PREPARATION OF STARCH-FILLED POLYISOCYANURATE FOAMS CATALYZED BY ZINC-AMMONIA COMPLEX/POTASSIUM OCTOATE

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A Thesis Submitted in Partial Fulfillment of the Requirements
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การเตรียมโฟมพอลิไอโซไซยานูเรตที่เติมแป้งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนซิงก์-แอมโมเนีย/ โพแทสเซียมออกโทเอต

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Thesis Title	PREPARATION OF STARCH-FILLED POLYISOCYANURATE FOAMS CATALYZED BY ZINC-AMMONIA COMPLEX/POTASSIUM OCTOATE
By	Miss Sirima Goonack
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Nuanphun Chantarasiri, Ph.D.

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ศิริมา กู้นาค : การเตรียมโฟมพอลิไอโซไซยานูเรตที่เติมแป้งเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนซิงก์-แอมโมเนีย/โพแทสเซียมออกโทเอต. (PREPARATION OF STARCH-FILLED POLYISOCYANURATE FOAMS CATALYZED BY ZINC-AMMONIA COMPLEX/POTASSIUM OCTOATE) อ.ที่ปรึกษาหลัก : รศ. ดร.นวลพรรณ จันทรศิริ

งานวิจัยนี้มีวัตถุประสงค์เพื่อลดความหนาแน่นและปรับปรุงการต้านการติดไฟของ โฟมพอลิไอโซไซยานูเรตโดยใช้สารประกอบเชิงซ้อนซิงก์-แอมโมเนียเป็นตัวเร่งปฏิกิริยาการเกิดเจลและปฏิกิริยาการฟู และใช้โพแทสเซียมออกโทเอตเป็นตัวเร่งปฏิกิริยาไตรเมอไรเซชัน การเตรียม โฟมพอลิโอโซไซยาเรตโดยเติมแป้งที่มีการผลิตในประเทศไทย 3 ชนิด คือ แป้งข้าวเหนียว แป้งข้าวเจ้า และแป้งถั่วเขียวเป็นสารตัวเติม ซึ่งศึกษาเอกลักษณ์ของโฟมพอลิไอโซไซยานูเรตที่เติมแป้งโดยใช้เทคนิคอินฟราเรดสเปกโทรสโกปี ศึกษาเวลาที่ใช้ในการเกิดปฏิกิริยาได้แก่ เวลาที่สารผสมเป็นครีม เวลาที่สารผสมเป็นเจล เวลาที่โฟมหยุดฟู และเวลาที่ผิวหน้าของโฟมไม่เกาะติดกับผิวสัมผัสของวัสดุ อัตราส่วนระหว่างพอลิไอไซยานูเรตต่อพอลิยูรีเทนโฟม ร้อยละไอโซไซยาเนต ความหนาแน่น ความต้านทานต่อแรงกดอัด ลักษณะสัณฐาน และสมบัติการติดไฟของโฟมพอลิไอโซไซยานูเรตที่เติมแป้ง จากผลการทดลองที่ได้พบว่า โฟมพอลิไอโซไซยานูเรตที่เติมแป้งมีความหนาแน่นลดลง และมีสมบัติการต้านการติดไฟเพิ่มขึ้นเมื่อเปรียบเทียบกับโฟมพอลิไอโซไซยานูเรตที่ไม่เติมแป้ง ซึ่งโฟมพอลิไอโซไซยานูเรตที่เติมแป้งสามารถดับไฟได้เอง

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Sirima Goonack : PREPARATION OF STARCH-FILLED POLYISOCYANURATE FOAMS CATALYZED BY ZINC-AMMONIA COMPLEX/POTASSIUM OCTOATE. Advisor: Assoc. Prof. Nuanphun Chantarasiri, Ph.D.

The research aimed to reduce apparent density and improve fire resistance of polyisocyanurate (PIR) foam. PIR foams were prepared using zinc-ammonia complex and potassium octoate as catalyst for gelling/blowing and trimerization reactions, respectively. Three types of starch produced in Thailand, namely glutinous rice flour, rice flour and mung bean starch, were used as additives for PIR foams. The characterized properties of PIR foams modified with starches are reaction times (cream time, gel time, rise time and tack free time), polyisocyanurate/polyurethane (PIR/PUR) ratio, %isocyanate conversion, apparent density, compressive property, morphology and fire behavior. These properties are compared with PIR foam without of starch. The experimental results showed that an addition of starches into PIR foams reduced apparent density and increased fire resistance property as compared to PIR foam without of starch. The PIR foam modified with starches showed self-extinguishing property.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature ....
Academic Year:	2019	Advisor's Signature ....

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Sirima Goonack

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LIST OF ABBREVIATIONS

Zn(Amm)	zinc ammonia complex
KOct	potassium octoate
PIR/PUR	polyisocyanurate/polyurethane ratio
PIR	polyisocyanurate
PUR	polyurethane
%NCO	%isocyanate conversion
NCO	isocyanate group
OH	hydroxyl group
CO_2	carbon dioxide
MDI	methane diphenyl diisocyanate
PMDI	polymeric methane diphenyl diisocyanate
mgKOH/g	milligrams of potassium hydroxide per gram
DEBCO	triethylenediamine
DMCHA	*N,N*-dimethylcyclohexylamine
H_2O	water
HCFCs	hydrochlorofluorocarbon
HFCs	hydrofluorocarbon
CFCs	chlorofluorocarbon
PFCs	perfluorocarbon
pbw	part by weight
KOH	potassium hydroxide
ATR-FTIR	attenuated total reflectance-flurier transform Infrared
NCO^i	peak area of initial isocyanate
NCO^f	peak area of final isocyanate
%	percentage

ASTM	American Society for testing and Material
wt%	weight percent
kg/m^3	kilogram per cubic metre
$Zn(OAc)_2 \cdot 2H_2O$	Zinc (II) acetate dihydrate
NH_3	ammonia
mmol	millimole
ml	milliliter
RT	room temperature
SEM	scanning electron microscope
rpm	revolution per minute
cm	centimeter
cm^{-1}	unit of wavenumber
mm	millimeter
min	minute
s	second
kV	kilovolt
O_2	oxygen
MPa	Megapascal Pressure Unit
kPa	Kilopascal Pressure Unit
V	vertical direction
H	horizontal direction
µm	micro metre
%LOI	Limit Oxygen Index

CHAPTER I

INTRODUCTION

Polyisocyanurate (PIR) foams are one of the most popular materials used in thermal insulation for buildings, packaging and other application. This is because PIR foams have outstanding properties such as closed-cell structure, good mechanical properties, high thermal properties and fire resistance [1, 2]. PIR foams contains higher amount of isocyanurate groups than polyurethane foams and therefore have better fire resistance than polyurethane foams. PIR foams are obtained from mixing polyol with excess amount of isocyanate, which forms the urethane and isocyanurate linkages. The excess amount of isocyanate compound gives isocyanurate linkage Thus, PIR foams are highly cross-linked as three-dimensional polymer. The isocyanurate groups can also react with water, which is a blowing agent, to generate carbon dioxide and leads to cellular structure of foam. Additional starting materials such as catalyst, surfactant and filler are added during production. However, The PIR foams have highly apparent density and brittleness, which are not suitable for application. Therefore, one promising route to produce PIR foam with lower density is the addition of natural filler [3-5]. Starches are one of the promising natural filler for reducing the apparent density of PIR foams. Starches are found in agricultural plants and they are inexpensive biopolymer. Starches contains amylose and amylopectin. Amylose is a linear polymer with α-1-4 linked glucopyranosyl unit and its molecular weight is 10^4 to 10^5. Amylopec- tin is a highly branch polymer with 1-4 linked α-D-glucopyranosyl unit. Starches also contains carbohydrates, amino groups, protein, fat and moisture [6, 7].

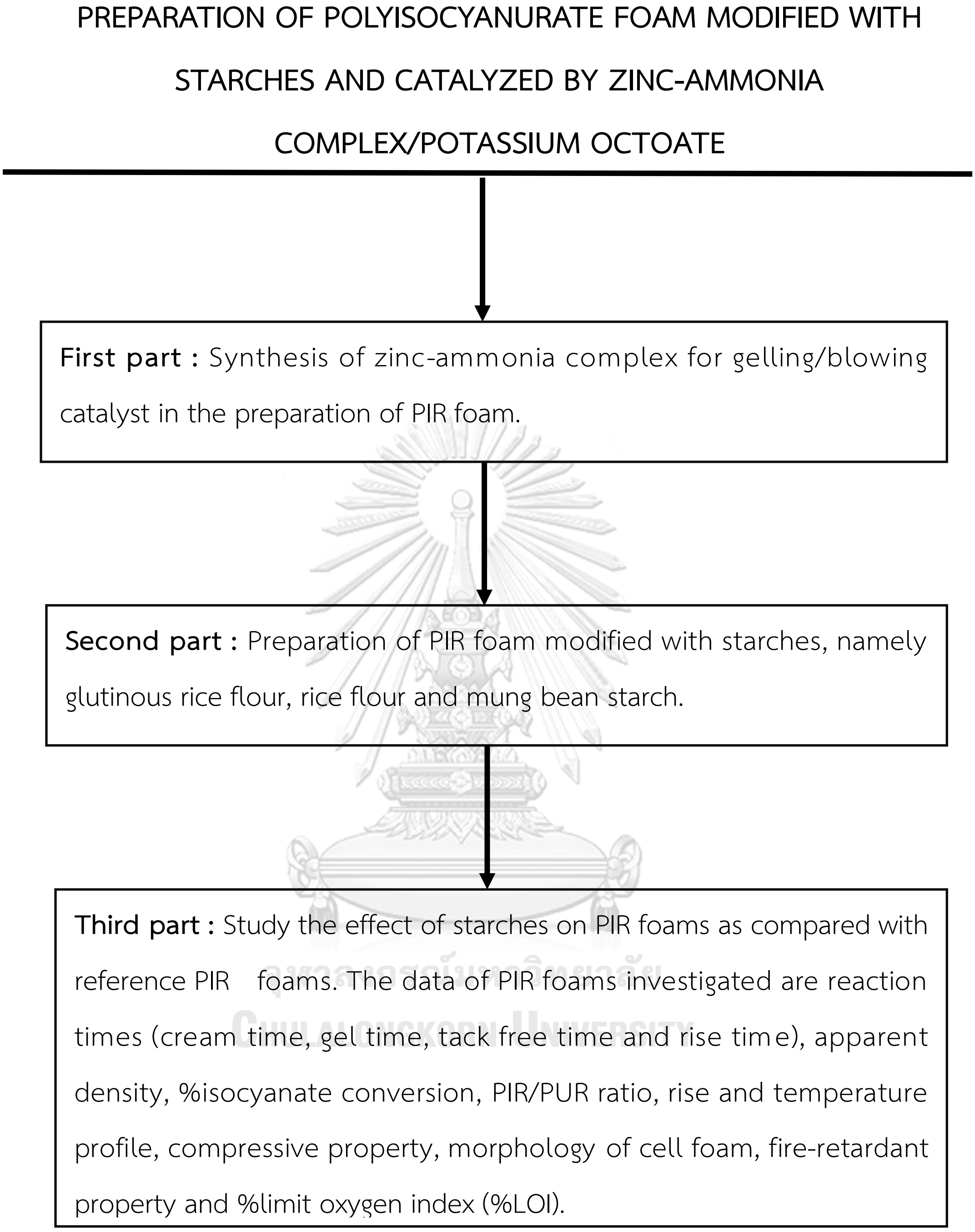
Starches has many hydroxyl groups per repeating unit, thus there can undergo various types of reactions such as oxidation, esterification and etherification. Starches leads to release incombustible gases products such as water, carbon dioxide and char forms on the foams surface to prevent oxygen and heat transfer [8-10].

1.1 Objective of the research

This work focuses on the preparation of PIR foam modified with starches. Glutinous rice flour, rice flour and mung bean starch are used as fillers in the preparation of PIR foams. PIR foams are prepared using zinc-ammonia complex and potassium octoate as gelling/blowing and trimerization catalysts, respectively. The purposes of this work are to reduce apparent density and improve fire resistance of PIR foams.

1.2 Scope of the research

The scope of the research divides into three parts (Figure 1.1). In the first part, the synthesis of zinc-ammonia complex [Zn(Amm)], which was used as gelling and blowing catalyst in the preparation of PIR foams, was done according to the method reported in the literature [11]. In the second part, PIR foams were prepared using zinc-ammonia complex and potassium octoate (KOct) as gelling/blowing and trimerization catalysts, respectively. In the preparation of PIR foams, starches were added as fillers. Three types of starches produced in Thailand, namely glutinous rice flour, rice flour and mung bean starch were used. PIR foams modified with starches were prepared using cup test method and prepared in a mold. In the last part, physical and mechanical properties of PIR foams modified with starches were studied. The reaction times, namely cream time, gel time, tack free time and rise time were recorded in order to study the effect of starches on PIR foams as compared with reference PIR foam prepared without starch. Polyisocyanurate/polyurethane (PIR/PUR) ratio, %isocyanate conversion, apparent density, compressive property, morphology and fire-retardant property of PIR foams modified with starches were studied and compared to those of reference PIR foams.



PREPARATION OF POLYISOCYANURATE FOAM MODIFIED WITH STARCHES AND CATALYZED BY ZINC-AMMONIA COMPLEX/POTASSIUM OCTOATE

First part : Synthesis of zinc-ammonia complex for gelling/blowing catalyst in the preparation of PIR foam.

Second part : Preparation of PIR foam modified with starches, namely glutinous rice flour, rice flour and mung bean starch.

Third part : Study the effect of starches on PIR foams as compared with reference PIR foams. The data of PIR foams investigated are reaction times (cream time, gel time, tack free time and rise time), apparent density, %isocyanate conversion, PIR/PUR ratio, rise and temperature profile, compressive property, morphology of cell foam, fire-retardant property and %limit oxygen index (%LOI).

Figure 1.1 Scope of research

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 General background

Polyisocyanurate (PIR) foams are used in wide range of application. PIR foams are mainly used as thermal insulation materials and parts in furniture. Figure 2.1 presents the advantages of sandwich panel PIR foam application. PIR foams are prepared with high isocyanate index (higher than 350), therefore, sandwich panel PIR foams are fire resistance and have low smoke index. A usual procedure for manufacturing PIR foams is obtained from trimerization reaction using high isocyanate index accompanying with the polymerization between hydroxyl groups of polyol and isocyanate groups. PIR foams contain both isocyanurate and urethane linkages in the structure. The isocyanurate group is a thermally stable structure and therefore, PIR foams are more thermally stable than polyurethane (PU) foams. The other starting materials of PIR foams are gelling/blowing catalyst, trimerization catalyst, surfactant, blowing agent and additive [12-15].

Although PIR foams have good fire-retardant properties, there are drawbacks from having isocyanurate groups in the foam structure. The mechanism properties of PIR foams decline and this leads to friability of the polymeric matrix [15]. In addition, the foams density is high and not suitable for application.

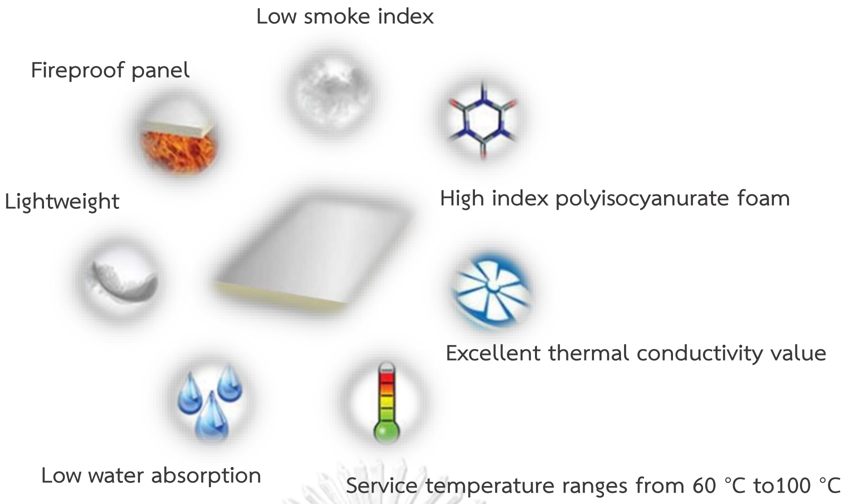


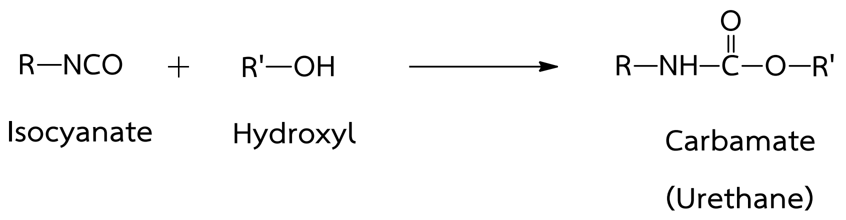
Figure 2.1 Sandwich panel PIR foams application [16]

2.2 Chemistry

The PIR foams are obtained for exothermic reaction of isocyanate compound with hydroxyl groups of polyols. Excessive amount of isocyanate is used to give urethane and isocyanurate linkages. When water is used as a blowing agent, isocyanate compound can react with water to release carbon dioxide and amine. The reaction involved in PIR formation are described as follow:

2.2.1 Reaction of isocyanate compound with polyol

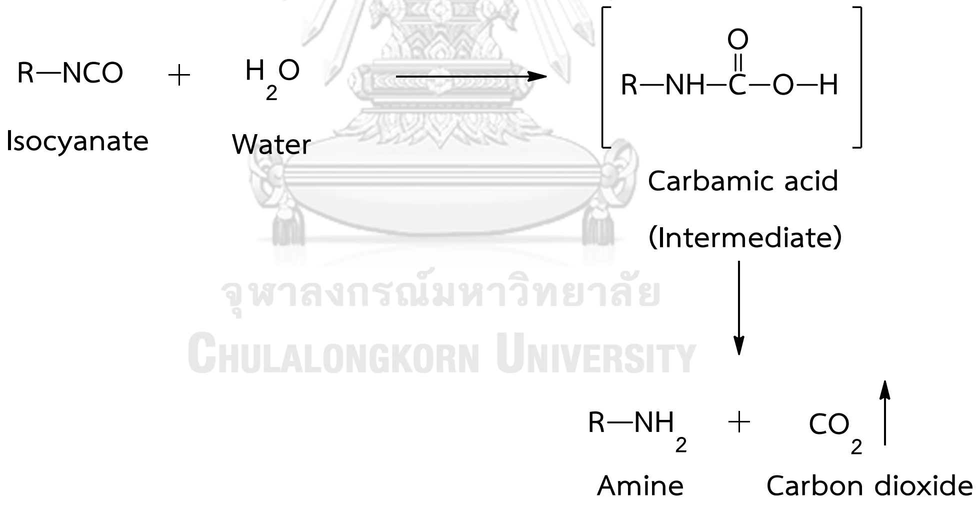
The reaction between isocyanate compound and hydroxyl group (scheme 2.1) is the polymerization reaction of gelling reaction. The carbamate or urethane linkage is a product of the reaction. The catalyst used in this reaction is called gelling catalyst [12, 15, 17]



Scheme 2.1 Reaction of isocyanate with polyol [17]

2.2.2 Reaction of isocyanate compound with water

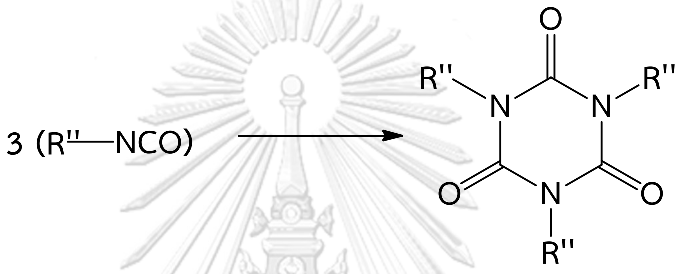
The reaction between isocyanate and water (Scheme 2.2) is called blowing reaction. This reaction gives carbamic acid as intermediate, which decomposes to give carbon dioxide gas (CO_2) and primary amine. The CO_2 acts as a blowing agent that blows up into the foam as air bubble during processing to generate the cellular structure. The water in reaction is used as chemical blowing agent [15, 17]



Scheme 2.2 Reaction of isocyanate with water [17]

2.2.3 Trimerization reaction

Trimerization reaction is obtained by three isocyanate molecules from the excessive isocyanate compound. The isocyanate compound can undergo a cyclization reaction to from a six-membered ring, which is called isocyanate group (Scheme 2.3). Polyisocyanurate groups can improve thermal stability and fire-retardant properties of PIR foams [15, 17, 18]



Scheme 2.3 Trimerization reaction of isocyanate compound [17]

2.3 Starting materials

The major of starting materials of PIR foams are isocyanate compound and polyol. In addition, other additives, namely catalyst, chemical blowing agent, surfactant and filler is used in preparation of the foam.

2.3.1 Isocyanate compound

There are many types of aromatic and aliphatic isocyanate which are commercially available. Examples of isocyanate compound used in the preparation of PIR foams are described as follows [12, 15, 17].

2.3.1.1 Methane diphenyl diisocyanate (MDI)

Methane diphenyl diisocyanate (MDI) is a solid at room temperature which has melting and boiling points of 38 and 195 °C, respectively. MDI is widely used in both polyurethane and PIR foam. The chemical structure of different types of MDI is shown in Figure 2.2

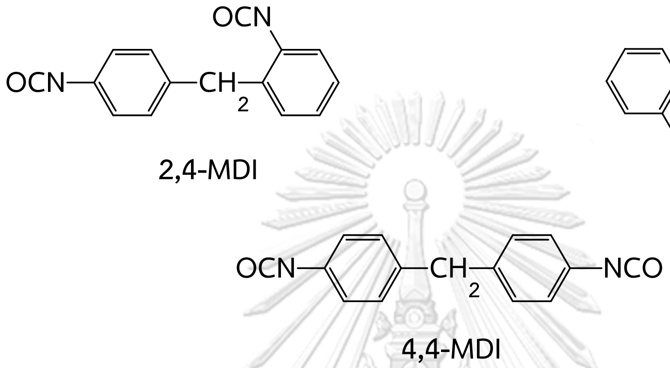
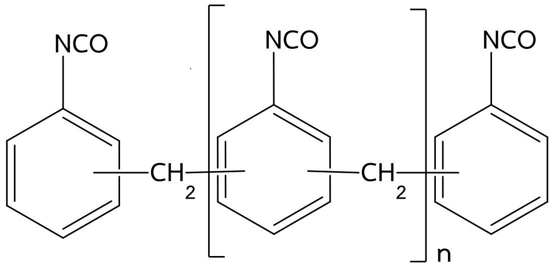


Figure 2.2 Chemical structure of MDI isomers

2.3.1.2 Polymeric methane diphenyl diisocyanate (PMDI)

Polymeric methane diphenyl diisocyanate (PMDI) composes of 4,4-and 2,4-diisocyanate isomers. The chemical structure of PMDI is shown in Figure 2.3. PMDI has low functionality and viscosity. The important properties of MDI and PMDI are shown in Table 2.1



Polymeric MDI (PMDI)

Figure 2.3 Chemical structure of PMDI [15]

Table 2.1 The important properties of MDI and PMDI [15]

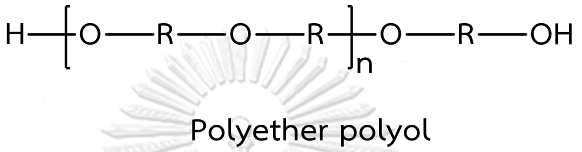
Properties	MDI	PMDI
Physical form	solid	liquid
Molecular weight	250	≈450
Equivalent weight	125	≈225
Functionality	2	2+
Boiling point (°C), at 760 mmHg	170	N/A
Flash point (°C), Cleveland open cup	213	210-230
Fire point (°C), Cleveland open cup	N/A	220-250

2.3.2 Polyols

Polyols contains many hydroxyl groups. Two main types of polyols used for the production of PIR foams are polyether-based and polyester-based polyols. These polyols have different for properties such as chemical structure, functionality, molecular weight and hydroxyl value, which have effect on the final properties of the foams. The polyols used for preparation of the rigid foams have high number of hydroxyl group while the polyols having low number of hydroxyl groups are used in the production for flexible foams. The polyols used for preparation of foam have functionality, molecular weight and hydroxyl value in range 2.5-8.0, 150-1,000 g/mol and 250-1,000 mgKOH/g, respectively [14, 15, 19]

2.3.2.1 Polyether polyols

Polyether polyols are long chain polymers which are synthesized from ring opening reaction using initiation such as ethylene oxide and propylene oxide. Polyether polyols have lower viscosity than polyester polyols. Some polyether polyols can be produced from natural oils, such as soybean, castor and rapeseed. The chemical structure of polyether polyols is presented in Figure 2.4

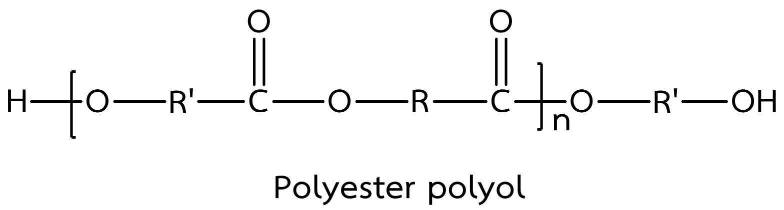


$H{-}[O{-}R{-}O{-}R]_n{-}O{-}R{-}OH$

Figure 2.4 Chemical structure of polyether polyol [17]

2.3.2.2 Polyester polyols

Polyester polyols are synthesized from the condensation reaction of diols and triols with acids such as adipic acid, phthalic acid and sebacic acid. Polyether polyols have higher viscosity and molecular weight than polyether polyols. The chemical structure of polyester polyols is presented in Figure 2.5 [20].



$$H{-}[O{-}R'{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}R{-}\overset{\overset{\large O}{\|}}{C}]_n{-}O{-}R'{-}OH$$

Figure 2.5 Chemical structure of polyester polyols [17]

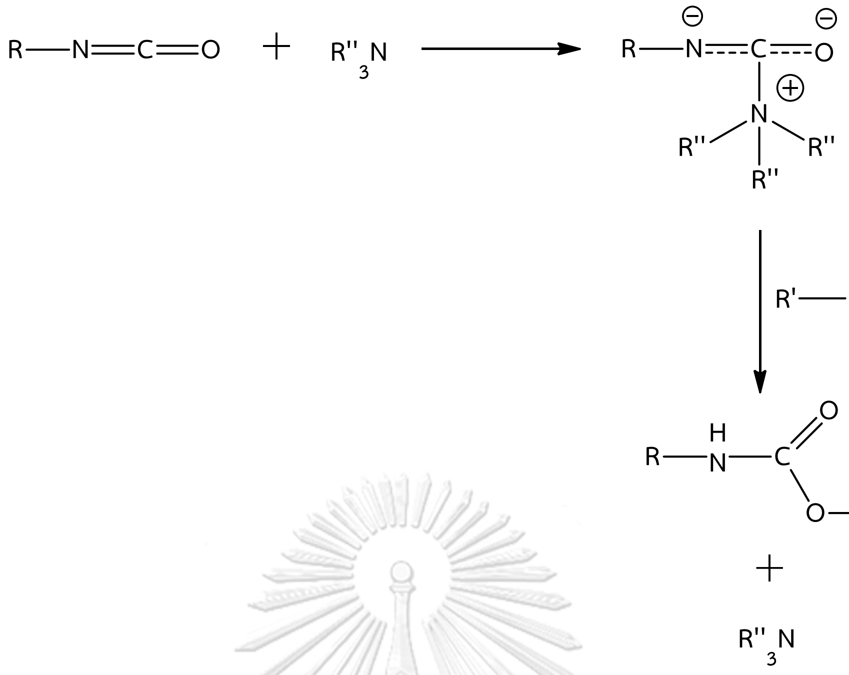
2.3.3 Catalysts

The catalyst used for preparation of the PIR foams accelerate many types of reactions. The gelling catalyst accelerates the reaction between isocyanate and polyols to give polyurethane linkage. The blowing catalyst accelerate the reaction between isocyanate and water to give CO_2. The trimerization catalyst accelerates the trimerization reaction between three isocyanate groups to form isocyanurate linkage [15, 21]. The details of different is described as follow:

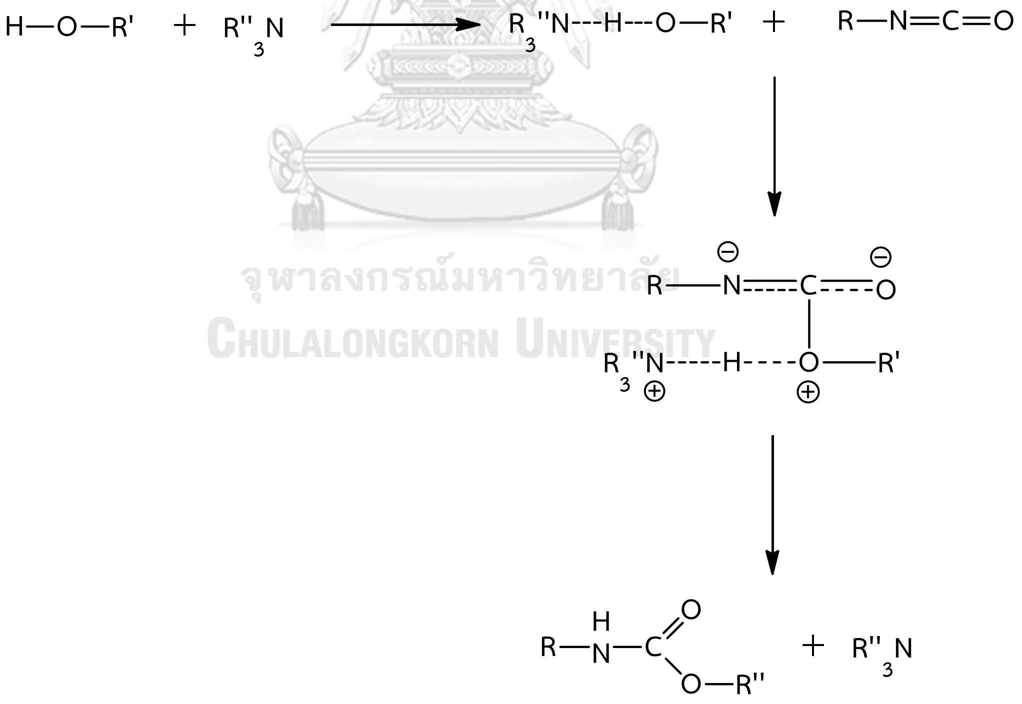
2.3.3.1 Tertiary amines catalysts

Tertiary amines catalysts are widely used for preparation of the foams because these catalysts can accelerate both gelling and blowing reaction. Example of these amine catalysts are triethylenediamine and *N,N*-dimethylcyclohexylamine. There are two catalytic mechanism proposed by Baker (Scheme 2.4) starts by using lone pair of nitrogen atom of tertiary amine to coordinate with carbonyl carbon of isocyanate group and forms an intermediate. Then, the intermediate reacts with the active hydrogen of polyol and water to give urethane linkage and carbon dioxide, respectively.

The catalytic mechanism proposed by Farka (Scheme 2.5) starts by the nitrogen atom of tertiary amine coordinating with hydrogen of polyol to form an intermediate and interacts with isocyanate group to produce urethane linkage [15, 17]



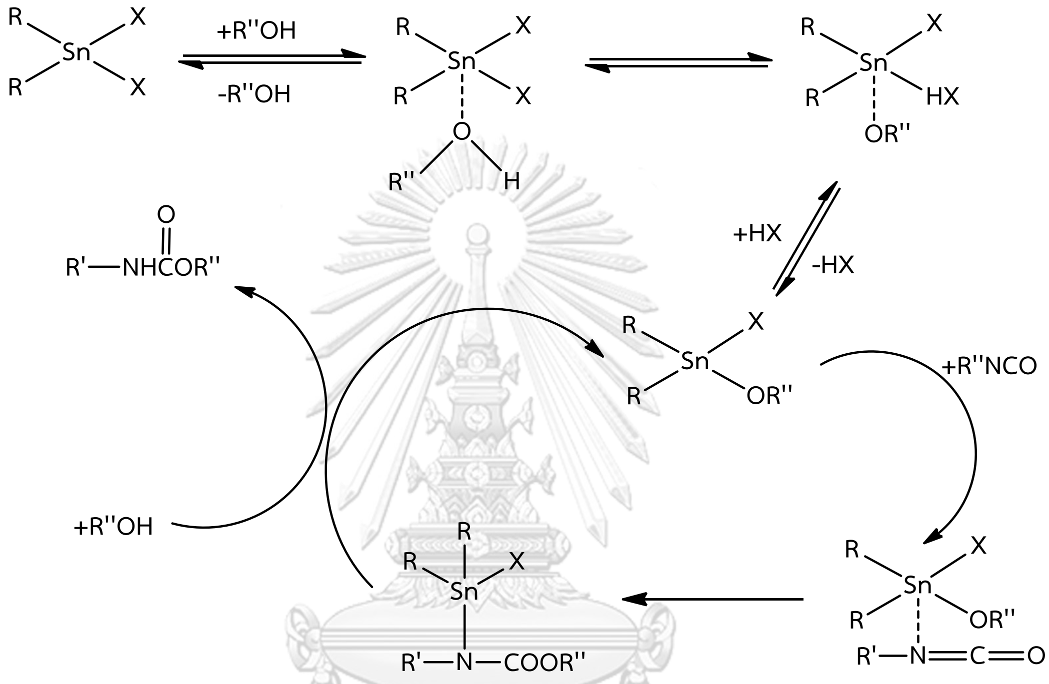
Scheme 2.4 Baker mechanism of amine catalyst [17]



Scheme 2.5 Farka mechanism of amine catalyst [17]

2.3.3.2 Organotin catalysts

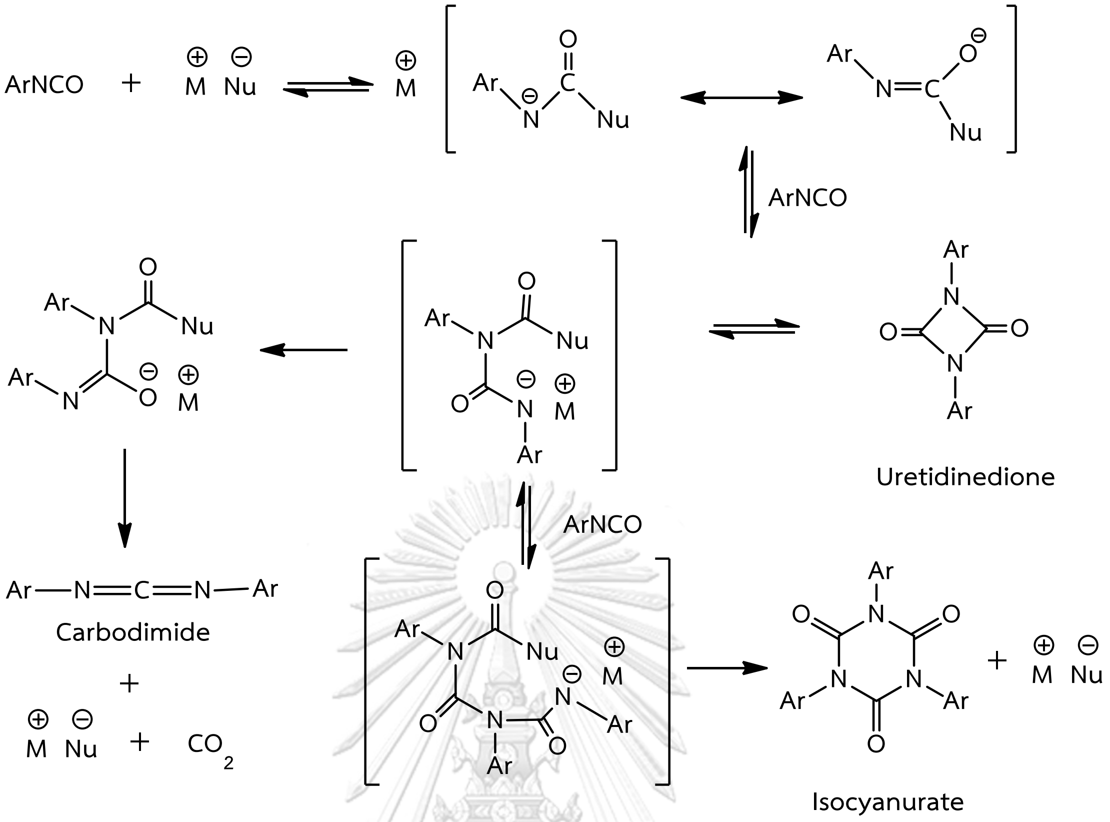
Organotin catalysts can accelerate gelling reaction. An example of organotin catalyst is dibutyltin dilaurate. The catalytic mechanism (Scheme 2.6) starts by reaction between tin and oxygen atom of polyols to form tin alkoxide anion. Then, tin alkoxide anion undergoes reaction with isocyanate to give urethane linkage.



Scheme 2.6 Mechanism of organotin catalyst [17]

2.3.3.3 Trimerization catalysts

Trimerization catalysts are used for accelerating trimerization reaction to produce isocyanurate groups for PIR foam. The widely used trimerization catalysts are potassium octoate, potassium acetate and quaternary ammonium salt. The catalytic mechanism of trimerization catalyst is shown in Scheme 2.7. The trimerization catalyst is nucleophilic and give anionic intermediate reacts with isocyanate and induces the cyclization isocyanate groups [12, 13, 15]



Scheme 2.7 Mechanism of trimerization catalyst [17]

2.3.4 Blowing agents

Blowing agents are used for generating gas bubble and expands the foam to create the cellular structure. The blowing agent can be categorized in two types: (i) physical blowing agents and (ii) chemical blowing agent. Water is the most widely used as chemical blowing agents due to low cost and environmentally friendly. Water cab react with isocyanate to generate CO_2 gas bubble. Hydrochlorofluorocarbon (HCRCs), hydrofluorocarbon (HFCs), chlorofluorocarbon (CFCs), and hydrofluoroflu orinate-hydrocarbon (PFCs), are physical blowing agents which create the cellular structure by evaporation process. The physical blowing agent give lower foam density than chemical blowing agent [22].

2.3.5 Surfactants

Surfactants are important additives for preparation of PIR foams. In foaming process, surfactants can reduce surface tension and stabilize gas bubble for nucleation process [13]. Figure 2.6 shows the chemical structure of silicone surfactant which is widely used for the production of foams. X and Y are the average number of repeating units. The amount of surfactant, which is added into the foam formulation, is 0.4-2.0 part by weight (pbw) of polyol [15, 17, 23].

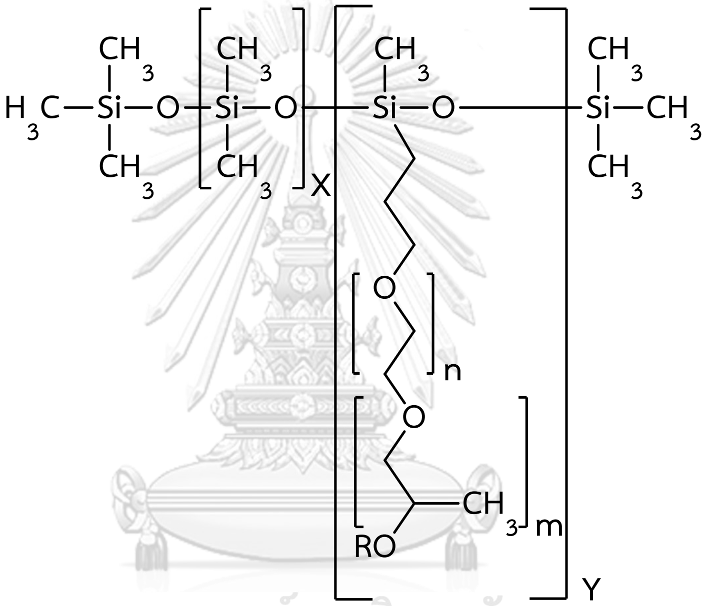


Figure 2.6 Chemical structure of silicone surfactant [17]

2.3.6 Fillers

Fillers are added in foam formation to improve mechanical, thermal and fire-retardant properties of foams. In addition, fillers can also reduce the cost for production of foam. However, addition of large amount of filler into the foams will reduce their compressive properties [24].

2.4 Foam Formulation

In foam formulation, the amount of isocyanate for the reaction with polyol and other starting materials is calculated to obtain stoichiometric equivalent in order to obtain the theoretical amount of isocyanate. The theoretical amount of isocyanate depends on several parameter, such as ambient conditions, amount of reactive functional groups and production scales. The amount of isocyanate is called the isocyanate index, which can be calculated by the equation as follows [13, 25]:

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

The equations for calculating the amount of other reactive starting materials, such as polyol, in parts by weight (pbw) unit are shown as follow:

Isocyanate value (%NCO) is the percentage of weight for reactive isocyanate group:

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

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

Hydroxyl value or hydroxyl number of the polyol is amount of reactive hydroxyl groups are unit weight of the polyol. The hydroxyl value is determined as the milligrams of potassium hydroxide (KOH) equivalent to the active hydroxyl content of 1 g of the polyol (mg KOH/g of polyol).

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

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

Water content is the amount of water which reacts with isocyanate groups. The equivalent weight of water is calculated as follow:

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

After the foaming reaction is finished, isocyanate conversion is calculated by peak area of ATR-FTIR method, which is defined as ratio between peak area of final isocyanate (NCO^f) and peak area of initial isocyanate (NCO^i) as follow:

Where: NCO^f = peak area of final isocyanate

NCO^i = peak area of initial isocyanate

2.5 starch

Starch is one of the most readily available inexpensive natural polymers which shows the advantage as biodegradable and non-toxic material. Example are corn, potato, rice and wheat starches. Starch contains two main types of polysaccharide units, namely amylose and amylopectin. Amylose is linear polysaccharide and is coiled like spring (Figure 2.7), which glucose units connect with α-1,4-glycosidic linkages. Amylopectin is highly branched-chain polysaccharide, which glucose units connect with α-1,4-glucoside and α-1,6-glycosidic linkages (Figure 2.8). Generally, starch consists of 20-25% of amylose and 75-80% of amylopectin [7, 26].

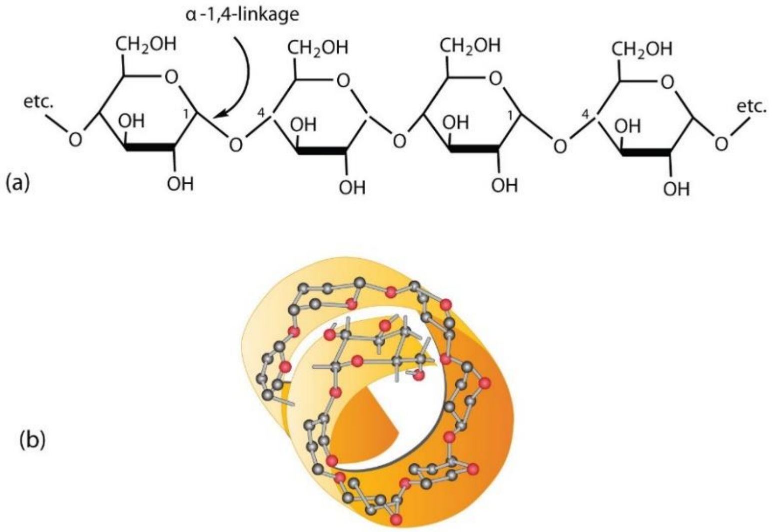


Figure 2.7 Chemical structure of amylose [27]

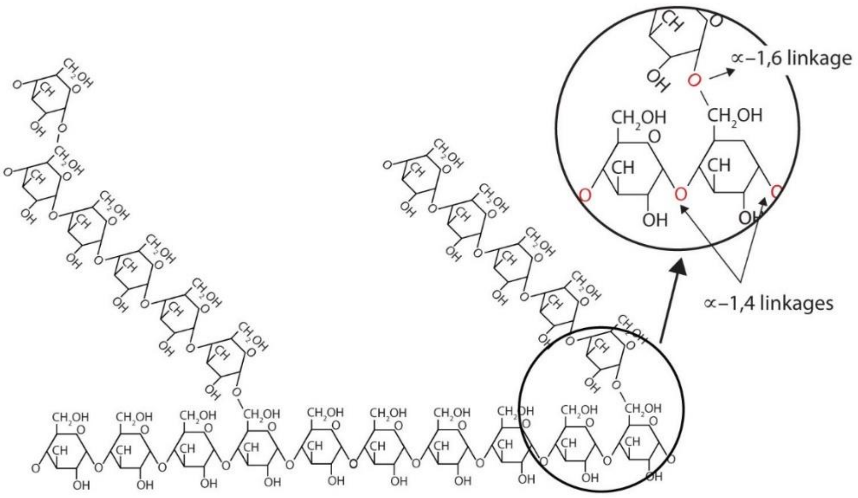


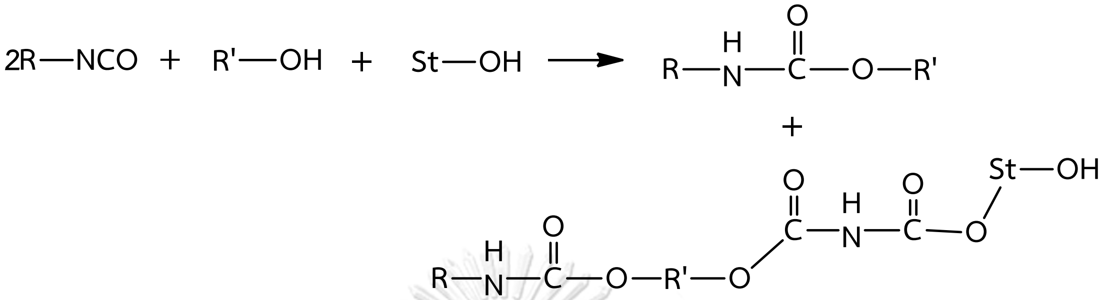
Figure 2.8 Chemical structure of amylopectin [27]

Molecular of starch compose of hundreds or thousands of glucose monomer. Other components of starch are protein, carbohydrate, fat and moisture, which depends on types of starch. Currently, the industry used starch for coating, binders and adhesive [28]. The components of starches used in this work, namely glutinous rice flour, rice flour and mung bean starch are presented in Table 2.2

Table 2.2 Component of starches [29-32]

Components	**Amount of component in starches (%)**		
	Glutinous rice flour	**Rice flour**	**Mung bean starch**
Amylose	5	24	45
Amylopectin	95	76	54
Protein	6.78	7.5	22
Moisture	7.21	10.25	12.72
Carbohydrate	87.23	81.55	59.77

Starch is reactive filler since it composes of hydroxyl group (OH). Therefore, starch can undergo reaction with isocyanate compounds in foam formation. The reaction of starch (St-OH) with isocyanate is shown in Scheme 2.8



Scheme 2.8 Reaction of starch with isocyanate [33]

Moreover, the advantage of starch is its fire-retardant property. Upon heating, starch can release incombustible gases as product, such as water and carbon dioxide and char forms cover the surface to prevent oxygen and heat transfer [28].

2.6 Compressive property

Compressive property is an essential mechanical property for PIR foams. The compressive property of PIR foams depends on density and morphology of foam cell. Rigid and flexible foams contain mostly closed-cell and opened-cell structure, respectively (Figure 2.9). The compression test can be measured according to ASTM D 1621-16. The tests are measured in two direction, namely parallel and perpendicular to foam rising direction. The compressive strength of cell structure in parallel rising direction is higher than that in perpendicular direction.

Energy absorption characteristic of PIR foams can be shown in terms of compression stress-strain curve (Figure 2.9). Compressive strength of the foams is reported at 10% deformation [34, 35].

Figure 2.9 Appearance of opened-cell (a) and closed-cell (b) [36]

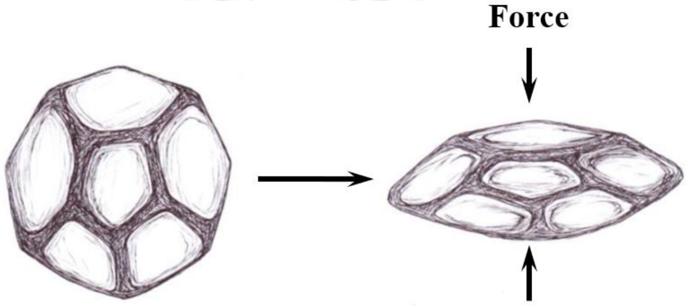


Figure 2.10 Appearance of closed-cell structure during compression test [36]

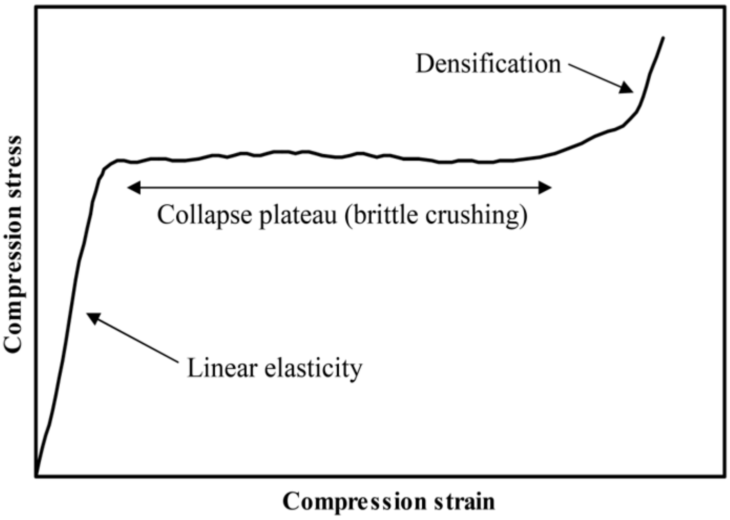


Figure 2.11 typical compressive stress-strain curve for rigid foam [37]

2.7 Literature reviews

The literature reviews are the previous researches about the catalyst and methods for preparation of PIR foams modified with different types of filler. These works are described as follow:

2.7.1 Catalyst for PIR foams

In 2019, our research group [11] reported the use of catalyst mixture between zinc-ammonia complexes and potassium octoate solution in diethylene glycol [Zn(Amm)+KOct] in the preparation of rigid polyisocyanurate-polyurethane (PIR-PUR) foams. Zn(Amm) was a gelling/blowing catalyst and KOct is a trimerization catalyst. The purpose of this research is to compare their catalytic activity with the commercial catalyst mixture, DMCHA+KOct, where DMCHA is *N,N*-dimethylcyclohexylamine which is a gelling/blowing catalyst. The properties of rigid PIR-PUR foams were also investigated. The result show that PIR-PUR foam prepared from [Zn(Amm) +KOct] had better compression property that that prepared from DMCHA+KOct. All PIR-PUR foams showed the self-extinguishing property.

Therefore, Zn(Amm)+KOct was used as catalyst for the preparation of PIR foams in this work. The synthesis of Zn(Amm) is shown in Figure 2.12

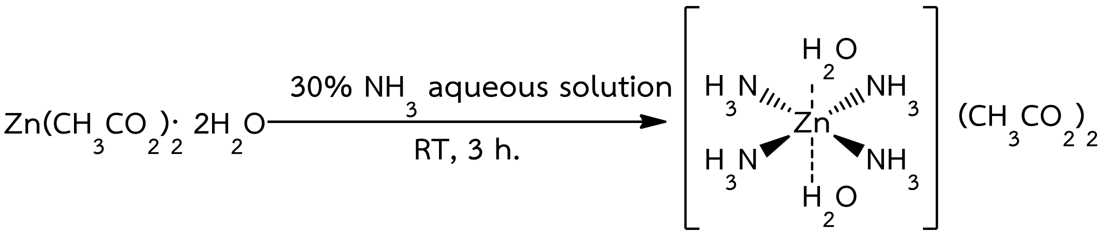


Figure 2.12 The synthesis of zinc-ammonia complex [11]

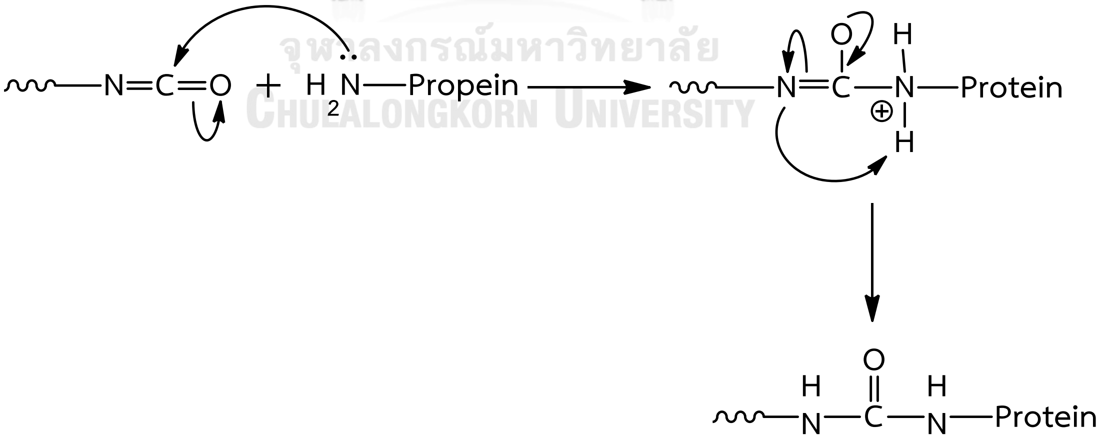
2.7.2 PIR foams modified with fillers

In 2019, Monika *et al.* [38] added fly ash at the amount of 5-20 wt% as compared with the mass of polyols for preparation of rigid PU foams. Fly ash is cheap and has good flame-retardant property. The fly ash composed of sulfur dioxide (SO_2) and calcium oxide (CaO), which can enhance the nucleation during foam formation process. Moreover, CaO can react with SO_2 and O_2 to from $CaSO_4$ which $CaSO_4$ is noncombustible. Thus, the addition of fly ash can improve thermal stability of rigid PU foam because fly ash gave barrier that protected the foam structure. However, the addition of fly ash over 10 wt% caused rupture of cell wall and decreased of mechanical properties for modified foam. It was found that addition of 20 wt% of fly ash reduced the compressive property from 216 to 188 MPa. The incorporation 10 wt% of fly ash was the suitable amount for rigid PU foam.

Acuna *et al.* [39] investigated effect of expandable graphite on flame retardancy and mechanical properties of rigid PU foam. Expandable graphite (0-10 wt% as compared with mass of isocyanate) was used as a filler. The foam modified with expandable graphite had higher density and viscosity than those without expandable graphite. Moreover, expandable graphite decreased the cell size and compressive strength of rigid PU foam. This is because of the poor compatibility between and PU foam matrix and expandable graphite. Therefore, rigid PU foam with expandable graphite was more heterogeneous than neat foam. However, there was advantages that the addition of expandable graphite increased thermal conductivity (from 43 to 47 mW/mK) and limit oxygen index (from 19.2 to 29.8) of rigid PU foam. The optimum amount of expandable graphite that can be added into rigid PU foam is 10 wt%.

Liszkowska *et al.* [40] studied the effect of cinnamon extract as filler in the range 5-15 wt% as compared with total mass of polyol and isocyanate on PIR-PUR foam properties. The cinnamon extract composition was 5% of polyphenol and small other composition (arsenic, chloride and sulphate). At 15 wt% of cinnamon extract, the apparent density of modified PIR-PUR foams decreased from 39.67kg/m^3 to 33.97 kg/m^3. Therefore, its compressive strength decreased from 251.63 kPa to 147.29kPa due to destruction of characteristic bond (cracking urethane bond). There was an advantage that the addition of 15 wt% of cinnamon extract increased limited oxygen index (LOI) of PIR-PUR foam from 18.5% to 20.2%.

In 2018, Czlonka *et al.* [41] prepared rigid PU foams and used protein from potato as a filler in the range 0-15 wt% of total polymer content in order to improve mechanical and thermal properties of PU foams. The chemical structure of potato protein contains reactive groups in the molecule, namely carboxyl group (-COO), primary and secondary amine (NH) and hydroxyl group (OH) in the side chain. Therefore, the reactive groups in potato protein can undergo reactions with isocyanate. Amine has higher reactivity in reaction with isocyanate than carboxyl and hydroxyl group. The mechanical between amine groups of potato protein and isocyanate is shown in Scheme 2.9



Scheme 2.9 Mechanism of reaction between amine groups and isocyanate [41]

It was found that the addition of 0.1 wt% of potato protein resulted in the increased in foam density (34.2 to 38.1 kg/m^3), compressive strength (187 to 230 kPa) and thermal conductivity (0.020 to 0.029 W/mK) as compared with unmodified foam. This is because the reactive group in potato protein can undergo reactions with isocyanate groups and therefore the modified PU foam has highly-crosslink structure. However, the addition of potato protein more than 0.1 wt% into PU foam caused the reduction of apparent density and compressive strength of modified foam. This was because the dispersion of potato protein was not homogeneous which resulted in smaller closed cell and thinner call wall.

In the same year, Czlonka *et al.* [42] prepared rigid PU foams and reinforced with buffing dust in the range 0.1-5 wt% of total polyol mass. Buffing dust is a solid waste generated in leather industry. Buffing dust, similar to potato protein, contains protein, fat, moisture and chromium (III) oxide. Therefore, the mechanism and effect of buffing dust on properties of modified foam are similar to those in the case of potato protein. It was found the addition of 0.1 wt% of buffing dust resulted in the increased in foam density (36.2 to 36.9 kg/m^3) and compressive strength (189 to 216 kPa) as compared with neat foam. The optimum amount of buffing dust that can be added into rigid PU foam is 0.1 wt%

Addition of buffing dust over the optimum amount leads to reaction of the mechanical of modified foam. For example, addition of 5 wt% buffing dust into PU foam caused irregular cell structure such as rupture of cell structure and defective shape (Figure 2.13a). This is because buffing dust can attach to the cell wall (Figure 2.13b)

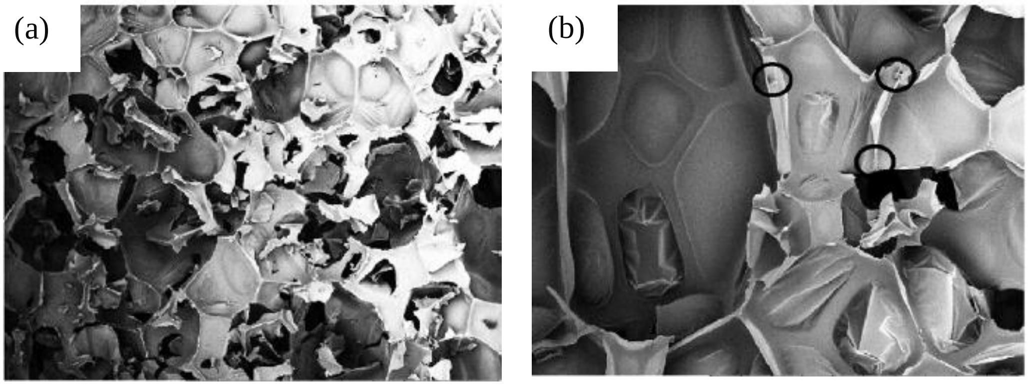
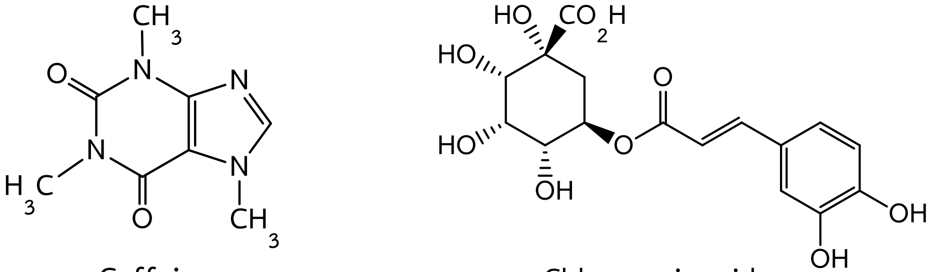


Figure 2.13 Foam morphology for 5 wt% of buffing dust [42]

In 2018, Liszkowaka [43] investigated the effect of ground coffee (2.5-15 wt% of total content of polyol) on the properties of rigid PIR-PUR foams. The coffee composes of organic compounds such as carbohydrate, caffeine and chlorogenic acid (Figure 2.14), which have reactive group. Thus, they can react with isocyanate group in system. When 2.5 wt% of ground coffee was added in foam formula, density of the modified foam increased from 46 to 54 kg/m^3 as compared with unmodified foam. In contrast, the compressive strength of foam modified with ground coffee decreased from 377 to 133 kPa as compared with unmodified foam. The ground coffee had effect on cell morphology of foam, which the ground coffee particle could attach on the cell walls and caused defect on cell structure.



Caffeine **Chlorogenic acid**

Figure 2.14 Chemical structure of caffeine and chlorogenic acid [43]

In 2016, Obaid *et al*. [44] used lignin as substitute for polyol and reinforcing agent to prepare PU foam. Lignin has complex structure, which composes of aliphatic and aromatic hydroxyl group. The aromatic groups of lignin cause stiffness of polymer chain, as the result, the obtained PU foam was brittle.

From the drawback of lignin as mentioned above. Butanediol was added as a chain extender to improve the compressive strength of PU foam-based lignin. The result showed that the compressive strength of butanediol modified foam increased from 350 to 375 kPa as compared with the unmodified. The proposed polyurethane network (Figure 2.15) indicates that the hydroxyl group of lignin can react with isocyanate group. Therefore, this work suggests that the hydroxyl group of starch can also react with isocyanate group.

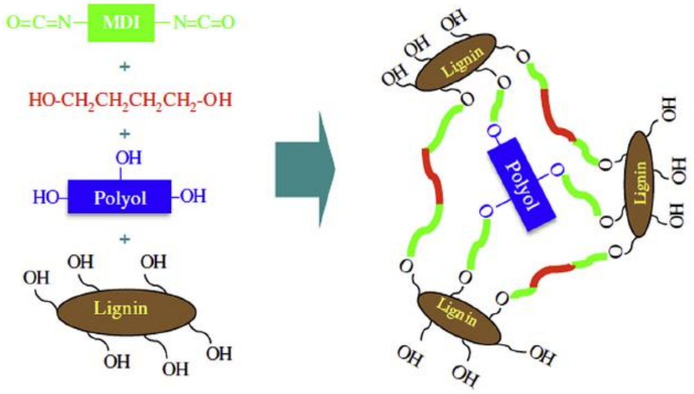


Figure 2.15 Reaction of lignin with isocyanate and polyol [44]

In 2014, Cabulis *et al.* [45] prepared PIR foam modified with organomodified montmorillonite clay loading at 1-5 wt% as composed to polyol mass to improve mechanical properties. However, the compressive strength of PIR foams decreased when increasing the amount of montmorillonite clay due to the presence of montmorillonite clay agglomerate.

Gao *et al*. [46] investigate effect of composite flame retardancy expandable graphite (10-30 wt% as compared to polyol mass) and diethyl ethylphosphonate (5-15 wt% as compared to polyol mass) on fire-retardant property of PIR foam. The results indicate that ratio of expandable graphite and diethyl ethylphosphonate as 2:1 improved fire-retardant property of PIR foams and increased limit oxygen index from 18 to 19% when compared with unmodified foam. This is due to thermal expandable graphite. Moreover, diethyl ethylphosphonate contains phosphorus which produces barrier layer to cover the surface of foams.

In 2012, Piszczyk *et al.* [47] prepared of PIR foam and used three types of montmorillonite clay, namely Cloiste 30B, Laponite RD and Bentonite as filler. The amount of fillers was 6 wt% as compared to polyol mass. It was found that the PIR foams modified filler showed increase in both density and compressive strength. Especially, in the case of PIR foam modified Cloisite 30B, which had the lowest density while having highest compressive strength (Table 2.3). This is due to Cloisite 30B contains hydroxyl groups which can form hydrogen bond with polyol.

Table 2.3 The average value of density and compressive strength of PIR foams modified with montmorillonite clay [47]

Montmorillonite clays	Density (kg/m^3)	Compressive strength (kPa)
Unmodified foam	21.7±0.69	100.0±3.4
Cloisite 30B	34.4±1,06	176.0±5.9
Laponite RD	36.1±1.11	146.0±6.1
Bentonite	41.6±1.91	174.0±5.3

In 2009, Czuprynski *et al*. [33] investigated the properties of rigid PIR-PUR foam modified with potato starch as a filler at 2.5-20 wt% as compared to the sum of mass of polyisocyanate and polyol. As compared with the unmodified foam, rigid

PIR-PUR foam modified with potato starch had decreased apparent density (from 38 to 30 kg/m^3) and compressive strength (from 221 to 122 kPa).

In 2007, Paciorek-sadowska *et al.* [48] investigating the preparation of rigid PIR-PUR foam by using wheat slop as a filler at 5-30 wt% in relation to the sum of isocyanate and polyether polyol content. Wheat slop is solid fraction obtained by fermentation of wheat starch milk. Wheat slop contains fat, fiber, protein and mineral compounds (phosphorus, sodium and chloride). As compared with the unmodified foam, the foam containing 30 wt% of wheat slops shows decrease in the brittleness (from 41.6% of unmodified foam to 16.9%). Other properties, namely compressive strength, apparent density and closed cell content also decreased.

Czuprynski *et al.* [49] investigated the preparation of PIR-PUR foams modified with potato slop in the range 5-30 wt% as compared with total polyisocyanate and oligodiol. Potato slop contains 94% of water and 6% of dry mass. The dry mass of potato slop contains fat, protein and mineral compounds (calcium, phosphorus, copper, iron and sodium) and was applied as a filler to reduce cost. The amount of potato slop increase, there was no change in apparent density and limit oxygen index of foam (36.2±0.1 kg/m^3 and 24.8±0.1% respectively). However, increasing amount of potato slop decreased the compressive strength of modified foam (from 196.1 kPa to 180.6 kPa) and softening point (221.5 °C to 203.0 °C)

Chen *et al*. [50] synthesized the modified polyol by ring opening of oxirane group in soy-based polyol with 2-carboxylphenyl phosphonic acid (CEPPA) (Figure 2.17). This modified polyol was used in the preparation of PIR foams (Bio-PIR) and expandable graphite (10-20 wt%) was added as a filler.

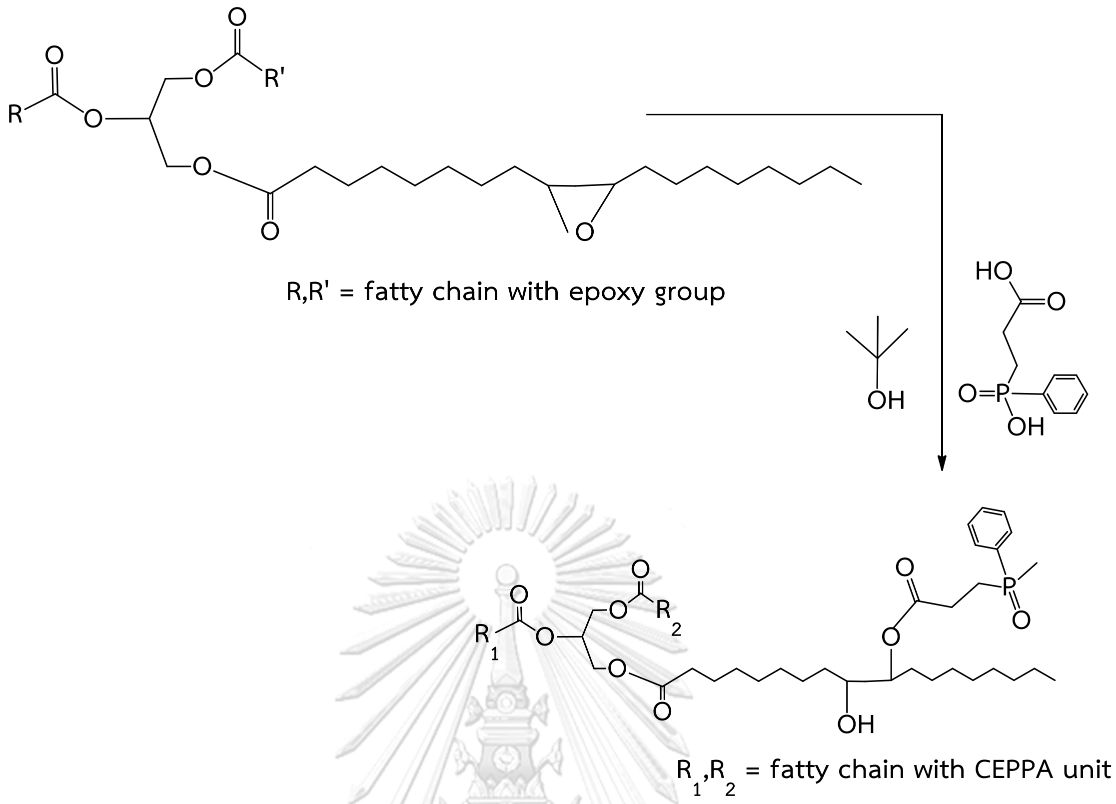


Figure 2.16 Synthesis of modified polyol having 2-carboxylethylphenyl phosphonic acid (CEPPA) unit [50]

As compared to the unmodified foam, the limit oxygen index of Bio-PIR foam was improved by 35% and the Bio-PIR foam had self-extinguish property. However, the compressive strength of Bio-PIR foam decrease. When added 20 wt% of expandable graphite because the addition of expandable graphite increased the brittleness of foam.

The mechanism of flame retardancy of Bio-PIR foam was proposed as known in Figure 2.17. The CEPPA unit in Bio-PIR foam (PCSO/BY30) caused the release of gaseous products and water to reduce pyrolysis process while expandable graphite upon heating and product char.

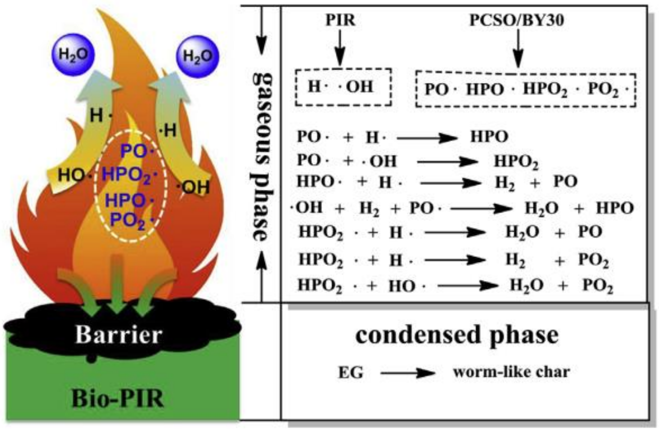
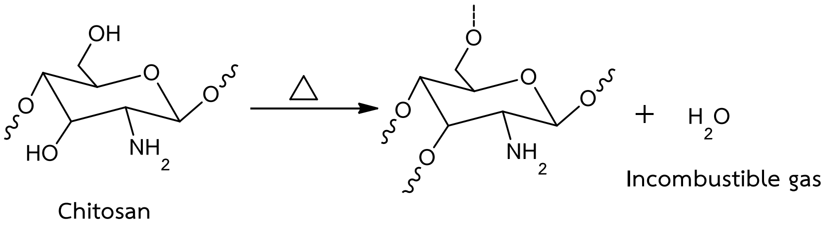


Figure 2.17 Mechanism of flame retardancy of Bio-PIR foam [50]

Prabhakar and Song [9] investigated flame-retardant property of starch/chitosan /flex fabric green composite. The hypothetical mechanism suggests three steps for the mechanism of flame retardant of chitosan structure during burning (Figure 2.18). In the first step, the chitosan structure promotes the release of water molecules. In the second step, chitosan undergoes ring opening reaction, promotes the formation of polyhydric alcohol and releases ammonia molecules. In the last step, the polyhydric alcohol can be self-condensed by absorb free radical to form as hexatomic ring or char structure.

In this investigation, starch/chitosan/flex fabric green composite, was found increased significantly of fire retardant at 6% and limit oxygen index from 21 to 48.7% as compared to without green composite. Moreover, the tensile strength was increased from 16.45 to 20.78 MPa.

First step



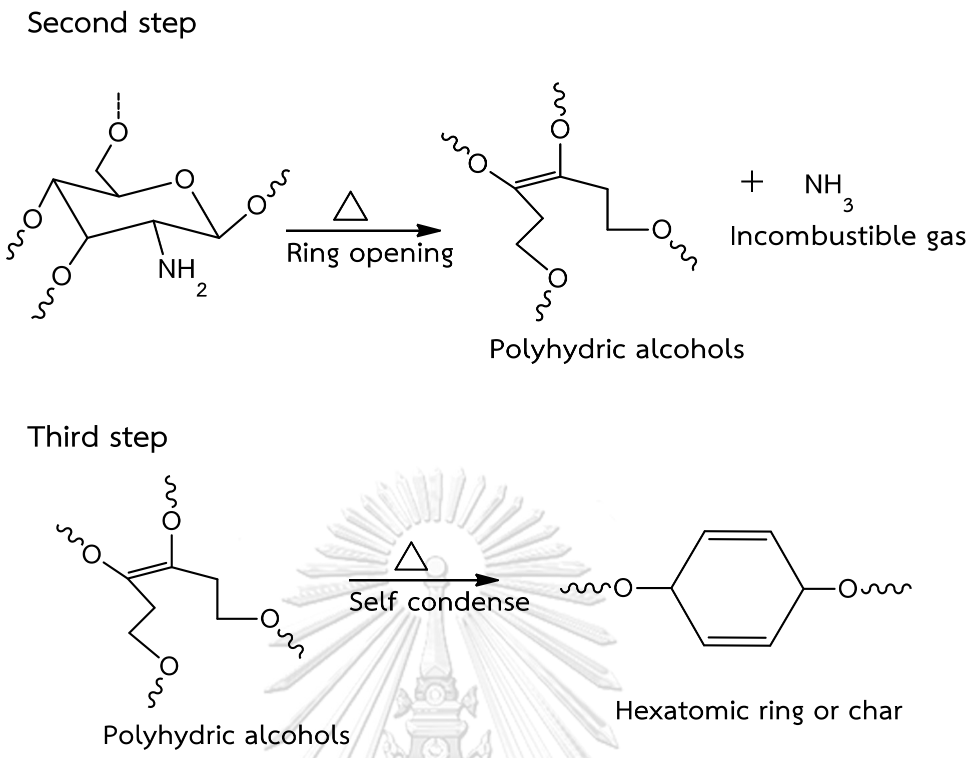


Figure 2.18 Flame-retardant mechanism of chitosan during combustion process [9]

Since the structure of starch is partly similar to that of chitosan. Therefore, the mechanism shown above suggest the possibility that the mechanism of starch during combustible process might be partly similar to that of chitosan. Therefore, addition of starch into PIR foams might enhance the fire-retardant property of PIR foams.

According to the above literature review, this research used starches as fillers in the preparation of PIR foams. PIR foams were prepared using the catalyst system [Zn(Amm)+KOct] developed in our research group [11]. These types of starch, which was produced in Thailand, namely glutinous rice flour, rice flour and mung bean starch were as filler. It was expected that PIR foams modified with starches would have less density and good fire retardancy

CHAPTER III

EXPERIMENT

3.1 Chemicals

3.1.1 Chemicals for zinc-ammonia complex preparation

Zinc (II) acetate dihydrate [$Zn(OAc)_2{\bullet}2H_2O$] and ammonia (NH_3) solution with 30% of concentration was obtained from Nacalai Tesque, Kyoto in Japan and Carlo Erba, Val de Reuil in France.

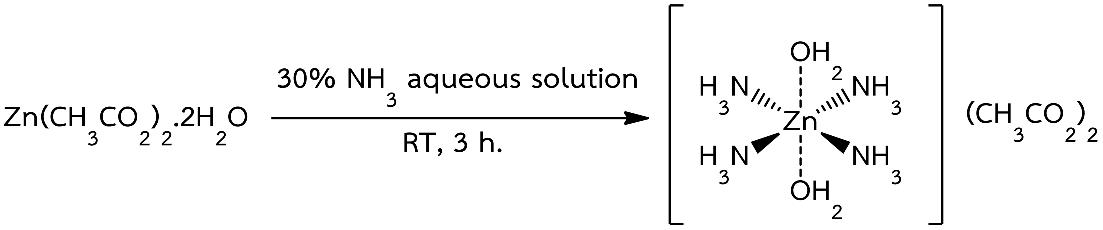
3.1.2 Chemicals for polyisocyanurate (PIR) foam preparation

Polymeric diphenyl methane diisocyanate (PMDI, B9001$^{\circledR}$, %NCO = 31.0 wt%, average functionality = 2.7), polyether polyol (Polymaxx$^{\circledR}$4221, hydroxyl value = 440 mg KOH/g, functionality = 4.3), potassium actuate with 70 wt% of concentration in diethylene glycol (Dabco$^{\circledR}$K-15, K-15:DEG = 70:30, trimerization catalyst) and polysiloxane surfactant (Tegostab$^{\circledR}$B8461) were obtained from IRPC Public Company Limited. Water was used as chemical blowing agent. Starches (glutinous rice flour, rice flour and mung bean starch) were used as filler. The starches were dried at a temperature of 80 °C before used.

3.2 Synthesis procedures

3.2.1 Synthesis of zinc-ammonia complex in aqueous solution

Zinc-ammonia complex was synthesized by reaction between $Zn(OAc)_2{\bullet}2H_2O$ and NH_3 solution with 30% concentration in water to obtain the 25 wt% aqueous solution of Zn(Amm) (Scheme 3.1) for using as catalyst in the preparation of PIR foam. The synthesis of Zn(Amm) was done following the method from previous research [11] as following: NH_3 solution with 30% of concentration (0.60 ml, 9.41 mmol) was added into water (3.63 ml). After that, $Zn(OAc)_2{\bullet}2H_2O$ (0.341 g, 1.55 mmol) was added and the solution was stirred at room temperature for 3 hour. The aqueous solution of Zn(Amm) was a colorless solution with low viscosity.



Scheme 3.1 Synthesis of zinc-ammonia complex in aqueous solution

3.2.2 Preparation of polyisocyanurate (PIR) foam

The PIR foams was prepared using two methods, namely cup test method and plastic molded method (Figure 3.1). PIR foams were prepared at isocyanate index of 200 and 300. Zn(Amm) (gelling/blowing catalyst) was mixed with potassium actuate (KOct, isocyanurate catalyst) as the catalyst system. PIR foams obtained from cup test method were used for investigation of reaction time, apparent density, rise profile, temperature profile, isocyanate (%NCO) conversion and ratio of polyisocyanurate per polyurethane (PIR/PUR) by using FTIR spectroscopy. PIR foams obtained from plastic molded method were used for investigation of compression strength, morphology by scanning electron microscope (SEM) and fire-retardant property.

3.2.2.1 Polyisocyanurate (PIR) foam preparation by cup test method

The cup test method was composed of two steps of mixing. Foam formulation in parts by weight (pbw) unit are shown in Table 3.1. The processing for PIR foams were carried out as follow: in the first step, polyol, starch (glutinous rice flour, rice flour and mung bean starch), catalyst (Zn(Amm) and potassium octoate) and surfactant were mixed by hand in paper cup (750 ml) to obtain homogeneous mixture. In the second step, PMDI was added into the polyol mixture in paper cup from the first step. Finally, the reaction mixture was mixed by mechanical stirrer at 2000 rpm for 20 second. PIR foams were allowed to rise freely at room temperature. The reaction time, namely cream time, gel time, rise time and tack free time were recorded. PIR foam were measured kept at room temperature for 48 hours before investigation of other properties. The foam samples were cut into a cubic shape of 3.0 × 3.0 × 3.0 cm (length × width × thickness) (Figure 3.2) for measurement of apparent density, %NCO conversion and PIR/PUR ratio.

3.2.2.2 Polyisocyanurate (PIR) foam preparation by plastic mold method

The preparation of PIR foams using plastic mold was carried out using the same method as cup test method, except the amount of all starting materials was increased 5 times as compared to cup test method. After the mixture was poured into the plastic mold with the dimension of 10 × 10 × 10 cm (length × width × thickness), the foam was allowed to rise freely at room temperature. The molded PIR foams were kept for 48 hours (Figure 3.3) then cut into cubic shape of 5.0 × 5.0 × 5.0 cm (length × width × thickness) for investigation of properties.

Table 3.1 Formulation for preparation of PIR foams (parts by weight unit, pbw)

Starting materials	NCO index (pbw)		
	200	**250**	**300**
Polyether polyol (Polymaxx®4221)	100	100	100
Polysiloxane surfactant (Tagostab®B8461)	2.5	2.5	2.5
Chemical blowing agent (H_2O)	4.0	4.0	4.0
Gelling and blowing reaction catalyst (Zn(Amm))	0.5	0.5	0.5
Trimerization catalyst (potassium actoate)	3.0	3.0	3.0
PMDI (B9001®)	313.68	392.10	470.52
Starch (glutinous rice flour, rice flour, mung bean starch compared to polyol mass)	10-30 wt%		

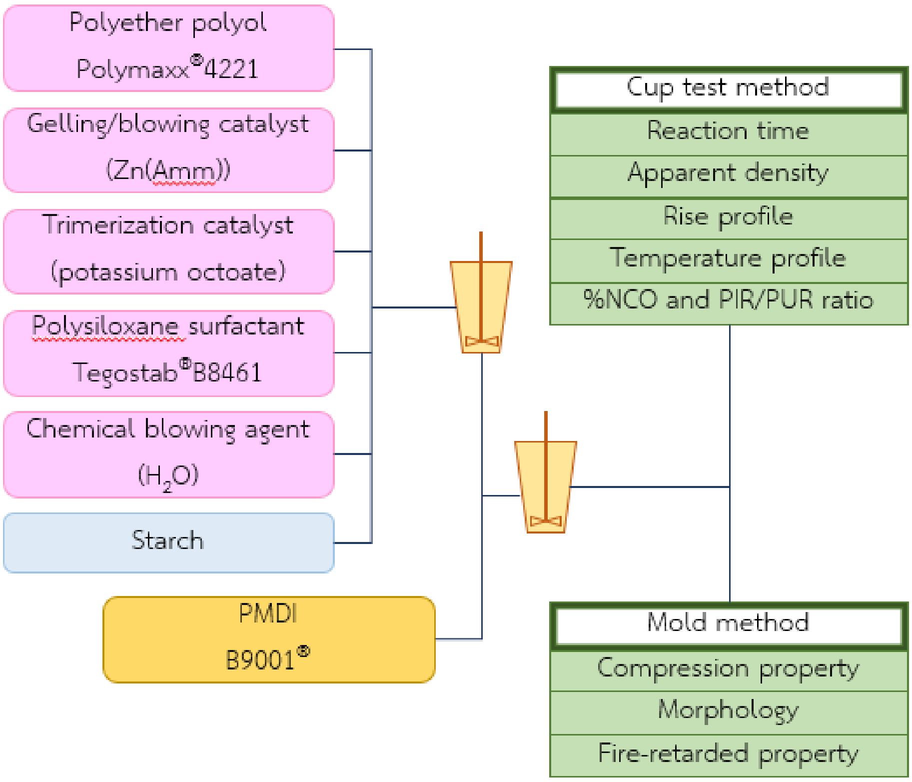


Figure 3.1 Processing step for preparation of PIR foams

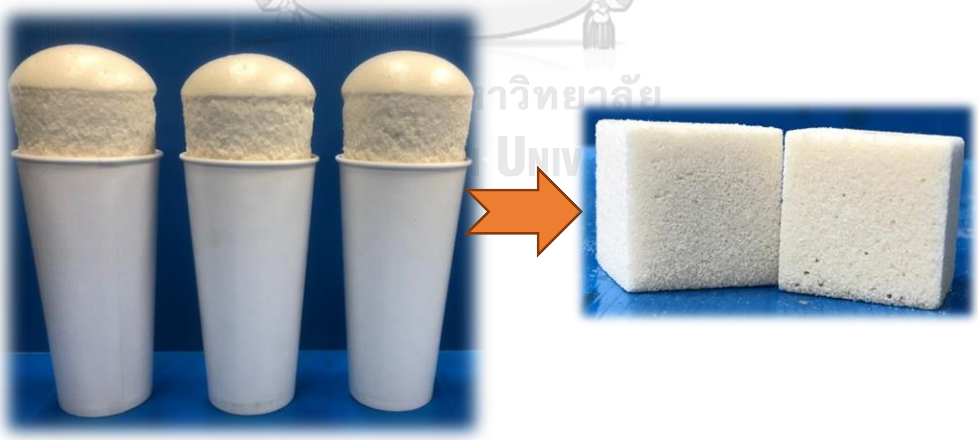


Figure 3.2 PIR foams prepared by cup test method and cut into the cubic shape

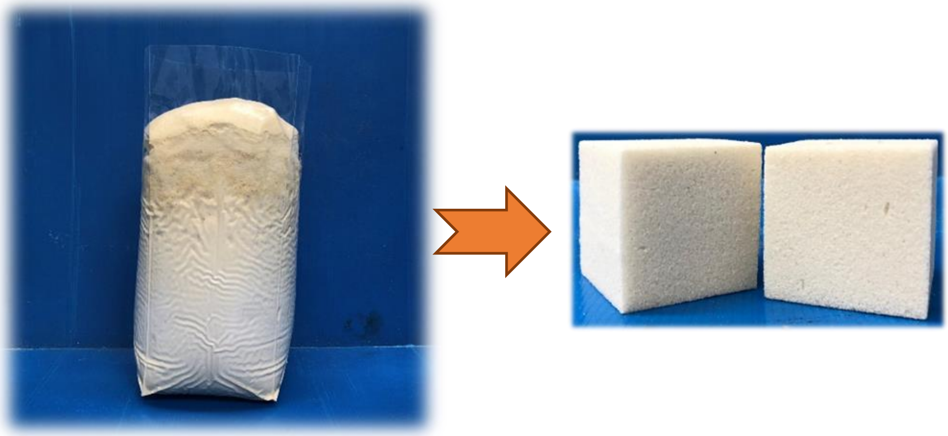


Figure 3.3 PIR foams prepared by plastic mold method and cut into the cubic shape

3.3 Characterization of PIR foams

3.3.1 Reaction times

The reaction times of PIR foams, namely cream time (the mixture of starting materials changes from clear liquid to creamy mixture and the foam height is 5% of the final foam height), gel time (the polymerization starts and the mixture appears like gel), rise time (generation of CO_2 stops and the foam expansion stops) and tack free time (polymerization reaction finishes and the foam surface is dry). All reaction times were measured by digital stopwatch in according to ASTM D7487-13.

3.3.2 Apparent density

The apparent density of PIR foams was measured according to ASTM D1622-08. The density was calculated from mass to volume ratio of sample. The sample of PIR foam were cut into a cubic shape of 3.0 × 3.0 × 3.0 cm (length × width × thickness)

3.3.3 %NCO conversion and PIR/PUR ratio

%NCO conversion and PIR/PUR ration of the foams was calculated from peak area in ATR-FTIR spectrum. The FTIR spectrometer range was 4000-800 cm^{-1} at a resolution of 4 and the number of scans were 16 scans. The IR peaks of functional group in PIR foams shown in Table 3.2 were used for calculation [25, 51]

Table 3.2 Characteristic IR peaks in PIR foam

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

3.3.4 Rise profiles

Rise profile of PIR foam were plotted between %height and time. The rise profiles were measured when the foam started to expand to the time when expansion was finished. The suitable catalyst should give the smooth graphs.

3.3.5 Temperature profiles

The temperature profiles were plotted between foaming temperature and time. The data were detected every 10 second by using Digicon DP-17 thermocouple, which its sensor was placed in the middle of foam sample. The highest of temperature was reported as the maximum core temperature.

3.3.6 Compression strength

The compression properties of PIR foam were investigated in two direction, namely parallel and perpendicular to foam rising direction (Figure 3.4) according to ASTM D1621-16 by universal testing machine (Hounsfield H 10 KM). The sample of PIR foam were cut into a cubic shape of 5.0 × 5.0 × 5.0 cm (height × width ×

thickness). The compression force is 0.100 N which moves at 2.54 mm/min. the data was recorded at 10% stain

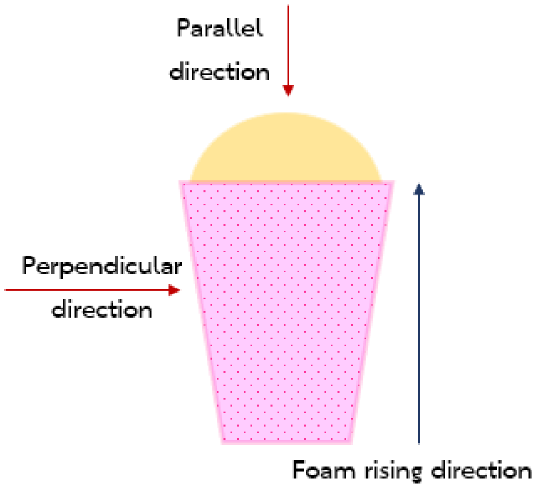


Figure 3.4 The direction of compression test for PIR foam

3.3.7 Morphology

The morphology of the PIR foam was investigated cellular of foams in two direction, namely side view and top view, by using JEOL JSM-6480 LV scanning electron microscope (SEM) at 40× times and voltage of 5 kV. The cell size and average cell diameter were calculated by using SEMAFORE 5.21 software.

3.38 Fire retardant properties

The fire-retardant properties of PIR foam were investigated by using UL-94 horizontal burning test according to ASTM D4986-03. The samples of foam were cut into the dimension of 15.0 × 5.0 × 1.3 cm (length × width × thickness) and were marked at 2.5, 6.0 and 12.5 cm of each sample. The foams were placed in horizontal direction in the test. Burning length and afterglow time were reported.

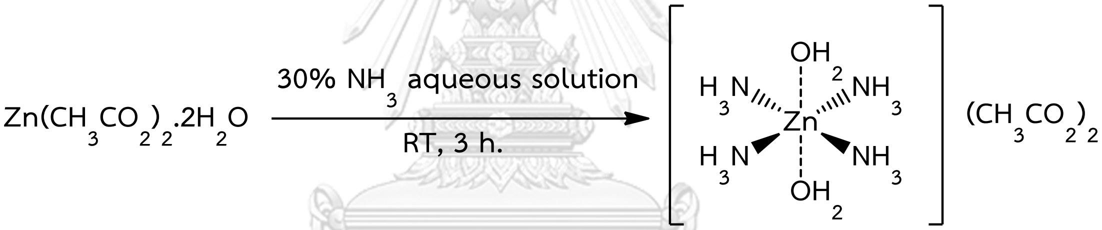
Limiting oxygen index (%LOI) was measured as the minimum amount of oxygen needed for ignition of foam by follow ASTM D2863-06. The sample of foam were cut into the dimension 12.5 × 1.0 × 1.0 cm (length × width × thickness). The samples were placed in vertical direction. After that, the fire was applied on the sample and the minimum O_2 concentration was recorded.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of zinc-ammonia complex using as gelling/blowing catalyst

The synthesis of zinc-ammonia complex Zn(Amm), which was used as gelling/ blowing catalyst for urethane group formation was done according to the method reported in the literature [11]. In this reaction, water was used as a solvent. In the first step, water and 30 wt% ammonia (NH_3) solution was mixed. Then, zinc acetate dihydrate [$Zn(OAc)_2{\bullet}2H_2O$] was added. After that, the reaction mixture was stirred for 3 hours at room temperature (Scheme 4.1). The aqueous solution of Zn(Amm) was obtained as homogeneous colorless liquid (Figure 4.1)



Scheme 4.1 Synthesis of zinc-ammonia complex for using as gelling/blowing catalyst [11]

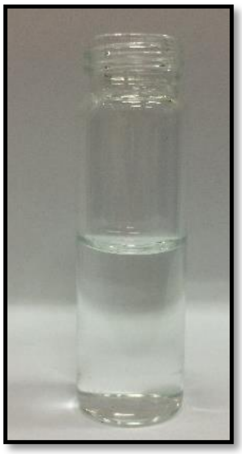


Figure 4.1 Zinc-ammonia complex Zn(Amm) aqueous solution

4.2 Preparation of PIR foam modified with starches and used a mixture of Zn(Amm) and potassium octoate (KOct) as catalysts

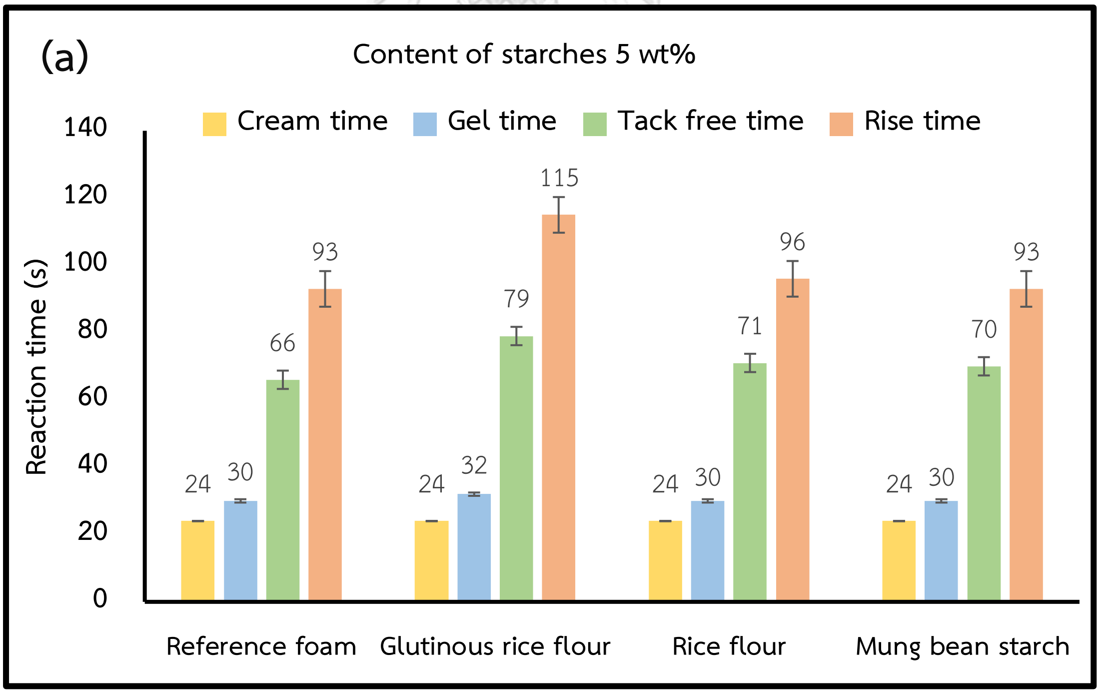
The PIR foam fill with starches produced in Thailand, namely glutinous rice flour, rice flour and mung bean starch were compared with reference foam (PIR foam without starch). The catalyst for gelling/blowing and trimerization reactions were Zn(Amm) and potassium octoate (KOct), respectively [11]. Gelling and blowing reaction are the reaction between isocyanate-polyol to give urethane linkage and isocyanate-water to give CO_2, respectively [52]. Trimerization reaction was the reaction between three isocyanate group to give isocyanurate linkage [15]. Therefore, PIR foams has highly crosslinked structure. The amount of starches added into the PIR foam was calculated based on mass of polyol in PIR foam formulation.

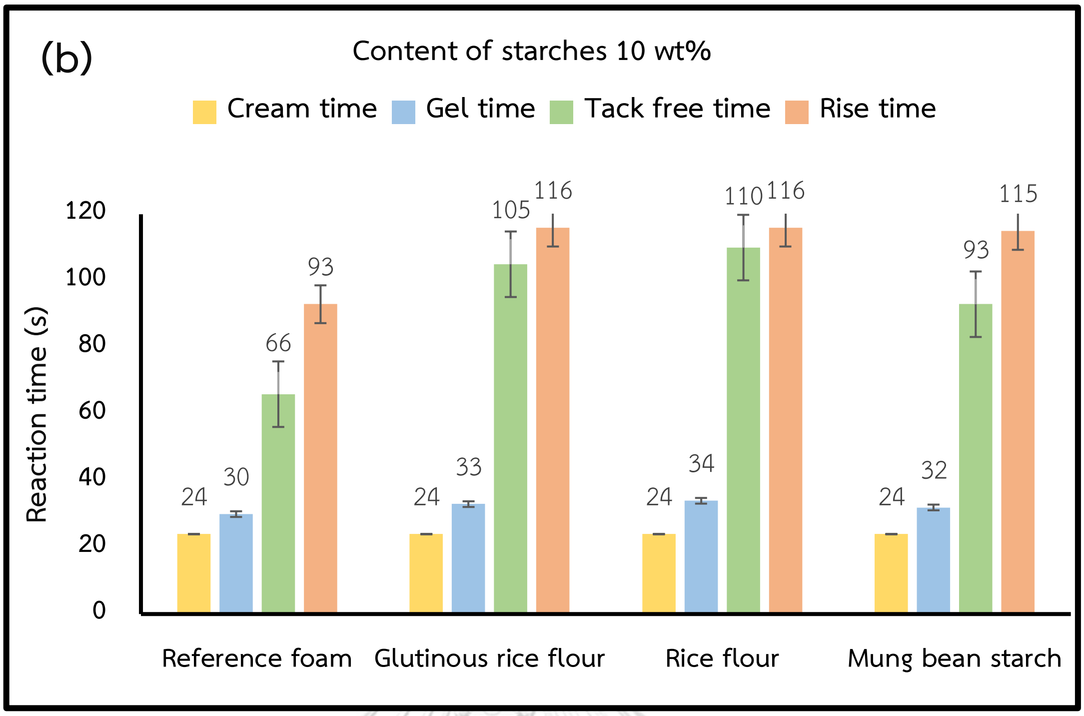
4.2.1 Reaction times of PIR foams

The reaction times of PIR foams prepared by using cup test method were recorded, namely cream time, gel time, rise time and tack free time. (Table 4.1). In comparison to the reference PIR foam, PIR foam prepared at the isocyanate index of 200 and modified with starches at the amount of 5, 10 and 15 wt% showed obvious increase in rise time and tack free time. In all case, cream time and gel time were unchanged (Figure 4.2). This is because the presence of starches in PIR foam system resulted in high viscosity, therefore, causing resistance to bubble and limiting diffusion of gases into the foam matrix [41]. Moreover, increasing the amount of starches in the foam system might cause aggregation and agglomeration.

Among three types of starch added into PIR foams, mung bean starch gave the shortest tack free time and rise time when compared to glutinous rice flour and rice flour. All starches compose of at different ratios. Amylose and amylopectin contain hydroxyl group that could with isocyanate group in starch can react with isocyanate group [3, 33]. Mung bean starch contains of higher amount of protein than glutinous rice flour and rice flour. Protein has NH_2 group which are more active than OH group toward the reaction with isocyanate group [33].

For all starches, water used in PIR foam formulation increased the solubility of starches, which caused activate swelling of starches in solution (Figure 4.3) [3]





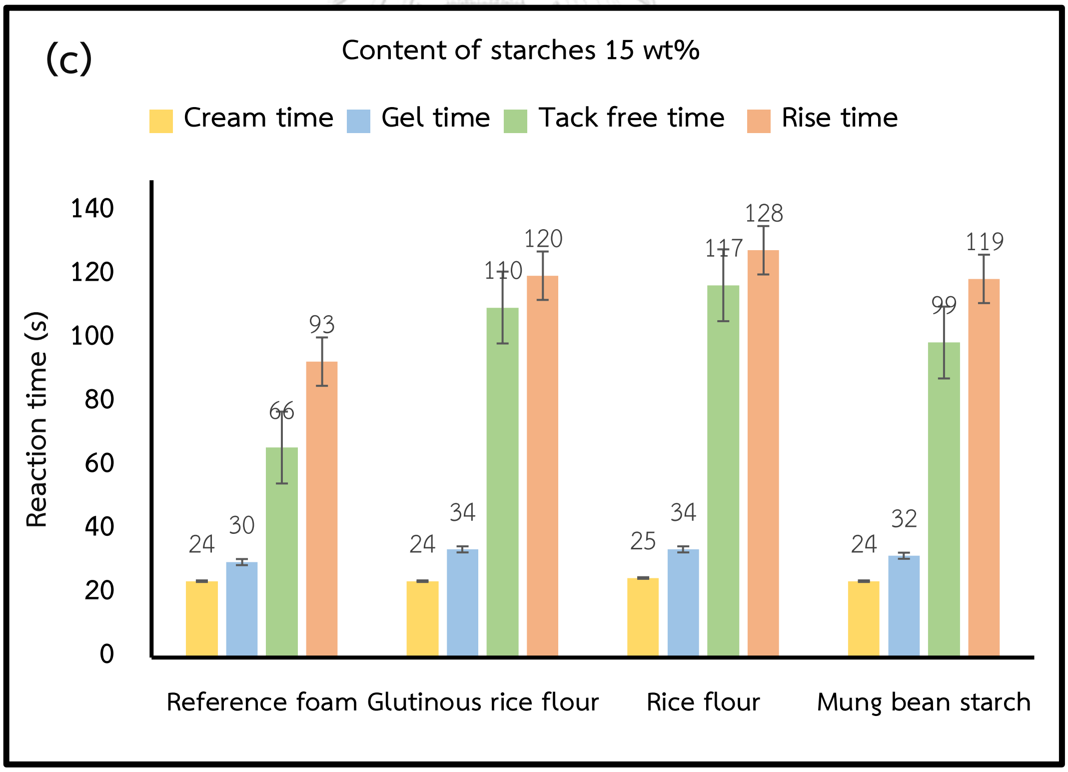


Figure 4.2 Reaction time of PIR foam modified with starches (a) 5 wt%, (b) 10 wt% and (c) 15 wt% at NCO index 200

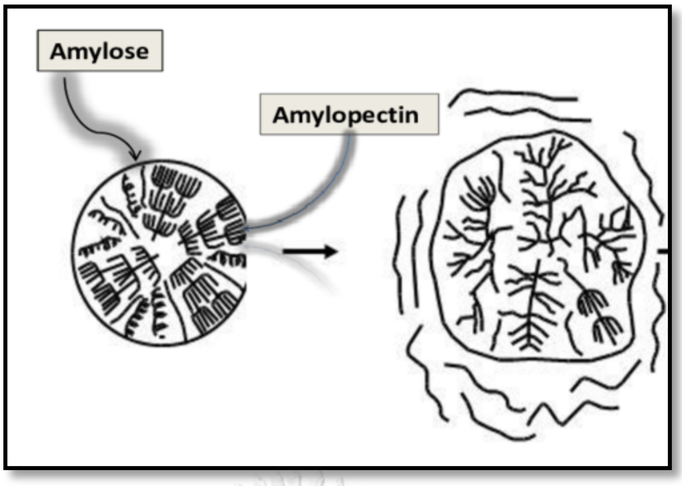


Figure 4.3 Dissolving and swelling in water of starches [53]

Table 4.1 Reaction times and density of PIR foam modified with starch (5-15 wt%) at %NCO index 200

Starch	Reaction time (s)				Density (kg/m^3)
	Cream time	Gel time	Tack free time	Rise time	
			5 wt%		
Glutinous rice flour	24.0±0.0	32.0±0.7	79.2±0.9	115.0±0.8	41.4±0.9
Rice flour	24.2±0.0	30.6±0.5	71.2±0.8	96.0±0.7	39.4±0.7
Mung bean starch	24.0±0.5	30.8±0.0	70.8±0.8	93.2±1.1	39.9±0.7
			10 wt%		
Glutinous rice flour	24.2±0.1	33.0±0.0	105.0±0.0	116.0±2.0	40.7±1.1
Rice flour	24.7±0.9	34.0±1.1	110.0±0.0	116.0±2.0	39.5±1.0
Mung bean starch	24.1±0.0	32.0±0.5	93.0±1.0	115.0±1.0	39.1±1.0
			15 wt%		
Glutinous rice flour	24.2±0.0	34.4±0.5	110.6±0.0	120.6±2.8	38.9±0.7
Rice flour	25.0±0.3	34.2±0.5	117.0±0.0	128.2±1.5	41.8±0.8
Mung bean starch	24.3±0.0	32.5±0.6	99.2±0.0	119.0±0.0	41.4±0.9
Reference foam	24.0±0.0	30.0±1.0	66.0±0.0	93.0±0.0	40.8±0.8

The same tendency was found in the literature. Prociak *et al.* [54] found that polyurethane foam filled of walnut shells resulted in increase of 60% in the reaction time, as compared with the neat foam. Formelar *et al.* [55] showed that addition ground tire rubber (GTR) into the polyurethane foam resulted in significant increase of rise time (67s to 120s) and tack free time (78s to 176s).

PIR foams prepared at the NCO index of 250 and modified with starches at the amount of 10 wt% were prepared and their result were compared with that the reference PIR foam (Table 4.2). It was found that PIR foams modified with all starches had increased reaction times, which was similar to the result obtained foam the PIR foam prepared at the NCO index of 200 (Table 4.1).

In comparison between the reaction times of PIR foams prepared at the NCO indexes of 200 and 250 (Figure 4.4), it was found that higher NCO index result in the increase of all reaction time (cream time, gel time, tack free time and rise time). This is because trimerization reaction is slower than gelling and blowing reaction. After the reaction between isocyanate-polyol and isocyanate-water were completed, the excess isocyanate group needed longer reaction time to complete trimerization. Higher of isocyanate index leads to higher amount of isocyanuarte group, cause crosslink in PIR structure [42].

Table 4.2 Reaction times and density of PIR foam filled with starches 10 wt% at NCO index 250

Starch	Reaction time (s)				Density (kg/m^3)
	Cream time	Gel time	Tack free time	Rise time	
Glutinous rice flour	28.8±0.0	40.0±0.7	235.0±0.0	157.0±0.0	49.4±1.3
Rice flour	28.0±0.0	39.4±0.5	235.0±0.0	145.0±0.0	48.4±1.1
Mung bean starch	28.0±0.0	39.0±1.0	233.0±0.9	143.0±0.0	49.9±1.4
Reference foam	26.2±0.2	34.6±0.6	106.0±1.1	120.0±0.0	53.6±0.8

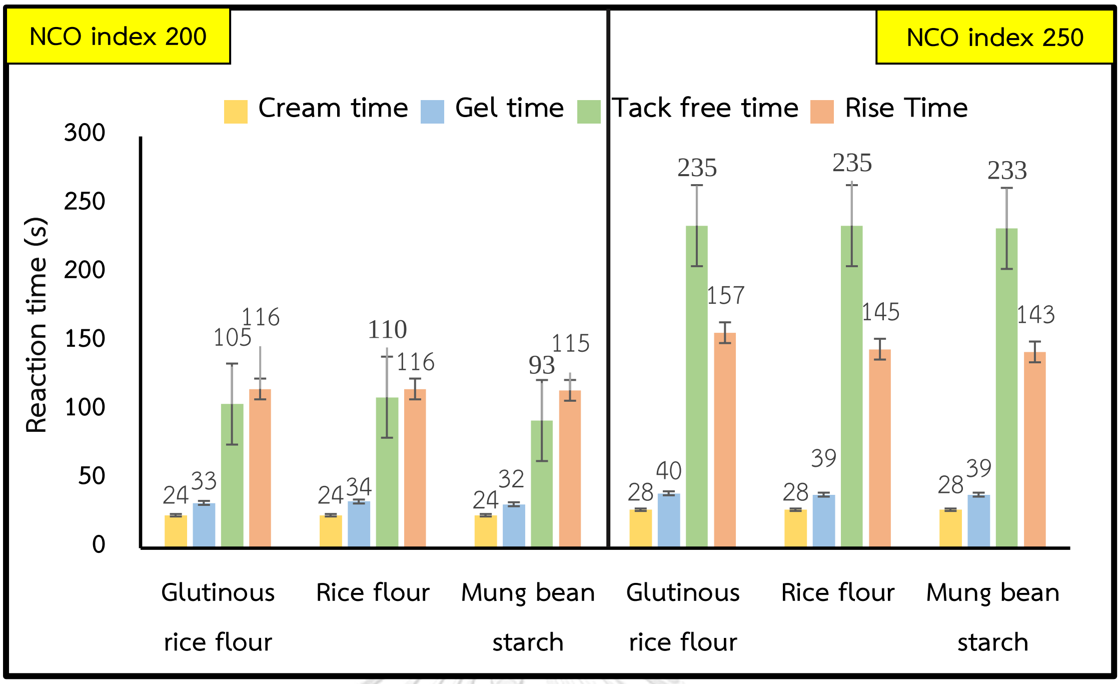


Figure 4.4 Comparing the reaction times of PIR foam modified with starches 10 wt% between NCO index 200 and 250

4.2.2 Apparent density of PIR foams

The apparent density is very important parameter which has influence on the withstand compressive loading [42]. PIR foam without starch prepared at the NCO index of 200 had density 40.8 kg/m^3. When starches were added into PIR foam at 5, 10 and 15 wt%, the foam density slightly change, and density value was in the range 38.9-41.8 kg/m^3. Density of all PIR foams was calculated from average of mass/volume ratio of each sample.

The density of PIR foams depended on part of sample (top, middle and bottom part in the foam rising direction). All PIR foam prepared at the NCO index of 200 and filled with starches at the amount of 10 wt% showed small increase from to bottom parts (Table 4.3). The bottom part of PIR foam had high for agglomeration of starches particles as the result of the gravity [42].

PIR foams filled with starches at the amount of 5 and 10 wt% had good appearance. PIR foams containing 15 wt% of starches were brittle material and had crack in the matrix (Figure 4.5). Therefore, the appropriate content of starches in PIR foam I 10 wt% (Figure 4.6) since PIR foam filled with maximum content of starches is the purpose of this research.

Table 4.3 Apparent density of PIR foams modified with starches of each part (top to bottom) at NCO index 200

Sample	**Density (kg/m^3)**		
	Upper	**Middle**	**Bottom**
	5 wt% of starches		
Glutinous rice flour	40.7±0.7	41.1±0.8	42.2±0.6
Rice flour	39.2±0.2	39.8±0.6	40.4±0.4
Mung bean starch	39.3±0.4	39.7±0.6	40.8±0.2
	10 wt% of starches		
Glutinous rice flour	39.3±0.8	40.3±0.6	41.2±0.7
Rice flour	39.1±0.4	39.7±1.3	40.9±0.6
Mung bean starch	39.1±1.3	39.5±1.2	40.5±1.6
	15 wt% of starches		
Glutinous rice flour	38.2±0.2	38.8±0.4	39.7±0.3
Rice flour	41.1±0.5	41.6±0.7	42.1±0.5
Mung bean starch	40.7±0.5	41.4±0.7	42.1±0.6

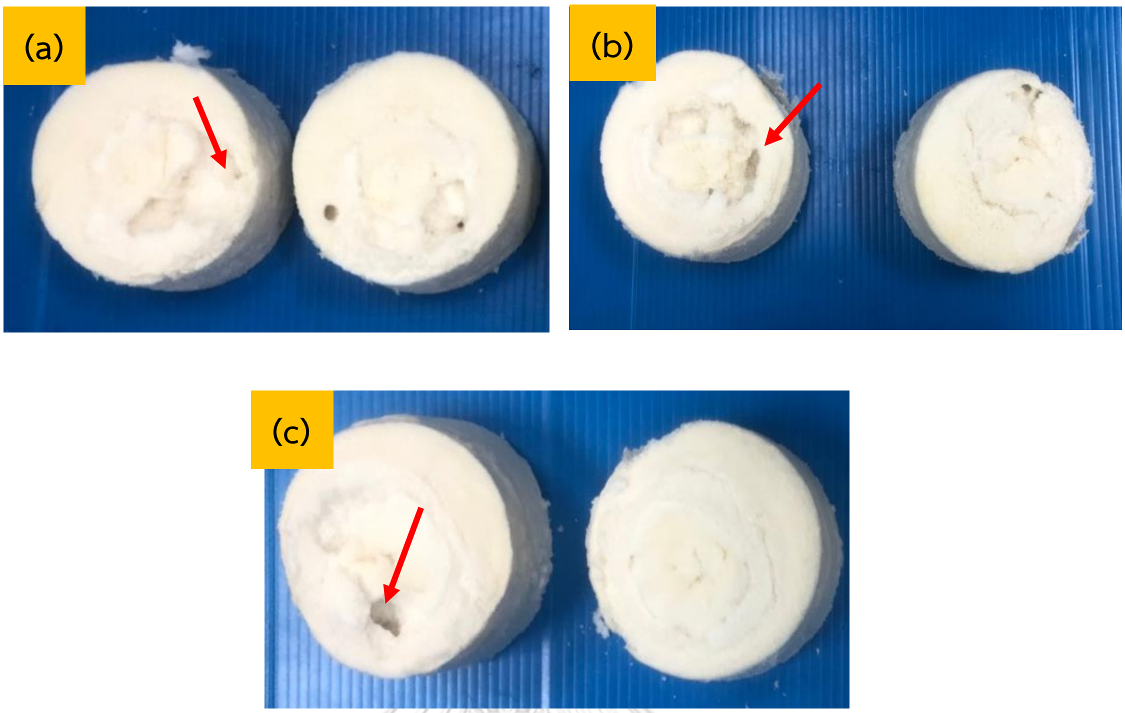
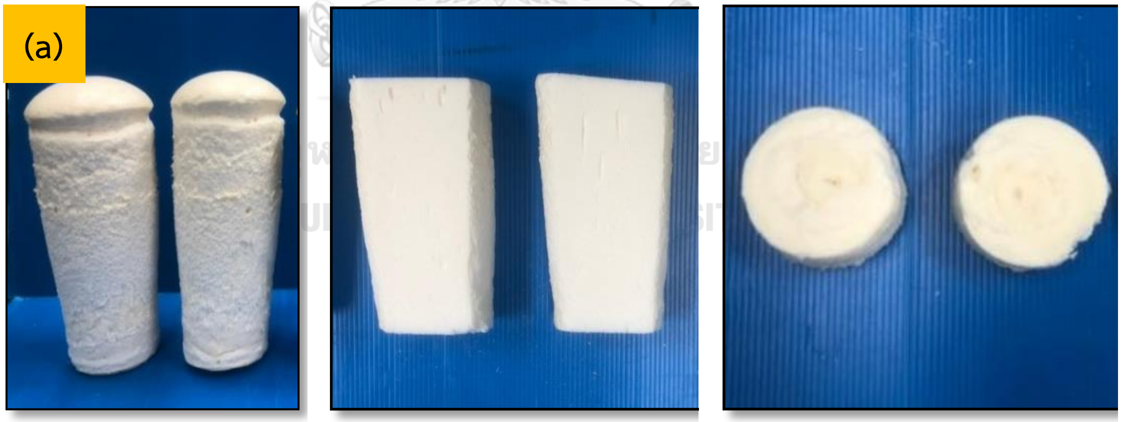


Figure 4.5 Hole of PIR foams modified with 15 wt% of (a) glutinous rice flour, (b) rice flour and (c) mung bean starch at NCO index 200



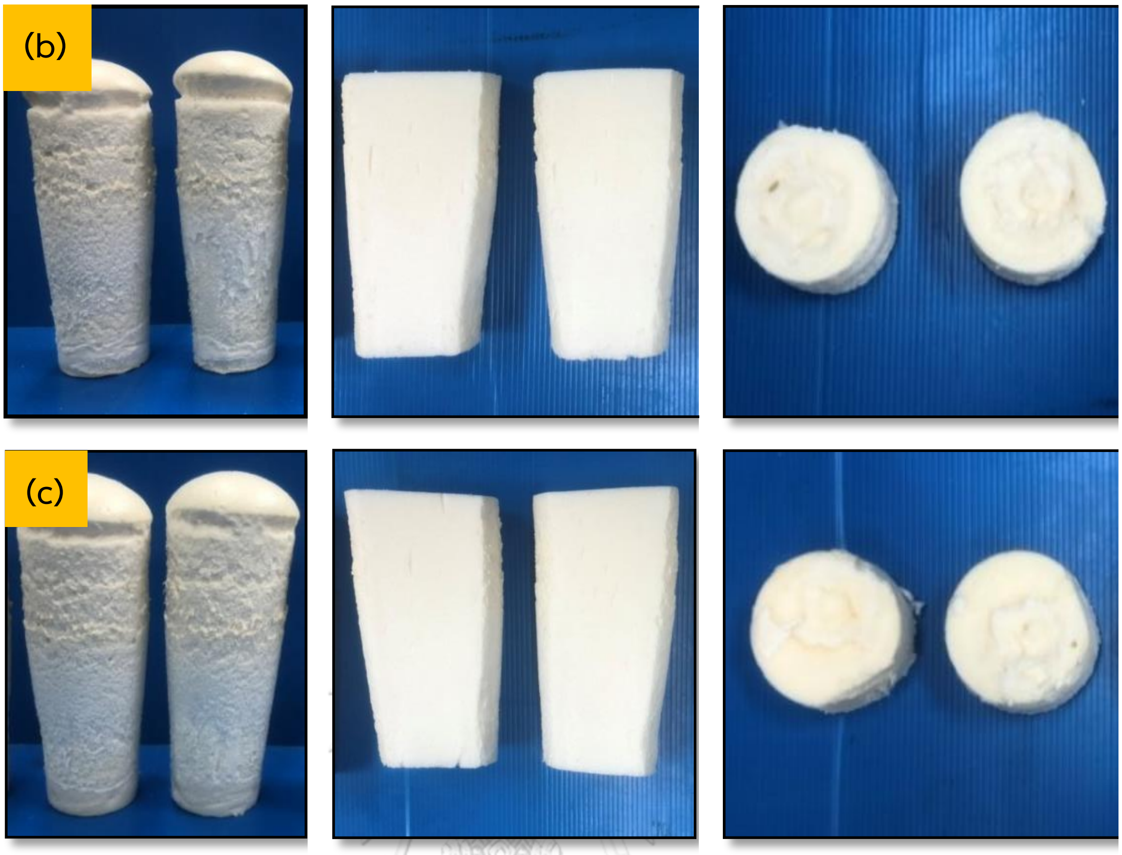


Figure 4.6 Appearance of PIR foams modified 10 wt% of (a) glutinous rice flour, (b) rice flour and (c) mung bean starch

When PIR foams were prepared at the NCO index of 250 and filled with starches at the amount of 10 wt%, the density of these PIR foam significantly decrease from 53.6 kg/m^3 (reference foam) to 48.4-49.4 kg/m^3 (Figure 4.7).

Comparing between PIR foams prepared at the NCO index 200 and 250, PIR foams prepared at the NCO index 250 had higher crosslink in PIR foam structure and therefore had higher density than those prepared at the NCO index of 200. The high crosslink was due to higher amount of isocyanate group that underwent trimerization reaction to give isocyanurate group.

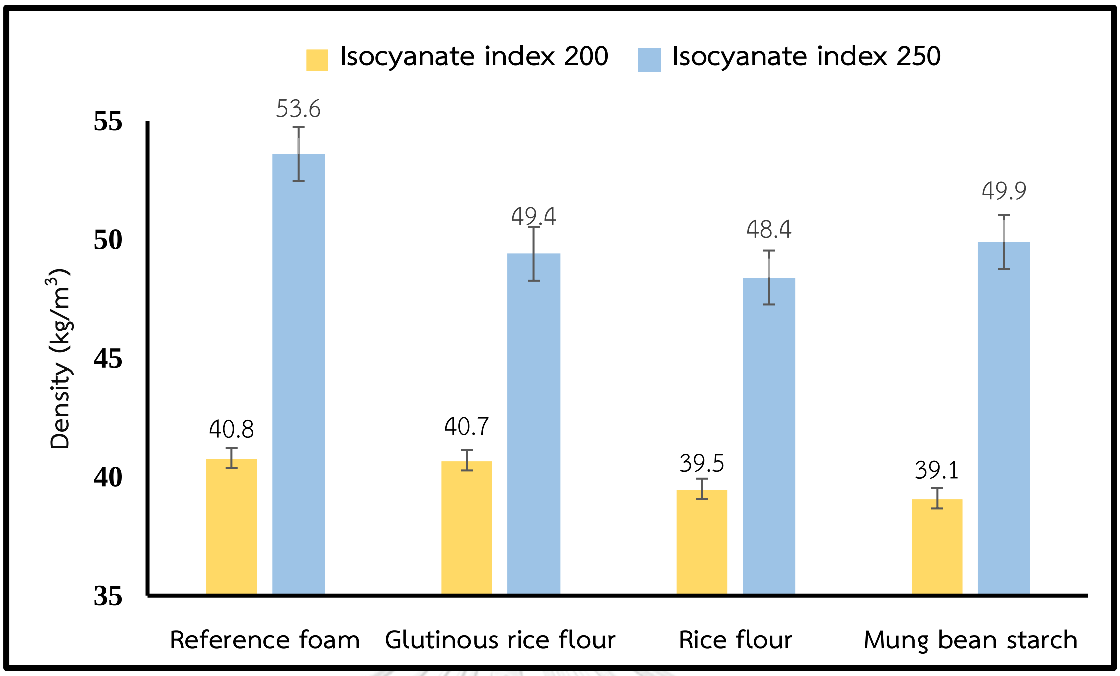


Figure 4.7 Density of PIR foam modified 10 wt% of starches at NCO index 250

4.2.3 Isocyanate conversion and PIR/PUR ratio of PIR foams

Figure 4.8 and 4.9 show FTIR spectra of PIR foams prepared at the NCO index of 200 and 250 and modified 10 wt% of starches. All PIR foams showed the same peaks. Isocyanate conversion and PIR/PUR ratio of PIR foam were calculated from paek area of FTIR spectrum. The peaks used for calculation are 2277, 1595, 1415 and 1220 cm^{-1}, which are due to isocyanate, phenyl, isocyanurate and urethane group, respectively [5]

Isocyanate conversion of all PIR foams modified was compute from the normalized final and initial of peak area of isocyanate group using the equation as follow:

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

Where NCO^f and NCO^i are normalized peak of isocyanate group at final time and initial time, respectively.

PIR foams prepared at the NCO index of 200 and 250 and filled with 10 wt% of starches had similar PIR/PUR ratio to those of reference foams prepared at the same NCO index. Isocyanate conversion of PIR foams modified with starches are lower than that of reference foams prepared at the same NCO index.

PIR/PUR ratio of PIR foams increased from 0.91-1.06 to 2.51-2.77 when increasing NCO index from 200 to 250 (Table 4.4-4.5). %NCO conversion decreased from 95.2-96.7 to 91.4-96.8 which cloud be observed by the higher intensity of NCO peak at 2227 cm^{-1} in FTIR spectra of PIR foams prepared at the NCO index 250. This is because the excess isocyanate group cloud slowly undergo trimerization reaction and highly crosslink structure also retard the reaction [5].

Table 4.4 %NCO conversion and PIR/PUR ratio of PIR foams modified 10 wt% of starches at NCO index 200

Starch	% NCO conversion	PIR/PUR ratio
Glutinous rice flour	95.2±0.4	1.04±0.1
Rice flour	95.4±0.2	1.03±0.0
Mung bean starch	95.8±0.3	1.06±0.0
Reference foam	96.7±0.2	0.91±0.1

Table 4.5 %NCO conversion and PIR/PUR ratio of PIR foam modified with starches 10 wt% at NCO index 250

Starch	% NCO conversion	PIR/PUR ratio
Glutinous rice flour	91.4±1.3	2.77±0.1
Rice flour	92.3±0.3	2.51±0.4
Mung bean starch	93.7±0.4	2.60±0.3
Reference foam	96.8±1.0	2.58±0.2

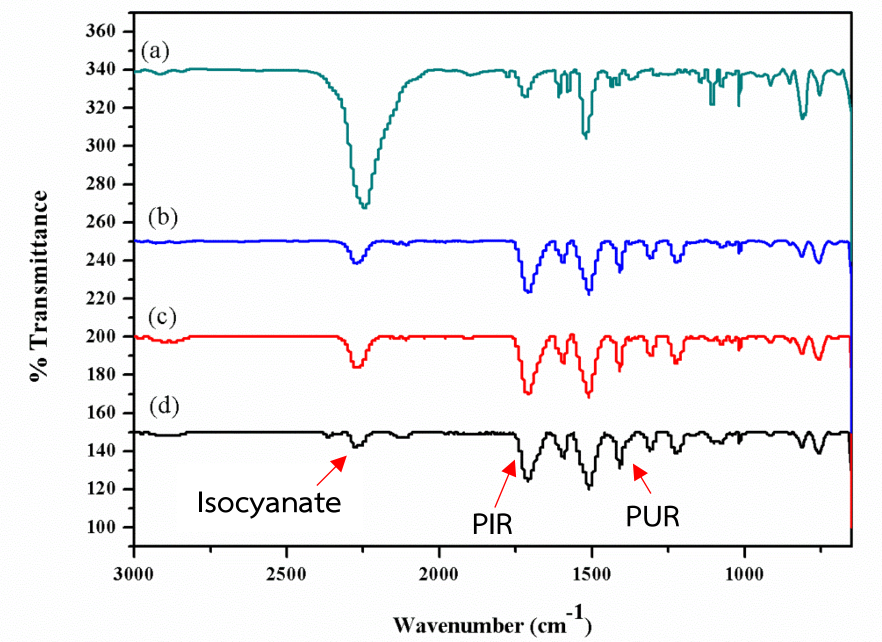


Figure 4.8 FTIR of isocyanate substance (a) compared with the PIR foam modified of starched at NCO index 200, (b) glutinous rice flour , (c) rice flour and (d) mung bean starch

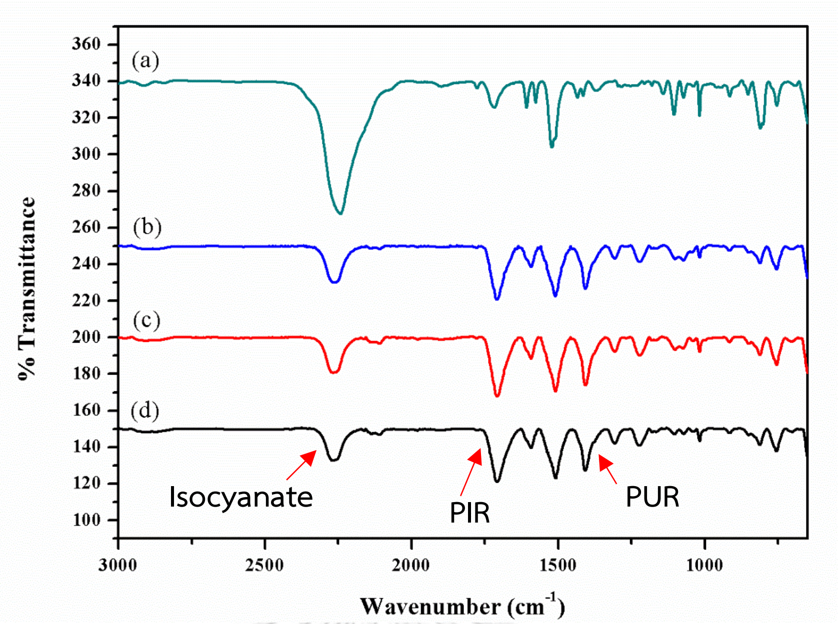


Figure 4.9 FTIR spectra of isocyanate substance (a) compared with the PIR foam modified of starches at NCO index 250, (b) glutinous rice flour, (c) rice flour and (d) mung bean starch

4.2.4 Rise profiles of PIR foams

The rise profiles of PIR foams prepared at the NCO index of 200 and modified with 10 wt% of starches were compared with that of reference foam as shown in Figure 4.10. It was found that the rise times of the all PIR foam filled with starches were longer than that of reference foam. This was because the starting materials of PIR foams modified with starches had high viscosity. This result in resistance to bubble expansion. Rise profiles of PIR foam filled with starches show slower rise rate in the beginning than that of reference foam. The rise rate in the early stage of PIR foam filled with glutinous rice flour is the slowest as compared with those of mung bean starch and rice flour. At the end, all PIR foams filled with starches had similar rise time. It was found that the trend of time to reach 100% height obtained from rise profile was the same as the rise time obtained from cup test experiment (Table 4.1)

The difference in rise time could be observed in PIR foams prepared at the NCO index 200 and filled with 10 wt% of starches (Table 4.6). The order of rise time of PIR foams filled with different starches in glutinous rice flour > mung bean starch ≅ rice flour.

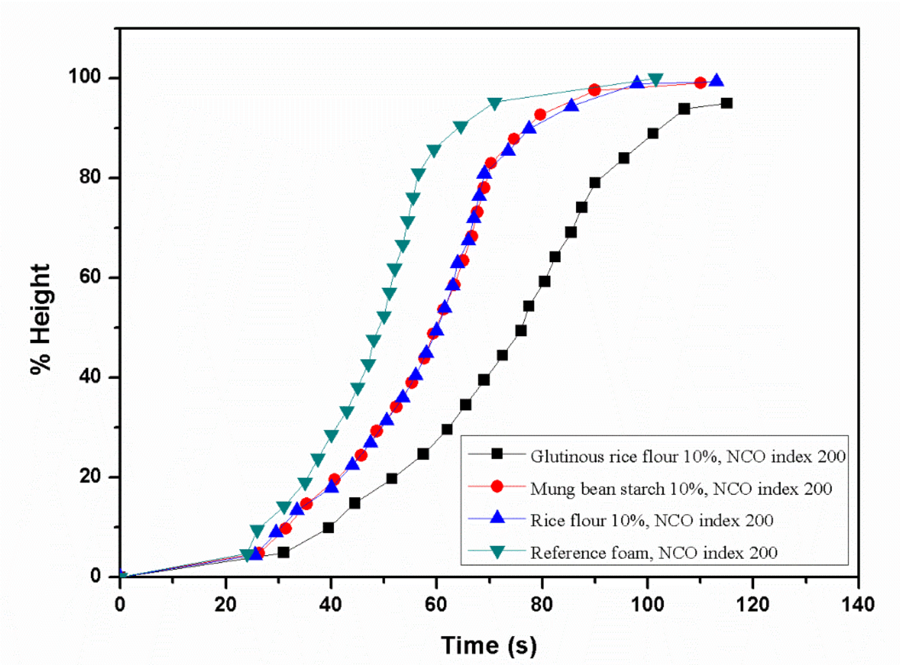


Figure 4.10 Rise profiled of PIR foam modified with starches (glutinous rice flour, rice flour and mung bean starch) compared with reference foam

Table 4.6 Comparing rise profiles of PIR foam modified with 10 wt% of starches with reference foam

Sample	Time to reach 100% height obtained from rise profile (s)	Rise time obtained from cup test experiment (s)
Glutinous rice flour	118	116
Rise flour	117	116
Mung bean starch	115	115
Reference foam	98	93

4.2.5 Temperature profiled of PIR foams

Temperature profiled of PIR foams prepared at the NCO index of 200 and modified with 10 wt% of starches were compared with that of reference foam as shown in Figure 4.11. Since the polymerization reaction is an exothermic reaction, temperature of PIR foam reaction mixture increased unit the reaction was complete. It was found that the temperature of PIR foam modified with starches was slightly lower than that of reference foam. It was found that the trend of the time to reach the maximum temperature was the same as the tack free time obtained from cup test experiment (Table 4.1). Higher reaction temperature is related to shorter time to reach the maximum temperature (Table 4.7)

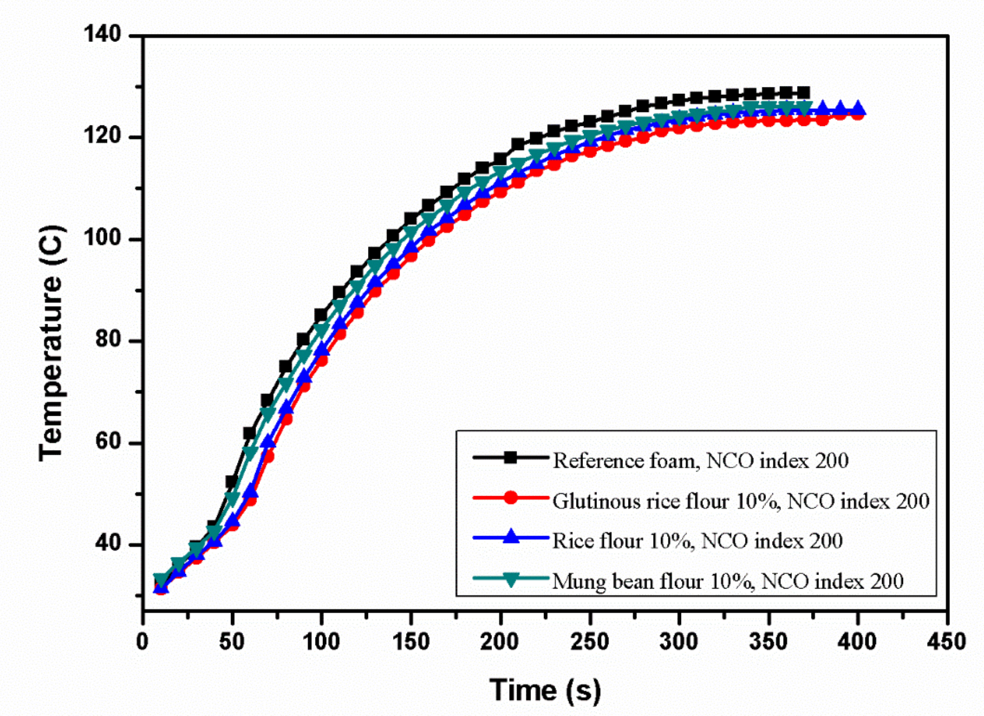


Figure 4.11 Temperature profiled of PIR foam modified of starches (glutinous rice flour, rice flour and mung bean starch) compared with reference foam

Table 4.7 Comparing temperature profiles of PIR foam modified with starches with standard foam

Sample	Maximum temperature obtained from temperature profile (°C)	Tack free time obtained from cup test experiment (s)
Glutinous rice flour	124.7	105
Rice flour	125.5	110
Mung bean starch	126.1	93
Reference foam	128.7	66

4.2.6 Compressive properties of PIR foams

Compressive strength is an important parameter of mechanical properties. PIR foams prepared at the NCO index of 200 and modified with 10 wt% of starches were chosen for the investigation of compressive properties. The compressive stress-strain curves of PIR foams were measured in both parallel and perpendicular to the foam rising direction. The compressive strength PIR foams modified with starches was compared with that of the reference foam, which was obtained from the literature [11]. The effect of starches on compressive strength of PIR foam is presented in Figure 4.12 and 4.13. The compressive strength of reference foam and PIR foam containing starches in the parallel direction was significantly greater than that perpendicular to the foam rising direction (Table 4.8 and Figure 4.14).

In the parallel of foam rising direction, the compression strength of all PIR foam filled with starches showed brittle property of the material. The order of compressive strength of PIR foams filled with starches in this direction is reference foam > mung bean starch > glutinous rice flour > rice flour. The compressive strength in the perpendicular of foam rising direction did not show brittle property of the material. The order of compressive strength of PIR foams filled with starches in this direction is reference foam > glutinous rice flour > rice flour > mung bean starch.

In comparison between the PIR foams filled with starches and reference foam, it was found that the compressive strength of PIR foams filled with starches is dramatically decreased in both parallel and perpendicular direction. This was because the starches added into the PIR foams had low dispersion. Therefore, the cellular structure of PIR foam modified with starches might be heterogeneous and rupture of cell wall occurred [56]. The same tendency was reported by Silva *et al.* [57], which showed that the addition 1-8 wt% of cellulose fiber to the polyurethane foam formulation caused a decreasing of 7% of compressive strength. On the other hand, compressive strength increased from 0.158 MPa to 0.170 MPa when cellulose fiber content was increase from 12 to 16 wt%. Czuprynski *et al.* [33], investigated the effect of potato starch on the mechanical property of polyurethane-polyisocyanurate foam. When the amount of potato starch was increased from 2.5 to 20 wt%, the compressive strength declined from 227.7 kPa to 120 kPa. Paciorek-Sadowska *et al.* [48] studied the influence of wheat slop content in polyurethane-polyisocyanurate foam. When 5 to 30 wt% of wheat slop were added, the compressive strength in the direction of foam expansion (parallel to the foam rising direction) declined from 221.7 kPa to 70 kPa.

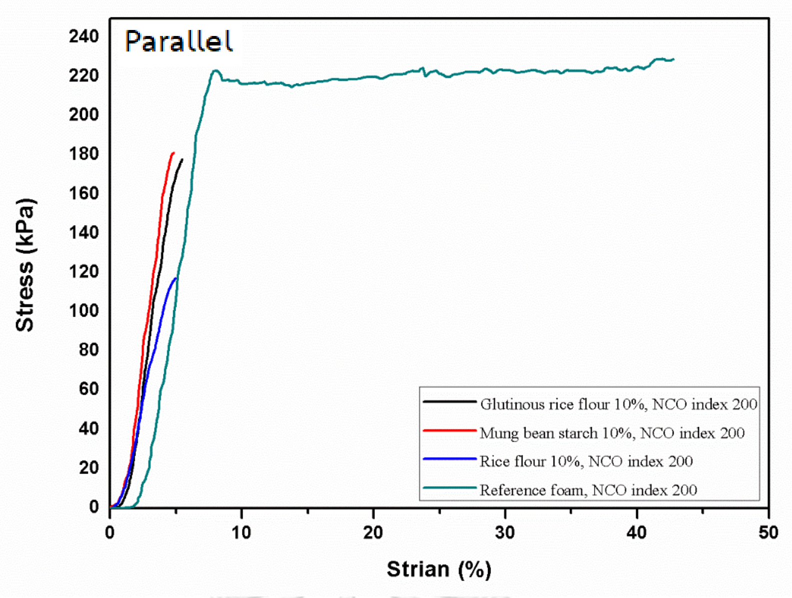


Figure 4.12 Compressive stress-stain graphs of PIR foam modified 10 wt% of starches at NCO index 200 in parallel of rising direction

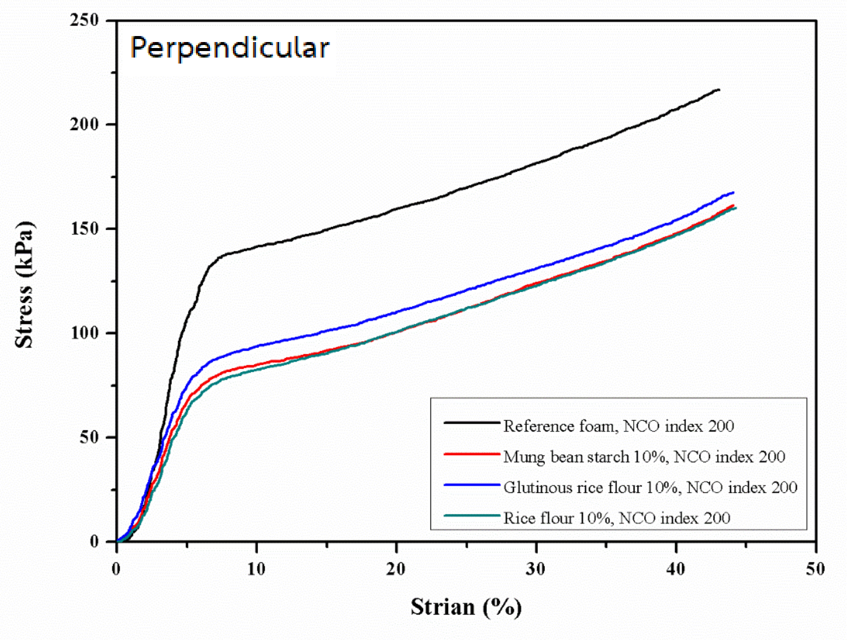


Figure 4.13 Compressive stress-stain graphs of PIR foam modified 10 wt% of starches at NCO index 200 in perpendicular of rising direction

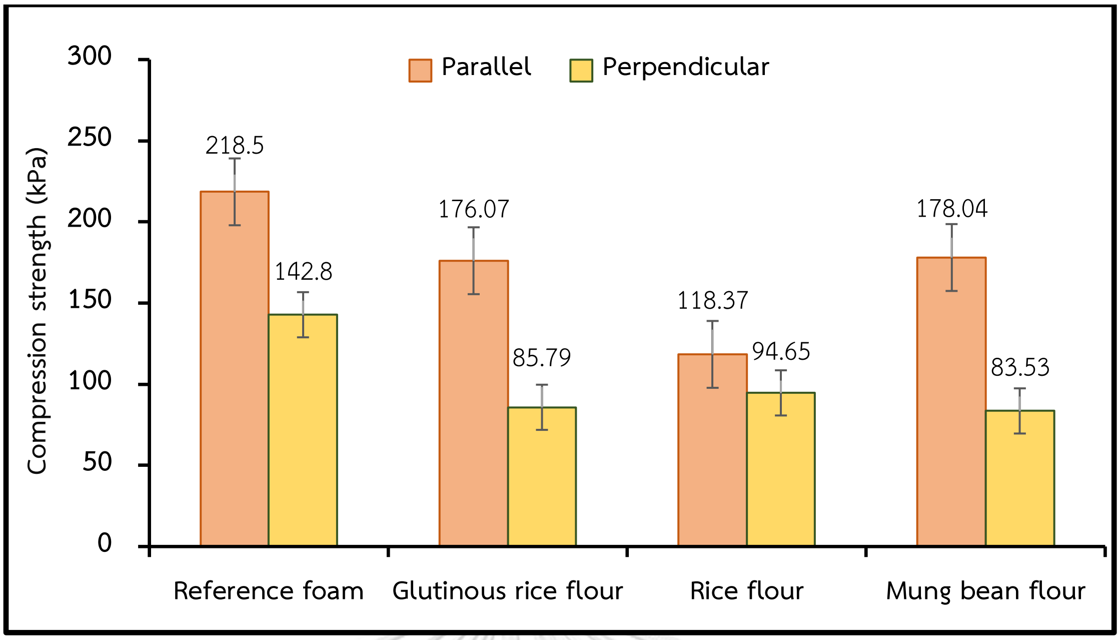


Figure 4.14 Comparing strength of PIR foam modified 10 wt% of starches at NCO index 200 in parallel and perpendicular in the foam rising direction

Table 4.8 Compressive strength of PIR foam modified 10 wt% of starches at NCO index 200

Starch	Compression strength (kPa)	
	Parallel	Perpendicular
Glutinous rice flour	176.07±1.65	85.79±0.24
Rice flour	118.37±4.47	94.65±8.60
Mung bean flour	178.04±1.94	83.53±4.48
Reference foam	218.50±5.61	141.80±2.51

4.2.7 Morphology of PIR foam

Morphology of PIR foams prepared at the NCO index of 200 and modified with 10 wt% of starches were investigated in order to explain the trend of their compressive properties. The cell morphology of PIR foams is one crucial parameter that related to their mechanical properties. Cell morphology of PIR foams modified with starches was investigated in both parallel and perpendicular to the foam rising direction. The cell morphology of PIR foams modified with starches was compared to that of the reference foam (Figure 4.15), which was obtained from the literature [11].

SEM of PIR foams modified with starches (Figure 4.16) indicates that the structure of all PIR foams was closed cell. The cell shape of samples in parallel and perpendicular to the foam rising direction were ellipsoidal and spherical, respectively. The average cell diameter in vertical (V) and horizontal (H) direction (Figure 4.17-4.18) per cell unit was measured (Table 4.9-4.10). It was found that all PIR foams modified 10 wt% of starches showed larger cell size, ruptured cell and less uniform cell wall in several points when compared with those of the reference foam.

Similar results were also reported by other research groups. *Kuznia et al.* [38] indicated that the addition of fly ash (5 to 10 wt%) into polyurethane foam caused destruction of cell walls. Moreover, the diameter of cell structure in vertical and horizontal direction decreased from 207.35 to 161.90 µm and 193.37 to 150.23 µm, respectively. Luo *et al.* [58] showed that the addition of lignin that was used as reinforce filler in polyurethane foam caused increase rupture of cell walls.

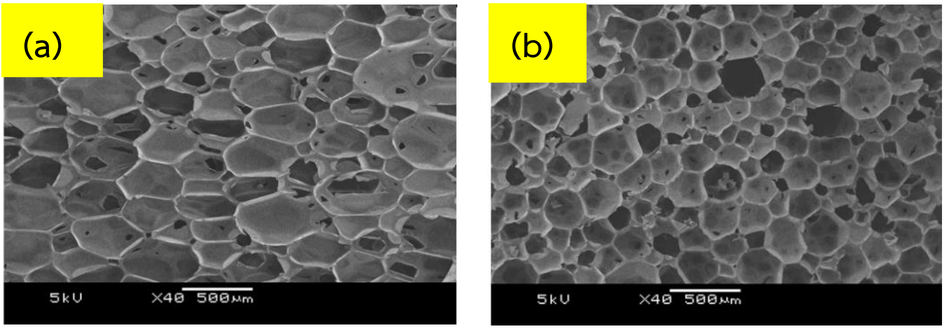


Figure 4.15 SEM of reference foam (a) perpendicular (b) parallel [11]

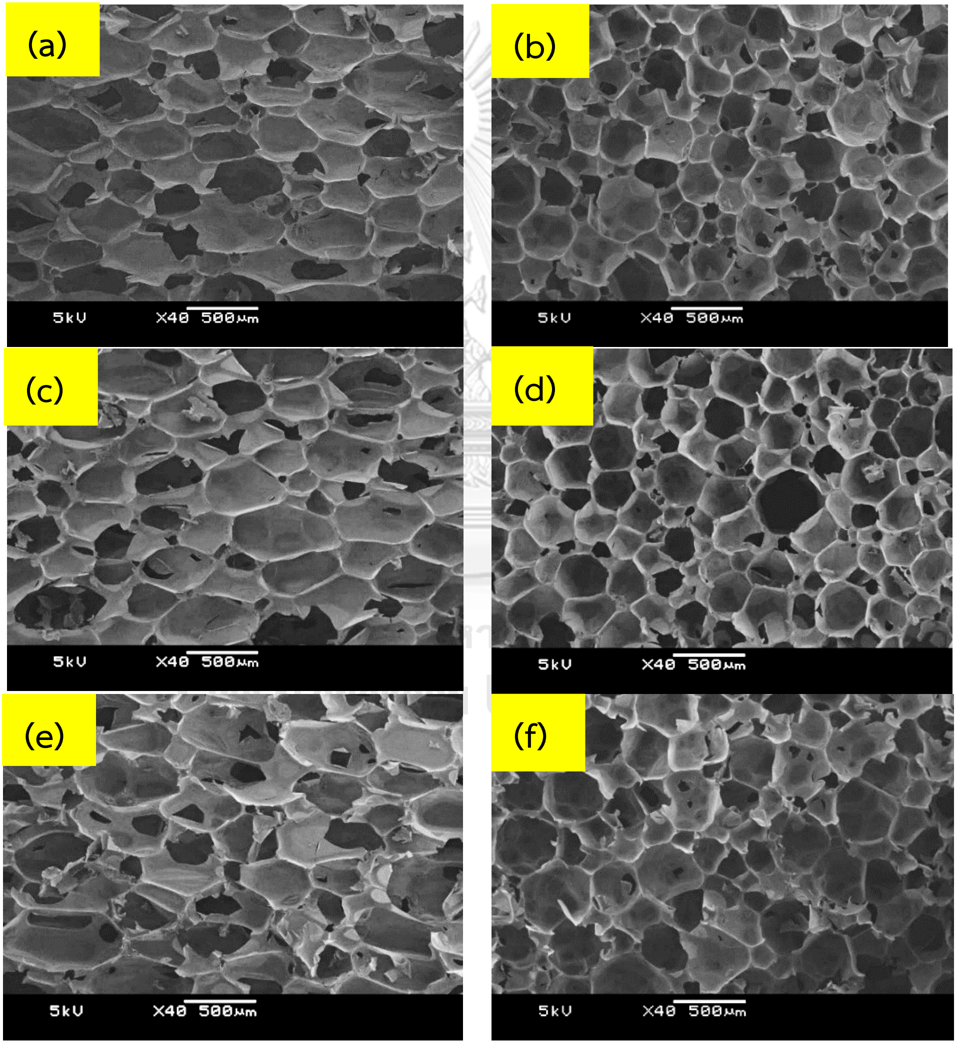


Figure 4.16 SEM of PIR foams modified with starches in parallel and perpendicular direction (a-b) glutinous rice flour, (c-d) rice flour and (e-f) mung bean flour

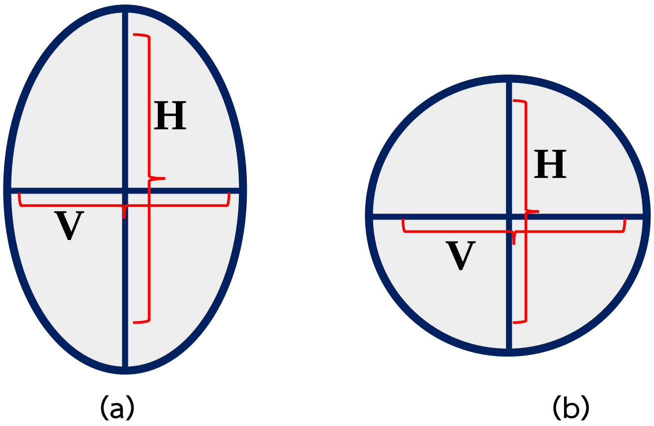


Figure 4.17 (a-b) measurement of cell size for PIR foam in both parallel and perpendicular direction respectively

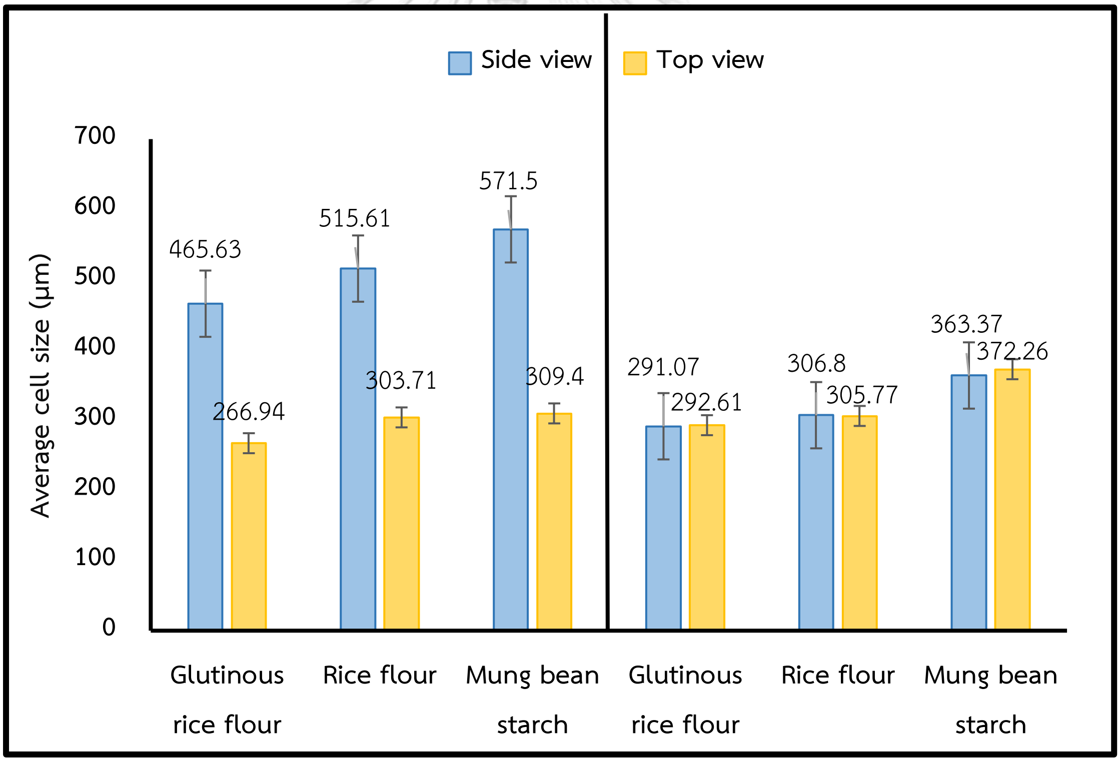


Figure 4.18 The comparison for average cell size of PIR modified with starches at NCO index 200 of parallel and perpendicular into the foam rising direction

Table 4.9 The average cell size of PIR modified with starches at NCO index 200 in parallel to foam rising direction

Starch	Average cell size (μm)	
	parallel	**perpendicular**
Glutinous rice flour	465.63±139.09	266.94±63.55
Rice flour	515.61±113.50	303.71±53.38
Mung bean starch	571.50±121.17	309.40±41.45
Reference foam	428.80±103.07	258.72±43.21

Table 4.10 The average cell size of PIR foam modified with starches at NCO index 200 in perpendicular to foam rising direction

Starch	Average cell size (μm)	
	parallel	**perpendicular**
Glutinous rice flour	291.07±80.55	292.61±75.25
Rice flour	306.80±53.04	305.77±68.59
Mung bean starch	363.37±96.96	372.26±81.15
Reference foam	230.20±68.73	265.40±53.28

4.2.8 Flammability properties of PIR foams modified with starches and %limit oxygen index (%LOI)

Fire-retardant property of PIR foams, which prepared at the NCO index of 200 and modified with 10 wt% of starches was investigated using horizontal test (Figure 4.19). It was found that the all PIR foams modified 10 wt% of starches were combustible but then self-extinguished before marked point at 2.5 cm. PIR foam prepared at NCO index 200 composed of isocyanurate ring which had fire-retardant property [2]. When 10 wt% of starches were added into the PIR foam system faster self-extinguishing property than that of the reference foam was observed (Figure

4.20). All three starches showed obvious effect on the fire-retardant property of PIT foam, which might be because the starches promoted incombustible gaseous (H_2O and CO_2) and char formation, thus reduce the convective heat transfer in pyrolysis zone [9, 28, 59]. The order of self-extinguishing properties and ignition length of the foam is glutinous rice flour-based foam > mung bean starch-based foam > rice flour-based foam (Figure 4.21-4.22). The result reveals that the starches were added into the foam as natural fire-retardant property.

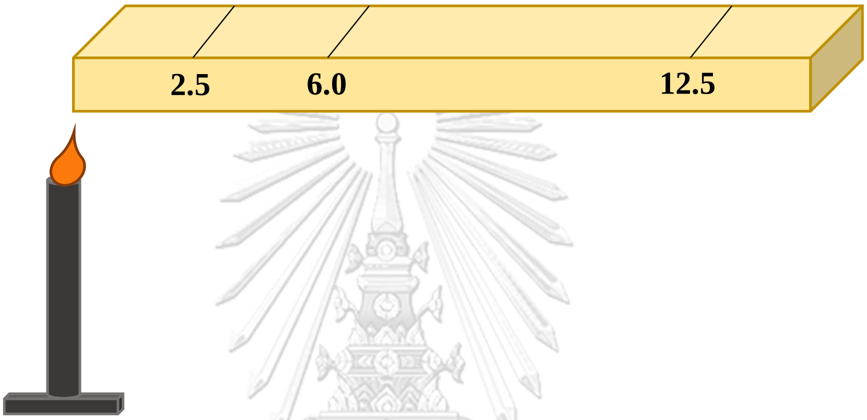


Figure 4.19 Displays the burning test in horizontal for PIR foams

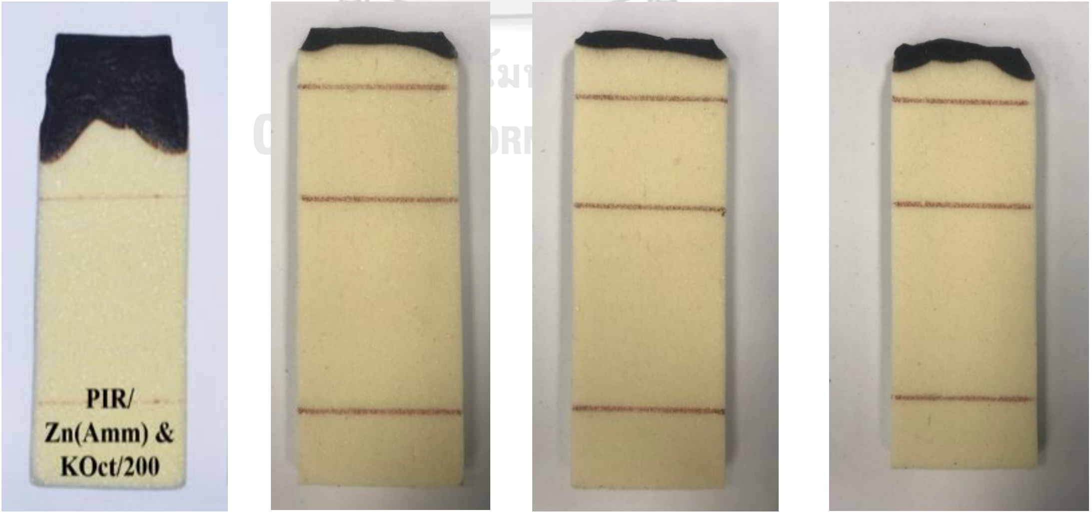


Figure 4.20 Appearance of PIR foams after burning test; (a) PIR foam is reference foam (b), (c) and (d) are PIR foams modified with glutinous rice flour, rice flour and mung bean starch respectively

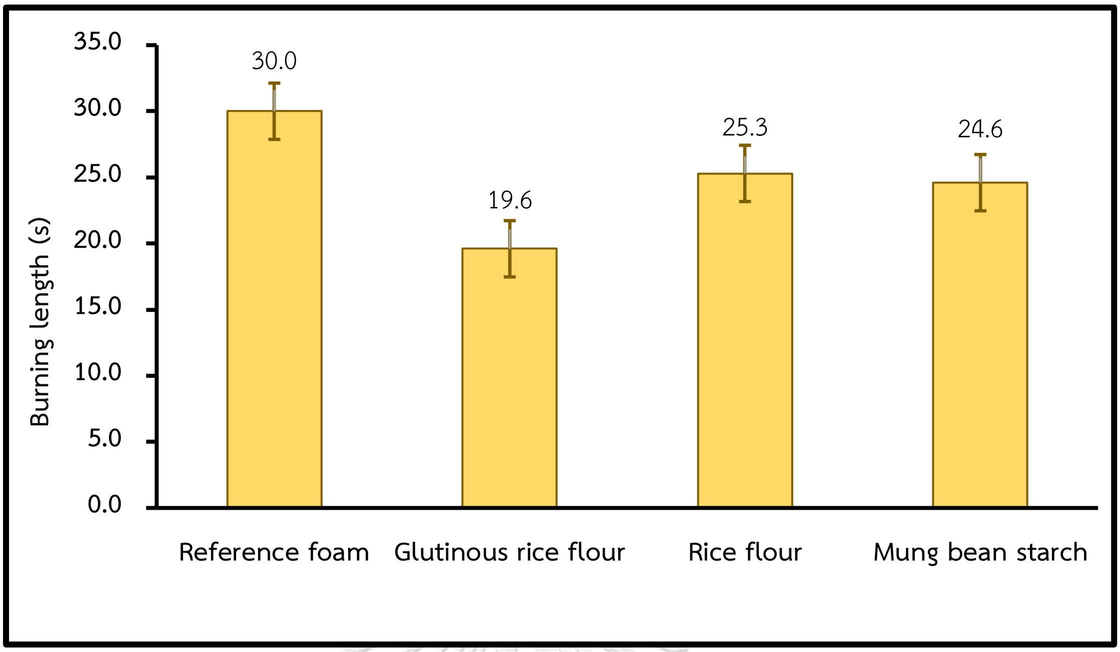


Figure 4.21 Times of self-extinguishing for PIR foam modified with starches

Figure 4.22 Ignition length for PIR foam modified with starches

%LOI of PIR foams (Figure 4.23) was investigated the minimum concentration of oxygen, which can be sustain combustion of PIR foams. The %LOI of PIR foams modified with starches are closely with reference foam. The maximum %LOI of PIR foam modified with glutinous rice flour, rice flour and mung bean starch was 20.6%, 20.5% and 20.5%, respectively. Thus, PIR foams modified with starches aren't effect on %LOI.

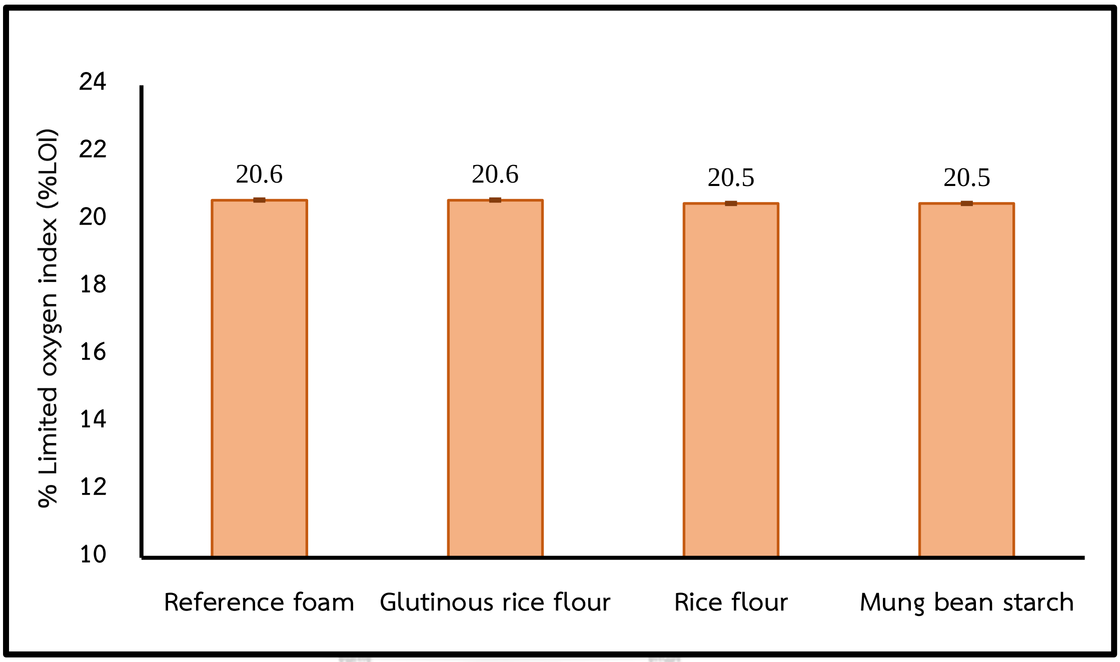


Figure 4.23 Comparison %LOI between PIR foam modified with starches and reference foam

CHAPTER
CONCLUSIONS

PIR foams were prepared using Zn(Amm) complex and potassium octoate as gelling/blowing and trimerization catalysts and three types of starches, namely glutinous rice flour, rice flour and mung bean starch, were used as filler. All PIR foams modified with starches showed longer reaction time, namely cream time, gel time tack free time and rise time, than PIR foam without starch. this result indicates that PIR foam formulation modified with starch has high viscosity, thus has resistant to dispersion of gas bubble into the foam cell. The order of reaction times was PIR foams modified with glutinous rice flour > rice flour > mung bean starch.

When PIR foams was prepared at the isocyanate index of 200 and the amount of starches in PIR foam formulation was 10 wt%, the PIR foams modified with starches showed exothermic reaction which was due to the released heat of gelling and blowing reaction. The maximum core temperature was in the range 124.7-126.1 °C. PIR foams modified with starches have lower core temperature than that PIR foam without starch. PIR foam modified with mung bean starch had the highest core temperature as composed with those modified with glutinous rice flour and rice flour. Density of PIR foams modified with starches slightly decreased when the amount of starch was increased. PIR foam modified with rice flour and mung bean starch at the amount of 15 wt% showed increased in density, therefore, the optimum amount of starches in PIR foam formulation was 10 wt%.

In comparison to PIR foam without starch, increasing of isocyanate index from 200 to 250 for resulted in decrease of density of PIR foam modified with starch. PIR foam density decreased from 53.6 to 49.9-48.4 kg/m^3. PIR/PUR ratio for PIR foams modified with starches at the isocyanate index of 200 to 250 was in the range 1.03-1.06 and 2.51-2.77, respectively. The isocyanate conversion for all PIR foam modified with starch was more than 90% at the isocyanate indexes of 200 and 250.

It was found that the compressive strength of PIR foam modified with starches in parallel direction was greater than in perpendicular to the foam rising direction. The order of compressive strength of PIR foam filled with starches in parallel direction in mung bean starch > glutinous rice flour > rice flour. However, compressive strength of all PIR foam filled with starches was showed dramatically decreased in both parallel and perpendicular direction when compared to PIR foam without starch. The morphology of PIR foams modified with starches showed larger cell size, rupture cell and less uniform cell wall in several point when compared with those of the PIR foam without starch.

All PIR foams modified with starches showed higher fire-retardant property and limit oxygen index than PIR foam without starch. The PIR foams modified with starches showed self-extinguishing property ahead of marked point. This is due to the release the incombustible gas such as carbon dioxide, water and char to prevent oxygen and heat transfer.

Suggestion for future work

The suggestion for future work is to improve the formulation of PIR foams modified with starch. As an example, decreasing the amount of starch might result in the increased of compressive strength of PIR foams, while good fire-retardant property.

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