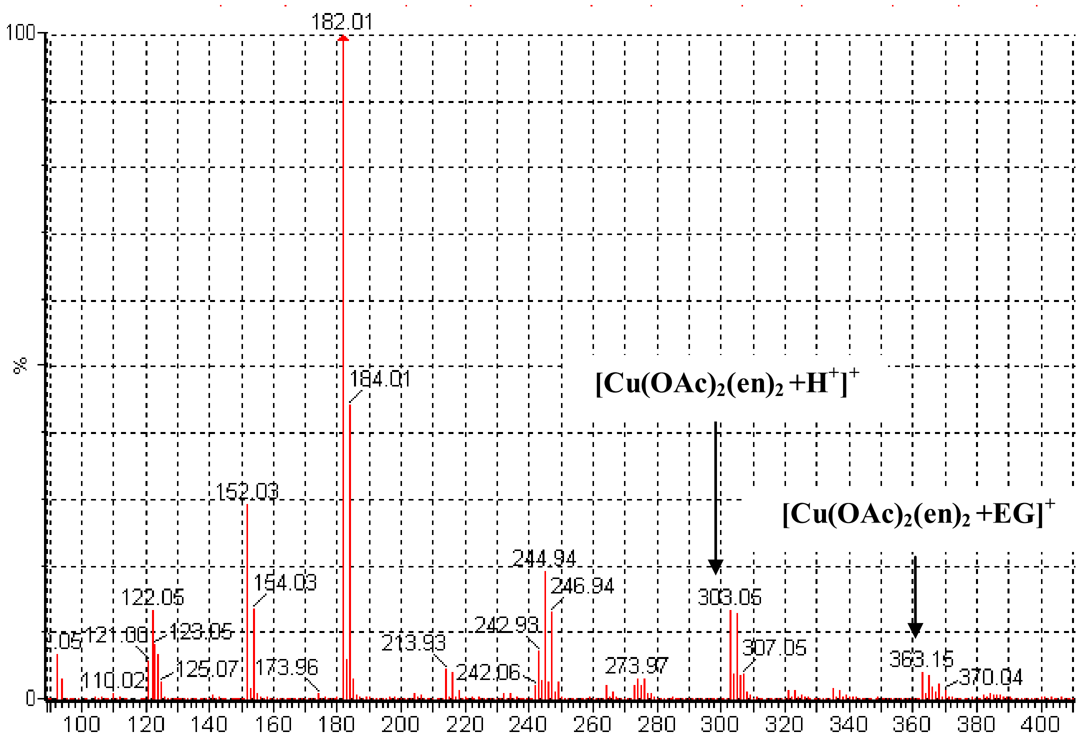


Figure 4.2 Positive ESI mass spectra of $Cu(OAc)_2(en)_2$ synthesized in ethylene glycol

4.2.2 Characterization of $Cu(OAc)_2(trien)$ synthesized in ethylene glycol

4.2.2.1 UV-visible spectroscopy of $Cu(OAc)_2(trien)$

UV-visible spectra of $Cu(OAc)_2$ and $Cu(OAc)_2(trien)$ synthesized in ethylene glycol and acetone are illustrared in Figure 4.3. The maximum wavelength of $Cu(OAc)_2$ appeared at 245 nm. It was found that the maximum wavelength of $Cu(OAc)_2(trien)$ in both solvents appeared at 258 nm and shifted from the typical maximum wavelength of $Cu(OAc)_2$ which indicated that $Cu(OAc)_2(trien)$ was formed in ethylene glycol.

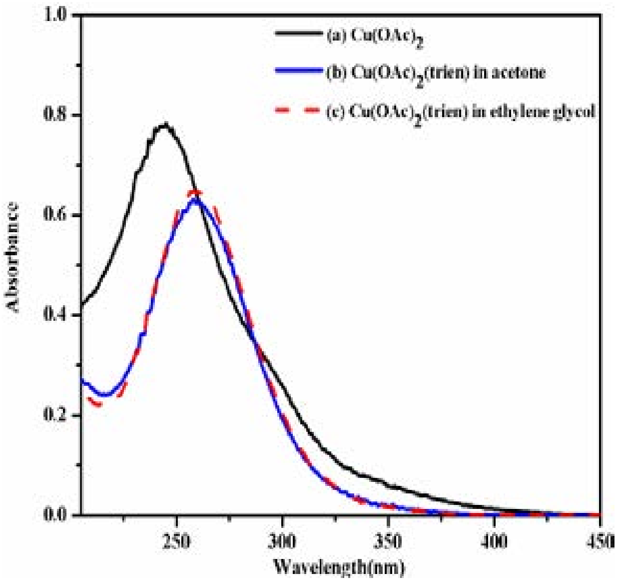


Figure 4.3 UV spectra of (a) Cu(OAc)$_2$; (b) Cu(OAc)$_2$(trien) synthesized in acetone and (c) Cu(OAc)$_2$(trien) synthesized in ethylene glycol

4.2.1.2 ESI mass spectroscopy of Cu(OAc)$_2$(trien)

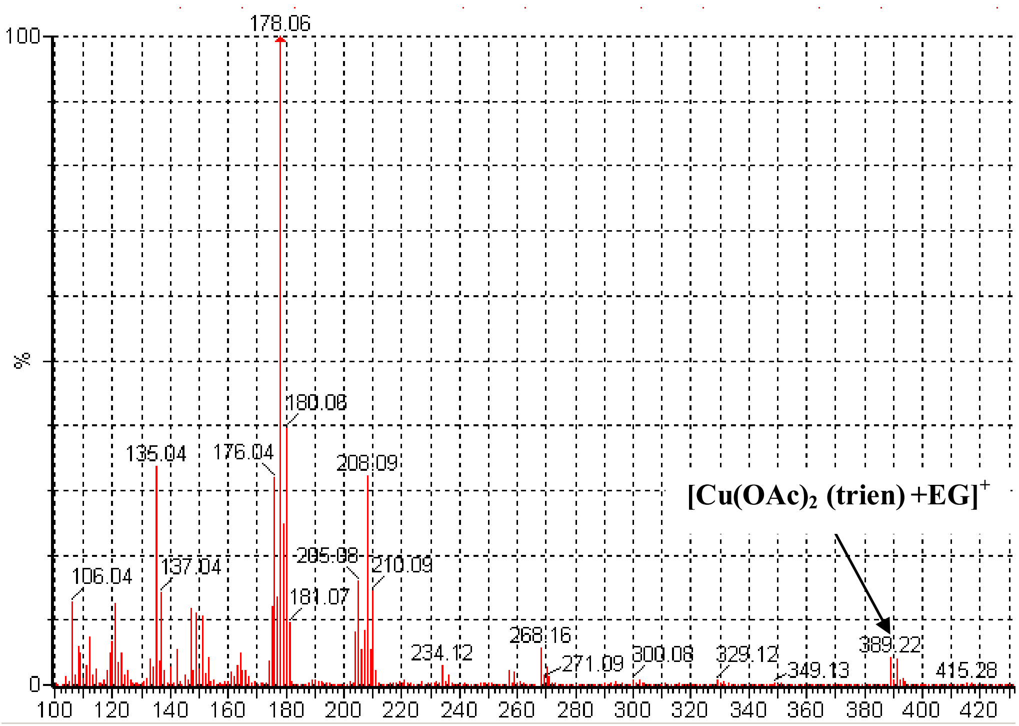


Figure 4.4 Positive ESI mass spectra of Cu(OAc)$_2$(trien) synthesized in ethylene glycol

4.2.3 Characterization of Cu(OAc)$_2$(tetraen) synthesized in ethylene glycol

4.2.3.1 UV-visible spectroscopy of Cu(OAc)$_2$(tetraen)

UV-visible spectra of Cu(OAc)$_2$ and Cu(OAc)$_2$(tetraen) synthesized in ethylene glycol and acetone are illustrared in Figure 4.5. The maximum wavelength of Cu(OAc)$_2$ appeared at 245 nm. It was found that the maximum wavelength of Cu(OAc)$_2$(tetraen) in both solvent appeared at 268 nm and shifted from the typical maximum wavelength of Cu(OAc)$_2$ which indicated that the complex was formed.

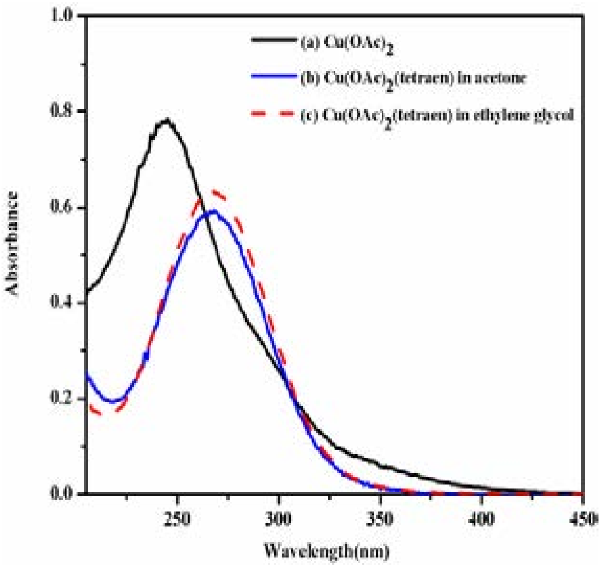


Figure 4.5 UV spectra of (a) Cu(OAc)$_2$; (b) Cu(OAc)$_2$(tetraen) synthesized in acetone and (c) Cu(OAc)$_2$(tetraen) synthesized in ethylene glycol

4.2.3.2 ESI mass spectroscopy of $Cu(OAc)_2$(tetraen)

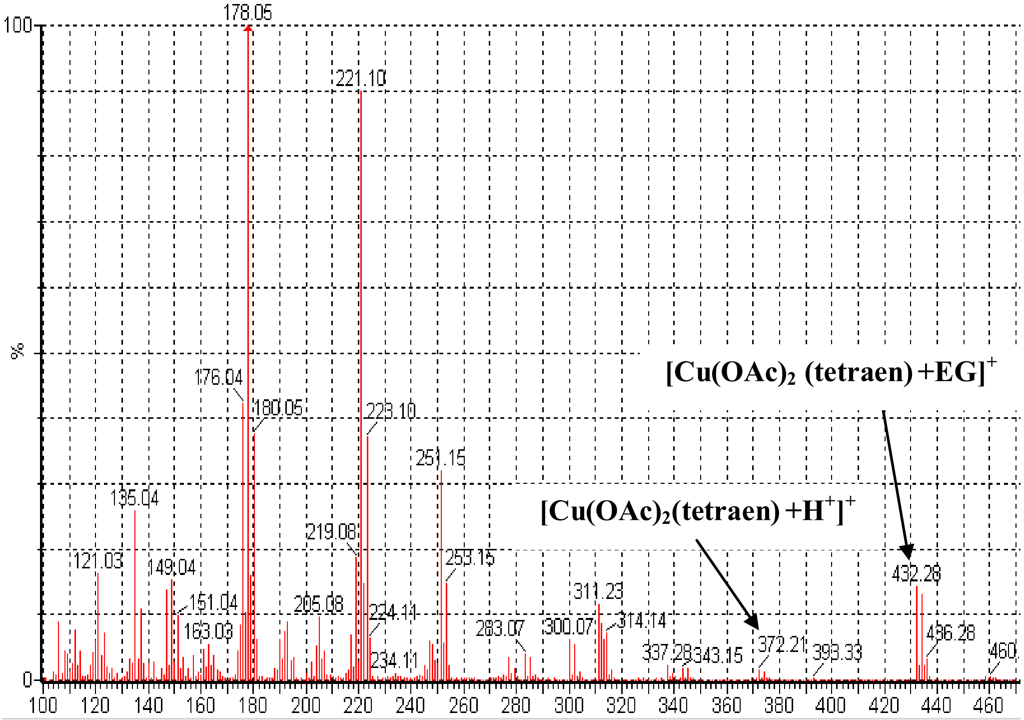


Figure 4.6 Positive ESI mass spectra of $Cu(OAc)_2$(tetraen) synthesized in ethylene glycol

4.2.4 Characterization of $Cu(OAc)_2$(pentaen) synthesized in ethylene glycol

4.2.4.1 UV-visible spectroscopy of $Cu(OAc)_2$(pentaen)

UV-visible spectra of $Cu(OAc)_2$ and $Cu(OAc)_2$(pentaen) synthesized in ethylene glycol and acetone are illustrared in Figure 4.7. The maximum wavelength of $Cu(OAc)_2$ appeared at 245 nm. It was found that the maximum wavelength of $Cu(OAc)_2$(pentaen) in both solvent appeared at 265 nm and shifted from the typical maximum wavelength of $Cu(OAc)_2$ which indicated that the complex was formed.

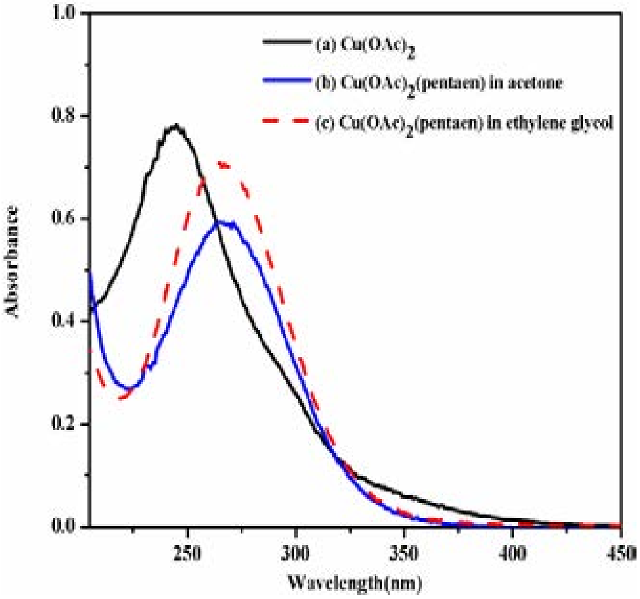
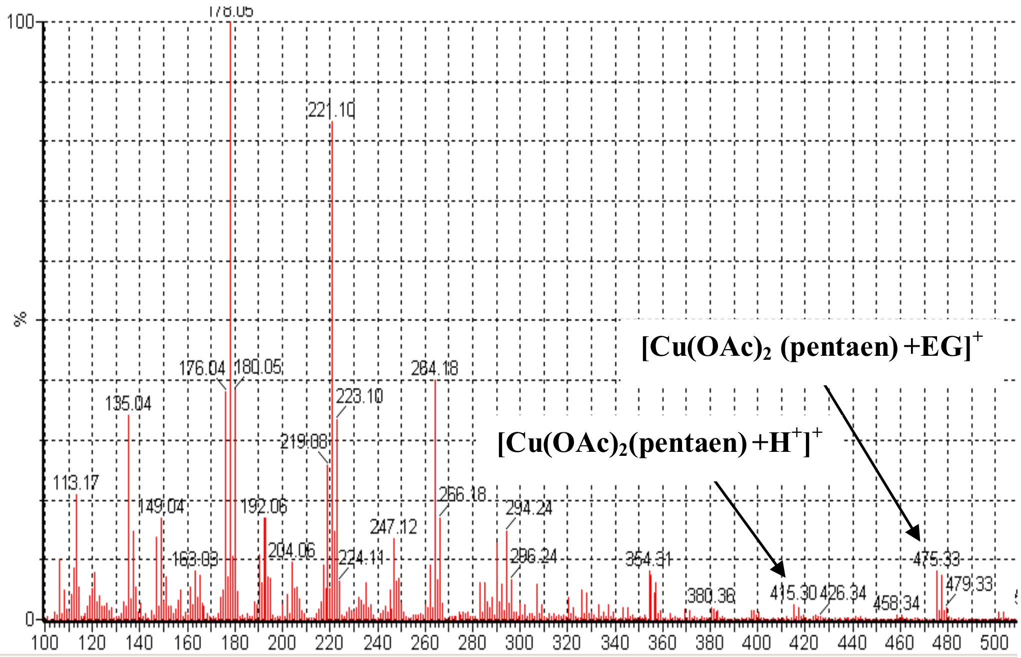


Figure 4.7 UV spectra of (a) $Cu(OAc)_2$; (b) $Cu(OAc)_2$ (pentaen) synthesized in acetone and (c) $Cu(OAc)_2$(pentaen) synthesized in ethylene glycol

4.2.4.2 ESI mass spectroscopy of $Cu(OAc)_2$(pentaen)



$[Cu(OAc)_2\ (pentaen) + EG]^+$

$[Cu(OAc)_2(pentaen) + H^+]^+$

Figure 4.8 Positive ESI mass spectra of $Cu(OAc)_2$(pentaen) synthesized in ethylene glycol

4.2.5 Characterization of $Cu(acac)_2(en)_2$ synthesized in ethylene glycol

4.2.5.1 UV-visible spectroscopy of $Cu(acac)_2(en)_2$

UV-visible spectra of $Cu(acac)_2$ and $Cu(acac)_2(en)_2$ synthesized in ethylene glycol and acetone are illustrared in Figure 4.9. The maximum wavelength of $Cu(acac)_2$ appeared at 295 nm. It was found that the maximum wavelength of $Cu(acac)_2(en)_2$ in both solvent appeared at 295 nm and shifted from the typical maximum wavelength of $Cu(acac)_2$ which indicated that the complex was formed.

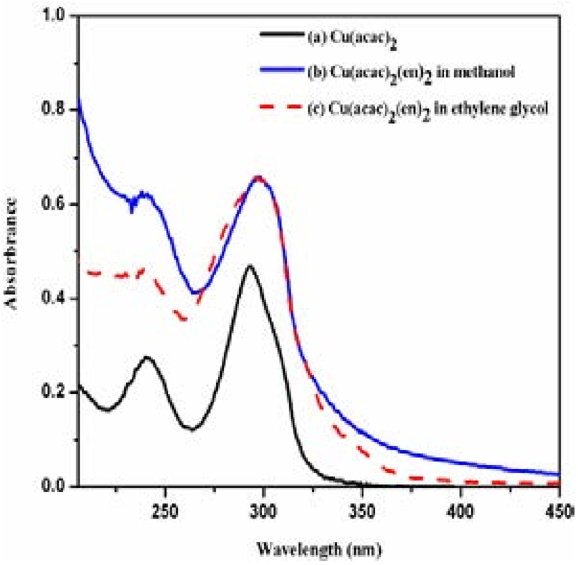
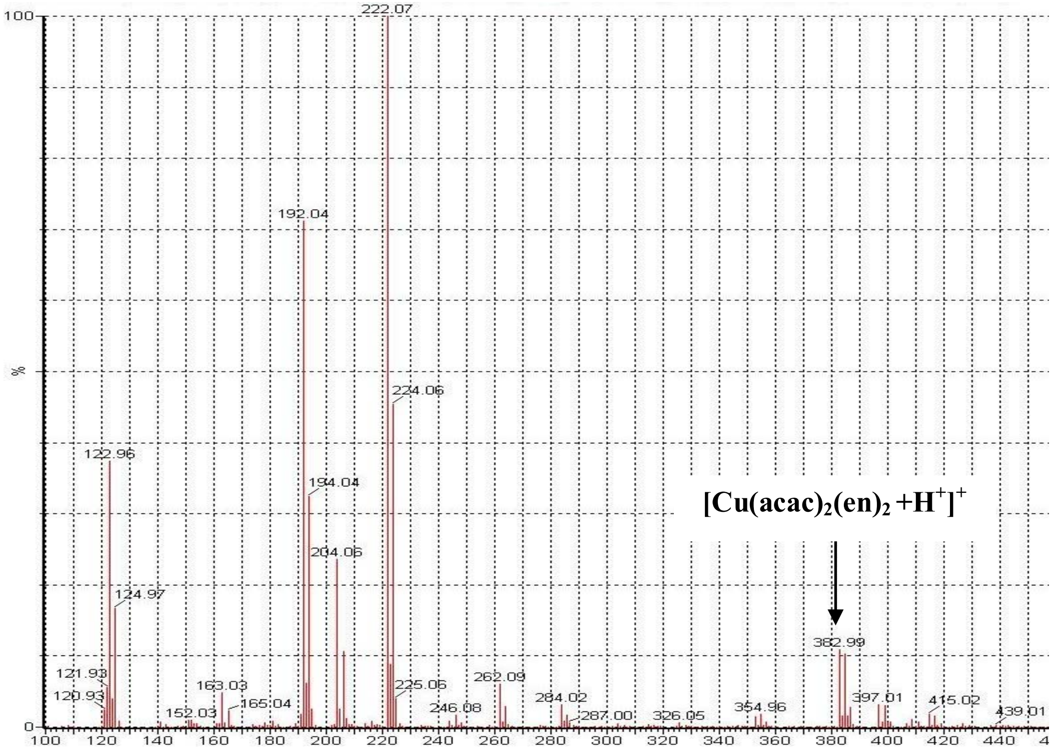


Figure 4.9 UV spectra of (a) $Cu(acac)_2$; (b) $Cu(acac)_2(en)_2$ synthesized in methanol and (c) $Cu(acac)_2(en)_2$ synthesized in ethylene glycol

4.2.5.2 ESI mass spectroscopy of $Cu(acac)_2(en)_2$



$[Cu(acac)_2(en)_2 + H^+]^+$

Figure 4.10 Positive ESI mass spectra of $Cu(acac)_2(en)_2$ synthesized in ethylene glycol

4.2.6 Characterization of $Cu(acac)_2(trien)$ synthesized in ethylene glycol

4.2.6.1 UV-visible spectroscopy of $Cu(acac)_2(trien)$

UV-visible spectra of $Cu(acac)_2$ and $Cu(acac)_2(trien)$ synthesized in ethylene glycol and acetone are illustrared in Figure 4.11. The maximum wavelength of $Cu(acac)_2$ appeared at 295 nm. It was found that the maximum wavelength of $Cu(acac)_2(trien)$ in both solvent appeared at 273 nm and shifted from the typical maximum wavelength of $Cu(acac)_2$ which indicated that the complex was formed.

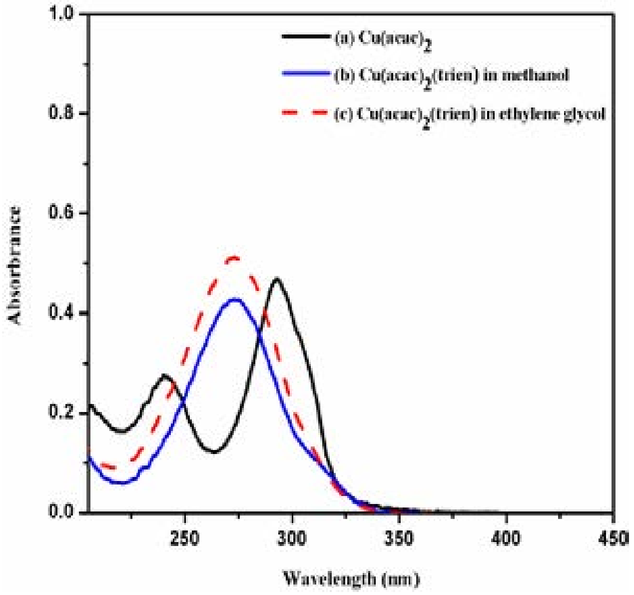


Figure 4.11 UV spectra of (a) $Cu(acac)_2$; (b) $Cu(acac)_2$(trien) synthesized in methanol and (c) $Cu(acac)_2$(trien) synthesized in ethylene glycol

4.2.6.2 ESI mass spectroscopy of $Cu(acac)_2$(trien)

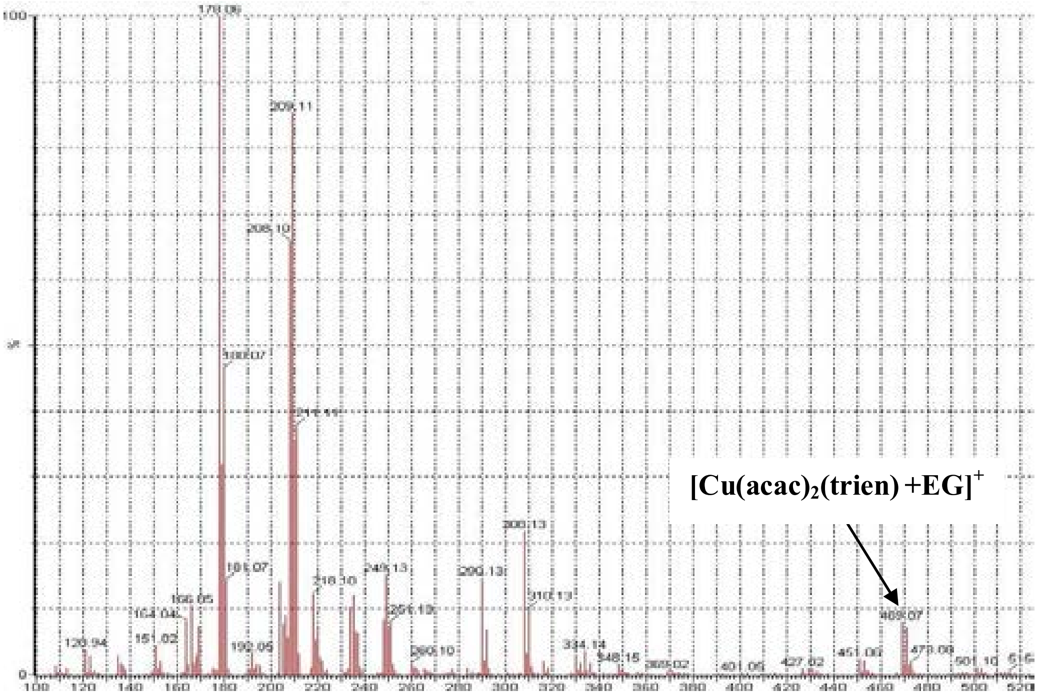


Figure 4.12 Positive ESI mass spectra of $Cu(acac)_2$(trien) synthesized in ethylene glycol

4.3 Preparation of rigid polyurethane (RPUR) foams

4.3.1 The optimum catalyst (copper-amine complex) content in copper complex-ethylene glycol (EG) solution in RPUR foam preparation

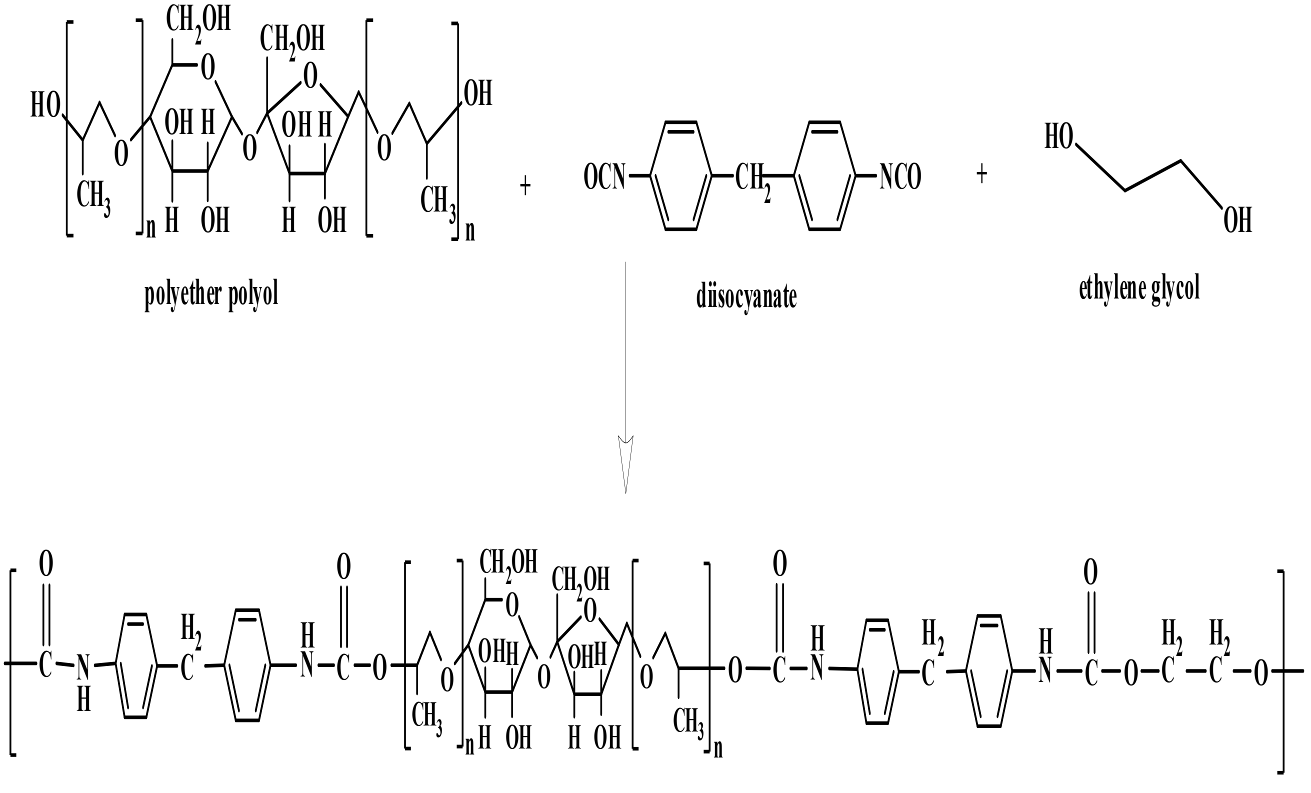
Table 4.2 Reaction profiles of RPUR foams catalyzed by copper-amine complexes synthesized in ethylene glycol at the different catalyst concentration

Catalyst concentration	Cream Time (min:sec)	Gel Time (min:sec)	Tack free Time (min:sec)	Rise Time (min:sec)	Density (kg/m^3)	Volume (V/8)
$Cu(OAc)_2(en)_2$						
60%wt in EG	0:30	0:51	1:19	1:44	37.0	7.25
30%wt in EG	0:31	0:46	1:08	1:37	37.1	7.25
15%wt in EG	0:28	0:35	0:45	1:07	37.1	8.0
$Cu(OAc)_2$(trien)						
60%wt in EG	0:32	0:58	1:32	2:15	37.4	7.0
30%wt in EG	0:35	0:55	1:31	2:11	38.5	7.0
15%wt in EG	0:32	0:40	0:55	1:23	38.4	7.5
$Cu(OAc)_2$(tetraen)						
60%wt in EG	0:35	1:18	1:56	2:44	38.7	7.0
30%wt in EG	0:35	1:10	1:41	2:20	39.5	7.0
15%wt in EG	0:34	0:54	1:13	1:45	39.2	7.25
$Cu(OAc)_2$(pentaen)						
60%wt in EG	0:36	1:26	2:26	3:09	39.1	6.50
30%wt in EG	0:37	1:14	1:56	2:37	39.8	6.50
15%wt in EG	0:35	1:04	1:25	1:54	39.6	7.0

Homogeneous mixing of raw materials is very important in the RPUR foams preparation because it affects on the properties and appearance of foam. From this reason, copper-amine complexes were prepared as the solution in ethylene glycol, which was a low viscosity liquid, in order to improve the mixing property. It was found that the use of ethylene glycol permitted copper-amine complexes to blend well with other ingredients in foam formulation (polyol, surfactant, blowing agent and PMDI) and gave the uniform mixing. The effects of copper-amine complex content in ethylene glycol, represented in the term of catalyst concentration (15, 30 and 60%wt), on the RPUR foams properties were investigated and the optimum content were chosen to synthesize other catalysts for RPUR foams. Table 4.2 shows the effects of catalyst content in ethylene glycol on the reaction profiles of RPUR foams. The foams were catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) at 15, 30, 60%wt in ethylene glycol.

4.3.1.1 The effect of catalyst (copper-amine complex) content in copper complex-ethylene glycol (EG) solution on the reaction times of RPUR foams

Reaction times of RPUR foams catalyzed by various concentration of $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) in ethylene glycol are shown in Figure 4.13. The reaction times measured were cream time (which is the time of the beginning of reaction or blowing reaction), gel time (which is the time of gel point of foam mixture or gelling reaction),tack free time (which is the time of the foam could not tack with other materials or crosslink reaction) and rise time (which is the time of the foam stop rising). It was found that the reaction times, especially gel time, tack-free time and rise time, decreased with decreasing catalyst concentration in ethylene glycol. Tack-free times and rise times occurred about two times faster with decreasing the catalyst concentration from 60%wt to 15%wt in ethylene glycol. This result implied that ethylene glycol content in copper complex-ethylene glycol solution effected on the kinetic rate of foaming reaction. Like polyol, ethylene glycol is an alcohol which also reacted with isocyanate group to form urethane or urea linkage [16,27]. But primary hydroxy groups contained in ethylene glycol are around three times more reactive in the reaction with isocyanate group than the secondary hydroxyl groups of polyether polyol [28]. Therefore, the addition of ethylene glycol would increase the urethane formation and gave faster kinetic rate of foaming. The urethane formation obtained by the reaction between ethylene glycol and isocyanate group is proposed in the Scheme 4.2. At high ethylene glycol content (15%wt of catalyst concentration), faster reaction times was obtained but gel time and tack free time were too short which caused difficulty in control. In the case of using 60%wt of catalyst, the catalyst solution had high viscosity which wasn't appropriate for foam preparation. It was found that 30%wt of catalyst was the optimum concentration for RPUR foam preparation.



Scheme 4.2 Reaction of isocyanate, polyether polyol and ethylene glycol

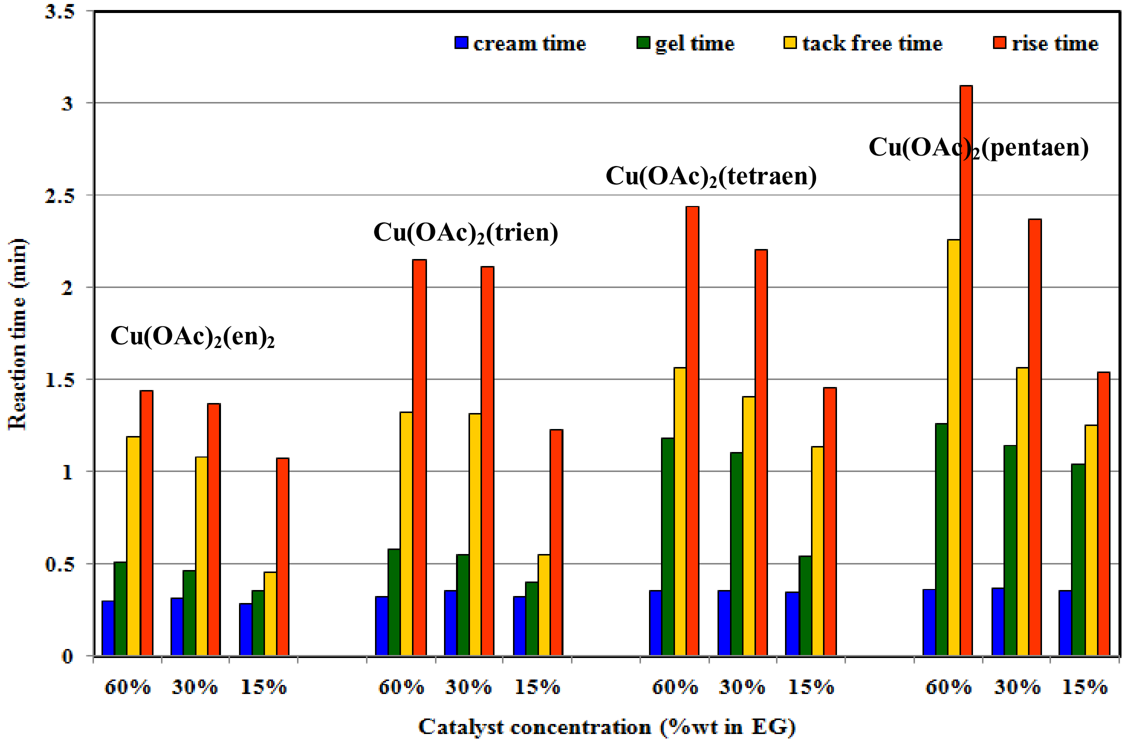


Figure 4.13 The effect of catalyst concentration on reaction times of RPUR foams prepared at NCO index of 100 and catalyzed by copper-amine complexes in ethylene glycol

4.3.1.2 The effect of catalyst (copper-amine complex) content in copper complex-ethylene glycol (EG) solution on the foaming temperature of RPUR foams

The maximum core temperature of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$ and $Cu(OAc)_2(pentaen)$ at different catalyst concentration was studied as shown in Table 4.3. The result indicated that the maximum core temperature increased with increasing the ethylene glycol content. From above result, ethylene glycol could react with isocyanate to give faster reaction of urethane formation. This reaction was exothermic reaction. Thus, increasing ethylene glycol amount would increase foaming temperature of foams.

Table 4.3 Maximum core temperature of RPUR foams catalyzed by copper-amine complexes at different catalyst concentration

Catalysts	concentration	Maximum core temperature (^{o}C)
$Cu(OAc)_2(en)_2$	15%wt in EG	145
	30%wt in EG	134
	60%wt in EG	128
$Cu(OAc)_2$(trien)	15%wt in EG	142
	30%wt in EG	130
	60%wt in EG	125
$Cu(OAc)_2$(tetraen)	15%wt in EG	137
	30%wt in EG	129
	60%wt in EG	127
$Cu(OAc)_2$(pentaen)	15%wt in EG	133
	30%wt in EG	124
	60%wt in EG	125

4.3.1.3 The effect of catalyst (copper-amine complex) content in copper complex-ethylene glycol (EG) solution on the density of RPUR foams

The apparent density of RPUR foams catalyzed by different concentration of catalyst was measured to study the effect of ethylene glycol content on density of foams as shown in Figure 4.14. It was found that the density of foam was not changed upon varying the catalyst concentration. This result implied that ethylene glycol content did not have effect on the density of foams.

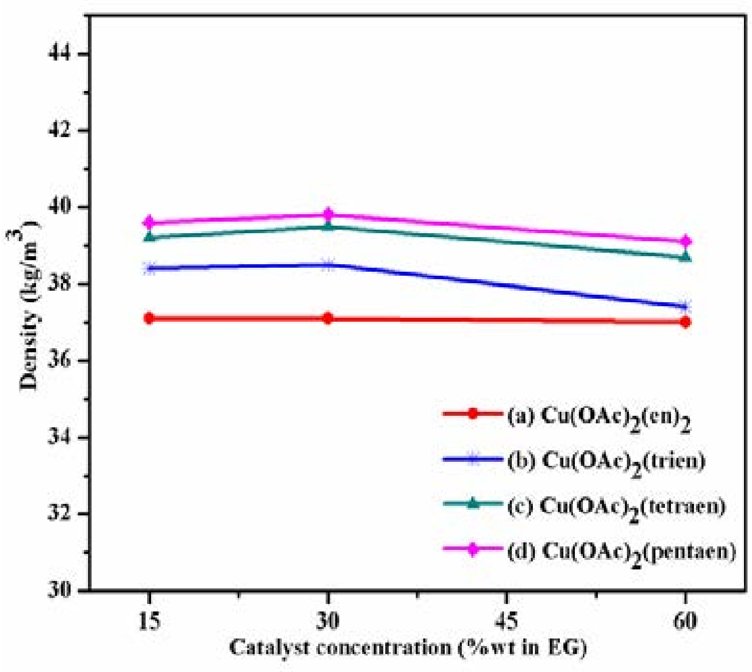


Figure 4.14 The effect of catalyst concentration on density of RPUR foams prepared at NCO index of 100 and catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$ and $Cu(OAc)_2(pentaen)$ in ethylene glycol

4.3.1.4 The effect of catalyst (copper-amine complex) content in copper complex-ethylene glycol (EG) solution on appearance of RPUR foams

The effect of ethylene glycol content on appearance of RPUR foams was observed as shown in Figure 4.15. It was found that all RPUR foams catalyzed by 30 and 60%wt of copper-amines complexes had similar external appearance. The foams obtained from those concentrations were good foam. On the other hand, foams catalyzed by 15%wt of copper-amines complexes had worse external appearance and foams catalyzed by 15%wt of $Cu(OAc)_2(en)_2$ had burning area due to the high temperature of polymerization reaction as illustrate in Figure 4.16(a). Another problem which was observed in using 15%wt of $Cu(OAc)_2(en)_2$ was the holes in the foam at the bottom of the mold. It was found that the foams catalyzed by 15%wt of $Cu(OAc)_2(en)_2$ had the hole at the bottom of the mold as shown in Figure 4.16(b). Less holes having smaller size were obtained when decreasing ethylene glycol content (or increasing catalyst content) in the foam formulation.

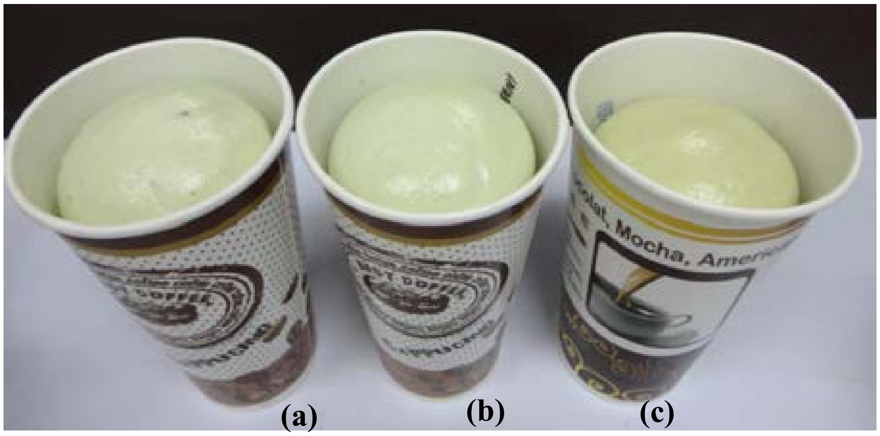


Figure 4.15 Appearance of RPUR foams catalyzed by $Cu(OAc)_2$(trien) in various catalyst concentration at NCO index of 100 (a) 15%wt ; (b) 30%wt and (c) 60%wt in ethylene glycol

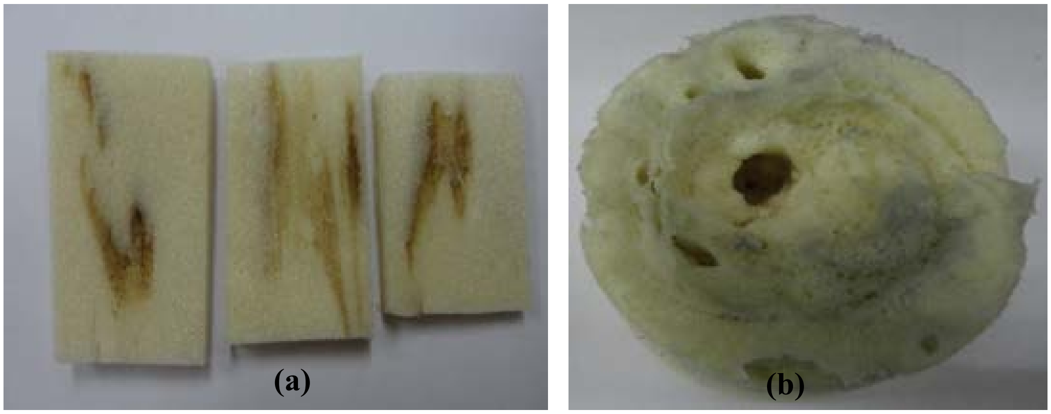


Figure 4.16 The defects of RPUR foam resulted from using $Cu(OAc)_2(en)_2$ 15%wt in ethylene glycol as a catalyst (a) burning area in the foam and (b) large holes in the foam at the bottom of the mold

4.3.1.5 The effect of catalyst (copper-amine complex) content in copper complex-ethylene glycol (EG) solution on morphology of RPUR foams

The effects of catalyst content on the cell size and morphology of RPUR foams analyzed by SEM are shown in Figure 4.17. Those morphologies belonged to RPUR foams catalyzed by $Cu(OAc)_2(trien)$ at different concentrations. The average cell diameter of RPUR foams catalyzed by $Cu(OAc)_2(trien)$ at 15, 30 and 60%wt in ethylene glycol were 537.8 µm, 317.9 µm, and 310.6 µm, respectively. The data informed that increasing of ethylene glycol content caused the increasing of cell size.

From all of above results in section 4.3.1.1-4.3.1.5, the suitable concentration for synthesizing copper-amine complexes catalyst was 30%wt in ethylene glycol.

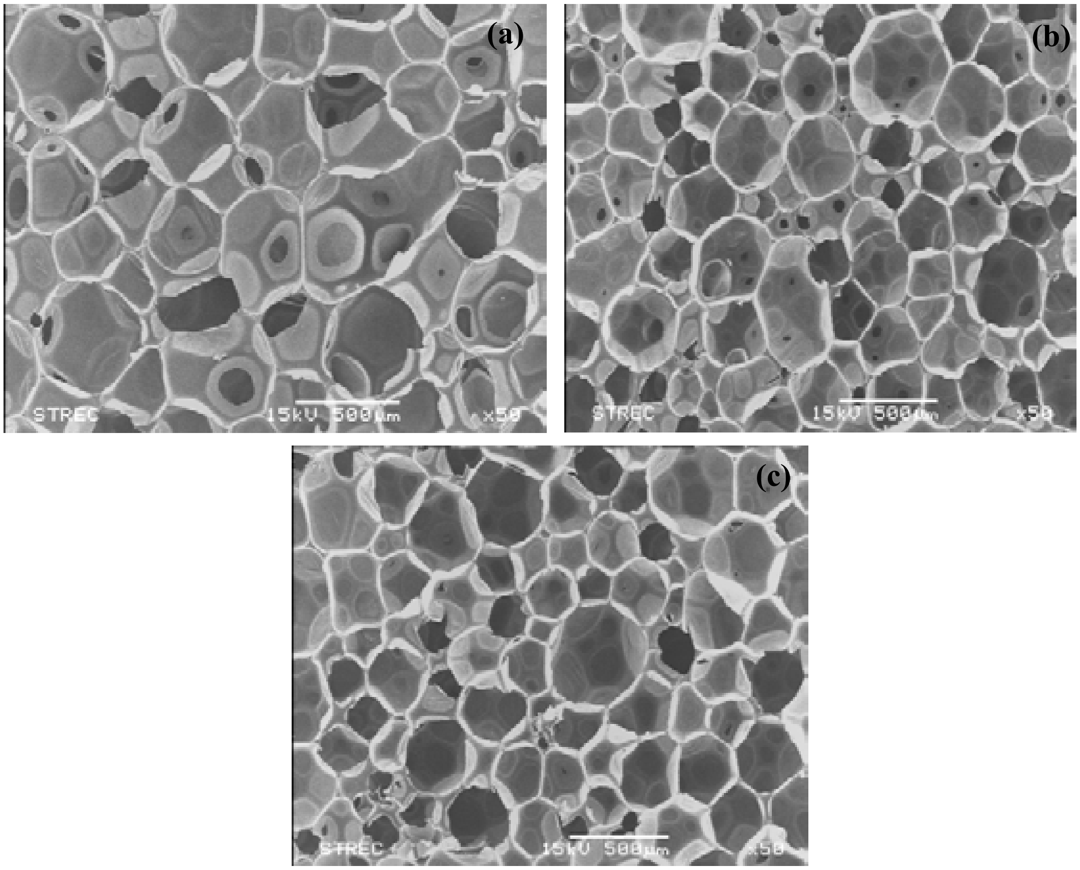


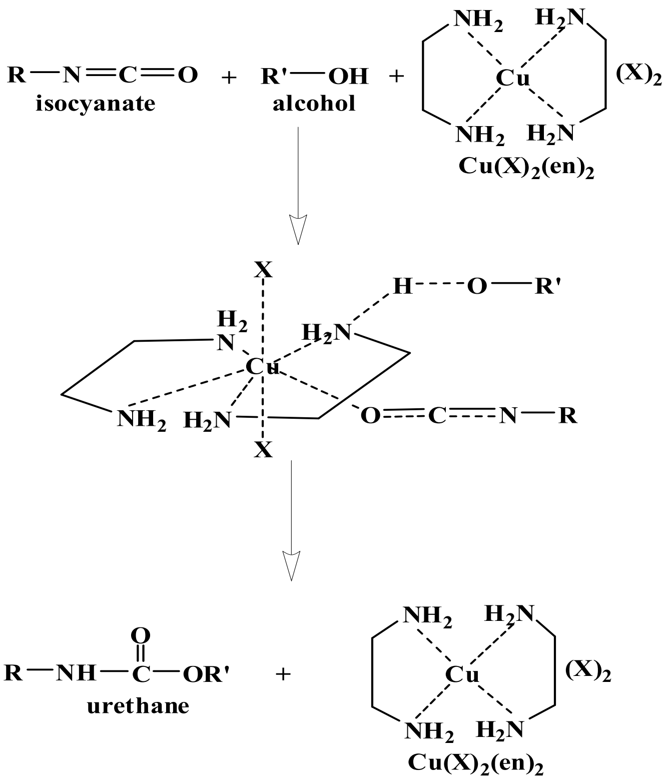
Figure 4.17 Morphology of foams catalyzed by $Cu(OAc)_2(trien)$ in various catalyst concentrations (a) 15%wt ; (b) 30%wt and (c) 60%wt in ethylene glycol

4.3.2 RPUR foams prepared from different types of copper-amine complex catalysts

Table 4.4 Reaction profiles of RPUR foams catalyzed by DMCHA and copper-amine complexes in ethylene glycol at NCO index of 100

Catalyst types	Cream Time (min:sec)	Gel Time (min:sec)	Tack free Time (min:sec)	Rise Time (min:sec)	Density (kg/m^3)	Volume (V/8)
DMCHA	0:22	0:32	2:34	1:55	37.1	7.0
$Cu(OAc)_2(en)_2$	0:31	0:46	1:08	1:37	37.1	7.25
$Cu(acac)_2(en)_2$	0:34	1:12	1:36	2:13	39.2	6.5
$Cu(NO_3)_2(en)_2$	0:41	2:23	3:18	4:02	41.1	6.25
$Cu(Cl)_2(en)_2$	0:53	3:44	11:16	7:48	49.6	4.5
$Cu(OAc)_2$(trien)	0:35	0:55	1:31	2:11	38.5	7.0
$Cu(acac)_2$(trien)	0:36	2:22	3:23	4:16	41.0	5.5
$Cu(NO_3)_2$(trien)	0:53	3:27	7:58	8:13	43.5	5.75
$Cu(Cl)_2$(trien)	0:57	4:17	11:54	8:32	44.5	5.25
$Cu(OAc)_2$(tetraen)	0:35	1:10	1:41	2:20	39.5	7.0
$Cu(acac)_2$(tetraen)	0:37	2:43	5:08	4:37	39.7	5.5
$Cu(NO_3)_2$(tetraen)	0:54	4:33	12:22	10:06	47.9	5.25
$Cu(Cl)_2$(tetraen)	1:05	4:08	13:51	9:33	46.1	5.0
$Cu(OAc)_2$(pentaen)	0:37	1:16	1:54	2:33	39.9	6.5
$Cu(acac)_2$(pentaen)	0:46	2:47	5:31	5:12	45.0	5.0
$Cu(NO_3)_2$(pentaen)	1:00	5:28	17:43	12:05	51.1	5.0
$Cu(Cl)_2$(pentaen)	0:58	4:23	14:43	10:02	46.7	5.25

Several types of copper salts and amines were chosen to synthesize copper-amine complexes for using as catalysts for RPUR foam preparation. The copper-amine complexes investigated were $Cu(X)_2(en)_2$, $Cu(X)_2(trien)$, $Cu(X)_2(tetraen)$ and $Cu(X)_2(pentaen)$, where X= OAc, acac, NO_3 and Cl; Y= en, trien, tetraen and pentaen). The reaction profiles of foams, such as reaction times, density and volume, are shown in Table 4.4. Copper-amine complexes could catalyze RPUR foam polymerization because the copper atom could act as a Lewis acid and coordinate to the oxygen atom of the NCO group, this caused the NCO carbon to be more electrophilic. The nitrogen atom of amine interacted with the proton of the hydroxyl group and caused the hydroxyl oxygen to be more nucleophilic, this oxygen then reacted with the NCO group to give a urethane linkage [9]. The reaction scheme for the urethane formation catalyzed by $Cu(X)_2(en)_2$ is proposed in the Scheme 4.3. The catalytic mechanism of $Cu(X)_2(trien)$, $Cu(X)_2(tetraen)$ and $Cu(X)_2(pentaen)$ were similar to that of $Cu(X)_2(en)_2$.



Scheme 4.3 Catalytic mechanism of $Cu(X)_2(en)_2$. Where; X= OAc, acac, NO_3 and Cl

To study the catalytic activity, the reaction time of foams catalyzed by each copper-amine complex was compared as shown in Figure 4.18. As a result, catalytic activity of catalyst depended on copper compound and amine types. In the case of copper-amine complexes prepared from different amine types, the order of catalytic activity was $Cu(X)_2(en)_2$ > $Cu(X)_2(trien)$ > $Cu(X)_2(tetraen)$ > $Cu(X)_2(pentaen)$, where X= OAc, acac, NO_3 and Cl, because of the steric hindrance of each amine. For copper-amine complexes prepared from different copper salts, the order of catalytic activity was $Cu(OAc)_2(Y)$ > $Cu(acac)_2(Y)$ > $Cu(NO_3)_2(Y)$ > $Cu(Cl)_2(Y)$, where Y= en, trien, tetraen and pentaen. This result was due to the ability of copper compound to form complexes with amine.

The catalytic activity of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$, $Cu(OAc)_2(pentaen)$ and $Cu(acac)_2(en)_2$ were comparable with the commercial reference 3° amine catalyst (DMCHA). Copper-amine complexes had shorter tack-free time than DMCHA. $Cu(acac)_2(trien)$ was interesting because this catalyst had the long gel time which resulted in the ease in pouring the starting materials into the mold.

The appearance of RPUR foams catalyzed by various copper-amine complexes was investigated as shown in Figures 4.19-4.20. It could be observed that some copper-amine complexes gave brittle foams with poor external appearance so they were not good for foam applications. The complexes which had effective catalytic property and gave good appearance of foam were $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$, $Cu(OAc)_2(pentaen)$, $Cu(acac)_2(en)_2$ and $Cu(acac)_2(trien)$. Therefore, those complexes were used to prepare RPUR foams in order to study the effect of raw material content on the property of RPUR foams.

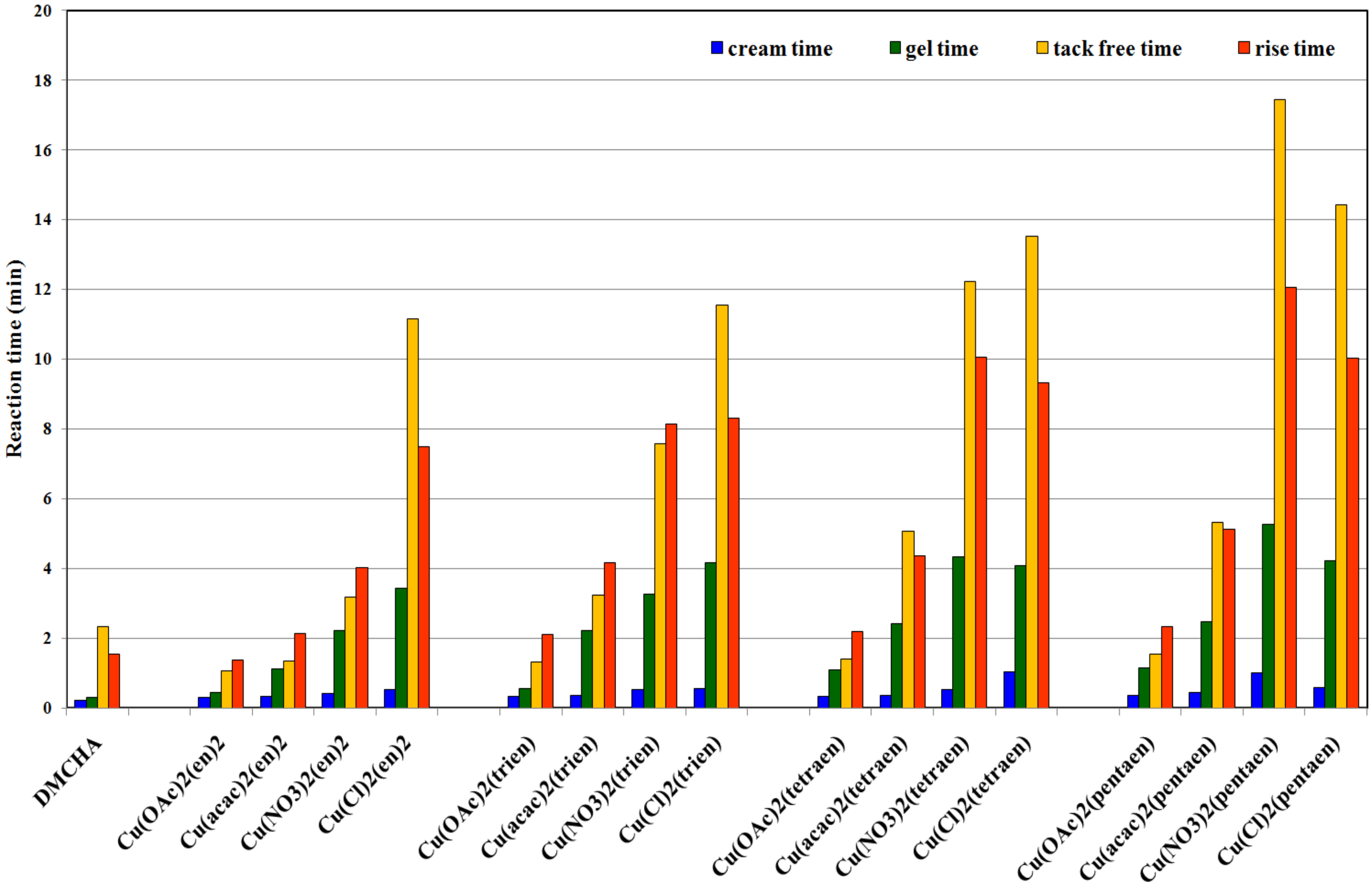
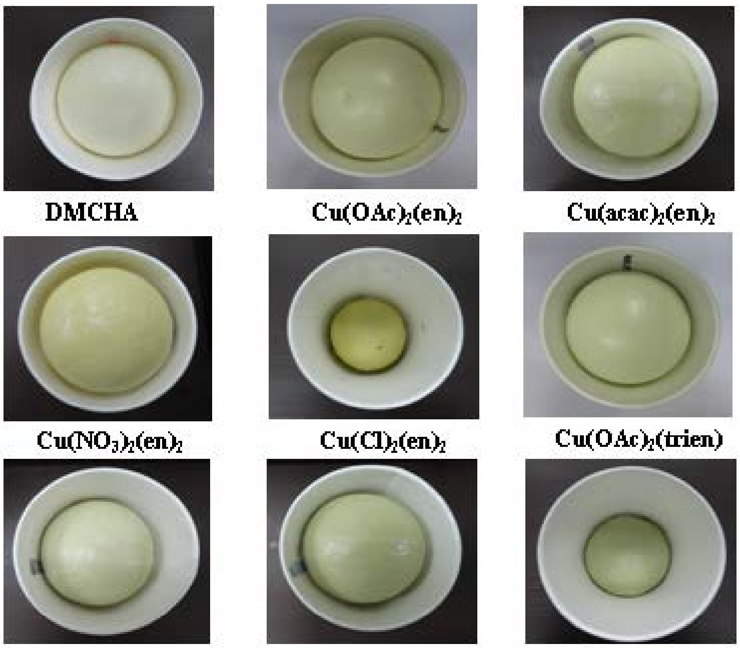


Figure 4.18 Reaction times of RPUR foams catalyzed by DMCHA and various copper-amine complexes synthesized in ethylene glycol at NCO index 100

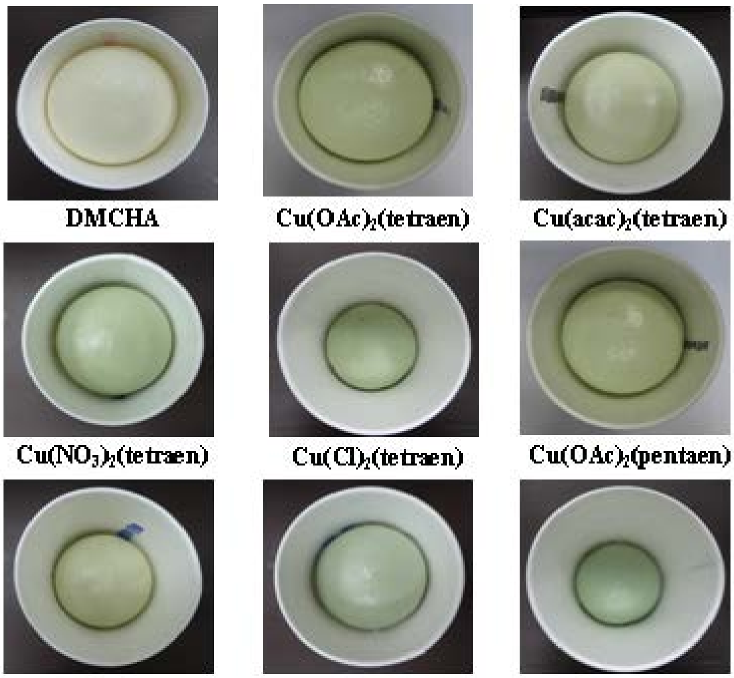


DMCHA **Cu(OAc)$_2$(en)$_2$** **Cu(acac)$_2$(en)$_2$**

Cu(NO$_3$)$_2$(en)$_2$ **Cu(Cl)$_2$(en)$_2$** **Cu(OAc)$_2$(trien)**

Cu(acac)$_2$(trien) **Cu(NO$_3$)$_2$(trien)** **Cu(Cl)$_2$(trien)**

Figure 4.19 External appearance of RPUR foams catalyzed by DMCHA and various copper-amine (en and trien) complexes in ethylene glycol



DMCHA **Cu(OAc)$_2$(tetraen)** **Cu(acac)$_2$(tetraen)**

Cu(NO$_3$)$_2$(tetraen) **Cu(Cl)$_2$(tetraen)** **Cu(OAc)$_2$(pentaen)**

Cu(acac)$_2$(pentaen) **Cu(NO$_3$)$_2$(pentaen)** **Cu(Cl)$_2$(pentaen)**

Figure 4.20 External appearance of RPUR foams catalyzed by DMCHA and various copper-amine (tetraen and pentaen) complexes in ethylene glycol

4.3.3 Rise profiles of RPUR foams

Rise profiles of RPUR foams catalyzed by copper-amine complexes prepared from $Cu(OAc)_2$ and $Cu(acac)_2$ are shown in Figures 4.21. and 4.22, respectively. The result indicated that the RPUR foams prepared from DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen),$Cu(OAc)_2$(pentaen) and $Cu(acac)_2(en)_2$ showed the similar rise profiles. However, DMCHA showed the a very fast rise at the initial of reaction, whereas copper-amine complexes had longer rise time at the initial of reaction and exhibited a very quick rise curve in the latter stage. In the case of $Cu(acac)_2$(trien), this complex showed longer initial time (which were cream time and gel time) than that of foam prepared from DMCHA. This result could explain the catalytic behavior of DMCHA, which is a tertiary amine-based catalyst, that it has strong catalytic activity towards both blowing and gelling reactions [14].

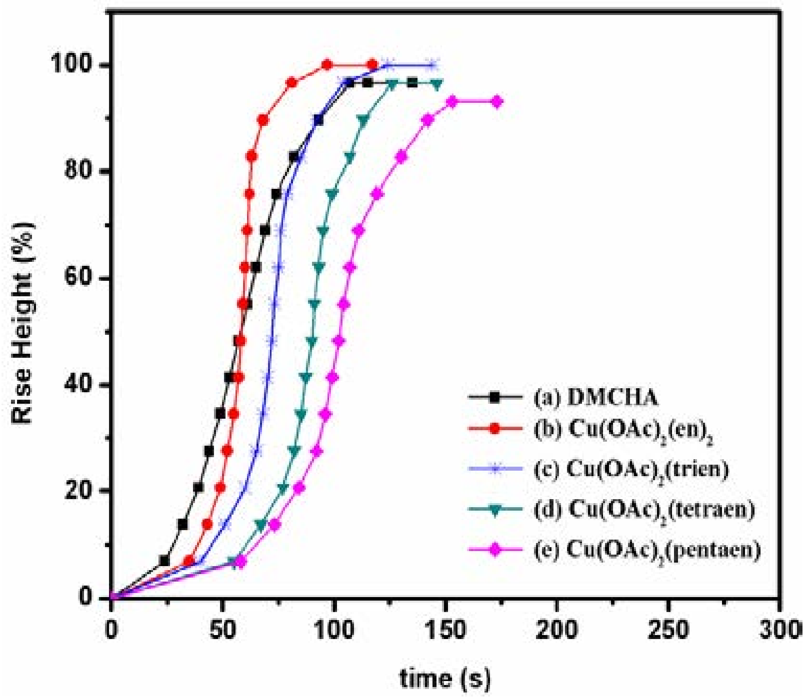


Figure 4.21 Rise profile of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2$(trien); (d) $Cu(OAc)_2$(tetraen) and (e) $Cu(OAc)_2$(pentaen) synthesized in ethylene glycol at NCO index 100

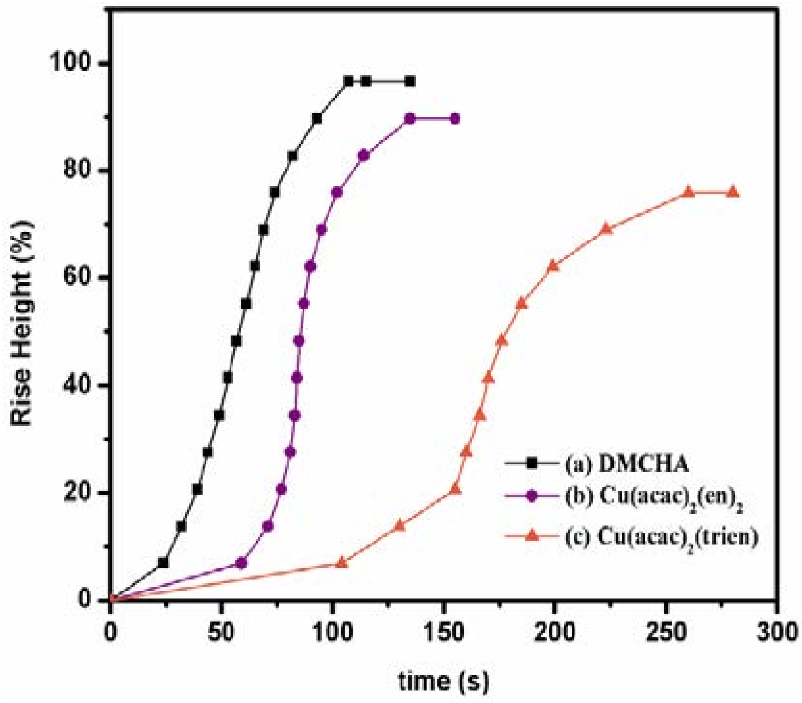


Figure 4.22 Rise profile of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(acac)_2(en)_2$; and (c) $Cu(acac)_2(trien)$ in ethylene glycol at NCO index 100

The maximum rise rate was calculated from maximum slope of rise profile of each catalyst as shown in Figure 4.23. It was found that the RPUR foams catalyzed by copper-amine complexes except $Cu(acac)_2(trien)$ showed higher maximum rise rate than that DMCHA. As a result, $Cu(OAc)_2(en)_2$ had the highest maximum rise rate. The results from the reaction times, rise profiles and maximum rise rates implied that copper-amine complex catalysts had comparable catalytic activity to DMCHA.

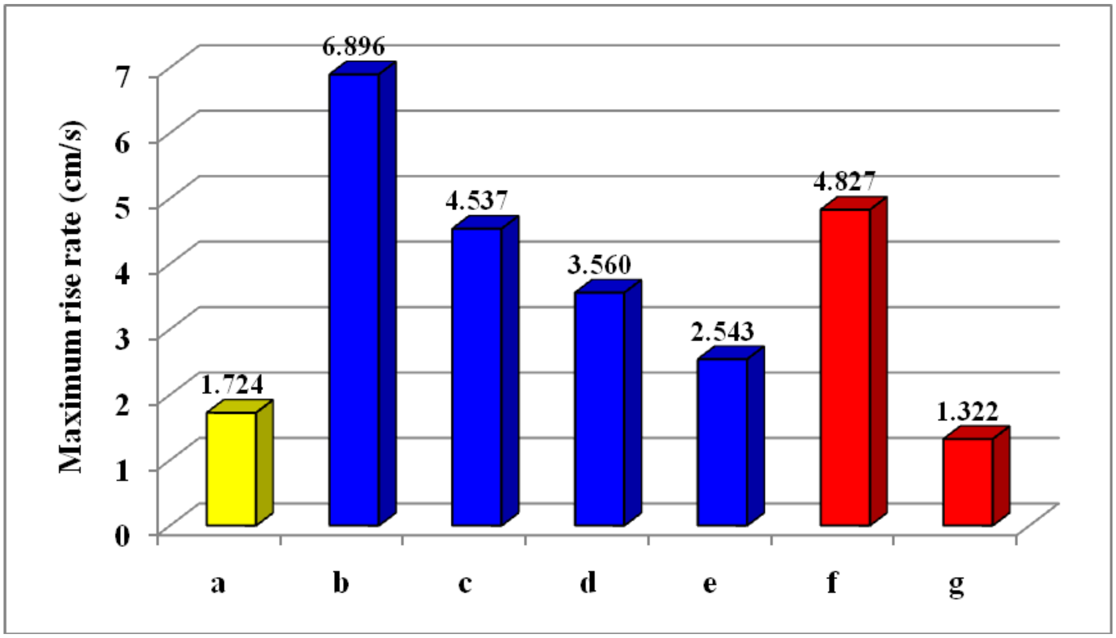


Figure 4.23 Maximum rise rates of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2$(trien); (d) $Cu(OAc)_2$(tetraen); (e) $Cu(OAc)_2$(pentaen); (f) $Cu(acac)_2(en)_2$; and (g) $Cu(acac)_2$(trien) in ethylene glycol at NCO index 100

4.3.4 Foaming Temperature

The temperature profiles of RPUR foams catalyzed by various copper-amine complexes at the NCO index of 100 were investigated as shown in Figures 4.24-4.25. It was found that the polymerization reaction is exothermic reaction and temperature profiles of RPUR foams catalyzed by copper-amine complexes were the same as that catalyzed by DMCHA. As a result, the maximum core temperatures of RPUR foams catalyzed by DMCHA and copper-amine complexes were 130 °C and 118-134 °C, respectively.

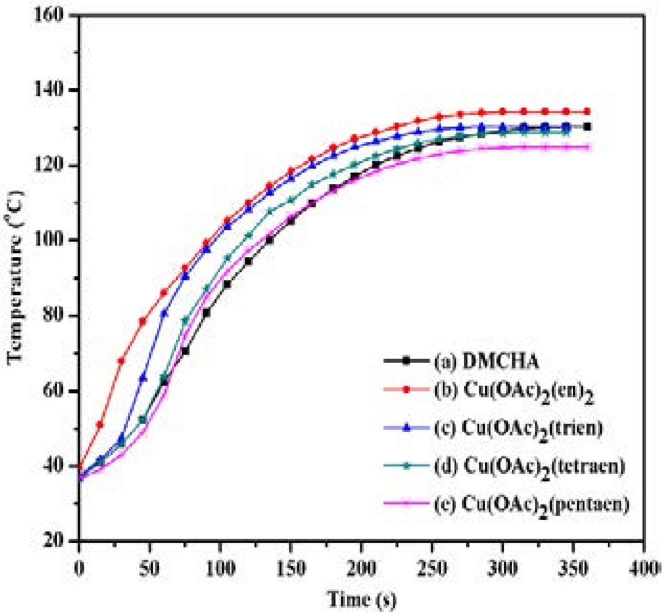


Figure 4.24 Temperature profile of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2$(trien); (d) $Cu(OAc)_2$(tetraen) and (e) $Cu(OAc)_2$(pentaen) in ethylene glycol at NCO index 100

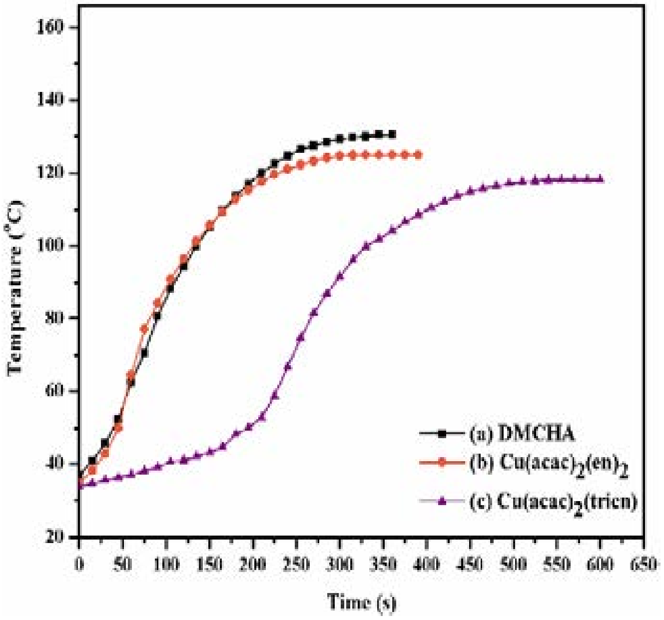


Figure 4.25 Temperature profile of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(acac)_2(en)_2$; and (c) $Cu(acac)_2$(trien) in ethylene glycol at NCO index 100

4.3.5 The effect of catalyst content in RPUR foam formulation on RPUR foam properties

Catalysts play an important role in control and balance between gelling and blowing reaction. The catalyst content affected reaction times and density and appearance of RPUR foam. Therefore, the optimum catalyst content was necessary for RPUR foam formulation to give the suitable reaction times and good quality foam. Tables 4.5-4.11 showed effect of catalyst content in RPUR foam formulation on reaction times, density and volume of RPUR foam.

Table 4.5 Reaction profiles of RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ in ethylene glycol at NCO index 100

Catalyst Content (pbw)	Catalyst type					
	$Cu(OAc)_2(en)_2$					
	Cream Time (min)	Gel Time (min)	Tack free Time (min)	Rise Time (min)	Density (kg/m^3)	Volume (V/8)
0.25	0:37	2:30	5:01	5:14	43.1	5.75
0.50	0:33	1:20	2:30	3:27	39.7	6.5
1.00	0:31	0:46	1:08	1:37	37.1	7.25
2.00	0:23	0:31	0:37	0:56	34.2	8.75

Table 4.6 Reaction profiles of RPUR foams catalyzed by $Cu(OAc)_2$(trien) in ethylene glycol at NCO index 100

Catalyst Content (pbw)	**Catalyst type**					
	$Cu(OAc)_2$(trien)					
	Cream Time (min)	**Gel Time (min)**	**Tack free Time (min)**	**Rise Time (min)**	**Density (kg/m^3)**	**Volume (V/8)**
0.25	0:37	2:43	5:09	5:31	43.6	5.5
0.50	0:35	1:46	2:52	3:44	41.4	6.25
1.00	0:35	0:55	1:31	2:11	38.5	7.0
2.00	0:27	0:37	0:49	1:15	35.1	8.5

Table 4.7 Reaction profiles of RPUR foams catalyzed by $Cu(OAc)_2$(tetraen) in ethylene glycol at NCO index 100

Catalyst Content (pbw)	**Catalyst type**					
	$Cu(OAc)_2$(tetraen)					
	Cream Time (min)	**Gel Time (min)**	**Tack free Time (min)**	**Rise Time (min)**	**Density (kg/m^3)**	**Volume (V/8)**
0.50	0:36	1:49	2:59	3:50	41.9	6.0
1.00	0:35	1:10	1:41	2:20	39.5	7.0
2.00	0:29	0:39	0:52	1:20	36.6	8.25

Table 4.8 Reaction profiles of RPUR foams catalyzed by $Cu(OAc)_2$(pentaen) in ethylene glycol at NCO index 100

Catalyst Content (pbw)	**Catalyst type**					
	$Cu(OAc)_2$(pentaen)					
	Cream Time (min)	**Gel Time (min)**	**Tack free Time (min)**	**Rise Time (min)**	**Density (kg/m^3)**	**Volume (V/8)**
0.50	0:38	2:03	3:47	4:36	41.5	6.0
1.00	0:37	1:16	1:54	2:33	39.9	6.5
2.00	0:30	0:48	1:06	1:33	37.2	8.0

Table 4.9 Reaction profiles of RPUR foams catalyzed by $Cu(acac)_2(en)_2$ in ethylene glycol at NCO index 100

Catalyst Content (pbw)	**Catalyst type**					
	$Cu(acac)_2(en)_2$					
	Cream Time (min)	**Gel Time (min)**	**Tack free Time (min)**	**Rise Time (min)**	**Density (kg/m^3)**	**Volume (V/8)**
0.25	0:43	3:26	8:21	7:25	47.3	5.25
0.50	0:37	2:10	3:33	4:01	43.1	5.75
1.00	0:34	1:12	1:36	2:13	39.2	6.5
2.00	0:20	0:28	0:39	0:54	38.2	6.75

Table 4.10 Reaction profiles of RPUR foams catalyzed by Cu(acac)$_2$(trien) in ethylene glycol at NCO index 100

Catalyst Content (pbw)	Catalyst type					
	Cu(acac)$_2$(trien)					
	Cream Time (min)	Gel Time (min)	Tack free Time (min)	Rise Time (min)	Density (kg/m^3)	Volume (V/8)
0.50	0:39	3:58	9:07	8:11	46.9	5.25
1.00	0:36	2:22	3:23	4:16	41.0	5.5
2.00	0:38	1:01	1:22	1:49	38.0	6.5

Table 4.11 Reaction profiles of RPUR foams catalyzed by DMCHA at NCO index 100

Catalyst Content (pbw)	Catalyst type					
	DMCHA					
	Cream Time (min)	Gel Time (min)	Tack free Time (min)	Rise Time (min)	Density (kg/m^3)	Volume (V/8)
0.25	0:32	2:21	9:38	6:17	42.5	6.25
0.50	0:26	1:27	6:11	4:21	40.3	6.5
1.00	0:22	0:32	2:34	1:55	37.1	7.0
2.00	0:16	0:25	1:36	1:27	35.4	8.0

4.3.5.1 Effect of catalyst content in RPUR foam formulation on reaction time of RPUR foams

The kinetic rate of foaming was assessed from the reaction times such as the cream time, gel time, tack free time and rise time. The effect of catalyst content on the reaction time of RPUR foam catalyzed by various types of copper-amine complex prepared from $Cu(OAc)_2$ and $Cu(acac)_2$ is shown in Figures 4.26-4.27. The results indicated that there was a large decrease in reaction time, especially gel time and tack-free time, with increasing content of catalyst in the foam formulation. For cream time, only a slight decrease was observed. This result revealed that all of copper-amine complexes were good catalyst for reaction between isocyanate group and hydroxyl groups. Moreover, tack free time of RPUR foam catalyzed by copper-amine complexes was shorter than rise time. It demonstrated that the blowing reaction still occurred for generating CO_2 gas while, the polymerization reaction almost completed. Consequently, the foam matrix would not collapse and effectively contained CO_2 gas. This result is needed for the insulating property of foams. Although a high catalyst content at 2.0 pbw gave faster reaction times, the gel time and tack free time were too short and, therefore, caused difficulty in foam preparation. From this reason, the optimum catalyst content for the foam formulation was 1.0 pbw.

The catalytic activities of copper-amine complexes were compared with reference commercial catalyst (DMCHA). It was shown that increasing of DMCHA content promoted the blowing and gelling reactions, which were confirmed by the faster cream time and tack-free time, respectively. Although DMCHA could catalyze both blowing and gelling reactions, but copper-amine complexes gave tack-free time much faster than DMCHA. This result was useful for reducing a cycle time in foam manufacturing.

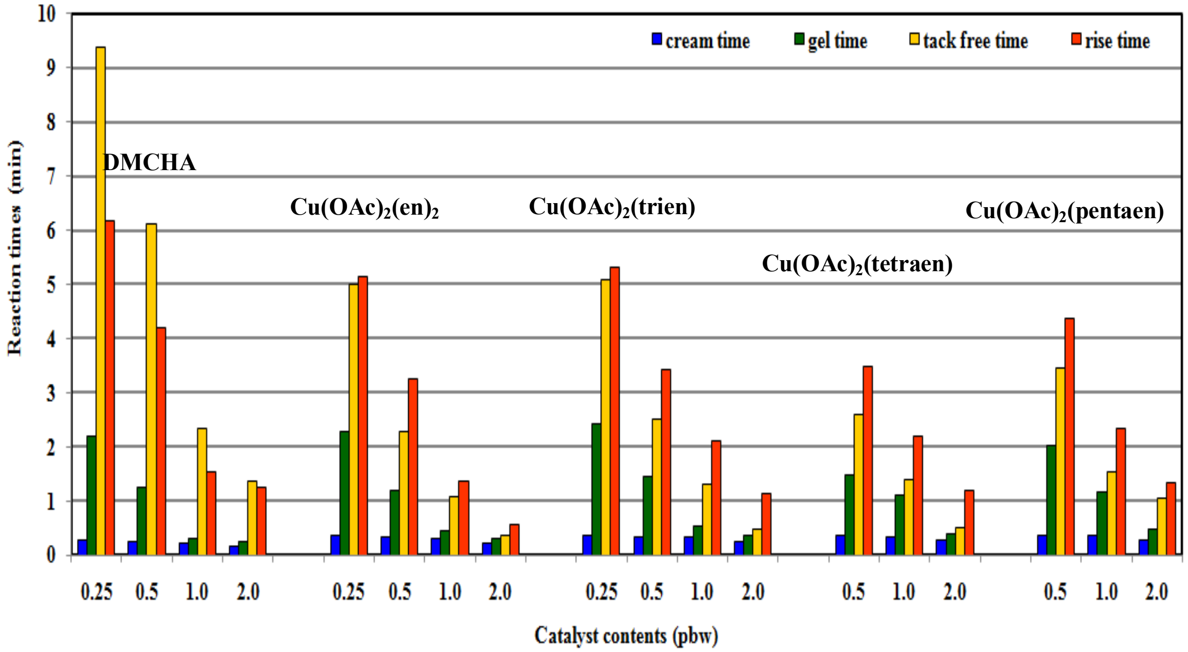


Figure 4.26 The effect of catalyst content on reaction times of RPUR foams catalyzed by DMCHA, Cu(OAc)$_2$(en)$_2$, Cu(OAc)$_2$(trien), Cu(OAc)$_2$(tetraen) and Cu(OAc)$_2$(pentaen) in ethylene glycol

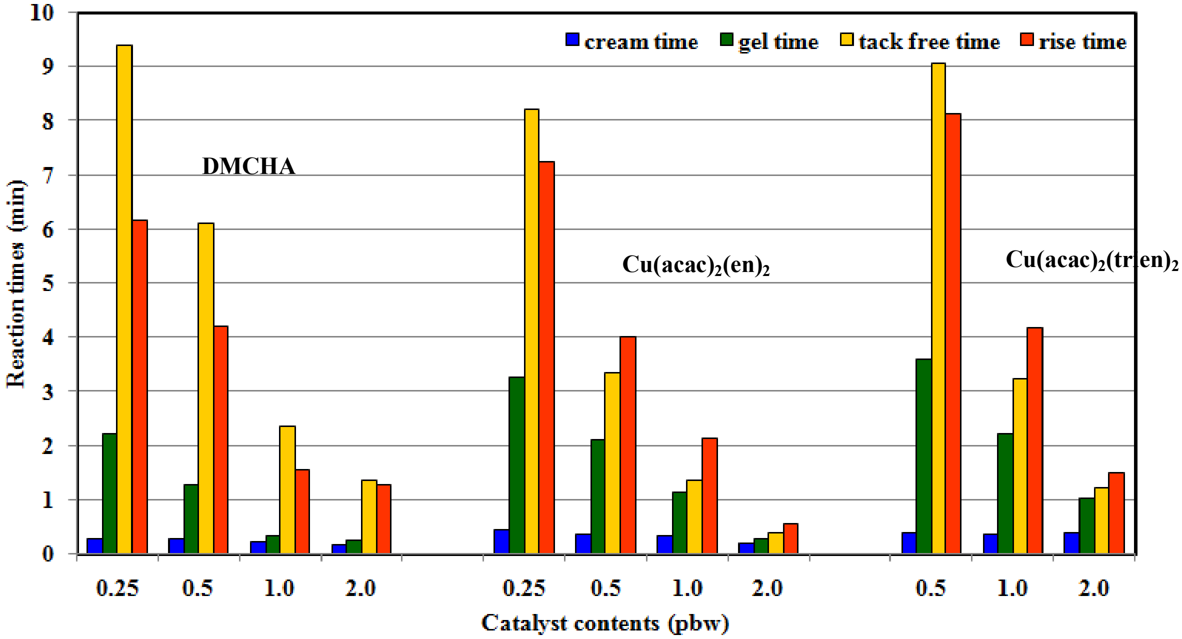


Figure 4.27 The effect of catalyst content on reaction times of RPUR foams prepared at NCO index of 100 and catalyzed by DMCHA, Cu(acac)$_2$(en)$_2$ and Cu(acac)$_2$(trien) in ethylene glycol

4.3.5.2 Effect of catalyst content in RPUR foam formulation on density of RPUR foams

The effect of catalyst content on density and apperance of RPUR foams catalyzed by various types of copper-amine complex prepared from $Cu(OAc)_2$ and $Cu(acac)_2$ were investigated as shown in Figures 4.28-4.29. It was found that the density of foam decreased with increasing catalyst content in foam formulation. This result could explain from the catalytic behavior of catalyst. The previous investigation referred that copper-amine catalyst was the good gelling catalyst which effectively increased the rate of gelling reaction and this reaction is exothermic. Consequently, increasing catalyst content, the temperature of system was risen due to increasing the gelling reaction rate. The kinetic rate of blowing reaction was promoted by a catalyst or by raising temperature [29]. Therefore, upon increasing catalyst content, more blowing reaction could occur and the foam density was decreased.

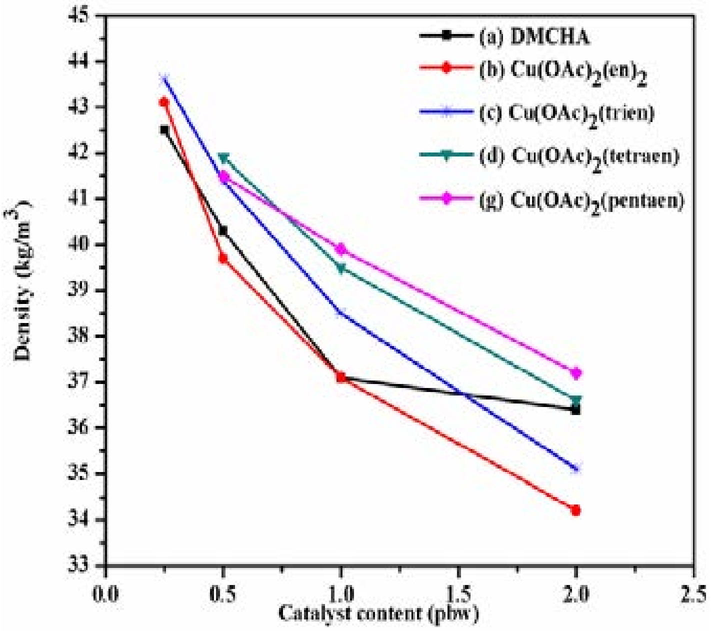


Figure 4.28 The effect of catalyst content on density of RPUR foams catalyzed by

(a) DMCHA; (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2(trien)$; (d) $Cu(OAc)_2(tetraen)$
and (e) $Cu(OAc)_2(pentaen)$ in ethylene glycol

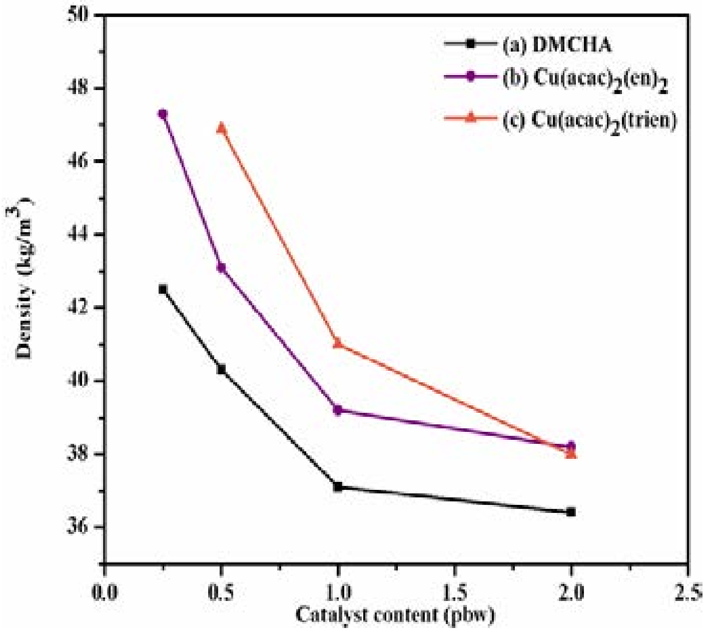


Figure 4.29 The effect of catalyst content on density of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(acac)_2(en)_2$ and (c) $Cu(acac)_2(trien)$ in ethylene glycol

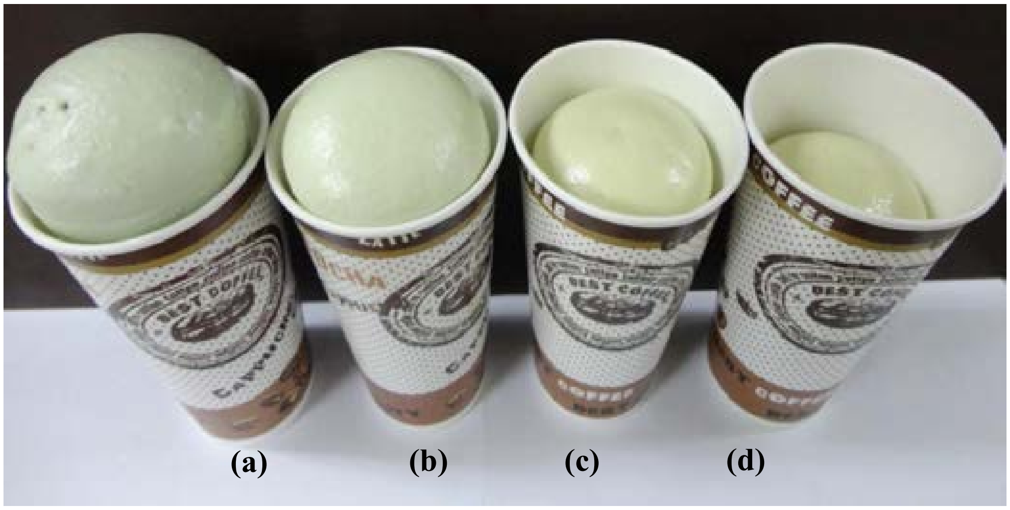


Figure 4.30 Appearance of RPUR foams catalyzed by $Cu(OAc)_2$(trien) in various catalyst contents (a) 2.0; (b) 1.0; (c) 0.5 and (d) 0.25 pbw

4.3.6 Effect of blowing agent content in RPUR foam formulation on density of RPUR foams

The next step of experiment was to investigate the effect of blowing agent content on density and apperance of RPUR foams catalyzed by various types of copper-amine complex prepared from $Cu(OAc)_2$ and $Cu(acac)_2$ were examined as shown in Figures 4.31-4.32. It was found that the density of RPUR foams decreased with increasing of blowing agent content. In this study, water was the chemical blowing agent which expanded RPUR foams by CO_2 gas generated by the reaction between water and isocyanate group, and this reaction is exothermic [29-30]. Thus, increasing of blowing agent content would reduce density of RPUR foams resulting from more CO_2 gas amount in the system. As a result, the proper density of RPUR foams (in the range of 35- 50 kg/m^3) was obtained from using 3.0 pbw of blowing agent, therefore, this blowing agent content was appropriate for the foam formulation.

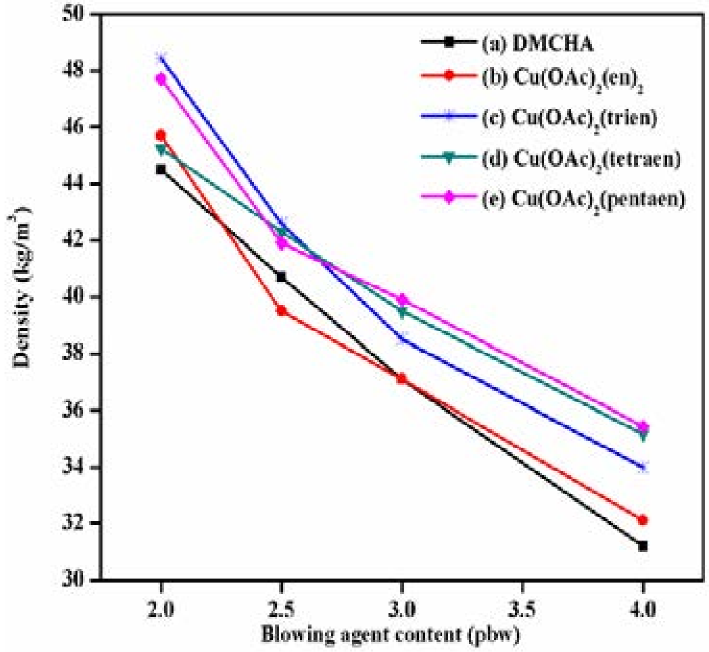


Figure 4.31 The effect of blowing agent content on densities of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2$(trien); (d) $Cu(OAc)_2$(tetraen) and (e) $Cu(OAc)_2$(pentaen) in ethylene glycol

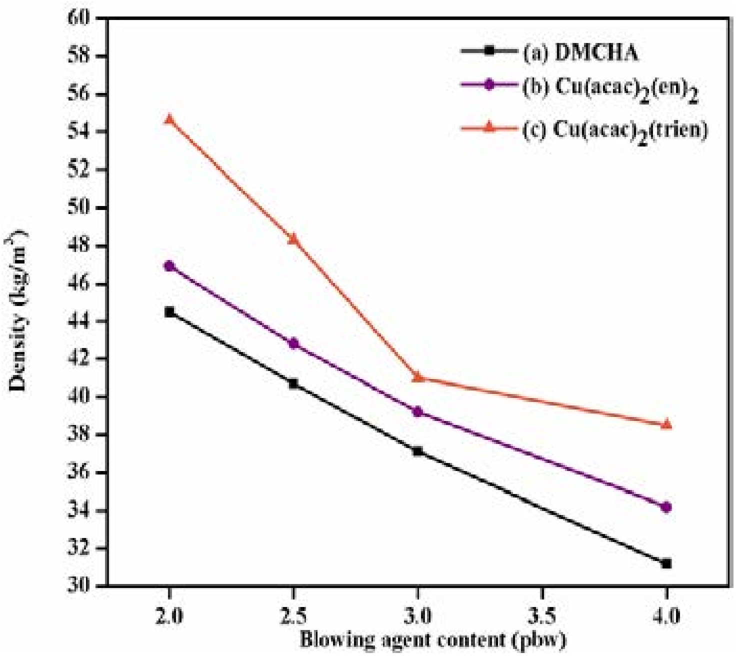


Figure 4.32 The effect of blowing agent content on densities of RPUR foams catalyzed by (a) DMCHA; (b) $Cu(acac)_2(en)_2$ and(c) $Cu(acac)_2$(trien) in ethylene glycol

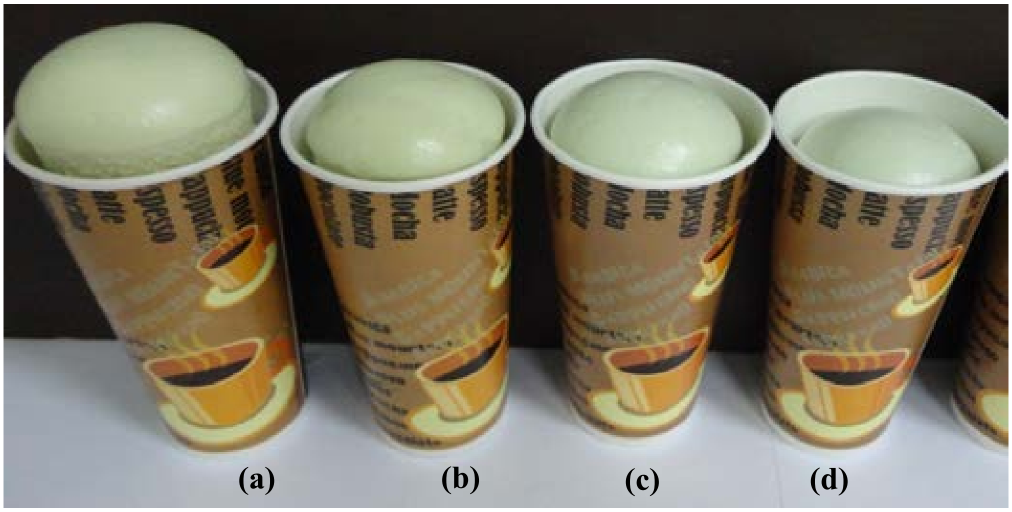


Figure 4.33 Appearance of RPUR foams catalyzed by Cu(OAc)$_2$(trien) in various blowing agent contents at NCO index of 100 (a) 4.0; (b) 3.0; (c) 2.5 and (d) 2.0 pbw

4.3.7 The effect of NCO indexes in RPUR foam formulation on RPUR Foam properties

The polymeric MDI content was varied to obtain the NCO indexes of 100 130 and 150. Other raw materials was fixed at the suitable amount as shown in RPUR foam formulation (Table 4.12) and their appearances are shown in Figures 4.34-4.35.

Table 4.12 RPUR foam formulation

Components (pbw*)	**NCO index****		
	100	**130**	**150**
Daltolac® R180	100	100	100
Catalyst			
- DMCHA (commercial catalyst)	1.0	1.0	1.0
- copper-amine complexes in EG			
Surfactant (Tegostab® 8460)	2.5	2.5	2.5
Blowing agent (water)	3.0	3.0	3.0
Polymeric MDI (PMDI, Supresec® 5005)	161	210	242

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

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

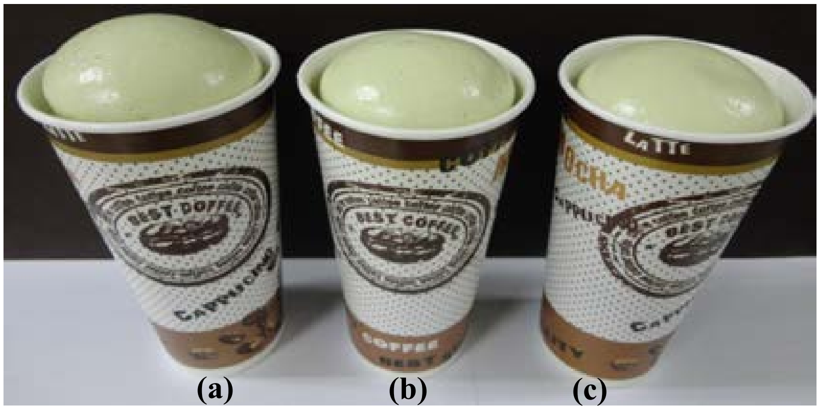


Figure 4.34 Appearance of RPUR foams catalyzed by Cu(OAc)$_2$(trien) in ethylene glycol at different NCO indexes (a) 150; (b) 130 and (c) 100

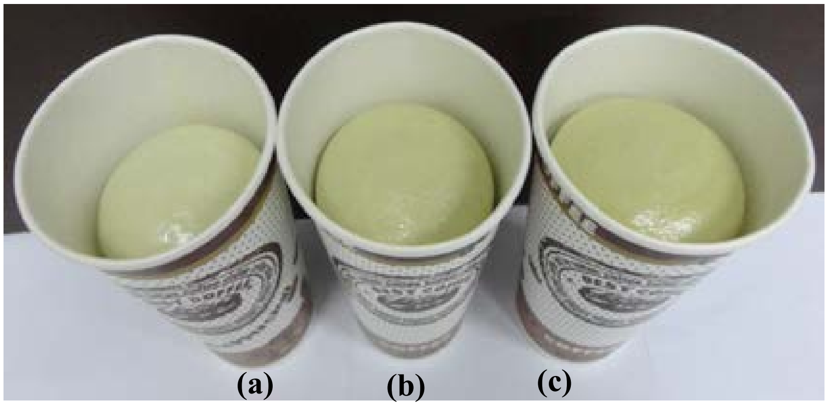


Figure 4.35 Appearance of RPUR foams catalyzed by Cu(acac)$_2$(trien) in ethylene glycol at different NCO indexes (a) 100; (b) 130 and (c) 150

From the above results of foam preparation, all RPUR foams catalyzed by Cu(OAc)$_2$(en)$_2$, Cu(OAc)$_2$(trien), Cu(OAc)$_2$(tetraen) and Cu(OAc)$_2$(pentaen) had good appearance and could be cut to measure the apparent density. RPUR foams catalyzed by those catalysts, gave the good foams at NCO indexes of 100-150. However, RPUR foams catalyzed by Cu(acac)$_2$(en)$_2$ and Cu(acac)$_2$(trien) gave good foams at NCO indexes of 100 and 130. In the case of Cu(acac)$_2$(en)$_2$ and Cu(acac)$_2$(trien), RPUR foams prepared at higher NCO index of 150 were harder and more brittle. Thus, they were not good for foam applications. RPUR foam catalyzed by copper acetylacetonate-amine complexes had less blowing reaction than those prepared copper acetate-amine complexes

4.3.7.1 The effect of NCO indexes in RPUR foam formulation on density of RPUR foams

The apparent density of RPUR foams catalyzed by copper-amine complexes at different NCO indexes is shown in Figures 4.36-4.37. It was found that the apparent density of RPUR foams increased with increasing the content of NCO indexes because the excess of isocyanate in PUR system could undergo further polymerization to give crosslinked structure [31]. RPUR foams catalyzed by $(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) had appropriate density when prepared at the NCO index of 100-150 while the foams catalyzed by $Cu(acac)_2(en)_2$ and $Cu(acac)_2$(trien) at the NCO index of 100 and 130 had suitable density.

In comparison between the densities of RPUR foams prepared from copper-amine complexes and reference commercial catalyst (DMCHA), it was found that foams catalyzed by $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen) and $Cu(OAc)_2$(pentaen) had density similarly to those catalyzed from DMCHA, especially NCO indexes of 130 and 150. Whereas the foams catalyzed by $Cu(OAc)_2(en)_2$ had lower density than those catalyzed by DMCHA. In the case of foams catalyzed by $Cu(acac)_2(en)_2$ and $Cu(acac)_2$(trien), they had higher density than those catalyzed by DMCHA in all of NCO indexes. Density of RPUR foams catalyzed by copper-aimne complexes at various NCO indexes 100-150 was in range of 35-50 kg/m3, which was the desirable density for foam applications [6,32].

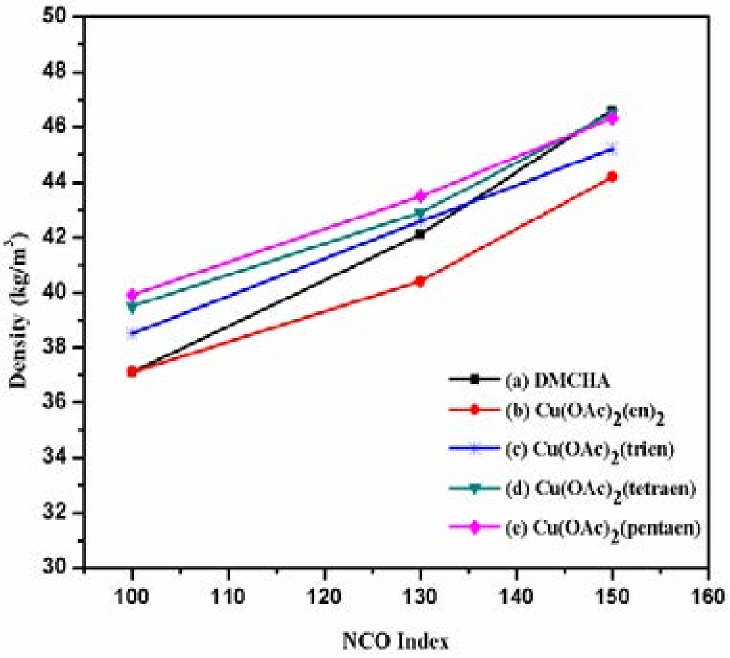


Figure 4.36 The effect of NCO index on densities of RPUR foams catalyzed by (a) DMCHA; (b) Cu(OAc)$_2$(en)$_2$; (c) Cu(OAc)$_2$(trien); (d) Cu(OAc)$_2$(tetraen) and (e) Cu(OAc)$_2$(pentaen) in ethylene glycol

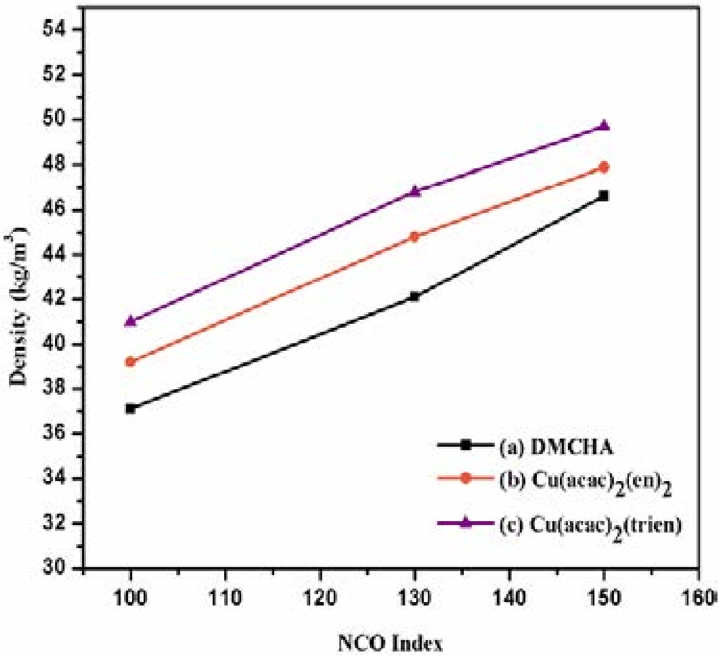


Figure 4.37 The effect of NCO index on densities of RPUR foams catalyzed by (a) DMCHA; (b) Cu(acac)$_2$(en)$_2$ and (c) Cu(cac)$_2$(trien) in ethylene glycol

4.3.7.2 The effect of NCO indexes in RPUR foam formulation on NCO conversions of RPUR foams

ATR-FTIR spectroscopy was useed to investigate the polymerization of RPUR foam system. IR spectra of polymeric MDI, polyether polyol and RPUR foams catalyzed by copper-amine complexes are illustrated in Figure 4.38. It was indicated that the absorption band of isocyanate could be observed at 2277 cm^{-1}. Therefore, the NCO conversion was calculated from FTIR spectra. The ratio of free NCO absorption band increased with increasing of NCO index in the foam formulation as shown in Figure 4.39.

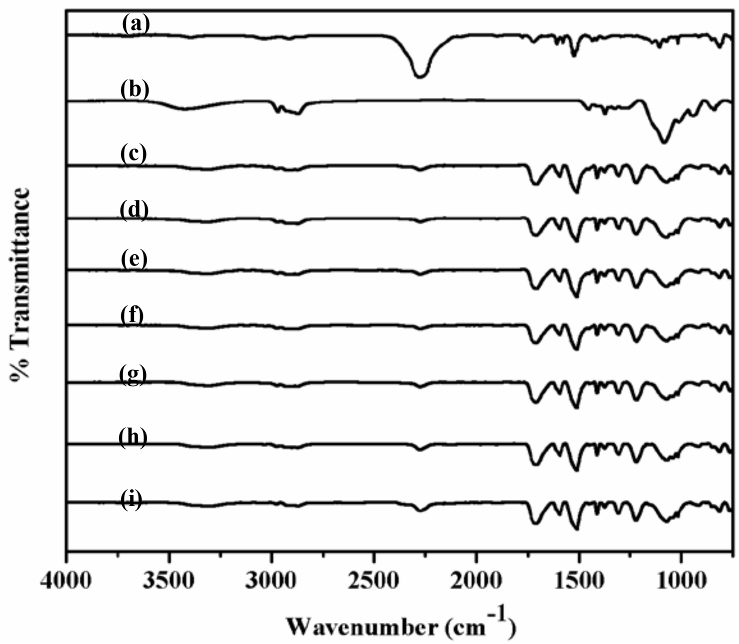


Figure 4.38 IR spectra of starting materials and RPUR foams catalyzed by copper-amine complexes in ethylene glycol at NCO index 100 (a) PMDI; (b) polyether polyol; (c) DMCHA; (d) Cu(OAc)$_2$(en)$_2$; (e) Cu(OAc)$_2$(trien);

(f) $Cu(OAc)_2(tetraen)$; (g) $Cu(OAc)_2(pentaen)$; (h) $Cu(acac)_2(en)_2$ and (i) $Cu(acac)_2(trien)$

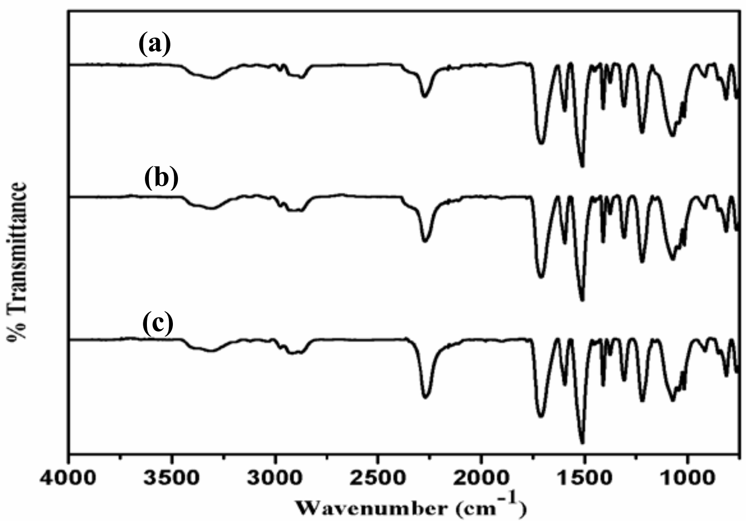


Figure 4.39 IR spectra of RPUR foams catalyzed by $Cu(acac)_2(trien)$ in ethylene glycol at different NCO indexes (a) 100; (b) 130 and (c) 150

The NCO conversion defined as the ratio between isocyanate peak area at time t and isocyanate peak area at time 0 as shown in following equation [31-36]:

$$\% \text{ conversion of isocyanate } (\alpha) = \left[1 - \frac{\text{NCO(f)}}{\text{NCO(i)}}\right] x100$$

where;

NCO(f) is the area of isocyanate absorbance peak area at time t (spectrum (b)-(i) in Figure 4.32)

NCO(i) is the area of isocyanate absorbance peak area at initial time 0 (spectrum (a) in Figure 4.32)

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

Polyisocyanate : polyurethane (PIR/PUR) ratio was calculated from the peak area of isocyanate and urethane at 1415 and 1220 cm^{-1}, respectively (Table 4.13).

Table 4.13 Wavenumber of the functional groups used in calculation [37]

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

The results of NCO conversion of RPUR foams catalyzed by copper-amine complexes are shown in Table 4.14 and Figure 4.40. It was found that NCO conversion was 96-99 % at various NCO indexes 100-150. Moreover, NCO conversion decreased with increasing of the content of NCO indexes. As a high NCO conversion of RPUR foams, it could be concluded that copper-amine complexes were good catalysts for polyurethane formation.

In this study, the polyisocyanurate:polyurethane (PIR:PUR) ratio of RPUR foams catalyzed by copper-amine complex was also investigated as shown in Table 4.14. It was found that PIR:PUR ratio was low and regardless with content of NCO indexes. It could be implied that the excess isocyanate could not undergo trimerization to give isocyanurate group since copper-amine complexes were not specific toward isocyanurate formation.

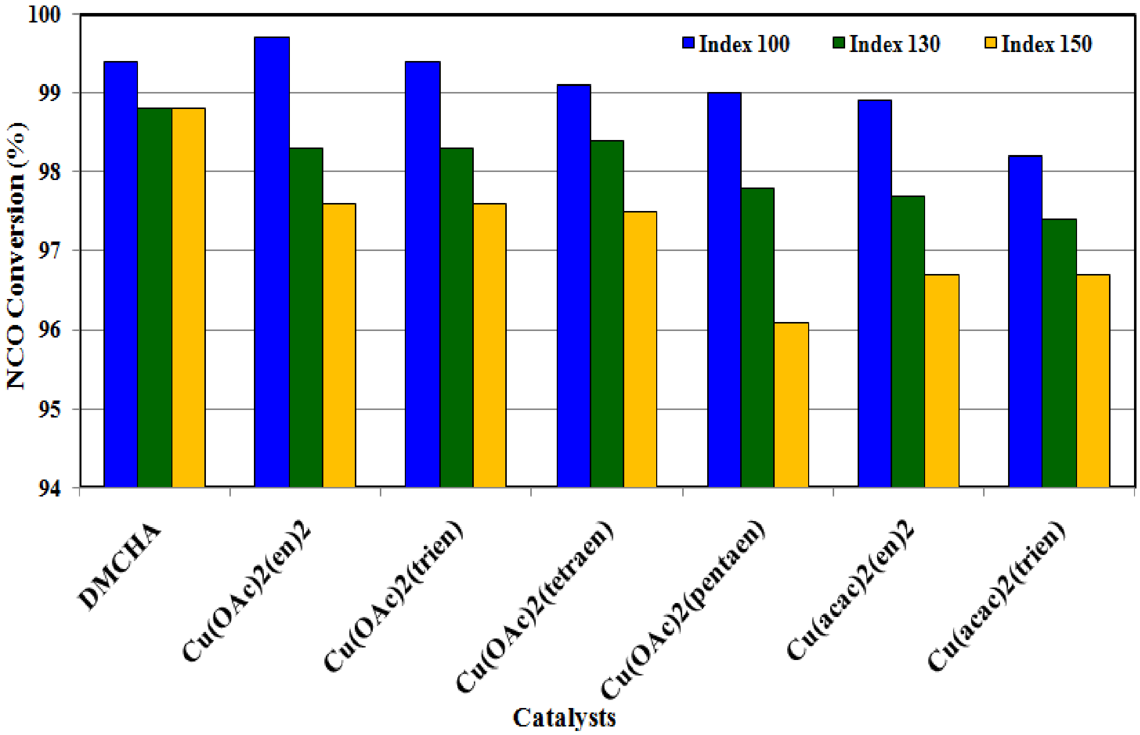


Figure 4.40 NCO conversions of RPUR foam catalyzed by different copper-amine complexes in ethylene glycol

Table 4.14 NCO conversions and PIR: PUR ratio of RPUR foams catalyzed by copper-amine complexes in ethylene glycol at different NCO indexes

Catalysts	**NCO indexes**	**NCO conversion (%)**	**PIR/PUR**
DMCHA (ref.)	100	99.4	0.205
	130	98.8	0.211
	150	98.4	0.223
$Cu(OAc)_2(en)_2$	100	99.7	0.176
	130	98.3	0.274

	150	97.6	0.246
Cu(OAc)$_2$(trien)	100	99.4	0.217
	130	98.3	0.286
	150	97.6	0.241
Cu(OAc)$_2$(tetraen)	100	99.1	0.182
	130	98.4	0.221
	150	97.5	0.180
Cu(OAc)$_2$(pentaen)	100	99.0	0.184
	130	97.8	0.229
	150	96.1	0.173
Cu(acac)$_2$(en)$_2$	100	98.9	0.177
	130	97.7	0.205
	150	96.7	0.258
Cu(acac)$_2$(trien)	100	98.2	0.190
	130	97.4	0.204
	150	96.7	0.230

4.3.7.3 The effect of NCO indexes in RPUR foam formulation on foaming temperature of RPUR foams

The maximum core temperature of RPUR foams catalyzed by various copper-amine complexes at different NCO indexes was studied as shown in Table 4.15. It was found that the NCO index effected on foaming temperature of foams. As increasing NCO indexes, the maximum core temperature of foams was increased. Since the excess isocyanate in formulation could react in other secondary reactions. For example, excess isocyanate might react with the active hydrogen atoms of urethane and urea linkages from the primary reactions to form allophonate and biuret, respectively. Those reactions were also exothermic reaction, which increased foaming temperature of RPUR foams

Table 4.15 Maximum core temperature of RPUR foam catalyzed by copper-amine complexes at different NCO indexes

Catalysts	**NCO indexes**	**Maximum core temperature (°C)**	**Starting times at T_{max} [sec(min)]**
DMCHA	100	130	345 (5:45)
	150	135	435 (7:15)
$Cu(OAc)_2(en)_2$	100	134	300 (5:00)
	150	141	360 (6:00)
$Cu(OAc)_2$(trien)	100	130	285 (4:45)
	150	142	360 (6:00)
$Cu(OAc)_2$(tetraen)	100	129	315 (5:15)
	150	136	360 (6:00)
$Cu(OAc)_2$(pentaen)	100	124	315 (5:15)
	150	135	375 (6:15)
$Cu(acac)_2(en)_2$	100	129	330 (5:30)
	150	141	375 (6:15)
$Cu(acac)_2$(trien)	100	118	555 (9:15)
	150	120	555 (9:15)

From above results, The optimum formulation of RPUR foams was obtained and demonstrated in Table 4.16.

Table 4.16 The optimum formulation of RPUR foams

Formulation	**pbw***
Daltolac® R180	100
Catalyst (copper-amine complexe 30%wt in ethylene glycol)	1.0

Surfactant (Tegostab® B8460)	2.5
Blowing agent (distilled water)	3.0
Polymeric MDI (PMDI, Suprasec® 5005) at NCO index 100	160.0

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

4.3.8. Preparation of RPUR foams using an plastic mold

In order to test the foam processing ability, RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ were selected for investigation. In the experiment, the foams were prepared at NCO index 100 using 10x10x10 cm plastic mold covered with aluminum foil instead of a paper cup. The starting materials were mixed in a paper cup and then poured into the large mold. The results showed that RPUR foams catalyzed by $Cu(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$ could be processed in the large mold and the appearance of foam was the same as that prepared in a paper cup. Appearances of RPUR foams prepared in plastic mold are illustrated in Figure 4.41.

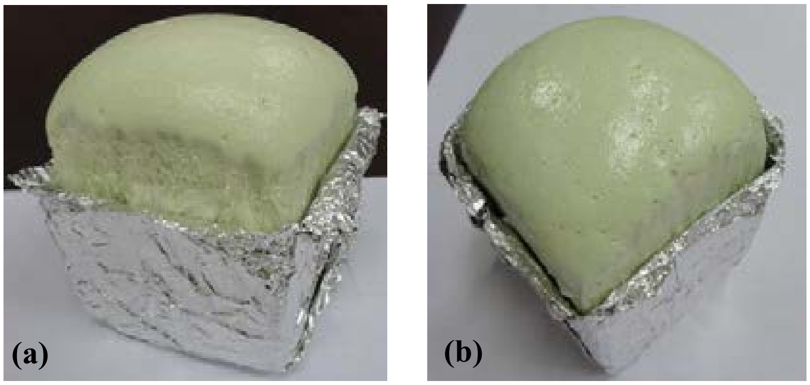


Figure 4.41 RPUR foams catalyzed by (a) $Cu(OAc)_2(en)_2$ and (b) $Cu(OAc)_2(trien)$ prepared in an plastic mold

4.4 Adjusting catalyst activity by using mixed metal-amine complexes

Although the catalytic activity of copper-amine complex catalysts was high, RPUR foams catalyzed by those catalysts had the problem about the formation of holes in RPUR foams at the bottom of the mold. This problem caused by unbalanced between gelling and blowing reaction. Copper-amine complexes accelerated effectively in gelling reaction but those catalysts had poor catalytic activity in blowing reaction. Moreover, the viscosity of liquid foams was rapidly increased at the initial of reaction due to the short gel time of foam catalyzed by copper-amine complexes. This high viscosity liquid foam could trap the air bubble, occurred from mixing process, and turn it into the large holes by exothermic heat of polymerization reaction.

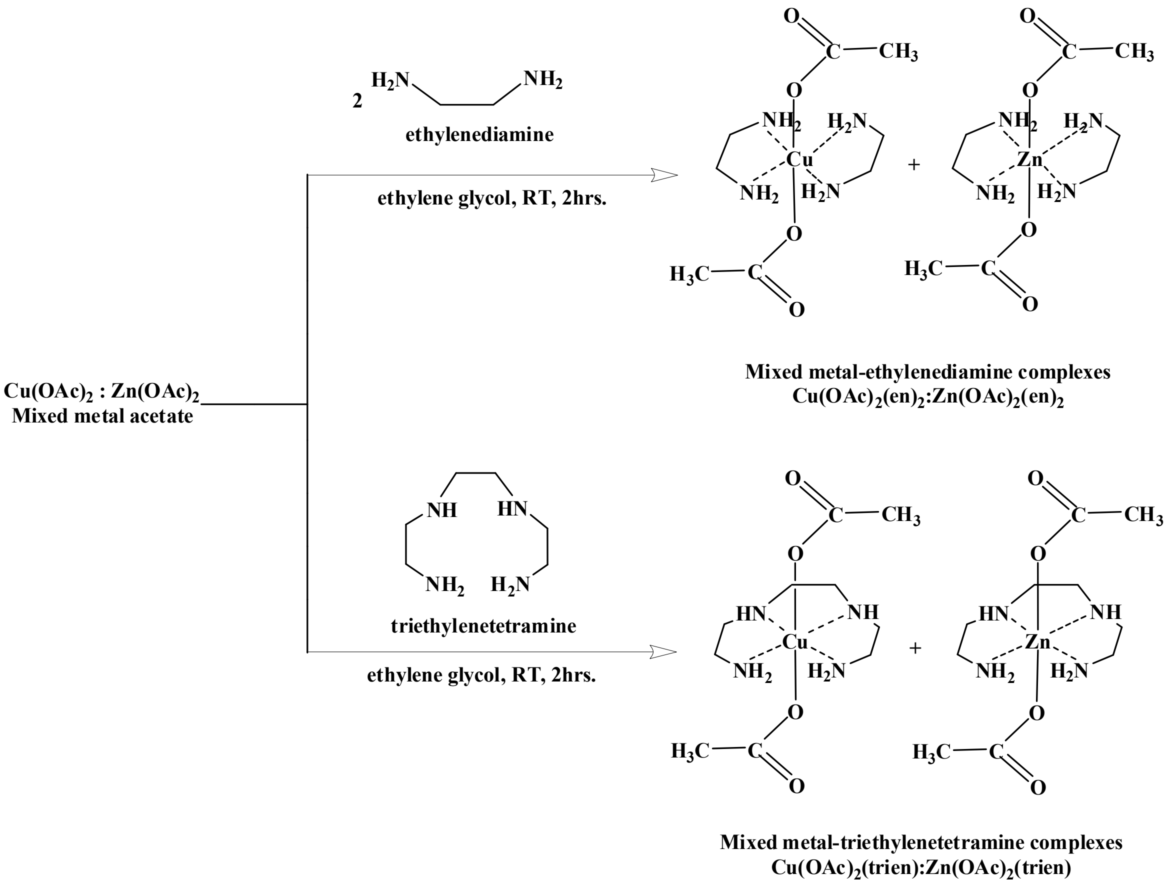
To solve this problem, $Zn(OAc)_2(en)_2$ and $Zn(OAc)_2(trien)$ were chosen to use as the co-catalyst for synthesizing mixed metal-amine complexes because the zinc-amine complexes synthesized from $Zn(OAc)_2$ compound were referred as the good blowing catalyst [38-39].

4.4.1 Synthesis of mixed metal-amine complexes [$Cu(OAc)_2(en)_2$:$Zn(OAc)_2(en)_2$] and $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$] in ethylene glycol

Mixed metal-amine complexes were synthesized with the same procedure used for copper-amine complexes. But the complexes were obtained from the reaction between the mixture of metal acetates, copper(II) acetate [$Cu(OAc)_2$] and Zn(II) acetate [$Zn(OAc)_2$], and aliphatic amine [ethylenediamine (en) or triethylenetetramine (trien)] and using ethylene glycol as a solvent. The mole ratios of $Cu(OAc)_2$:$Zn(OAc)_2$:en and $Cu(OAc)_2$:$Zn(OAc)_2$:trien employed in the synthesis of mixed metal complexes were 0.5:0.5:2 and 0.5:0.5:1, respectively. The reactions between mixed-metal

compounds and aliphatic amines gave $Cu(OAc)_2(en)_2$:$Zn(OAc)_2(en)_2$ and $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$] as shown in Scheme 4.4

As the same result, mixed metal-amine complexes were obtained as odorless with low viscosity. The solution containing mixed metal-amine complexes could be further used in the preparation of RPUR foam without purification.



Scheme 4.4 Synthesis of $Cu(OAc)_2(en)_2$:$Zn(OAc)_2(en)_2$] and $Cu(OAc)_2$(trien):$Zn(OAc)_2$(trien) complexes

4.4.2 Preparation of rigid polyurethane (RPUR) foams

The reaction profiles of RPUR foams catalyzed by copper-amine, zinc-amine and mixed metal-amine complexes synthesized in ethylene glycol are shown in Table 4.17. Comparison of reaction times (Figure 4.42) showed that the order of catalytic activity was copper-amine complexes > mixed metal complexes > zinc-amine complexes.

This result indicated that mixed metal-amine complexes had the catalytic activity between copper and zinc-amine complexes. Both Cu(OAc)$_2$(en)$_2$:Zn(OAc)$_2$(en)$_2$ and Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) had longer gel time than their copper-amine complexes, which could reduce the air trapping at the initial of reaction.

The comparison of RPUR foams density is shown in Figure 4.43. It was found that density of foams catalyzed by mixed metal-amine complexes was lower than those catalyzed by only copper or zinc-amine complexes. Since more blowing reaction could take place with using zinc-amine complexes as a co-catalyst. This reaction decreased the density of foams by generating more CO$_2$ gas. The result confirmed that mix metal-amine complexes could balance the reaction of RPUR foams due to accelerating both gelling and blowing reaction.

Table 4.17 Reaction profiles of RPUR foams catalyzed by DMCHA, copper-amine complexes and mixed metal-amine complexes synthesized in ethylene glycol

Catalyst types	Cream Time (min:sec)	Gel Time (min:sec)	Tack-free Time (min:sec)	Rise Time (min:sec)	Density (kg/m^3)	Volume (V/8)	Height of hole in the mold (cm)
Cu(OAc)$_2$(en)$_2$	0:31	0:46	1:08	1:37	37.1	7.25	5.0
Cu(OAc)$_2$(trien)	0:35	0:55	1:31	2:11	38.5	7.0	4.0
Zn(OAc)$_2$(en)$_2$	0:22	1:30	2:48	3:17	37.6	6.75	2.0
Zn(OAc)$_2$(trien)	0:35	1:50	3:04	3:42	38.0	6.75	No hole
Cu(OAc)$_2$(en)$_2$: Zn(OAc)$_2$(en)$_2$*	0:29	1:14	1:57	2:38	35.9	7.25	3.5

Cu(OAc)$_2$(trien): Zn(OAc)$_2$(trien)*	0:35	1:45	2:29	3:13	35.4	7.0	1.5

* Mole ratio of Cu(OAc)$_2$:Zn(OAc)$_2$:en and Cu(OAc)$_2$:Zn(OAc)$_2$:(trien) is 0.5:0.5:2 and 0.5:0.5:1 respectively.

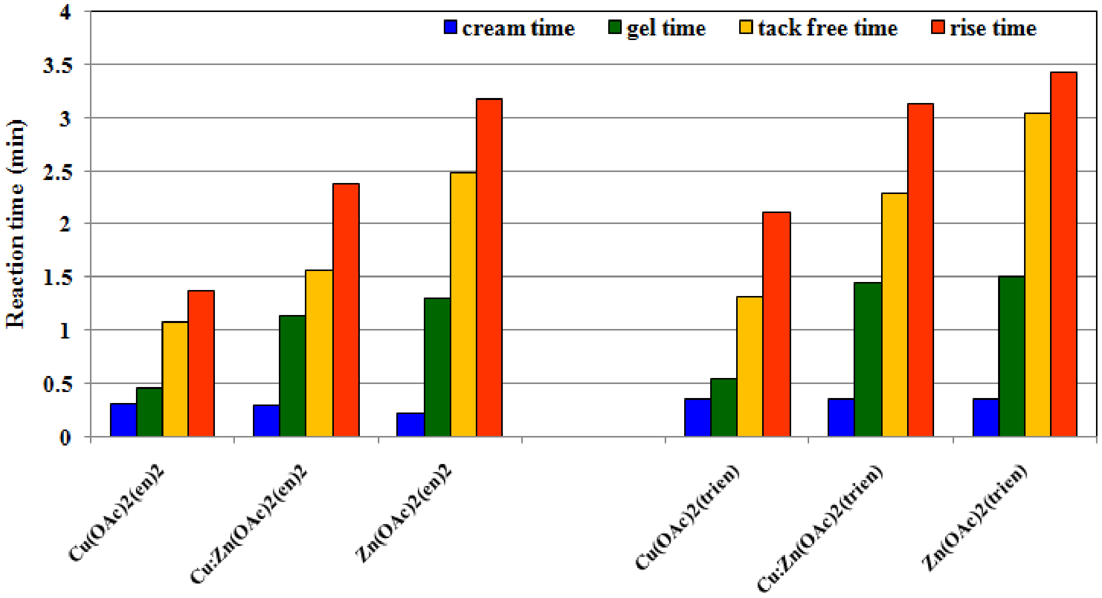


Figure 4.42 Reaction times of RPUR foams catalyzed by DMCHA, copper-amine complexes and mixed metal-amine complexes in ethylene glycol at NCO index 100

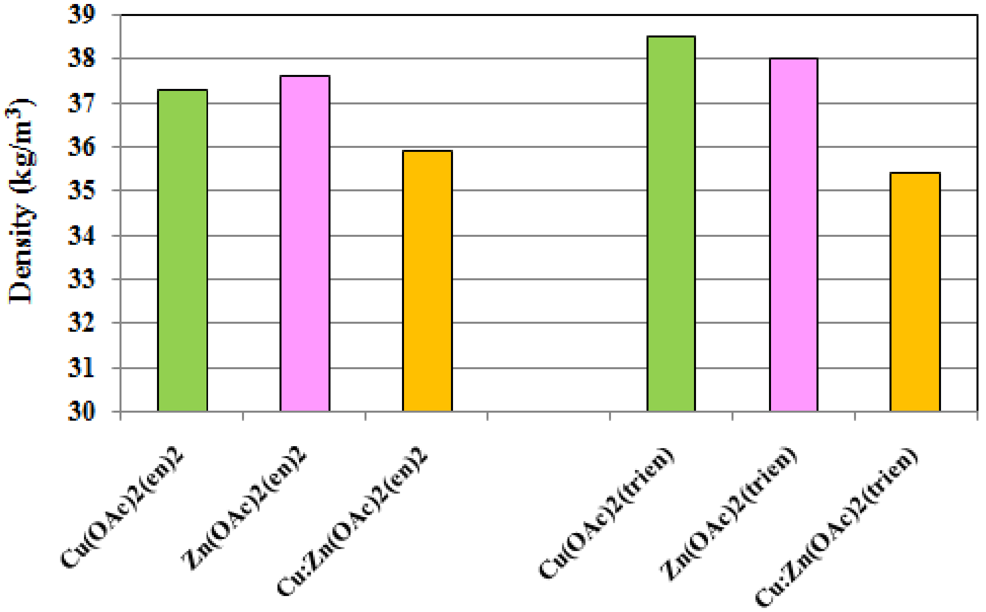


Figure 4.43 Density of RPUR foams catalyzed by DMCHA, copper-amine complexes and mixed metal-amine complexes in ethylene glycol at NCO index 100

The appearances of those foams are illustrated in Figure 4.44. It was found that all RPUR foams catalyzed by mixed metal-amine complexes were good foams. Figure 4.45 showed that the holes in the foams at the bottom of the mold were minimized with using zinc-amine complexes as a co-catalyst. Although, the holes of foams catalyzed by $Cu(OAc)_2(en)_2$:$Zn(OAc)_2(en)_2$ were smaller than those catalyzed by $Cu(OAc)_2(en)_2$, but it was too large for foam application. In the case of $Cu(OAc)_2$(trien):$Zn(OAc)_2$(trien), the holes were obviously smaller. The hole height was reduced from 4.0 to 1.5 cm when used $Cu(OAc)_2$(trien):$Zn(OAc)_2$(trien) instead of $Cu(OAc)_2$(trien). From the above results, $Cu(OAc)_2$(trien):$Zn(OAc)_2$(trien) had high catalytic activity, gave good foams and could minimized the hole on bottom foams. Thus, this catalyst was chosen to characterize and study rise profiles and temperature profiles in the next step.

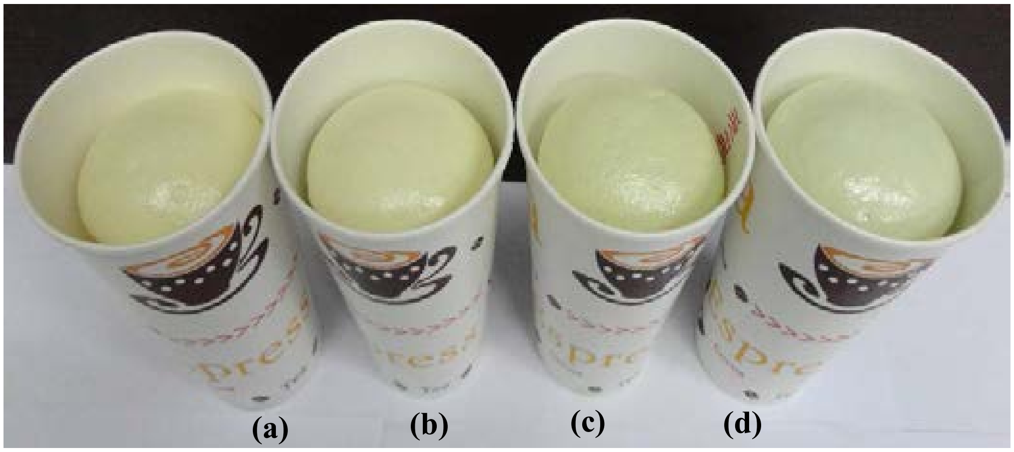


Figure 4.44 Appearance of RPUR foams prepared at NCO index of 100 catalyzed by (a) $Zn(OAc)_2(en)_2$; (b) $Zn(OAc)_2(trien)$; (c) $Cu(OAc)_2(en)_2$:$Zn(OAc)_2(en)_2$ and (d) $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$

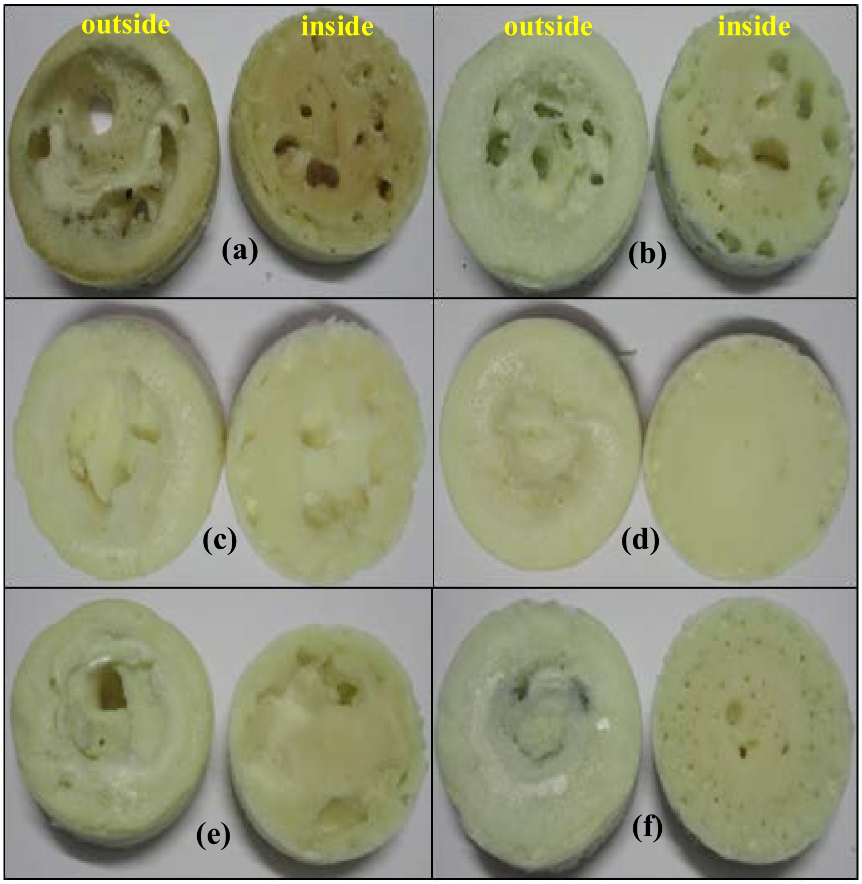


Figure 4.45 Appearance of the RPUR foam bottoms prepared at NCO index of 100 catalyzed by (a) $Cu(OAc)_2(en)_2$; (b) $Cu(OAc)_2(trien)$; (c) $Zn(OAc)_2(en)_2$; (d) $Zn(OAc)_2(trien)$; (e) $Cu(OAc)_2(en)_2$:$Zn(OAc)_2(en)_2$ and (f) $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$

4.4.3 Characterization of $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$ synthesized in ethylene glycol using UV-visible spectroscopy

The complex formation was confirmed using UV-visible spectroscopy. UV-visible spectra of $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$ synthesized in ethylene glycol is illustrared in Figure 4.46. The maximum wavelength of $Cu(OAc)_2$ and $Zn(OAc)_2$ appeared at 245 nm and 203, respectively. It was found that the maximum wavelength of $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$ appeared at 259 nm and shifted from the typical maximum wavelength of $Cu(OAc)_2$ and $Zn(OAc)_2$ which indicated that the complexes were formed.

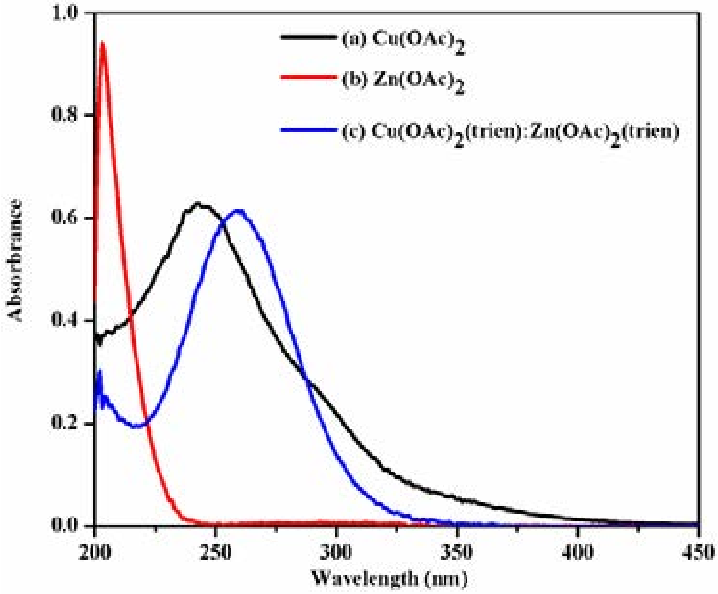


Figure4.46 UV spectra of (a) $Cu(OAc)_2$; (b) $Zn(OAc)_2$ and (c) $Cu(OAc)_2(trien)$:$Zn(OAc)_2(trien)$ in ethylene glycol

4.4.4 Rise profiles of RPUR foams catalyzed by mixed metal-amine complexes

Rise profile of RPUR foams catalyzed by Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) was investigated and compared with those foams catalyzed by their copper and zinc-amine complexes as shown Figure 4.47. It was found that all of foams catalyzed by different catalysts had the similar reaction profiles but the rise profile of foams catalyzed by Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) was more smoother curve than those foams catalyzed by Cu(OAc)$_2$(trien). The rise height of foams accelerated by Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) could be comparable with those foams catalyzed by Cu(OAc)$_2$(trien). The maximum rise rate of foams was calculated as shown in Figure 4.48. The order of maximum rise rate was copper-amine complexes > mix metal complexes > zinc-amine complexes. The result demonstrated that adding Zn(OAc)$_2$(trien) into Cu(OAc)$_2$(trien) could adjust the reaction rate of copper-amine catalyst.

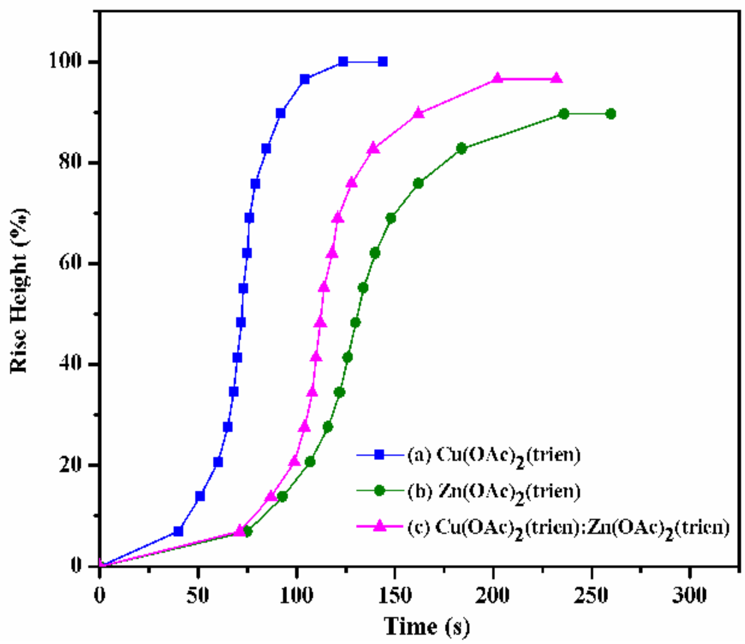


Figure 4.47 Rise profile of RPUR foams catalyzed by (a) Cu(OAc)$_2$; (b) Zn(OAc)$_2$ and (c) Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) in ethylene glycol at NCO index 100

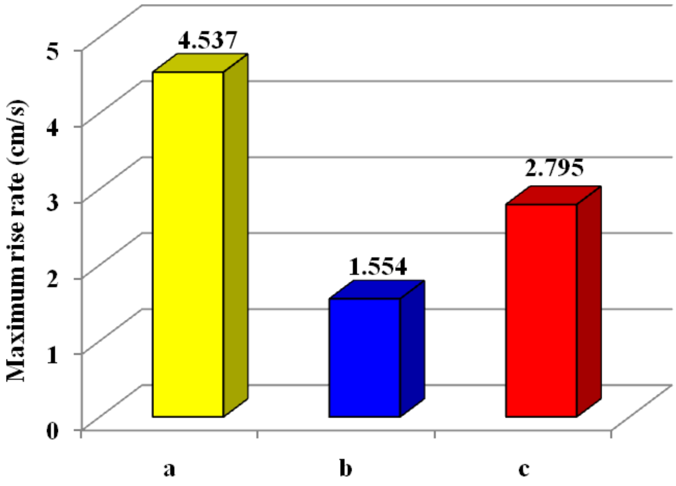


Figure 4.48 Maximum rise rates of RPUR foams catalyzed by (a) Cu(OAc)$_2$; (b) Zn(OAc)$_2$ and (c) Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) in ethylene glycol at NCO index 100

4.4.5 Temperature profiles of RPUR foams catalyzed by mixed metal-amine complexes

Figure 4.49 shows the temperature profiles of RPUR foams catalyzed by different catalysts at NCO index 100. It was found that the temperature profiles of RPUR foams catalyzed by Cu(OAc)$_2$(trien):Zn(OAc)$_2$(trien) were the same as those catalyzed by Cu(OAc)$_2$(trien) and Zn(OAc)$_2$(trien). The maximum core temperature of foams catalyzed by $Cu(OAc)_2$(trien):$Zn(OAc)_2$(trien), $Cu(OAc)_2$(trien) and $Zn(OAc)_2$(trien) were 135.6, 130.3 and 130.3 °C, respectively.

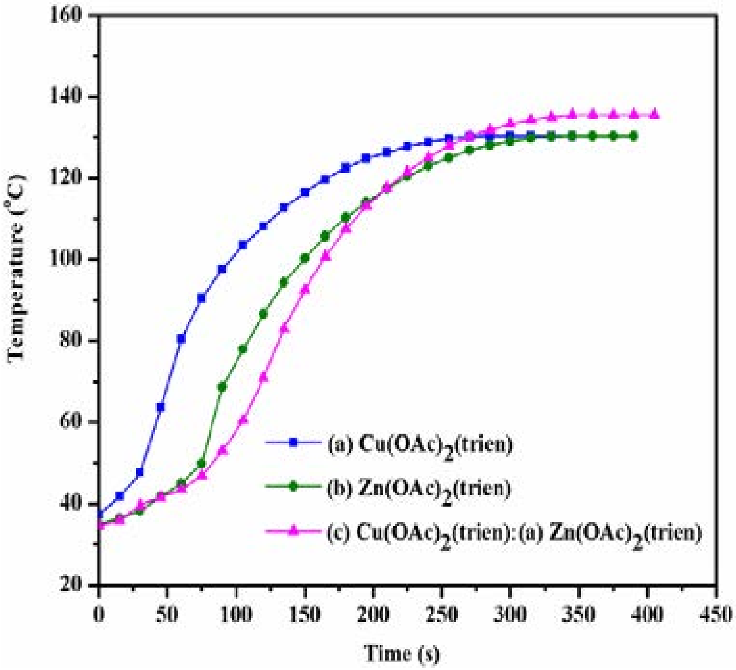


Figure 4.49 Temperature profile of RPUR foams catalyzed by (a) $Cu(OAc)_2$; (b) $Zn(OAc)_2$ and (c) $Cu(OAc)_2$(trien):$Zn(OAc)_2$(trien) in ethylene glycol at NCO index 100

4.5. Morphology of RPUR foams

4.5.1. Morphology of RPUR foams catalyzed by various catalysts

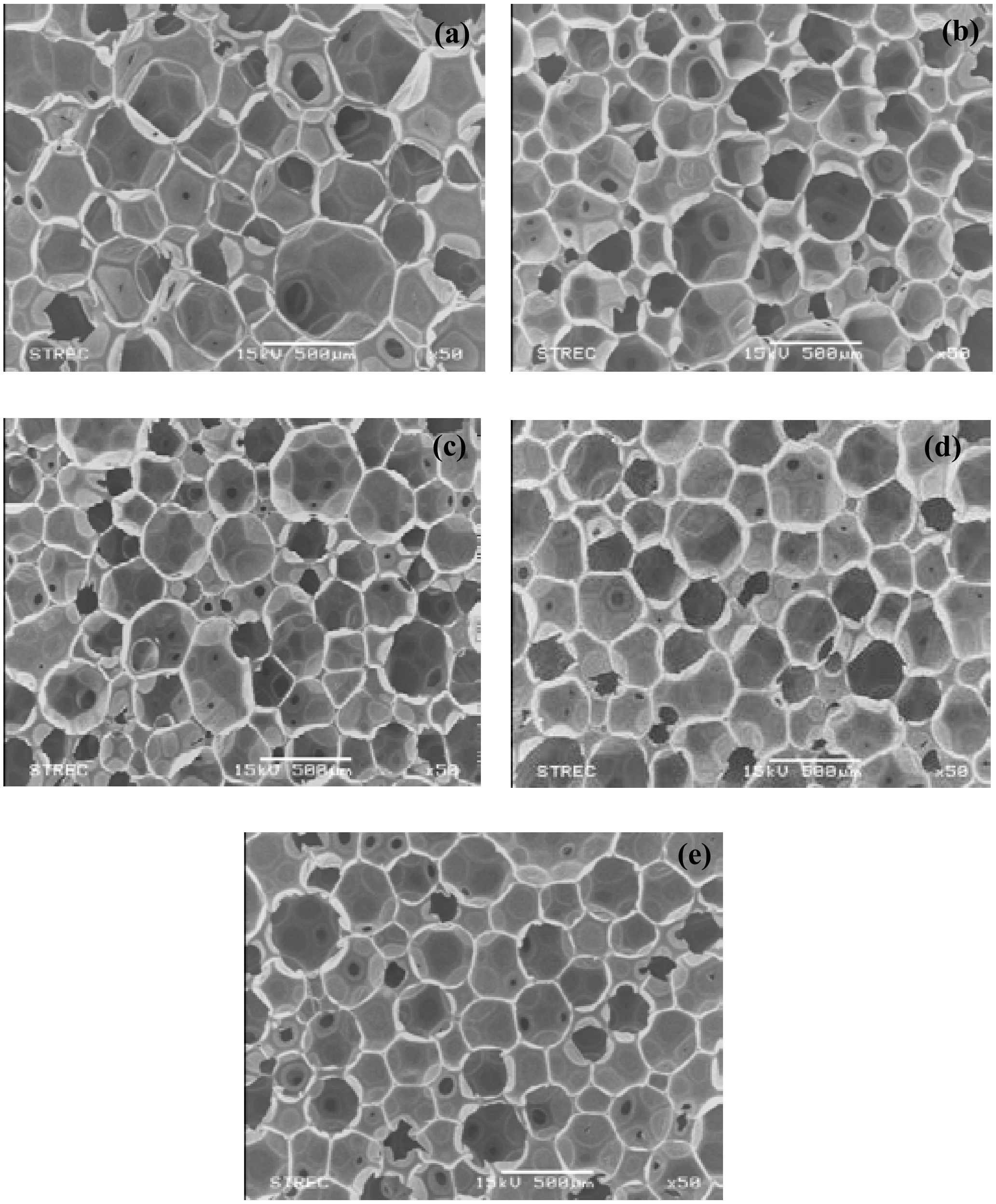


Figure 4.50 SEM of RPUR foams catalyzed by (a) $Cu(OAc)_2(en)_2$; (b) $Cu(OAc)_2(trien)$; (c) $Cu(OAc)_2(tetraen)$; (d) $Cu(OAc)_2(pentaen)$ and ; (e) $Cu(acac)_2(en)_2$

Morphology of RPUR foams catalyzed by various copper-amine complexes in perpendicular direction of foam rising is shown in Figure 4.50. It was found that RPUR foams catalyzed by all copper-amine complexes had closed cell, which structure were believed to contain CO_2 gas providing the insulation property of foam [1,6]. The foam cells had spherical shape and the average cell size of foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2$(trien), $Cu(OAc)_2$(tetraen), $Cu(OAc)_2$(pentaen) and $Cu(acac)_2(en)_2$ were 383.8, 317.9, 335.5, 329.9 and 284.0 μm.

4.5.2. Morphology of RPUR foams in different rising direction

Morphology of RPUR foam catalyzed by $Cu(OAc)_2$(trien) in parallel and perpendicular direction of foam rising is shown in Figure 4.51. It was found that cell morphology of foam showed spherical cell in parallel direction and elongated cell in perpendicular direction. This indicated that the foams were anisotropic materials.

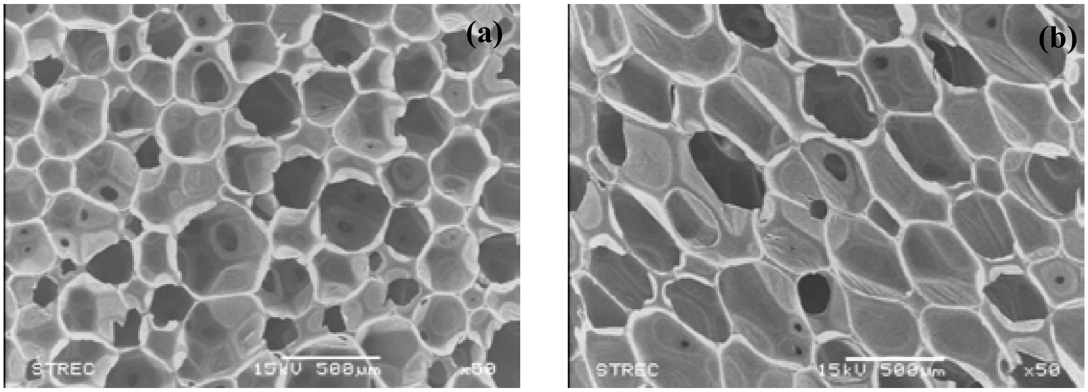


Figure 4.51 SEM of RPUR foams catalyzed by $Cu(OAc)_2$(trien) prepared at the NCO index 100; (a) perpendicular direction; (b) parallel direction

4.6 Compressive properties of RPUR foams

Compressive properties are the most important mechanical properties for RPUR foams. The compressive stress-strain curves of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien)$: $Zn(OAc)_2(trien)$ are shown in Figure 4.52. The stress-strain curves of foams catalyzed by varying catalysts showed different number of deformation stage. The foams prepared from $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien)$: $Zn(OAc)_2(trien)$ showed three typical stages of deformation; initial linear behavior, linear plateau region and finally, densification. Whereas, the foam prepared from DMCHA and $Cu(OAc)_2(en)_2$ showed only two stages, namely initial linear behavior and densification. The initial linear behavior corresponds to the elasticity of foams. The linear plateau corresponds to cell deformation occurring as combination of cell bending and collapse. The densification corresponds to the resistance of foam deformation at final stages of compression due to the entrapped air in closed cell structure of foams [9].

The intersection point between the initial slope and plateau slope was used to calculate the compressive strength, which determined the load-bearing properties of RPUR foams [40]. In this experiment, the compressive strength was reported at 10% deformation as shown in Figure 4.53. It was shown that RPUR foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien)$: $Zn(OAc)_2(trien)$ showed higher compressive strength than the foam prepared from a commercial reference catalyst (DMCHA) at both parallel and perpendicular direction of foam rising. Moreover, it was observed that the parallel compressive strength of foams was higher than that of perpendicular compression direction. Because of this, the foam cells were elongated in the direction of the rise [41]. All foams were anisotropic materials, which the compressive properties depend on direction of measurement [42]. Generally, a high compressive strength in one direction occurred at the expense of the compressive strength in the other directions which were could be explained by the foam cell model as shown in Figure 4.54.

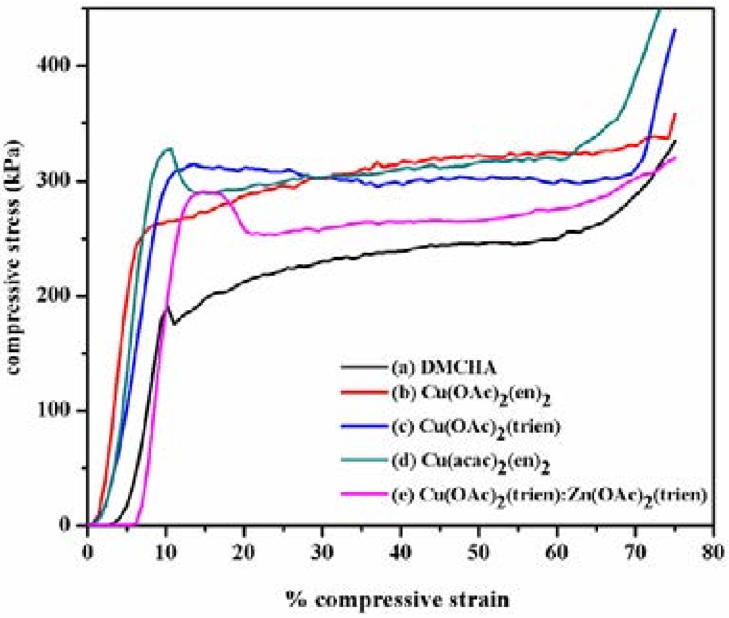


Figure 4.52 Parallel compression stress-strain curve of RPUR foams catalyzed by (a) DMCHA; (b) Cu(OAc)$_2$(en)$_2$; (c) Cu(OAc)$_2$(trien); (d) Cu(acac)$_2$(en)$_2$ and (e) Cu(OAc)$_2$(trien): Zn(OAc)$_2$(trien)at the NCO index of 100

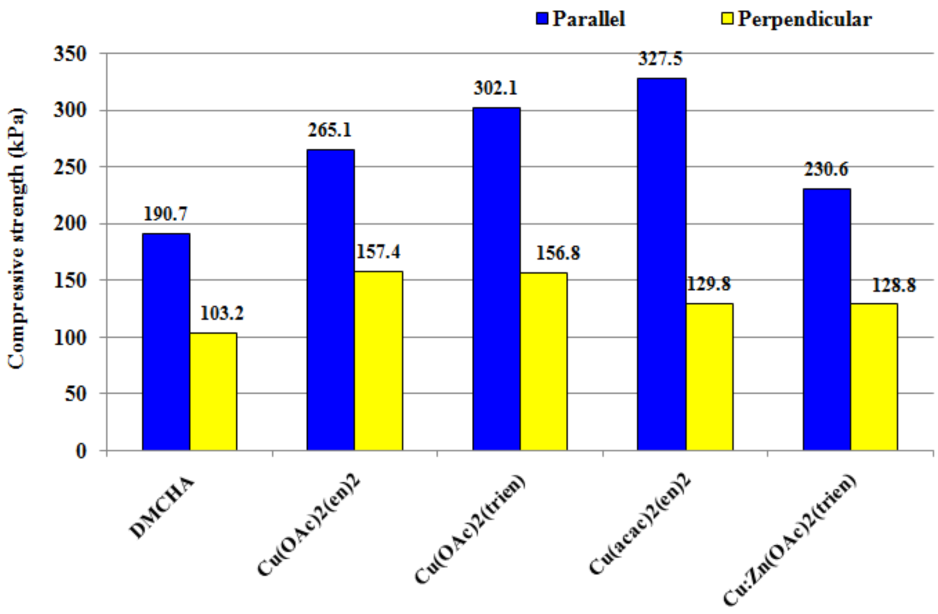


Figure 4.53 Comparison of compressive strength of RPUR foams between parallel and perpendicular direction of foam rising at the NCO index of 100

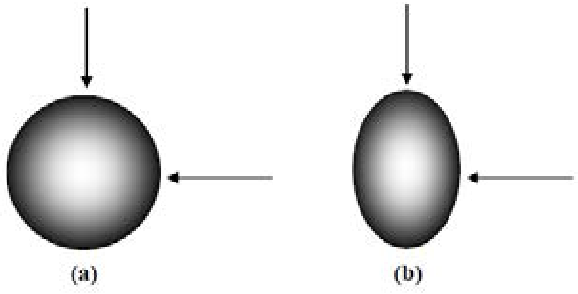


Figure 4.54 Isotropic foam (a): spherical cells, equal properties in all directions; anisotropic foam (b): ellipsoid cells, properties depend on direction [8]

4.7. Thermal stability of RPUR foams

Thermal stability of RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien)$: $Zn(OAc)_2(trien)$ at NCO index of 100 was analyzed by thermogravimetric analysis (TGA). The thermogram and TGA data of RPUR foams are shown in Figure 4.55 and Table 4.18, respectively. TGA thermograms of all RPUR foams showed the decomposition of foams in one step. The initial decomposition temperature (IDT), which is determined as the temperature at 5% weight loss, was found in the range of 258.7-282.8 °C. This decomposition step was attributed to bonds dissociation of urethane groups [43]. The residual weights at 550 °C were in the range of 16.4-25.3%. Moreover, RPUR foams catalyzed by DMCHA, $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien)$: $Zn(OAc)_2(trien)$ showed their maximum decomposition temperature (T_{max}) in the range of 343.6-349.4 °C. As a result, the foams prepared from copper-amine and mixed metal-amine complexes catalysts showed similar thermal decomposition with that prepared from DMCHA catalyst. This indicated that the copper-amine and mixed metal-amine complexes showed similar catalytic reaction to that of DMCHA.

Table 4.18 TGA data of RPUR foam catalyzed by various catalysts

RPUR foams catalyzed by various catalysts	IDT (^{o}C)	Weight residue (%) at different temperatures (^{o}C)				T_{max} (^{o}C)
		250	350	450	550	
DMCHA (ref.)	282.8	100	53.2	28.6	25.3	343.6
$Cu(OAc)_2(en)_2$	268.7	97.7	49.7	25.2	21.2	347.2
$Cu(OAc)_2$(trien)	270.8	98.3	48.5	24.6	20.8	349.4
$Cu(acac)_2(en)_2$	277.9	99.6	49.7	24.0	18.9	347.4
$Cu(OAc)_2$(trien): $Zn(OAc)_2$(trien)	258.7	96.3	49.6	22.9	16.4	348.5

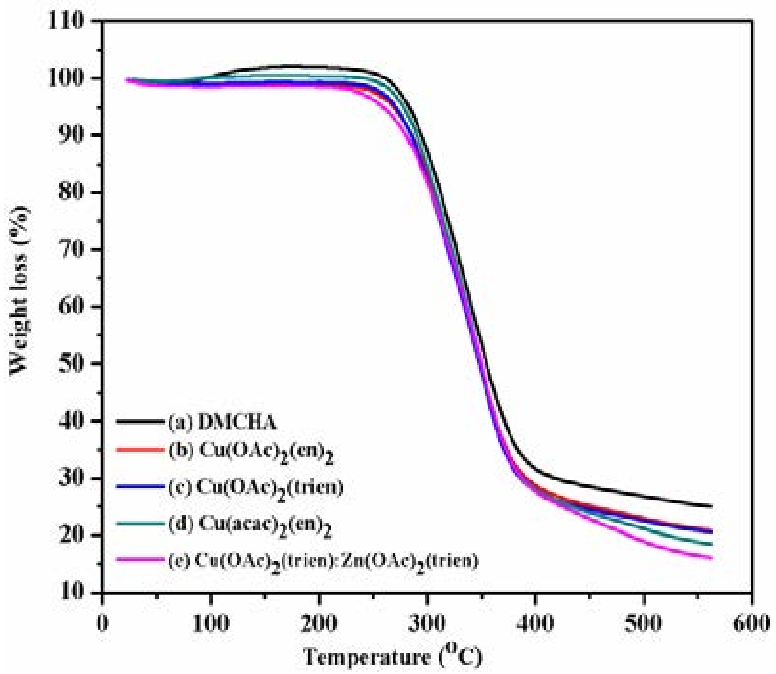


Figure 4.55 TGA thermograms of RPUR foams catalyzed by (a) DMCHA (ref.); (b) $Cu(OAc)_2(en)_2$; (c) $Cu(OAc)_2$(trien); (d) $Cu(acac)_2(en)_2$ and (e) $Cu(OAc)_2$(trien): $Zn(OAc)_2$(trien) at the NCO index of 100

CHAPTER V

CONCLUSION

5.1 Conclusion

Copper-amine complexes solution, namely $Cu(X)_2(en)_2$, $Cu(X)_2(trien)$, $Cu(X)_2(tetraen)$ and $Cu(X)_2(pentaen)$ (where X= OAc, acac, NO_3 and Cl) were synthesized using ethylene glycol as a solvent and they were used as catalyst for rigid polyurethane foam preparation. The complex catalysts were obtained as odorless solution in ethylene glycol and having low viscosity. UV-visible spectroscopy and electrospray ionization (ESI) mass spectroscopy were used to characterize the synthesized copper-amine complexes. UV spectra confirmed that the same complexes could be formed in ethylene glycol, acetone and methanol. Mass spectra showed the molecular peak of copper-amine complexes, which could use to identified the copper-amines complex structures.

Rigid polyurethane (RPUR) foam preparations were carried out by two shot and free rise method. Copper-amine complexes solution had homogeneous solubility in the starting materials of foam formulation, which resulted in good foam appearance. Ethylene glycol, which was use as solvent in catalyst synthesizing, effected on reaction times, foaming temperature and morphology of foams. $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(OAc)_2(tetraen)$, $Cu(OAc)_2(pentaen)$ and $Cu(acac)_2(en)_2$ showed comparable catalytic activity to a reference commercial catalyst (DMCHA). Although $Cu(acac)_2(trien)$ showed lower catalytic activity than DMCHA, but it might be suitable for some applications which required longer gel time. Among all complexes, $Cu(OAc)_2(trien)$ was the best catalyst because it showed high catalytic activity and gave good appearance of foams. The reaction time and density decreased as the catalyst content in the foam formulation was increased. Apparent density of RPUR foams increased with increasing of the NCO content. The NCO conversion of RPUR foams slightly decreased with increasing of the NCO content. The polymerization of RPUR foams was exothermic reaction. The maximum core temperature was in the range of 118-134 °C and these temperature increased with increasing of NCO content.

The formation of holes in RPUR foams at the bottom of the mold could be minimized with using zinc-amine complexes as a co-catalyst. The mixed metal-amine complexes, especially $Cu(OAc)_2(trien):Zn(OAc)_2(trien)$, could adjust the suitable catalytic activity of synthesized catalyst by balancing between gelling and blowing reaction.

The compressive strength of foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien):Zn(OAc)_2(trien)$ complexes were higher than that catalyzed by DMCHA. In addition, the compressive strength in parallel direction of foam rising was higher than that in perpendicular direction, which indicated that RPUR foams were anisotropic materials.

TGA results indicated that RPUR foams catalyzed by $Cu(OAc)_2(en)_2$, $Cu(OAc)_2(trien)$, $Cu(acac)_2(en)_2$ and $Cu(OAc)_2(trien):Zn(OAc)_2(trien)$ complexes showed similar thermal stability to the foam catalyzed by DMCHA.

5.2 Suggestion for future work

From the results, it is concluded that copper-amine complexes solution can be used to catalyze rigid polyurethane foam reactions. The advantages of these catalysts are their comparable catalytic activity to DMCHA, a reference commercial catalyst, and their easy usage. Therefore, the suggestion for future work is to develop the copper-amine complexes solution and use them as catalysts for the other foam systems such as semi-rigid and flexible polyurethane foams.

REFERENCES

[1] Wood, G. *The ICI polyurethane book*. 2nd Edition. London: Jonh Wiley & Sons, 1990.

[2] Singh, H. Sharma, T. P. and Jain, A. K. Reactivity of the raw materials and their effects on the structure and properties of rigid polyurethane foams. *J. Appl. Polym. Sci.* 106 (2007): 1014-1023.

[3] Schaumstoff, P. Polyurethane rigid foam, a proven thermal insulating material for applications between +130°C and -196°C. *Cryogenics* 38 (1998): 113-117.

[4] Choe, K. H.; Lee, D. S.; Seo, W. J.; and Kim, W. N. Properties of rigid polyurethane foams with blowing agents and catalyst. *Polym. J.* 36 (2004): 368-373.

[5] Inoue, Sh. I.; Nagai, Y. and Okamoto, H. Amine-manganese complexes as a efficient catalyst for polyurethane syntheses. *Polym. J.* 34 (2002): 298-301.

[6] Randall, D. and Lee, S. *The polyurethane book*. London: Jonh Wiley & Sons, 2002.

[7] Pentrakoon, D. and Ellis, J.W. *An introduction to plastic foams*. Chulalongkorn University Press, 2005.

[8] Oertel, G. *Polyurethane handbook*. New York: Hanser, 1985.

[9] Pengjam, W. preparation of rigid polyurethane foam catalyzed by Cu-amine and Mn-amine complexes. Master's Thesis, Science Program in Petrochemistry and Polymer Science. Chulalongkorn University, 2009.

[10] Kim, S. H.; Lim, H. and Song, J. Ch. Effect of blowing agent type in rigid polyurethane foam. *J. Macromol. Sci.* 45(2008): 323-327.

[11] Thirumal, M., S., H. and Kim, B. K.; et al. Effect of foam density on the properties of water blown rigid polyurethane foams. *J. Appl. Polym. Sci.* 108 (2008): 1810-1817.

[12] Han, M. S.; Choi S. J.; Kim, J. M.; et al. Effects of silicone surfactant on the cell Size and thermal conductivity of rigid polyurethane foams by environmentally friendly blowing agents. *Macromol. Res.* 17 (2009) 44-50.

[13] Lee, S.T. and Ramesh N.S. *Polymeric foams*. New York: *CRC Press*, 2004.

[14] Maris, R. V.; Tamano, Y.; Yoshimura, H. and Gay, K. Polyurethane catalysis by tertiary amines. *J. Cell. Plast.* 41 (2005): 305-322.

[15] Barnes, R. K. *The encyclopedia of chemistry*. New York: Van Nostrand Reinhold, 1973.

[16] Cunningham, R. L.; Gordon, S. H.; Felker, F. C. and Eskins, K. Glycols in polyurethane foam formulations with a starch-oil composite. *J. Appl. Polym. Sci.* 69 (1998): 957-964.

[17] Firdaus, F. E. Chain extender on property relationships of polyurethane derived from soybean oil. *World Academy of Science, Engineering and Technology.* 81 (2011): 191-194.

[18] Triwulandari, E.; Prihastuti, H. Haryono, A. and Susilo, E. Synthesis and structure properties of rigid polyurethane foams from palm oil based polyol. *J. Mater. Sci.*ISSN :1411-1098, (2008): 31-36.

[19] Modesti, M. and Lorenzetti, A. An experimental method for evaluating isocyanate conversion and trimer formation in polyisocyanurate-polyurethane foams. *Eur. Polym. J.* 37 (2001): 949-954.

[20] Deanin, D. J.; Murarka, M.R. and Kapasi, V.C. Structure and properties of Thermoplastic polyurethane elastomers. *Antech.* 85 (1985): 1297-1299.

[21] Harris, R.F. Polyurethane elastomer base on molecular weight advanced poly(ethylene ether carbonated)diols. I. comparison to commercial diols. *J. Appl. Polym. Sci.* 41 (1990): 487-508.

[22] Petrovic, Z.C. and Simendic, J.B. Study of the effect of soft-segment length and concentration on properties of polyetherurethane. II. the effect on mechanical properties. *Rubb. Chem. Techol.* 58 (1985): 701-713.

[23] Lim, H.; Kim, S. H. and Kim, B. K. Effects of silicone surfactant in rigid polyurethane foams. *Express. Polym. Lett.* 2 (2008): 194-200.

[24] Lim, H.; Kim, E. Y. and Kim, B. K. Polyurethane foams blown with various types of environmentally friendly blowing agents. Plast. Rubber Compos. 39 (2010): 364-369.

[25] Strachota, A.; Strachotova, B. and Spirkova, M. Comparison of environmentally friendly, selective polyurethane catalysts. *Mater. Manuf. Process.* 23 (2008): 566-570.

[26] Kurnoskin, A. V. Metalliferous epoxy chelate polymers: 1. synthesis and properties. *Polymer.* 34 (1993): 1060-1067.

[27] Zia, K.M.; Barikani, M.; Zuber, M.; Bhattil, I.A. and Bhattil, H.N. Morphological studies of polyurethane elastomers extended with α,ω alkane diols. *Iranian Polym. J.* 17 (2008): 61-72.

[28] Yang, L.T.; Zhao, Ch. Sh.; Dai, Ch. L.; Fu, L. Y. and Lin, Sh. Q. Thermal and mechanical properties of polyurethane rigid foam based on epoxidized soybean oil. *J. Polym. Environ.* 20 (2012): 230–236

[29] Choe, K. H.; Lee, D. S.; Seo, W. J.; and Kim, W. N. Properties of rigid polyurethane foams with blowing agents and catalysts. *Polym. J.* 36 (2004): 368-373.

[30] Seo, W. J.; Park, J. H.; Sung Y. T.; Hwang D. H.; Kim W. N. and Lee H. S. Properties of water-blown rigid polyurethane foams with reactivity of raw materials.. *J. Appl. polym. Sci.* 93 (2004): 2334-2342.

[31] Kim, S. H. and Kim, B. K. Effect of isocyanate index on the properties of rigid polyurethane foams blown by HFC 365mfc. *Polym. Adv. Technol.* 19 (2008): 1729-1738.

[32] Landrock, H. *Handbook of plastic foams*. USA: Noyes Publication, 1995.

[33] Romero, R. R., Robert, A., Grigsby, J. R., Ernest, L., Rister, J. R., Rratt, J. K., and Ridgway, D. A study of the reaction kinetics of polyisocyanate foam formulations using real-time FTIR. *J. Cell. Plast.* 41(2005):339-359.

[34] Elwell, M. J. and Ryan, A. J. An FTIR study of reaction kinetics and structure development in model flexible polyurethane foam system. *Polymer.* 37 (1996): 1353-1361.

[35] Thomson, M. A., Melling, P. J., and Slepski, A. M. Real time monitoring of isocyanate chemistry using a fiber-optic FTIR probe. *Polymer Preprints.* 42 (2001): 310-311.

[36] Modesti, M., and Lorenzetti, A. An experimental method for evaluating isocyanate conversion and trimer formation in polyisocyanurate-polyurethane foams. *Eur. Polymer. J.* 37 (2001): 949-954.

[37] Modesti, M.; Lorenzetti, A.; Simioni, F. and Checchin, M. Influence of different flame retardants on fire behaviour of modified PIR/PUR polymers. *Polym. Degrad. Stabil.* 74 (2001): 475–479.

[38] Poomsuk, J. preparation of rigid polyurethane foam using mixed metal complexes and ethylenediamine as catalysts. Master's Thesis, Science Program in Chemistry. *Chulalongkorn University,* 2010.

[39] Promnimit, R. preparation of rigid polyurethane foam using mixed metal complexes and pentaethylenehexaamine as catalysts. Science Program in Petrochemistry and Polymer Science. Chulalongkorn University, 2011.

[40] Saha, M. C.; Kabir, M. E. and Jeelani, S. Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles, *Mat. Sci. Eng.* 479 (2008): 213–222.

[41] Goto, A.; Yamashita, K.; Nonomura, Ch.; Yamaguchi, K. Modeling of cell structure in polyurethane foam. *J. Cell. Plast.* 40 (2004): 481-488.

[42] Tu, Z. H.; Shim, V P. W.; Lim, C. T. Plastic deformation modes in rigid polyurethane foam under static loading. *Inter. J. Sol. Struct.* 38 (2001): 9267-9279.

[43] Rashmi, B. J.; Rusu, D.; Prashantha, K.; Lacrampe, M. F. and Krawczak, P. Development of water-blown bio-based thermoplastic polyurethane foams using bio-derived chain extender. *J. Appl. Polym. Sci.* published online (2012): DOI: 10.1002/app.38183.

APPENDICES

Appendix A

NCO index and NCO conversion Calculations

NCO index calculation

#Example Calculate the parts by weight (pbw) of PMDI (Suprasec® 5005), molar mass = 365.8, 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® R180 (OHV = 440 mgKOH/ g, functionality = 4.3)	100.0
Catalysts (30%wt in ethylene glycol)	1.0
Surfactant	2.5
Blowing agent (water, Mw = 18 g/mole, functionality = 2)	3.0
PMDI (Suprasec® 5005), NCO indexes of 100, 130, and 150	?

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

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

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

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

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

Equivalent in the above formulation:

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

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

$$\text{Ethylene glycol (solvent)} = \frac{1.98}{31.0} = 0.064$$

$$\text{Total equivalent weight} = 1.181$$

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

Thus:

$$\text{PMDI (pbw)} = 1.181 \times \frac{\text{PMDI molar mass}}{\text{functionality}} = 1.181 \times \frac{365.8}{2.7} = 160.0$$

Note: 160.0 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 ;

$$\text{Isocyanate actual} = \frac{160.0}{100} \times 100 = 160.0 \text{ pbw}$$

Isocyanate index = 130 ;

$$\text{Isocyanate actual} = \frac{160.0}{100} \times 130 = 208.0 \text{ pbw}$$

Isocyanate index = 150 ;

$$\text{Isocyanate actual} = \frac{160.0}{100} \times 150 = 240.0 \text{ pbw}$$

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

Formulation (pbw)	**NCO indexes**		
	100	**130**	**150**
Polyol (Daltolac® R180)	100	100	100
Catalysts	1.0	1.0	1.0
Surfactant	2.5	2.5	2.5
Blowing agent	3.0	3.0	3.0
PMDI (Suprasec® 5005)	**160.0**	**208.0**	**240.0**

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:

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

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 IR-ATR

PMDI (MR-200) spectra	**NCO Absorbance peak area Normalized @ 1.0 Ar-H peak area**
1	97.620
2	98.556
3	97.824
Average (NCO^i); ATR-IR	98.0

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

Conversion of isocyanate (%)

Data at **Table A2**

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

The data from **Table A5** at NCO index 100, absorbance peak area of free NCO was normalized by aromatic ring quantity:

Absorbance peak area of final NCO = 0.6363 = NCO^f

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

$$= \left[1 - \frac{0.6363}{98.0}\right] \times 100$$

$$\text{\% NCO conversion} = 99.4$$

PIR:PUR ratio

Absorbance peak area of PIR (polyisocyanurate) = 0.847

Absorbance peak area of PUR (poluurethane) = 3.905

$$\text{Thus, PIR:PUR} = \frac{0.847}{3.905} \quad 0.217$$

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	0.997	1.765	0.871	4.253	0.5649	99.4	0.205
130	2.434	2.103	1.055	4.999	1.1574	98.8	0.211
150	3.091	2.022	1.058	4.736	1.5287	98.4	0.223

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

NCO indexes	**Peak Area**					**NCO conversion (%)**	**PIR/PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
100	0.879	1.688	0.739	4.192	0.5207	99.5	0.176
130	3.360	1.970	1.305	4.769	1.7056	98.3	0.274
150	4.556	1.946	1.182	4.810	2.3412	97.6	0.246

Table A5 NCO conversion of RPUR foam catalyzed by $Cu(OAc)_2$(trien) at different NCO indexes

NCO indexes	**Peak Area**					**NCO conversion (%)**	**PIR/PUR**
	NCO 2277 cm^{-1}	**Ar-H 1595 cm^{-1}**	**PIR 1415 cm^{-1}**	**PUR 1220 cm^{-1}**	**NCO^f (Ar-H=1.0)**		
100	2.703	1.480	0.523	2.404	1.8264	98.1	0.2176
150	1.061	0.848	0.321	1.412	1.2515	98.7	0.2270

Table A6 NCO conversion of RPUR foam catalyzed by $Cu(OAc)_2$(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	1.373	1.509	0.756	4.147	0.9099	99.1	0.182
130	3.263	2.056	1.011	4.575	1.5871	98.4	0.221
150	5.075	2.033	0.893	4.953	2.4963	97.5	0.1803

Table A7 NCO conversion of RPUR foam catalyzed by $Cu(OAc)_2$(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	1.809	1.759	0.772	4.193	1.0284	99.0	0.184
130	4.389	1.995	1.008	4.408	2.2000	97.8	0.229
150	7.599	2.004	0.828	4.801	3.7919	96.1	0.173

Table A8 NCO conversion of RPUR foam catalyzed by $Cu(acac)_2(en)_2$ at different NCO indexes

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	1.983	1.886	0.829	4.689	1.0514	98.9	0.177
130	3.921	1.761	0.788	3.848	2.2266	97.7	0.205
150	6.072	1.884	0.927	3.599	3.2229	96.7	0.258

Table A9 NCO conversion of RPUR foam catalyzed by $Cu(acac)_2$(trien) at different NCO indexes

NCO indexes	Peak Area					NCO conversion (%)	PIR/PUR
	NCO 2277 cm^{-1}	Ar-H 1595 cm^{-1}	PIR 1415 cm^{-1}	PUR 1220 cm^{-1}	NCO^f (Ar-H=1.0)		
100	3.472	1.913	0.850	4.482	1.8150	98.2	0.190
130	4.933	1.972	0.864	4.243	2.5015	97.5	0.204
150	6.277	1.948	0.918	3.987	3.2223	96.7	0.230

Appendix B
Compression Curves and Data

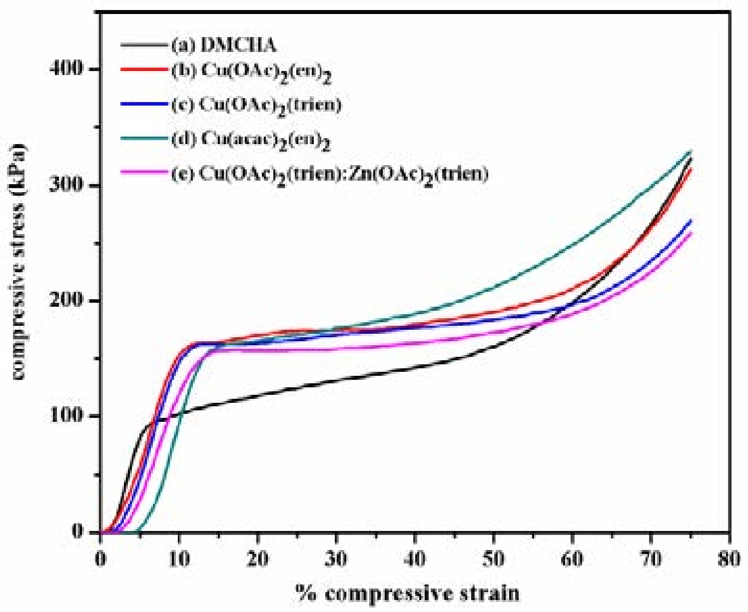


Figure B1 Perpendicular compression stress-strain curve of RPUR foams catalyzed by different catalysts at NCO index of 100

Table B2 Formulations, reaction times, physical and mechanical properties of RPUR foams catalyzed by reference commercial catalyst (DMCHA)

Formulations (pbw)	**Catalysts at different NCO indexes**					
	DMCHA (Ref.)					
	100		**130**		**150**	
Polyol (Daltolac® R180)	100		100		100	
Catalysts	1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5	
Blowing agent	3.0		3.0		3.0	
PMDI (Suprasec® 5005)	151.3		196.7		226.9	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times						
Cream time (min.)	0:22	0.03	0:26	0.05	0:26	0.02
Gel time (min.)	0:32	0.03	0:44	0.03	0:51	0.03
Tack free time (min.)	2:34	0.04	3:14	0.17	3:46	0.09
Rise time (min.)	1:55	0.30	2:27	0.48	2:50	0.51
Density (kg/m^3)	37.1	0.6	42.1	0.7	46.6	0.9
Mechanical properties						
// Compressive strength (kPa)	190.7	-	-	-	-	-
<u>//</u> Compressive modulus (kPa)	103.2	-	-	-	-	-

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

Formulations (pbw)	**Catalysts at different NCO indexes**											
	$Cu(OAc)_2(en)_2$						**$Cu(OAc)_2(trien)$**					
	100		**130**		**150**		**100**		**130**		**150**	
Polyol (Daltolac® R180)	100		100		100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5		2.5		2.5		2.5	
Blowing agent	3.0		3.0		3.0		3.0		3.0		3.0	
PMDI (Suprasec® 5005)	160.0		208.0		240.0		160.0		208.0		240.0	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times												
Cream time (min.)	0:31	0.05	0:31	0.07	0:31	0.03	0:35	0.05	0:33	0.03	0:35	0.04
Gel time (min.)	0:46	0.07	0:50	0.03	0:57	0.03	0:55	0.10	1:06	0.07	1:14	0.07
Tack free time (min.)	1:08	0.05	1:12	0.15	1:17	0.29	1:31	0.09	1:38	0.07	1:48	0.14
Rise time (min.)	1:37	0.24	1:43	0.44	1:58	0.38	2:11	0.24	2:21	0.34	2:39	0.52
Density												
Density (kg/m^3)	37.1	0.5	40.4	0.3	44.2	0.6	38.5	0.4	42.6	0.5	45.2	1.0
Mechanical properties												
// Compressive strength (kPa)	265.1	-	-	-	-	-	302.1	-	-	-	-	-
// Compressive modulus (kPa)	157.4	-	-	-	-	-	156.8	-	-	-	-	-

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

Formulations (pbw)	**Catalysts at different NCO indexes**											
	$Cu(OAc)_2$(tetraen)						**$Cu(OAc)_2$(pentaen)**					
	100		**130**		**150**		**100**		**130**		**150**	
Polyol (Daltolac® R180)	100		100		100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5		2.5		2.5		2.5	
Blowing agent	3.0		3.0		3.0		3.0		3.0		3.0	
PMDI (Suprasec® 5005)	160.0		208.0		240.0		160.0		208.0		240.0	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times												
Cream time (min.)	0:35	0.04	0:37	0.03	0:37	0.07	0:37	0.03	0:37	0.09	0:38	0.08
Gel time (min.)	1:10	0.03	1:23	0.05	1:34	0.04	1:16	0.05	1:41	0.15	1:58	0.07
Tack free time (min.)	1:41	0.31	2:01	0.08	2:15	0.27	1:54	0.18	2:26	0.20	2:50	0.19
Rise time (min.)	2:20	0.48	2:52	0.16	3:20	0.50	2:33	0.09	3:23	0.22	3:53	0.42
Density												
Density (kg/m^3)	39.5	0.4	42.9	0.6	46.5	1.0	39.9	0.9	43.5	1.0	46.3	0.7
Mechanical properties												
// Compressive strength (kPa)	-	-	-	-	-	-	-	-	-	-	-	-
// Compressive modulus (kPa)	-	-	-	-	-	-	-	-	-	-	-	-

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

Formulations (pbw)	**Catalysts at different NCO indexes**											
	Cu(acac)$_2$(en)$_2$						**Cu(acac)$_2$(trien)**					
	100		**130**		**150**		**100**		**130**		**150**	
Polyol (Daltolac® R180)	100		100		100		100		100		100	
Catalysts	1.0		1.0		1.0		1.0		1.0		1.0	
Surfactant	2.5		2.5		2.5		2.5		2.5		2.5	
Blowing agent	3.0		3.0		3.0		3.0		3.0		3.0	
PMDI (Suprasec® 5005)	160.0		208.0		240.0		160.0		208.0		240.0	
Efficiency parameters	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**	**Data**	**S.D.**
Reaction times												
Cream time (min.)	0:34	0.09	0:37	0.11	0:37	0.06	0:36	0.05	0:42	0.04	0:41	0.06
Gel time (min.)	1:12	0.17	1:43	0.05	1:53	0.04	2:22	0.10	3:17	0.02	3:45	0.13
Tack free time (min.)	1:36	0.24	2:12	0.18	2:34	0.38	3:23	0.09	5:35	0.16	6:24	0.21
Rise time (min.)	2:13	0.46	2:54	0.22	3:22	0.30	4:16	0.22	6:21	0.41	6:41	0.14
Density												
Density (kg/m^3)	39.2	0.9	44.8	0.7	47.9	0.7	41.0	0.4	46.8	1.0	49.7	1.1
Mechanical properties												
// Compressive strength (kPa)	327.5	-	-	-	-	-	-	-	-	-	-	-
// Compressive modulus (kPa)	129.8	-	-	-	-	-	-	-	-	-	-	-

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