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PREPARATION OF FLEXIBLE POLYURETHANE FOAM CATALYZED
BY COPPER-AMINE AND ZINC-AMINE COMPLEXES

Mr. Nuttawut Chueasakol

A Thesis Submitted in Partial Fulfillment of the Requirements
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งานวิจัยนี้ได้พัฒนาตัวเร่งปฏิกิริยาสำหรับใช้เตรียมโฟมพอลิยูรีเทนชนิดยืดหยุ่นเพื่อลดปริมาณการใช้ของตัวเร่งปฏิกิริยาทางการค้าที่มีราคาสูง โดยตัวเร่งปฏิกิริยาดังกล่าวเป็นสารประกอบเชิงซ้อนโลหะ-แอมีน คือ $M(OAc)_2(Y)_2$ เมื่อ $M = Cu$ และ Zn และ $Y =$ เอทิลีนไดแอมีน (en), ไตรเอทิลีนเตตระมีน (trien) และ ไดเอทิลแอมีน (dea) การสังเคราะห์ $M(OAc)_2(Y)_2$ ใช้ปฏิกิริยาระหว่างโลหะแอซิเตตและแอมีนโดยใช้เอทิลีนไกลคอลเป็นตัวทำละลาย การพิสูจน์เอกลักษณ์ของสารประกอบเชิงซ้อนโลหะ-แอมีนใช้ยูวี-วิสลิเบิลสเปกโทรสโกปีและแมสสเปกโตรเมตรี โฟมพอลิยูรีเทนชนิดยืดหยุ่นได้เตรียมขึ้นจากปฏิกิริยาระหว่างเมทิลีนไดไอโซไซยาเนตพรีพอลิเมอร์และเอทิลีนออกไซด์ไทรออล โดยใช้สารประกอบเชิงซ้อนโลหะ-แอมีนเป็นตัวเร่งปฏิกิริยา เปรียบเทียบประสิทธิภาพในการเร่งปฏิกิริยากับตัวเร่งปฏิกิริยาทางการค้า คือ 1,4-ไดเอซาไบโซโคล (2.2.2) ออกเทน (Dabco[®] EG) โดยศึกษาเวลาที่ใช้ในการเกิดปฏิกิริยา สมบัติเชิงกายภาพและสมบัติเชิงกลของโฟมพอลิยูรีเทนชนิดยืดหยุ่น จากผลการทดลองพบว่า สารละลายของ $M(OAc)_2(Y)_2$ ในเอทิลีนไกลคอลสามารถผสมเข้ากันกับสารตั้งต้นในสูตรการเตรียมโฟมได้ดี โดย $Cu(OAc)_2(en)_2$ มีความว่องไวในการเร่งปฏิกิริยาสูงที่สุด แต่โฟมที่ได้มีความหนาแน่นต่ำ เมื่อนำ Dabco[®] EG: $Cu(OAc)_2(en)_2$ ซึ่งเป็นสารผสมระหว่าง Dabco[®] EG และ $Cu(OAc)_2(en)_2$ ในอัตราส่วนโมล 0.5 : 0.5 มาใช้เป็นตัวเร่งปฏิกิริยา พบว่ามีความว่องไวในการเร่งปฏิกิริยามากกว่า Dabco[®] EG หรือ $Cu(OAc)_2(en)_2$ Dabco[®] EG: $Cu(OAc)_2(en)_2$ ให้โฟมที่มีสมบัติเชิงกายภาพและสมบัติเชิงกลที่ดี ดังนั้น Dabco[®] EG: $Cu(OAc)_2(en)_2$ จึงมีความเหมาะสมสำหรับใช้เป็นตัวเร่งปฏิกิริยาของโฟมพอลิยูรีเทนชนิดยืดหยุ่น

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NUTTAWUT CHUEASAKOL: PREPARATION OF FLEXIBLE
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AND ZINC-AMINE COMPLEXES. ADVISOR: ASSOC. PROF.
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In this research, catalysts for flexible polyurethane (FPUR) foam preparation were developed in order to reduce the use of the expensive commercial catalysts. These catalysts were metal-amine complexes, namely $M(\text{OAc})_2(\text{Y})_2$, where $M = \text{Cu}$ and Zn ; $\text{Y} =$ ethylenediamine (en), triethylenetetramine (trien) and diethylamine (dea). $M(\text{OAc})_2(\text{Y})_2$ could be synthesized from the reaction between metal acetates and amines using ethylene glycol as a solvent. UV-visible spectroscopy and mass spectrometry were used to characterize the metal-amine complexes. FPUR foams were prepared by the reaction between methylene diphenyl diisocyanate prepolymer (MDIP) and ethylene oxide triol in the presence of metal-amine complexes as catalysts. The catalytic activity was compared with that of commercial catalyst, namely 1,4-diazabicyclo(2.2.2)octane (Dabco[®] EG) by investigation of the reaction time, physical and mechanical properties of FPUR foams. The experimental results showed that the solution of $M(\text{OAc})_2(\text{Y})_2$ in ethylene glycol could be easily dissolved in the raw materials of FPUR foam formulation. $\text{Cu}(\text{OAc})_2(\text{en})_2$ had the highest catalytic activity, however, the foam had low density. When Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$, which was a mixture of $\text{Cu}(\text{OAc})_2(\text{en})_2$ and Dabco[®] EG at the mole ratio of 0.50 : 0.50 was used as a catalyst, higher catalytic activity than Dabco[®] EG or $\text{Cu}(\text{OAc})_2(\text{en})_2$ was obtained. Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$ gave the foam having good physical and mechanical properties. Therefore, Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$ was a suitable catalyst for FPUR foam.

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

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LIST OF ABBREVIATIONS

%	percentage
ϵ	molar absorptivity
ATR-IR	attenuated Total Reflectance-Infrared
AA	atomic absorption
BDMAEE	bis(N,N-dimethylaminoethyl)ether
cm	centimeter
cm^{-1}	unit of wavenumber
$^{\circ}\text{C}$	degree Celsius (centigrade)
CFC	chlorofluorocarbons
Cu	copper
DABCO	1, 4-diazabicyclo(2.2.2)octane
DBTDL	dibutyltin dilaurate
DMCHA	N,N-dimethylcyclohexylamine
DMEA	N,N-dimethylethanolamine
EA	elemental Analysis
FPUR	flexible polyurethane
FTIR	fourier transform infrared spectrophotometer
g	gram
h	hour
HCFCs	hydrochlorofluorocarbons
IDT	initial decomposition temperature
KOH	potassium hydroxide
kg	kilogram
kV	kilovolt
M	metal
$\text{M}(\text{OAc})_2$	metal acetate
m^3	cubic meter
MDI	methylene diphenyl diisocyanate
MDIP	methylene diphenyl diisocyanate prepolymer

mA	milliampere
mg	milligram
min	minute
ml	milliliter
mm	millimeter
mmol	millimole
N	newton unit
NCO	isocyanate
OHV	hydroxyl value
pbw	part by weight
PDMS	polydimethylsiloxane
pentaen	pentaethylenehexamine
PEO	polyethylene oxide
PIR	polyisocyanurate
PMDI	polymeric 4,4'-methane diphenyl diisocyanate
PPO	polypropylene oxide
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
Zn	zinc

CHAPTER I

INTRODUCTION

Polyurethanes are versatile materials and can be manufactured in wide range of grades, namely elastomers, foams, fibers and coatings. Polyurethane foams can be divided into three major classes, namely low-density flexible foam, high-density flexible foam and rigid foams.

High-density flexible foams are defined as those have density above 100 kg/m^3 . It can be easily produced in a variety of shapes by molding or cutting. The major demand for high-density flexible foams are in cushioning applications such as bedding, mattresses, pillows and furnitures. In the mattress market, the advantages of flexible polyurethane foams are low cost and low weight [1].

Polyurethane foams are produced by the reaction between liquid polyols and isocyanates in the presence of catalysts, surfactants and other additives in widely varying processing procedures to make the final commercial products [2].

The properties of polyurethane foams depend on the type of isocyanates and polyols used. The key factors are functionality and molecular weight of polyols. Polyols having higher functionality give rigid foam with improved mechanical properties such as tensile strength, modulus and compression set. Polyols with a higher molecular weight give flexible foams which are soft and more elastic. The foam stability during processing is controlled by the combination of catalysts to promote both blowing reaction and gelling reaction. Tertiary amines are used as blowing catalysts and organometallic compounds are used as gelling catalysts. The excess blowing reaction results in foams splitting and collapse and eventually cracking of surface, while excess gelling results in shrinking foams [3].

At present, tin compounds and tertiary amines are mainly used as commercial catalysts because of their excellent catalytic activities. However, tertiary amines have strong odor and release volatile organic compound (VOC) while tin compounds are toxic. Tertiary amines without odor are expensive. Therefore, new types of catalyst are needed to substitute these commercial catalysts [3].

Objective

The aim of this research was to develop a new catalyst for flexible polyurethane (FPUR) foams. In our previous research, metal-amine complexes synthesized from copper acetate and aliphatic amines had high catalytic activity in the preparation of rigid polyurethane (RPUR) foams [4]. In the preparation of rigid and flexible polyurethane foams, the isocyanates and polyols used in FPUR foams have higher molecular weight than those used in RPUR foam. Therefore, the reactivity of foaming reaction in FPUR foam is lower than that of RPUR foam. The commercial catalyst used in FPUR foam, such as 1,4-diazabicyclo(2.2.2)octane (Dabco[®] EG), must have high catalytic activity and therefore expensive. Therefore, the objective of this research was to use metal-amine complexes as catalysts in the preparation of FPUR foams. Metal-amine complexes are less expensive than Dabco[®] EG. Metal-amine complexes could be easily synthesized from the reaction between metal acetates and aliphatic amines. The metal acetates used were copper acetate and zinc acetate. The aliphatic amines used were ethylenediamine (en), triethylenetetramine (trien) and diethylamine (dea). Metal-amine complexes would be synthesized as solutions of metal-amine complexes in ethylene glycol. This metal-amine complex-ethylene glycol solution was obtained as an odorless and low viscous solution and could be easily dissolved in the raw materials of RPUR foam formulation [5].

Scope of the research

The scope of this research consists of two parts. In the first part, the metal-amine complexes, namely $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$, $\text{Cu}(\text{OAc})_2(\text{dea})_4$, $\text{Zn}(\text{OAc})_2(\text{en})_2$, $\text{Zn}(\text{OAc})_2(\text{trien})$, $\text{Zn}(\text{OAc})_2(\text{dea})_4$, were synthesized. UV-visible spectroscopy and mass spectrometry were used to characterize these metal complexes. Mixed metal-amine complexes, namely $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$, would also be synthesized and characterized.

In the second part, the metal-amine complexes were used as catalysts in the preparation of FPUR foams. The foaming reaction time, physical and mechanical properties of FPUR foams were investigated and compared with FPUR foams prepared from 1,4-diazabicyclo(2.2.2)octane (Dabco[®] EG), which is a commercial tertiary amine catalyst.

CHAPTER II

THEORY AND LITERATURE REVIEWS

Polyurethane is prepared by polyols and isocyanate as the main components and other components such as surfactant, blowing agent, chain extender, catalysts and other additives are also employed to regulate the properties of foams. The polyurethane foams can be divided into three major classes, low-density flexible foam, high-density flexible foam and low-density rigid foams.

Flexible polyurethane (FPUR) foams are one of the most versatile materials in many applications [6]. FPUR foams having large industrial production because of their high strength to weight ratio, excellent mechanical properties and can be easily cut or molded to almost any shape [7]. The properties of polyurethane foam can be modified within wide limits depending on the raw materials used for their synthesis. The polyols and isocyanates are the major raw materials which largely influence the properties of the foam. The changes in FPUR foam properties are mainly due to the differences in chemical structure, equivalent weight and functionality of polyols or combination of polyols which decides flexibility or rigidity of the foam [8].

2.1 Raw materials

FPUR foams are obtained by the reaction between isocyanate compounds and polyols having active hydroxyl groups to form the urethane linkages. The physical character, morphology, and molecular size of these compounds influence the polymerization reaction as well as final foam properties. Additives, catalysts, blowing agents, surfactants and chain extender are used to control and modify the foaming reaction and characteristics of foam [9].

2.1.1 Isocyanates

The main isocyanates employed are aromatic isocyanates, methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), which have high reactivity in foaming reaction. Aliphatic isocyanates react slowly with hydroxyl groups [10].

2.1.1.1 Toluene diisocyanate (TDI)

Toluene diisocyanate (TDI) is colorless liquid produced by phosgenation of diaminotoluene, which is obtained by the reduction of nitrotoluene. Commercial TDI is available as a mixture of 2,4-isomers and 2,6-isomers in mole ratio of 80:20 or 65:35. Isomeric structures of toluene diisocyanate are shown in Figure 2.1. The mixture of TDI has toxic hazard since it causes irritation the skin and has a marked effect on the respiratory system [6]. While the methylene diphenyl diisocyanate (MDI) based on diaminodiphenylmethane is considerable safer in used and has lower volatile organic than TDI.

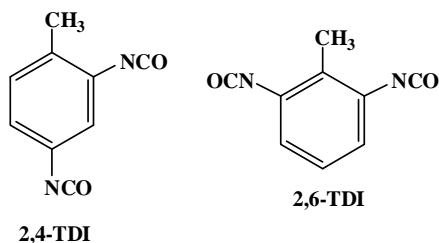


Figure 2.1 Isomeric structures of toluene diisocyanate [6]

2.1.1.2 Methylene diphenyl diisocyanate (MDI)

Methylene diphenyl diisocyanate (MDI) is produced by the phosgenation of the condensation product of aniline with formaldehyde [11]. The MDI mainly used in polyurethane manufacture are monomeric MDI or pure MDI, polymeric MDI and MDI prepolymers.

Monomeric MDI is a crystalline solid at room temperature, thus it must be heated slightly to convert into liquid form. The production of MDI by the reaction of aniline with formaldehyde, using hydrochloric acid as a catalyst, to produce a diamine precursor, the diamine is then treated with phosgene to form an MDI. The isomer ratio is determined by the isomeric composition of the diamine. The isomeric structures of monomeric MDI are shown in Figure 2.2. Then, distillation of MDI mixture gives polymeric MDI (a mixture of oligomeric polyisocyanates). Polymeric MDI may contain 55% of 4,4'-diisocyanate and 2,4'-diisocyanate, 20-25% of triisocyanate and small quantity of the 2,2'-diisocyanate. Another form of MDI is pure MDI, which is produced by distillation from polymeric MDI. It is mainly 4,4'-isomer based and usually contains a small amount of 2,4'-isomer. The chemical structure of polymeric MDI is shown in Figure 2.3 [6].

The modified MDI or MDI prepolymer (MDIP) has been developed for the production of FPUR foams by increasing soft segment in polyurethane to improve resilience properties. Isocyanate prepolymer are synthesized by the reaction between excess diisocyanate and low molecular weight diol or triol. For MDI prepolymer, excess methylene diphenyl diisocyanate (MDI) reacts with polypropylene glycol to form the prepolymer with isocyanate-terminated end groups. The structure MDI prepolymer (Suprasec[®] 2449) is shown in Figure 2.4 [7].

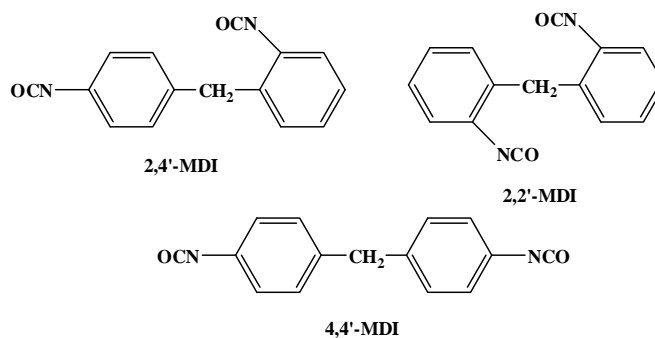


Figure 2.2 Isomeric structures of monomeric MDI [6]

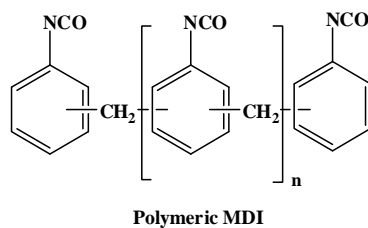


Figure 2.3 Structure of polymeric MDI [6]

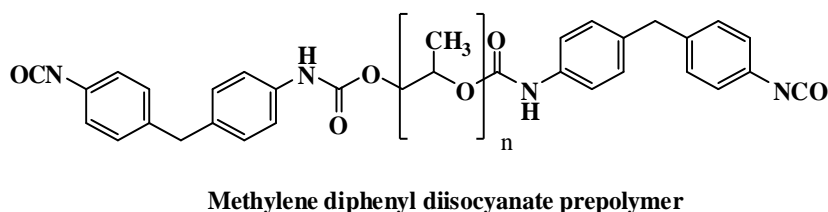


Figure 2.4 Structure of MDI prepolymer (Suprasec[®] 2449) [7]

2.1.2 Polyols

The polyols used in manufacture of polyurethane foams are classified in two types, polyether polyols and polyester polyols. The structure, functionality and average molecular weight of polyol influences the final properties of polyurethane foam. Polyols usually have functionality 2.0-8.0 and molecular weight of 200-8000. Polyether polyols give softer and more resilient foam with better hydrolysis resistance than polyester polyols, while polyester polyols give the foam with greater mechanical properties and better resistance to oils, oxidation and solvents [12]. Higher functionality and lower molecular weight polyols are used in the production of rigid polyurethane foams, while the production of flexible foams uses lower functionality and higher molecular weight polyols in order to get the higher chain length of polymer for better resilience properties.

2.1.2.1 Polyether polyols

Polyether polyols are low molecular weight polyols. Their stages range from low viscous liquid to solid which depend on molecular weight and chemical structure. Polyether polyols are produced by ring opening reaction of ethylene oxides or propylene oxides. The polyfunctional initiators such as glycerol, ethylene glycol, sucrose, sorbitol and trimethylolpropane are used. The structures of poly(ethylene oxide)triols and poly(propylene oxide)triols based on glycerol initiator are shown in Figure 2.5 [13].

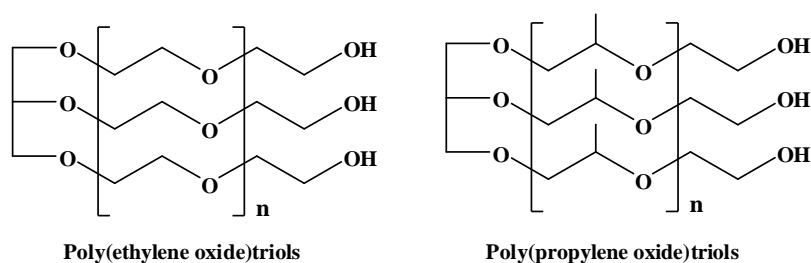


Figure 2.5 Structures of poly(ethylene oxide)triol and poly(propyleneoxide)triol based on glycerol initiator [13]

2.1.2.2 Polyester polyols

Another class of polyol is polyester polyol. Polyesters polyols are formed by condensation or step-growth polymerization of diols (or triols) and dicarboxylic acids such as adipic acid, sebacic acid and phthalic acids [7]. Polyester polyols have higher viscosity than polyether polyols. Therefore, the use of polyesters polyols in FPUR foams is limited as compared with polyether polyols [14].

2.1.3 Surfactants

Silicone surfactants, which consist of polydimethylsiloxane (PDMS) backbone and polyethylene oxide-co-propylene oxide (PEO-PPO) random copolymer grafts, are used as surfactants in polyurethane foam systems. An example of silicone surfactant is shown in Figure 2.6. Surfactants do not alter the reaction time in the foam formation. In the absence of surfactants, the foaming process will have catastrophic coalescence and finally causes foam collapse. Silicone surfactants have significant effect on bubble generation and the cell window stabilization steps in the foam process [15]. The largest commercial application of silicone surfactants are their use as additives of polyurethane foams. They are regularly added in the amount of 0.4-2.0% w/w in the polyol formulation [14].

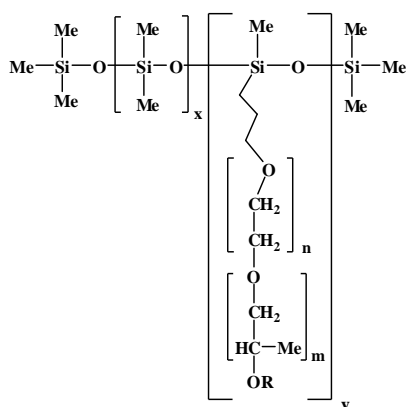


Figure 2.6 An example of silicone surfactant [14]

2.1.4 Blowing agents

The properties of polyurethane foams are considerably influenced by types of the blowing agents and their contents in foam formulations. Two types of blowing agents, physical and chemical blowing agents, are used for the production of polyurethane foams.

Carbon dioxide (CO₂) generated from reaction between water and isocyanate during the foaming reaction is normally used as a chemical blowing agent [6, 16].

Physical blowing agents are low molecular weight compounds having boiling point around room temperature, non-flammability, low toxic hazard, low thermal conductivity for insulation and do not react with isocyanate group. The physical blowing agents used in industry are chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), perfluorinated hydrocarbons (PFCs) and hydrofluorocarbons (HFCs). These compounds cause depletion of the ozone layer and their uses are regulated in many countries. Thus, other type of physical blowing agent, such as cyclopentane, starts to replace such environmentally hazardous blowing agents [6].

2.1.5 Chain extenders

Chain extenders are low molecular weight polyfunctional compounds. They are active towards the reaction with isocyanate and are also known as curing agents. Chain extenders having two functionalities, such as difunctional glycol and diamine are usually used in the preparation of FPUR foam and polyurethane elastomer. Chain extenders react with isocyanate to produce polyurethane or polyurea segment in polyurethane backbone. The commercial chain extenders used in the preparation of polyurethane foams are shown in Figure 2.7.

Crosslinking agents have three or more functionalities. They are used to increase crosslinking or branching in polyurethane networks through the formation of urethane bonds. Crosslinking agents are usually used in the preparation of rigid polyurethane foams [6].

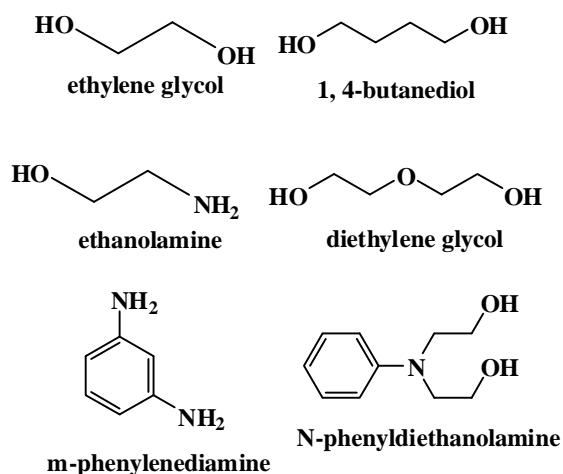


Figure 2.7 Commercial chain extenders used in the preparation of polyurethane foams [6]

2.1.6 Catalysts

The catalysts control balance rate of chemical reaction between isocyanate with polyol and water. The important role of catalyst affects not only the rate of reaction, but also influences the final properties of polyurethane foams.

The catalysts for flexible polyurethane foam consist of amine and organometallic catalysts (Table 2.1). The activity of catalysts depends on their basicity, with steric hindrance on the active site playing a secondary role [6]. The selection of catalysts depends on their selectivity, toxicity, odor, and solubility. The selection of catalysts could be divided into two categories as gelling and blowing catalysts. The relationship between gelling and blowing activity and properties of polyurethane foam is shown in Figure 2.8. Normally, strong gelling catalysts gave higher foam density and adhesive strength foam due to the small cell size, but the reacting mixture has poor flowability and the obtained foam exhibit poor dimensional stability and isotropy cell structure. Strong blowing catalysts provide lower foam density and better dimensional stability because of the excellent flowability and isotropy cell structure. However, they give worse adhesive strength [10]. The structure of commercial catalysts used in preparation of polyurethane foams is shown in Figure 2.9.

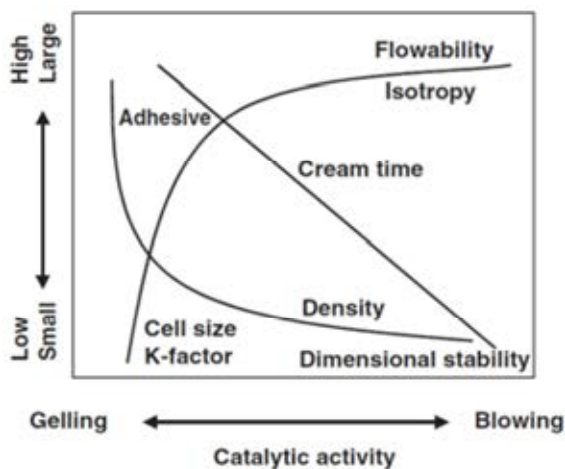


Figure 2.8 The relationship between gelling and blowing activity and properties of polyurethane foam [6]

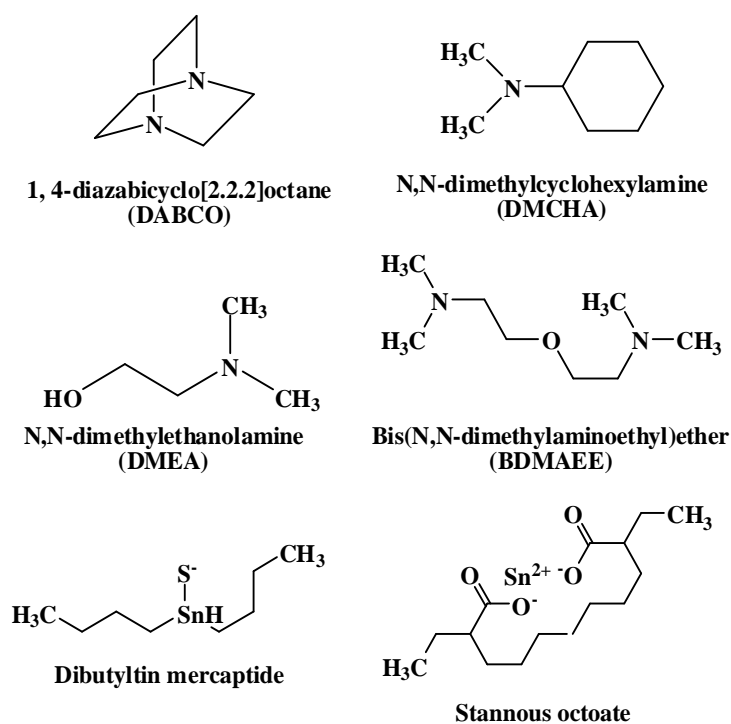


Figure 2.9 Commercial catalysts used in preparation of polyurethane foams [6]

Table 2.1 Frequently used tertiary amine and organometallic catalysts [6]

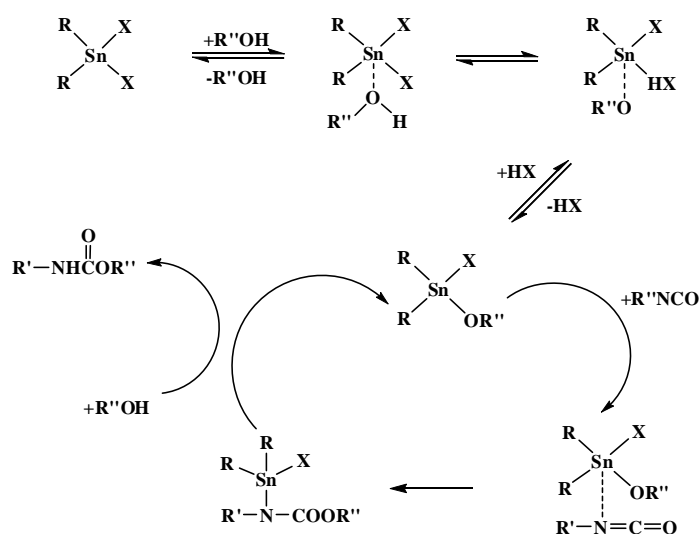
Catalysts	Characteristic and use
<ul style="list-style-type: none"> • 1, 4-diazabicyclo[2.2.2]octane (DABCO) 	<ul style="list-style-type: none"> • Very good amine gelation catalyst used in all foam types
<ul style="list-style-type: none"> • N,N-dimethylcyclohexylamine (DMCHA) 	<ul style="list-style-type: none"> • Inexpensive, has a high odor, used in mainly rigid foam
<ul style="list-style-type: none"> • Bis(N,N-dimethylaminoethyl)ether (BDMAEE) 	<ul style="list-style-type: none"> • Excellent blowing catalyst in flexible foam
<ul style="list-style-type: none"> • N,N-dimethylethanolamine (DMEA) 	<ul style="list-style-type: none"> • Inexpensive, used in flexible and rigid foam
<ul style="list-style-type: none"> • Stannous octoate 	<ul style="list-style-type: none"> • Gelling catalyst used in molded polyether-based flexible foams
<ul style="list-style-type: none"> • Dibutyltin dilaurate (DBTDL) 	<ul style="list-style-type: none"> • Gelling catalyst used in elastomer and microcellular flexible foams
<ul style="list-style-type: none"> • Dibutyltin mercaptide 	<ul style="list-style-type: none"> • Hydrolysis resistant catalysts for storage stable two component foams

2.1.6.1 Amine catalysts

Tertiary amines are mainly used as blowing catalysts for polyurethane foam since they can catalyze isocyanate-water reaction better isocyanate-polyol reaction [6].

Two catalytic mechanisms have been proposed for tertiary amine catalysis. The first mechanism was proposed by Baker (Scheme 2.1). The nitrogen of amine using its lone pair of electrons to coordinate with carbonyl carbon of the isocyanate group, afterwards complex intermediate is formed. This intermediate then reacts with active hydrogen from alcohol to generate a urethane group [1, 7]. The second mechanism was proposed by Farka (Scheme 2.2), which is supported in the more recent literature. The nitrogen of amine interacts with the proton source (polyols, amine, water) to form the complex intermediate and then reacts with the isocyanate to generate a urethane group [1, 7]. The factors that influence the activity of tertiary amine are basicity and steric hindrance of nitrogen atom in amine.

The proposed catalytic mechanism for the tin (IV) catalysts, such as dialkyltin dialkylthiolate and dialkyltin dicarbonate, is shown in Scheme 2.3. Tin compound reacts with polyol to form tin alkoxide. The alkoxide anion is transferred onto the co-ordinated isocyanate to afford an N-stannylurethane, which then undergoes alcoholysis to produce the urethane group and the original tin alkoxide [1].



Scheme 2.3 Catalytic mechanism of tin (IV) catalyst [1]

2.1.6.3 Metal-amine catalysts [1]

Since tertiary amine catalysts are selective towards blowing reaction while organotin catalysts are selective towards gelling reaction, the synergy between these two types of catalysts is necessary to control the balance of gelling and blowing reaction. Metal-amine catalyst system is commercially used in the preparation of polyurethane foam to obtain effective gelling and blowing reactions. The proposed mechanism of organotin-tertiary amine synergism in urethane formation is shown in Scheme 2.4. The metal coordinates to the oxygen of the isocyanate group to make the carbon more electrophilic. At the same time, amine coordinates to the hydrogen of the hydroxyl group to make the oxygen more nucleophilic.

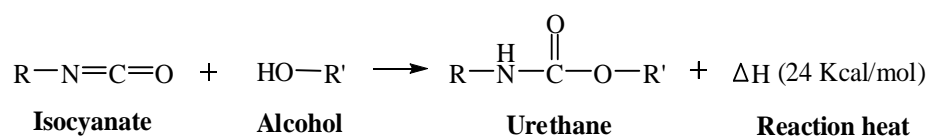
more reactive than aliphatic isocyanates (R = alkyl). Steric hindrance at -NCO or HO-R' groups markedly reduces the reactivity.

2.2.1 Primary reaction of isocyanates

The primary reactions of isocyanate with polyols and water to produced urethane and CO₂, respectively, strongly influence the mechanical properties of polyurethane foams.

2.2.1.1 Reaction of isocyanate with polyols

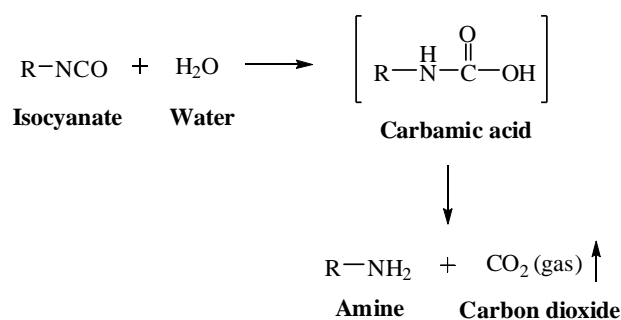
The reaction between isocyanate with polyols gives polyurethane. This reaction is known as the “gelling reaction” and must be temperature controlled because it is an exothermic reaction. The rate of polymerization is affected by steric hindrance of isocyanate group and the type of the hydroxyl group (primary or secondary). Catalyst must be used to accelerate the rate of reaction.



2.2.1.2 Reaction of isocyanate with water

The reaction between isocyanate with water leads to production of unstable carbamic acid, which immediately decomposes into CO₂ and amine. This reaction is a source of CO₂, which is necessary to generate the cellular structure of polyurethane foams.

This reaction is called the “blowing reaction” because the carbon dioxide gas produced is used for blowing the polyurethane foams. Water is called “blowing agent”. The reaction rate must accelerated by suitable choice of catalyst system.

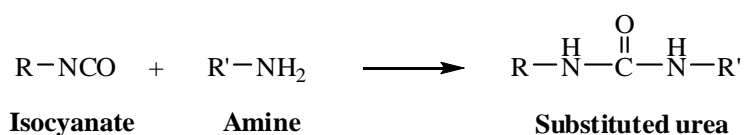


2.2.2 Secondary reaction of isocyanates

Excess amount isocyanate in polyurethane foam formulation will react with amine and urethane occurred from the primary reactions as follows:

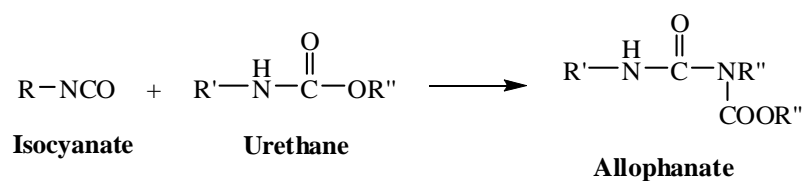
2.2.2.1 Reaction of isocyanate with amines

The reaction between isocyanate with amine forms the urea linkage. Since the reaction of isocyanate with amine occur faster than that with primary alcohols, amine is used as chain extender and curing agent in polyurethane foams manufacture.



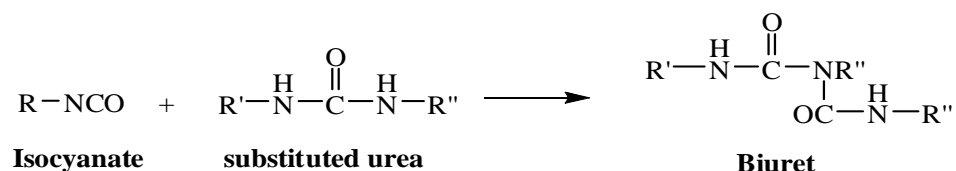
2.2.2.2 Reaction of isocyanate with urethane

The reaction between isocyanate with the nitrogen atom of the urethane group gives an allophanate group.



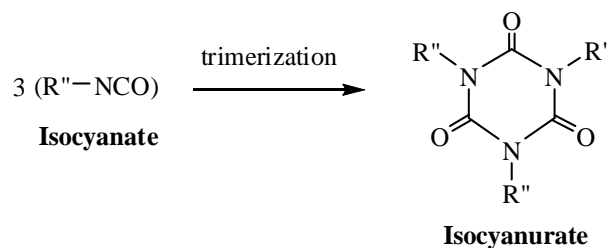
2.2.2.3 Reaction of isocyanate with urea

The biuret formation is similar to the allophanate formation. Isocyanate reacts with the nitrogen atom of substituted urea to produce a biuret structure.



2.2.2.4 Trimer formation

Isocyanurate trimer could be formed by further polymerization of isocyanate oligomers at higher temperature, especially in the presence of basic catalysts such as potassium and sodium salts of carboxylic acid. Isocyanurate trimer is thermally stable and contribute to fire resistance of polyurethane foams.



2.3 Formulations [4-6]

The amount of isocyanate needed to react with polyols and other active hydroxyl components could be calculated to gain chemically stoichiometric equivalents. This theoretical the amount of isocyanate could be adjusted to increase or decrease depended on the foam formulation, properties required, scale of production and surrounding conditions. The amount of isocyanate used is referred to “isocyanate index”.

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

The calculation of the component ratio for polyurethane manufacture is to calculate number of part by weight of the isocyanate needed to react with 100 parts by weight of polyol and hydroxyl additives. The analytical data needed for the calculation are the isocyanate value and hydroxyl value, residual acid value and water amount of the polyols and other reactive additives.

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

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

Hydroxyl value (hydroxyl number, OHV)

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

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

Acid value is also expressed as mg KOH/g of polyols and numerically equal to hydroxyl value in isocyanate used.

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

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

Isocyanate conversion (α), isocyanate conversion could be calculated by ATR-FTIR method, defined as the ratio between isocyanate peak area at final time and isocyanate peak area at initial time :

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

Where,

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

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

2.4 Mechanical properties

The mechanical properties of flexible and rigid polyurethane foam are different. Compression set is used to determine the compression load per unit of original area at a specified deformation. Test on flexible and rigid foams can be determined according to ASTM C165 [18], which is the standard test method for measuring compression properties of thermal insulations. This test method covers two procedures for determining the compression resistance of thermal insulations. The universal testing machine fitted with a compression rig (cage) consisting of two parallel flat plates (Figure 2.10) is used for the tests [20].

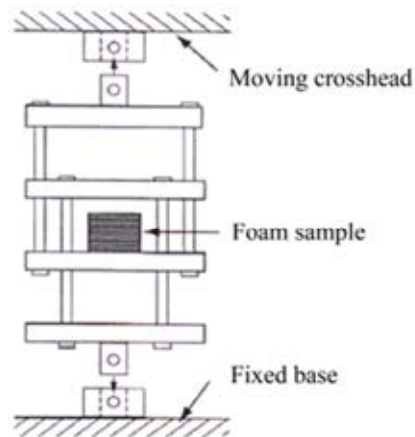


Figure 2.10 Compression load deflection test rig [20]

Compression properties are important mechanical properties for cellular polymers. Compression energy absorption characteristics and deformation characteristics of foam depend on density of foam, chain length and functionality of raw materials and the predominance of either open or closed cells. In simple terms, open cell foam (invariably flexible) relies on cell walls buckling and bending, which is essentially a reversible process (Figure 2.11).

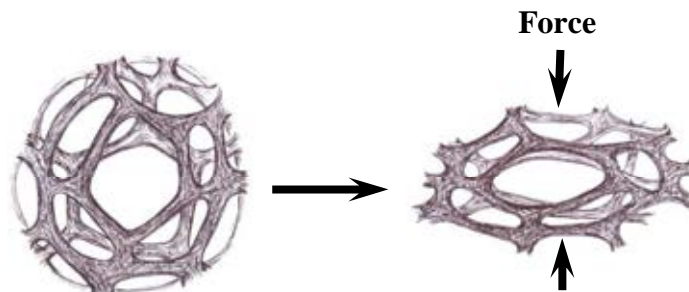


Figure 2.11 Schematic representation of open cell deformation [20]

On the other hand, air flow is not the consideration with closed cell foams. In this case (Figure 2.12) deformation involves cell wall bending/buckling (reversible), gas compression, cell wall stretching/yielding (non-reversible). Severe compression causes cell rupture.

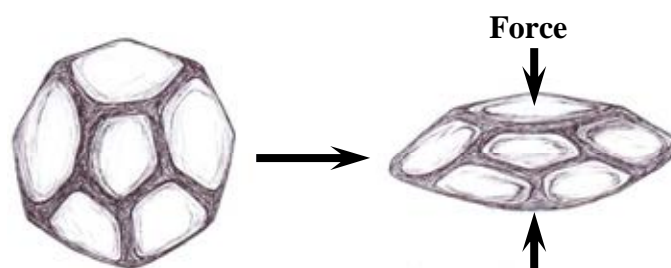


Figure 2.12 Schematic representation of closed cell deformation [20]

Tensile properties are mostly used for characterization of flexible foam and elastomer in polyurethane according to ASTM D412, which is the standard method of tensile testing for vulcanized rubber. This method covers the effect of the application of a tension load to vulcanized rubber and similar rubber-link materials. Samples are tests for tensile strength, which is the maximum tensile stress applied during stretching a specimen to rupture. Tensile stress is the applied force per unit of original cross sectional area of specimen and elongation at break, which is the extension of a uniform section of a specimen by tensile force applied to the specimen. Tensile stress is expressed as a percentage of original length of the section [19].

2.5 Literature reviews

In the polyurethane industry, new catalyst systems that have less volatile organic compound (VOC) emission in FPUR foams are needed. These FPUR foams are used for automotive seating, furniture, bedding and carpet industries. The researches on the attempt to reduce VOC from amine catalysts, which was the main source of VOC emission were done by Rothe *et al.* [21]. New amine catalysts were developed to replace commercial tertiary amine catalysts, which cause of VOC emission in flexible slabstock foam. Primary and secondary amines, which are reactive amine that can react with NCO group, were used in the preparation of FPUR foam. The results showed that when replacing the commercial amine catalysts with reactive amine catalysts, the total VOC was reduced by 30-75% and FPUR foam properties were not significantly affected.

Sikorski *et al.* [22] prepared high-resilience molded FPUR foam by using primary and secondary reactive amines as catalysts. The results showed that replacement of commercial catalyst (triethylenediamine; TEDA) by active amine catalyst, N-(2-hydroxy)-propyl-imidazone (PC CAT[®] HPI), the released VOC in molded foam was reduced. Combination of PC CAT[®] HPI with a non reactive amine blowing catalyst resulted in 15-20% VOC reduction. Combination of PC CAT[®] HPI with a reactive amine blow catalyst, bis(dimethylamino)-2-propanol (PC CAT[®] BDP), resulted in 50% VOC reduction without significant deterioration of processing and mechanical foam properties.

However, catalysts containing reactive groups, namely primary amine, secondary amine and hydroxyl group, that react with the isocyanate to become a part of the polymer matrix do not evaporate. The obvious disadvantage of these catalysts is loss of catalytic activity [2]

Active polyols (Voranol[®]) are the polyols which amine catalyst is built into the polyols. Active polyols could be used to prepare flexible slabstock foams in order to eliminate the use of volatile amine catalyst, which will reduce VOC emission. Fabio *et al* [23] studied the effect of using active polyols (Voranol[®]) in the preparation of flexible slabstock foam as compared with commercial polyether polyol. These results showed use of active polyols resulted in significant reduction of VOC without reduction in physical properties of foam.

Casati *et al.* [24] studied the effect of active polyols as a partial substitute for fugitive catalyst or tertiary amine catalyst (commercial catalyst) in automotive flexible molded polyurethane foams. Active polyols and non-fugitive catalyst were used to prepare the foam. The reaction time and mechanical properties were investigated and compared with fugitive catalyst. The results showed that VOC emission of foam catalyzed by active polyols with non-fugitive catalyst was reduced. The reaction time and foam densities of all formula gave similar results. The foam prepared from active polyols and non-fugitive catalyst had poor mechanical properties while the foam catalyzed by fugitive catalyst had good properties.

Inoue *et al.* [25] studied the catalytic activity of new catalyst system, $M(\text{acac})_n$ -amine catalysts, which were co-catalysts of metal acetylacetonate [$M(\text{acac})_n$, where $M = \text{Mn, Cu, Co, Ni}$ and Fe] and tertiary amines, namely triethylenediamine (TEDA), N,N,N',N'',N''' -pentamethyldiethylenetriamine (DT), N,N,N',N' -tetramethylethylenediamine (TE), bis(2-dimethylaminoethyl) ether (ETS) and N,N',N' -trimethylaminoethylpiperazine. $M(\text{acac})_n$ -amine catalysts were used as a catalysts for the reaction between hexamethylene diisocyanate (HDI) with diethylene glycol (DEG) and their catalytic activities were compared with that of dibutyl dilaurate (DBTDL). When different $M(\text{acac})_n$ were used, the order of catalytic activity was $\text{TEDA-Mn}(\text{acac})_2 > \text{TEDA-Fe}(\text{acac})_3 > \text{TEDA-Co}(\text{acac})_2 > \text{TEDA-Ni}(\text{acac})_2 > \text{TEDA-Cu}(\text{acac})_2$. When different amines were used, it was found that $\text{TEDA-Mn}(\text{acac})_2$ had higher catalytic activity than $\text{DT-Mn}(\text{acac})_2$ and $\text{TE-Mn}(\text{acac})_2$. However, $\text{TEDA-Mn}(\text{acac})_2$ had lower catalytic activity than DBTDL.

The work in our research group focuses on using metal-amine catalysts as new catalysts to replace N,N -dimethylcyclohexylamine (DMCHA), which is a commercial tertiary amine in rigid polyurethane (RPUR) foam manufacture. DMCHA has good catalytic activity, however, it has strong amine odor. The metal-amine catalysts were modified from the work of Kurnoskin *et al.* [26]. Various metal complexes were synthesized from transition metal salts and aliphatic amines (Figure 2.12). These metal complexes were used in the preparation of thermally stable metal-containing epoxy polymers.

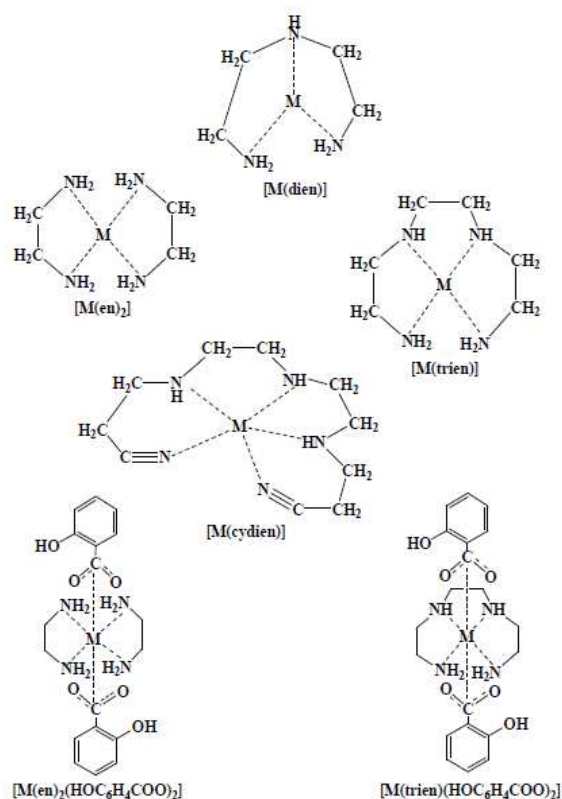


Figure 2.13 Structures of metal complexes in the work of Kurnoskin *et al* [26]

Pengjam *et al.* [4] synthesized metal-amine complexes as catalysts for rigid polyurethane foams. These metal-amine complexes were synthesized by the reaction of metal acetates, namely $M(\text{OAc})_2$ (where $M = \text{Cu}, \text{Ni}, \text{Mn}$ and Co), with aliphatic amines, namely ethylenediamine (en) and triethylenetetramine (trien) using methanol or acetone as solvents. The results showed that $\text{Cu}(\text{OAc})_2(\text{en})_2$ had comparable catalytic activity to DMCHA. Although metal-amine complexes synthesized in methanol or acetone had good catalytic activity, but methanol and acetone had to be removed from metal complexes before using and this purification took a long time. Moreover, the metal-amine complexes were obtained in viscous liquid or powder forms, which were difficult to obtain homogeneous mixing with the other components in foam formulation.

Following the work of Pengjam *et al.* [4], Sukkaneewat *et al.* [5] developed new method for the synthesis of metal-amine complexes using ethylene glycol as a solvent. Various metal-amine complexes were obtained as odorless solutions in ethylene glycol. The synthesis of these metal-amine complex solutions required no purification and could be used as catalysts for rigid polyurethane foams. The metal-amine complexes were synthesized from copper acetate with different aliphatic amines, namely ethylenediamine (en), triethylenetetramine (trien), tetraethylenepentamine (tetraen) and pentaethylenhexamine (pentaen). It was found that rigid polyurethane foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{trien})$ gave the best results because $\text{Cu}(\text{OAc})_2(\text{trien})$ showed high catalytic activity and the foam had good properties.

From the works Pengjam *et al.* [4] and Sukkaneewat *et al.* [5], it is of interest to use metal-amine complex solutions in ethylene glycol in the preparation of flexible polyurethane (FPUR) foams. The common commercial catalysts used in flexible polyurethane foam is 1,4-diazabicyclo(2.2.2)octane (Dabco[®] EG), which is a tertiary amine. Dabco[®] EG is a strong gelation catalyst without strong odor, however, it is expensive. Therefore, the objective of this research was to synthesize metal-amine complexes as solution in ethylene glycol and used as catalysts for FPUR foams and compared with Dabco[®] EG catalyst. Metal-amine complexes would be synthesized from the reaction of metal acetates, namely copper acetate and zinc acetate, with the aliphatic amines, namely ethylenediamine (en), triethylenetetramine (trien) and diethylamine (dea). Copper-amine and zinc-amine complexes were chosen since these metal complexes could be easily prepared and they are stable in air [26]. The amines chosen were primary and secondary amine because secondary amine has higher catalytic activity than primary amine, however, it has higher steric hindrance than primary amine. Ethylenediamine (en) is a primary amine. Diethylamine (dea) is a secondary amine. Triethylenetetramine (trien) contains both primary and secondary amines. The catalytic activity of metal-amine complexes prepared from different amines would be studied.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and raw materials

3.1.1 Metal-amine complex synthesis

Ethylene glycol was obtained from Carlo Erba. Copper(II) acetate monohydrate [Cu(OAc)₂·H₂O] was obtained from TCI Tokyo Kasei. Zinc acetate dihydrate [Zn(OAc)₂·2H₂O], ethylenediamine (en), triethylenetetramine (trien) and diethylamine (dea) were obtained from Fluka and Aldrich.

3.1.2 FPUR Foam preparation

3.1.2.1 Starting materials for flexible polyurethane foam preparation

Polyether polyol (Jeffol[®] G-31-35, glycerine initiated ethylene oxide triol), molecular weight = 4800 g/mole, hydroxyl value (OHV) = 35 mgKOH/g, average functionality = 3; 4,4'-methane diphenyl diisocyanate prepolymer (Suprasec[®] 2449), %NCO = 18.9 (%wt.); 1,4-diazabicyclo(2.2.2)octane (Dabco[®] EG, commercial reference catalyst); silicone surfactant (Dabco[®] DC193); chain extender (mono ethylene glycol) was supplied from Huntsman (Thailand) Co., Ltd. Distilled water was used as a chemical blowing agent. Copper-amine and zinc-amine complexes were synthesized and used as catalysts.

3.2 Synthetic procedures

The metal-amine and mixed metal-amine complexes were synthesized using ethylene glycol as a solvent to obtain odorless and low viscosity solution. The procedure was modified from the synthetic procedure reported in the literature [5]. The solution of metal-amine and mixed metal-amine complexes in ethylene glycol were used to prepare the free rise and molded FPUR foams.

3.2.1 Synthesis of metal-amine complexes (copper-amine and zinc-amine complexes)

Metal-amine complexes synthesized were $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$, $\text{Cu}(\text{OAc})_2(\text{dea})_4$, $\text{Zn}(\text{OAc})_2(\text{en})_2$, $\text{Zn}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{dea})_4$.

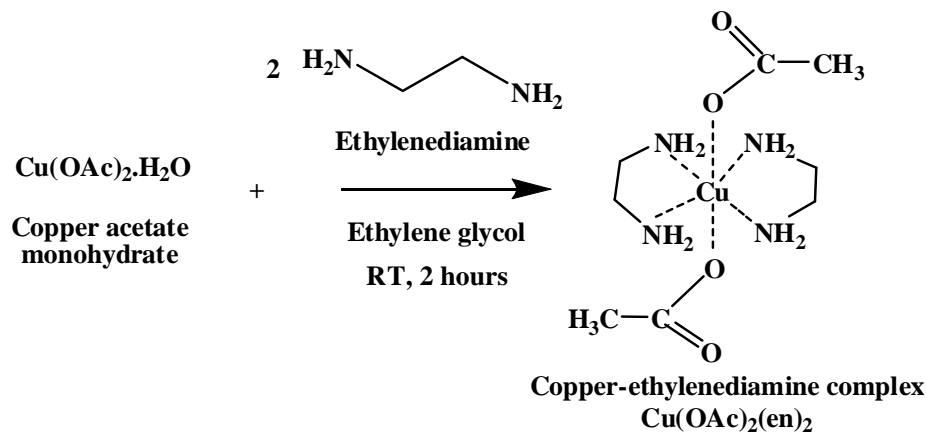
3.2.1.1 Synthesis of copper-amine complexes [$\text{Cu}(\text{OAc})_2(\text{Y})_2$] (Y = en, trien and dea)

The composition of chemicals in synthesis 33%wt copper-amine complex solution in ethylene glycol is shown in Table 3.1.

Table 3.1 The composition of chemicals in the synthesis of 33%wt copper-amine complex solution in ethylene glycol (EG).

Metal complexes	Amount of $\text{Cu}(\text{OAc})_2$ (mol)	Amount of amine (mol)			Appearance
		en	trien	dea	
$\text{Cu}(\text{OAc})_2(\text{en})_2$	0.312	0.628	-	-	dark blue solution
$\text{Cu}(\text{OAc})_2(\text{trien})$	0.289	-	0.289	-	dark blue solution
$\text{Cu}(\text{OAc})_2(\text{dea})_4$	0.203	-	-	1.148	dark brown solution

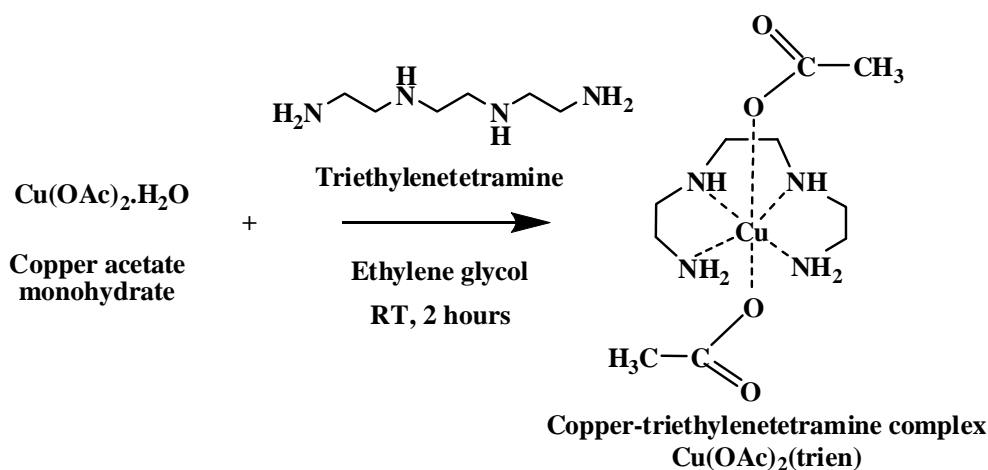
3.2.1.1.1 Synthesis of copper-ethylenediamine complex, $\text{Cu}(\text{OAc})_2(\text{en})_2$ [5]



Scheme 3.1 Synthesis of copper-ethylenediamine complex, $\text{Cu}(\text{OAc})_2(\text{en})_2$ [5]

Ethylenediamine (en) (0.42 ml, 0.313 mol) was dissolved in ethylene glycol (2.4 ml) at room temperature for 20 minutes. After that, copper (II) acetate monohydrate (0.624 g, 0.698 mol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33% wt of $\text{Cu}(\text{OAc})_2(\text{en})_2$ in ethylene glycol was obtained as a low viscous and odorless dark blue solution.

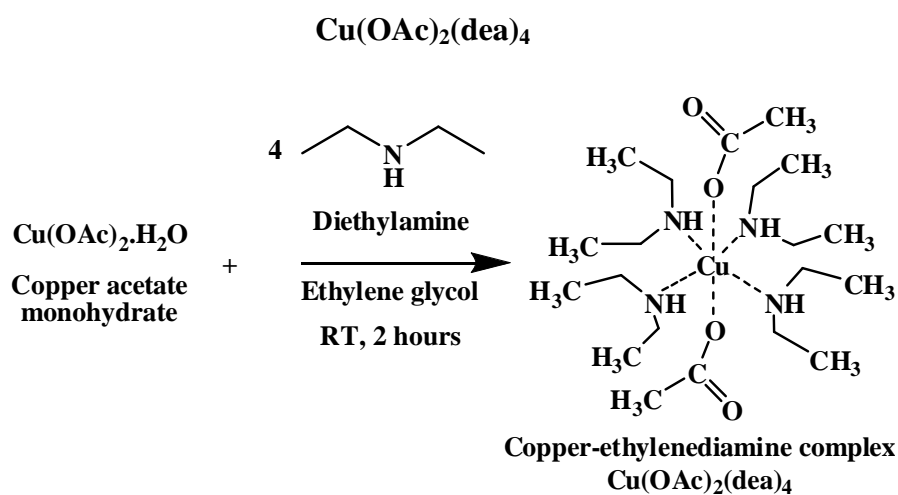
3.2.1.1.2 Synthesis of copper-triethylenetetramine complex, $\text{Cu}(\text{OAc})_2(\text{trien})$ [5]



Scheme 3.3 Synthesis of copper-triethylenetetramine complex, $\text{Cu}(\text{OAc})_2(\text{trien})$ [5]

Triethylenetetramine (trien) (0.423 ml, 0.289 mol) was dissolved in ethylene glycol (2.05 ml) at room temperature for 20 minutes. After that, copper (II) acetate monohydrate (0.577 g, 0.289 mol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33%wt of $\text{Cu}(\text{OAc})_2(\text{trien})$ in ethylene glycol was obtained as a low viscous and odorless dark blue solution.

3.2.1.1.3 Synthesis of copper-diethylamine complex



Scheme 3.5 Synthesis of copper-diethylamine complex, $\text{Cu}(\text{OAc})_2(\text{dea})_4$

Diethylamine (dea) (0.840 ml, 0.203 mol) was dissolved in ethylene glycol (2.05 ml) at room temperature for 20 minutes. After that, copper (II) acetate monohydrate (0.406 g, 1.148 mol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33%wt of $\text{Cu}(\text{OAc})_2(\text{dea})_4$ in ethylene glycol was obtained as a low viscous and odorless dark brown solution.

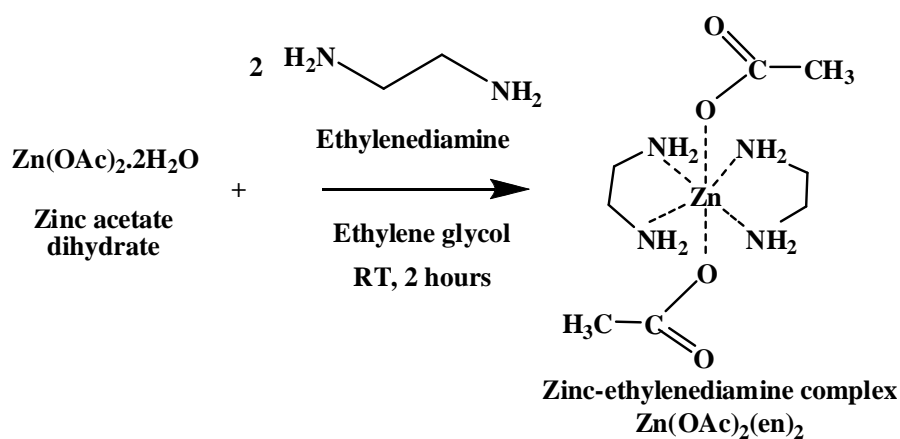
3.2.1.2 Synthesis of zinc-amine complexes, $\text{Zn}(\text{OAc})_2(\text{Y})_2$ (Y = en, trien and dea)

Zinc-amine complexes were synthesized using the same procedure as copper-amine complexes. The composition of chemicals in synthesizing zinc-amine complexes are shown in Table 3.2

Table 3.2 The composition of chemicals in the synthesis of 33% wt zinc-amine complex solution in ethylene glycol (EG)

Metal complexes	Wt. of $\text{Zn}(\text{OAc})_2$ (mol)	Weight of composition (mol)			Appearance
		en	trien	dea	
$\text{Zn}(\text{OAc})_2(\text{en})_2$	0.294	0.648	-	-	colorless solution
$\text{Zn}(\text{OAc})_2(\text{trien})$	0.273	-	0.273	-	pale yellow solution
$\text{Zn}(\text{OAc})_2(\text{dea})_4$	0.194	-	-	1.113	pale orange solution

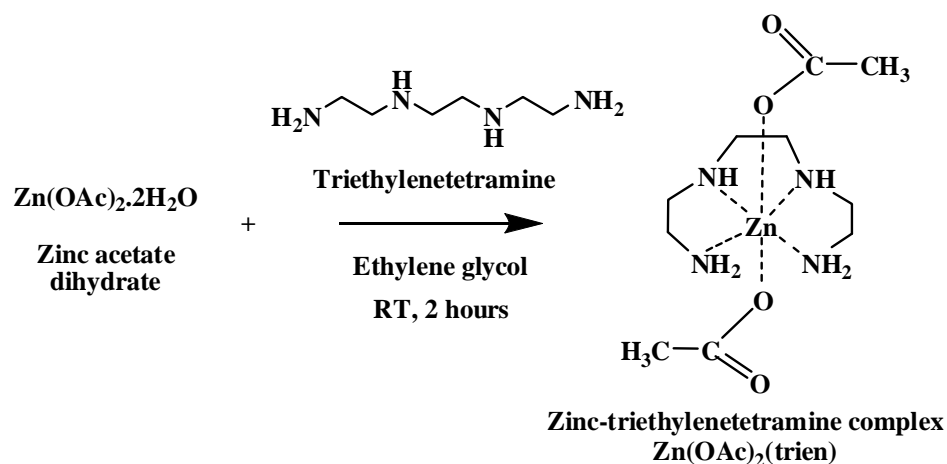
3.2.1.2.1 Synthesis of zinc-ethylenediamine complex, $\text{Zn}(\text{OAc})_2(\text{en})_2$ [5]



Scheme 3.2 Synthesis of zinc-ethylenediamine complex, $\text{Zn}(\text{OAc})_2(\text{en})_2$ [5]

The mole ratio of zinc acetate dihydrate to ethylenediamine (en) was (1 : 2). The solution of 33%wt of $\text{Zn}(\text{OAc})_2(\text{en})_2$ in ethylene glycol was prepared using the following procedure : A solution of ethylenediamine (en) (0.39 ml, 0.294 mol) was dissolved in ethylene glycol (2.05 ml) at room temperature for 20 minutes. After that, zinc (II) acetate dihydrate (0.646 g, 0.648 mol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33%wt of $\text{Zn}(\text{OAc})_2(\text{en})_2$ in ethylene glycol was obtained as a low viscous and odorless colorless solution.

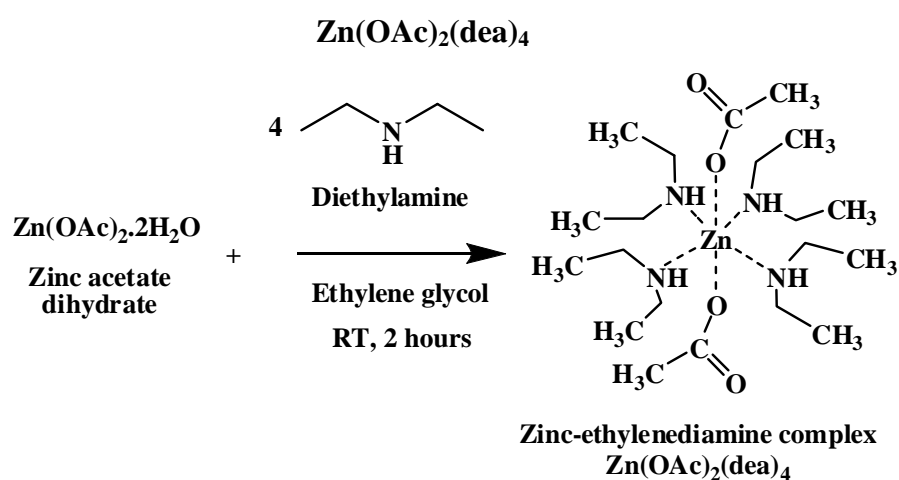
3.2.1.2.2 Synthesis of zinc-triethylenetetramine complex, $\text{Zn}(\text{OAc})_2(\text{trien})$ [5]



Scheme 3.4 Synthesis of zinc-triethylenetetramine complex, $\text{Zn}(\text{OAc})_2(\text{trien})$ [5]

The mole ratio of zinc acetate dihydrate to triethylenetetramine (trien) was (1 : 1). The solution of 33%wt of $\text{Zn}(\text{OAc})_2(\text{trien})$ in ethylene glycol was prepared using the following procedure : A solution of triethylenetetramine (trien) (0.400 ml, 0.273 mol) was dissolved in ethylene glycol (2.05 ml) at room temperature for 20 minutes. After that, zinc (II) acetate dihydrate (0.600 g, 0.273 mol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33%wt of $\text{Zn}(\text{OAc})_2(\text{trien})$ in ethylene glycol was obtained as a low viscous and odorless pale yellow solution.

3.2.1.2.3 Synthesis of zinc-diethylamine complex,



Scheme 3.6 Synthesis of zinc-diethylamine complex, $\text{Zn}(\text{OAc})_2(\text{dea})_4$

The mole ratio of zinc acetate dihydrate to diethylamine (dea) was (1 : 4). The solution of 33%wt of $\text{Zn}(\text{OAc})_2(\text{dea})_4$ in ethylene glycol was prepared using the following procedure : A solution of diethylamine (dea) (0.814 ml, 0.194 mol) was dissolved in ethylene glycol (2.05 ml) at room temperature for 20 minutes. After that, zinc acetate dihydrate (0.427 g, 1.113 mol) was added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33%wt of $\text{Zn}(\text{OAc})_2(\text{dea})_4$ in ethylene glycol was obtained as a low viscous and odorless pale orange solution.

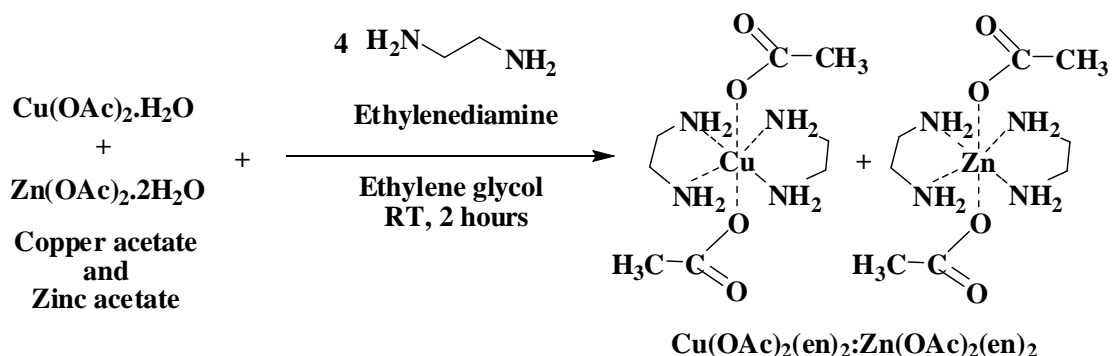
3.2.2 Synthesis of mixed metal-amine complexes

Mixed metal-amine complexes were synthesized using the same procedure as copper-amine and zinc-amine complexes. The compositions of chemicals in synthesizing mixed metal-amine complex solution in ethylene glycol are shown in Table 3.3.

Table 3.3 The composition of chemicals in the synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1 : 1 : 4, 1.5 : 0.5 : 4$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$

Catalysts	Wt. of copper acetate (mol)	Wt. of zinc acetate (mol)	Vol. of en (mol)	Vol. of trien (mol)	Appearance
$\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en}$ 1 : 1 : 4	0.151	0.151	0.682	-	dark blue solution
$\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en}$ 1.5 : 0.5 : 4	0.230	0.077	0.682	-	dark blue solution
$\text{Cu}(\text{OAc})_2:\text{en}:\text{trien}$ 2 : 2 : 1	0.230	-	0.095	0.366	dark blue solution

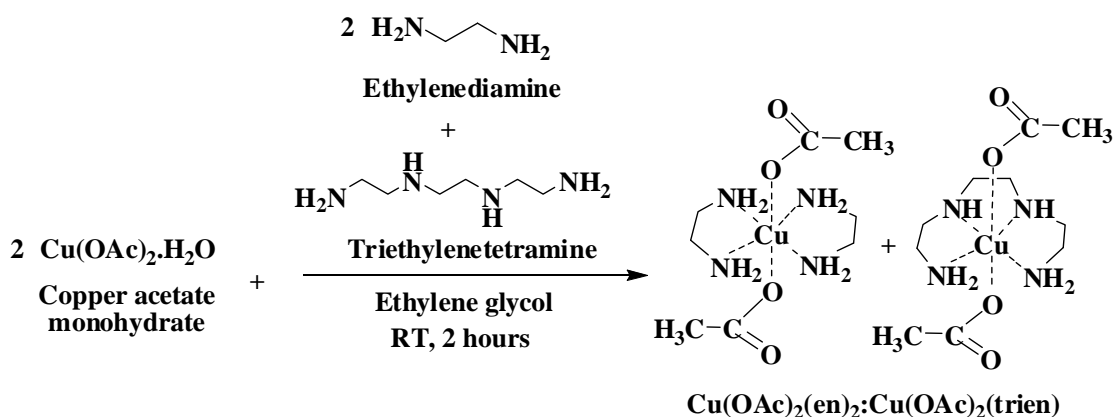
3.2.2.1 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ [5]



Scheme 3.7 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ [5]

The mole ratio of copper(II) acetate monohydrate to zinc(II) acetate dihydrate to ethylenediamine was 1 : 1 : 4. The solution of 33%wt of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ in ethylene glycol was prepared using the following procedure: ethylenediamine was dissolved in ethylene glycol at room temperature for 10 minutes. After that, copper(II) acetate monohydrate and zinc(II) acetate dihydrate were added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33%wt of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ in ethylene glycol was obtained as a low viscous and odorless blue solution. The series of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ in 33%wt in ethylene glycol were chosen to study about the reaction times and density of FPUR foams compared with foams catalyzed by Dabco[®] EG.

3.2.2.2 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$



Scheme 3.8 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$

The fraction ratio of copper(II) acetate monohydrate to ethylenediamine (en) to triethylenetetramine (trien) was 2 : 2 : 1. The solution of 33% wt of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ in ethylene glycol was prepared using the following procedure: ethylenediamine and triethylenetetramine was dissolved in ethylene glycol at room temperature for 10 minutes. After that, copper(II) acetate monohydrate were added and the reaction mixture was stirred continuously at room temperature for 2 hours. Solution of 33% wt of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ in ethylene glycol was obtained as a low viscous and odorless purple solution. $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ in 33%wt in ethylene glycol were chosen to study about the reaction times and density of FPUR foams compared with foams catalyzed by Dabco[®] EG.

3.3 Flexible polyurethane (FPUR) foam preparation [5]

The preparation of FPUR foams used a two-step method. Two types of foam samples were prepared in this research. The first type, which was free rise foams prepared in paper cup, was used for investigation of the reaction time, free rise density, height of foams, rise profile, temperature profile, NCO conversion and morphology. The second type, which was molded foams prepared in aluminum molded, was used for investigation of thermal stability and mechanical properties, tensile strength, modulus, elongation at break and compression properties.

Reaction times in foaming reaction studied 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), rise time (which is the time of the foam stop rising), tack-free time (which is the time of the foam could not tack with other materials or crosslink reaction) and demolded time (which is the time of foam curing).

3.3.1 Free rise flexible polyurethane foam prepared by cup test method

The preparation of free rise FPUR foams using two-step method is shown in Figure 3.1. The formulations used for foam preparation are presented in Tables 3.4. In the first step, polyol, catalysts (Dabco[®] EG or metal-amine complexes), surfactant, chain extender and blowing agent were mixed in a paper cup (700 ml). In the second step, MDIP was added into the polyol mixture. Then, the mixture was mixed to obtain for homogeneous mixture by a mechanical stirrer at 2000 rpm for 10 seconds. The mixture was poured into a paper cup. During the foaming reaction, reaction time was measured. After that, the foams were kept for 48 hours at room temperature in order for complete all of the polymerization reactions. After 48 hours, the foams were cut by saw for measurement of free rise density. The foams were kept for 5 days for investigation of the NCO conversion by infrared spectroscopy.

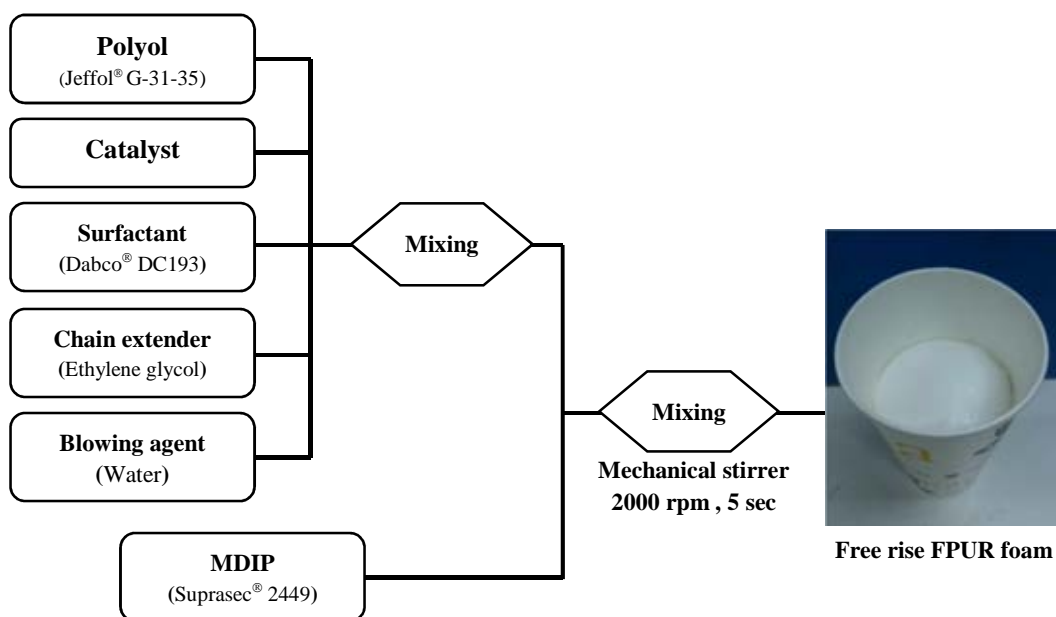


Figure 3.1 Procedure for the preparation of flexible polyurethane foam [4]

Table 3.4 FPUR foam formulations (in parts by weight unit, pbw)

Formulation (NCO index = 100)	pbw*
• Poly(ethylene oxide) triol, (Jeffol [®] G-31-35, Molecular weight = 4,800 g/mole, OH Number = 35 mg KOH/g)	100.0
• Metal complex catalysts or reference catalyst (Dabco [®] EG)	0.3-0.8
• Silicone surfactant (polysiloxane, Dabco [®] DC193)	0.5
• Crosslinking agent (ethylene glycol)	3.0-5.0
• Blowing agent (water)	0.3-0.5
• Diphenylmethane diisocyanate prepolymer (MDI prepolymer, MDIP, Suprasec [®] 2449, isocyanate index = 18.9)	69.3

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

3.3.2 Molded flexible polyurethane foam prepared by molded method

The preparation of the molded foams used the same mixing step in the preparation of free rise foams. After all components were mixed by mechanical stirrer at 2000 rpm for 10 seconds, the liquid was poured into an aluminum mold with a dimension of 20 cm x 10 cm x 0.6 cm. (width x length x thickness). After that, demolded time was measured. After the foams were demolded, the foams were trimmed into a regular rectangular blocks. After that, FPUR foams were allowed to cure at room temperature for at least 48 hours before foam specimens was cut from the foam slap for mechanical testing.

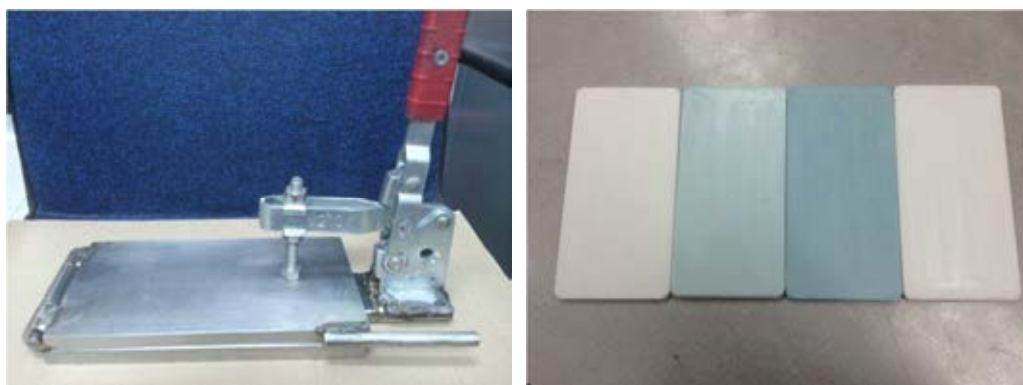


Figure 3.2 FPUR foam mold and flexible polyurethane foam slap

3.4 Characterization of metal-amine complexes and mixed metal-amine complexes

3.4.1 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy was routinely used in the quantitative determination of solutions of transition metal ions conjugated organic compounds. UV-visible 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 200-800 nm at a medium speed. The solvent used was methanol (spectroscan grade).

3.4.2 Mass spectrometry

Electrospray ionization (ESI) mass spectrometry was used to confirmed complex formations by their unique mass (mass-to-charge ratio). The method relies on the fact that every compound had 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 (spectroscan grade) was used as a solvent.

3.5 Characterization of FPUR foams

3.5.1 Infrared spectroscopy

The infrared spectroscopy was used to characterize the functional groups and study about NCO conversion of FPUR foams. Attenuated total reflectance fourier transformed infrared spectroscopy (ATR-FTIR) was recorded on a Nicolet 6700 FTIR spectrometer, over the range 700-4000 cm^{-1} at a resolution of 16 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 measurement surface that is in contact with the foam sample. 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.

3.5.2 Kinetic of foaming

The kinetic of FPUR foaming was studied through the reaction times for instance cream time, gel time, rise time and tack-free time by using a digital stopwatch.

3.5.3 Foaming temperature

The measurement of foaming temperature used as a thermocouple, Digicon DP-71 was widely used to detected foaming temperatures of FPUR foams. Those foaming temperature is represented by the maximum core temperature and the temperature profiles.

3.5.4 Apparent density

The apparent density of FPUR foams was measured in accordance with ASTM D3574 [27]. The size of specimen was 3.0 cm x 3.0 cm x 3.0 cm (width x length x thickness) and the average values of three samples was reported.

3.5.5 Scanning electron microscope (SEM)

The cell size and morphology of FPUR foams were measured on a Hitachi/S-4800 scanning electron microscope (SEM). The thickness of FPUR foams sample was prepared for SEM analysis by coating with gold before scanning in order to provide an electrically conductive surface. The samples were done at magnification of 25x and accelerating of 20 kV.

3.5.6 Mechanical properties

3.5.6.1 Tensile testing [19]

The tensile testing of FPUR foams investigated tensile strength, modulus and elongation at break properties of foams using universal testing machine, Hounsfield H 10 KM in accordance with ASTM D412-68, The piece of foams to be tested should be flat, not less than 1.5 mm or more than 3 mm in thickness and of a size which will permit cutting by a Dumbbell die C cutter following ASTM D412. The speed of measurement was 250 mm/min and the average values of three samples were reported.



Figure 3.3 Dumbbell die C cutter following ASTM D412 and FPUR foams

3.5.6.2 Compression set testing [18]

The compression set of FPUR foams investigated the compression set at 25% thickness of foams using universal testing machine, Hounsfield H 10 KM in accordance with ASTM C165-95. The specimen with the dimension of 3.0 cm x 3.0 cm x 3.0 cm (width x length x thickness) at perpendicular to the foam rise direction were analyzed. The rate of crosshead movement was fixed at 1 mm/min.

CHAPTER IV

RESULTS AND DISCUSSION

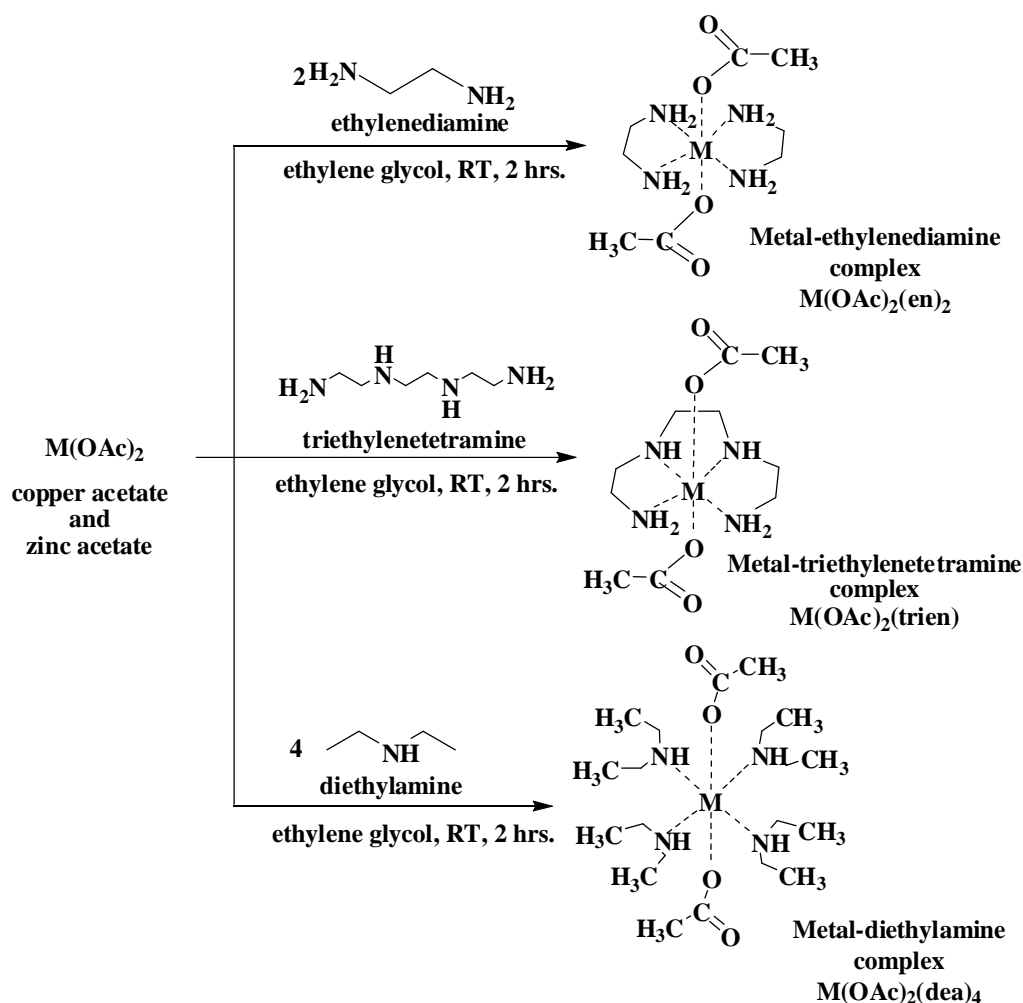
4.1 Synthesis of metal-amine complexes and mixed metal-amine complexes

4.1.1 Metal-amine complexes

The study of catalytic activity of the metal-amine complexes towards polymerization reaction to give polyurethane foam was carried out. Metal-amine complexes employed in this research were $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$, $\text{Cu}(\text{OAc})_2(\text{dea})_4$, $\text{Zn}(\text{OAc})_2(\text{en})_2$, $\text{Zn}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{dea})_4$. Catalytic activity of these metal complexes was compared with the commercial catalysts, 1,4-diazabicyclo(2.2.2)octane (Dabco[®] EG).

4.1.1.1 Synthesis of copper-amine and zinc-amine complexes

Synthesis of metal-amine complexes was done by using ethylene glycol as a solvent. The metal compounds used were copper(II) acetate monohydrate $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$ and zinc(II) acetate dihydrate $[\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}]$. The aliphatic amines used were ethylenediamine (en), triethylenetetramine (trien) and diethylamine (dea). Mole ratios of copper acetate or zinc acetate to en, trien and dea were 1 : 2, 1 : 1 and 1 : 4, respectively. The procedure of synthesized was applied from the synthetic reported in the literature [5]. The reactions between metal compounds with aliphatic amines gave $\text{M}(\text{OAc})_2(\text{en})_2$, $\text{M}(\text{OAc})_2(\text{trien})$ and $\text{M}(\text{OAc})_2(\text{dea})_4$ as shown in Scheme 4.1. The solution of copper-amine and zinc-amine complexes was obtained as an odorless, low viscosity homogeneous liquid and could be easily dissolved in the raw materials of FPUR foam formulation. UV-visible spectroscopy and mass spectrometry were used to identify the complex formation of copper-amine and zinc-amine complexes.



Scheme 4.1 Synthesis of $M(OAc)_2(en)_2$, $M(OAc)_2(trien)$ and $M(OAc)_2(dea)_4$
 (M = Copper and Zinc)

4.1.1.2 Characterization of copper-amine and zinc-amine complexes

UV-visible spectroscopy and mass spectrometry were used to identify the complex formation of copper-amine and zinc-amine complexes. UV-visible spectra of copper-amine and zinc-amine complexes were compared with those of copper acetate and zinc acetate to observe the shift of the maximum wavelength (λ_{max}) of the metal complex. Mass spectrometry was used to identify the complexes of copper-amine and zinc-amine.

The appearances of copper-amine complexes and zinc-amine complexes are shown in Figures 4.1 and 4.2 respectively, it was found that all copper-amine complexes 33% wt in ethylene glycol were obtained as dark blue or dark brown liquid and could be easily dissolved in the raw materials of FPUR foam formulation. Zinc-amine complexes 33% wt in ethylene glycol were obtained as pale yellow or pale orange solution.

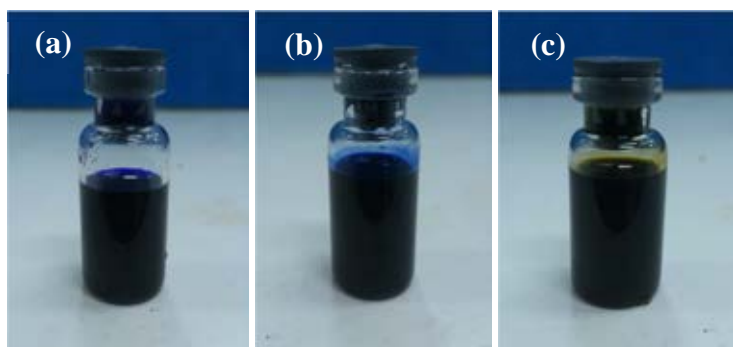


Figure 4.1 Copper-amine complexes 33% wt in ethylene glycol
(a) $\text{Cu}(\text{OAc})_2(\text{en})_2$, (b) $\text{Cu}(\text{OAc})_2(\text{trien})$ and (c) $\text{Cu}(\text{OAc})_2(\text{dea})_4$

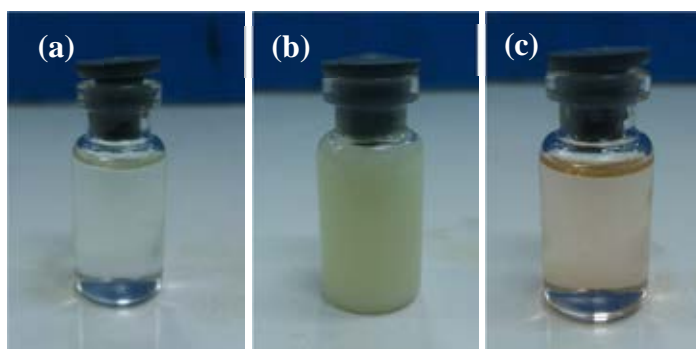


Figure 4.2 Zinc-amine complexes 33% wt in ethylene glycol (a) $\text{Zn}(\text{OAc})_2(\text{en})_2$,
(b) $\text{Zn}(\text{OAc})_2(\text{trien})$ and (c) $\text{Zn}(\text{OAc})_2(\text{dea})_4$

4.1.1.2.1 UV-visible spectroscopy of copper-amine complexes and zinc-amine complexes

UV-visible spectra of copper-amine complexes are shown in Figure 4.3. The maximum wavelength (λ_{\max}) of $\text{Cu}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Cu}(\text{OAc})_2(\text{dea})_4$ appeared at 245, 232, 259 and 246 nm, respectively. The λ_{\max} of $\text{Cu}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$ at 232 to 259 nm, respectively, shifted from the λ_{\max} of $\text{Cu}(\text{OAc})_2$ which suggested the complex formation. These λ_{\max} of $\text{Cu}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$ occurred from ligand to metal charge transfer and could be clearly observed since the electron configuration of Cu is $4s^2 3d^9$. The λ_{\max} of $\text{Cu}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$ were slightly different. This is because both $\text{Cu}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$ have 6 coordinations and the structure of amine donors, en and trien, are similar. The λ_{\max} of $\text{Cu}(\text{OAc})_2(\text{dea})_4$ appeared at the same wavelength as that of $\text{Cu}(\text{OAc})_2$. This indicated that the complex formation did not occur which might be due to the steric hindrance of dea.

UV-visible spectra of zinc-amine complexes are shown in Figure 4.4. It was found that the λ_{\max} of $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{OAc})_2(\text{en})_2$, $\text{Zn}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{dea})_4$ appeared approximately between 205 to 210 nm. The λ_{\max} of zinc-amine complexes occurred from ligand to metal charge transfer. However, they could not be clearly observed since the electron configuration of Zn is $4s^2 3d^{10}$. Zinc-amine complexes were synthesized using the same condition as copper-amine complexes to ensure the complex formation.

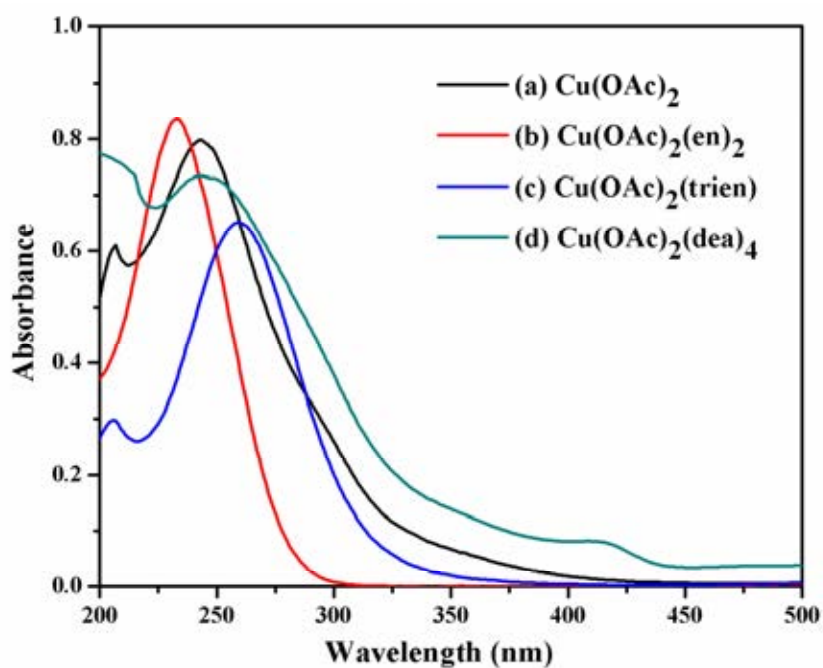


Figure 4.3 UV spectra of (a) $\text{Cu}(\text{OAc})_2$, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$, (c) $\text{Cu}(\text{OAc})_2(\text{trien})$ and (d) $\text{Cu}(\text{OAc})_2(\text{dea})_4$

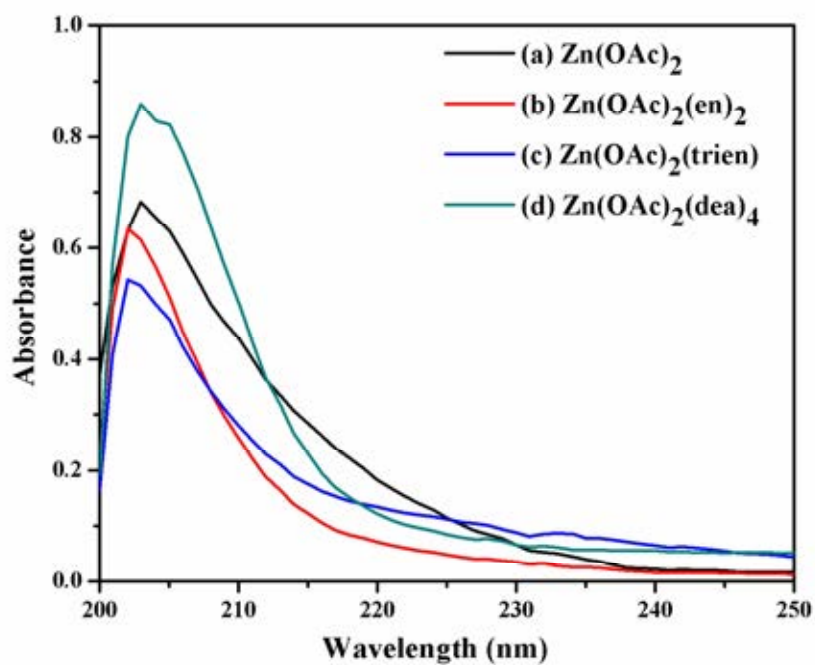


Figure 4.4 UV spectra of (a) $\text{Zn}(\text{OAc})_2$, (b) $\text{Zn}(\text{OAc})_2(\text{en})_2$, (c) $\text{Zn}(\text{OAc})_2(\text{trien})$ and (d) $\text{Zn}(\text{OAc})_2(\text{dea})_4$

4.1.1.2.2 Mass spectroscopy of copper-amine complexes and zinc-amine complexes

Mass spectrometry was also used to identify complexes of copper-amine and zinc-amine. Mass spectra peak corresponded to the molecular weight of copper-amine and zinc-amine complexes, which could use to identify the copper-amines and zinc-amine complexes structures and confirmed the complex formation. The molecular ion peak of $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{en})_2$ are shown in Figures 4.5 and 4.6 respectively [5]. 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-amines and zinc-amine complexes

Molecular ion peak	m/z (Calculated)	m/z (Found)
$[\text{Cu}(\text{OAc})_2(\text{en})_2+\text{H}^+]^+$	302.86	303.05
$[\text{Cu}(\text{OAc})_2(\text{en})_2+\text{EG}]^+$	363.85	363.15
$[\text{Cu}(\text{OAc})_2(\text{trien})+\text{EG}]^+$	389.89	389.22

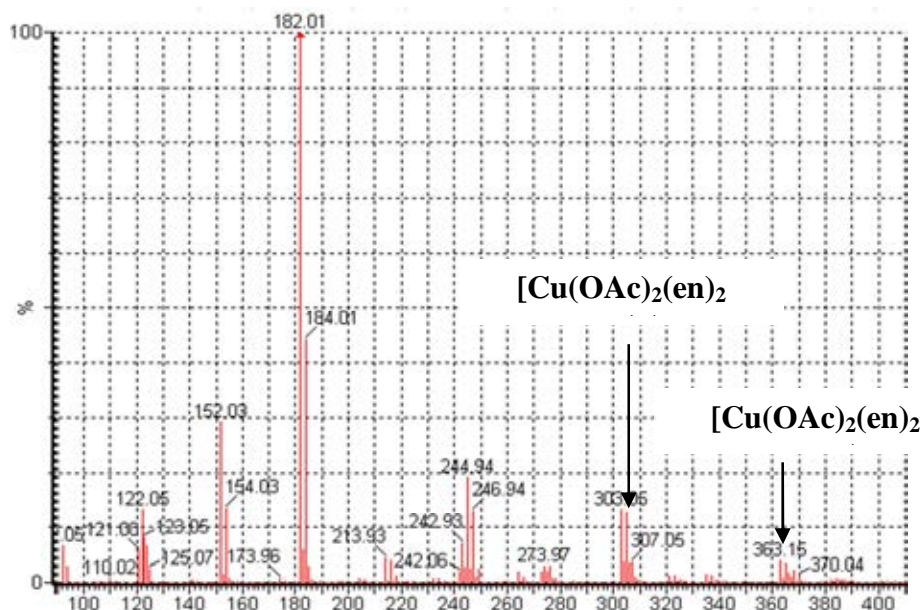


Figure 4.5 Positive ESI mass spectra of $\text{Cu}(\text{OAc})_2(\text{en})_2$ [5]

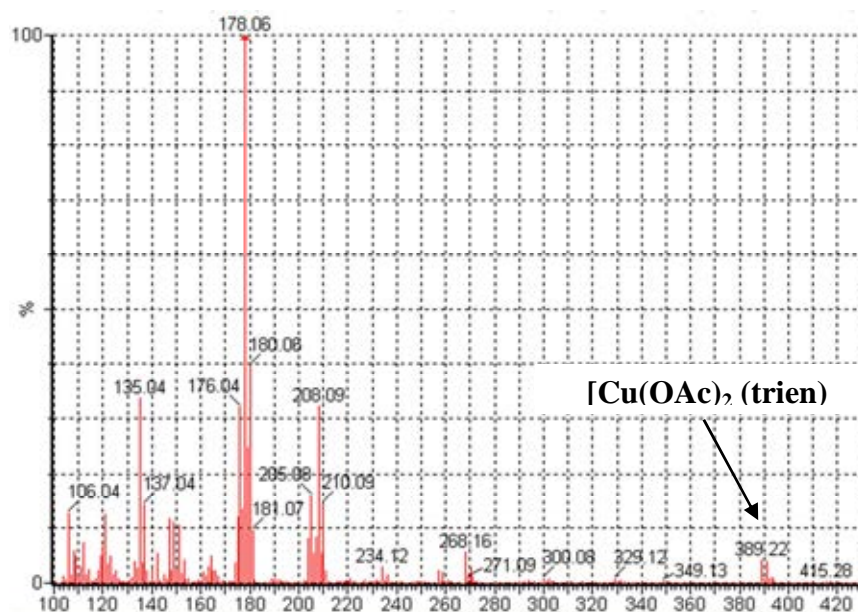


Figure 4.6 Positive ESI mass spectra of $\text{Cu}(\text{OAc})_2(\text{trien})$ [5]

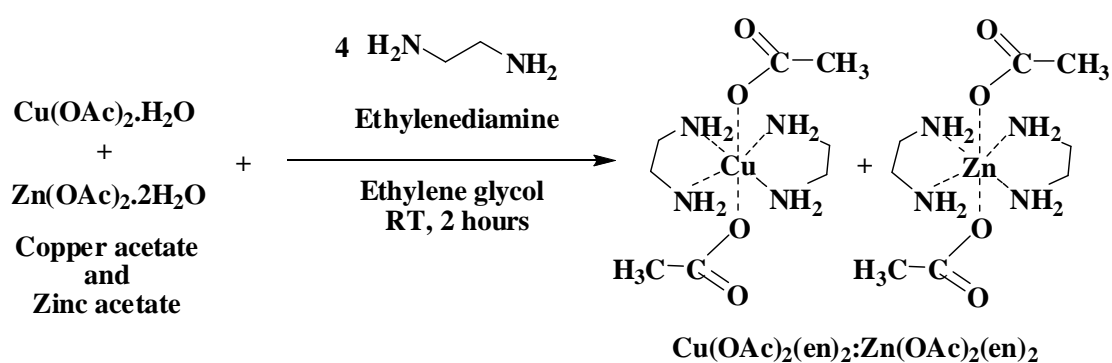
Based on the mass data obtained from the previous work [5], the characterization of the metal-amine complexes by UV-visible spectroscopy and mass spectroscopy, it could conclude that, the results could use to identify the copper-amines and zinc-amine complexes and suggested the complex formation.

4.1.2 Mixed metal-amine complexes

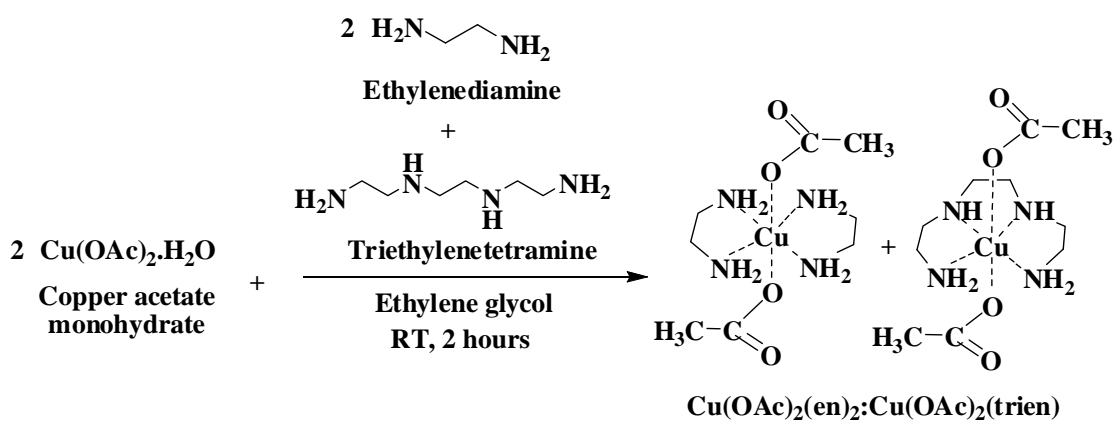
The mixed metal-amine complexes used in this study were $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$.

4.1.2.1 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ complexes

The synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ in ethylene glycol are shown in Schemes 4.2 and 4.3 respectively.



Scheme 4.2 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$



Scheme 4.3 Synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$

4.1.2.2 Characterization of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ complexes

The appearances of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ 33% wt in ethylene glycol are shown in Figure 4.7. These mixed metal-amine complexes were synthesized at different mole ratios of metal acetates and amines. All mixed metal-amine complex solutions were obtained as an odorless, low viscous dark blue solution and could be easily dissolved in the raw materials of foam formulation.

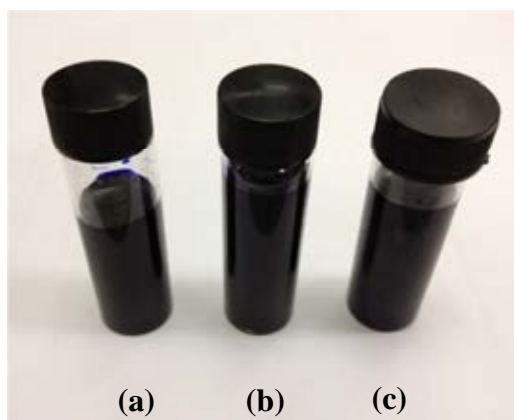


Figure 4.7 The mixed metal-amine complexes (33% wt in ethylene glycol)
 (a) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1 : 1 : 4$, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1.5 : 0.5 : 4$, (c) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$

**4.1.2.2.1 UV-visible spectroscopy of $\text{Cu}(\text{OAc})_2(\text{en})_2$:
 $\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2$:
 $\text{Cu}(\text{OAc})_2(\text{trien})$ complexes**

UV-visible spectra of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1 : 1 : 4$ and $1.5 : 0.5 : 4$ (Figure 4.8) gave λ_{max} due to $\text{Cu}(\text{OAc})_2(\text{en})_2$ at 242 and 246 nm, respectively.

UV-visible spectra of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$ (Figure 4.9) gave λ_{max} due to $\text{Cu}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$ at 230 nm.

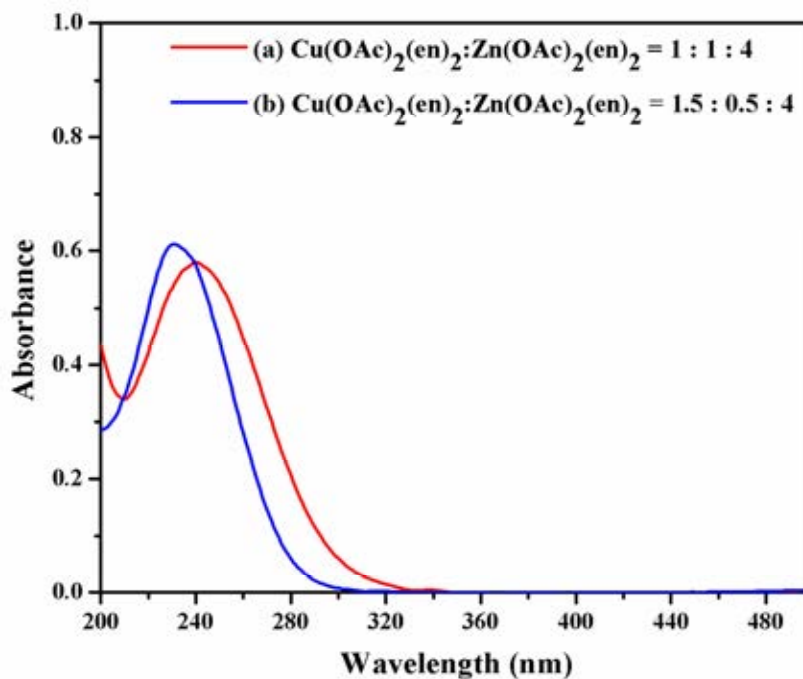


Figure 4.8 UV spectra of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} =$ (a) $1 : 1 : 4$ and (b) $1.5 : 0.5 : 4$

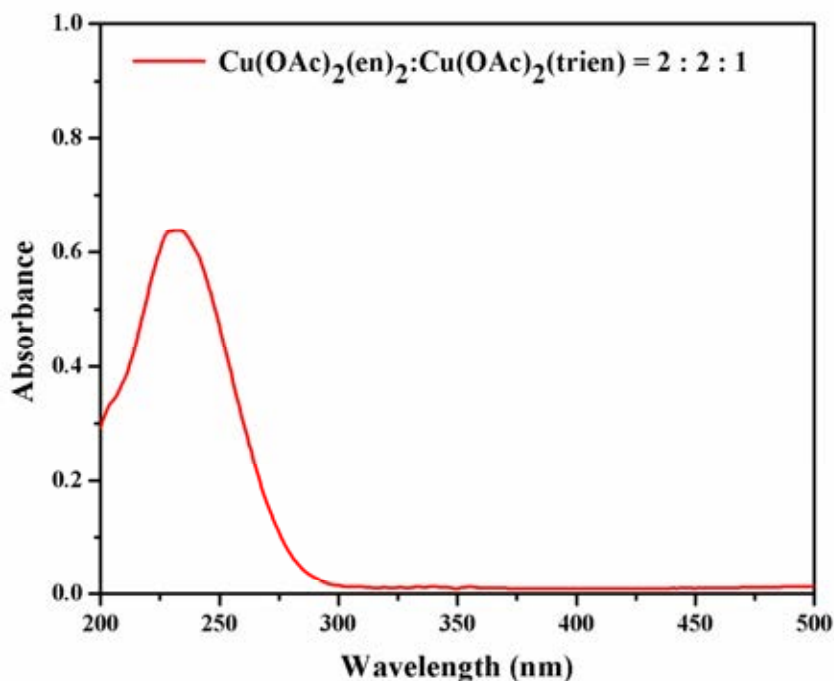


Figure 4.9 UV spectra of $\text{Cu(OAc)}_2(\text{en})_2:\text{Cu(OAc)}_2(\text{trien})$ prepared at the mole ratio of $\text{Cu(OAc)}_2:\text{en}:\text{trien} = 2 : 2 : 1$

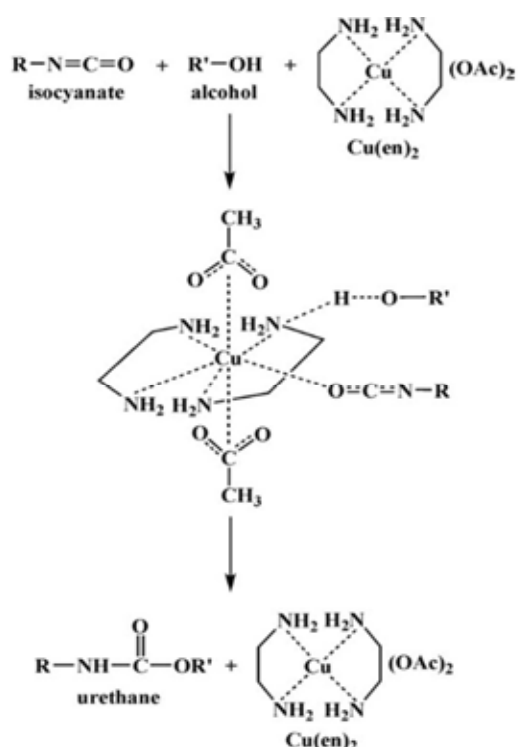
4.2 Preparation of FPUR foams

4.2.1 The effect of metal-amine complexes on the reaction time of FPUR foams

The metal-amine complexes, $\text{Cu(OAc)}_2(\text{en})_2$, $\text{Cu(OAc)}_2(\text{trien})$, $\text{Cu(OAc)}_2(\text{dea})_4$, $\text{Zn(OAc)}_2(\text{en})_2$, $\text{Zn(OAc)}_2(\text{trien})$ and $\text{Zn(OAc)}_2(\text{dea})_4$ had a different structure. Hence, it is necessary to study the catalytic activity of these metal-amine complexes.

Two types of metal acetates and three types of amines were chosen to synthesize the metal-amine complexes for using as catalysts for FPUR foam preparation. The metal-amine complexes investigated were $\text{M(OAc)}_2(\text{Y})_2$ where ($\text{M} = \text{Cu}$ and Zn), ($\text{Y} = \text{en}$, trien and dea). The reaction time, density and foam height of FPUR foams are shown in Table 4.2. The results showed that both copper-amine and zinc-amine complexes could catalyze polymerization of FPUR foams because the metal atom can act as a Lewis acid and can coordinate to oxygen atom of

the NCO group thus, the NCO carbon to be more electrophilic. Nitrogen atom of amine interacted to proton of the hydroxyl group and caused the hydroxyl oxygen to be more nucleophilic, this oxygen then reacted with the NCO group to produce a urethane linkage [4,5]. The reaction scheme for the urethane formation catalyzed by $M(OAc)_2(Y)_2$ is proposed in Scheme 4.2. The catalytic mechanism of $M(OAc)_2(trien)$ and $M(OAc)_2(dea)_4$ is similar to that of $M(OAc)_2(en)_2$.



Scheme 4.2 The catalytic mechanism of $Cu(OAc)_2(en)_2$ [4]

The reaction time of FPUR foaming reaction, namely cream time, gel time, rise time and tack-free time, catalyzed by the metal-amine complexes was investigated by cup test method and compared with that of Dabco[®] EG as shown in Figure 4.10. The results showed that the catalytic activity depended on both metal acetate and amine types. The order of catalytic activity was $Cu(OAc)_2(Y)_2 > Zn(OAc)_2(Y)_2$, where $Y = en, trien$ and dea . In the case of metal-amine complexes prepared by different amine types, the order of catalytic activity was $M(OAc)_2(en)_2 > M(OAc)_2(trien) > M(OAc)_2(dea)_4$, where $M = Cu$ and Zn . This result was due to of the steric hindrance of amine [4, 5].

The catalytic activity of FPUR foams catalyzed by copper-amine and zinc-amine complexes was compared with that of Dabco[®] EG. The results showed that $\text{Cu}(\text{OAc})_2(\text{en})_2$ had slightly faster tack-free time than Dabco[®] EG, while $\text{Cu}(\text{OAc})_2(\text{trien})$, $\text{Cu}(\text{OAc})_2(\text{dea})_4$, $\text{Zn}(\text{OAc})_2(\text{en})_2$, $\text{Zn}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{dea})_4$ had lower catalytic activity than Dabco[®] EG.

The density of foam varied inversely with foam height because the catalyst caused more blowing reaction and therefore more CO_2 was generated, thus, the height of foam was increasing while the foam density was decreased. In comparison between the density of FPUR foams catalyzed by Dabco[®] EG, copper-amine and zinc-amine complexes (Table 4.3 and Figure 4.10), the density of foam catalyzed by copper-amine and zinc-amine complexes had a wide range. The foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2$ had much lower density to that catalyzed by Dabco[®] EG. This suggested that $\text{Cu}(\text{OAc})_2(\text{en})_2$ was a good blowing catalyst since it gave more blowing reaction than Dabco[®] EG. $\text{Zn}(\text{OAc})_2(\text{en})_2$ gave the foam with much higher density than the foam catalyzed by Dabco[®] EG and the cracks on the foam surface was found due to unbalance between blowing and gelling reaction, The excess blowing reaction results in foam splitting and collapse eventually with cracking of surface [1, 6].

External appearance of FPUR foams catalyzed by Dabco[®] EG, copper-amine complexes and zinc-amine complexes (Figure 4.11) showed that all FPUR foams catalyzed by zinc-amine complexes gave similarly colors of foams to that catalyzed by Dabco[®] EG, however, the foams had poor external appearance with cracks on the foam surface. Therefore, zinc-amine complexes were poor catalysts. The foams catalyzed by copper-amine complexes had good appearance, however, the foam had darker color than that catalyzed by Dabco[®] EG.

Table 4.2 Reaction times and density of FPUR foams catalyzed by 0.5 pbw of copper-amine and zinc-amine complexes at NCO index 100

Catalysts	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack-free time (min:sec)	Free rise density (kg/m ³)	Foam height (cm)
Dabco [®] EG	0:18	0:34	1:04	1:33	266	11.0
Cu(OAc) ₂ (en) ₂	0:17	0:30	0:45	1:13	179	13.0
Cu(OAc) ₂ (trien)	1:02	2:02	3:27	11:30	227	11.6
Cu(OAc) ₂ (dea) ₄	1:20	3:56	7:01	19:39	267	9.7
Zn(OAc) ₂ (en) ₂	1:08	2:04	4:20	8:13	359	7.7
Zn(OAc) ₂ (trien)	1:54	6:59	12:33	31:32	212	9.7
Zn(OAc) ₂ (dea) ₄	0:57	5:27	7:44	24:29	269	10.5

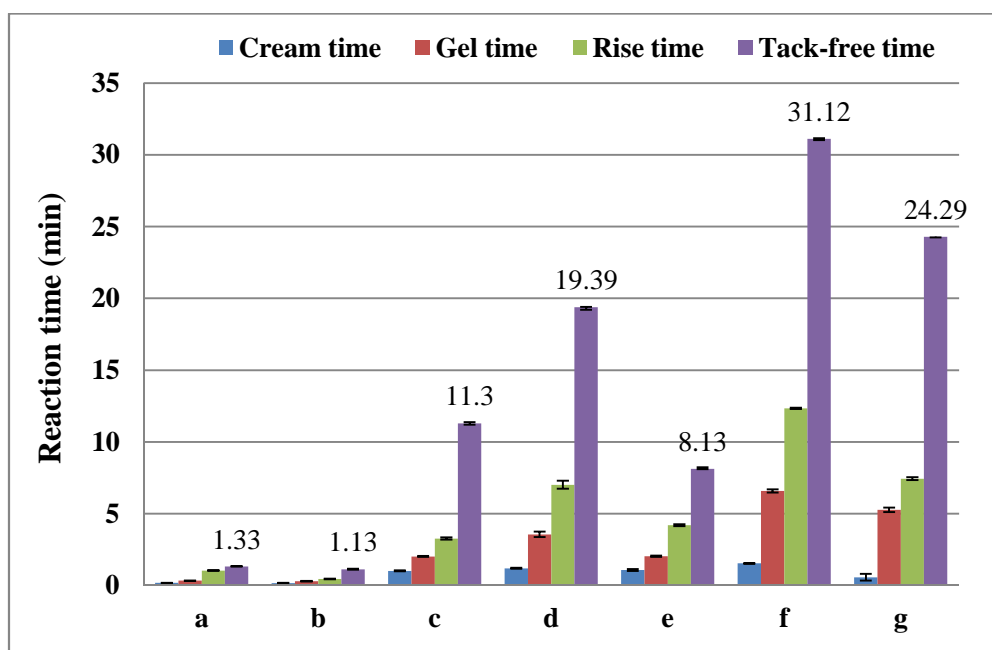


Figure 4.10 Reaction times of FPUR foams catalyzed by 0.5 pbw of (a) Dabco[®] EG, (b) Cu(OAc)₂(en)₂, (c) Cu(OAc)₂(trien), (d) Cu(OAc)₂(dea)₄, (e) Zn(OAc)₂(en)₂, (f) Zn(OAc)₂(trien) and (g) Zn(OAc)₂(dea)₄

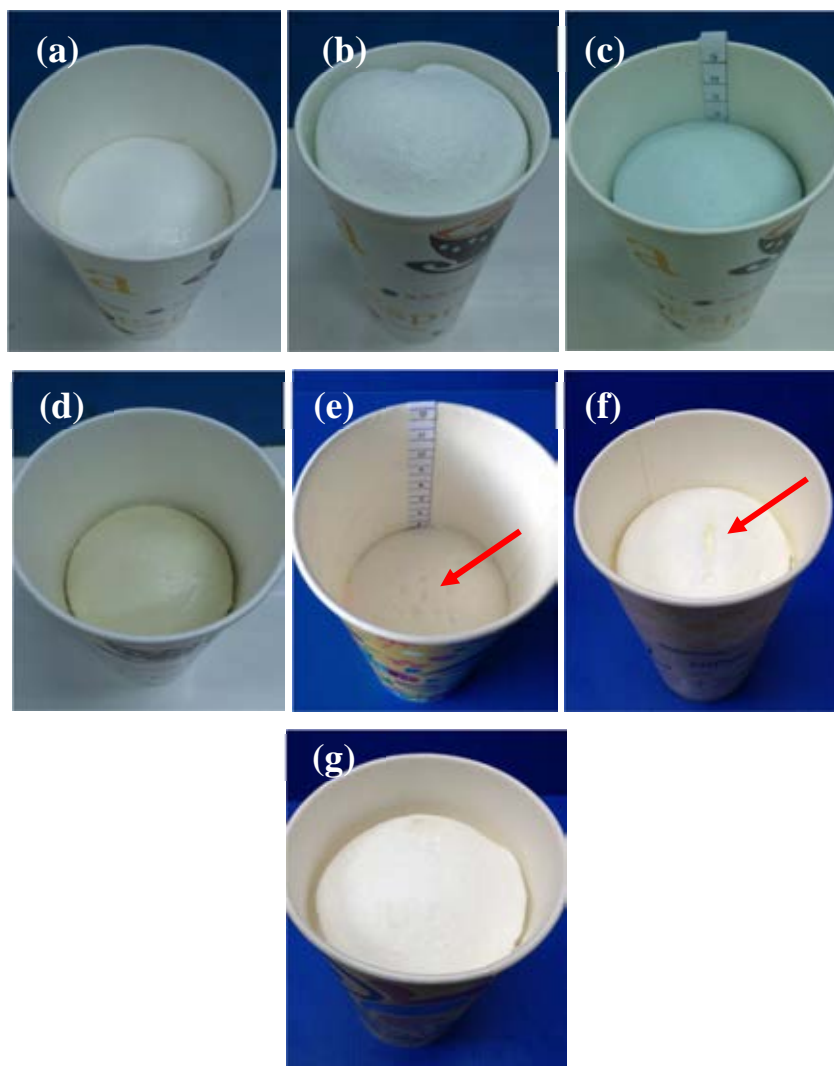


Figure 4.11 External appearance of FPUR foams catalyzed by 0.5 pbw of (a) Dabco[®] EG, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$, (c) $\text{Cu}(\text{OAc})_2(\text{trien})$, (d) $\text{Cu}(\text{OAc})_2(\text{dea})_4$, (e) $\text{Zn}(\text{OAc})_2(\text{en})_2$, (f) $\text{Zn}(\text{OAc})_2(\text{trien})$ and (g) $\text{Zn}(\text{OAc})_2(\text{dea})_4$

Since $\text{Cu}(\text{OAc})_2(\text{en})_2$ showed the best catalytic activity. Thus, further study about the catalytic behavior of $\text{Cu}(\text{OAc})_2(\text{en})_2$ was done by using variable amounts of chain extender and blowing agent in the FPUR foam formulation. For $\text{Cu}(\text{OAc})_2(\text{trien})$, since it had less catalytic activity than $\text{Cu}(\text{OAc})_2(\text{en})_2$, the amount of $\text{Cu}(\text{OAc})_2(\text{trien})$ in FPUR foam formulation was increased to obtain faster foaming reaction.

4.2.1.1 The effect of chain extender (ethylene glycol) and blowing agent (water) amounts in FPUR foam formulation

Polyurethane foam was prepared by polyols and isocyanate as the main components. Other important components, such as catalysts, surfactant, blowing agent and chain extender, are employed to define the properties of foams [1, 6]. Since the catalyst was changed from Dabco[®] EG to $\text{Cu}(\text{OAc})_2(\text{en})_2$, suitable amount of blowing agent and chain extender in foam formulation was investigated to obtain FPUR foam with suitable foaming reaction times and good properties.

4.2.1.1.1 The effect of chain extender (ethylene glycol) amount in FPUR foam formulation

Effect of chain extender amount in FPUR foam formulation was done with fixed catalyst and blowing agent amounts at 0.5 pbw and 0.5 pbw, respectively. $\text{Cu}(\text{OAc})_2(\text{en})_2$ was used as a catalyst. Chain extender amount in FPUR foam formulation was varied from 3 to 7 pbw.

Reaction time, density and foam height of FPUR foams prepared by 3 to 7 pbw of chain extender are shown in Table 4.3 and Figure 4.12. The results showed that the reaction times decreased with increasing ethylene glycol amount. Because ethylene glycol is a primary alcohol which could also react with isocyanate group to form urethane linkage [5]. Since the primary OH group in ethylene glycol underwent faster reaction with isocyanate group than the secondary OH group of polyol, addition of ethylene glycol would increase the urethane formation and gave faster rate of foaming reaction [5].

It was observed that the highest foam density was obtained at 5 pbw of ethylene glycol. There was a large decrease in the reaction time with increasing amount of ethylene glycol from 3 to 5 pbw while the reaction time slightly decreased with increasing amount of ethylene glycol from 5 to 7 pbw. Thus, ethylene glycol amount of 5 pbw was optimum for FPUR foam formulation.

Table 4.3 Reaction times and density of FPUR foams prepared by various amounts of chain extender (ethylene glycol)

Chain extender content (pbw)	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack-free time (min:sec)	Free rise density (kg/m ³)	Foam height (cm)
3	0:27	1:08	1:40	3:06	167	12.8
5	0:24	0:35	0:55	1:14	196	13.0
7	0:26	0:35	0:49	1:04	185	13.1

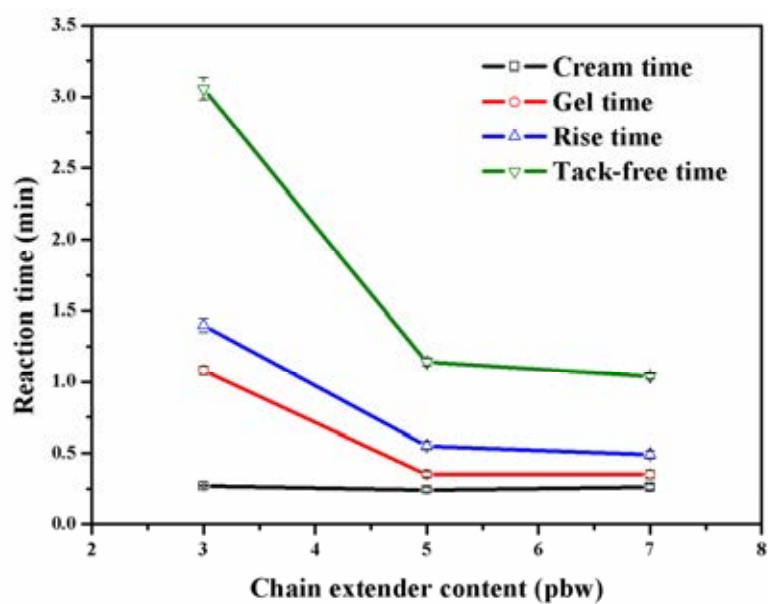


Figure 4.12 Reaction times of FPUR foams prepared by 3, 5 and 7 pbw of chain extender (ethylene glycol)

4.2.1.1.2 The effect of blowing agent (water) amount in FPUR foam formulation

Effect of blowing agent amount in FPUR foam formulation was done with fixed catalyst and chain extender amounts at 0.5 pbw and 5 pbw, respectively. $\text{Cu}(\text{OAc})_2(\text{en})_2$ was used as a catalyst. Blowing agent amount in FPUR foam formulation was varied from 0.3 to 0.7 pbw.

Reaction times, density and foam height of FPUR foams prepared from 0.3 to 0.7 pbw of blowing agent are shown in Table 4.4 and Figure 4.13. The results showed that there was a slight increase in the reaction time with increasing amount of water from 0.3 to 0.7 pbw. Water was the chemical blowing agent which expanded foams by CO_2 gas generated by the reaction between isocyanate group and water, and this reaction is exothermic. Thus, increasing of blowing agent amount would reduce density of FPUR foams resulting from more CO_2 gas amount in the system [5, 6]. The foam prepared by increasing water amount had increase surface roughness.

Table 4.4 Reaction times and density of FPUR foams prepared by various amounts of blowing agent (water)

Blowing agent content (pbw)	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack-free time (min:sec)	Free rise density (kg/m^3)	Foam height (cm)
0.3	0:22	0:31	0:50	1:08	222	11.2
0.5	0:24	0:35	0:55	1:14	196	13.0
0.7	0:25	0:37	0:56	1:17	184	14.8

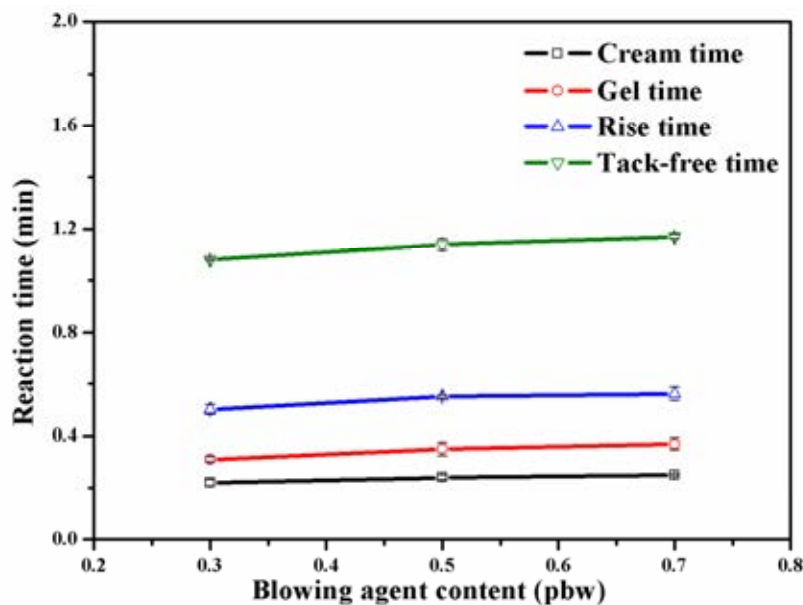


Figure 4.13 Reaction times of FPUR foams prepared by 0.3, 0.5 and 0.7 pbw of blowing agent (water)

From the effect of blowing agent amount in FPUR foam formulation. It could be concluded that the suitable amount of blowing agent was 0.5 pbw because 0.3 pbw of blowing agent in foam formulation gave hard foam and 0.7 pbw gave poor external appearance of foam.

From the above results in the preparation of FPUR foam using 0.5 pbw $\text{Cu}(\text{OAc})_2(\text{en})_2$ as a catalyst, it could be concluded that the suitable amount of chain extender and blowing agent was 5 and 0.5 pbw, respectively.

4.2.2 Preparation of FPUR foams catalyzed by mixed metal-amine complexes

The preparation of FPUR foams catalyzed by the mixed metal-amine complexes, namely $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$, used the same amount of chain extender and blowing agent at 5 and 0.5 pbw, respectively. The catalyst amount in foam formulation was 0.5 pbw. It was expected that the foam would have good morphology.

4.2.2.1 The effect of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ complexes on the reaction time of FPUR foams

Reaction times, density and foam height of FPUR foams catalyzed by different mole ratios of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ were investigated and compared with the foam catalyzed by Dabco[®] EG as shown in Table 4.6 and Figure 4.14. The reaction times of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ occurred faster with increasing of $\text{Cu}(\text{OAc})_2(\text{en})_2$ amount in $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ from the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en}$ was 1 : 1 : 4 to 1.5 : 0.5 : 4. However, all mixed metal-amine complexes, $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ had low catalytic activity than Dabco[®] EG. The FPUR foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ had higher density than $\text{Cu}(\text{OAc})_2(\text{en})_2$.

The external appearance of FPUR foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ are shown in Figure 4.15. It was found that all FPUR foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ gave poor external appearance with cracks on the foam surface. In the case of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ gave good external appearance of foam.

Table 4.5 Reaction times, density and foam height of FPUR foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1 : 1 : 4$, $1.5 : 0.5 : 4$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$

Catalysts	Cream time	Gel time	Rise time	Tack-free time	Density (kg/m^3)	Foam height
Dabco [®] EG	0:18	0:34	1:04	1:33	266	11.0
$\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en}$ 1 : 1 : 4	0:59	1:27	2:26	5:09	283	9.1
$\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en}$ 1.5 : 0.5 : 4	0:39	1:03	1:41	4:37	239	12.2
$\text{Cu}(\text{OAc})_2:\text{en}:\text{trien}$ 2 : 2 : 1	0:35	1:22	2:16	8:23	216	11.9

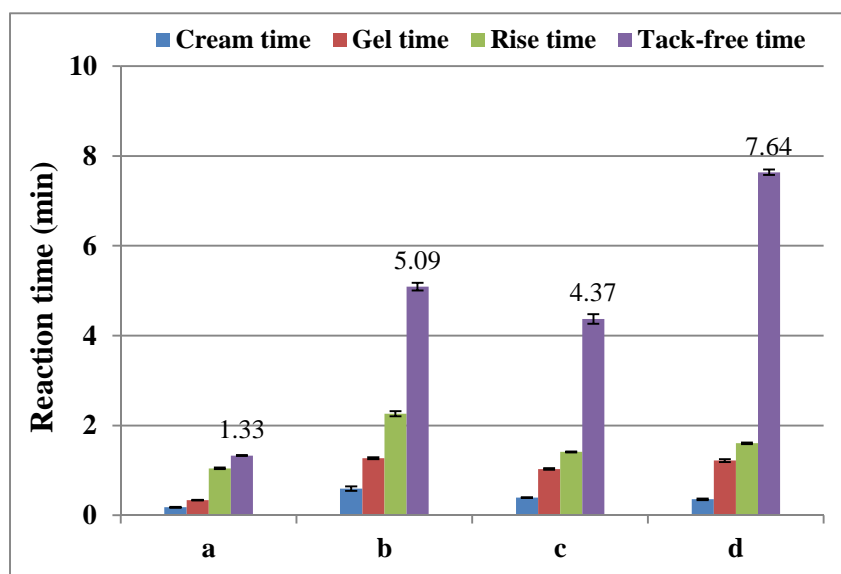


Figure 4.14 Reaction times of FPUR foams catalyzed by 0.5 pbw of (a) Dabco[®] EG, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1 : 1 : 4$, (c) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1.5 : 0.5 : 4$, (d) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$

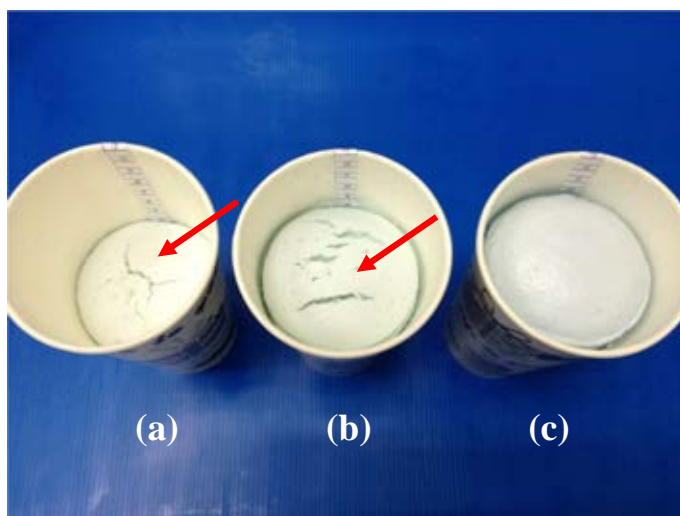


Figure 4.15 External appearance of FPUR foams catalyzed by
 (a) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ prepared at the mole ratio of
 $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1 : 1 : 4$, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$
 prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{Zn}(\text{OAc})_2:\text{en} = 1.5 : 0.5 : 4$,
 (c) $\text{Cu}(\text{OAc})_2(\text{en}):\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of
 $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$

The mixed metal-amine complexes gave higher foam density than $\text{Cu}(\text{OAc})_2(\text{en})_2$, however, they had low catalytic activities than $\text{Cu}(\text{OAc})_2(\text{en})_2$. It could be concluded that both $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ were not suitable catalysts for preparation of FPUR foams because they had low catalytic activity than Dabco[®] EG and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ gave poor external appearance.

$\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ gave a good external foam appearance and gave higher foam density than $\text{Cu}(\text{OAc})_2(\text{en})_2$ however, they also had low catalytic activities than $\text{Cu}(\text{OAc})_2(\text{en})_2$. Thus, $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ were chosen to the study effect of catalysts amount in the preparation of FPUR foams to decrease the reaction time in foaming reaction.

4.2.3 The effect of catalysts amount in the preparation of FPUR foams

The catalysts employed were $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Cu}(\text{OAc})_2(\text{en})_2$: $\text{Cu}(\text{OAc})_2(\text{trien})$. The amounts of blowing agent and chain extender were fixed at 0.5 pbw and 5 pbw, respectively. The catalyst amount was varied from 0.5 to 1.1 pbw.

4.2.3.1 The effect of $\text{Cu}(\text{OAc})_2(\text{trien})$ amount on the reaction time of FPUR foams

Reaction times, density and foam height of FPUR foams catalyzed by 0.5, 0.7, 0.9 and 1.1 pbw of $\text{Cu}(\text{OAc})_2(\text{trien})$ are shown in Table 4.6 and Figure 4.16. The results showed that there was a large decrease in tack-free time with increasing content of $\text{Cu}(\text{OAc})_2(\text{trien})$ in the foam formulation from 0.5 to 1.1 pbw. Only a slight decrease was observed in cream time, gel time and rise time. Further increase in the amount of the $\text{Cu}(\text{OAc})_2(\text{trien})$ beyond 1.1 pbw resulted in poor external appearance of FPUR foams.

For comparison, 0.5 pbw of Dabco[®] EG was used in the foam formulation. It was found that 0.5 pbw of Dabco[®] EG had higher catalytic activity than 1.1 pbw $\text{Cu}(\text{OAc})_2(\text{trien})$.

The foam density decreased with the increasing of $\text{Cu}(\text{OAc})_2(\text{trien})$ amount. The foam catalyzed by $\text{Cu}(\text{OAc})_2(\text{trien})$ had lower density than those catalyzed by Dabco[®] EG.

Table 4.6 Reaction times, density and foam height of FPUR foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{trien})$ in various amounts

$\text{Cu}(\text{OAc})_2(\text{trien})$ amount (pbw)	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack- free time (min:sec)	Free rise density (kg/m^3)	Foam height (cm)
Dabco [®] EG 0.5	0:18	0:34	1:04	1:33	266	11.0
0.5	1:02	2:02	3:27	11:30	227	11.6
0.7	0:53	1:45	2:52	7:59	220	11.8
0.9	0:50	1:26	2:14	6:04	215	11.9
1.1	0:46	1:13	1:56	4:58	204	12.2

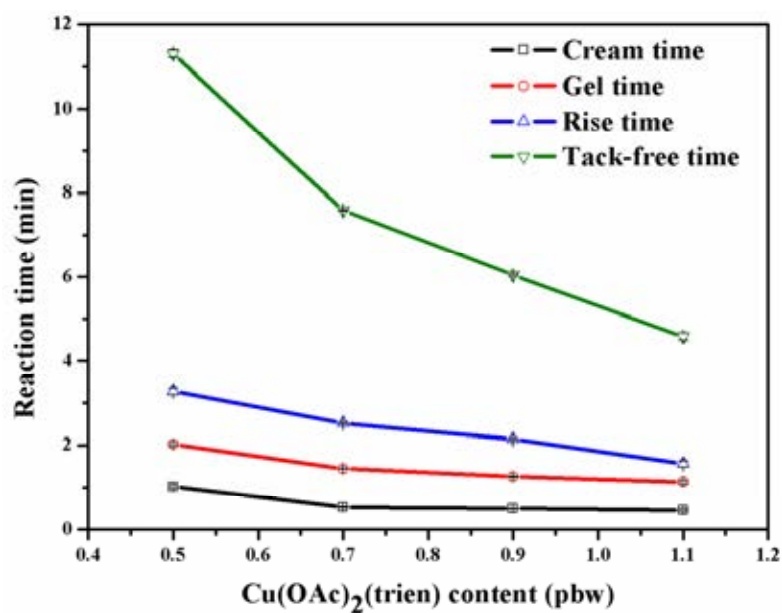


Figure 4.16 Reaction times of FPUR foams catalyzed by 0.5, 0.7, 0.9 and 1.1 pbw of $\text{Cu}(\text{OAc})_2(\text{trien})$

**4.2.3.2 The effect of Cu(OAc)₂(en)₂:Cu(OAc)₂(trien)
amount on the reaction time of FPUR foams**

The results in Table 4.8 and Figure 4.17 showed the same trend as in the case of Cu(OAc)₂(trien) in section 4.2.3.1. Increasing the amount of Cu(OAc)₂(en)₂:Cu(OAc)₂(trien) decreased tack-free time. Cu(OAc)₂(en)₂:Cu(OAc)₂(trien) had less catalytic activity than Dabco[®] EG. Further increase in the amount of the Cu(OAc)₂(en)₂:Cu(OAc)₂(trien) beyond 1.1 pbw resulted in poor external appearance of FPUR foams.

Table 4.7 Reaction times, density and foam height of FPUR foams catalyzed by Cu(OAc)₂(en):Cu(OAc)₂(trien) prepared at the mole ratio of Cu(OAc)₂:en:trien = 2 : 2 : 1

Cu(OAc) ₂ (en) ₂ : Cu(OAc) ₂ (trien) amount (pbw)	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack- free time (min:sec)	Free rise density (kg/m ³)	Foam height (cm)
Dabco [®] EG 0.5	0:18	0:34	1:04	1:33	266	11.0
0.5	0:35	1:22	2:16	8:23	216	11.9
0.7	0:33	1:18	2:13	6:27	194	12.1
0.9	0:33	1:10	1:53	5:05	187	12.3
1.1	0:31	1:06	1:50	4:24	185	12.4

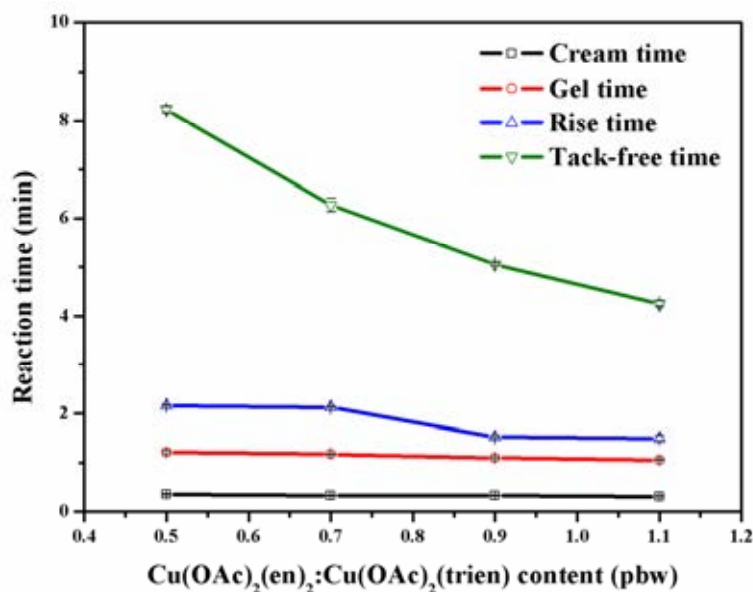


Figure 4.17 Reaction times of FPUR foams catalyzed by 0.5, 0.7, 0.9 and 1.1 pbw of $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ prepared at the mole ratio of $\text{Cu}(\text{OAc})_2:\text{en}:\text{trien} = 2 : 2 : 1$

4.2.4 Preparation of FPUR foams catalyzed by the mixture of Dabco[®] EG and metal-amine complexes (Dabco[®] EG:metal-amine complexes)

Since Dabco[®] EG more expensive than metal-amine complexes, the reduction of Dabco[®] EG in FPUR foam formulation is of interest. The experiments were done using similar approach as described in section 4.2.2. The mixture of Dabco[®] EG and metal-amine complexes (Dabco[®] EG:metal-amine complexes) was employed as catalyst in FPUR foam formulation. Metal-amine complexes chosen for this study were $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{en})_2$.

The study was divided into three stages. The first study varied the metal-amine complexes types in Dabco[®] EG:metal-amine complexes. The second study varied amount of Dabco[®] EG:metal-amine complexes. The last study varies the ratio between Dabco[®] EG and the metal-amine complexes in Dabco[®] EG:metal-amine complexes.

4.2.4.1 The effect of Dabco[®] EG:metal-amine complexes on the reaction time of FPUR foams

Dabco[®] EG:metal-amine complexes at the mole ratio of 0.5 : 0.5 was employed as catalysts and the amount of Dabco[®] EG:metal-amine complexes in FPUR foam formulation was 0.5 pbw (Table 4.8 and Figure 4.18).

Dabco[®] EG:metal-amine complexes can catalyze polymerization of FPUR foams because the metal atom in metal-amine complexes acts as a Lewis acid and coordinates to oxygen atom of the NCO group, therefore, the NCO carbon is more electrophilic. While nitrogen atom of Dabco[®] EG is a tertiary amine which is very active towards the proton of hydroxyl group and causes the hydroxyl oxygen to become more nucleophilic. This hydroxyl oxygen then reacts with the NCO group to produce a urethane linkage.

The results showed that Dabco[®] EG:Cu(OAc)₂(en)₂ and Dabco[®] EG:Cu(OAc)₂(trien) had more catalytic activity than Dabco[®] EG or metal-amine complexes. The order of catalytic activity was Dabco[®] EG:Cu(OAc)₂(en)₂ > Dabco[®] EG:Cu(OAc)₂(trien) > Dabco[®] EG:Zn(OAc)₂(en)₂.

The order of foam densities was Dabco[®] EG:Zn(OAc)₂(en)₂ > Dabco[®] EG:Cu(OAc)₂(trien) > Dabco[®] EG:Cu(OAc)₂(en)₂. The FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ had densities in the range around 200-250 kg/m³, which was the desirable density for cushioning applications such as mattresses and furnitures.

The external appearances of all FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ at the mole ratio of = 0.50 : 0.50 (Figure 4.19) had good appearance.

Table 4.8 The reaction times, density and foam height of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes

Catalysts	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack-free time (min:sec)	Density (kg/m ³)	Foam height (cm)
Dabco [®] EG	0:18	0:34	1:04	1.33	266	11.0
Cu(OAc) ₂ (en) ₂	0:17	0:30	0:45	1:13	179	13.0
Cu(OAc) ₂ (trien)	1:02	2:02	3:27	11:30	227	11.6
Zn(OAc) ₂ (en) ₂	1:08	2:04	4:20	8:13	359	7.7
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	0:10	0:19	0:33	0:41	199	12.0
Dabco [®] EG: Cu(OAc) ₂ (trien)	0:15	0:24	0:39	0:45	215	11.5
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	0:27	0:46	1:23	2:15	246	10.8

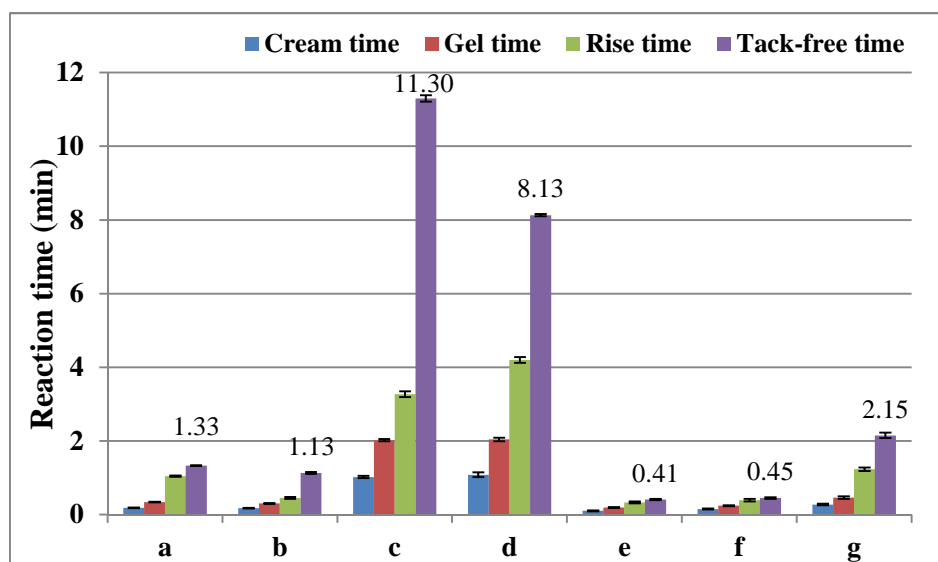


Figure 4.18 Reaction times of FPUR foams catalyzed by (a) Dabco[®] EG; (b) Cu(OAc)₂(en)₂, (c) Cu(OAc)₂(trien), (d) Zn(OAc)₂(en)₂, (e) Dabco[®] EG:Cu(OAc)₂(en)₂, (f) Dabco[®] EG:Cu(OAc)₂(trien) and (g) Dabco[®] EG:Zn(OAc)₂(en)₂

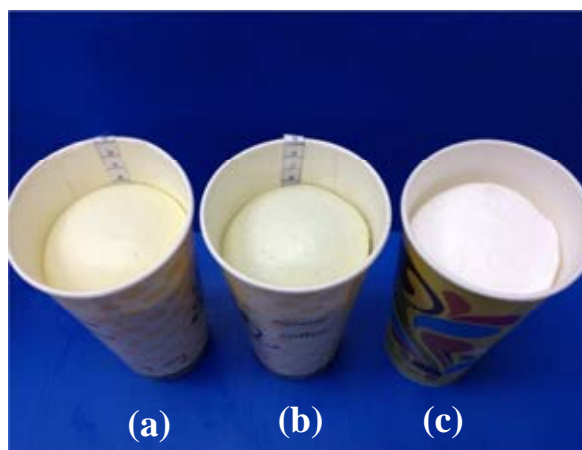


Figure 4.19 External appearance of FPUR foams catalyzed by (a) Dabco[®] EG:Cu(OAc)₂(en)₂, (b) Dabco[®] EG:Cu(OAc)₂(trien) and (c) Dabco[®] EG:Zn(OAc)₂(en)₂

4.2.4.2 The effect of Dabco[®] EG:metal-amine complexes amount on reaction time of FPUR foams

This study adjusted the catalyst amounts in FPUR foam formulation. Since Dabco[®] EG:Cu(OAc)₂(en)₂ and Dabco[®] EG:Cu(OAc)₂(trien) had higher catalytic activity than Dabco[®] EG, therefore, the catalysts amount was decreased from 0.5 to 0.1 pbw. Dabco[®] EG:Zn(OAc)₂(en)₂ had less catalytic activity than Dabco[®] EG and therefore the catalyst amount was increased from 0.5 to 0.7 pbw. Mole ratio of Dabco[®] EG:metal-amine complexes was fixed at 0.50 : 0.50.

The results in Table 4.9 and Figure 4.20 showed that there was a large increase in tack-free time with decreasing amount of catalysts from 0.5 to 0.1 pbw. For Dabco[®] EG:Zn(OAc)₂(en)₂, tack-free time decreased with increasing catalysts amount from 0.5 to 0.7 pbw. For all catalysts, the foam density increased with decreasing catalyst amount.

Table 4.9 Reaction times of FPUR foams catalyzed by 0.1-0.5 pbw of Dabco[®] EG:
 Cu(OAc)₂(en)₂, 0.1-0.5 pbw of Dabco[®] EG:Cu(OAc)₂(trien) and
 0.5-0.7 pbw of Dabco[®] EG:Zn(OAc)₂(en)₂

Catalyst amount (pbw)	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack-free time (min:sec)	Free rise density (kg/m ³)	Foam height (cm)
Dabco[®] EG:Cu(OAc)₂(en)₂						
0.5	0:11	0:20	0:36	0:42	195	12.0
0.4	0:15	0:28	0:41	0:51	204	10.8
0.3	0:17	0:36	0:61	1:13	217	10.2
0.2	0:25	0:53	1:23	2:15	228	10.0
0.1	0:45	1:40	2:58	5:45	238	9.5
Dabco[®] EG:Cu(OAc)₂(trien)						
0.5	0:13	0:24	0:38	0:46	218	11.5
0.4	0:19	0:31	0:56	1:07	221	10.5
0.3	0:23	0:43	1:13	1:24	231	10.0
0.2	0:38	1:03	2:10	2:21	250	9.7
0.1	0:54	1:46	3:54	6:05	257	9.4
Dabco[®] EG:Zn(OAc)₂(en)₂						
0.5	0:27	0:46	1:23	2:15	246	10.8
0.6	0:22	0:39	1:06	1:34	226	11.0
0.7	0:20	0:34	0:56	1:20	224	11.1

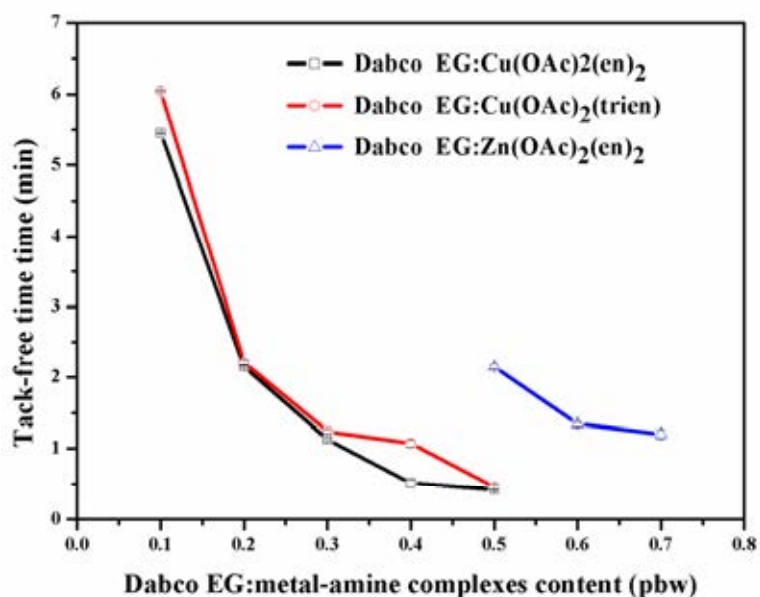


Figure 4.20 Tack-free time of FPUR foams catalyzed by 0.1-0.7 pbw of Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂

4.2.4.3 The effect of Dabco[®] EG:metal-amine complexes at different mole ratios on reaction of FPUR foams

Since Dabco[®] EG:Cu(OAc)₂(en)₂ had the better catalytic activity than Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(en)₂ was chosen in this study. The amount of Dabco[®] EG:Cu(OAc)₂(en)₂ in FPUR formulation was fixed at 0.5 pbw. Mole ratio of Dabco[®] EG:Cu(OAc)₂(en)₂ was varies at 0.50 : 0.50, 0.25 : 0.75 and 0.10 : 0.90 (Table 4.10). The results showed that there was a slight increase in tack-free time with decreasing amount of Dabco[®] EG in Dabco[®] EG:Cu(OAc)₂(en)₂ (Figure 4.21). Density of FPUR foams decreased with decreasing amount of Dabco[®] EG in Dabco[®] EG:Cu(OAc)₂(en)₂.

Table 4.10 Reaction times and density of FPUR foams catalyzed by 0.5 pbw of Dabco[®] EG:Cu(OAc)₂(en)₂ at mole ratios of 0.50 : 0.50, 0.25 : 0.75 and 0.10 : 0.90

Dabco [®] EG: Cu(OAc) ₂ (en) ₂	Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack- free time (min:sec)	Free rise density (kg/m ³)	Foam height (cm)
0.50 : 0.50	0:11	0:20	0:36	0:42	195	12.0
0.25 : 0.75	0:12	0:26	0:39	0:47	194	12.2
0.10 : 0.90	0:17	0:31	0:50	0:55	180	12.6

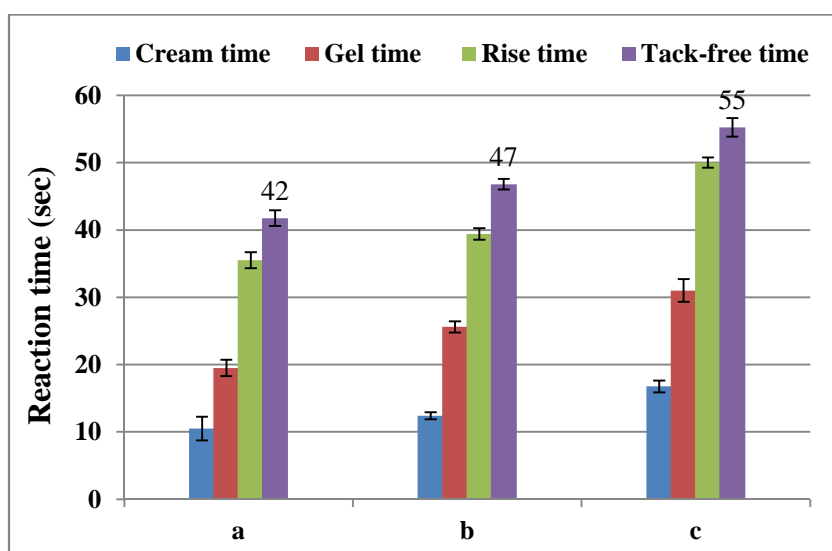


Figure 4.21 Reaction times of FPUR foams catalyzed by 0.5 pbw of Dabco[®] EG:Cu(OAc)₂(en)₂ at the mole ratios of Dabco[®] EG to Cu(OAc)₂(en)₂ were (a) 0.50 : 0.50, (b) 0.75 : 0.25 and (c) 0.10 : 0.90

4.3 Characterization of FPUR foams

The characterization of FPUR foams catalyzed by Dabco[®] EG: metal-amine complexes were investigated since they were efficient catalysts for FPUR foam preparation.

Rise profile, temperature profile, NCO conversions, morphology and mechanical properties of FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ at the mole ratio of 0.50 : 0.50 and fixed catalyst amount of 0.5 pbw was investigated and compared with FPUR foam catalyzed by Dabco[®] EG, Cu(OAc)₂(en)₂, Cu(OAc)₂(trien) and Zn(OAc)₂(en)₂.

4.3.1 Rise profile of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes

Rise profile of FPUR foams catalyzed by Cu(OAc)₂(en)₂, Cu(OAc)₂(trien) and Zn(OAc)₂(en)₂ was investigated and compared with the foam catalyzed by Dabco[®] EG as shown in Figure 4.22. It was found that the FPUR foams catalyzed by Dabco[®] EG showed very fast rise at the initial of reaction, whereas Cu(OAc)₂(en)₂ had longer rise time at the initial of reaction and exhibited a very quick rise curve in the latter stage.

Rise profile of FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ was investigated and compared with the foam catalyzed by Dabco[®] EG as shown in Figure 4.23. It was found that the FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂ and Dabco[®] EG:Cu(OAc)₂(trien) showed very fast rise rate at the middle of reaction while Dabco[®] EG showed slightly longer rise rate at the initial of reaction and very fast rise rate in the latter stage.

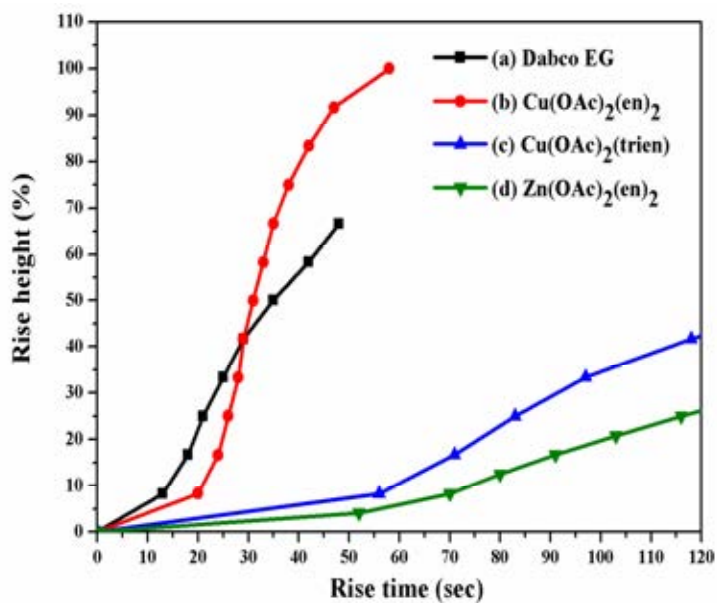


Figure 4.22 Rise profiles of FPUR foams catalyzed by (a) Dabco[®] EG, (b) Cu(OAc)₂(en)₂, (c) Cu(OAc)₂(trien) and (d) Zn(OAc)₂(en)₂

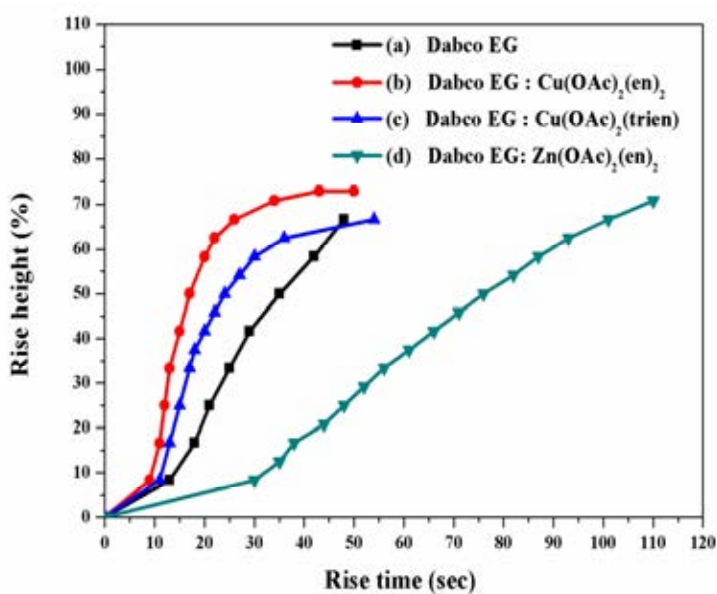


Figure 4.23 Rise profiles of FPUR foams catalyzed by (a) Dabco[®] EG, (b) Dabco[®] EG:Cu(OAc)₂(en)₂, (c) Dabco[®] EG:Cu(OAc)₂(trien) and (d) Dabco[®] EG:Zn(OAc)₂(en)₂

4.3.2 Foaming temperature of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes

Temperature profile of FPUR foams catalyzed by Dabco[®] EG: Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ were investigated and compared with the foam catalyzed by Dabco[®] EG, Cu(OAc)₂(en)₂, Cu(OAc)₂(trien) and Zn(OAc)₂(en)₂ as shown in Figure 4.24. It was found that the polymerization reaction was exothermic and all foams had similar temperature profiles. The maximum core temperature was in the range of 93-100 °C (Table 4.11) which was suitable for polymerization of FPUR foam because the foam did not burn at this maximum temperature.

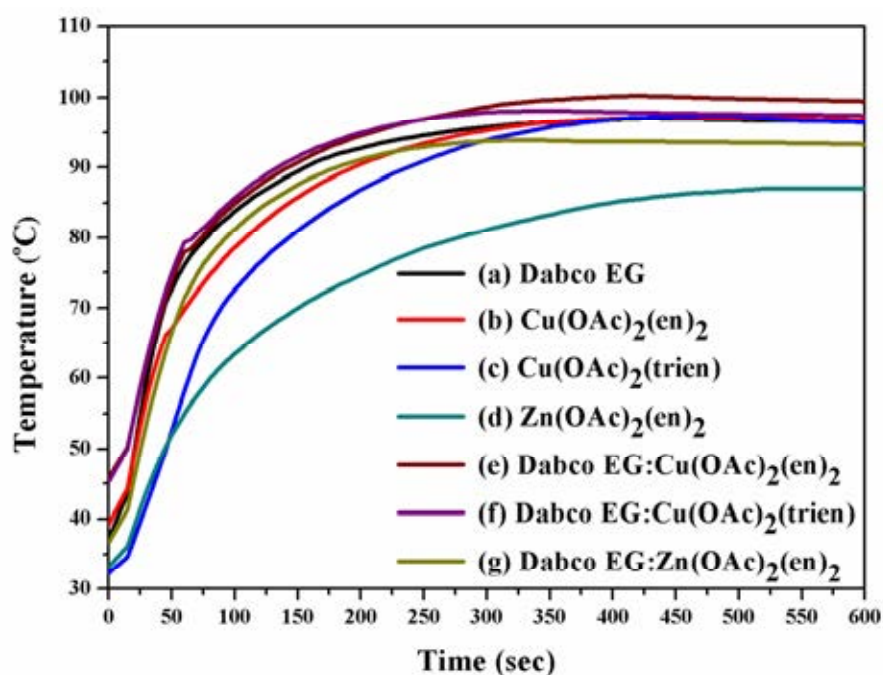


Figure 4.24 Temperature profiles of FPUR foams catalyzed by 0.5 pbw of (a) Dabco[®] EG, (b) Cu(OAc)₂(en)₂, (c) Cu(OAc)₂(trien), (d) Zn(OAc)₂(en)₂, (e) Dabco[®] EG:Cu(OAc)₂(en)₂, (f) Dabco[®] EG:Cu(OAc)₂(trien) and (g) Dabco[®] EG:Zn(OAc)₂(en)₂

Table 4.11 The maximum core temperature of FPUR foams catalyzed by Dabco[®] EG, metal-amine complexes and Dabco[®] EG:metal-amine complexes

Catalysts	Maximum core temperature (°C)	Starting times (min) at T _{max}
Dabco [®] EG	97.0	415 (6:55)
Cu(OAc) ₂ (en) ₂	97.2	425 (7:05)
Cu(OAc) ₂ (trien)	97.4	470 (7:50)
Zn(OAc) ₂ (en) ₂	87.1	525 (8:45)
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	100.3	405 (6:45)
Dabco [®] EG: Cu(OAc) ₂ (trien)	98.1	325 (5:25)
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	93.9	315 (5:15)

4.3.3 NCO conversion of FPUR foams catalyzed by Dabco[®] EG: metal-amine complexes

NCO conversion of FPUR foams catalyzed by Dabco[®] EG: Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ at NCO index of 100 was investigated and compared with the foam catalyzed by Dabco[®] EG Cu(OAc)₂(en)₂, Cu(OAc)₂(trien) and Zn(OAc)₂(en)₂ as shown in Figure 4.25 and Table 4.12. It was found that all Dabco[®] EG:metal-amine complexes gave approximately 99% of NCO conversion. It could be concluded that all Dabco[®] EG: metal-amine complexes were good catalysts for foam formation.

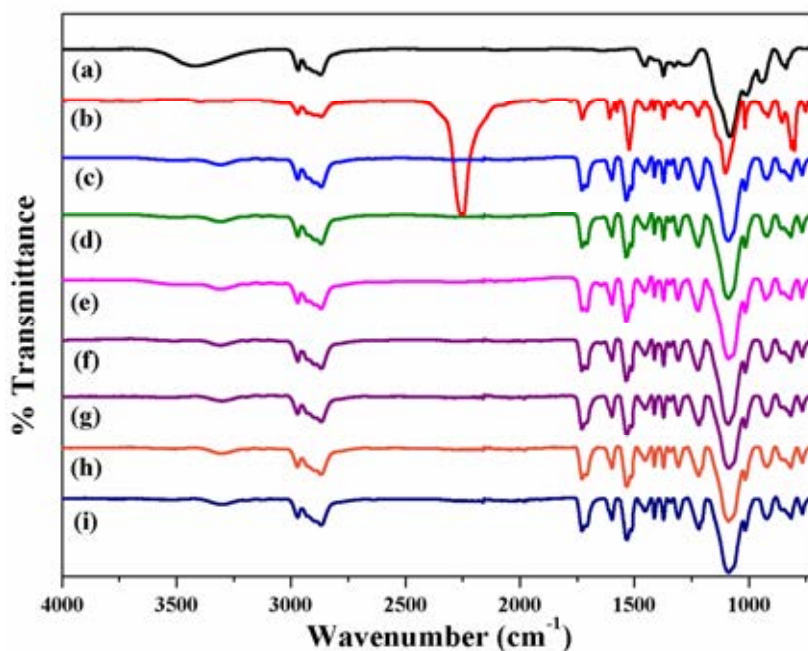


Figure 4.25 IR spectra of starting materials and FPUR foams catalyzed by 0.5 pbw of various catalysts at NCO index 100 (a) Polyether polyol, (b) MDI prepolymer, (c) Dabco[®] EG, (d) Dabco[®] EG:Cu(OAc)₂(en)₂ (e) Dabco[®] EG:Cu(OAc)₂(trien) and (f) Dabco[®] EG:Zn(OAc)₂(en)₂

Table 4.12 NCO conversion of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes at NCO index 100

Catalysts	NCO conversion (%)
Dabco [®] EG	99.81
Cu(OAc) ₂ (en) ₂	99.82
Cu(OAc) ₂ (trien)	99.88
Zn(OAc) ₂ (en) ₂	99.75
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	99.95
Dabco [®] EG: Cu(OAc) ₂ (trien)	99.97
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	99.94

4.3.4 Morphology of FPUR foams

4.3.4.1 Morphology of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes (cup test)

Morphology of cup test FPUR foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{en})_2$ was investigated and compared with the foam catalyzed by Dabco[®] EG (Figure 4.26). It was found that Dabco[®] EG and $\text{Cu}(\text{OAc})_2(\text{en})_2$ gave good morphology of FPUR foams with small average cell size while $\text{Cu}(\text{OAc})_2(\text{trien})$ had a larger cell size. $\text{Zn}(\text{OAc})_2(\text{en})_2$ gave poor morphology of FPUR foams with irregular cell size.

Morphology of cup test FPUR foams catalyzed by Dabco[®]EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$, Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{trien})$ and Dabco[®] EG: $\text{Zn}(\text{OAc})_2(\text{en})_2$ (Figure 4.27) showed better morphology of FPUR foams than $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$ and $\text{Zn}(\text{OAc})_2(\text{en})_2$ because morphology of foam had spherical shape and the smaller average cell size of foams.

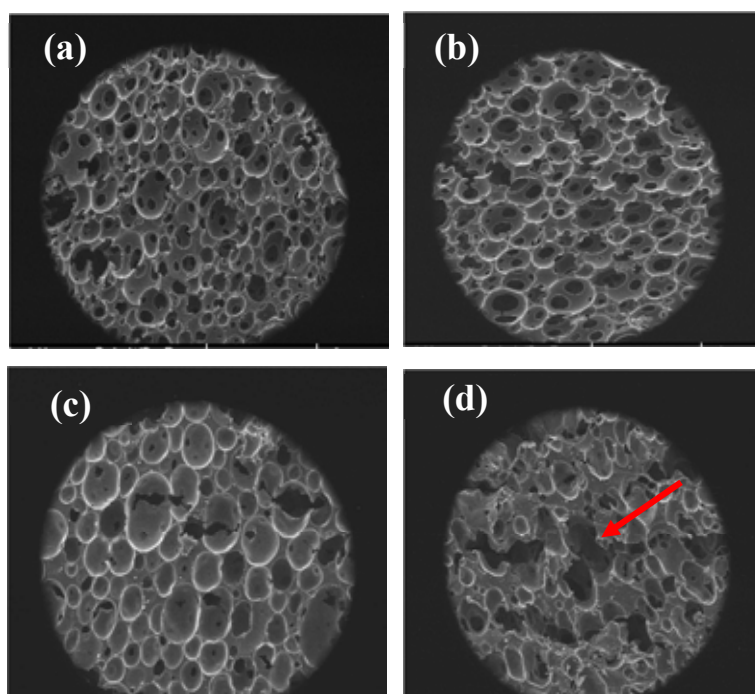


Figure 4.26 SEM images of cup test FPUR foams catalyzed by (a) Dabco[®] EG, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$, (c) $\text{Cu}(\text{OAc})_2(\text{trien})$ and (d) $\text{Zn}(\text{OAc})_2(\text{en})_2$

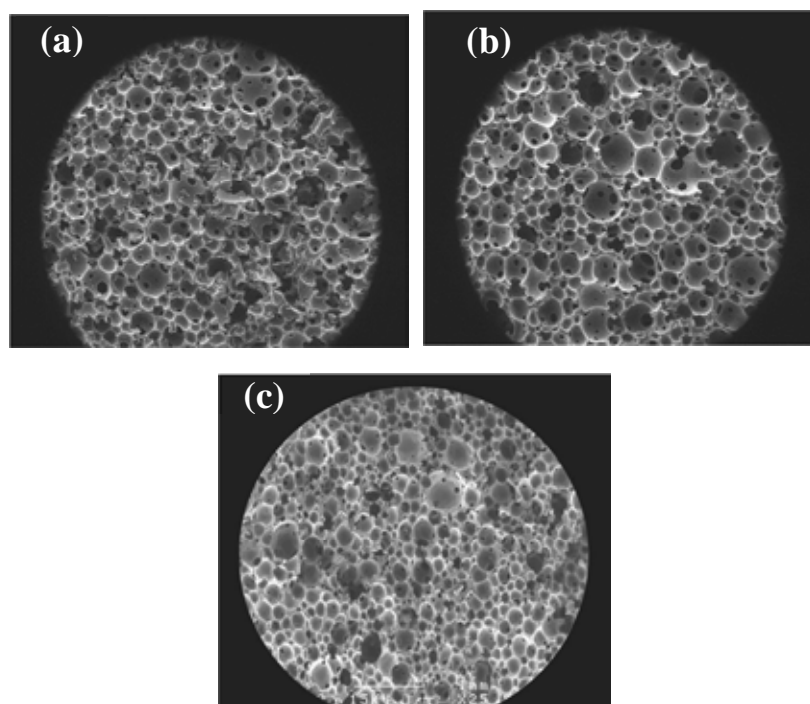


Figure 4.27 SEM images of cup test FPUR foams catalyzed by (a) Dabco[®] EG:Cu(OAc)₂(en)₂, (b) Dabco[®] EG:Cu(OAc)₂(trien) and (c) Dabco[®] EG:Zn(OAc)₂(en)₂

4.3.4.2 Morphology of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes (mold test)

Morphology of molded FPUR foams catalyzed by Cu(OAc)₂(en)₂ and Dabco[®] EG:Cu(OAc)₂(en)₂ was investigated and compared with the foam catalyzed by Dabco[®] EG (Figure 4.28). It was found that FPUR foams prepared by mold test method had smaller cell size than those prepared by cup test method (Figures 4.26 and 4.27). FPUR foam catalyzed by Dabco[®] EG and Dabco[®] EG:Cu(OAc)₂(en)₂ showed better morphology than that prepared from Cu(OAc)₂(en)₂. This might be because Cu(OAc)₂(en)₂ was a better catalyst for blowing reaction, which is isocyanate-water reaction, than Dabco[®] EG. Therefore, Cu(OAc)₂(en)₂ generated more CO₂ than Dabco[®] EG and caused too high pressure in the mold, which resulted in poor morphology of foam.

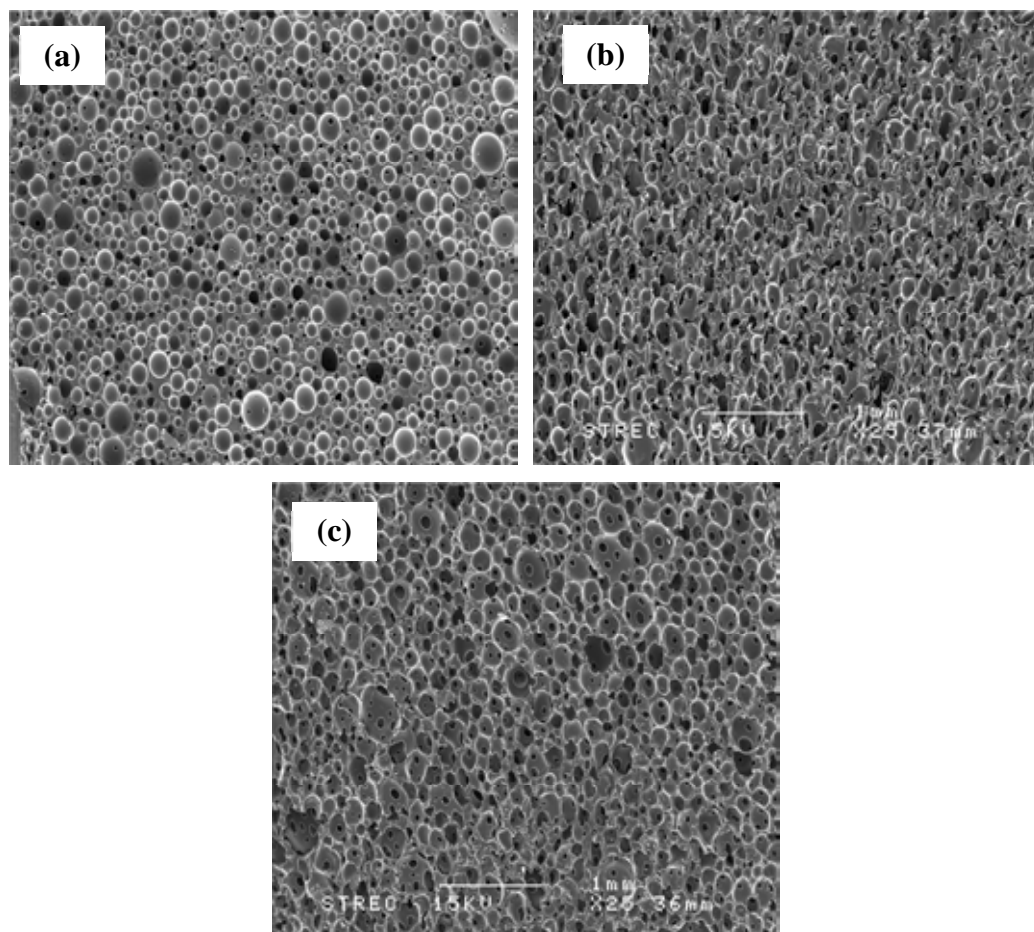


Figure 4.28 SEM images of FPUR foams catalyzed by (a) Dabco[®] EG, (b) Cu(OAc)₂(en)₂ and (c) Dabco[®] EG:Cu(OAc)₂(en)₂

4.3.5 Mechanical properties of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes

The catalysts control the rate of chemical reactions between isocyanate with polyol and water. The important function of catalyst is not only affects the rate of reaction but also influence the final properties of polyurethane foams [1, 6]. FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ were chosen to study mechanical properties, namely tensile properties and compression properties, and compared with the foams catalyzed by Dabco[®] EG, Cu(OAc)₂(en)₂, Cu(OAc)₂(trien) and Zn(OAc)₂(en)₂.

The study of mechanical properties of polyurethane foam was done on the molded FPUR foams and fixed catalyst amount at 0.5 pbw and the mole ratio of Dabco[®] EG:metal-amine complexes was fixed at 0.50 : 0.50.

4.3.5.1 Tensile properties of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes

Table 4.13 and Figure 4.29 showed tensile properties of FPUR foams. Young's modulus of FPUR foams catalyzed by the metal-amine complexes and Dabco[®] EG:metal-amine complexes was higher than that of the foam catalyzed by Dabco[®] EG.

For tensile strength and elongation at break, the foams catalyzed by the metal-amine complexes had lower tensile strength and elongation at break than the foam catalyzed by Dabco[®] EG. Addition of Dabco[®] EG into Dabco[®] EG:metal-amine complexes improved both tensile strength and elongation at break. The foam catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂ had the highest of tensile strength and elongation at break.

Table 4.13 Tensile testing of molded FPUR foams catalyzed by various catalysts.

Catalysts	Molded density (kg/m ³)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Dabco [®] EG	484	0.116	2.158	252
Cu(OAc) ₂ (en) ₂	454	0.154	0.982	137
Cu(OAc) ₂ (trien)	465	0.240	1.602	167
Zn(OAc) ₂ (en) ₂	646	0.302	1.679	104
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	497	0.152	2.539	255
Dabco [®] EG: Cu(OAc) ₂ (trien)	520	0.177	2.067	197
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	531	0.208	2.407	193

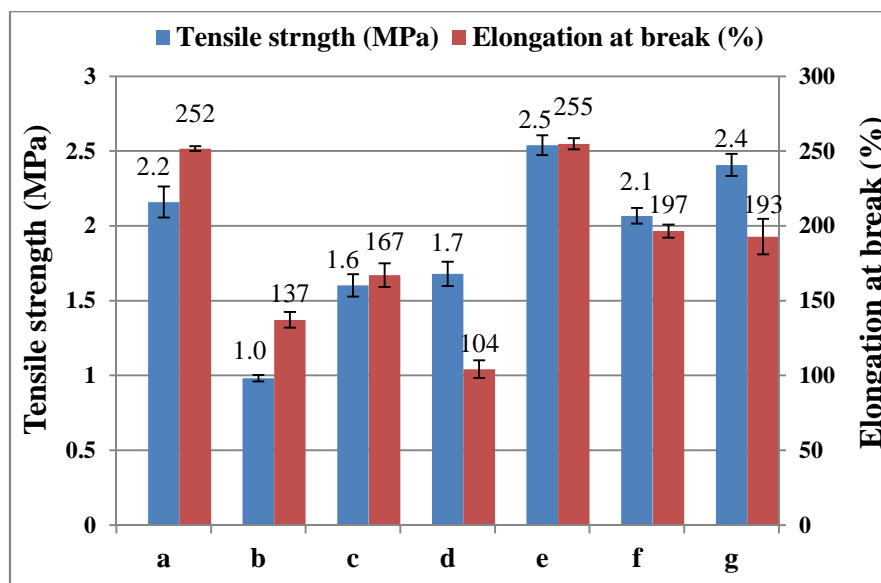


Figure 4.29 Tensile strength and elongation at break of molded FPUR foams catalyzed by (a) Dabco[®] EG, (b) Cu(OAc)₂(en)₂, (c) Cu(OAc)₂(trien), (d) Zn(OAc)₂(en)₂, (e) Dabco[®] EG:Cu(OAc)₂(en)₂, (f) Dabco[®] EG:Cu(OAc)₂(trien) and (g) Dabco[®] EG:Zn(OAc)₂(en)₂

4.3.5.2 Compression properties of FPUR foams catalyzed by Dabco[®] EG:metal-amine complexes

Compression properties of FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ was investigated and compared with those foam catalyzed by Dabco[®] EG, Cu(OAc)₂(en)₂, Cu(OAc)₂(trien) and Zn(OAc)₂(en)₂ as shown in Figure 4.30. The results in Table 4.14 show that the compression set of FPUR foams catalyzed by all catalysts had similar compression set. Except for Zn(OAc)₂(en)₂, which gave higher compression set than other metal complexes because FPUR foam catalyzed by Zn(OAc)₂(en)₂ had higher density.

Table 4.14 Compression set testing at 25% thickness of molded FPUR foams catalyzed by various catalysts

Catalysts	Molded density (kg/m ³)	Compression set @25% (MPa)
Dabco [®] EG	484	26.45
Cu(OAc) ₂ (en) ₂	454	26.53
Cu(OAc) ₂ (trien)	465	27.45
Zn(OAc) ₂ (en) ₂	646	28.71
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	497	26.82
Dabco [®] EG: Cu(OAc) ₂ (trien)	520	26.71
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	531	26.62

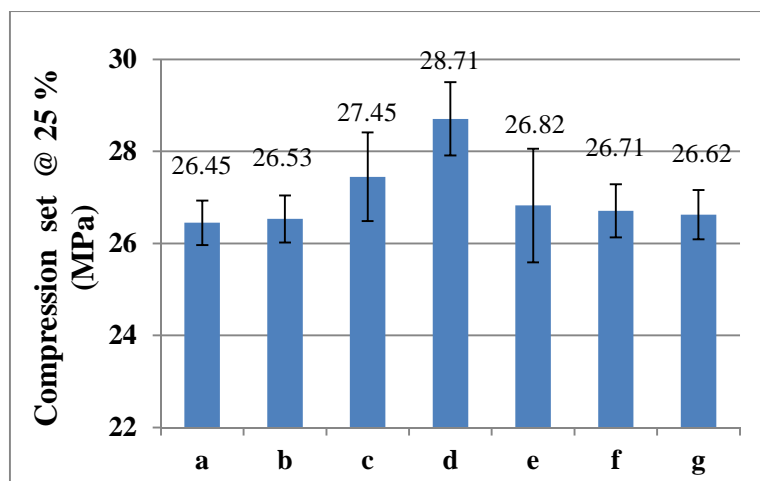


Figure 4.30 Compression set at 25% thickness of molded FPUR foams catalyzed by 0.5 pbw of (a) Dabco[®] EG, (b) Cu(OAc)₂(en)₂, (c) Cu(OAc)₂(trien), (d) Zn(OAc)₂(en)₂, (e) Dabco[®] EG:Cu(OAc)₂(en)₂, (f) Dabco[®] EG:Cu(OAc)₂(trien) and (g) Dabco[®] EG:Zn(OAc)₂(en)₂

4.3.6 FPUR foam appearances prepared from cup test method

$\text{Cu}(\text{OAc})_2(\text{en})_2$ was a good catalysts for FPUR formation because it had catalytic activity than commercial catalysts, Dabco[®] EG. However, the foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2$ and Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$ had brown color in the middle of the foam sample while the foam catalyzed by Dabco[®] EG did not have brown color (Figure 4.31). Therefore, compression set of these FPUR foams was investigated (Table 4.15) and it was found that the foams catalyzed by Dabco[®] EG, $\text{Cu}(\text{OAc})_2(\text{en})_2$ and Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$ had similar compression set. This suggested that the brown color in the center of foam sample might be the color of $\text{Cu}(\text{OAc})_2(\text{en})_2$.

Table 4.15 Compression set testing at 25% of thickness of FPUR foams prepared from cup test method

Catalysts	Free rise density (kg/m ³)	Compression set @25% (MPa)
Dabco [®] EG	266	26.21
$\text{Cu}(\text{OAc})_2(\text{en})_2$	179	26.97
Dabco [®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$	199	26.59

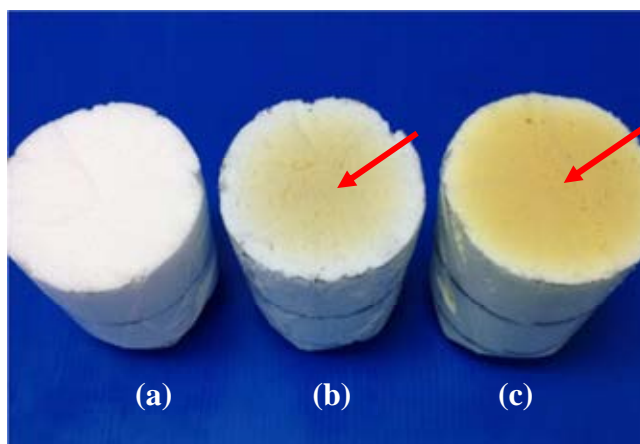


Figure 4.31 Free rise FPUR foams (a) Dabco[®] EG (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$ and (c) Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$

4.3.7 FPUR foam appearances prepared from mold test method

In the preparation of FPUR foams by using cup test method, the foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2$ and Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$ had brown color in the middle of the foam sample. The brown color was the color of $\text{Cu}(\text{OAc})_2(\text{en})_2$ (Figure 4.31). When using mold test method, FPUR foams prepared by $\text{Cu}(\text{OAc})_2(\text{en})_2$ (Figure 4.32) and Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$ (Figure 4.33) did not have brown color. The foams had uniform blue color of $\text{Cu}(\text{OAc})_2(\text{en})_2$ in the foam sample.

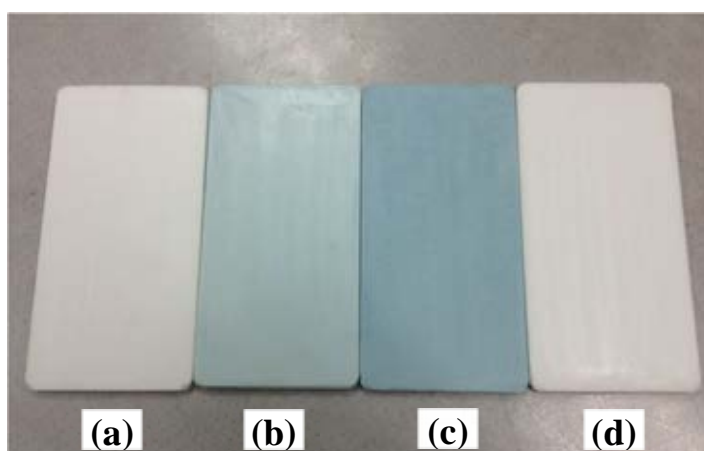


Figure 4.32 Mold FPUR foams (a) Dabco[®] EG (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$ (c) $\text{Cu}(\text{OAc})_2(\text{en})_2$ and (d) $\text{Zn}(\text{OAc})_2(\text{en})_2$

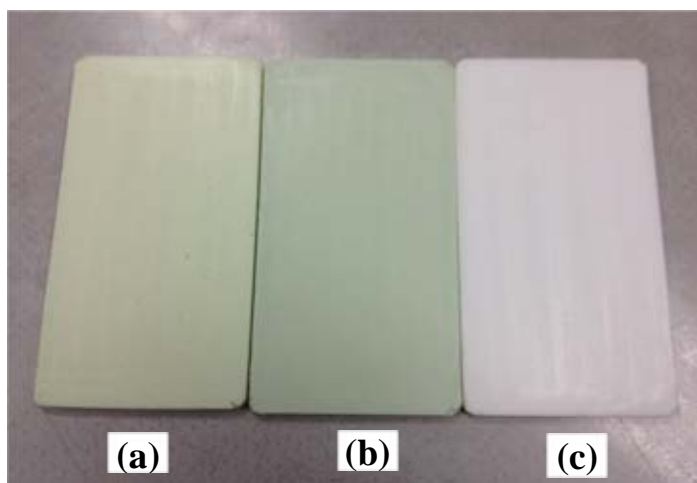


Figure 4.33 Mold FPUR foams (a) Dabco[®] EG:Cu(OAc)₂(en)₂, (b) Dabco[®] EG:Cu(OAc)₂(trien) and (c) Dabco[®] EG:Zn(OAc)₂(en)₂

CHAPTER V

CONCLUSION

5.1 Conclusion

Metal-amine and mixed metal-amine complexes, namely $\text{Cu}(\text{OAc})_2(\text{en})_2$, $\text{Cu}(\text{OAc})_2(\text{trien})$, $\text{Cu}(\text{OAc})_2(\text{dea})_4$, $\text{Zn}(\text{OAc})_2(\text{en})_2$, $\text{Zn}(\text{OAc})_2(\text{trien})$, $\text{Zn}(\text{OAc})_2(\text{dea})_4$, $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ were prepared as solutions in ethylene glycol and were used as catalyst for FPUR foam preparation. The obtained metal-amine and mixed metal-amine complex-ethylene glycol solutions were odorless, low viscous and could be easily dissolved in the raw materials of FPUR foam formulations. UV-visible spectroscopy and mass spectrometry confirmed the complex formation. The catalytic activity of the metal-amine complexes was evaluated from the tack-free time. Among all metal complexes, $\text{Cu}(\text{OAc})_2(\text{en})_2$ showed the highest catalytic activity and had comparable catalytic activity to Dabco[®] EG.

For FPUR foam formulation using $\text{Cu}(\text{OAc})_2(\text{en})_2$ as a catalyst, the optimum amount of chain extender (ethylene glycol) and blowing agent (water) in FPUR foam formulation was investigated. It was found that the suitable amount of chain extender and blowing agent was 5 and 0.5 pbw, respectively. Although $\text{Cu}(\text{OAc})_2(\text{en})_2$ showed good catalytic activity and gave good appearance of foam, however, the foam had low density than that prepared from Dabco[®] EG.

Therefore, the mixed metal-amine complexes were prepared by mixing of $\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{trien})$ into $\text{Cu}(\text{OAc})_2(\text{en})_2$. The mixed metal-amine complexes, namely $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ were used to prepare FPUR foam. It was found that both $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Zn}(\text{OAc})_2(\text{en})_2$ and $\text{Cu}(\text{OAc})_2(\text{en})_2:\text{Cu}(\text{OAc})_2(\text{trien})$ were not suitable catalyst because they had low catalytic activity than Dabco[®] EG and gave poor external appearance of FPUR foams.

Since Dabco[®] EG is expensive, the amount of Dabco[®] EG in FPUR foam formulation was reduced by using the mixtures of Dabco[®] EG:Cu(OAc)₂(en)₂, Dabco[®] EG:Cu(OAc)₂(trien) and Dabco[®] EG:Zn(OAc)₂(en)₂ as catalysts. It was found that Dabco[®] EG:Cu(OAc)₂(en)₂ and Dabco[®] EG:Cu(OAc)₂(trien) had higher catalytic activity than Dabco[®] EG and gave suitable foam density.

Rise profile of FPUR foaming reaction catalyzed by Dabco[®] EG: metal-amine complexes showed slow rate at initial of reaction and very fast rate in the middle of the reaction. The maximum core temperature during foaming reaction was in the range of 93-100 °C which suitable for polymerization of FPUR foam because the foam did not decompose at this temperature range. The NCO conversion was approximately 99% at the NCO index of 100.

Morphology of FPUR foams catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂ and Dabco[®] EG:Cu(OAc)₂(trien) were similar to that of Dabco[®] EG. The foam catalyzed by Dabco[®] EG:Cu(OAc)₂(en)₂ had the highest tensile strength and elongation at break.

Among all catalysts, Dabco[®] EG:Cu(OAc)₂(en)₂ is the most suitable catalyst for preparation of FPUR foams because it gives the highest catalytic activity and mechanical properties of FPUR foam. The advantage of Dabco[®] EG: Cu(OAc)₂(en)₂ is the price of Cu(OAc)₂(en)₂ is lower than that of Dabco[®] EG. The amount of Dabco[®] EG in FPUR foam formulation can be reduced by use of Dabco[®] EG:Cu(OAc)₂(en)₂.

In summary, the best FPUR foam formulation, reaction times of FPUR foaming reaction, physical and mechanical properties of FPUR foams are shown in Tables 5.1-5.3.

Table 5.1 The best FPUR Foam formulation

Starting materials	pbw
Poly(ethylene oxide)triol (Jeffol [®] G-31-35)	100.0
Catalyst [Dabco [®] EG:Cu(OAc) ₂ (en) ₂ , mole ratio = 0.5 : 0.5]	0.5
Silicone surfactant (Dabco [®] DC193)	0.5
Crosslinking agent (ethylene glycol)	5.0
Blowing agent (water)	0.5
Diphenylmethane diisocyanate prepolymer (MDIP Suprasec [®] 2449)	69.3

Table 5.2 The best reaction times of FPUR foaming reaction

Reaction time	(min:sec)
Cream time	0:10
Gel time	0:19
Rise time	0:33
Tack-free time	0:41

Table 5.3 The best physical and mechanical properties of FPUR foams

Properties	Values
Density (Cup test, kg/m ³)	199
Density (Mold test, kg/m ³)	497
Young's modulus (MPa)	0.152
Tensile strength (MPa)	2.539
Elongation at break (%)	255
Compression set @25% (MPa)	26.820

5.2 Suggestion for future work

The suggestion for future work is to apply this methodology to rigid polyurethane foam. The mixture of metal-amine complex, such as $\text{Cu}(\text{OAc})_2(\text{en})_2$, and commercial catalyst will be used as catalyst in the preparation of rigid polyurethane foam.

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APPENDICES

Appendix A

NCO index and NCO conversion calculations

NCO index calculation

#Example Calculate the parts by weight (pbw) of MDIP (Suprasec[®] 2449), NCO value = 18.9% at isocyanate indexes of 100 required to react with the following formulation:

Formulation (pbw)	Part by weight (g)
• Jeffol [®] G-31-35 (OHV = 35 mgKOH/ g, functionality = 3, Mw = 4800)	100.0
• Catalysts (33% wt in ethylene glycol)	0.5
• Surfactant (silicon surfactant)	0.5
• Blowing agent (water, Mw = 18 g/mole, functionality = 2)	0.5
• Chain extender (ethylene glycol, Mw = 62.10 g/mole, functionality = 2)	5.0
• MDIP (Suprasec [®] 2449), NCO indexes of 100	?

$$\text{Equivalent weight of Jeffol}^{\text{®}} \text{ G-31-35} = \frac{56.1}{35} \times 1000 = 1602.85$$

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

$$\text{Equivalent weight of ethylene glycol} = \frac{62.07}{2} = 31.035$$

$$\text{Equivalent weight of Suprasec}^{\text{®}} \text{ 2449} = \frac{4200}{18.9} = 222.22$$

Note: Surfactants is 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:

$$\text{Polyol (Jeffol® G-31-35)} = \frac{100}{1602.85} \times 222.22 = 13.864$$

$$\text{Water (blowing agent)} = \frac{0.5}{9.0} \times 222.22 = 12.345$$

$$\text{Ethylene glycol (chain extender + solvent)} = \frac{5 + 1.015}{31.035} \times 222.22 = 43.069$$

$$\text{Total equivalent weight} = 69.278$$

Note : 69.278 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:

$$\text{Actual amount of isocyanate} = \frac{69.278}{100} \times 100 = 69.278 \text{ pbw}$$

Table A1 Isocyanate quantity at difference amounts of catalyst in the above formulations

Formulation (pbw)	NCO indexes = 100						
Polyols	100						
Catalysts	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Surfactant	0.5						
Blowing agent	0.5						
Chain extender	5						
Isocyanate	63.5	64.9	66.4	67.8	69.3	70.7	72.2

Table A2 Isocyanate quantity at difference amounts of blowing agent in the above formulations

Formulation (pbw)	NCO indexes = 100		
Polyols		100	
Catalysts		0.5	
Surfactant		0.5	
Blowing agent	0.3	0.5	0.7
Chain extender		5	
Isocyanate	64.3	69.3	74.2

Table A3 Isocyanate quantity at difference amounts of chain extender in the above formulations

Formulation (pbw)	NCO indexes = 100		
Polyols		100	
Catalysts		0.5	
Surfactant		0.5	
Blowing agent		0.5	
Chain extender	3	5	7
Isocyanate	55.0	69.3	83.6

NCO conversion calculation

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

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

where;

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

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

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

Table A4 Free NCO absorbance peak area in MDIP (Suprasec[®] 2449) from IR-ATR

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

Example Calculate the conversion of isocyanate (α) of flexible polyurethane foams catalyzed by $\text{Cu}(\text{OAc})_2(\text{en})_2$ at NCO index 100

Conversion of isocyanate (%)

Data at **Table A4**

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 = 0.184 = NCO^f

$$\begin{aligned} \text{Thus, conversion of isocyanate (\%)} &= \left[1 - \frac{\text{NCO}^f}{\text{NCO}^i} \right] \times 100 \\ &= \left[1 - \frac{0.814}{98.0} \right] \times 100 \end{aligned}$$

$$\% \text{ NCO conversion} = 99.81$$

Table A5 The NCO conversion of FPUR foams catalyzed by different catalyst types.

Foam catalyzed by		Peak area			NCO Conversion (%)
		NCO 2277 cm ⁻¹	Ar-H 1595 cm ⁻¹	NCO ^f AR-H=1	
Dabco [®] EG	Mean	0.263	1.399	0.188	99.81
	SD	0.009	0.015	0.008	0.005
Cu(OAc) ₂ (en) ₂	Mean	0.253	1.426	0.177	99.82
	SD	0.023	0.047	0.015	0.018
Cu(OAc) ₂ (trien)	Mean	0.198	1.659	0.118	99.88
	SD	0.062	0.108	0.029	0.031
Cu(OAc) ₂ (dea) ₄	Mean	0.272	1.394	0.195	99.80
	SD	0.022	0.011	0.017	0.014
Zn(OAc) ₂ (en) ₂	Mean	0.321	1.307	0.247	99.75
	SD	0.050	0.070	0.049	0.049
Zn(OAc) ₂ (trien)	Mean	0.312	1.438	0.217	99.78
	SD	0.049	0.015	0.032	0.032
Zn(OAc) ₂ (dea) ₄	Mean	0.309	1.399	0.220	99.78
	SD	0.049	0.015	0.032	0.032
Cu(OAc) ₂ : Zn(OAc) ₂ :en 1 : 1 : 4	Mean	0.253	1.426	0.177	99.82
	SD	0.023	0.047	0.015	0.018
Cu(OAc) ₂ :en: trien 2 : 2 : 1	Mean	0.198	1.659	0.118	99.88
	SD	0.062	0.108	0.029	0.031
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	Mean	0.074	1.420	0.052	99.95
	SD	0.015	0.043	0.011	0.069
Dabco [®] EG: Cu(OAc) ₂ (trien)	Mean	0.045	1.446	0.031	99.97
	SD	0.009	0.070	0.049	0.071
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	Mean	0.081	1.410	0.057	99.94
	SD	0.011	0.047	0.015	0.050

Appendix B

Calculations of metal-amine complexes

- Calculation of metal-amine complexes

Example Calculate the composition in synthesis of $\text{Cu}(\text{OAc})_2(\text{en})_2$

$$\text{The ratio of } \text{Cu}(\text{OAc})_2 : \text{ethylenediamine} = 1 : 2$$

$$\begin{aligned} \text{Total molecular weight} &= (199.65) + (2 \times 60.10) \\ &= 319.65 \text{ g/mol} \end{aligned}$$

$$\% \text{wt of } \text{Cu}(\text{OAc})_2 = 199.65 / 319.65 = 0.624$$

$$\% \text{wt of ethylenediamine} = (2 \times 60.10) / 319.65 = 0.376$$

- Calculation of ethylene glycol amount in 33%wt of $\text{Cu}(\text{OAc})_2(\text{en})_2$

$$\% \text{ Weight} = \frac{\text{solute}}{\text{solute} + \text{solvent}} \times 100$$

Note : solute = weight of metal + amine = 0.624 + 0.376 = 1

solvent = ethylene glycol amount in 33%wt of $\text{Cu}(\text{OAc})_2(\text{en})_2$ (X)

$$33 = \frac{1}{(1 + X)} \times 100$$

$$X = 2.03 \text{ g.}$$

Density of ethylene glycol = 1.113 kg/m³

$$X = 1.82 \text{ ml.}$$

The composition in synthesis of 33%wt of $\text{Cu}(\text{OAc})_2(\text{en})_2$:

$$\text{Cu}(\text{OAc})_2 = 0.624 \text{ g.}$$

$$\text{Ethylenediamine} = 0.374 \text{ ml.}$$

$$\text{Ethylene glycol} = 1.820 \text{ ml.}$$

Appendix C

The reaction time of metal-amine and mixed metal-amine complexes

Table C1 Reaction time of FPUR foams catalyzed by various types of catalysts

Catalyst types		Cream time (min:sec)	Gel time (min:sec)	Rise time (min:sec)	Tack-free time (min:sec)
Dabco [®] EG	Mean	0:17	0:30	0:45	1:13
	SD	0:01	0:01	0:03	0:03
Cu(OAc) ₂ (en) ₂	Mean	0:17	0:30	0:45	1:13
	SD	0:01	0:01	0:03	0:03
Cu(OAc) ₂ (trien)	Mean	1:02	2:02	3:27	11:3
	SD	0:03	0:03	0:08	0:09
Cu(OAc) ₂ (dea) ₄	Mean	1:2	3:56	7:01	19:39
	SD	0:03	0:19	0:28	0:19
Zn(OAc) ₂ (en) ₂	Mean	1:08	2:04	4:2	8:13
	SD	0:07	0:05	0:08	0:03
Zn(OAc) ₂ (trien)	Mean	1:54	6:59	12:33	31:12
	SD	0:04	0:11	0:04	0:10
Zn(OAc) ₂ (dea) ₄	Mean	0:57	5:27	7:44	24:29
	SD	0:23	0:15	0:10	0:04
Cu(OAc) ₂ : Zn(OAc) ₂ :en 1 : 1 : 4	Mean	0:59	1:27	2:27	5:10
	SD	0:05	0:02	0:06	0:09
Cu(OAc) ₂ : Zn(OAc) ₂ :en 1.5 : 0.5 : 4	Mean	0:39	1:03	1:41	4:37
	SD	0:01	0:02	0:01	0:10
Cu(OAc) ₂ :en: trien 2 : 2 : 1	Mean	0:35	1:22	1:60	7:64
	SD	0:02	0:03	0:02	0:06
Dabco [®] EG: Cu(OAc) ₂ (en) ₂	Mean	0:11	0:20	0:36	0:42
	SD	0:02	0:01	0:01	0:01
Dabco [®] EG: Cu(OAc) ₂ (trien)	Mean	0:09	0:18	0:31	0:40
	SD	0:00	0:00	0:02	0:02
Dabco [®] EG: Zn(OAc) ₂ (en) ₂	Mean	0:27	0:46	1:23	2:15
	SD	0:02	0:04	0:05	0:07

Appendix D

Tensile and compression curves and data

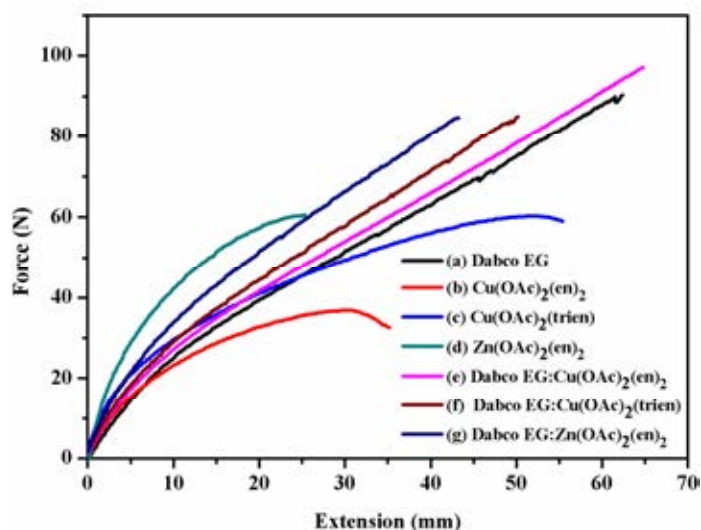


Figure D1 Tensile force-%extension curve of FPUR catalyzed by (a) Dabco[®] EG, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$, (c) $\text{Cu}(\text{OAc})_2(\text{trien})$, (d) $\text{Zn}(\text{OAc})_2(\text{en})_2$, (e) Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$, (f) Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{trien})$ and (g) Dabco[®] EG: $\text{Zn}(\text{OAc})_2(\text{en})_2$

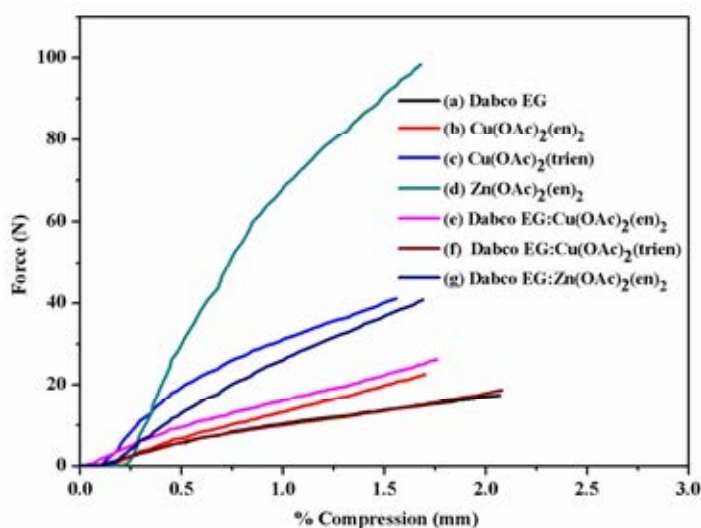


Figure D2 Compression set force-%compression curve of FPUR catalyzed by (a) Dabco[®] EG, (b) $\text{Cu}(\text{OAc})_2(\text{en})_2$, (c) $\text{Cu}(\text{OAc})_2(\text{trien})$, (d) $\text{Zn}(\text{OAc})_2(\text{en})_2$, (e) Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{en})_2$, (f) Dabco[®] EG: $\text{Cu}(\text{OAc})_2(\text{trien})$ and (g) Dabco[®] EG: $\text{Zn}(\text{OAc})_2(\text{en})_2$

Table D1 Tensile properties of FPUR foams catalyzed by various types of catalysts

Catalysts	Molded density	Modulus @5%	Modulus @25%	Tensile strength (MPa)	Elongation at break (%)
Dabco[®] EG	mean	0.116	0.414	2.158	252
	SD	0.009	0.015	0.104	2
Cu(OAc)₂(en)₂	mean	0.154	0.473	0.982	137
	SD	0.021	0.016	0.021	5
Cu(OAc)₂(trien)	mean	0.240	0.600	1.602	207
	SD	0.019	0.044	0.074	8
Zn(OAc)₂(en)₂	mean	0.302	0.895	1.679	104
	SD	0.022	0.038	0.082	6
Dabco[®] EG: Cu(OAc)₂(en)₂	mean	0.002	0.017	0.066	4
	SD	0.150	0.540	2.582	251
Dabco[®] EG: Cu(OAc)₂(trien)	mean	0.177	0.529	2.067	197
	SD	0.013	0.021	0.053	4
Dabco[®] EG: Zn(OAc)₂(en)₂	mean	0.208	0.641	2.207	188
	SD	0.007	0.014	0.073	12

Table D2 compression properties of FPUR foams catalyzed by various types of catalysts

Catalysts	Molded density	Modulus (MPa)	Compression (MPa)
Dabco[®] EG	mean	1.042	26.45
	SD	0.206	0.480
Cu(OAc)₂(en)₂	mean	1.605	26.530
	SD	0.222	0.513
Cu(OAc)₂(trien)	mean	3.607	27.446
	SD	0.673	0.962
Zn(OAc)₂(en)₂	mean	9.654	28.706
	SD	0.645	0.796
Dabco[®] EG: Cu(OAc)₂(en)₂	mean	1.327	26.82
	SD	0.376	1.230
Dabco[®] EG: Cu(OAc)₂(trien)	mean	1.236	26.706
	SD	0.268	0.579
Dabco[®] EG: Zn(OAc)₂(en)₂	mean	2.151	26.622
	SD	0.491	0.534

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