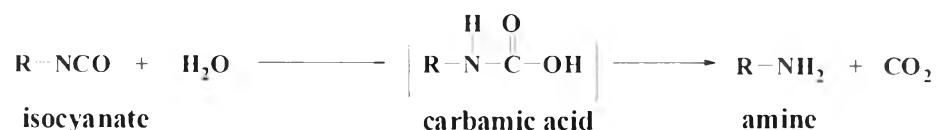# CHAPTER II

THEORY AND LITERATURE REVIEWS

Polyurethane foams can be separated into three types: low density flexible polyurethane foams, low density rigid polyurethane foams and high density rigid polyurethane foams. Low density rigid polyurethane foams are highly crosslinked polymers with an essentially closed cell structure and a density range of 28-50 kg/m^3. The foams are widely used as many applications such as insulation materials, construction and transportation. The general class of low density rigid polyurethane foams can be divided into rigid polyurethane foams (RPUR foams) and polyisocyanurate foams (PIR foams). RPUR foams are produced by reaction of isocyanate (usually MDI) with polyols while PIR foams result from reactions in which MDI is used at levels substantially higher than stoichiometric ratio [2, 4].
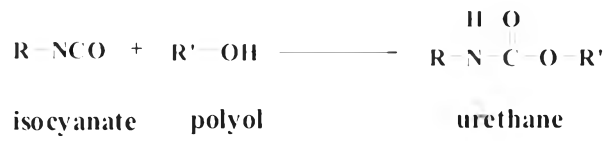
2.1 Chemistry

2.1.1 Chemical Reactions

There are three steps of chemical reactions that occur during foam formation. The first reaction is blowing reaction (Scheme 2.1), which is the reaction of isocyanate with water. Initially, unstable carbamic acid is formed. This decomposes to an amine and carbon dioxide, which blows the foam. The amine will then react immediately with another isocyanate to form symmetric urea [5]. The second reaction is urethane reaction or gelling reaction (Scheme 2.2), resulting from the reaction of isocyanate with hydroxyl groups of polyol. This reaction is exothermic reaction.

$$R-NCO \ + \ H_2O \ \longrightarrow \ R-\overset{H}{\underset{}{N}}-\overset{O}{\overset{\|}{C}}-OH \ \longrightarrow \ R-NH_2 \ + \ CO_2$$

isocyanate   carbamic acid   amine

Scheme 2.1 Blowing reaction [2]

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

isocyanate   polyol   urethane

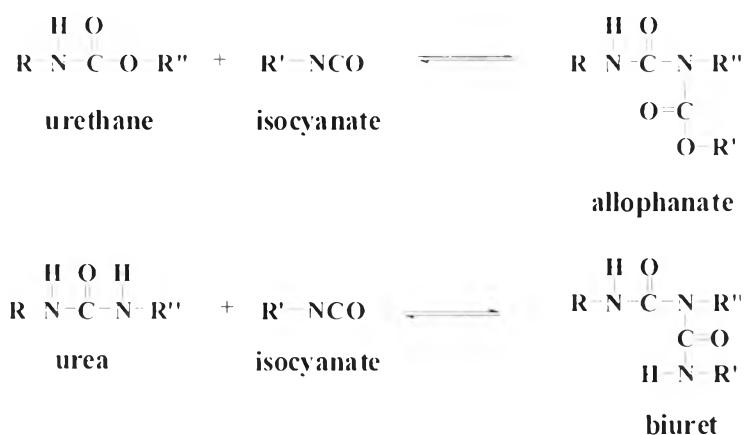**Scheme 2.2** Urethane reaction [2]

The last reaction. three isocyanates can undergo a cyclization reaction across the C=N bond resulting in six-membered ring called a trimer or isocyanurate (Scheme 2.3). It is used in manufacture of rigid foams, where the cross-linked structure contributes to fire resistance.
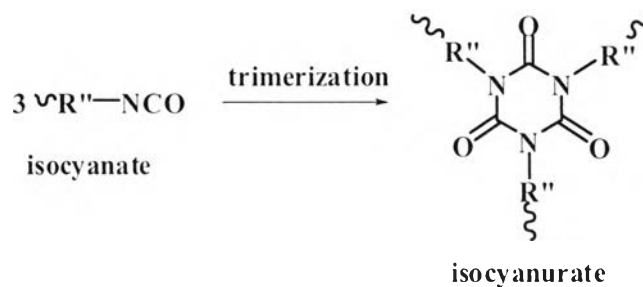
isocyanurate

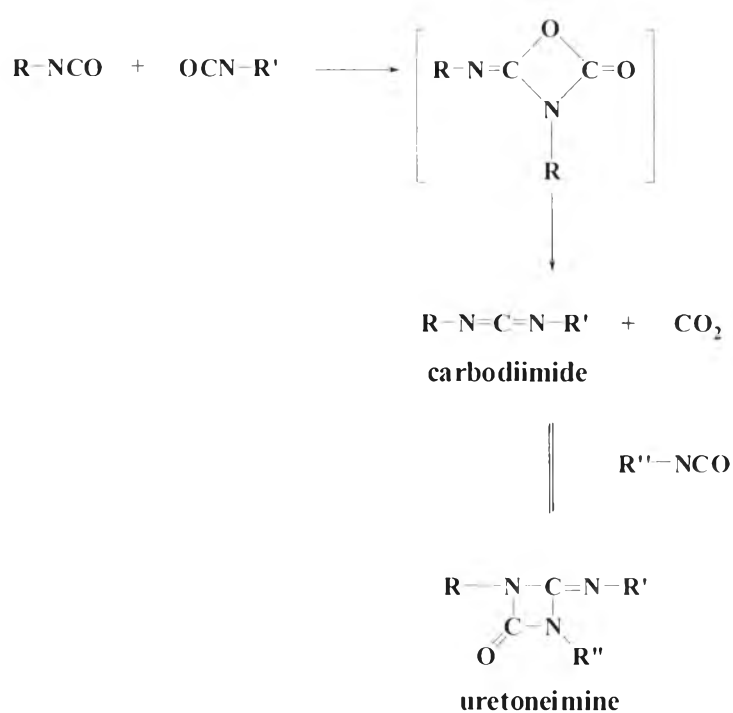**Scheme 2.3** Isocyanurate reaction [2]

2.1.2 Other Reactions of Isocyanate

Isocyanate can react with the active hydrogen atoms of urethane and urea linkages to form allophanate and biuret reactions (Scheme 2.4), which increase cross-linking in polyurethane systems. Allophanate and biuret reactions can be formed under suitable conditions.

H O
R—N—C—O—R" + R'—NCO ⇌ R—N—C—N—R"
                                        |
urethane   isocyanate   O=C
                                        |
                                       O—R'

allophanate

H O H
R—N—C—N—R" + R'—NCO ⇌ R—N—C—N—R"
                                       |
urea   isocyanate   C=O
                                       |
                                     H—N—R'

biuret

Scheme 2.4 Allophanate and biuret reactions [2]

Moreover, isocyanate can react at high temperature to form carbodiimide. It will react with another isocyanate in a cycloaddition reaction across the C=N bonds forming uretoneimine (Scheme 2.5).

R—NCO + OCN—R' ⟶ [R—N=C⟨O⟩C=O]
                              |
                              N
                              |
                              R

↓

R—N=C=N—R' + CO₂
carbodiimide

‖ R"—NCO

R—N—C=N—R'
     |
     C—N
    ‖   \
   O   R"
uretoneimine

Scheme 2.5 Carbodiimide and uretoneimine reactions [2]

2.2 Raw Materials

2.2.1 Polyols

Polyols play an important role in urethane industries and conventionally, a majority of them derived from petrochemical crude oils and coals. Polyols are also prepared from vegetable oils such as soybean oil, castor oil and palm oil. Polyether and polyester polyols are the main compounds used in both rigid and flexible polyurethane foams. Polyols used for the production of polyurethane foams are oligomer, which contain at least two hydroxyl groups. Table 2.1 shows some polyol characteristics.

Table 2.1 Polyos for polyurethane foams [2, 3]

Characteristic	Flexible foams and Elastomers	Rigid foams, rigid plastics and stiff coatings
Molecular weight range	1,000 – 6,500	150 – 1,600
Functionality range	2.0-3.0	3-8
Hydroxyl value range (mg KOH/g)	28-160	250-1,000

The hydroxyl value is used as a measure of the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol and is expressed as mg/KOH. Polyols sold for use in polyurethanes are invariably characterized by hydroxyl value as this is convenient for calculation of the stoichiometric formulation. The measured hydroxyl value of polyol is associated with its molecular weight and functionality [2]:

$$\text{Hydroxyl value,(mg KOH/g)} = \frac{56.1 \times \text{functionality}}{\text{molecular weight}} \times 1000$$

2.2.1.1 Polyether Polyols

Polyether polyols are formed by anionic polymerization of ethylene oxides or propylene oxide in the presence of an initiator and catalyst. The functionality and equivalent weight of the polyol can be controlled within wide limits and

the materials are widely used for both rigid and flexible polyurethane foams. Moreover, mixture of amines and alcohols as starters provide a useful way of adjusting the performance of the polyol in the urethane reaction. Since amine-based polyols are self-catalytic in their reaction with isocyanate compared with nitrogen-free polyols. Table 2.2 reveals some typical polymerization initiators [3, 4].

Sucrose and sorbital based polyols are usually used for preparing rigid polyurethane foams since they have shot chain oligomers with functionality between six and eight. Figure 2.1 shows the structure of poly(propyleneoxy) sucrose and poly(propyleneoxy) sorbitol.

Table 2.2 Examples of starter compounds for polyether polyols [2, 4]

Alcohols	Amines	Functionality
Water		2
Ethylene glycol		2
Diethylene glycol		2
Glycerol	Triethanolamine	3
Trimethylolpropane		3
Pentaerythritol	Toluene diamine	4
	Ehtylene diamine	4
	4, 4´-diaminodiphenyl-Methane	4
	Diethylene triamine	5
Sorbitol		6
Sucrose		8

poly(propyleneoxy) sucrose
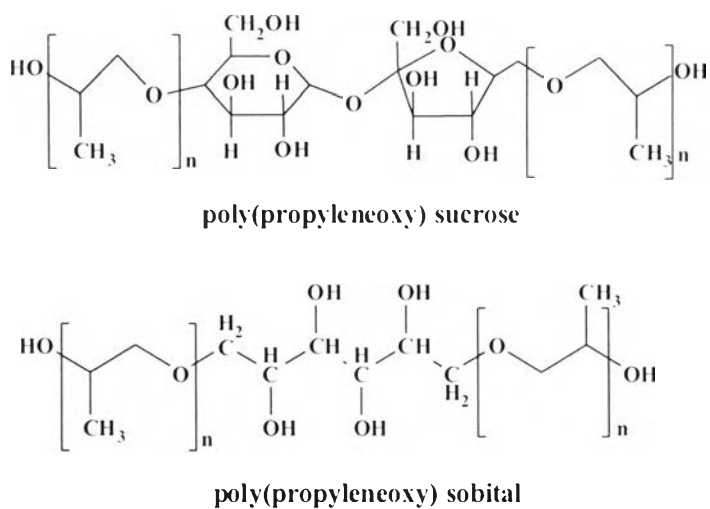
poly(propyleneoxy) sobital

Figure 2.1 Structure of poly(propyleneoxy) sucrose and poly(propyleneoxy) sorbitol [2]

2.2.1.2 Polyester Polyols

Aliphatic polyester polyols are usually used for making flexible polyurethane foam, polyurethane elastomers and polyurethane coating. On the other hand, aromatic polyester polyols are used for preparing rigid polyurethane foams. Polyester polyols for polyurethane foams can be prepared by dibasic acid (adipic acid or phthalic acid) with glycols (ethylene glycol or propylene glycol). The raw materials and structure for polyester polyol are shown in Table 2.3 and Figure 2.2, respectively.

Table 2.3 Example of raw materials for polyester polyols [2]

Dibasic acids	Glycols	Branching agents
Adipic acid	Ethylene glycol	Glycerol
AGS mixed acids	Diethylene glycol	Trimethylolpropane
	Propylene glycol	Pentaerythritol
	Dipropylene glycol	
	1,4-butane diol	
	1,6-hexane diol	
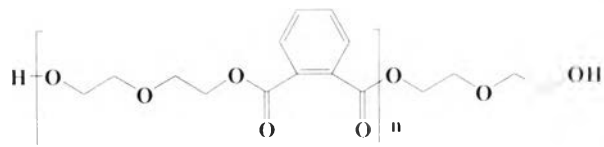
phthalic anhydride based polyester polyol

Figure 2.2 Structure of phthalic anhydride based polyester polyol [2]

2.2.2 Isocyanate

Diisocyanates are compounds with two isocyanate groups in the molecule. Industrially important diisocyanates include 2,4- and 2,6-toluene diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI) and 1,6-hexamethylene diisocyanate (HDI). The structure of general diisocyantes is shown below. The R groups can be aromatic rings or alkyl chains in order to increase rigidity and flexibility, respectively.

$$O=C=N-R-N=C=O$$

Figure 2.3 Structure of general diisocyanates [4]

2.2.2.1 Toluene Diisocyanate (TDI)

TDI is chiefly used as a mixture of the 2,4-and 2,6-isomers in the ratio of 80:20 and less commonly as 65:35 and pure 2,4-compound (Figure 2.4). TDI serves mostly for the production of flexible polyurethane foams.
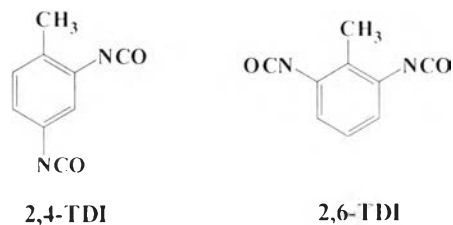

2,4-TDI   2,6-TDI

Figure 2.4 Structure of TDI isomers [4]

2.2.2.2 Methylene Diphynylene Diisocyanate (MDI)

MDI is a mixture of isocyanates with two or more aromatic rings. 4,4'-MDI and 2,4'-MDI are mainly type of MDI (Figure 2.5). Their average functionality is in a range of 2.2 to 3.0. The high functionality of MDI can be facilitate the production of a rigid. crosslinked, network coupled with a highly aromatic character which contributes to flame resistance. Beside. MDI is the choice for preparing rigid polyurethane foams.
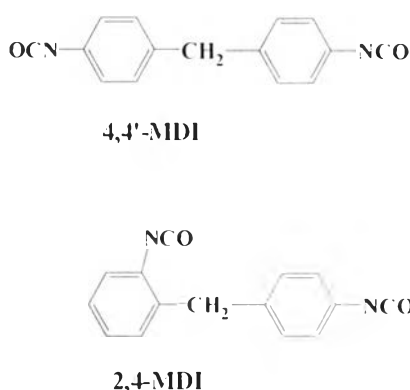

4,4'-MDI

2,4-MDI

Figure 2.5 Structure of MDI isomers [4]

2.2.2.3 Hexamethylene Diisocyanate (HDI)

HDI is a flexible, linear, symmetrical molecule with two primary aliphatic isocyanate groups of equal reactivity. The reactivity is at least two orders of magnitude lower than that in the 4-position of MDI. All the commercially available polyisocyanates, it has the highest isocyanate content because it is totally aliphatic, it gives rise to light-stable polyurethanes. The formula of HDI is shown in Figure 2.6.
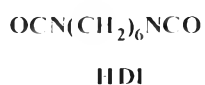
$$OCN(CH_2)_6NCO$$

HDI

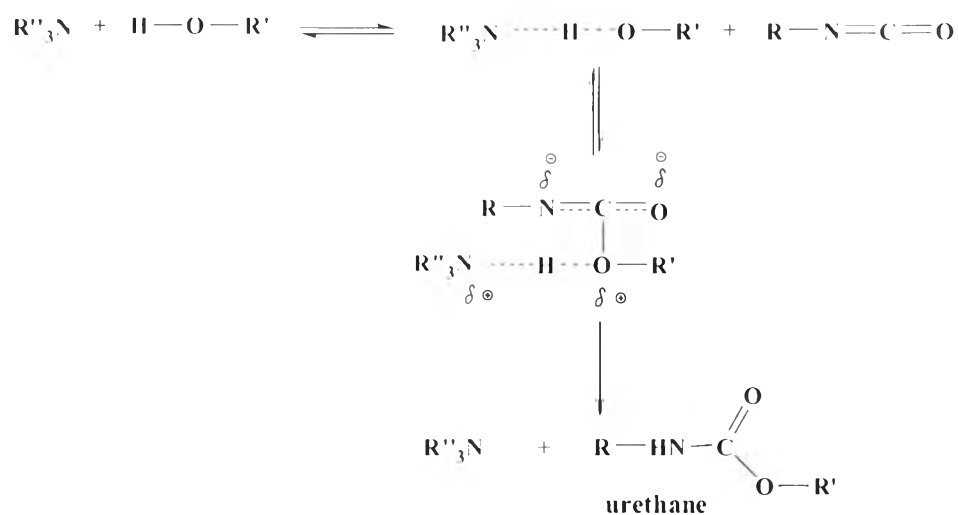**Figure 2.6** The formula of HDI

2.2.3   Catalysts

In the production of polyurethane foams, catalysts play an important role in the control and balance between blowing and gelling reactions (Scheme 2.1-2.2) [6]. With a suitability of the catalyst, the desired profile in reaction, blowing, foaming, and foam properties can be obtained. The selection of catalyst is based on its activity and performance on physical foam properties. Tertiary amine and organometallic catalysts are widely used for preparation of polyurethane foams.

2.2.3.1   Tertiary Amine Catalysts

Tertiary amine catalysts are mainly selected in making polyurethane foams. The choice of catalysts for preparing rigid, closed-cell, polyurethane foams from PMDI is usually concerned with obtaining the gelation, foam rise profile and cure rate most suitable for the process application. Mainly catalysts are tertiary amine listed in Table 2.4. Tertiary amine mechanism is shown in Scheme 2.6 proposed by Farka. The activation starts by the proton source (polyol, water, amine) to form a complex, which then reacts with the isocyanate.

Table 2.4 Tertiary amine catalysts and their applications [2]

Catalysts	Formula	Principal applications
N,N-dimethylcyclohexylamine (DMCHA)	$C_6H_{11}N(CH3)_2$	Rigid foams
1,4-diazabicyclooctoate (DABCO)	$N(CH_2CH_2)_3N$	All types of foams
N,N-dimethylethanolamine (DMEA)	$(CH_3)_2NCH_2CH_2OH$	Flexible and rigid foams
N,N'-diethylpiperazine	$C_6H_5CH_2N(CH_3)_2$	Polyester based flexible foams

$$R''_3N \ + \ H-O-R' \ \rightleftharpoons \ R''_3N \cdots H \cdots O-R' \ + \ R-N=C=O$$

$$R-\overset{\ominus}{\underset{\delta}{N}}=\overset{}{\underset{\delta}{C}}=\overset{\ominus}{\underset{\delta}{O}}$$

$$R''_3N \cdots H \cdots O-R'$$
$$\overset{}{\underset{\delta \, \oplus}{}} \qquad \overset{}{\underset{\delta \, \oplus}{}}$$

$$R''_3N \ + \ R-HN-C\overset{O}{\underset{O-R'}{\diagup}}$$

urethane

Scheme 2.6 Farka mechanism amine catalysts [2]

The catalytic activity depends on structure, basicity and steric hindrance of tertiary amine. N-methylmorpholine and N-methylpiperidine show similar structures (Figure 2.7). The N-methylpiperidine has a pKa of 10.1 is six time as fast as N-methylmorpholine which has a pKa of 7.4. Since two structures are similar the one with the higher pKa will be more reactivity.
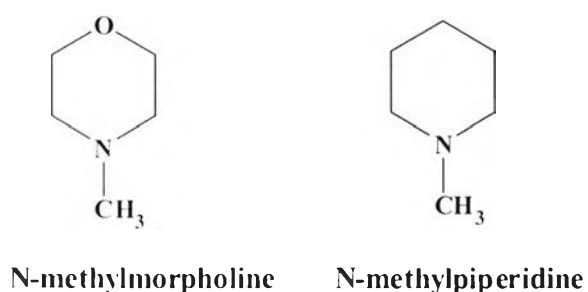
N-methylmorpholine **N-methylpiperidine**

Figure 2.7 Structure of N-methylmorpholine and N-methylpiperidine

The spacing of the heteroatoms has a definite effect on the gelling and blowing reaction. Amines with an ethylene linkage between heteroatoms are much better blowing catalysts than amines with a propylene linkage between atoms. The Figure 2.8 displays the structures of bis(N,N-dimethylaminoethyl)ether (BDMAEE) and N,N-dimethylaminoethyl N,N-dimethylaminopropyl ether (DMAEDMAPE). Therefore,

BDMAEE, which contain an ethylene linkage are faster blowing reaction than propylene linkage (BMAEDMAPE).
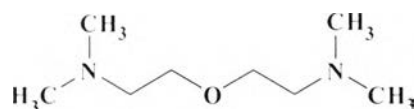
bis(N,N-dimethylaminoethyl)ether
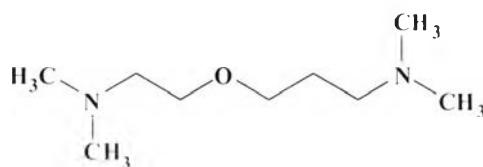
N,N-dimethylaminoethyl N,N-dimethylaminopropyl ether

Figure 2.8 Structure of bis(N,N-dimethylaminoethyl)ether and N,N-dimethylaminoethyl N,N-dimethylaminopropyl ether [2]
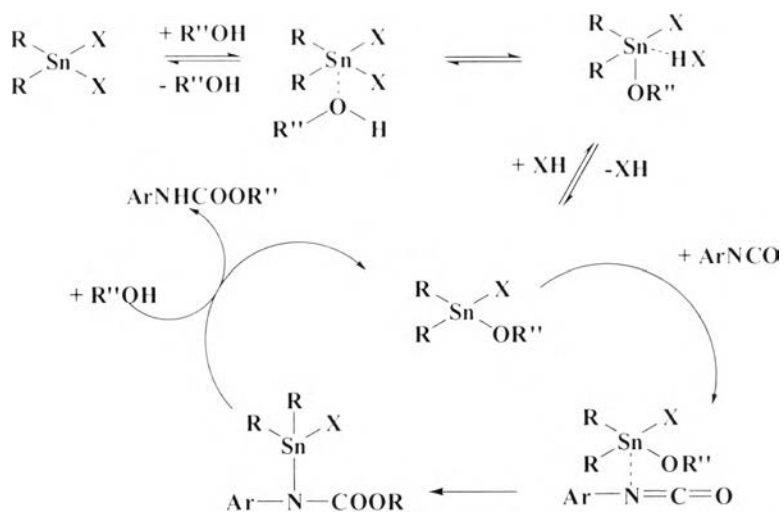
2.2.3.2 Organometallic Catalysts

Organometallic catalysts are used to accelerate the urethane reaction. Stannous octoate and dibutyltin dilaurate are the most popular. Mercury catalysts play an important role for preparing elastomers because they give a long reaction time with a rapid cure and show very good selectivity toward the gelling reaction. Moreover, the lead catalysts are usually used in spray foams. Table 2.5 shows some commercially available organometallic catalysts. Scheme 2.7 proposes tin II salts catalyst. Isocyanate, polyol and tin catalyst form a complex, which then gives the urethane product. Scheme 2.8 explains mechanism of tin IV catalyst, which interacts with polyol to form a tin alkoxide. Then, it reacts with isocyanate to form a complex. Transfer of the alkoxide anion onto the coordinated isocyanate affords an N-stannylurethane, which then undergoes alcoholysis to produce the urethane group and original tin alkoxide.

Table 2.5 Some commercially available organometallic catalysts [3]

Catalysts	Formula	Principal applications
Stannous octoate	$Sn(OCOC_7H_{15})_2$	Slabstock polyether-based flexible foams, moulded flexible foams
Dibutyltin dilaurate	$(C_4H_9)_2 Sn$ $(OCO(CH_2)_{10}CH_3)_2$	Microcellular foams, elastomer, moulding system
Lead octoate	$(C_7H_{15}COO)_2Pb$	Rigid spray foams
Potassium acetate	CH_3CO_2K	Isocyanurate foams
Ferric acetylacetonate	$C_{15}H_{21}FeO_6$	Catalysts for cast elastomer system, especially those based on TDI
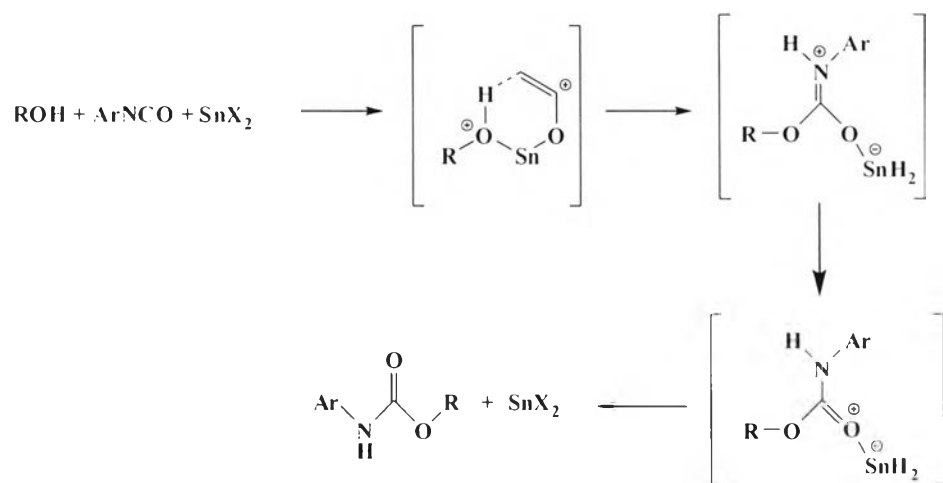
Scheme 2.7 Mechanism for tin II salts [2]

Scheme 2.8 Mechanism for tin IV compounds [2]

In some case. a combination of tertiary amine and organometallic catalysts is required to maintain a balance between the reaction of isocyanate with alcohol, and the reaction of the isocyanate with water. Mechanism of tin-amine catalyst is shown below.
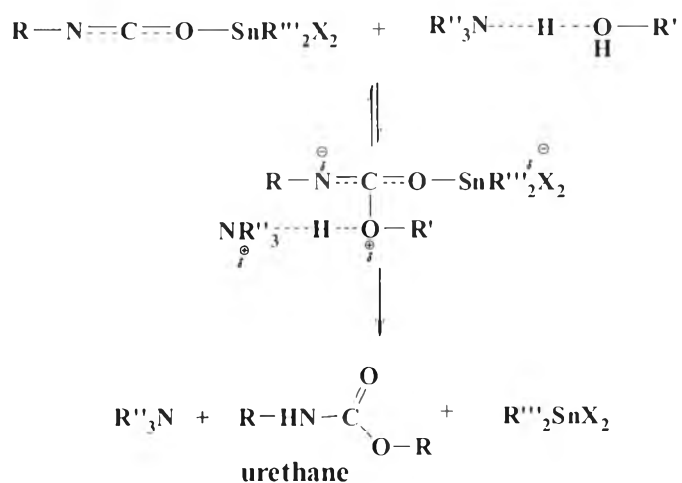
Scheme 2.9 Mechanism of tin-amine catalyst [2]

2.2.4 Surfactants

Surfactants play an important role in obtaining required cell structure. fine cells, coarse cell, closed cells and open cells. These cell sizes are influential in foam properties. Silicone surfactants are commonly used in the manufacture of polyurethane foams. They are polydimethyl siloxanes on which random or block copolymers of ethylene and propylene oxide are grafted [7]. The general structure of silicone surfactants is shown in Figure 2.9.

Silicone surfactants reduce the polyol surface tension and thereby facilitate generation of a large number of small bubbles during initial mixing. During the foam rising they stabilize these gas bubbles and prevent coalescence. To obtain the most efficient bubble stability and prevent coalescence the correct balance of foam reactivity and surfactant activity must be obtained. In most polyurethane systems the surfactant must act within a few minutes since if this balance is not optimized the surfactant will not be able to do its job and surface film rupture and defoaming will occur [8, 9].
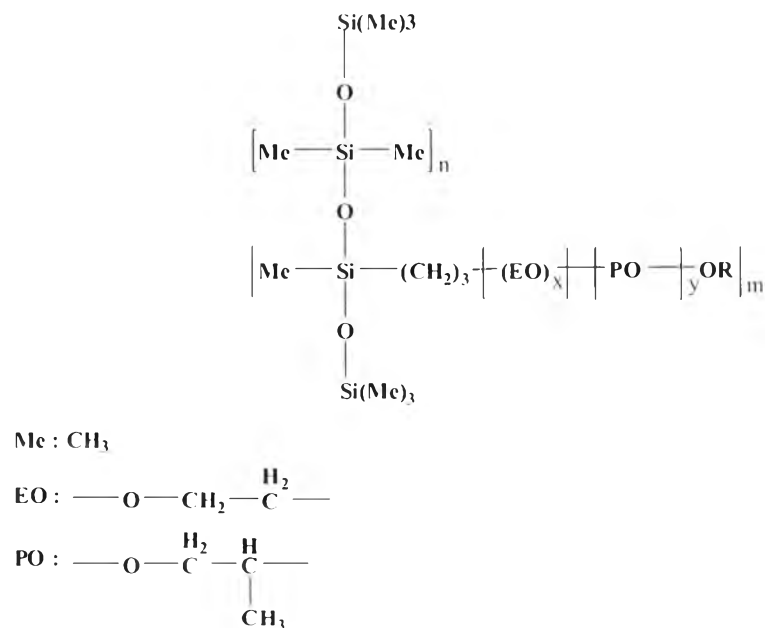

Figure 2.9 The general structure of silicone surfactants [9]

2.2.5 Blowing Agents

Gas generation is the important part of RPUR foam formation. Preparation of rigid polyurethane foams usually used physical and chemical blowing agents of combination of both. Major blowing agents are listed in Table 2.6. The widely used physical blowing agents are cyclopentane and HFCs. These blowing agents provide endothermic reaction. On the other hand, chemical blowing agents such as water expand foams by carbon dioxide gas result from the reaction between water and isocyanate. This reaction is exothermic reaction [1].

Table 2.6 Physical and chemical blowing agents [6]

Blowing agent	Types	Formula
Physical blowing agent	CFCs	
	CFC-11	CCl_3F
	CFC-12	CCL_2F_2
	HCFCs	
	HCFC-22	$CHClF_2$
	HCFC-142b	CH_3CClF_2
	HFCs	
	HFC-134a	CH_2FCF_3
	HFC-152a	CHF_2CH_3
	HCs	
	Iso-butane	C_4H_{10}
	Iso-pentane	C_5H_{12}
	n-pentane	C_5H_{12}
Chemical blowing agent	Azodicarbonamides	$C_2H_4N_2O_2$
	Water	H_2O

Almost physical blowing agents content halogens, which may deplete the ozone layer and cause the global warming. Therefore, water is usually used for preparing rigid polyurethane foams. Since water is a non ozone, non toxic and cheap blowing agent [10].

2.3 Formulations

2.3.1 The Reactive Components

The amount of isocyanate required to react with polyol and any other reactive additives, is calculated in the usual way to obtain the chemically stoichiometric equivalents. This theoretically stoichiometric amount of isocyanate can be adjusted upwards or downwards, depending on the polyurethane system, the properties required of the polymer product and known effects such as the scale of manufacture and ambient conditions.

2.3.2 Isocyanate Index (Index number) [2, 3]

The amount of isocyanate used relative to the theoretical equivalent amount, is known as the Isocyanate index or Index number. An isocyanate index of 110 indicates that there is ten percent excess of isocyanate.

$$\text{Isocyanate index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate}} \times 100$$

2.3.3 Isocyanate Value [2, 3]

The isocyanate value is the weight percentage of reactive isocyanate (NCO) groups in an isocyanate, modified isocyanate or prepolymer and is determined using the following equation, where the molecular weight of the NCO group is 42.

$$\text{Isocyanate value} = \% \text{ NCO groups} = \frac{42 \times \text{Functionality}}{\text{Molecular weight}} \times 100$$

2.3.4 Hydroxyl Value [2, 3]

The hydroxyl value (OHv) of a polyol, sometimes called the hydroxyl number, is determined by acetylating the polyol with pyridine and acetic anhydride and then titrating the excess acetic anhydride with KOH solution, measuring the difference between a blank solution and one containing polyol.

$$\text{Hydroxyl value} = \frac{56.1 \times \text{Functionality} \times 1000}{\text{Molecular weight}}$$

2.3.5 Acid Value [2, 3]

The acid value (Av) of a polyol, sometimes called the acid number, is determined by measuring the difference between titrating, with a standard KOH solution, a blank solution and one containing polyol. The Av is defined as the weight of KOH, in milligram, that neutralizes the acid in one gram of polyol.

2.3.6 Water Content [2, 3]

Water reacts with isocyanate groups and equivalent of water is thus:

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Functionality}}$$

2.3.7 Isocyanate Conversion [11, 12]

Isocyanate conversion can be calculated by FTIR spectroscopy, defined as the ratio between isocyanate peak area at time t and isocyanate peak at time 0:

$$\text{Isocyanate conversion} = \left[1 - \frac{\text{NCO}^t}{\text{NCO}^i} \right] \times 1000$$

Where;

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

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

2.4 Properties of Rigid Polyurethane Foams

2.4.1 Isotropy-Anisotropy

The cell morphology has a very significant influence on the properties. The cells are usually elongated or elliptical in the direction of foam rising. The ellipsoid cells give aspect ratio more than 1. Aspect ratio can be calculated by the ratio of the diameters of the major and minor ellipse axes. The compressive strength in the direction of foam rising can be about twice, the E-modulus about three times as high at the values measured perpendicular to the direction of rise [13-14]. A spherical, isotropic cell structure is most likely to occur when the foam system reacts slowly and uniformly and if there are no influences from the surrounding surfaces. The cell deviates from a spherical shape more and more as the reaction become faster and as the influence of the surfaces or mold wall increases. Round cells exhibit the same properties in all directions [6]. The cells in two major directions are shown below.
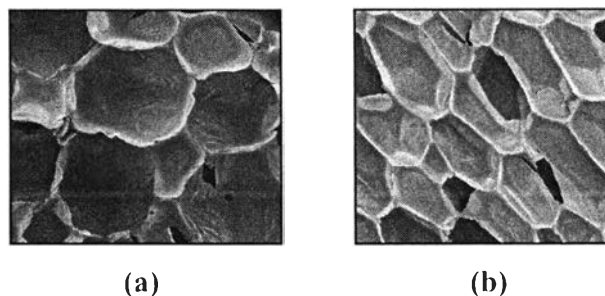

(a)   (b)

Figure 2.10 Cell structure of RPUR foams (a) spherical cells in the parallel of foam rise; (b) ellipsoid cells in the perpendicular of foam rise [7]

2.4.2 Compressive Strength

The compressive strength of RPUR foams can be measured in order to determine the apparent density of the foam. The compressive strength increase with the increasing of densitiy and the foam cells are oriented in the direction of foam rising, the compression parallel to rise has much higher than the one perpendicular to rise [15]. As Figure 2.11, the compression stress-strain curve can be separated into three regions. In region 1, linear elastic behaviour is controlled by cell wall bending and cell face

stretching due to the contained gas pressure. In region 2. the cells collapse through cell wall buckling. or in brittle foams, by cell crushing and cell wall fracture. In region 3, densification occurs. As foam density increases. Young's modulus increases in region 1, the plateau stress value increases and the strain at which densification starts reduces. In closed cell structure, the compression of gas in the cells also contributes, more so in regions 2 and 3 than 1 [2. 4].
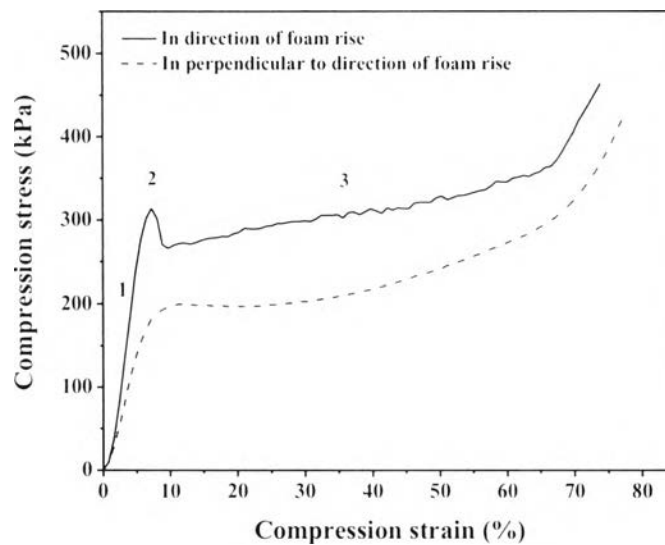

Figure 2.11 Stress-strain curve of RPUR foams [7]

2.4.3 Thermal Conductivity

RPUR foam is one of the best thermal insulation materials. The low thermal conductivity of the RPUR foam results from its low density and fine closed-cell structure filled gas. A typical of RPUR foam with a density of 32 kg/m^3 consists of 3% polymer and 97 % gas (by volume) trapped within the closed cells. Clearly, the thermal conductivity of the foam will depend to a large extent on the conductivity of the gas within the cells. The thermal conductivity of a foamed material (λ_f) may be expressed as the sum of four components:

$$\lambda_f = \lambda_G + \lambda_R + \lambda_S + \lambda_C$$

Where, λ_G is thermal conductivity of the cells gas, λ_R is thermal radiation, λ_S is thermal conductivity of the cell material and λ_C is convection of the cell gas. The

largest variations in thermal conductivity are attributable to variations in λ_g resulting from changes in the composition of the gas in the closed cells of the foam. Table 2.7 lists the thermal conductivities of the gases that may be present in RPUR foam.

Table 2.7 The thermal conductivity of the gases in RPUR foam [3]

Temperature (°C)	CFM-11	CFM-12	Air	CO_2	Water vapour
-17.8	0.00571	0.00778	0.0227	0.0133	0.0145
-6.7	0.00623	0.00813	0.0235	0.0141	0.0154
0	0.00643	0.00844	0.0240	0.0146	0.0159
4.4	0.00657	0.00864	0.0244	0.0149	0.0163
15.6	0.00692	0.00899	0.0253	0.0157	0.0170
26.7	0.00743	0.00951	0.0260	0.0166	0.0179
37.8	0.00778	0.00958	0.0269	0.0157	0.0188

2.4.4 Dimensional Stability

If the gas pressure difference between the internal cell gas pressure and atmospheric pressure has greater than the strength of the cell structure, it can start to deform and the dimensional stability test measures the tendency of the foam to shrink or expand under service conditions. As diffusion of the different gases takes place, the internal gas pressure in the cells can change. Taking into account the relative rates of diffusion of the different gases, the total cell gas pressure will usually exhibit a minimum value when all the carbon dioxide has left the foam and only minor amounts of air (N_2 and O_2) have entered the foam. This critical point for shrinkage will occur at any time dependent on how fast the diffusion processes take place [6, 16]

2.5 Literature Reviews

Water is one of the most widely used chemical blowing agents. It reacts with isocyanate and then produces carbon dioxide gas and amine (Scheme 2.1). The widely used physical blowing agents are CFCs and cyclopentane which were considered to be undesirable mainly because of environment problems. Physical blowing agents deplete

the ozone layer and cause global warming. Li *et al.* [10] prepared RPUF blown by varying water level. They explained that density of RPUF samples decreased with the increase of water level. Compressive strength showed the similar behavior with density. T_g shifted to a higher temperature with increasing of isocyanate when more water as a chemical blowing agent was used. Water blown RPUF samples usually have poor dimensional stability due to fast diffusion rate of carbon dioxide gas out of the foams. Dimensional stability became poorer with the increase of water level.

Mechanical properties should be studied due to the measurement of properties may also indicate the suitability of material for applications. The most important quality control tests are the determination of apparent density of foams, the measurement of compression strength and dimensional stability of foams under conditions of temperature and humidity that are related to applications. Hawkins *et al.* [17] investigated the relationships between cell morphology, density and mechanical properties in a molded polyurethane material. These relationships could be used for mechanical designers to analyze and predict the responses of foam components accurately. They found that the cells showed more elongated at the bottom of the mold at parallel to the rise direction. The cells were much more uniform at perpendicular to the foam rising. The density did not change significantly from the top to the bottom of the mold. Mohan *et al.* [18] determined the effect of processing temperature on the physical and mechanical properties of polyurethane foam. The polyurethane foaming process manipulated to change the foam's density and mechanical properties. They reported that the mean densities and compressive modulus decreased with the increase of processing temperature from 25 to 85 °C.

Catalysts are necessary for preparation RPUR foams due to the reaction of isocyanate with water (blowing reaction) and polyol (gelling reaction) are slow (Schemes 2.1-2.2). Tertiary amines and tin catalysts are usually used in industries. On the other hand, they show toxic to human beings and have strong smell. Inoue *et al.* [19] studied the activities of M(acac)$_n$ and tertiary amine-M(acac)$_n$ catalysts. These catalysts accelerated the reaction between hexamethylene diisocyanate (HDI) and diethylene glycol (DEG). It was indicated that TEDA-Mn(acac)$_2$ had better catalytic activity than

other $M(acac)_n$ complexes (M = Fe, Co, Ni and Cu) and showed comparable catalytic activity to DBTDL, which is a commercial catalyst.

Sardon et al. [20] compared the effectiveness of tin compound and zirconium compound in the polymerization of isophorone diisocyanate (IPDI) based waterborne polyurethanes. Sardon and coworkers found that isophorone diisocyanate (IPDI) based waterborne polyurethanes could be synthesized using zirconium compound as catalyst. This catalyst had less toxic than comparable tin compound.

Zelenak et al. [21] synthesized and characterized copper acetate complexes, namely $Cu(CH_3COO)_2(en)_2.2H_2O$ (I), $Cu(CH_3COO)_2(tn)_2$ (II) and $Cu_2(CH_3COO)_4(pyz)$ (III) (where en=ethylenediamine, tn=1,3-diaminopropane, pyz=pyrazine). The complexes were investigated by TG/DTG-DTA-EGA methods on heating in argon to characterize their thermal stability. The results indicated that complex III showed the highest thermal stability. Thermal stability of complexes I and II was lower and determined by the dehydration and evolution of the amines.

Cara et al. [22] reported the characterization of $[Ni(trien)(en)]X_2$ complexes (en = ethylenediamine, trien = triethylenetetramine); X = Cl, Br, I, SCN, NO_3, AcO, ClO_4 and BPh_4 and $[Cu(trien)(en)]X_2$ complexes (X = ClO_4 and BPh_4). They studied the stereochemistry of these compounds both in solution and in solid state. It was found that $[Ni(trien)(en)]X_2$ and $[Cu(trien)(en)]X_2$ complexes were racemic mixtures in solution.

Blank et al. [23] developed new catalysts for isocyanate-hydroxyl reaction by non-tin catalysts. Tin catalysts showed excellent catalytic activity but had strong smell and toxicity. Blank and coworkers found that zirconium chelates could activate the hydroxyl groups and catalyze the isocyanate-hydroxyl reaction by an insertion mechanism. This reaction was selective and preferred over the isocyanate-water reaction.

Choe et al. [1] prepared RPUR foams by variation of amine catalysts. Triethylene dianine and pentametylenetriamine were gelling and blowing catalysts, respectively. Water was used as chemical blowing agent. They found that kinetic rate of gelling and blowing reactions of RPUR foams increased with increasing of triethylenediamine and

pentametylenetriamine, respectively. Since triethylenediamine promoted gel time and tack free time, and pentametylenetriamine promoted cream time.

Maris *et al.* [5] reported the catalytic activities of tertiary amine catalysts by titration and HPLC methods. It was found that triethylenediamine (TEDA) showed a strong gelling catalyst, while pentamethyldiethylenetriamine (TOYOCAT-DT) and bis(2-dimethylaminoethyl(ether) (ETS) were all strong blowing catalysts that produced more open cell foam inflexible foam applications and provided excellent flowabitily of foam. Moreover, the strong gelling catalyst showed high adhesive strength and lower K-factor due to the small cell size. The strong blowing catalyst produced low density foam with better dimensional stability because of the excellent flowability and isotropic cell structure.

Catalyst content plays an important role not only on reaction time, but also on cell window areas. Mondal *et al.* [24] studied the effect of DBTDL content on network formation. The optimum of catalyst content provided small cells and narrow struts. The window areas of foam decreased with the increase of DBTDL proportion due to the rate of network formation was slightly faster than blowing reaction. This would prevent bubble coalescence and slow down cell window drainage. The small cell windows could increase the hydraulic resistance of foam which used in subsea vehicles.

Kurnoskin [25, 26] synthesized metal-containing epoxy polymers by hardening of the diglycidyl ether of bisphenol A (DGEBA) with the chelates of metals (Mn^{4+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) and aliphatic amines (ethylenediamine, diethylenetriamine, triethylenetetraamine and cycloethylated diethylenetriamine). The copper-containing polymers exhibited a significant increased in thermal oxidative stability, which could be compared with the heat resistance of well known epoxy-anhydride systems.

Pengjam [27] prepared RPUR foams from metal complexes [$M(OAc)_2(en)_2$] (where M = Cu and Mn) and synthesized in acetone. It was found that $Cu(OAc)_2(en)_2$ showed the best catalytic activity. RPUR foams prepared from metal complexes were compared to those prepared from dimethylcyclohexylamine (DMCHA), which is a commercial catalyst.

The research of Ionue and Pengjam indicated that the metal complexes between transition metal and amine could be synthesized and catalyzed urethane formation. Therefore, metal-amine complexes and mixed metal-amine complexes between $M(OAc)_2$ (where M = Cu, Zn, Ni, Co and Mn) and tetraenethylenepentamine (tetraen) were investigated as catalysts for preparing RPUR foams in order to obtain good catalytic activity and mechanical properties.