

CHAPTER 2

THEORY

The urethane-producing reaction was well known in the nineteenth century until the late 1930s the commercial potential of polyurethane (PU) was made by Otto Byer and his co-workers at Leverkusen, Germany. Most applications of PU such as fibers, adhesive, coating and foam have been developed during the past 30 years. The development of PU is showed in Table 2.1. The PU forming system has received in many specialized forms, and fibers. The range of end-products derived from polymers is shown in Figure 2.1

Table 2.1 Illustrates some highlight in the development of polyurethane

(Wood, 1987)

1937-40	Otto Bayer and co-workers made polymers by polyaddition processes from various diisocyanates with glycols and/or diamines.	1960	ICI introduces the first polymeric MDI-based semi-rigid energy absorbing foam for vehicles.
1940-5	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).	1960-5	Rigid foam blowing by chlorofluoromethanes.
1945-7	Manufacture of millable polyurethane elastomers, coatings and adhesives.	1962	First production line moulded 'deep seat' flexible polyurethane car cushions at Austin-Morris (U.K.).
1950	Cast elastomers from polyester diols, diisocyanate prepolymers and chain extenders.	1963	ICI demonstrates production line manufacture of refrigerators using MDI-based polyurethane foam.
1953	First flexible polyurethane foam manufacture with a Bayer system using a high pressure machine, a polyester polyol and TDI.	1963	First cold-store built entirely from metal-faced polyurethane rigid foam laminate made continuously (Australia).
1956	First manufacture of polyether-based flexible polyurethane foam in the U.S.A. using a two stage or 'pre-polymer' process.	1964	ICI inverse- and floating-platen systems for the continuous manufacture of rigid polyurethane foam-cored building boards in production.
1957	ICI introduces the first commercially available polymeric MDI composition for rigid polyurethane foam manufacture.	1965	First commercial production of self-skinning flexible foam (Soc. Quillery, France).
1959	ICI introduces the first rigid foam system based on polymeric MDI and a polyether polyol.	1968	ICI introduces isocyanurate rigid foams.
1959	'One-shot' system for flexible polyether-based foam introduced in the U.S.A.	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.

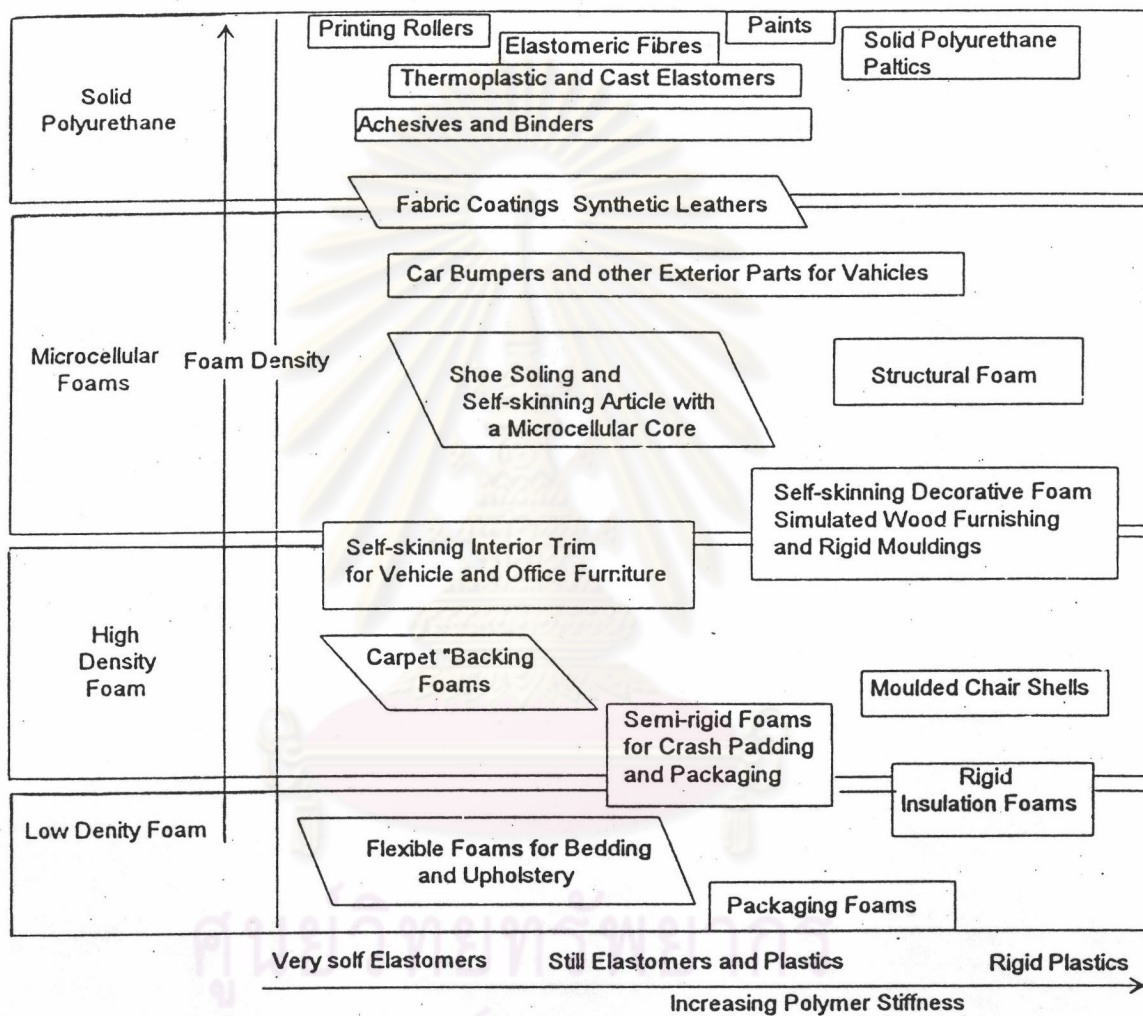


Figure 2.1 Structure - property relationship in Polyurethane

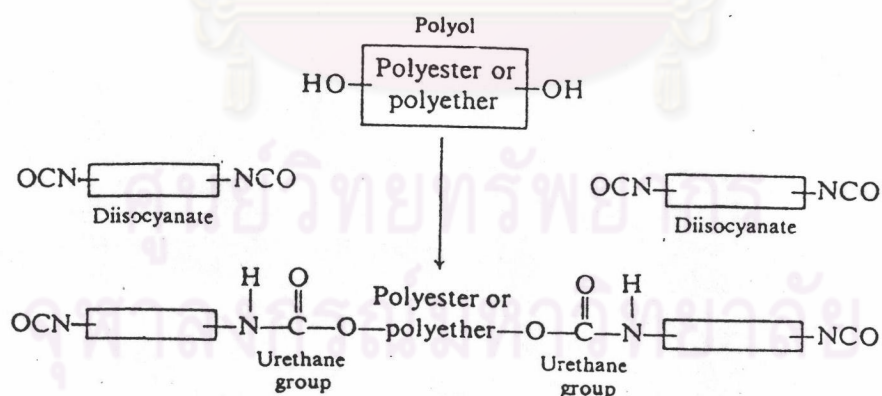
(Hepburn, 1992)

2.1 Basic Chemistry

A urethane group is formed by the chemical reaction between alcohol and isocyanate. PU result from the reaction alcohols with two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate). This is known as addition polymerization. No by-product are given off. The diisocyanate will react with any compound having an active hydrogen, such as hydroxyl-terminated epoxies, hydroxyl-terminated polyester, and hydroxyl-terminated furanes, and will even react with cellulose, rubbers, or other materials containing hydrogen groups. The reactions which produce a solid polymer are rapid and complete in two minutes, rates can be varied by type of catalyst and its concentration. The reactions are exothermic, the heat generated may be used to vaporize a liquid "blowing agent" and produce a polyurethane foam. Alternatively, some water may react with the polyisocyanate to release carbon dioxide gas.

The reaction of diisocyanate with polyol is shown in equation below.

(Hepburn, 1992)



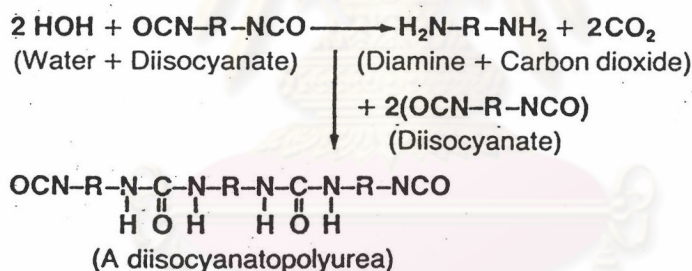
The rate of polymerization is influenced by the structure and functionality of both isocyanate groups and polyols. Aliphatic polyols with primary hydroxyl groups are the most reactive.

A few of the basic reaction would be

1. Diisocyanate + water = urea (RNH_2) + carbon dioxide (CO_2)
2. Diisocyanate + hydroxyl = urethane ($\text{RNHCOOR}'$)
3. Diisocyanate + amine = disubstituted urea ($\text{RNHCONHR}'$)
4. Diisocyanate + urethane = allophanate ($\text{RNHCOHR}'\text{COOR}'$)
5. Diisocyanate + disubstituted urea = substituted biuret

Reaction of isocyanate with water (Wood, 1987)

The reaction of isocyanates and water yields a substituted urea and carbon dioxide. This reaction provides the principal source of gas for blowing in the manufacture of low density foams. The amine then reacts with further isocyanate to yield the substituted urea as the equation below. In the absence of catalysts, both TDI and MDI react with water slowly because the low solubility.

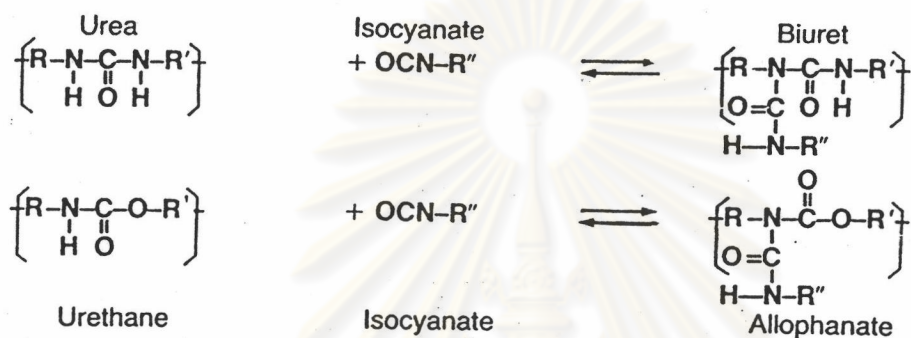


Reaction of isocyanate with amines

The reaction of diisocyanates with primary and secondary amine compounds, especially diamines, is the important reaction in practical polyurethane chemistry. Diamines are used as chain extending and curing agents in polyurethane manufacture. The reactivity of amines increases with the basicity of the amine, and aliphatic amines react much faster than aromatic amines. Tertiary amines, because they contain no active hydrogen atoms, do not react with isocyanates, but they are powerful catalyst for many other isocyanate reactions.

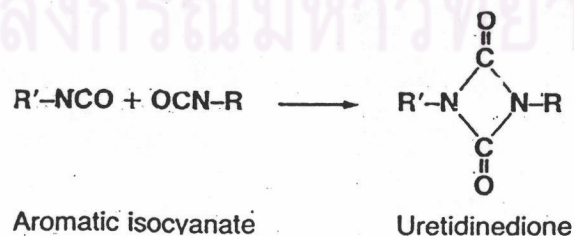
Secondary reaction of isocyanate

Isocyanate may react with the active hydrogen atom of the urethane, and urea and amide groups already introduced during the initial polymer formation to form allophanate, biuret and acylurea, respectively. Both reactions are cross-linking reactions. The reaction of isocyanate with urea groups is significantly faster and occurs at lower temperature than that with urethane groups.



Isocyanate polymerization reactions

Amyl isocyanates readily polymerize in the presence of catalyst giving uretidines (commonly called dimers). Some diisocyanate such as 4,4'-diphenylmethane diisocyanate (MDI) dimerises slowly when left standing at room temperature so they have a limited storage life, losing activity at different rates. The reaction and structure is generally considered to be:



Both aliphatic and aromatic isocyanate can also form isocyanurates (normally called trimers). The reaction is accelerated by basic catalysts. Isocyanurate formation gives very stable branch points, the reaction is not easily reversed.

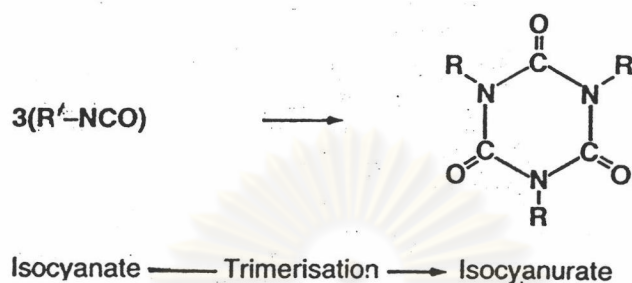


Figure 2.2 Isocyanurate formation (Wood, 1987)

2.2 Raw material for Polyurethanes

The polymerized urethane may have a widely varying structure, depending on type of raw material. Most polyurethane are made from aromatic isocyanates reacted with aliphatic polyols. In order to obtain a well balanced formulation for any specific and product, a wide range of auxiliary chemicals (additives) may be added to isocyanate and polyol.

2.2.1 Isocyanates

Several aromatic and aliphatic diisocyanate are available, but some 95% of polyurethanes are based upon the two aromatic diisocyanates, toluene diisocyanate (MDI) and its derivatives

Two isomers of TDI exist. The different species of TDI are based on the different ratio of the two isomers. The 80:20 mixture of 2,4-TDI and 2,6-TDI (80:20-TDI) is today the most important commercial product, but a 65:35 ratio mixture, the 2,4 and 2,6 isomers (65:35-TDI) is also available from some supplies.

TDI mixtures can occur 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 considerably safer to use, having as much lower volatility but its 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).

Diphenyl methane diisocyanate is another important isocyanate. Isocyanate MDI is available in several forms based on two types of product purified monomeric MDI and polymeric MDI. Pure MDI is substantially 4,4'-diisocyanatodiphenylmethane (4,4'-diphenylmethanediisocyanate or 4,4'-MDI). It usually contains a small amount of the 2,4-isomer.

Pure MDI is a white to pale yellow solid of melting point about 38°C and its shelf life is poor. It tends to form insoluble dimer when stored. The difficulty of handling solid pure MDI and its increased tendency to form dimer when stored as liquid at over 40°C, have led to the development of modified pure MDI. Both methods involve reacting part of the pure 4,4'-MDI. One method is to react some of the isocyanate groups with an aliphatic diol having low molecular weight or with a mixture of such diols, to yield a solution of diurethanes having isocyanate end-groups (e.g. Figure 2.3) in 4,4'-MDI.

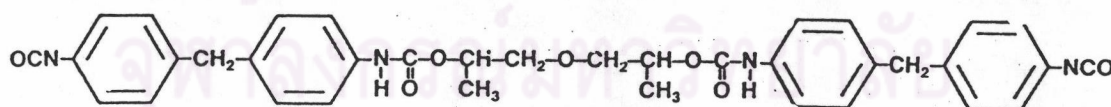


Figure 2.3 Modified pure MDI. (Wood, 1987)

This type of liquid diisocyanate mixture has an effective functionality of 2.0 and is useful in the production of polyurethane elastomers of high quality.

Table 2.2 MDI-based isocyanates for polyurethane manufacture (Wood, 1987)

Product name	Isocyanate value (NCO by wt.)	Viscosity (mPas at 25°C)	Average functionality	Main application area
'Suprasec'MPR	33.4	solid at 25°C 4.7 at 50°C	2.00	High grade elastomer
'Suprasec'ML	33.2	5.0 at 50°C	2.00	Binder for rubber granules
'Suprasec'VM02 1	23.0	1000	2.01	Polyester-based shoe soling.
'Suprasec'VM05 1	18.0	190 at 50°C	2.01	Polyether-based shoe soling
'Suprasec'VM10	26.0	150	2.07	'Suprasec'VM051
'Suprasec'VM20	29.0	50	2.13	RIM elastomer
'Suprasec'VM25	24.3	170	2.21	Cold-cure auto seating cushions
'Suprasec'VM50	30.6	130	2.49	Semi-rigid foams. Carpet backing
'Suprasec'DND	30.7	230	2.7	Rigid foams
'Suprasec' VM85HF	30.4	550	2.9	Rigid foams for construction applications.
'Suprasec' VM90HF	30.2	900	3.0	Rigid foams for construction applications

'Suprec" is trade marks of Imperial Chemical Industries PLC.

Polymeric MDI are undistilled MDI compositions made by the phosgenation of polyamine mixtures. Polymeric MDI compositions are available with effective mean functionalities from about 2.5 to over 3.0. A typical functionality distribution is illustrated diagrammatically in Figure 2.5. Polymeric MDI composition are characterized by their viscosity increases with increasing mean molecular weight and polymeric isocyanate content.

The wide range of MDI-based isocyanates available is illustrated in Table 2.2

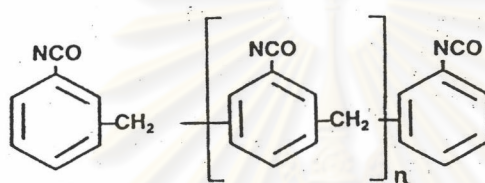


Figure 2.4 Structural formula of polymeric MDI (Wood, 1987)

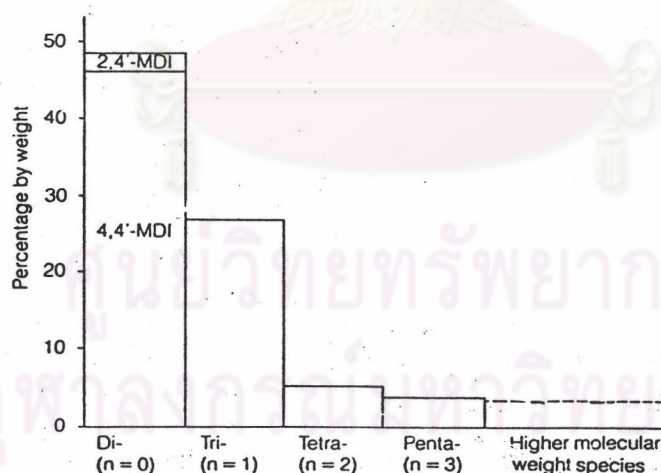


Figure 2.5 The functionality distribution of a typical polymeric MDI (Wood, 1987)

Table 2.3 Range of MDI variants (Hepburn, 1992)

Average functionality	Product description	Polyurethane type	Main application
2.0	Pure MDI	High performance elastomers	Shoe-soling. Spandex fiber Coatings
2.01-2.1	Modified, liquid pure MDI	High performance elastomers. Microcellular elastomers	Shoe-soling RIM and RRIM. Cast elastomers
2.1-2.3	Liquid, low functionality polyisocyanates	Flexible, semi-rigid and rigid foams	Automotive parts Cabinets for electronic equipment Insulating Sealants Cast elastomers
2.5	Low viscosity liquid polyisocyanate	High density flexible foams. Structural foams	Foam-backs for carpet/vinyls. Computer carbinets
2.7	Low viscosity polymeric MDI	Low density rigid foams. Semi-rigid foams.	Insulating foams Energy absorbing foams
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.

Naphthalene diisocyanate (NDI), available commercially as the 1,5 derivative, is employed only in special products, mainly elastomers. Hexamethylene diisocyanate (HDI) made from the nylon 66 intermediate hexamethylene diamine, being normally less reactive than the aromatic counterparts (but additionally more volatile and thus presenting a greater toxic hazard), is again of somewhat specialized interest for Spandex fiber manufacture and surface coating and paints. The rigid, rod-like

structures such as that of paraphenylene diisocyanate (PPDI), are known to give PUs of particularly good resistance to high temperatures.

Although most widely used, the aromatic diisocyanates lead to polyurethanes that turn yellow on exposure to light, and recent developments have been directed to intermediates in which the NCO groups are aliphatic or not attached directly to an aromatic nucleus. HDI is an obvious isocyanate to consider in this respect, particularly with the finding that its activity can be promoted by use of catalysts. Other diisocyanates used for the production of polyurethane having improved resistance to discoloration and thermal and hydrolytic attack include the 4,4'-dicyclohexylmethane diisocyanates (based on the mixed stereoisomers obtained on hydrogenation of 4,4'-diaminodiphenyl-methane), 70:30 meta/para xylylene diisocyanate (which gives good light stability even when used in conjunction with TDI), isophorone diisocyanate (IPDI), and 2,2,4-trimethyl-1,6-hexamethylene diisocyanate. The structural formulae of this other industrially important diisocyanates are given in Figure 2.6 and 2.7.



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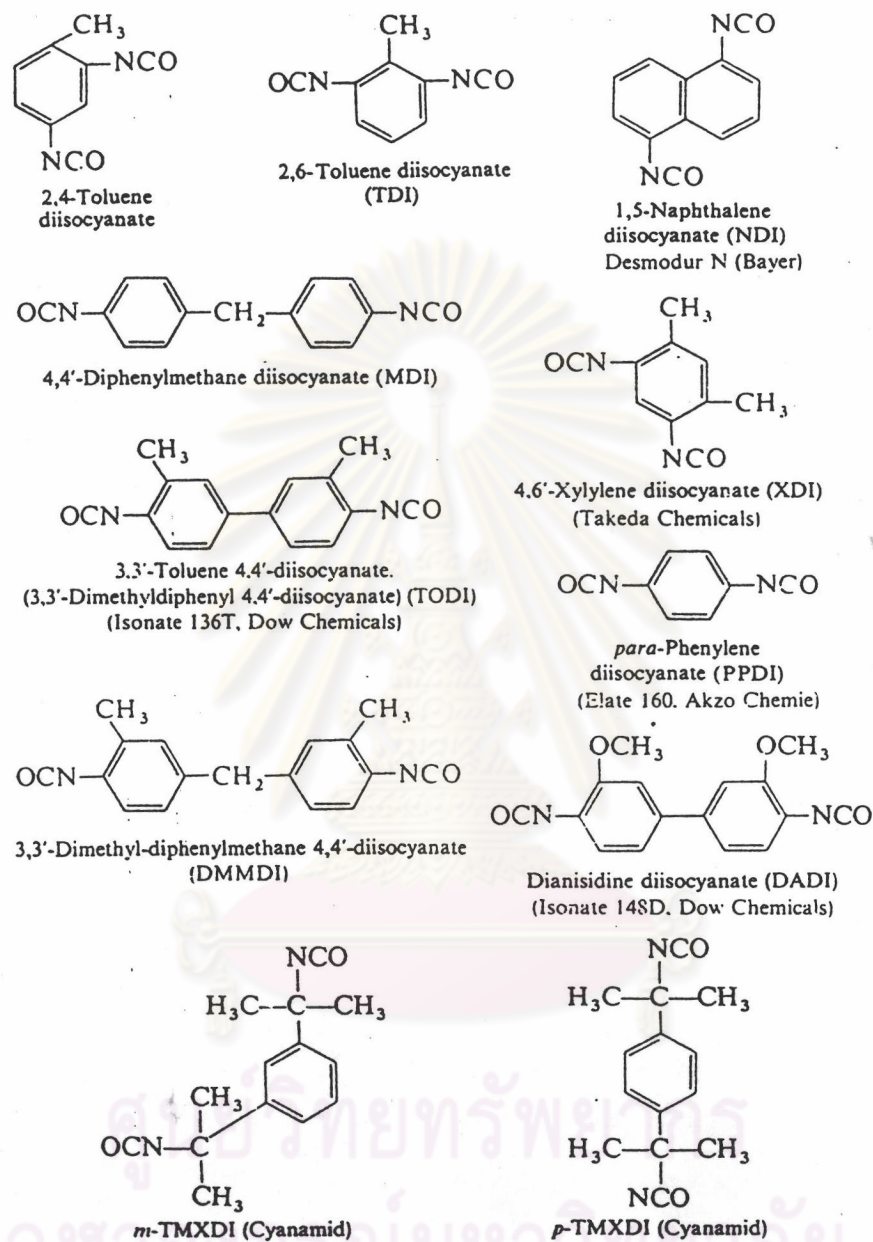


Figure 2.6 Aromatic diisocyanates used in polyurethane elastomer synthesis
(Hepburn, 1992)

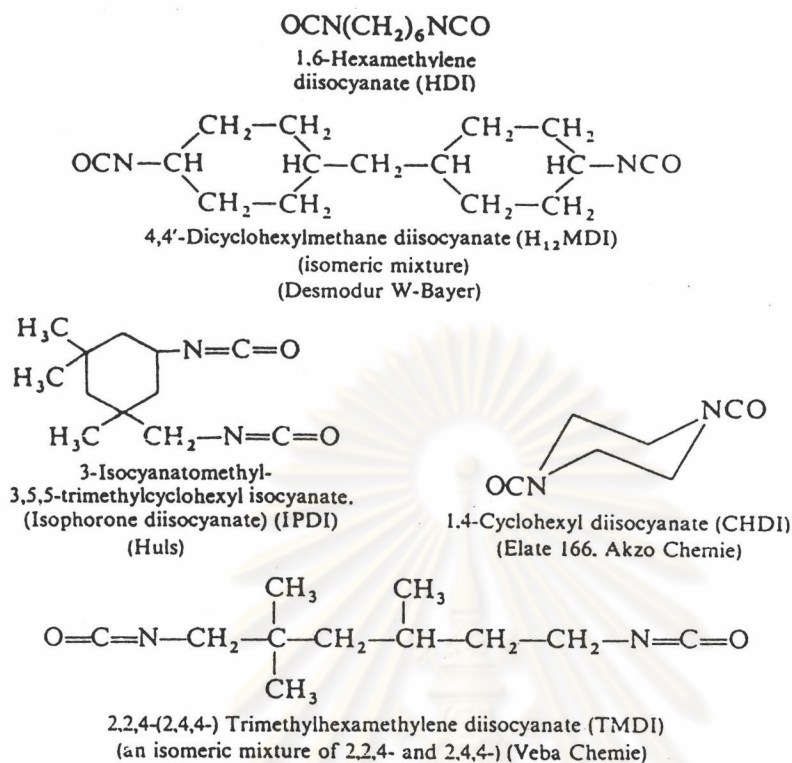


Figure 2.7 Aliphatic diisocyanates used in polyurethane synthesis.

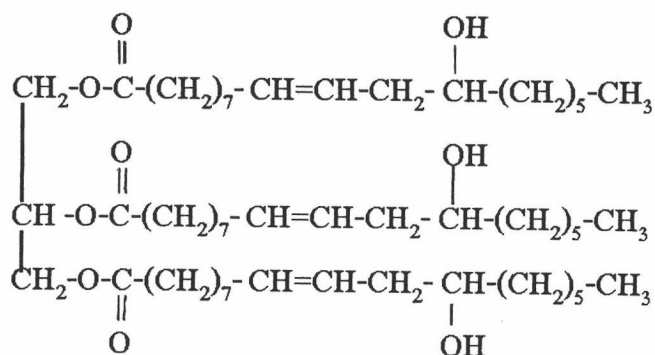
(Hepburn, 1992)

2.2.2 Polyols

The multitude of different polyurethanes are based on the large number of different polyols that are available for polyurethane synthesis. Polyols that are used commercially for polyurethane synthesis from a separate class:

Polyols which are suitable for polyurethane synthesis include both polyols based on natural products and polyols prepared synthetically. (Kircher, 1987)

As a proven natural polyol, castor oil has been proven successful. It contains three available hydroxyl groups which produce cross-linked polymers.



castor oil (Kircher, 1987)

The literature describes the use of tall oil, which is a by-product in the manufacture of cellulose, for the synthesis of polyurethane. In principle, the following polyols can also be used: sugar, starch, cellulose, and lignin. These compounds are solids, and they are suitable as reactive fillers.

The synthetically prepared polyols are much more important. They are divided into two groups:

- Polyester polyols
- Polyether polyols

The structure of polyol plays a large part in determining the properties of the final urethane polymer. The molecular weight and functionality of the polyol are the main factors, but the structure of the polyol chains is also important. The characteristics of the polyols used to make the two main classes of flexible and rigid polyurethanes are shown in Table 2.4

Table 2.4 Polyols for polyurethane manufacture (Wood, 1987)

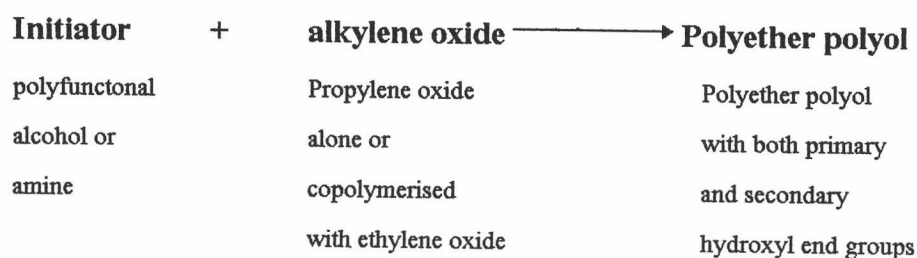
Characteristic	Flexible foams and elastomers	Rigid foams, rigid plastics and stiff coatings
Molecular weight range	1,000 to 6,500	150 to 1,600
Functionality range	2.0 to 3.0	3 to 8
Hydroxyl value range (mg KOH/g)	28 to 160	250 to 1,000

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/g. 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 a polyol is related to its molecular weight and functionality: (Wood, 1987)

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

Polyether polyols

About 90% of polyols used in polyurethane manufacture are hydroxyl-terminated polyethers. These are made by the addition alkylene oxides, usually propylene oxide, onto alcohols or amine which are usually called starters or 'initiators'



It can be polymerized by basic or acidic catalysts, but in general basic catalyst are employed. The epoxide ring of propylene oxide may theoretically open at either of two positions reaction but, in practice, the ring opens preferentially at the less sterically-hindered position with base catalysis. Polyethers based propylene oxide thus contain predominantly secondary hydroxyl end-groups. Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups and for some applications polyether polyols based only on propylene oxide may have inconveniently reactivity.

The primary hydroxyl content may be increased by the separate reaction of the polyoxypropylene polyols with ethylene oxide to form a block copolymer with an oxyethylene. By this means the primary hydroxyl end-group content may be varied from about 5% to over 80% of the total hydroxyl end-groups.

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The polymerization of propylene oxide and ethylene oxide

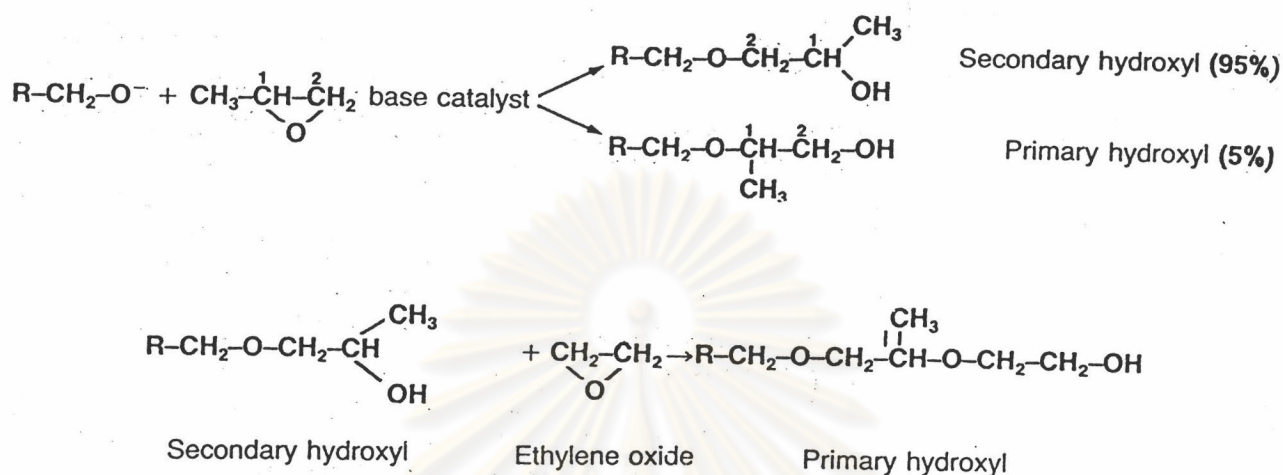


Figure 2.8 The manufacture of polyether polyols. (Wood, 1987)

Polyether polyols for flexible polyurethanes.

Most of the polyether polyols used to make flexible polyurethane foams and elastomers are triols based on trifunctional initiators, mainly glycerol or trimethylpropane. Polyether diols, made using glycol initiators, are also frequently used, often together with triols, in making high-elongation foams and elastomers. These high molecular weight polyether polyols are made mainly from propylene oxide but are usually modified by the co-polymerisation of 5% to 20% of ethylene oxide.

The many polyether triols used to make flexible polyurethanes include specialty products for the production of flat-top slabstock foam, polyether polyols for molded flexible and semi-rigid foams, and specially developed polyethers for elastomers, RIM products, adhesives and coatings.

The majority of flexible foam is made from 80:20-TDI and polyether triols with molecular weights in the range from 3000 to 4000. A typical triol with molecular weight of 3500 is made by the addition polymerization of 50 to 55 moles of propylene oxide and 10 to 15 moles of ethylene oxide onto 1 mole of glycerol or trimethylpropane.

The epoxide monomers and the polyether polyols are easily oxidised. Air is excluded from the manufacturing process and, when polymerisation is complete, antioxidants are added to prevent oxidation of the polyether. Much work has been done to develop efficient antioxidants that not only protect the polyol from oxidation during storage, but also protect low density foam from oxidative scorch at the high curing temperature immediately after manufacture.

Polyether polyols for making rigid polyurethanes. The polyether polyols used to make rigid polyurethane foams, rigid polymers and hard surface coatings, have a lower equivalent weight than those used to make flexible polyurethanes. The properties of these polyols vary with the choice of polyol initiator, either an alcohol or an amine and with the composition and the length of the oxyalkylene chain. Polyethers based on aminic initiators have a significantly higher reactivity with isocyanates than similar polyethers based on alcohols. Some typical polymerisation initiators are listed in Table 2.5

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Table 2.5 Polymerisation initiators: Polyether polyols for rigid polyurethanes
 (Wood, 1987)

Alcohols	Amines	Functionality
Water		2
Ethylene glycol		2
Diethylene glycol		2
Glycerol	Triethanolamine	3
Trimethylopropane		3
Pentaerythritol	Toluene diamine	4
	Ethylene diamine	4
	4,4'-diaminodiphenyl methane	4
Sorbitol		6
Sucrose		8

The weight of the starter may represent over one third of the weight of polyol. The choice of the starter is thus a very important factor in controlling the cost as well as the performance of the polyol. For these reasons a common starter is sucrose which is available in pure form at low cost and yields polyols with a satisfactory performance. Blends of polyols are often used to obtain the best combination of processability, cost and the properties of the final product, and for general application a mixture having an average functionality of 4 to 5 is often used. 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 isocyanates compared with nitrogen-free polyols, they tend to be less affected by tertiary amine catalysts and by changes in temperature. Polyols based upon aromatic diamine starters yield polyurethane systems that cure quickly to form a strong polymers.

Polyester polyols

Saturated polyesters with terminal hydroxyl-groups are used to make both flexible and rigid polyurethane polymers. Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and therefore more difficult to handle. They also yield polyurethane polymers which are more easily hydrolyzed. Consequently they are only used to make polyurethanes for demanding applications where the particular physical properties obtainable from polyesters are important. Polyester-based polyurethane elastomers combine high levels of tensile property with resistance to flexing and abrasion. They also have good resistance to many types of oil. Flexible foams made with polyester polyols and TDI combine high elongation with resistance to dry cleaning solvents. Polyesters are also less easily oxidised and resist higher temperature than polyethers.

Polyesterpolyols for making flexible polyurethanes include:

- Poly (ethylene adipates), which are wax-like solids at room temperature and are mostly used in manufacture of polyurethane elastomers and adhesives.
- Lightly branched poly (diethyleneglycol adipates), which are used mainly to make flexible foams.
- Aromatic polyester polyols are used in rigid polyurethane and polyisocyanurate foam. Polyesters based partly on scarp PET and/or DMT process waste are also used in rigid foam.
- Polycarbonate diols, which are waxy solids at room temperature, are also used to make polyurethanes-mainly for coating and adhesives. They have significantly improved resistance to hydrolysis under humid conditions.
- Halogen containing polyester, made from halogenated diols and diacids, may be used to reduce the flammability of heat-resistant polyurethanes.

Generally, the hydrolysis resistance of polyesters increase with increasing length of the chain between the polyester linkages and also with reducing residual acidity. The resistance to hydrolysis and to swelling by solvents and oils is also increased by increased branching of the polyester chains.

Table 2.6 Typical properties of polyester polyols (Wood, 1987)

Application	Type	Hydroxyl no. (mgKOH/g)	Viscosity (MPa at 25°C)	Acid value (mgKOH/g)
Flexible foam	Linear	45 to 60	10,000 to 20,000	< 2.0
Flexible foam	Branched	60 to 70	15,000 to 20,000	< 5.0
Low density semi-rigid foam	Highly branched	200	20,000	< 10
Elastomer	linear	50 to 60	3,000 to 10,000	< 1.0

2.2.3 Auxiliary material (additives)

For polyurethane manufacturing, a wide range of auxiliary chemicals may be added to control and modify both the polyurethane reaction and the properties of the final polymer.

These additives include catalysts, chain extenders, cross-linking agents, surface-active materials, flame-retardants, coloring materials and fillers.

Catalyst

Catalysts are widely used to give desired reaction rate and direction of the polymer-forming process. Catalysts regulate the reaction rates between the hydroxyl groups of polyol and the isocyanate groups in the di- or polyisocyanate, as well as the reaction of isocyanate groups with water. In addition, catalysts influence the rates of other crosslinking reactions, such as the formation of allophanate or biuret groups. A proper balance between chain extension crosslinking and gas evolution is necessary to effect an optimum foam rise and cure to minimize gas loss and foam

collapse. Insufficient catalysis may result coarse cell structure, while an excess may cause scorching of the foam. The most common types of catalysts can be used include aliphatic and aromatic tertiary amines, and organo-metallic compounds, especially tin compounds, although compounds of mercury or lead are also used. Alkali metal salts of carboxylic acids and phenols, and symmetrical triazine derivatives are used to promote the polymerisation of isocyanates. In the case of amines, promotion of urethane links is related to the strength of the base and structural effects.

While a number of organometal compounds, e.g. ferric acetylacetonate and cobalt naphthenate, will catalyze isocyanate reaction, those based on tin show remarkable activity, promoting reactions of NCO with OH groups in preference to reaction with water. For this reason, dibutyltin dilaurate and tin octoate are widely used; they are readily soluble in the reaction mixtures and have the advantage of low volatility and little odour.

Reviewing catalysts in general, tertiary amines favour NCO/OH and NCO/H₂O combination, while organotin catalysts are most effective for the NCO/OH reaction.

Temperatures of reaction can be important. At up to 50 °C the linear chain-forming reaction predominates but as higher temperatures (up to 150 °C) are reached then biuret and isocyanurate formation become effective and branching occurs. At above 150 °C some of the less stable links are affected and reversion or degradation can then take place. (Hepburn, 1992)

Table 2.7 Some tertiary-amine catalysts (Wood, 1987)





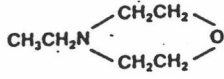
Catalyst	Application
1 N,N-Dimethylaminoethanol $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$	Inexpensive, low-odour, isocyanate reactive, mobile liquid catalyst used in polyether-based flexible foams.
2 N,N-Dimethylcyclohexylamine, (Catalyst SFC)  $\text{N}(\text{CH}_3)_2$	Liquid with an intense 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 polyester-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 Diaminobicyclooctane (DABCO) 	Solid, soluble in water, glycols and polyethers. May be used in most types of polyurethanes.
8 N-Ethylmorpholine 	Volatile, low viscosity liquid with characteristic odour. Used as synergistic catalyst in flexible foams and in prepolymer preparation.

Table 2.8 Some commercially available organo-metallic catalysts
(Wood, 1987)

Catalyst	Principle 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 thiocarbonylates Dioctyltin thiocarbonylates	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, e.g. CH_3COOK , K_2CO_3 NaHCO_3 and NaCO_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 for isocyanate polymerisation.
Ferric acetylacetonate	Catalyst for cast elastomer systems, especially those based on TDI

Cross-linking agents and chain-extenders.

These are low molecular weight polyols or polyamines. They are also sometimes known as curing agents. Chain-extenders are difunctional substances, glycols, diamines or hydroxy amines; cross-linking agents have a functionality of three or more.

The chain-extender reacts with diisocyanate to form a polyurethane or polyurea segment in the urethane polymer. It is usually added in sufficient amount to permit hard-segment segregation that results in an increase in the modulus and the hard-segment glass transition temperature (T_g) of the polymer.

Cross-linkers are used to increase the level of covalent bonding in rigid polyurethanes such as some rigid foams and also as additives in many semi-rigid foam systems.

Chain-extenders and curing agents are used in both single shot and prepolymer processes for making polyurethanes. Aromatic and aliphatic diamines are each used as curing agents. Simple diamines are too reactive to permit high level of addition in microcellular elastomers and special derivatives have been developed. A wide range of aliphatic, aromatic, arakyl and alicyclic diols have been used as chain extenders for urethanes.

Aromatic diols, e.g. quinol; 1,5-naphthalene diol; bisphenol A ,give tougher elastomers than aliphatic diols because of their bulky and relatively inflexible units. Table 2.9 lists some common chain-extending and cross-linking agents.



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Table 2.9 Chain-extending agents, cross-linking agents and curing agents and their diisocyanate equivalents. (Wood, 1987)

Additive	Functionality	Molecular weight	OH value (mgKOH/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 $C_3H_6(OH)_2$	2	76.11	1474	229	329
Dipropylene glycol $O(C_3H_6OH)_2$	2	134.18	836	130	186
1,4-Butane diol $C_4H_8(OH)_2$	2	90.12	1245	193	278
Polypropylene glycol 400	2	400	280	43.5	62
<i>m</i> -Pnylene diamine $C_6H_4(NH_2)_2$	2	108.15	1037	161	231
Diethyltoluene diamine $C_6HCH_3(C_2H_5)_2(NH_2)_2$	2	178.27	629	97.7	140
Dimethylthiotoluene diamine $C_6HCH_3(SCH_3)_2(NH_2)_2$	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

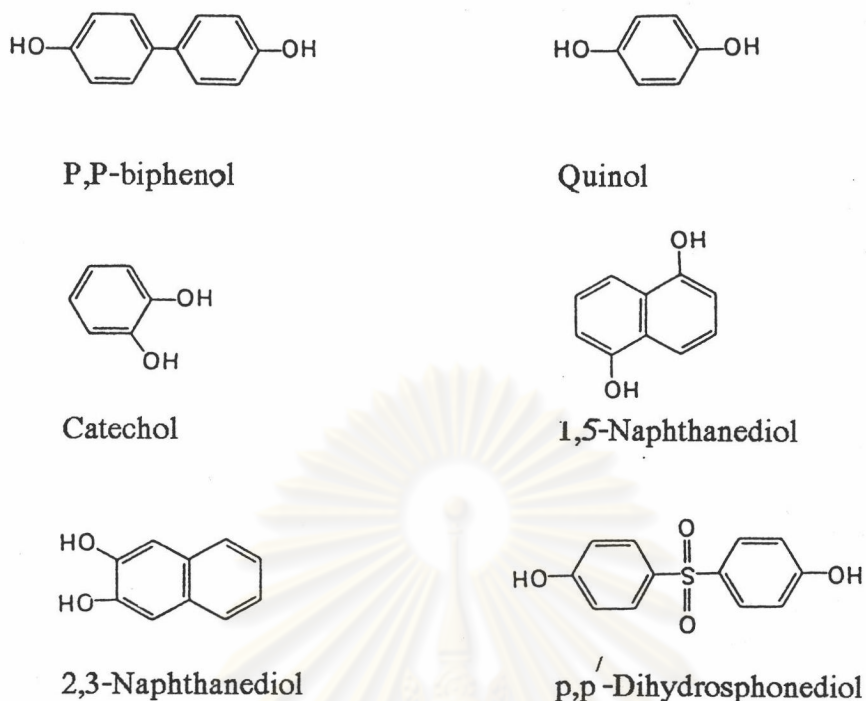


Figure 2.9 Structural formula of aromatic diol used as chain extender

(Hepburn, 1992)

Blowing agent

Cellular polyurethanes are manufactured by using blowing agents to form gas bubbles in the polymerising reaction mixture. There are two general types of blowing agent used in the manufacture of urethane foams. Carbon dioxide is generated *in situ* by the reaction of isocyanate with water, or volatile liquids such as fluorocarbons, particularly trichlorofluoromethane, are volatilized by the exothermic reaction between the isocyanate and hydroxyl components. High-density foams are most frequently made using carbon dioxide as blowing agent, while low-density foams with the best insulation properties are generally prepared employing fluorocarbons for purpose. Flexible polyurethane foams are usually made using the carbon dioxide formed in the reaction of water diisocyanate (water blowing). Rigid foams, because they are made with polyols having functionality and higher order of hydroxyl group content than those used in flexible polyurethanes, yield sufficient exothermic heat from the urethane reaction alone to allow foam expansion simply by vaporising an inert

blowing agent. The usual blowing agent for rigid foams is CFM-11, sometimes mixed with dichlorodifluoromethane (CFM-12) which has lower boiling point.

Unfortunately, CFC-11 and fully halogenated chlorofluorocarbons (CFCs) deplete the ozone layer and their continue use has been severely limited. In accordance with the invention, it has been discovered that a polyurethane foam having physical properties comparable to that of the current commercial products and low ozone depletion potential (ODP) can be obtained by using the two-carbon hydrogen-containing halocarbon, such as HCFC-123 or HCFC-141b. These materials have a lower ODP compared to CFC-11.

Table 2.10 Non-reactive blowing agents for polyurethanes (Wood, 1987)

Blowing agent	Trichloromono- fluoromethane (CFC-11)	Dichlorodi- fluoromethane (CFC-12)	Methylene chloride
Molecular weight	137.38	120.92	84.94
Density at 20°C (g/m)	1.488	1.486	1.336
Boiling point at 1 atm.(°C)	23.8	-29.8	40.1
Freezing point (°C)	-111	-160	-96.7
Solubility (g/100 g solvent at 20°C)			
Water	Insoluble	Insoluble	2
Ethanol	∞	∞	∞
Polyethers	Adequately soluble for all applications		

Table 2.11 The different of properties between CFC-11 and HCFC

	CFC-11	HCFC-123	HCFC-141b
Molecular formula	CCl_3F	CHCl_2CF_3	CH_3CFCl_2
Molecular weight	137.4	152.9	116.9
Boiling point ($^{\circ}\text{C}$)	23.8	28	32
Heat conductivity of gas (Btu/hr.ft. $^{\circ}\text{F}$)	0.0045 @ 25 $^{\circ}\text{C}$	0.0054 @ 30 $^{\circ}\text{C}$	0.0053 @ 32 $^{\circ}\text{C}$
Heat of evaporation (cal/g)	43.1	40	53
Life in atmosphere (years)	60	2	5
Relative ozone depletion potential	1	<0.05	<0.05
Relative green house effect	0.4	<0.1	<0.1

Source : Patent Number : 5,114,980

Surfactant

Surface-active materials are particularly useful in foam making where they help to control the size of the foam cells by stabilising the gas bubbles formed during nucleation and may stabilise the rising foam by reducing stress-concentrations in the thinning cell-walls. Most flexible and rigid foams are now made using organosiloxanes or silicone-based surfactants. The first silicone polymers to be used in production of polyurethane foams, especially in two-stage processes, were poly(dimethylsiloxanes), (PDMS) and poly(phenylmethylsiloxanes) having viscosities from about 2000 to 14000 mPas at 25 $^{\circ}\text{C}$. Silicone surfactants for rigid foams have a greater surface activity than those used for flexible foam.

Coloring materials

Specialised products, such as foams for textile laminating and for packaging, may be highly colored to meet the requirements of the application. Rigid foams, being mostly made from brown-colored polymeric MDI and sold enclosed within opaque covering materials, are often made without added colorants. The usual method of coloring is by the addition of pigment pastes to the foam reaction mixture.

Organic and inorganic pigments are both used. The pigments used must not react with isocyanates and must be stable at the high curing temperature reached in the manufacture of low density foams. The most widely used coloring material is carbon black which, at levels above 0.1 part per 100 parts of the polyol used, gives some protection against surface discoloration of the foam caused by UV light.

Fillers

Fillers are generally used either to reduce costs or to impart specially desired properties to the foam. When fillers are employed for cost reduction, any significant increase in density should be taken into account. Particulate and fibrous fillers may each be used in flexible polyurethane foams to reduce their flammability and to increase weight of seat cushions for furniture and to increase their resistance to compression. fibrous fillers are reinforcing : they give increased stiffness and they increase the range of operating temperature. Mineral fillers are sometimes used to reduce costs and to increase the compressive strength of rigid foams used in composite building panels.

Typical classes of fillers which have been used with urethane foam systems are the following : (Benning, 1969)

- **Cellulosic and Other Wood Derivattived Fillers.** Cellulosic fillers, such as wood flour, contain reactive hydroxyl groups. Because of their low reactivity in the solid state, reaction with isocyanate groups is very slow; thus these fillers act more like inert fillers. In addition to increasing foam density this group of fillers usually imparts greater moisture absorption to foams since they are sensitive to moisture.

- **Synthetic Fibers.** Fibers (e.g., nylon, acrylic, and polyesters) have been added to impart better dimensional stability and greater strength properties.

- **Inorganic Salt and Oxides.** A number of inorganic salts and oxides have been used either as extender fillers or to impart flame resistance. In the latter category are materials such as ammonium phosphate and antimony oxide. Heavier metal oxides have also been employed to modify electrical properties.

- **Inorganic Flakes and Fibers.** A considerable amount of development work is going on with various types of glass flakes, and fibers to provide reinforcement and to achieve improved strength properties.

- **Miscellaneous Fillers.** Coal tars can be used with rigid foams for applications such as sound absorption, insulation, and void filling. Other bulk fillers, including phenolic and polystyrene beads, have been evaluated but generally lead to foams with inferior properties. The use of glass microballons in rigid foams has been found to impart improved fire resistance.

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Table 2.12 Some fillers and their application in polyurethanes (Wood, 1987)

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.
Clay (China clay, kaolins, ect.)	Flexible systems
Expanded silicas, colloidal silicas	Flexible foams, cast elastomers
Clay balls, vermiculite, expanded mica, ect.	Rigid foams
Glass micro-spheres	Flexible, microcellular foams, RIM
Glass flakes	Elastomeric RIM
Silicates, cements	Rigid foams, sealants, grouting compounds
Short fibers, milled and chopped glass-fibre, Aramid fibres, carbon fibres, conducting fibres, (aluminum, coated glass, steel)	Elastomeric RIM, rigid foams
Glass cloths and scrim, wire mesh, organic fibres, ect.	Encapsulation in rigid foams, reinforcement of low density flexible foam mouldings.

Finely-divided fillers with a particle size ranging from a few microns up to about 100 microns are usually added as dispersions in the polyol component of the polyurethane mix. Fillers for use in polyurethanes must be dry. Some low-cost mineral fillers such as china clay, kaolins and other aluminum silicates, which contain both free and combined water, that would otherwise be satisfactory, may be difficult to dry reproducibly and economically.

Flame Retardants.

Polyurethanes, in common with all other organic materials, will burn given the application of sufficient heat in presence of oxygen. Flame retardants are added to polyurethanes to reduce the flammability.

The most widely used flame-retardants in both flexible and rigid foam systems are chlorinated phosphate esters. They can reduce in the rate of burning without adverse effects upon the processability of the foam system and the properties of the product.

The addition of aluminum trihydrate gives a further reduction in flammability and minimises the increase in smoke formation on burning, resulting from the addition of halogenated organic phosphates. Melamine is also used, together with phosphate flame retardants such as ammonium polyphosphate, in flexible foams for furniture cushions. It gives good resistance to smouldering combustion.

Table 2.13 list examples of flame-retardants in three classes: non-reactive liquid flame retardants; compounds that react with isocyanates to become bound into the polymer network; and some other materials that reduce the rate of burning.

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Table 2.13 Some flame retardants for polyurethanes (Wood, 1987)

Additive	Typical application
A. Non-reactive liquids	
Tris (2-chloropropyl) phosphate.	All polyurethane foams including polyester-based foams and microcellular elastomers.
Tris (2-chloroethyl) phosphate.	Polyether-based flexible and rigid foams.
Tris (2,3-dichloropropyl) phosphate.	Polyether-based flexible and rigid foams.
Tetrakis (2-chloroethyl)-2,2-bis-(chloromethyl) propylene phosphate.	Low volatility material for flexible and rigid foams.
Dimethyl methyl phosphate.	Rigid foams.
B. Isocyanate-reactive additives	
Tris (polyoxyalkyleneglycol) phosphonates and phosphite esters.	Flexible and semi-rigid foams.
Tris (halogenate polyol) phosphonates.	Flexible and rigid foams.
Dibromoneopentyl glycol.	Polyether-based polyurethane.
Brominated polyester and polyether diols.	Rigid polyurethane and polyisocyanurate foam.
Tetrabromobisphenol A.	Rigid polyurethane and polyisocyanurate foam.
Tetrabromophthalic anhydride	Rigid polyurethane and polyisocyanurate foam.
C. Fillers	
Ammonium salt, sulphate, polyphosphate, ect.	Together with halogenated additive in rigid polyurethanes.
Aluminium hydroxide.	All polyurethanes but especially in low density flexible foams for ignition and smoke supression.
Melamine.	
Calcium carbonate.	Heat absorbing filler.

2.3 Molasses

Molasses, another type of syrup, is a by-product of the sugar industry; it is the mother liquor remaining after crystallization and removal of sucrose from the juices of sugar cane or sugar beet and is used in a variety of food and non-food applications. Molasses was first produced from sugarcane in China and India centuries ago, later spread into Europe and Africa, and was introduced as the by-product of cane-sugar production into Santo Domingo by Columbus in 1493. During Colonial times, molasses was very important to the American colonies for the production of rum.

Manufacture

Raw sugar is produced from sugarcane by a process that involves extraction of sugar in water, treatment to remove impurities, concentration, and several crystallizations. After the first crystallization and removal of "first sugar," the mother liquor is called first molasses. First molasses is recrystallized to obtain a second lower quality sucrose (second sugar) and a second molasses. After a third crystallization, the third molasses is sold as blackstrap, final, or cane molasses.

Molasses from other sources include citrus and corn sugar molasses. Citrus molasses is produced from citrus waste and contains 60-75% sugars. Corn sugar molasses is the mother liquor remaining after dextrose crystallization and contains a minimum of 43% reducing sugars expressed as dextrose.

Molasses is shipped in drums, barrels, tank trucks, tank cars, barges, and ocean-going vessels. Blackstrap molasses is generally stored long periods of time in round tanks resembling gasoline or fuel oil tanks. After blackstrap has been separated in centrifugals from low grade sugar it is pumped into the storage tanks, which may hold as much as 2,000,000 gal. each. As a general rule molasses is stored at 85-88 ° Brix. At

this high level of concentration the final molasses is immune to bacteriological decomposition.

Composition

Molasses composition depends on several factors, e.g. locality, variety, soil, climate, and processing. Cane molasses is generally at pH 5.5-6.5 and contains 30-40% sucrose and 15-20% reducing sugars. Cane molasses contains less ash, less nitrogenous material, but considerably more vitamins than beet molasses. Composition of selected molasses products is listed in Table 2.14

Table 2.14 Analyses of Molasses Samples. (Othmer, 1983)

Molasses type	Solid %	Total sugar wt%	Crude protein %	Total ash wt%
cane (Louisiana)	80.8	59.5	3.0	7.2
beet (Wisconsin)	78.6	52.7	11.4	9.3
corn	74.9	50.3	0.4	8.9
citrus	71.4	42.4	4.7	4.8

Composition of cane molasses.

Water	17-25 %
Sucrose	30-40 %
Reducing sugar	10-25 %
Ash	7-15 %
Organic non-sugar	10-20 %

Uses.

The primary use of molasses is in animal feed. Molasses provides a carbohydrate source, salt, protein, vitamins, and palatability and may be used directly or mixed with other feeds.

The second main use for molasses is in various fermentation processes as an inexpensive source of carbohydrate. Molasses is the basic raw material for rum production and is also used for production of yeast and citric acid. Molasses is also used in confections such as toffees and caramels, and in baked and glazes.

The mainly use of molasses in Thailand is in alcohol production. In 1975 molasses is used to produce alcohol for 218,400 tons and to produce monosodiumglutamate about 20,000 tons, molasses is also used in animal feed 50,000 tons. Molasses can be used in other industry such as vinegar, sweet sauce and Soya sauce.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

2.4 Chemistry and biochemistry of polymer biodegradation

Biodegradation is an event which takes place through the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, ect.) or their secretion products. Microbiological deterioration can be achieved by exo- and endo-enzymes or by products secreted biochemically from these. Microorganisms can also eat and, sometimes digest polymers and give a mechanical, chemical or enzymatic ageing. There are many different degradation modes that in nature combine synergistically to degrade polymers. Biodegradation might be better used as a term only when it is essential to distinguish clearly might be better used as a term only when it is essential to distinguish clearly between the action of living organisms and other degradation modes (e.g. photolysis, oxidation, hydrolysis).

The accessibility of a polymer to degradative attack by living organisms has no direct relation to its origin and not all biopolymers are truly biodegradable. Complex macromolecules such as lignin are extremely inert while synthetic polymers with hydrolysable backbones, such as aliphatic polyesters, are accessible to the biodegradative action of esterases despite the usual specificity of these particular enzymes. (Albertson and Karlsson, 1994)

Enzymes

Enzymes are biological catalysts, with the same action as chemical catalysts, i.e. by lowering the activation energy they can induce increases in reaction rates in an environment. Enzymes are among the most potent catalysts known, a rise in reaction rate of 10^8 - 10^{20} can often be observed in the presence of enzymes. All enzymes are proteins; a polypeptide chain with a complex three-dimensional structure. The enzymes activity is closely related to the conformational structure, even small changes in temperature, pH or osmolarity can result in changes in the conformational structure rendering the enzyme inactive. Their action is regulated, i.e. they can change

from a period of low activity to periods of high activity, through the influence of hormones, pH changes or other factors.

The three-dimensional structure of enzymes with folds and pockets creates certain regions at the surface with characteristic primary structure (i.e. specific amino acid sequence) which form an active site. At the active site the interaction between enzyme and substrate takes place leading to the chemical reaction, eventually giving a particular product. Some enzymes contain regions with absolute specificity for a given substrate while others can recognize a series of substrates. The initial contact between enzyme and substrate forms an optimal orientation at the active site giving good possibilities for maximal bonding (enzyme-substrate), often the cofactor induces these changes when binding to the enzyme.

Enzyme nomenclature

All enzymes, except those few retaining historically important trivial name (trypsin, pepsin, ect.), are named according to rules adopted by the International Enzyme Commission. The names give the nature of the chemical reaction catalyzed and also describe the substrate. All new enzymes end with the suffix -ase, but shorter names are often used as some enzyme names become very long, e.g. hexokinase for ATP: hexose-phosphotransferase. Typical enzyme classes, together with the reactions catalyzed and the reactive bonds, are shown in Table 2.15

Table 2.15 Reactions catalyses and reactive bonds of different classes of enzyme (Albertson and Karlsson, 1994)

Enzyme class	Reaction catalyzed	Reactive bonds
1. Oxidoreductase	Redox reactions	-C=O -C-NH ₂
2. Transferase	Transfer of functional groups	One C-groups Acetyl groups
3. Hydrolase	Hydrolysis	Esters Peptides
4. Lyase	Addition to double bonds	-HC=CH- -C=O
5. Isomerase	Isomerisation	Racemases
6. ligase	Formation of new bonds using ATP	-C-O- -C-S- -C-N-

Physical factors affecting the activity of enzymes

All enzymes are adjusted to a specific environment in which their activity and three-dimensional structure are optimal for the purpose. An extremely small change in some parameter may render the enzyme totally inactive and sometimes even destroy it irreversibly. Other solvents than water, especially organic solvents, are also lethal to many enzymes but, on the other hand, there are enzymes active in quite extreme environments, e.g. in hot water springs or salt deserts.

Enzyme mechanisms

Different enzymes have different actions, some enzymes change the substrate through some free radical mechanism while others follow alternative chemical routes. Typical examples are biological oxidation and biological hydrolysis.

1. Biological oxidation. Several enzymes can react directly with oxygen, the classical example being cytochromoxidase which is active in the respiratory chain.

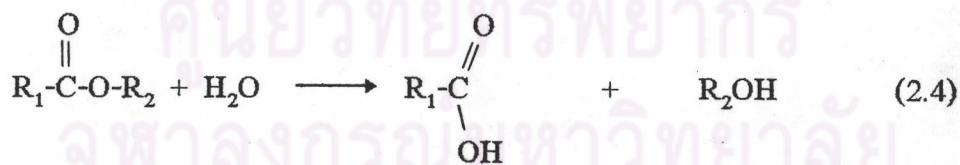
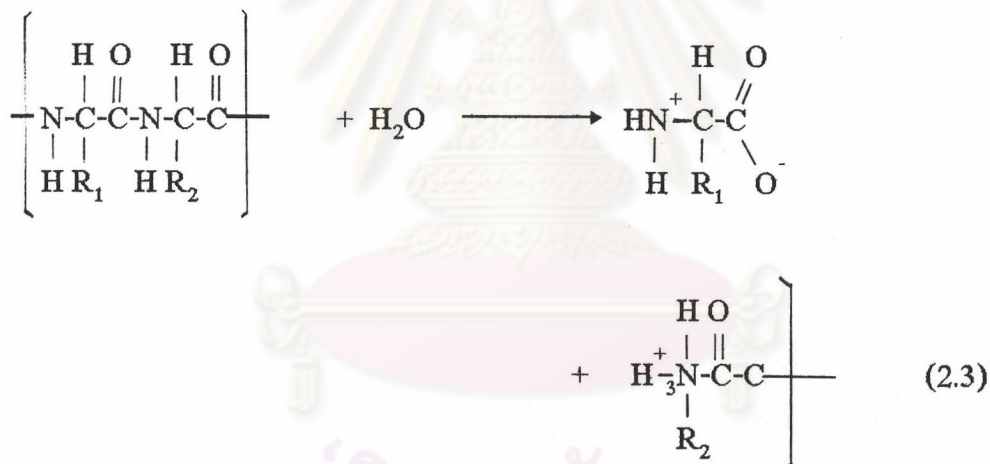
In several cases oxygen is directly incorporated into substrate. The enzymes can be hydroxylases (equation 2.1) or oxygenase (equation 2.2). (Albertson and Karlsson, 1994)



Hydroxylases are sometimes called monooxygenases and catalyze the insertion of a single atom of oxygen in the substrate A as a part of the hydroxyl group. The monooxygenases require a second reduced substrate BH_2 which simultaneously undergoes oxidation (i.e. dehydrogenation).

Oxygenases, also called dioxygenase, catalyse the insertion of the whole oxygen molecule into the substrate; sometimes the product is dihydroxy derivative but more often the oxygen atoms are incorporated as part of a carbonyl (-CO) or a carboxyl (-COO-) grouping. One example of an oxygenase enzyme is that capable of catalysing the splitting of the aromatic structure producing two (C=O) groups instead of the (-HC=CH-) group.

2. Biological hydrolysis. Several different hydrolysis reactions occur in biological organism. Proteolytic enzymes (proteases) catalyse the hydrolysis of peptide bonds (equation 2.3) and also the related reaction hydrolysis of an ester bond (equation 2.4). (Albertson and Karlsson, 1994)



Chemical degradation initiates biodegradation

The initial step in oxidation should be compared with the initial step in degradation of lignin and other rather inert natural products such as rubber and gutta percha. It is also possible to compare this oxidation step with the degradation of polymer films implanted in the tissues of living animals as well as the oxidation in landfill.

In many landfills, especially at depths of 1 to 2 meters below the surface, or in deep soil burial especially in waterlogged land, anaerobic conditions can develop which then decrease the initial oxidation of polymers. Certain microorganisms can, however, utilize oxygen in chemically bound form from nitrate, sulphate, carbonate and fumarate anion and also, probably, from ferric ions in an anaerobic way without gaseous oxygen.

Initial photooxidation has been demonstrated to have a profound effect on the degradability of polyethylene in soil even after 10-year period of incubation. Polyethylene without prior photooxidation degrades by some 0.2 % during a 10-year period, while polyethylene photoxidised for 42 days before incubation in soil degrades by about 2 %.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย