

CHAPTER 2

THEORY AND LITERATURE REVIEW

The original discovery leading to the world-wide interest in all class of polyurethane was made by Otto Bayer and his co-workers of I.G. Farbenindustrie at Leverkusen, Germany in 1937 that commercial potential of polyurethanes as fibres, adhesives, coating and foams began to be recognized. In fact, most polyurethanes application have been developed during the past 30 years. Table 2.1 shows progressive of polyurethanes.

2.1 Reaction of isocyanate

G. Woods (1987) described that polyurethanes contain carbamate groups in their backbone structure. They are obtained by the reaction between isocyanate with more than one reactive isocyanate group per molecule (diisocyanate or polyisocyanate) and alcohols that have two or more reactive hydroxyl group per molecule (diols or polyols). This kind of polymerization is called addition polymerization. All polyurethanes are based on exothermic reaction of diisocyanate or polyisocyanate with polyols molecules. The rate of polyaddition reaction is influenced by the structure and functionality of both isocyanate groups and polyols, including the location of substituents in proximity to the reactive isocyanate group (steric hindrance) and the nature of the hydroxyl group (primary or secondary). Relative few basic isocyanates and a range of polyols of different molecular weight and functionalities are used to produce various kinds of polyurethane products in an extremely wide range of grade that is stiffness from

very flexible elastomer to rigid, hard plastics. The range of end products which is derived from polyurethanes is shown in Figure 2.1.

Table 2.1 Illustrates some highlights in the development of polyurethanes
(Wood G., 1987)

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

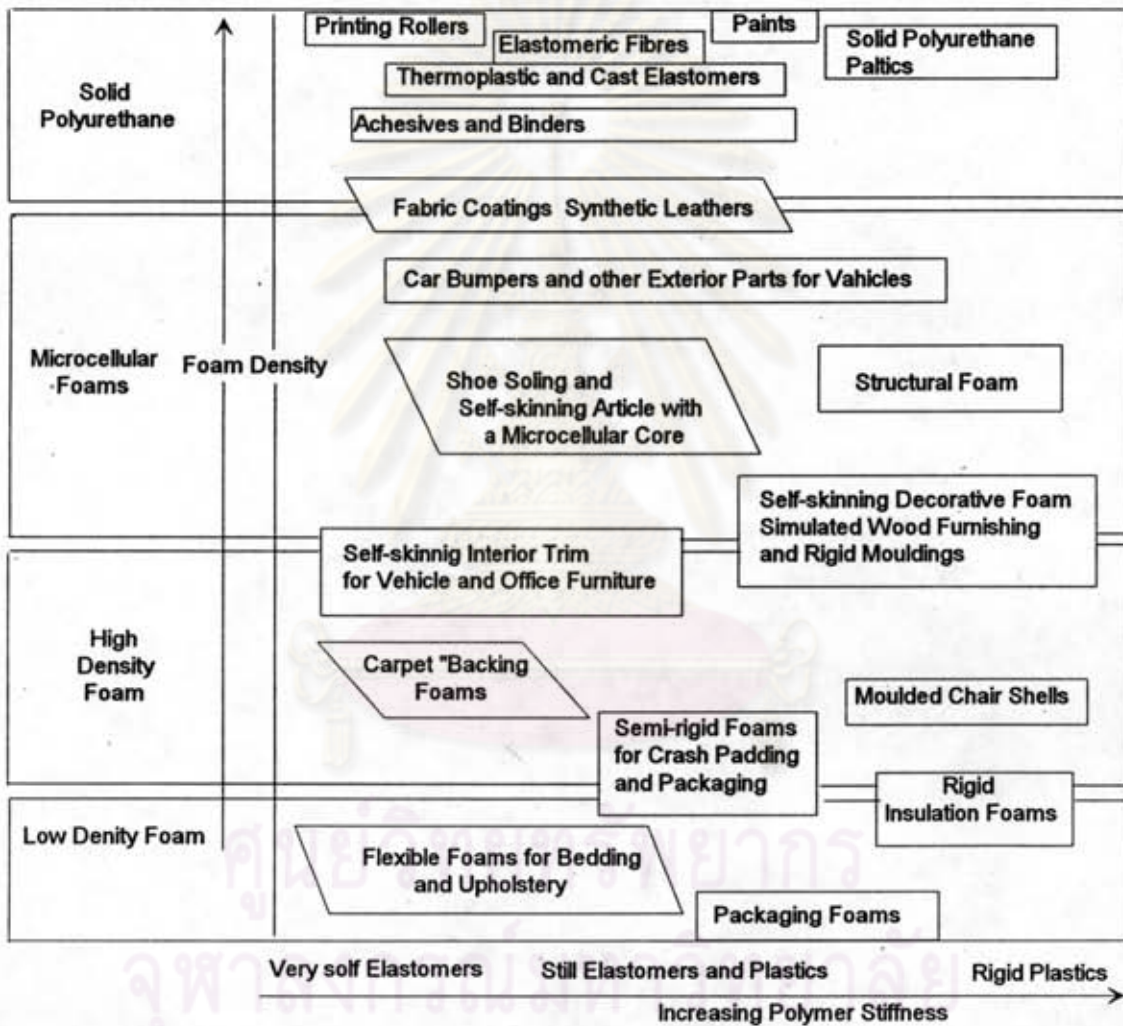
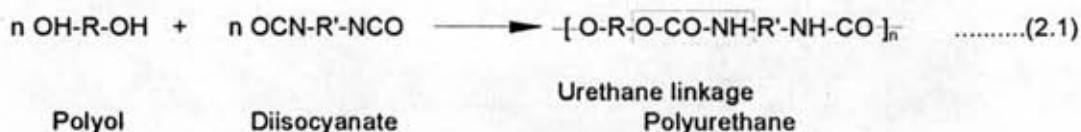
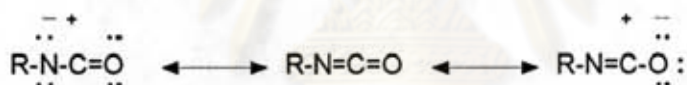


Figure 2.1 Properties matrix of Polyurethane

The reaction of diisocyanate with polyol is shown in Equation (2.1).



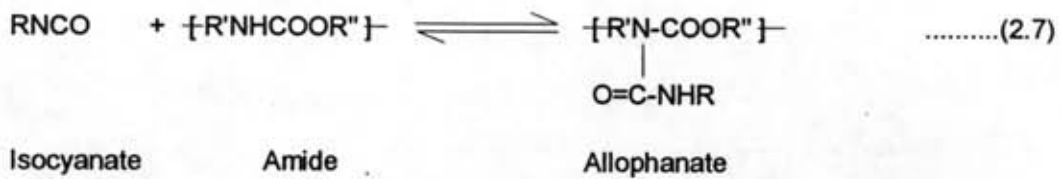
The key to the manufacturing of polyurethane is the unique reactivity of the heterocumulene groups in diisocyanate toward nucleophilic addition which reactive hydrogen atom is transferred to the nitrogen of the isocyanate and the remainder is attached to the carbonyl. The formation of the polymer is by a step-wise process (G.Norman and S.Gerald,1985). The polymerization of the isocyanate group enhances the addition across the carbon-nitrogen double bond which allows rapid formation of addition polymer from diisocyanate and macroglycols (O. Kirk,1983).



The important characteristic of reaction is giving no by-product of a small molecule is formed.

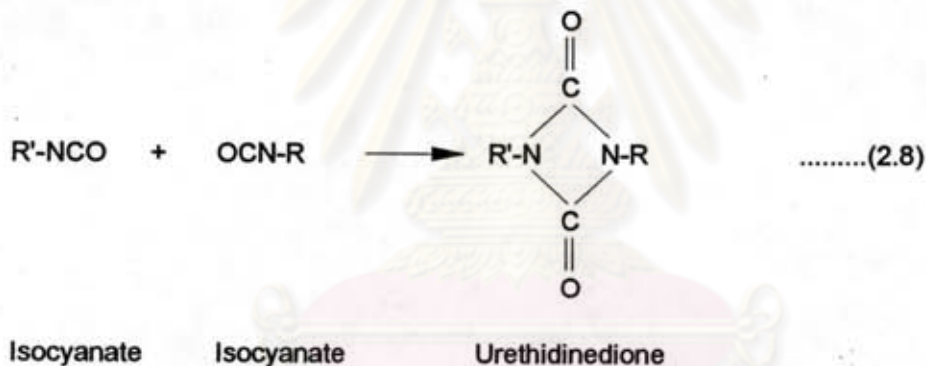
The reaction of isocyanates with compounds containing active hydrogen atoms i.e. amine, water etc. was capable of much wider application in polymer formation.

Reaction with amines: diamines are used as chain-extending and curing agent in polyurethane manufacturing. It can increase the potential for both primary (covalent) and secondary, or hydrogen-bonded, crosslinking and resulting urea segments in polymer as shown in Equation 2.2.

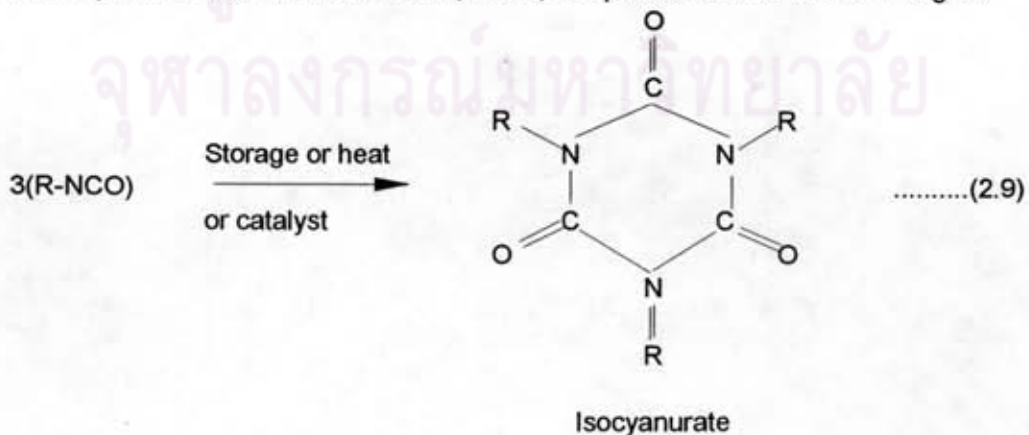


Isocyanate polymerization reactions

Some isocyanate also react with themselves to form thermally reversible dimer structure, the so-called uretidinediones, and isocyanurated. Thus 2,4- and 2,6-TDI do not forms dimers at normal temperature but 4,4'-diphenylmethane diisocyanate (MDI) dimerizes slowly when left standing at room temperature. After that, a storage life of MDI is limited because of dimerization. At higher temperature insoluble polymeric material are formed.



Isocyanurate are formed on heating both aliphatic or aromatic isocyanate. The reaction is accelerated by basic catalysis. Isocyanurate formation gives very stable branch point unlike the uretidinedione, biuret, allophanate and urethane linkages.

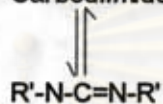


In the presence of special catalysts, isocyanate can react to form carbodiimide with eliminate carbon dioxide and then react reversible with further isocyanate to give a uretonimime. Polycarbodiimides are used as anti-hydrolysis additives in polyester based urethanes.



Isocyanate

Carbodiimide



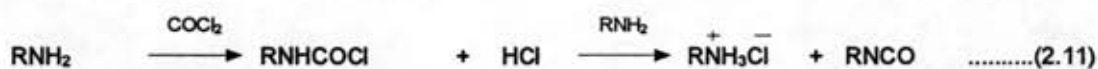
Uretonimine

2.2 Raw material for polyurethanes

The starting materials for produce polyurethane are the two main participants, namely isocyanate and polyol. In addition to the isocyanate and polyol, auxiliary materials (additives) are added to control the process of reaction and to obtain particular characteristics of final polymer.

2.2.1 Isocyanate

Isocyanates are made by phosgenation of primary amine or amine hydrochlorides in an inert medium (O-dichlorobenzene). The reaction proceeds in two stages : first at room or higher temperature to generate the carbamyl chloride and HCl; further treatment with phosgene at temperature of the order of 150-170°C , then forms the isocyanate according to the reaction 2.11 and 2.12.



The structural formula of diisocyanate are given in Figure 2.2 which includes TDI, MDI, NDI, HDI, H₁₂MDI, XDI, IPDI, TMDI, PPDl, CHDI, TODI, but about 95% of all polyurethanes are based on toluene diisocyanate (TDI), 4,4'-Diphenylmethane diisocyanate (MDI) and its derivatives. Both of them are derived from petrochemical intermediates.

TDI is prepared by direct nitration of toluene to give 80:20 mixture of 2,4- and 2,6-dinitroderivatives, followed by hydrogenation to diaminotoluenes. The diamine mixtures are treated with phosgene at temperature up to 140°C and the derived diisocyanate mixture is isolated and purified by distillation. Flowsheet and diisocyanate preparation route for production TDI are detailed in Figure 2.3 and Figure 2.4, respectively.

TDI mixtures can occurred a serious toxic hazard in use, having a marked effect on the respiratory system and the skin, and care is very necessary in handling if damage to health is to be avoided. On the other hand, the diisocyanate MDI based on diaminodiphenylmethane is considerable safer to use, having as much lower volatile but it is manufacturing is more complex than that of TDI. Otherwise, the disadvantage is less easily purified and consequently MDI is often used in the crude (undistilled form). The manufacture of MDI is shown in Figure 2.5.

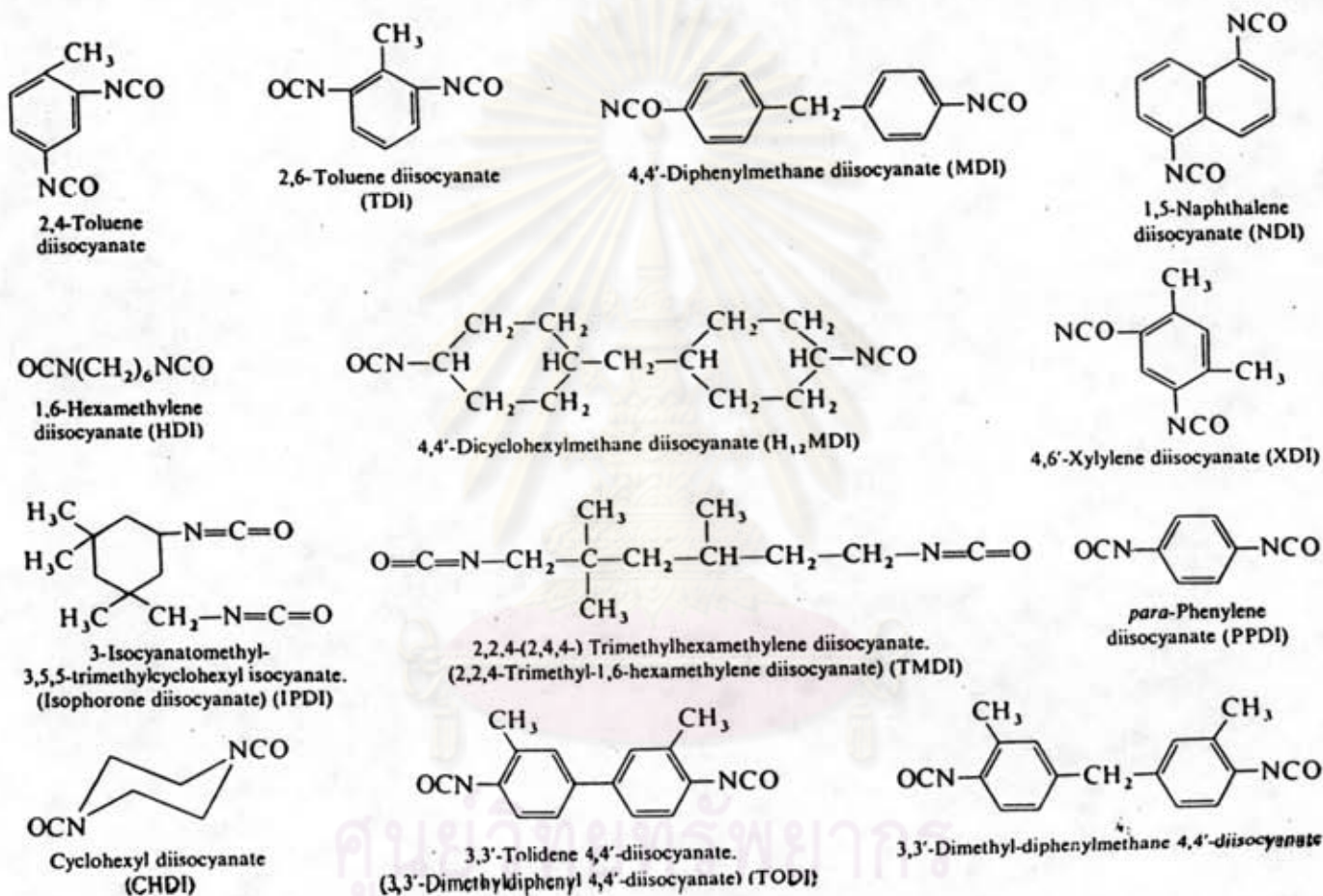


Figure 2.2 Structural formula of diisocyanate

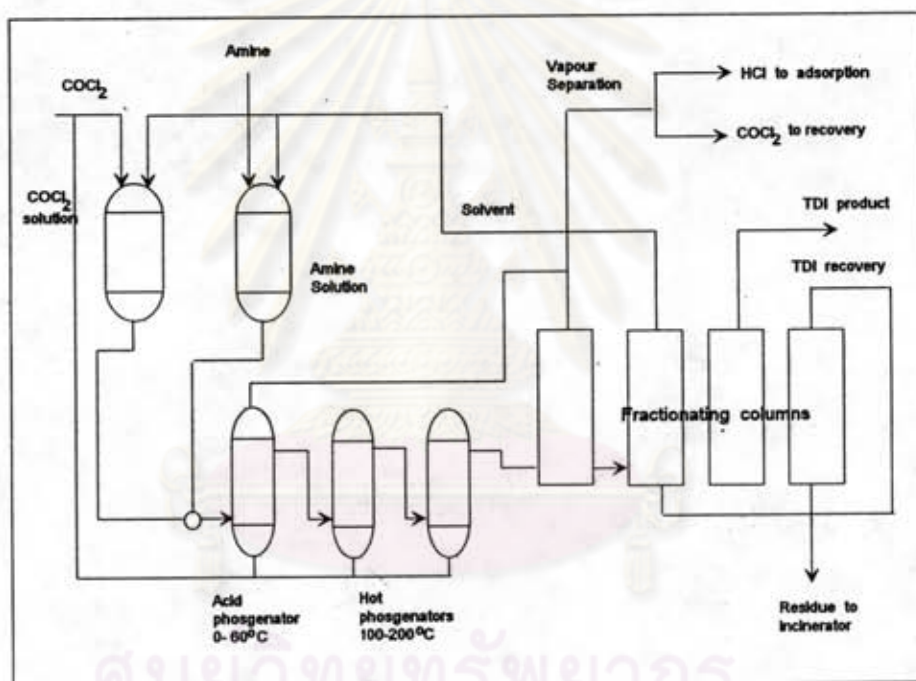


Figure 2.3 Flowsheet for the production of toluene diisocyanate

(P.Wright and A.P.Cumming, 1969)

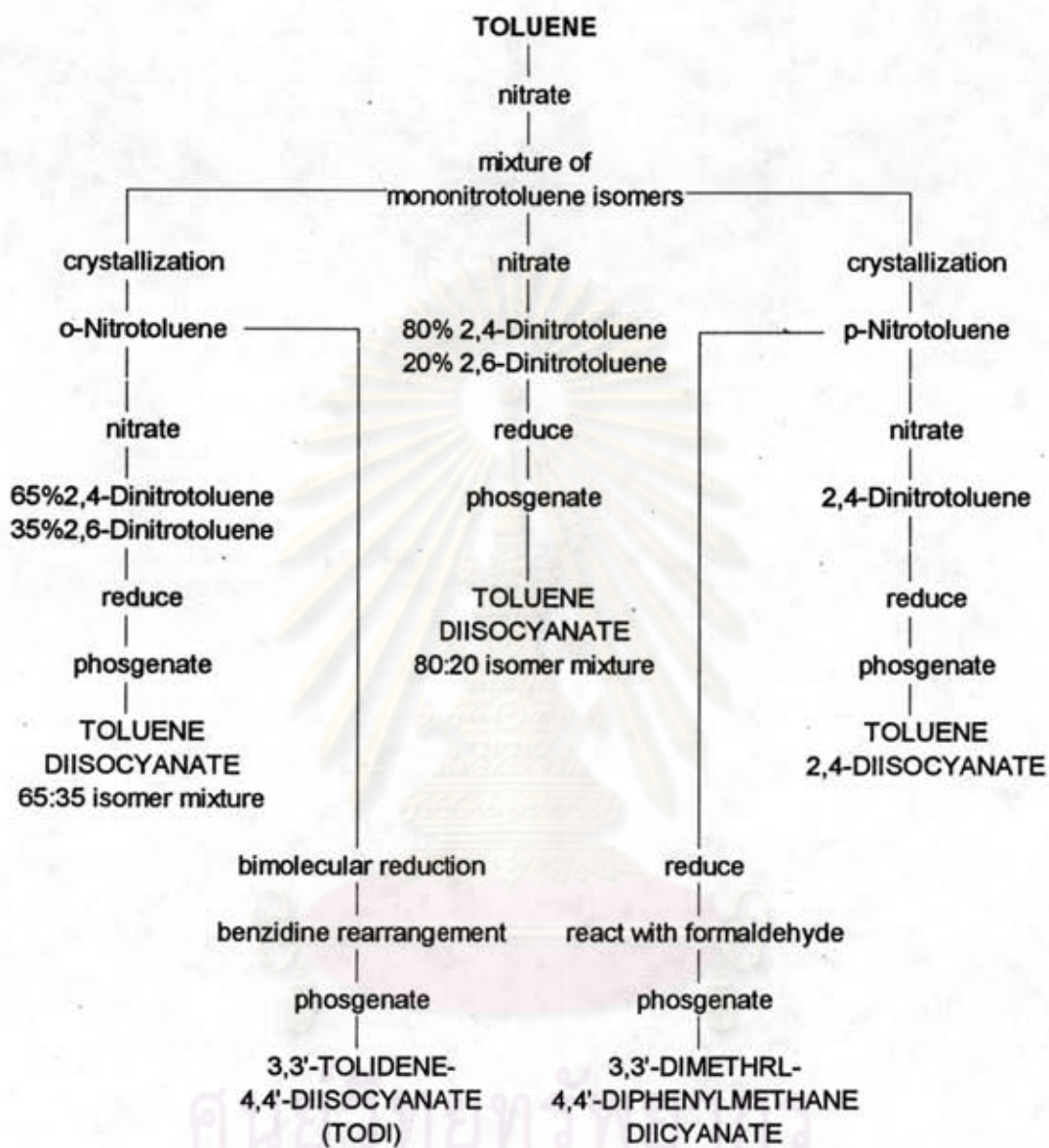
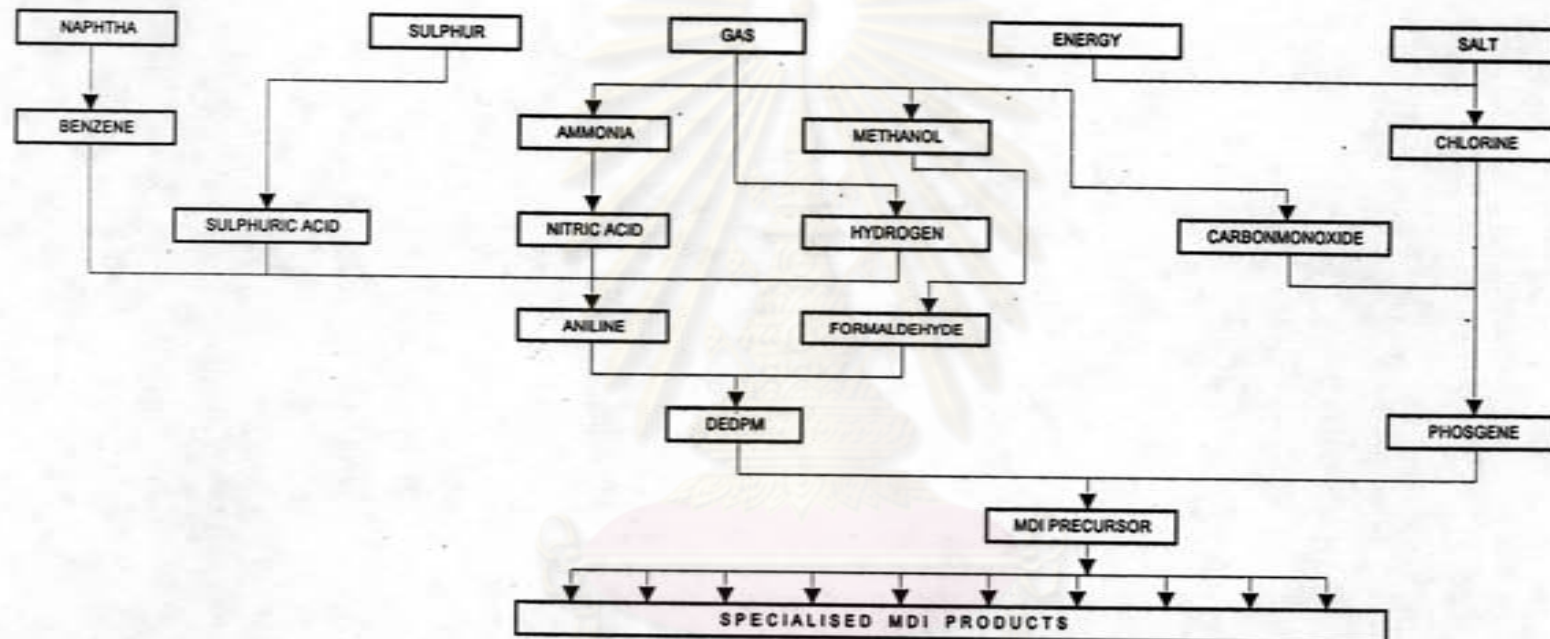


Figure 2.4 Diisocyanate preparation routes for production of TDI



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Figure 2.5 The manufacture of MDI

MDI is produced from aniline and formaldehyde by using hydrochloric acid as a catalyst. This condensation reaction produced a complex mixture of polyamide which are phosgenated to obtain a polyisocyanate mixture as shown in Equation 1.13 and 1.14. The product, known as the polymeric MDI as shown in Figure 2.6 (L.F. Hatch and S.Matar,1981)

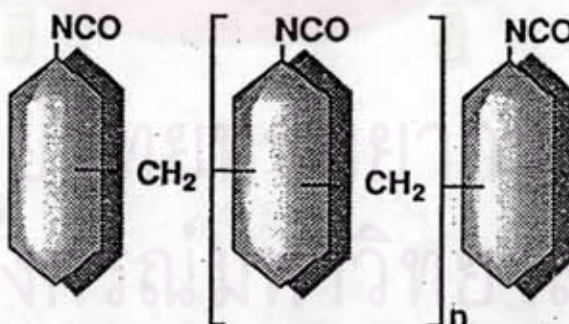
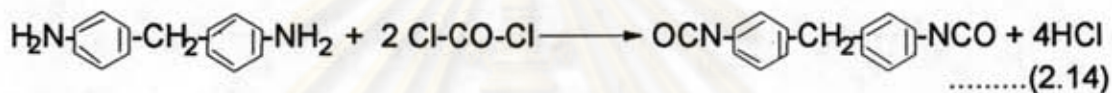
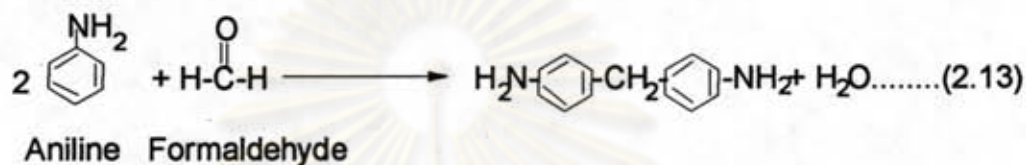


Figure 2.6 Structure of polymeric MDI

Polymeric MDI may contain 55 % of the 4,4' and 2,4'-diisocyanate and 20-25 % of triisocyanates and the remainder being polyisocyanates. Another form of MDI is pure MDI, a low melting solid (m.p. 38°C) is available and is produced by separation from a polymeric MDI precursor. It usually contain small amount of the 2,4' isomer.

Because of different range of functionality, structure and compositions, the selection of MDI may obtain the different kinds of polyurethane. Table 2.2 shown the suitable applications which are effect on properties of polyurethane.

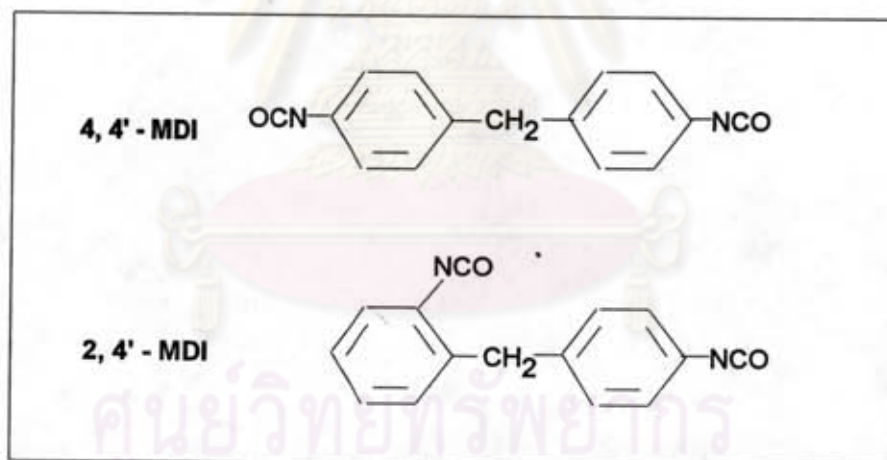


Figure 2.7 Structures of pure MDI

Table 2.2 Range of MDI variants

Average functionality	Product description	Polyurethane type	Main application
2.0	Pure MDI	High performance elastomers	Shoe-soling. Spandex fibers. Flexible Coatings thermoplastics
2.01-2.1	Modified, liquid pure MDI	High performance elastomers. microcellular elastomers	Shoe-soling Flexible Coatings. RIM and RRIM. Cast elastomers
2.1-2.3	Liquid, low functionality polyisocyanates	Flexible, semi-rigid and rigid foams one component froth.	Automotive parts Cabinets for electronic equipment Insulating sealants Cast elastomers
2.5	low viscosity liquid polyisocyanates	High density flexible foams. Structural foams	Foam-backs for carpet/vinylns. Computer carbinets and other moulded articles.
2.7	Low viscosity polymeric MDI	Low density rigid foams.Semi-rigid foams. Isocyanurate foams. Particle binders.	Insulating foams Energy absorbing foams Isocyanurate foam building panels. Mine-face consolidation Clipboard and foundry sand binders
2.8-3.1	High functionality polymeric MDI	Rigid polyurethane isocyanate foams	Continuous lamination of rigid foam and foam slabstock

Remarks : Functionality is defined as the average number of chemically-reactive groups on each individual molecule present.

2.2.2 Polyols

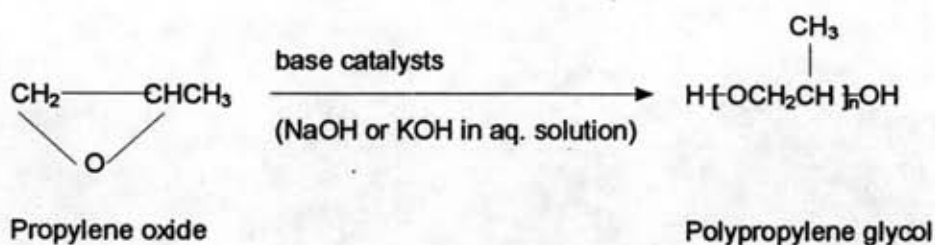
Most of the polyols used in making polyurethanes are classified in two types : hydroxyl-terminated polyethers and hydroxyl-terminated polyesters. The structure of polyol influences on the properties of the final urethane polymer.

2.2.2.1 Polyether polyols

Polyether polyols are high molecular weight polyols that range from viscous liquid to waxy solids, depending on structure and molecular weight. Commercial polyether polyols are shown in Table 2.3. Most polyethers polyols used in polyurethane manufacturing are polypropylene glycols which are derived from propylene oxide.

Table 2.3 Commercial Polyether polyols (M. Morton, 1987)

Common Chemical Name	Type	Structure
Poly(tetramethylene adipate) glycol	Polyester	$\text{HO}[(\text{CH}_2)_4\text{OCO}(\text{CH}_2)_4\text{COO}]_n(\text{CH}_2)_4\text{OH}$
Poly(ϵ -caprolactone) glycol	Polyester	$\text{H}[\text{O}(\text{CH}_2)_5\text{CO}]_x\text{ORO}[\text{CO}(\text{CH}_2)_5\text{O}]_y\text{H}$
Poly(hexamethylene carbonate) glycol	Polyester	$\text{HO}[(\text{CH}_2)_6\text{OCOO}]_n(\text{CH}_2)_6\text{OH}$
Poly(oxytetramethylene) glycol	Polyether	$\text{HO}[(\text{CH}_2)_4\text{O}]_n\text{H}$
Poly(1,2-oxypropylene) glycol	Polyether	$\text{HO}[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]_n\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$
Poly(butadiene) glycol	Polyhydro-carbon	$\text{HO}(\text{CH}_2\text{CH}=\text{CHCH}_2)_x\text{OH}$



Propylene oxide is produced from propylene via a chlorohydrin intermediate and polymerized by basic catalysts.

The manufacturing of propylene glycol uses ethylene glycol or propylene glycol or diethylene glycol as initiator and uses catalyst in a common solvent. Then pump into a catalyzing vessel heated to 80-100°C under vacuum where the solvent is removed and the alcoholate formed, and transferred to the reactor vessel at 90-120°C. Propylene oxide is pumped into a pressure of 10-50 psi which is maintained until the desired molecular weight is reached, when any excess propylene oxide is distilled off and the polyether mixture transferred to a neutralizing vessel and neutralized by sulfuric acid. Then the mixture is filtered and remaining water reduced to 0.05% maximum. Antioxidants are added to prevent storage stability. Polypropylene glycol flowsheet is given in Figure 2.8 and Figure 2.9, respectively.

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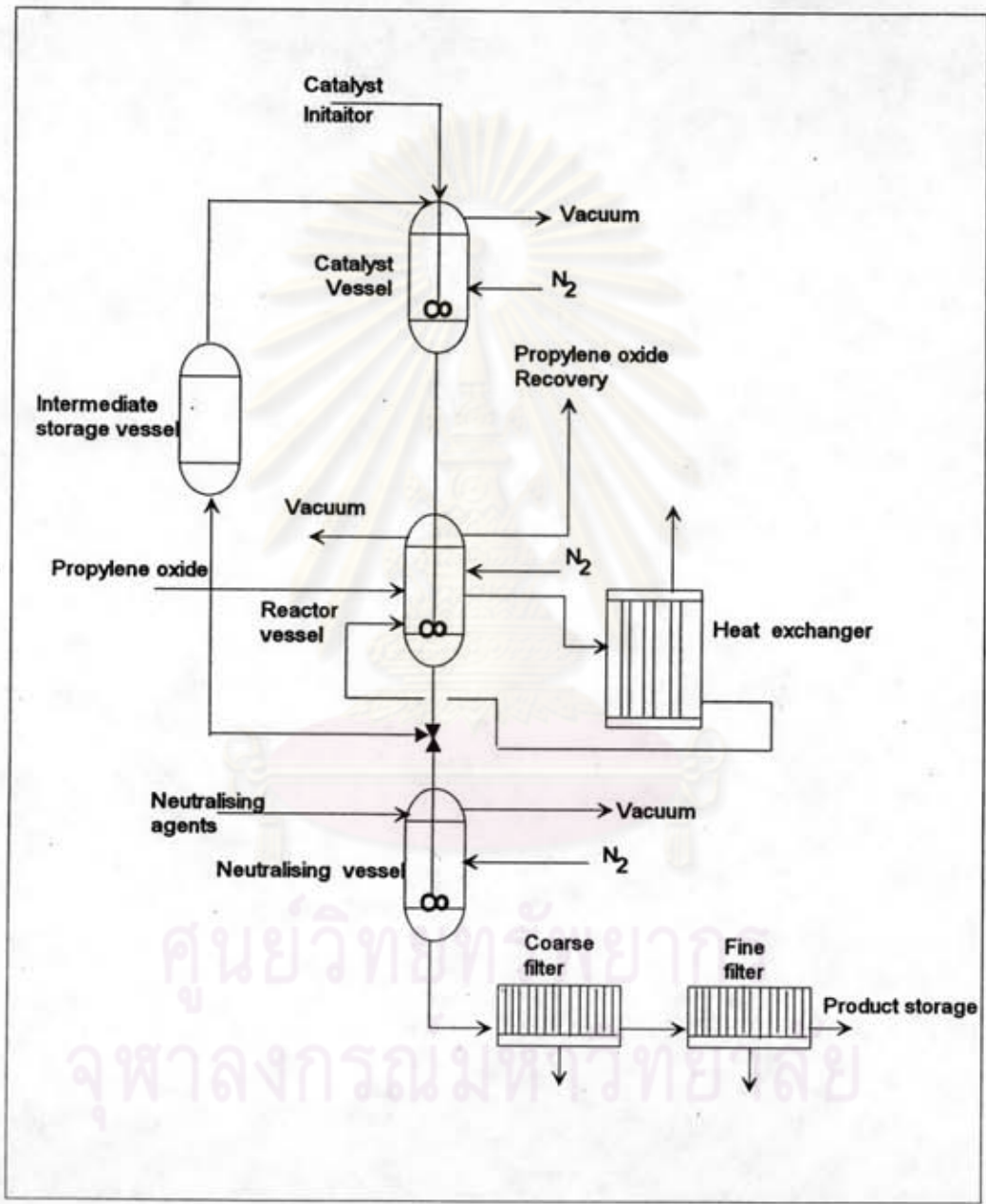
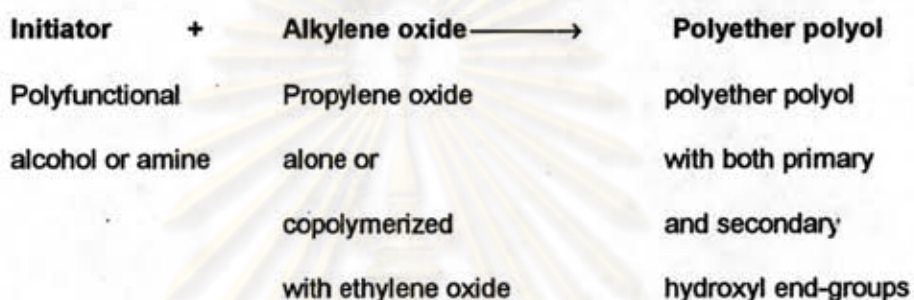


Figure 2.8 Polyether (polypropylene) glycol manufacture flowsheet.



The polymerization of Propylene oxide and Ethylene oxide

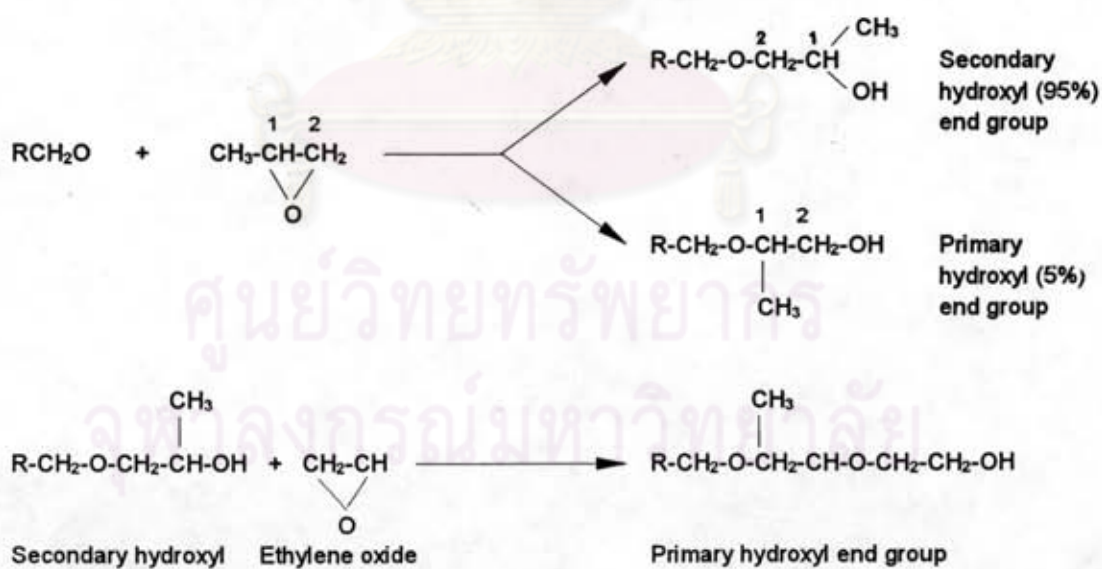


Figure 2.9 The manufacture of polyether polyols



Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups.

Table 2.4 Advantage and disadvantage of polyester polyols compare with polyether polyols

Type of Polyols	Advantage	Disadvantage
Polyester polyols	<ul style="list-style-type: none">-Greater mechanical strength-Oil resistance and dry cleaning solvent resistance-Stable to oxidation and higher temperature resistance	<ul style="list-style-type: none">-Higher cost-More difficult to handle (more viscous)-Sensitive to hydrolysis
Polyether polyols	<ul style="list-style-type: none">-Lower cost-Hydrolysis resistant	<ul style="list-style-type: none">-Inferior mechanical strength-Sensitive to oxidation

For preparation of polyesters, conventional methods of polyesterification, i.e. reaction between acid and diol or polyol, are used, the water of condensation being removed by distillation and the reaction help by use of vacuum or an azeotrope. The molecular weight can be controlled by the molar ratio of the reactants and the reaction conditions, but it is essential that the terminal groups should be hydroxyl terminated so as to react an excess of the stoichiometric amount of the difunctional glycol with the dibasic acid as shown in equation 2.15.



Condensation polymerization manufacturing of polyester polyols is shown in Figure 2.10 .

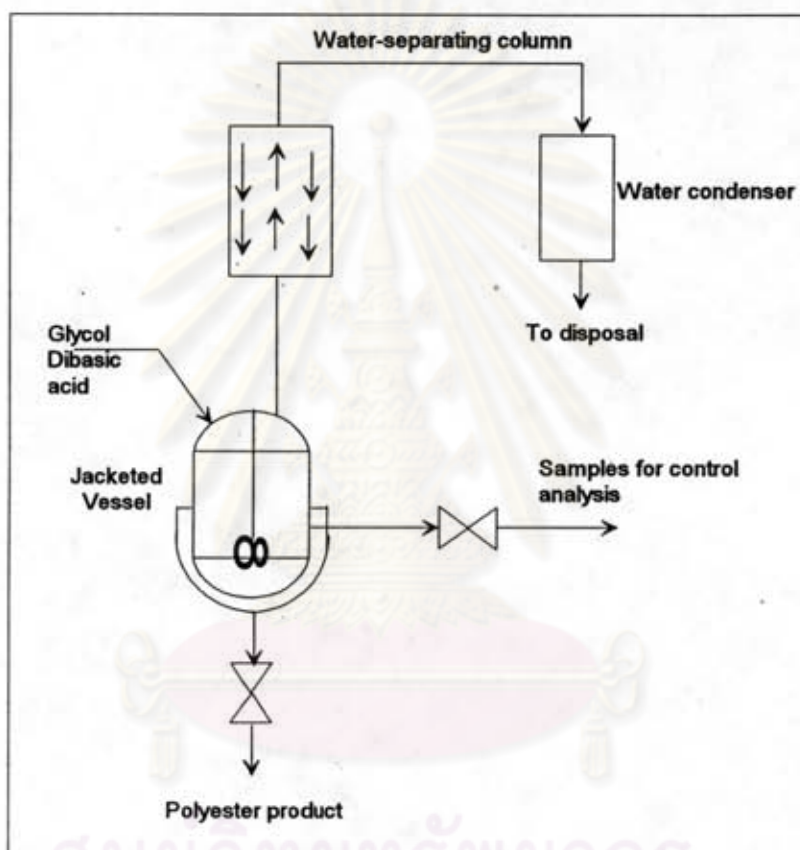
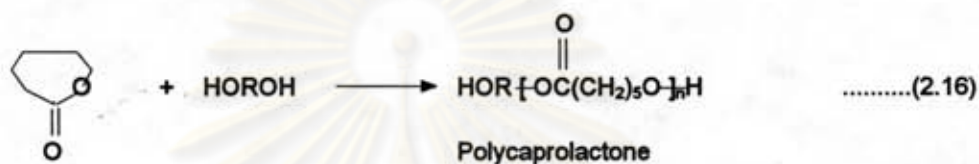


Figure 2.10 Condensation polymerization equipment for manufacture of polyesters(courtesy of Wright and Cumming, reproduced with permission).

A molar excess of glycol over acid in the range of 5-20 % is required to be heated to 200-500°C under vacuum to prevent oxidation discoloration. Water is removed during the reaction and any glycol evaporated returned by the use of a fractionating column.

Polyester polyols is used in production of specialty polyurethane flexible foam and thermoplastic polyurethane elastomers and fibres. Polyester polyols are also made by the reaction of caprolactone with suitable glycols. The reduction of ester groups in the macromolecule improves the hydrolytic stability of the products.



The "hydroxyl value" is used as measure of the concentration of isocyanate reactive hydroxyl groups per unit weight of the polyol and is expressed as mg KOH/g. The measured hydroxyl value of polyol is related to its molecular weight and functionality.

$$\text{Hydroxyl Value (mg KOH/g)} = \frac{56.1 \times (\text{functionality})}{\text{Molecular weight}} \times 100$$

Hydroxyl Value is convenient for calculation of the stoichiometric formulation of manufacturing polyurethane. In order to achieve the chemically stoichiometric equivalents of hydroxyl to isocyanate group, the isocyanate index is specified.

Isocyanate index is defined as the amount of isocyanate used relative to the theoretical equivalent amount of isocyanate required.

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

$$\begin{aligned} \text{Isocyanate Value} = \% \text{ NCO groups} &= \frac{42 \times (\text{functionality})}{\text{Molecular weight}} \times 100 \\ &= \frac{4200}{\text{Equivalent weight}} \end{aligned}$$

Calculating the ratio of the components required for polyurethane manufacturing is to calculate the number of parts by weight of the isocyanate that are required to react with two parts by weight (pbw) of the polyol and proportionate amounts of additives.

2.2.3 Auxiliary material (additives)

For polyurethane manufacturing, in addition to the isocyanate and polyol, a wide variety of auxiliary chemicals may be added to control and modify both the polyurethane reaction and the properties of final polymer.

These additives include catalyst, chain extenders, cross-linking agents, flame retardants, colouring material and fillers which are shown in Table 2.5.

2.2.3.1 Catalyst

In urethane technology catalysts are widely used to give desired balance of reaction rate between compound of differing active hydrogen activity. The important role of catalyst is not only affects the rate of chemical reaction, responsible for chain propagation, extension, and cross-linking but also influence the ultimate properties of the final polymers.

Choice of the catalyst depend on catalyst activity, odour, vapour pressure, toxicity, solubility, processing, cost etc.

The commonly used catalyst can be divided into two categories:

1. Tertiary amines (see Table 2.6) which promote OH/NCO reaction (blowing).

The mechanism of this catalyst involve the donation by the tertiary nitrogen to the carbonyl carbon of the isocyanate group, then formation of a complex intermediate. The efficiency of tertiary amine increase with the basicity of the amine, and decrease with increasing steric shielding of the amino nitrogen.

2. Organometallic compounds (see Table 2.7) which promote OH/NCO reactions (polymer forming).

Organometallic compounds are much more efficient catalysts than the amines, especially for the hydroxyl/isocyanate reaction (S.J. Blunden, 1976). This allows the polymer-formation polyol/isocyanate reaction to proceed at a sufficient rate to increase viscosity rapidly to a state where gas is effectively trapped, as well as to developed enough gel strength to prevent the foam from collapsing after gas evolution has ceased.

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Table 2.5 Reasons for using additive

Additives	Type of Material	Purpose
Catalyst	Tertiary amines Organometallic compounds	To speed up the reaction of isocyanate and polyol
Cross-linking chain-extending agents	Polyols Polyamines	To give polymer cross-linking or to introduce specialised polymer segments
Blowing agents	Water (reacts with isocyanate giving carbon dioxide gas). Chlorofluoromethanes	To produce foamed structures
Surfactants	Silicone fluids	To aid and help foam-forming processes
Colours	Various pigments Carbon black	To identify different foam grades and for aesthetic reasons
Fillers	Particulate inorganic materials Fibres (chopped, milled or as continuous fibres, nets or scrims)	To modify properties (stiffness, fire performance etc.)
Flame retardants	Phosphorus or halogen-containing molecules	To reduce flammability
Smoke suppressants	Particulate inorganic and/or organic materials (polycarboxylates, hydrated oxides, borates etc.)	To reduce the amount of smoke or to slowdown the rate of smoke production on burning

Table 2.6 Some tertiary-amine catalysts



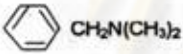

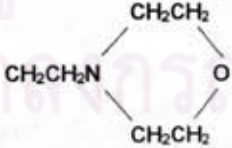
Catalyst	Application
1. N,N-Dimethylaminoethanol $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$	Inexpensive, low-odour, isocyanate reactive, mobile liquid catalyst used in polyether-based flexible foams.
2. N,N-Dimethylcyclohexylamine (Catalyst SFC)  $\text{N}(\text{CH}_3)_2$	Liquid with an intense odour Rigid foams, polyester-based flexible foams and some semi-rigid foams.
3. Bis-(2-dimethylaminoethyl)ether $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Low-odour, mobile liquid used in high resilience and cold-cure flexible foams.
4. N,N,N',N',N"-Pentamethyl-diethylene-triamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  CH_3	Flexible foams and semi-rigid foams.
5. N,N-Dimethylbenzylamine, (Catalyst SFB)  $\text{CH}_2\text{N}(\text{CH}_3)_2$	Liquid with characteristic smell used in polyether-based flexible foams, semi-rigid foams and for prepolymer making.
6. N,N-Dimethylcetylamine $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}(\text{CH}_3)_2$	Viscous liquid with a low odour used in polyester-based flexible foams and some potting compounds.
7. Diaminibicyclooctane (DABCO) 	Solid, soluble in water, glycols and polyethers. May be used in most type of polyurethanes.
8. N-Ethylmorpholine 	Volatile, low viscosity liquid with characteristic odour. Used as synergistic catalyst in flexible preparation.

Table 2.7 Some commercially available organometallic catalysts

Catalyst	Principal applications
Stannous octoate	Slabstock polyether-based flexible foams, moulded flexible foams
Dibutyltin dilaurate	Microcellular foams, RIM, two-pot moulding systems, elastomers.
Dibutyltin mercaptide	Hydrolysis resistant catalyst for storage stable two-pot systems
Dibutyltin thiocarboxylates Diocetylthiocarboxylates	Delayed action (hindered) catalysts for RIM and high resilience foams
Phenylmercuric propionate	In glycol solution for potting compounds, as a powder for delayed action catalysis.
Lead octoate	Urethane chain extension catalyst
Alkali-metal salts eg. CH_3COOK , K_2CO_3 NaHCO_3 and Na_2CO_3	General catalysts for the urethane reaction and for isocyanate polymerisation
Calcium carbonate	A common filler with a catalytic effect on the urethane reaction and on the urethane reaction and on the cure rate of polyurethanes.
Ferric acetylacetonate	Catalyst for cast elastomer systems, especially those based on TDI.

2.2.3.2 Chain- extenders and crosslinking agents

Chain-extenders are difunctional substances, glycols, diamines or hydroxy amines which a diamine chain extender give more excellent physical properties results than if a diol were used, probably due to the introduction of urea linkages which enter strong hydrogen bonded interaction as shown in Figure 2.11. Chain-extenders are used in flexible polyurethanes such as flexible foams; microcellular elastomer, cast elastomer and RIM systems. Some chain-extending agents and cross-linking agent are shown in Table 2.8.

Crosslinking agents having a functionality of three or more are used to increase the level of covalent bonding in rigid polyurethane foam.

2.2.3.3 Blowing agents

Cellular polyurethanes are manufactured by using blowing agents to form gas bubbles in the polymerizing reaction mixture. Blowing agents may be considered in two types as physical and chemical blowing agent.

Water can react with diisocyanate to generate carbondioxide as gas bubbles in "flexible foam". In addition to generating carbon dioxide, the water/isocyanate reaction produces not only polyureas, an essential part of polymer hard segment, but also the exothermic heat required to complete the polymerization and vaporise any non-reactive blowing agent used. Physical blowing has no effect upon the hard segment of polymer chain but tend to reduce the stiffness of polymer. On the other hand, chemical blowing stiffens the polymer by increasing the polyurea content of the polymer structure and the degree of the secondary bonding between polymer chains. Some non-reactive blowing agents are given in the Table 2.9.

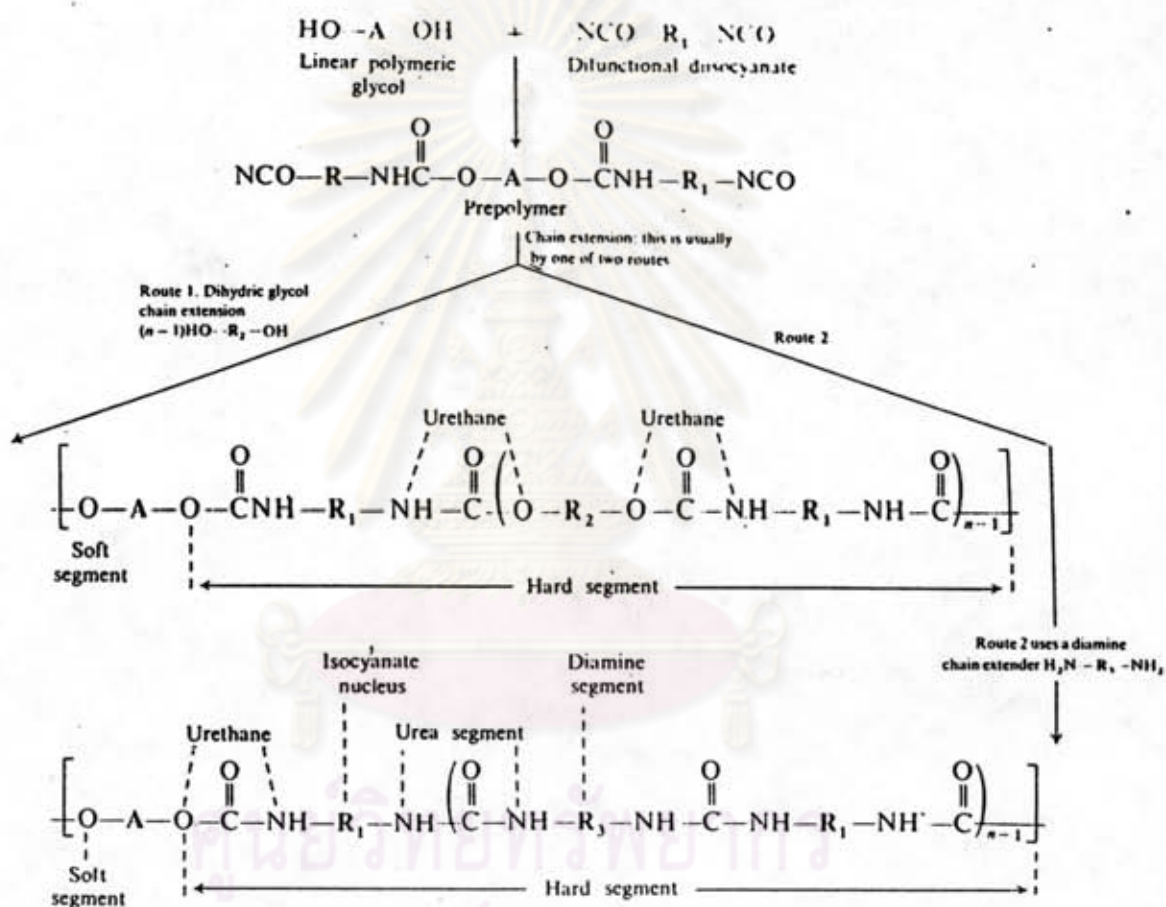


Figure 2.11 Prepolymer reaction sequence for elastomer synthesis

Table 2.8 Chain-extending agents, cross-linking agents and curing agents and their diisocyanate equivalents

Additive	Functionality	Mole Weight	OH Value (mg KOH/g)	Weight of diisocyanate (g per 100 g of required additive)	
				TDI	MDI
Ethylene glycol $C_2H_4(OH)_2$	2	62.07	1801	280	401
Diethylene glycol $O(C_2H_4OH)_2$	2	106.12	1057	164	235
Propylene glycol $C_3H_8(OH)_2$	2	76.11	1474	229	329
Dipropylene glycol $O(C_3H_8OH)_2$	2	134.18	836	130	186
1,4-Butane diol $C_4H_{10}(OH)_2$	2	90.12	1245	193	278
Polypropylene glycol 400	2	400	280	43.5	62
<i>m</i> -Phenylene diamine $C_6H_4(NH_2)_2$	2	108.15	1037	161	231
Diethyl toluene diamine $C_6H_4CH_2(C_2H_5)_2(NH_2)_2$	2	178.27	629	97.7	140
Dimethylthio toluene diamine $C_6H_4CH_2(SCH_3)_2(NH_2)_2$	2	214.34	523	81.2	116
Water HOH	2	18.01	6230	968	1389
Diethanolamine $HN(CH_2CH_2OH)_2$	3	105.14	1601	248	357
Triethanolamine $N(CH_2CH_2OH)_3$	3	149.19	1128	175	252
Glycerol $CH_2OHCHOHCH_2OH$	3	92.11	1827	284	407
'Daltolac' C4	3	168	1000	155	223
'Daltolac' C5	3	150	1125	175	251
'Daltolac' 50	4	498	480	75	107
'Uropol' G 790	4	280	800	124	178

Table 2.9 Non-reactive blowing agents for polyurethanes

Blowing agent	Trichloro- monofluoro- methane (CFM-11)	Dichloro- difluoro- methane (CFM-12)	Methylene chloride
Molecular weight	137.38	120.92	84.94
Density at 20°C(g/ml)	1.488	1.486	1.366
Boiling point at 1 atm (°C)	23.8	-29.8	40.1
Freezing point (°C)	-111	-160	-96.7
Threshold limit value (TVL*,ppm)	1000 ppm	1000 ppm	50 ppm A ₂
Solubility (g/100 g solvent at 20 °C)			
Water	Insoluble	Insoluble	2
Ethanol	∞	∞	∞
Polyethers	Adequately soluble for all applications		

2.2.3.4 Flame Retardant

Polyurethane will burn given the application of sufficient heat in the presence of oxygen. Flame retardants are added to polyurethanes to reduce the flammability, ignitability and the burning rate of polyurethanes which operate through one or more of the following mechanisms:

- Provision of a heat sink by filling with incombustible materials to delay ignition and reduce the rate of burning.
- Provision of an energy sink and means of diluting the combustion gases by filling with substances that decompose on heating to give incombustible products such as water and carbon dioxide.
- Modification of the mechanism of burning by filling with materials, such as halogenated flame-retardants, that react with the polymer or that produce a gas.
- Including char formation by the use of additives.

The most widely used flame-retardants are chlorinated phosphate esters. The common flame-retardants are shown in Table 2.10.

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Table 2.10 Some flame retardants for polyurethanes

Additives	Typical application
<p>A. Non-reactive liquids</p> <p>Tris(2-chloropropyl) phosphate 'Daltogard'F</p> <p>Tris(2-chloropropyl) phosphate, (T.C.E.P.)</p> <p>Tris(2,3-dichloropropyl) phosphate, 'Fyrol'FR2 'Celluflex'FR-2</p> <p>Tetrakis(2-chloromethyl)-2,2- bis-(chloromethyl) propylene- phosphate 'Phosgard'2XC20</p> <p>Dimethyl methyl phosphonate</p>	<p>All polyurethane foams including polyester-based foams and microcellular elastomers.</p> <p>Polyether-based flexible and rigid foams.</p> <p>Polyether-based flexible and rigid foams.</p> <p>Low volatility material for flexible and rigid foams.</p> <p>Rigid foams</p>
<p>B. Isocyanate-reactive additives</p> <p>Tris(polyoxyalkyleneglycol)- phosphonates and phosphite esters.</p> <p>tris(halogenated polyol)- phosphonates.</p> <p>Dibromoneopentyl glycol. 'FR'1138</p> <p>Brominated polyester and polyether diols. 'Saytech'RB-79 and 42-43</p> <p>Tetrabromobiphenol A Tetrabromophthalic anhydride</p>	<p>Flexible and semi-rigid foams.</p> <p>Flexible and rigid foams.</p> <p>Polyether-base polyurethanes.</p> <p>Rigid polyurethane and polyisocyanurate foams.</p> <p>Rigid polyurethane and polyisocyanurate foams.</p>
<p>C. Fillers</p> <p>Ammonium salts sulphate, polyphosphate, etc.</p> <p>Aluminium hydroxide. Melamine.</p> <p>Calcium carbonate.</p>	<p>Together with halogenated additives in rigid polyurethanes.</p> <p>All polyurethanes but especially in low density flexible foams for ignition and smoke suppression.</p> <p>Heat absorbing filler.</p>

2.2.3.5 Colouring materials

During manufacturing low density flexible foam, it usually add pigment pastes in order to identify the grade and the density of the foam. The pigment are also used in both organic and inorganic pigments. The characteristic of pigment used must not react with isocyanates and must be stable at the high curing temperatures reached in the manufacture of low-density foams. The most widely used colouring material is carbon black which gives some protection against surface discolouration of foam cause by UV. light. Polyurethane foam is easily coloured by dyeing but its disadvantage is high cost.

2.2.3.6 Fillers.

Particulate and fibrous fillers may be used in most kinds of polyurethanes. Particulate fillers are used in flexible polyurethane foams to reduce their flammability and increased stiffness and increase the range of operating temperature of rigid foams, Mineral fillers are used to reduce costs and to increase the compressive strength of rigid foam. R. Gachter et.al. (1987) introduced and guided for the selection and usage of fillers. Some fillers and their application are listed in Table 2.11 and 2.12, respectively.

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Table 2.11 Some fillers and their application in polyurethanes

Filler	Typical applications
Calcium carbonate, (Ground chalk,ground limestone, whiting)	Flexible foams,semi-rigid foams, binder compositions, rigid self- skinning mouldings.
Barium sulphate,(Barytes)	Flexible foams,semi-rigid foams, especially for sound-absorbing.
Clays(China clay,kaolins,etc.)	Flexible systems
Expanded silicas, colloidal silicas	Flexible foams, cast elastomers
Clay balls, vermiculite, expanded mica,etc.	Rigid foams
Glass micro-spheres	Flexible,microcellular foams,RIM
Glass flakes	Elastomeric RIM
Silicates,cements	Rigid foams,sealants,grouting Compounds
Short fibres,milled and chopped glass-fibre,Aramid fibres, carbon fibres,conducting fibres, (aluminium,coated glass,steel)	Elastomeric RIM, rigid foams
Glass cloths ans scrim, wire mesh,organic fibres,etc	Encapsulation in rigid foams, reinforcement of low density flexible foam mouldings.

Table 2.12 Some high modulus reinforcing fibres

Fibre	Young's modulus (ϵ)	Specific gravity (s.g.)	ϵ / s.g.
'E'-glass fibre	70	2.55	27
Aluminium	70	2.7	26
Aramid fibre 'Kevlar'29	80	1.3	61
'Kevlar'2	120	1.4	86
Carbon fibre (PAN)	250-400	1.8-1.9	140-210
Carbon fibre (Pitch)	200	1.9	105
Steel	200	7.8	26
Alumina fibres	350	4.0	88
Polyethylene fibres	30-70	0.96	31-73
Boron fibres	400	2.5	160

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2.3 Literature review

Nierzwichi and Wysocka (1980) studied about varying amount of chemical composition (NCO/OH ratio) revealed a joint action of crosslinkage and microphase separation in determining mechanical properties, swelling behavior and glass transition temperature of the system. The analysis showed that the investigated system of NCO/OH ratio at 1 was preferred for optimum properties. Thus polyurethane were prepared from poly(ethylene adipate)glycol, 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, or 3,3-dichloro-4,4-diaminodiphenylmethane. This work summarized that mechanical properties of urethane are influenced directly to NCO/OH ratio and microphase separation.

Llavsky and Dusek (1983) studied the equilibrium mechanical and optical behaviour of polyurethane networks prepared from poly(oxypropylene) triols and 4,4-diphenylmethane diisocyanate at various molar ratio of reactive groups, $r_H = [\text{OH}]/[\text{NCO}]$, in the range $0.6 < r_H < 1.75$ and studied comparison between experimental and theoretical dependences of equilibrium mechanical and optical behaviour. In the range $r_H > 1$, the result were concluded that the theory adequately describes experimental dependences, while in the range r_H excess crosslinking take place, obviously due to the formation of allophanate groups.

Harris, Joseph, Davidson, Deporter and Dais (1990) studied the effect of variation in chemical composition of 4,4-methylene-di(phenylisocyanate) and 1,4-butanediol on properties which had constant quantity of poly (ethylene ether carbonate) diol. The properties such as rubbery plateau modulus, solvent resistance, melting point, hardness, tensile strength were improve with result of increasing composition of 4,4'-methylene-di(phenylisocyanate) and 1,4-butanediol concentration.

Petrovic and Simendic (1985) studied about the effect of variation in chemical composition of three polytetramethylene oxide diols of $M_n = 650, 1000$ and 2000 on mechanical, thermochemical and dynamicmechanical properties. It was shown that maximum tensile strength obtained when concentration of polytetramethylene diol was 40-50% at a fixed ratio of NCO/OH at 1. This can be explained by a specific interlocking morphology. Thus, elongation at break increased linearly with polytetramethylene oxide diol concentration. On the other hand, hardness, modulus, and tear strength were affected by quantity of 4,4 MDI and 1,4 butanediol.

Buchhiktz, Rambosek and Drew (US. Pat. No. 3,272,098) investigated the preparation of tough resilient paving surfacing from polyurethane. This polyurethane production was produced by organic polyol and organic isocyanate in amounts providing an approximately equivalent number of NCO/OH groups and incorporated resilient aggregate. The quantity and size of resilient aggregate were about 10% to 50% by volume and average size in the range of 1/16 inch to 1/3 inch. The advantage of resilient aggregate for paving surface was good non-slip characteristic and simple to repair.

Verdol and Ryan(US. Pat. NO. 3,427,366) improved the properties such as improved hydrocarbon oils and solvent resistance, increased abrasion resistance, and high tensile strength of polyurethane by using rubber composition. It contained hydrocarbon rubber and urethane resin. The urethane polymer is produced by reaction of a diisocyanate with an intermediate polyhydroxy polymer having a viscosity at 30°C about 5-20,000 poise number average molecular weight of about 400-25,000.

Sapp and Goodrich(US. Pat. No. 3,869,421) studied preparation of resilient surface which is obtained by casting a mixture containing an oil-extended polyurethane and a resilient aggregate. The compositions contained polyisocyanate, resilient rubber particle, extender oil, carbon black, mineral filler and drying agent. The mixture was cast onto a surface to provide a rapid curing to form a resilient surface. The surface are porous, non-skid, resistant to were non-flammables and easy to install for running track, athletic field, golfs tee house stable, playground surface.

Coke and Gill(US. Patent No. 4,420,513) studied improvement of composition for synthetic running surface by a layer of urethane elastomer having totally encapsulated granules of elastomeric material which provided suitable surface for runner traction. Otherwise; improved apparatus for mixing and applying the batching a liquid elastomer having granular material dispersed through out., which apparatus was easily loaded and provided for continuous self-cleaning, as well as easy batching operations.

Coke and Gill (US. Patent No. 4,614,686) studied preparation a running track of polyurethane elastomer with dispersed granular particles throughout the polyurethane. The size of particle was 0.0625-0.125 inch and constitute 26-30 weight percentage of the granular rubber (styrene-butadiene-rubber or natural rubber) to provide a roughened traction surface. Average track thickness was preferred 0.38-0.5 inch and there are two layers of encapsulated rubber particles and a layer of encapsulated polyurethane elastomer particles. The advantage of these running track was provided cushioned track with traction surface.