

CHAPTER II

THEORY

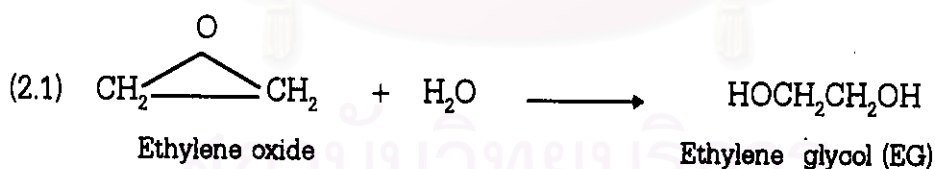
2.1 Poly(ethylene terephthalate) (PET)

2.1.1 Raw materials

Poly(ethylene terephthalate) may be obtained from ethylene glycol and either terephthalic acid or its ester, dimethyl terephthalate. Until the mid-1960s, all poly(ethylene terephthalate) was produced from the ester, mainly because the acid then available was difficult to obtain with sufficiently high purity whereas the ester was readily purified. This situation changed when discovery of purely fibre - grade terephthalic acid and at the present time approximately equal amounts of the polymer are made from acid and ester .

2.1.1.1 Ethylene glycol

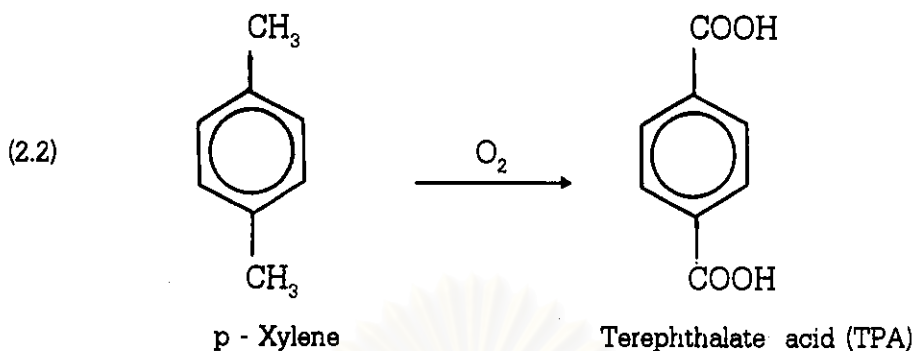
Ethylene glycol is prepared by the hydration of ethylene oxide



This reaction is carried out in a manner comparable to that described for the preparation of propylene glycol from propylene oxide. Ethylene glycol is a colorless liquid, with the boiling point of 197 °C.

2.1.1.2 Terephthalic acid

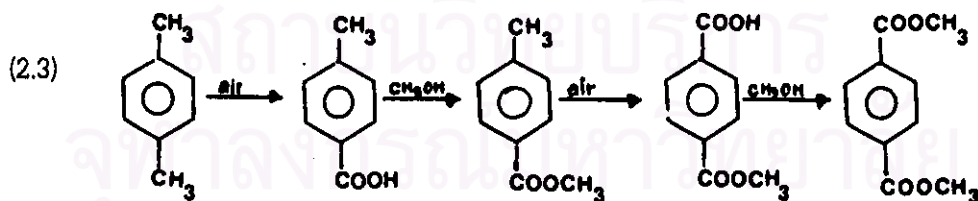
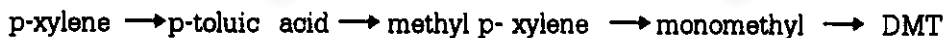
The major commercial route to terephthalic acid which is suitable for the direct preparation of poly(ethylene terephthalate) is from p-xylene :



p-Xylene is obtained largely from petroleum sources, being a product of the fractionation of reformed naphthas. The oxidation is carried out in the liquid phase. Typically, air is passed into a solution of p-xylene in acetic acid at about 200 °C and 2 MPa. in the presence of a catalyst system containing cobalt and manganese salts and source of bromide ions. The terephthalic acid produced contains only small amounts of impurities (mainly p-carboxybenzaldehyde), which are readily removed. The acid is dissolved in water at about 250 °C and 5 MPa and treated with hydrogen. The solution is then cooled to 100 °C and pure terephthalic acid crystallizes. Terephthalic acid is a white solid which sublimates at 300 °C.

2.1.1.3 Dimethyl terephthalate

Several processes have been developed for the preparation of dimethyl terephthalate from p-xylene, but the most important processes are as follows :

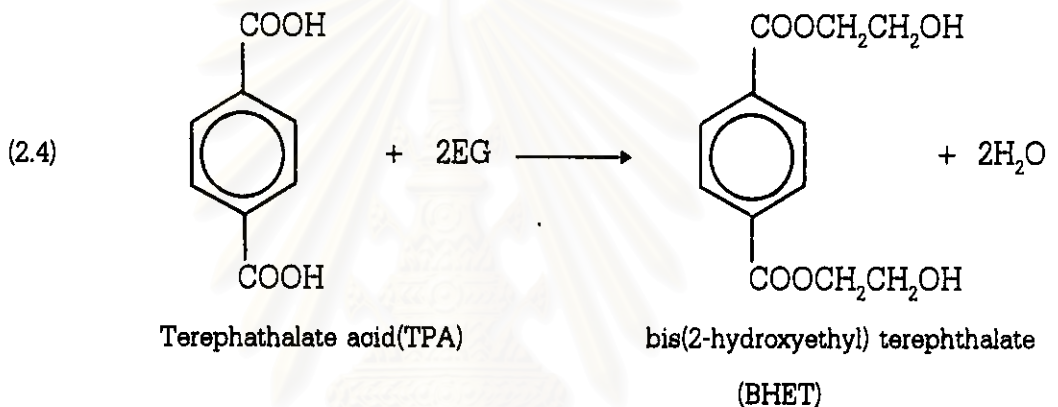


The oxidation steps are carried out in the liquid phase at about 170 °C and 1.5 MPa in the presence of a cobalt acetate or naphthenate catalyst whilst the esterifications are conducted at about 150 °C. Dimethyl terephthalate may also be produced by esterification of terephthalic acid. Dimethyl terephthalate is a white solid, with the melting point of 142 °C.

2.1.2 Preparation

2.1.2.1 Polymerization

Poly(ethylene terephthalate) can be prepared from either terephthalic acid or dimethyl terephthalate. With both starting materials, the polymerization is carried out in two steps. In the acid based process, the initial step is esterification to give mainly bis(2-hydroxyethyl terephthalate). Equation 2.4 shows the esterification between terephthalic acid and ethylene glycol.



In addition to bis(2-hydroxyethyl) terephthalate, oligomers up to about the hexamer are formed, these have the general formula as shown in figure 2.1.

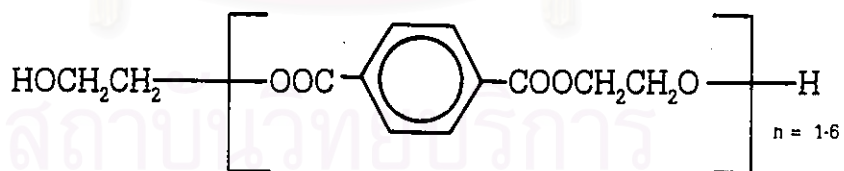
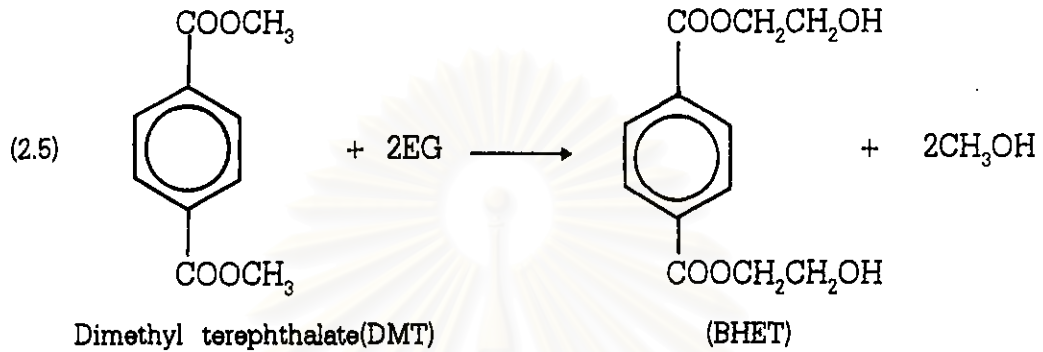


Figure 2.1 The general formula of the oligomer of bis(2-hydroxyethyl)

Typically, terephthalic acid is treated with an excess of ethylene glycol (1:1.5 molar) at about 250 °C and 0.4 MPa and water is allowed to evaporate as reaction proceeds.

In the ester-based process, the initial step is ester interchange and again the principle product is bis(2-hydroxyethyl)terephthalate. Equation 2.5 represents the ester interchange between dimethyl terephthalate and ethylene glycol.



Also, some oligomers are formed. In a typical process, dimethyl terephthalate is heated with an excess ethylene glycol (1:2.2 molar) at 140-220 °C and atmospheric pressure in the presence of a catalyst usually manganese acetate. Methanol is removed as reaction proceeds. Whether the starting material is terephthalate acid, the second step in the polymerization sequence is the same. An ester interchange reaction occurs, in which the bis(2-hydroxyethyl)terephthalate serves as both ester and alcohol. Successive interchanges result in the formation of polyester, as represented in equation 2.6 and figure 2.2.

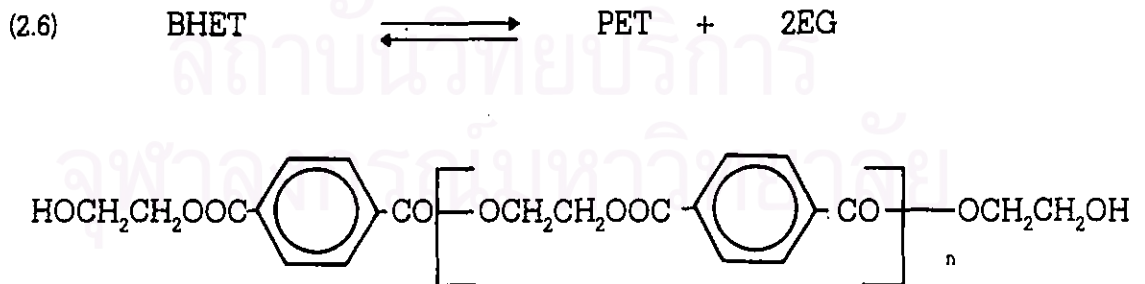


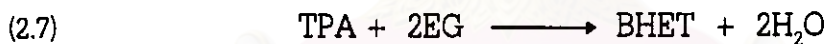
Figure 2.2 The general formula of PET

Under the reaction conditions employed, the ethylene glycol which is eliminated is removed continuously from the system, thus there is a progressive increase in molecular weight. Of course, ester interchange reactions also occur at non-terminal ester linkages, but such reactions do not lead to formation of ethylene glycol and so do not change the average molecular weight of the mixture. The bis (2-hydroxyethyl) terephthalate is heated at about 290 °C in the presence of a catalyst such as antimony trioxide while the pressure is lowered to about 0.1 KPa. Ethylene glycol is distilled off as reaction proceeds. Polymerization is continued until the molecular weight reaches the desired level (2000 for fiber and film, 3000 for molding material). The molten polymer is either spun directly into fiber or extruded and disintegrated. Compared to the ester-based process, the acid-based process avoids costs involved in using and recycling methanol and gives higher yields. On the other hand, the ester-based process is somewhat easier to carry out.

2.1.2.2 Depolymerization

The study of Balica and Wong (1989)

In their study, PET was depolymerized by glycolysis in excess ethylene glycol. Equation 2.4 and 2.6 are rearranged into a simple form of equation 2.7 and 2.8



Polymerization of PET has two steps. Equation 2.7, the reaction between one mole of TPA and two mole of EG occur in the presence of a catalyst. BHET are polymerized to form PET and ethylene glycol occurs. The equation is the reversible reaction. From the theoretical kinetics, the reaction of PET and excess ethylene glycol can occur at suitable condition. From the experiment, the reaction of PET and excess ethylene glycol occurred at the presence of catalyst. The product of the reaction depended on the condition. The reversible reaction is named depolymerization. Depolymerization of PET in excess ethylene glycol can be perform at , the ratio of PET to EG of 1:4 and the temperature for depolymerization at 190 °C. The depolymerization occurred in the atmospheric pressure. When the time

passed to 8 hours, the equilibrium of the reaction occurred. The final product consisted of BHET, dimer and excess ethylene glycol, with an equilibrium constant lying between 1.13 to 1.53 .

The study of J.Y. Chen and the others (1991)

Depolymerization of PET in excess ethylene glycol was occurred at the high temperature and at higher than atmospheric pressure. The final product consisted of BHET, oligomers and excess ethylene glycol. They found that a definite amount of ethylene glycol was needed in order to obtain a given length of oligomers. The mechanism of pressurized depolymerization of PET resin can be provided into two steps.



According to their kinetic studies, as shown in figure 2.4-2.6 ,the depolymerization rate is dependent on pressure , temperature ,and EG/PET ratio ,respectively ,as represented by equation 2.11 .

$$(2.11) \quad \text{Depolymerization rate} \propto (P)(T)[\text{EG}]/[\text{PET}]$$

The depolymerization rate was expressed as the number of hydroxyl value /hour, where [EG] was defined as the molar concentration of ethylene glycol based on unit mole of PET, and [PET] was defined as the molar concentration of PET based on unit mole of ethylene glycol. Under the constant pressure and temperature and PET concentration ,equation 2.11 can be reduced to equation 2.12.

$$(2.1.2) \quad \text{Depolymerization rate} = k[\text{EG}]^2$$

A plot of depolymerization rate against the square of ethylene glycol concentration shows a linear relationship as shown in figure 2.6. Based on the kinetics ,it was believed that the depolymerization of PET resin was catalyzed by ethylene glycol . The reaction step

of equation 2.9 was very fast. After the scission reaction on the polymer chains was completed, it must exist an equilibrium reaction between BHET and oligomers (mostly dimer and trimer) as shown in equation 2.10. Because the scission reaction happened so quickly and randomly, the oligomer which had repeating unit higher than trimer were too minute to be detected in the case of high EG/PET ratio. However, in a low EG/PET ratio, the glycolyzed product consisted of oligomers had a high molecular weight. This implied that the degree of polymerization of product may be regulated easily by the EG/PET ratio used in glycolysis.

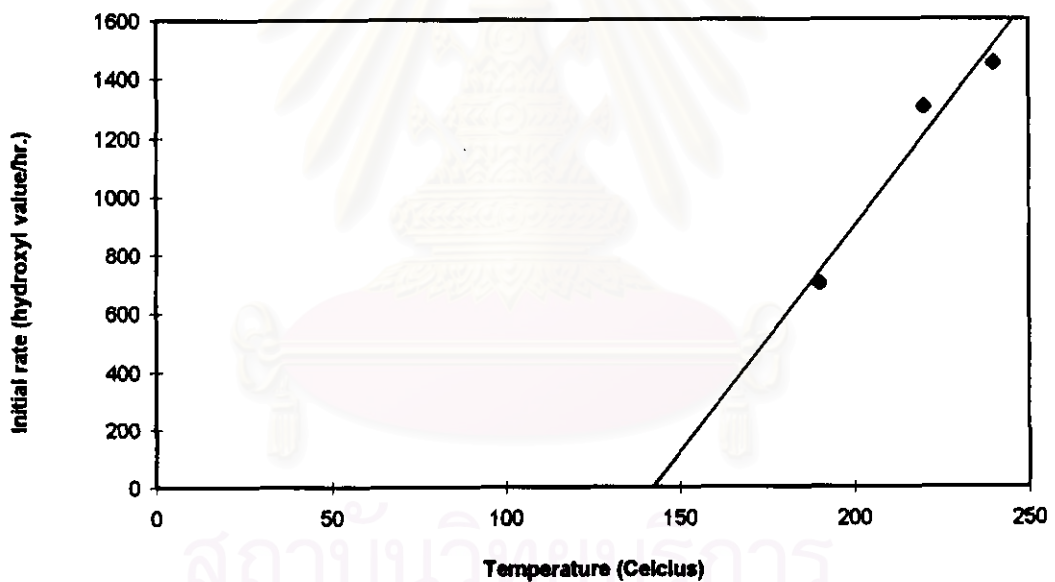


Figure 2.4 Depolymerization rate versus temperature (Chen and the others, 1991)

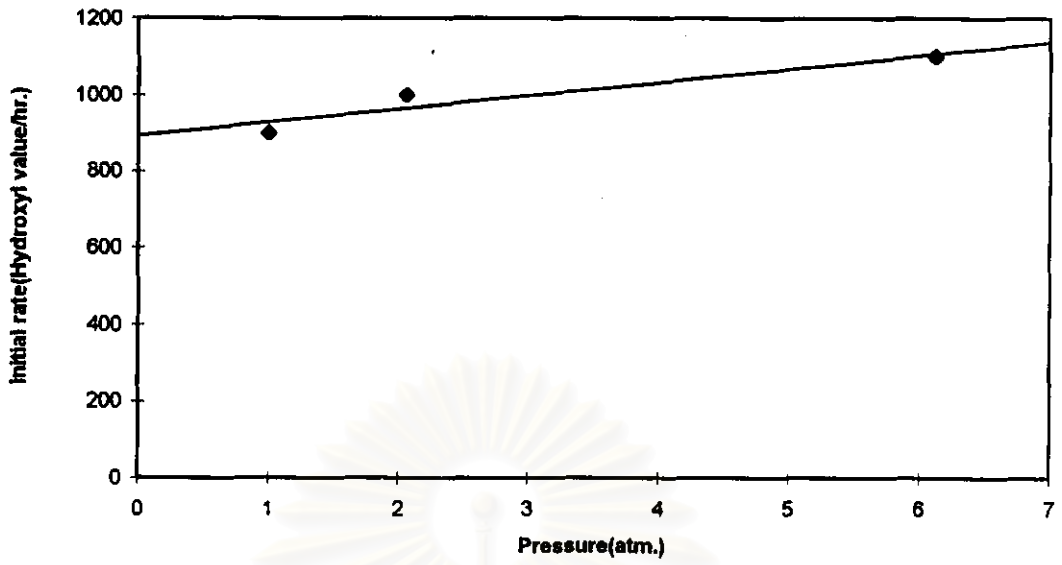


Figure 2.5 Depolymerization rate versus pressure (Chen and the others ,1991)

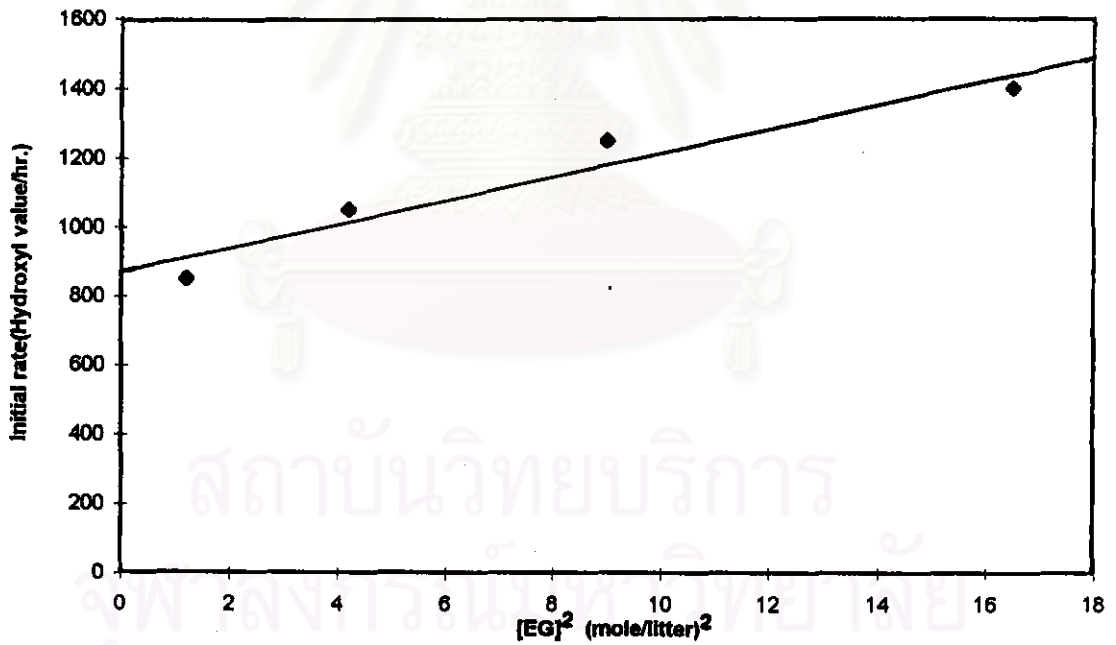


Figure 2.6 Depolymerization rate versus $[EG]^2$ (Chen and the others ,1991)

2.1.3 Properties of Poly(Ethylene Terephthalate)

2.1.3.1 Structure of polyethylene terephthalate

As a result of various methods of investigation, it is possible to represent the structure of poly(ethylene terephthalate) in figure 2.7.

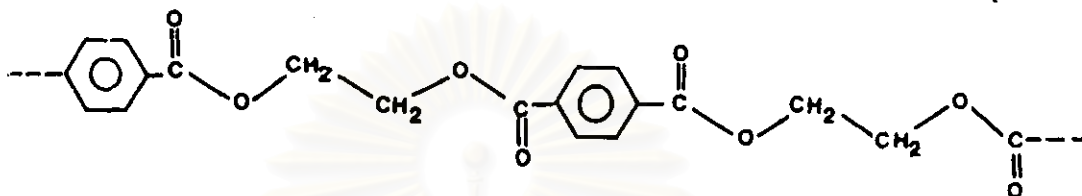


Figure 2.7 Illustration of the structure of poly(ethylene terephthalate)

(Korshark V.V. and Vinogradova S.V.,1965)

Poly(ethylene terephthalate) consists of a mixture of crystalline and amorphous regions the relative proportions of which depend on the method of preparation. The molecule has extended rectilinear shape. The macromolecules are linked only Van der Waals forces and the high melting point is due solely to the rigidity of the aromatics-nucleus-containing chain.

2.1.3.2 Physical Properties

Ordinary poly(ethylene terephthalate) has a specific gravity of 1.38. It is a polymer which contains a considerable amount of crystalline fraction. However, on rapidly cooling from molten state, poly(ethylene terephthalate) can be obtained as a completely amorphous polymer in the form of perfectly transparent samples with sp.gr. of 1.33. The specific gravity of the completely crystalline fraction is 1.455. The change in the specific gravity has been used in the study of the process of crystallization of poly(ethylene terephthalate). On immersion in water at 25°C for a week, it absorbs less than 0.5 percent of water. The mechanical properties remain virtually unchanged. The wettability of poly(ethylene terephthalate) has been investigated and it has been found that it is wet by liquids which form hydrogen bonds better than polystyrene and polyethylene.

2.1.3.3 Optical Properties

The refractive indices for poly(ethylene terephthalate) in a form of a film are perpendicular to the plane of the film -1.64, parallel to the plane of the film -1.51.

2.1.3.4 Thermal properties

The melting point of poly(ethylene terephthalate) lies within the range 250-265 °C. Zero strength for poly(ethylene terephthalate) is at 248°C. The viscosity of molten poly(ethylene terephthalate) has been determined in a capillary viscometer, it is found that the activation energy of viscous flow is 40 kcal/mole in consequence of a decrease in the viscosity of the melt. The second-order transition point (glass point) has been determined by the following methods : from the change in the dielectric constant with temperature, the variation of the dynamic modulus with temperature and the specific volume. For amorphous unorientated poly(ethylene terephthalate), the second-order transition point is 81°C, for crystalline unorientated material it is 100°C and for a crystalline orientated sample it is 125°C. At a temperature of 240-245°C a poly(ethylene terephthalate) film contracts and becomes wrinkled and brittle. Poly(ethylene terephthalate) ignites with difficulty and having ignited it burns. Slowly and readily goes out since the burning portion melts and falls away. The resistance to cold of poly(ethylene terephthalate) is fairly high, since a film remains elastic at -50°C and at -60°C no appearance of brittleness is observed.

2.1.3.5 Mechanical Properties

Poly(ethylene terephthalate) is in the form of a film, fiber or massive objects. It has a high strength. In table 2.1, a comparative data on the mechanical properties for films of poly(ethylene terephthalate), polyethylene, cellulose acetate and cellophane, determined by Frierl's method is given.

Table 2.1 Comparative mechanical properties of films
(25°C:35 percent relative humidity) (Korshak V.V. and Vinogradova S.V.,1965)

Properties of the polymer	Poly(ethylene terephthalate)	Polyethylene	Cellulose acetate	Cellophane
Thickness, (mm.)	0.0254	0.0381	0.0223	0.0254
Tensile strength,(kg/cm ²)	1638.2	168.7	633.0	563.0
Elongation, (%)	70	700	20	30
Tensile modulus,(kg/cm ²)	35200	1336	24610	28100
Tear strength,(g.)	18	175	4	5
Impact strength, (kg-cm ²)	90	15	10	15
Flex,(cycles)	20000	26000	300	600

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2.1.3.6 Electrical Properties

In table 2.2, the comparative characteristics of electrical properties of a poly(ethylene terephthalate) film (thickness 1 mil at 25°C), polyethylene and cellulose acetate films are given.

Table 2.2 Comparative electrical characteristics

(Korshark V.V. and Vinogradova S.V.,1965)

Properties of the polymer	Poly(ethylene terephthalate)	Polyethylene	Cellulose acetate
Dielectric constant at 60 cycle/sec	3.2	2.25	3.5-6.5
Tangent of the loss angle at 60	0.003	0.0005	0.03-0.06
Dielectric strength, (KV/mm.)	180	160	120
Volume resistibility, (ohm/cm.)	1×10^{19}	4×10^{15}	1×10^{10}
Surface resistibility at 100% relative humidity, (ohm.)	4.8×10^{11}	-	-

2.1.3.7 Permeability

poly(ethylene terephthalate) film is almost impermeable to water vapor and the vapor of organic solvents. The vapor permeability of such film compared with polyethylene, cellophane, butvar and cellulose acetate are shown in table 2.3. The permeability is expressed in grams of vapor passing through a given area in a definite time. Table 2.4 gives the permeability of films of poly(ethylene terephthalate), polyethylene and cellophane for the vapors of organic solvents. The comparative penetration of vapors of strong-smelling substances through various film is given in table 2.5.

Table 2.3 Penetration of water vapor through a film
(Korshark V.V. and Vinogradova S.V.,1965)

Material of the film	Permeability (g./100 m ² .hr)
Water - impermeable cellophane	30
Polyethylene	100
Poly(ethylene terephthalate)	160
Butvar (89% of molecules substituted)	1200
Cellulose acetate	5000

Table 2.4 Permeability of films for vapors of organic solvents
(g/100 m².hr at 35°C) (Korshark V.V. and Vinogradova S.V.,1965)

Solvent	Poly(ethylene terephthalate)	Polyethylene	Water-impermeable cellophane
Ethyl alcohol	0	2800	2800
Ethyl acetate	4	9500	20
Carbon tetrachloride	7	65000	30
Benzene	6	37000	27
Acetone	18	36000	21

Table 2.5 Permeability of films for vapors of strong-smelling substance.
[time (hours) necessary for the passage of the smell, that is the vapors, through the film]
(Korshark V.V. and Vinogradova S.V.,1965)

Material of the film	Thickness of the film	Vanillin	Pinene	Methyl salicylate	Ethyl butyrate	propylene diamine
PET	0.75	140	140	120	20	96
Polyethylene	2.0	1/4	1/2	1/10	1/10	1/5

Various oils and fats do not pass through a poly(ethylene terephthalate) film with a thickness of 1 mil after two months' action at a temperature of 29 °C. Poly(ethylene terephthalate) film is almost impermeable to such gases as oxygen and nitrogen. Films with a thickness of 0.5 mil at 100 percent relative humidity pass oxygen to the amount of 5.7 g/100 m².hr and nitrogen to the amount of 5.2 g /100 m².hr.

2.1.3.8 Resistance to the Action of chemical Reagent

Poly(ethylene terephthalate) is unaffected at room temperature and even at a temperature close to the boiling under the action of such solvents as ethyl acetate, acetone, xylene, deoxan trichloroethane and glacial acetic acid. Acid can act more weakly than alkalines. A strong solution of ammonia has a particularly powerful action. Nitric acid also decomposes PET. Phenols dissolve poly(ethylene terephthalate). Strong sulfuric acid simultaneously dissolves and decomposes it. Table 2.6 shows the solubility of poly(ethylene terephthalate) in various solvents.

Table 2.6 Solubility of poly(ethylene terephthalate) in various solvents
(Korshark V.V. and Vinogradova S.V.,1965)

Solvent	Solubility
Hydrochloric acid (conc.)	insoluble
Sulfuric acid (conc.)	soluble
Nitric acid (conc.)	soluble on warming
Potassium hydroxide (40%KOH)	swells and disintegrates on heating, partially dissolving
Acetone	insoluble
Cyclohexane	insoluble
Formic acid (98-100%)	insoluble
Acetic acid	insoluble
Benzene	insoluble
Toluene	insoluble
Xylene	insoluble
Phenol	solution on heating
m-Cresol	solution on heating

2.2 Polyurethane Elastomer

2.2.1 Introduction

Thermoplastic polyurethane elastomer is a member in the family of polyurethane, which was discovered by Otto Bayer in 1937. Originally, polyurethane elastomers were considered to be chemical cross-linked, thermosetting materials. Only in the late fifties was it found that essentially linear polyurethane elastomers based on 4,4'-diphenylmethane diisocyanate could be processed like thermoplastics. Indeed, the segmented structure of the polyurethane elastomer, containing crystalline hard segments, led to completely new model for scientific understanding of elastomers in general. The basic ingredients of polyurethane elastomers are diisocyanates and long-chain and short-chain diols. The diisocyanate and short-chain diol form hard segments, while the long-chain diols provide the basis of segment. Because the hard and the soft segment are incompatible, the polyurethane elastomers exhibits a two-phase structure. The unusual properties of polyurethane elastomers can be attributed to formation of domain microstructures.

Polyurethane can be categorized into polyester and polyether types. Polyester-based polyurethane elastomers generally have better physical properties, thermooxidative stability, and oil resistance. At a similar hardness, polyether-based polyurethane elastomers exhibit better low temperature properties, hydrolytic stability, and resistance to microbial attack. Polyurethane elastomers have been widely used in automotive applications, hosing, tubing, blown film and sheet, animal tags, wire and cable, caster wheel, compounding, mining screens, shore soles, and so on. A more detailed description of polyurethane elastomer such as raw materials, additives, chemistry, structure and properties, processing and applications is presented in following sections.

2.2.2 Raw materials (Wood G.,1987)

Polyurethane is produced from the chemical reaction between a polyol and a diisocyanate. The reaction starts spontaneously when two components are blended together in a presence of a suitable catalyst. The polymerization, once started, is exothermic completion.

2.2.2.1 Polyols

A wide range of polyols is used in polyurethane manufacture. Most of the polyols used ,however, fall into two classes: hydroxyl-terminated polyether or hydroxyl-terminated polyester. The structure of the 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 polyurethane are shown in table 2.7

The hydroxyl value is used as a measurement of concentration of isocyanate-reactive hydroxyl groups per unit weight of polyol and is expressed as mg.KOH/g. Polyol sold for use in polyurethane is invariably characterized by hydroxyl value as this is convenient for calculation of stoichiometric formulation. The measured hydroxyl value of a polyol is related to its molecular weight and functionality :

$$(2.13) \text{ Hydroxyl Value, (mg.KOH/g.)} = \frac{56.1 \times \text{functionality}}{\text{molecular weight}} \times 1000$$

Equation 2.13 expresses for relating the hydroxyl value, functionality and molecular weight.

Table 2.7 Polyol for polyurethane manufacture

(Wood G.,1987)

Characteristic	Flexible foams and elastomer	Rigid foams, rigid plastics and stiff coatings
Molecular weight range	1000 to 6500	150 to 1600
Functionality range	2.0 to 3.0	3.0 to 8.0
Hydroxyl value range(mg. OH/g.)	28 to 160	250 to 1000

Polyether polyol

About 90% of the polyols used in polyurethane manufacture are hydroxyl-terminated polyethers. They are made by the addition of alkylene oxides, usually propylene oxide, onto alcohols or amines which are usually called starters or initiators. The addition polymerization of propylene oxide occurs by base catalysis. The epoxide ring of propylene oxide may theoretically open at either of two positions reaction but, in practice, the open preferentially at the less sterically-hindered position with base catalysis. Polyether based on propylene oxide contained predominantly secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups and for some application polyether polyol based only on propylene oxide to form a block copolymer with an oxyethylene tip. By this mean, the primary hydroxyl end-group content may be varied from about 5% to over 80% of the total hydroxyl end group.

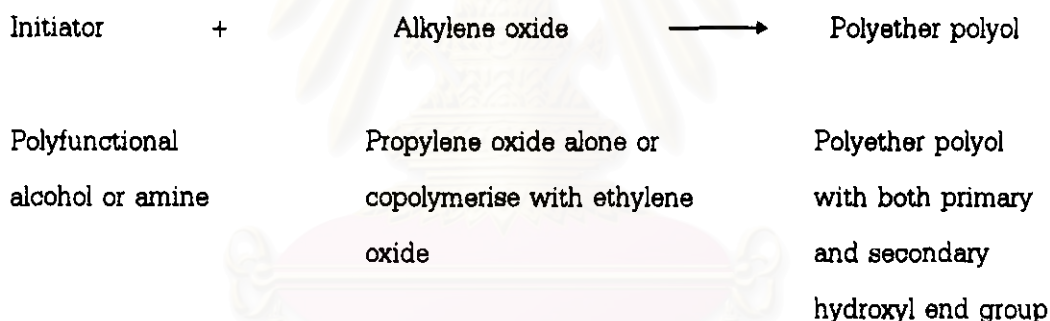


Figure 2.8 The chart expresses the manufacture of polyether polyols.

(Wood G.,1987)

Polyester polyols

Saturated polyester 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 yield polyurethane polymers which are more easily hydrolyzed. Consequently they are only used to make polyurethane for demanding applications where the particular physical properties obtainable from polyesters are important. Polyester based polyurethane

elastomers combine high levels of tensile properties with resistance to flexing and abrasion. They also have good resistance to many types of oil.

Polyesters are typically made from the condensation reaction between glycols and di-carboxylic acids, Branching can be introduced by the addition of small amount of triol to the reaction mixture. As the esterification proceeds the water produced is removed from the reaction. Water commonly represents up to 15% of the reaction product in making oligomeric polyesters so that the maximum yield of useful product is about 85% by weight of the raw materials used. This contrasts with the production of polyether polyols where yields may approach 100%. This lower yeild, combine with the fact that the raw materials trend to be more expensive, explains the higher cost of many polyesters compared with polyethers.

Relatively low cost polyester polyols, based on recovered materials are also available. Mixed adipic, glutaric and succinic acid polyester are made using purified nylon waste acid (AGS acids). Aromatic polyester polyols made from dimethyl terephthalate(DMT),process waste, have been available for several years but more recently, a number of low cost polyester polyols have been produced using a proportion of materials obtained by depolymerising wasted PET, recovered from scrap bottles and film. Table 2.8 presents the properties of polyester polyols which are used in each type of polyurethane.

Table 2.8 Typical properties of polyester polyols(Wood G.,1987)

Application	type	Hydroxyl number (mg.KOH / g.)	Viscosity (at 25°C)	Acid value (mg. KOH)
Flexible foams	Linear	45 to 60	10000 to 20000	< 2.0
Low density semi rigid foam	Highly branched	200	20000	< 1.0
Elastomer	Linear	50 to 60	3000 to 10000	< 1.0

2.2.2.2 Diisocyanate

Another major method of varying the properties of the final polyurethane is by varying the type of isocyanate used. Isocyanate may be modified in many ways to give products with different physical and chemical properties. Several aromatic and aliphatic isocyanate are available, but about 95% of polyurethane are based on two of them. These are toluene diisocyanate(TDI) and diisocyanate-diphenylmethane(MDI) and its derivatives. Both materials are derived from readily available petrochemical intermediates and are manufactured by well understood and closely defined chemical processes.

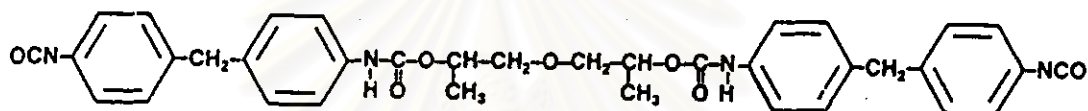


Figure 2.9 Modified pure MDI(Wood G.,1987)

Development of MDI was necessary as the volatility caused severe problems when TDI rigid foams were sprayed in enclosed spaces. The production chemistry of MDI is considerable more complex than that of TDI. MDI is produced from aniline and formaldehyde, reacted together using hydrochloric acid as a catalyst. The condensation reaction produces a complex mixture of polyamines which are phosgenated to obtain a polyisocyanate mixture. The product is known as polymeric MDI. MDI is available in several forms based on two types of product purified monomeric MDI and polymeric MDI. Pure MDI is a white to pale yellow and tends to form insoluble dimer when stored. The difficulty of handling solid pure MDI and its increase tendency to form dimer when stored as liquid at over 40 °C have led to development of modified pure MDIs which are liquid at ordinary temperature and reduced tendency to dimerise.

2.2.3 Additives

In addition to isocyanates and polyols - the basic materials for making polyurethane - a wide range of auxiliary chemical 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 and fillers. All practical polyurethane systems include some of auxiliary chemicals.

2.2.3.1 Catalyst

A number of catalysts can be used for the reaction of isocyanates with water and with polyols and this included 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 polymerization of isocyanate. Organo-metallic are used to accelerate the urethane reaction. The most popular are stannous octoate and dibutyltin dilaurate. Stannous octoate is used in most flexible foam systems, except pre-blended two-pack system where its low hydrolytic stability is unacceptable. Microcellular elastomer and cast elastomer are often catalysed by low level of dibutyltin dilaurate or dibutyltin mercaptide. Organo-metallic catalyst forms an intermediate complex with an isocyanate group and a hydroxyl group of the polyol. This complex formation is inhibited by steric hindrance of the Sn atom. This steric effect is used in one type of delay action catalyst, i.e. a catalyst that is not very active at room temperature but becomes effective when the reaction temperature rises. Table 2.9 presents some commercially available catalyst

2.2.3.2 Cross - linking agents and chain - extender

These are low molecular weight polyol or polyamines. They are also sometimes known as curing agents. Chain extenders are difunctional substances, glycols, diamines or hydroxylamines, cross linking agents have a functionality of three or more. Chain-extenders are used in flexible polyurethane such as flexible foams, microcellular elastomers, cast elastomers and RIM systems.

The chain extender reacts with diisocyanate to form polyurethane or polyurea segment in urethane polymer. It is usually added in sufficient amount to permit hard-

segment segregation that results in an increase in modulus and the hard-segment glass transition temperature(T_g) of the polymer. The T_g provides a measure of the polymer softening point and some indication of the upper limit of its working temperature. When diamines are used as additives, instead of glycols of similar molecular weight, they give faster reaction with isocyanates. The resulting polyurea hard-segment has a higher density of secondary bonding so that the T_g and the thermal stability of the polymer are both increased.

Cross-linkers are used to increase the level of covalent bonding in rigid polyurethane such as some rigid foams and also as additives in many semi-rigid foam systems. Chain extenders and curing agents are used in both the single shot and prepolymer processes for making polyurethane. Aromatic and aliphatic diamines are each used as curing agent but the former are more favoured because of their lower reactivity with isocyanates. A high level of polyurea hard-segment separation is required in order to obtain elastomers having a high modulus and this necessitates at least 3 to 4 molecular equivalents of chain extender per oligomer chain. Simple diamine is in general too reactive to permit. The table 2.10 lists of some common chain extender and cross linking agent together with the stoichiometric weight of TDI and MDI .

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Table 2.9 Some commercially available catalyst (Wood G.,1987)

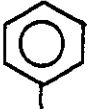
Catalyst	Application
<p>1. N,N - Dimethylaminoethanol $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$</p>	<p>Inexpensive, low odor, isocyanate reactive, mobile liquid catalyst used in polyether-based flexible foams.</p>
<p>2. N,N - Dimethylcyclohexylamine</p>  <p style="text-align: center;">$\text{N}(\text{CH}_3)_2$</p>	<p>Liquid with intense odor. Rigid foams, polyester-based flexible foams and some semi rigid foams.</p>
<p>4. N,N,N',N',N'' - Pentamethyl - diethylene - triamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ <div style="margin-left: 150px;">CH_3</div></p>	<p>Flexible foams and semi rigid foams</p>
<p>5. N,N - Dimethylcetylamine $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}(\text{CH}_3)_2$</p>	<p>Viscous liquid with low odor used in polyester-based flexible foams and some plotting compounds.</p>
<p>6. N,N,N',N'',N''' -pentamethyl- dipropylene- triamine $(\text{CH}_3)_2\text{NC}_3\text{H}_6\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$ <div style="margin-left: 150px;">CH_3</div></p>	<p>Liquid with strong ammoniaical odor used in polyether based slabstock foams and in semi-rigid foam molding</p>

Table 2.9 Some commercially available catalyst
(continue) (Wood G.,1987)

Catalyst	Application
7. Stannous octoate	Slabstock polyether-based flexible foams, molded flexible foams.
8. Dibutyltin dilaurate	Microcellular foams, RIM, two-pot molding systems, elastomer.

2.2.3.3 Surfactants

Surface-active materials are essential ingredients in the manufacture of most polyurethanes. Selected surfactants, or mixture of surfactants, help in mixing incompatible components of the reaction mixture. They are particularly useful in foam making where help to control the size of the foam cells by stabilizing the gas bubbles formed during nucleation and may stabilize the rising foam by reducing stress-concentration in the thinning cell-walls. Surfactants for use with in making conventional flexible polyether foams have longer grafted polyether chain with higher polyoxypropylene content. Polyester-based flexible foams, on the other hand, require surfactants of lower activity with much shorter polyether chains.

Table 2.10 Chain extender, cross linking agents and curing agents and their diisocyanate equivalent (Wood G.,1987)

Additive	Functionality	Mole weight	OH value (mgKOH/g.)	Weight of diisocyanate (g./100g. of required additive)	
				TDI	MDI
Ethylene glycol	2	62.07	1801	280	401
Diethylene glycol	2	106.12	1057	164	235
Propylene glycol	2	76.11	1474	229	329
Dipropylene glycol	2	134.18	836	130	186
1,4 -Butane diol	2	90.12	1245	193	278
Polypropylene glycol	2	400	280	43.5	62

2.2.3.4 Fillers

Particulate and fibrous fillers may each be used in most kind of polyurethane. There are many reasons for adding fillers. Particulate filler are used in flexible polyurethane foams to reduce their flammability and particular in the USA, to increase the 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 of rigid foams, self-skinning foams and flexible RIM products. Mineral filler are sometimes used to reduce costs and increase the compressive strength of rigid foams used in composite building panels. Continuous fibers, netting or scrims encapsulated in rigid

foams, improve the stiffness and heat resistance of insulating panels and, in low density flexible foam moldings, their use increases the tensile strength at highly stressed positions. Some fillers and their application are listed in table 2.11

Table 2.11 Some filler and their application in polyurethane
(Wood G.,1987)

Filler	Typical applications
Calcium carbonate	Flexible foam and semi-rigid foam, binder composition, rigid self-skinning moldings.
Barium sulfate	Flexible foam and semi-rigid foam especially for sound-absorbing.
Clays	Flexible system
Expanded silicas, colloidal silicas	Flexible foams, cast elastomers
Glass micro-spheres	Flexible, microcellular foams, RIM
Glass flakes	Elastomeric RIM
Silicates , cements	Rigid foams, sealants, grouting compounds
Short fibers, milled and chopped glass-fiber, Aramid fibers, carbon fibers, conducting fibers	Elastimeric RIM

2.2.4 Chemistry (Hebbum C., 1992)

polyurethane synthesis can be occurred by reaction of chloroformic esters with diamines and of carbanic esters with diols:

(2.14)

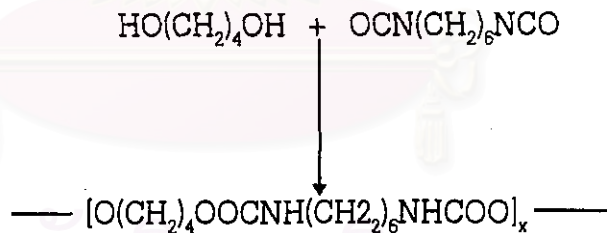


(2.15)

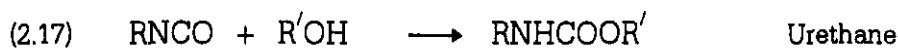


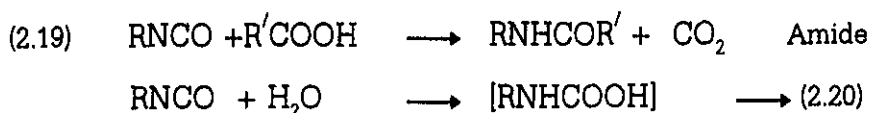
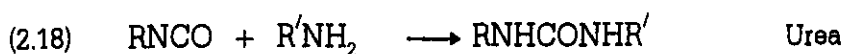
Development has depended basically on the chemistry of isocyanates. First investigated well over a hundred years ago by Wurtz and Hofmann, but only directed to polymer formation when Otto Bayer, in 1938, during research on fiber-forming polymers analogous to the polyamide, prepared a number of linear polyurethane from diisocyanates and diols. One of these, the polyurethane was made from 1,4-butane diol and hexamethylene diisocyanate: was selected for development in monofilaments and fibers (Perlon U).

(2.16)



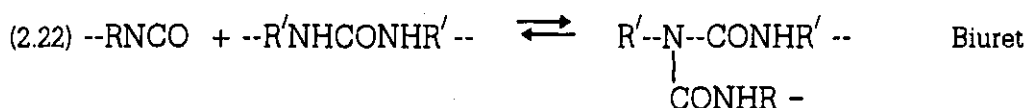
It was quickly realized that reaction of isocyanates with compounds containing OH groups was capable of much wider application in polymer formation. The NCO group can react generally with compounds containing active hydrogen atoms, i.e. according to the following:

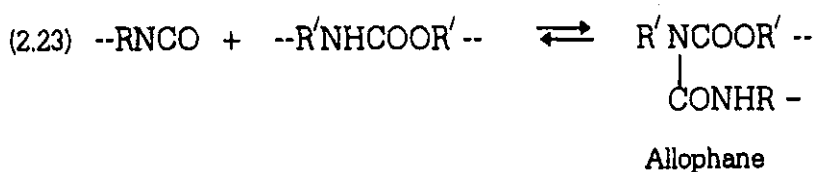




Thus, if the reagents are di- or polyfunctional polymer formation can take place. While these reactions normally occur at different rates, eqn. (2.18) being the most rapid, they can be influenced appreciably and controlled by use of catalysts. Reaction (2.19) and (2.20) also give rise to carbon dioxide, a feature of value when forming foamed products but introducing difficulty if bubble-free castings and continuous surface coatings are required. In the reactions noted there is the advantage that, unlike polycondensation, the processes normally give rise to no by-product that require removal as the macromolecules are built up.

The reactants are bifunctional or higher functionality leads to the formation of branched chain or crosslinked materials. Again, additional reaction of the isocyanate with the urea, urethane and amide groups already introduced during the initial polymer formation is also possible. Chain branching or cross linking then occurs, due to the formation of acylurea, biuret and allophanate links onto the main chain :





The initial studies on polyurethane synthesis were based on simple diisocyanates and diols but the main importance of the reaction is now concerned with the use of intermediates which are often polymeric in character (polyesters, polyethers) and carry terminal groups (usually-OH or -NCO) capable of further reaction and thus of increasing the molecular size, often during the actual fabrication processing, by chain extension, branching or cross linking according to the reaction noted in the above eqns (2.17)-(2.23). Some of the reactions are reversible under the action of heat, thus introducing the possibility of molecular rearrangement during processing. The polyurethanes can therefore have a preponderance of other linking groups, i.e. be essentially copolymers such as polyester urethanes or polyether urethane and be branched or crosslinked through groups formed in reactions (2.21)-(2.23). The whole macromolecule system in these polymers can accordingly be designed so as to incorporate links or chain segments which provide the required molecular flexibility or rigidity, and the chain order, branching or crosslinking necessary to give the properties sought in the finished product.

2.2.5 Basic Structure Of A Polyurethane Elastomer(Hepburn C.,1992)

A urethane elastomer can be regarded as a linear block copolymer of the type shown in figure 2.10. This segmented polymer structure can vary its properties over a vary wide range of strength and stiffness by modification of its three basic building blocks: the polyol, diisocyanate and chain extender. Essentially the hardness range covered is that of soft jelly-like structures to hard rigid plastics. Properties are related to segmented flexibility, chain entanglement, inter chain forces and crosslinking.

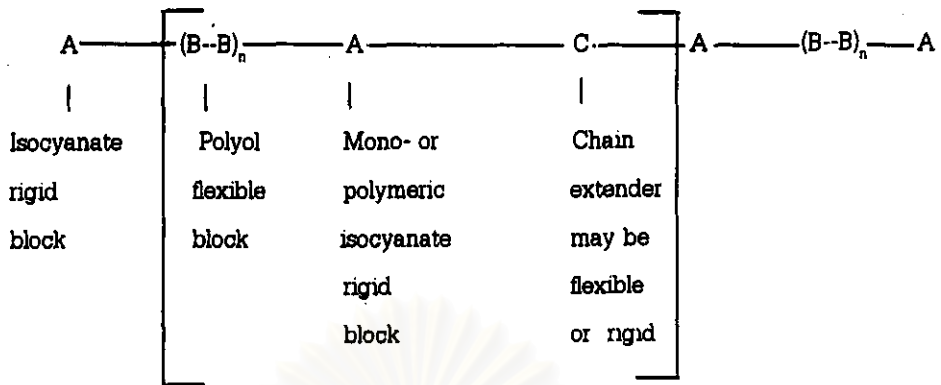


Figure 2.10 The basic unit in a urethane block copolymer.

(Hepburn C.,1992)

Evidence from X-ray diffraction, thermal analysis, birefringence and mechanical properties strongly supports the view that these polymers can be considered in terms of long(1000-2000 nm) flexible segments and much shorter (150 nm) rigid units which are chemically and hydrogen bonded together, the whole undergoing orientation on extension as indicate in figure 2.11 Modulus-temperature data usually show at least two definite transitions, one below room temperature and relate to segmental flexibility of the polyol and one above 100°C due to dissociation of the inter chain forces in the rigid units. Multiple transitions may also be observed if mixed polyols and rigid units are present in the polymer structure.

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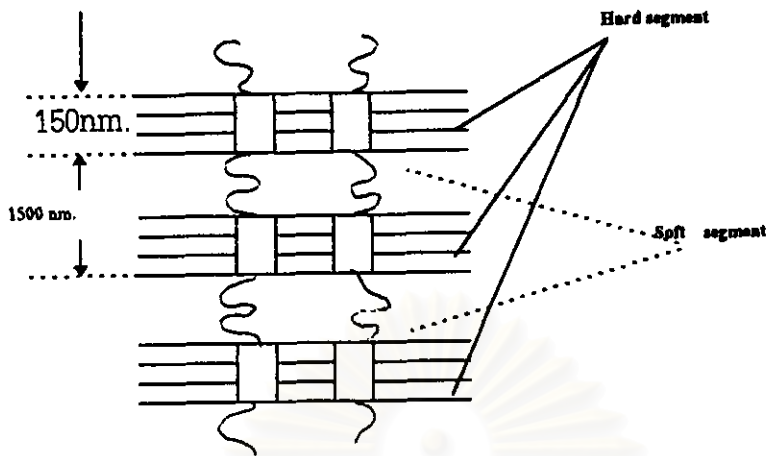


Figure 2.11 Flexible and rigid segments in a polyurethane elastomer.

(Heppburn C.,1992)

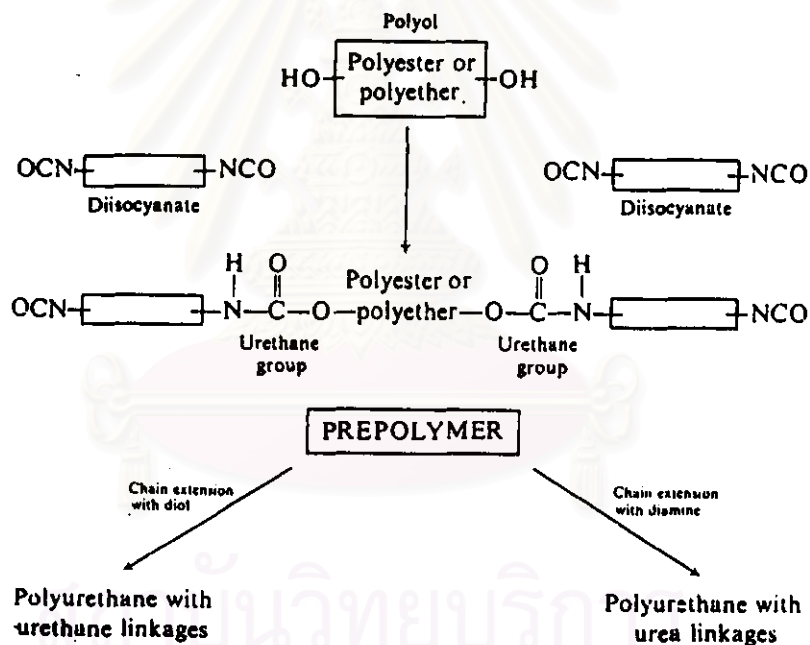


Figure 2.12 Prepolymer route for the formation of a polyurethane elastomer.

(Heppburn C.,1992)

The usual route of chemical formation for all urethanes is illustrated in figure 2.12. It is referred to as the prepolymer method, since the final polymer is formed into separate steps. Initially the diisocyanate and polyol are reacted together to form an intermediate

polymer of molecular weight 15000-20000 which is called a prepolymer and is normally a thick viscous liquid or low-melting-point solid of low or no strength. This prepolymer, sometimes shelf-stabilized by means of 0.01-0.1 % of an acid chloride (e.g. acylchloride) for storage purposes, is then converted into the final high molecular weight polymer by further reaction with a diol or diamine chain extender; this step is usually referred to as the chain extension stage. Though sometimes the term crosslinking is used if this better represents the elastomeric character of the final polymer. Also catalyst is often, though wrongly, used by some workers to describe this chain extension step. Alternatively the entire polymer formation may be carried out by simultaneously mixing together polyol, diisocyanate and chain extender (in the presence of catalysts), where upon the reaction is referred to as the one-shot process or polyurethane formation schematically represented in figure 2.13

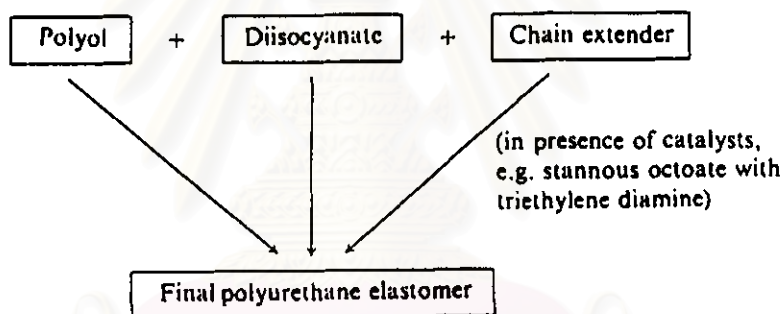


Figure 2.13 One-shot process for polyurethane elastomer preparation.

(Hepburn C.,1992)

2.2.6 Structure and properties of polyurethane elastomer

Block copolymers have gained substantial attention in recent years because of the uniqueness of their structures and properties. As one of the important block copolymers, the typical polyurethane consist of an amorphous phase (soft block) and a crystalline phase (hard block) due to the incompatibility of the adducts of short-chain versus long-chain diols with diisocyanates. As noted earlier, the two-phase structure of polyurethane consists of short-chain diols and diisocyanates as hard segments are generally dispersed in the amorphous

phase(continuous phase).The chemical composition and the molecular weight of long-chain diols greatly affect the extent of phase separation of the polyurethane. Because of stronger hydrogen bonding, the phase mixing of a polyester-based polyurethane is generally greater than that of a polyether-based polyurethane.

In a typical polyurethane, the hard segments determine the hardness, modulus, tear strength ,and upper use temperature, while the soft segments determine the elastic and low temperature properties.

2.2.6.1 Isocyanate to Hydroxy Ratio

The highest-molecular-weight condensation polymers as described by Flory (1953) under the assumption that all the functional groups react equally, are obtained with balanced stoichiometry. In the preparation of polyurethane ,the isocyanate-to-hydroxy (NCO/OH) ratio plays an important role in controlling molecular weight. The initial molecular weights of polyurethane , as shown in figure 2.14 , decrease with increase or decrease of NCO/OH ratios from the equivalence point (NCO/OH =1). However, the molecular weights of polyurethane elastomer manufactured above the equivalence point ultimately will increase because of the reaction of excess isocyanate with moisture, urethane and urea groups, to give urea, allophanate ,and biuret, respectively. The effect of the molecular weight on the physical properties of polyurethane elastomer has been studied by Schollenberger(1974). The results indicated that the specific gravity, processing temperature, tensile strength, modulus, and abrasion resistance of solution-polymerized polyurethane, based on poly(tetramethylene adipate),MDI and 1,4-butanediol, increased with increasing molecular weight and then leveled off at M_n (number average molecular weight) of 35,000 to 40,000. In a later study, Redman showed that the hardness, tensile strength, and tear strength of polyurethane, which were also based on poly(tetramethylene adipate),MDI, and 1,4-buatnediol, increased with increasing NCO/OH ratio and then leveled off in the neighborhood of the equivalence point (NCO/OH =1)

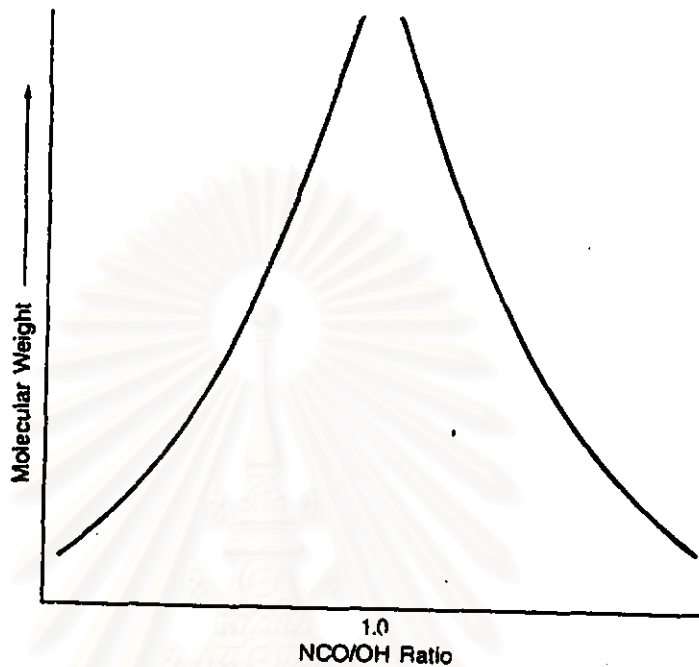


Figure 2.14 The relationship of the initial molecular weight of polyurethane and the NCO/OH Ratio.

2.2.6.2 Postcuring of polyurethane elastomer

The properties of polyurethane are strongly affected by domain morphology. Phase mixing takes place during the heat processing or treatment of the polyurethane, while phase separation occurs upon rapid cooling. The phase separation process of polyurethane (demixing process) has been shown to be time-dependent because of their high viscosity. Wilkes showed that the mechanical properties of polyurethane are strongly related to the time-dependent formation of domain morphology. Therefore, postcuring of a polyurethane after thermal formation is recommended in order to obtain optimum properties. The postcuring conditions vary with the polyurethane material. The optimum properties of a

polyurethane can be achieved either by storing it at ambient conditions for one week or by curing it at elevated temperature for a much shorter period of time.

2.2.6.3 Specific Gravity

The specific gravity of a polyurethane which is determined by ASTM method D 792, is defined as a unit volume weight ratio of the TPI to water at 23°C. This property is important in both purchasing and production control because polyurethane are sold by weight rather than volume. The specific gravity of polyurethane vary from 1.10 to 1.25. The ester-based polyurethane, because of their stronger hydrogen-bonding abilities, generally have higher specific gravity than ether-based polyurethane with a similar hard segment content. The specific gravity of polyurethane decrease with increasing soft segment content.

2.2.6.4 Hardness

Hardness is an indication of the ability of an material to resist deformation, indentation, or scratching. The durometer type A and type D tests (ASTM D 2240) are most commonly used with polyurethane. The softer polyurethane are generally measured in Shore A hardness, and the harder ones in Shore D hardness. Because of their block copolymer nature, polyurethane with a hardness of 70 Shore A to 80 Shore D can be obtained by varying the ratios of hard segment to soft segment. The hardness-along with modulus, load-bearing capacity (compressive stress), tear strength, and specific gravity -of a polyurethane elastomer normally increases with increasing hard segment content.

2.2.6.5 Stiffness

Although the hardness of a polyurethane elastomer is related to its flexibility, it is not directly indicative of its stiffness. The stiffness of polyurethane elastomer is normally expressed by flexural modulus, which is a measure of the stiffness during the initial bending of a test specimen. In many ways the flexural modulus of a polymer is similar to Young's modulus (tensile modulus). The flexural modulus of polyurethane elastomers, which is specially important in automotive applications, is obtained according to ASTM D 790.

2.2.6.6 Stress-Strain Relationship

Miller et al. have shown that the hard segment length distribution in polyurethane elastomer will affect the stress and elongation at break as well as Young's modulus (tensile modulus). Smith indicated that the ultimate properties are closely related to morphology of the polyurethane elastomer. The stress-strain curve of polyurethane elastomer is generally believed to be affected by the hard segment to soft segment ratio, soft segment length, hard segment crystallinity, and susceptibility of the hard segment to reorientation and alignment. The stress-strain curve of a polyurethane elastomer is normally measured by ASTM method D 412. A dumbbell specimen with either die C (0.25 inch width and 0.08 inch thickness) or die D (0.125 inch width 0.08 inch thickness) dimensions has been employed with an extension rate of 20 in./min. The tensile strength (at yield or at break), tensile strain and tensile set at break, tensile modulus, modulus at different strains, and toughness (area under stress-strain curve) can be obtained from the stress-strain test. However, one should bear in mind that the stress (in psi) obtained from a die D sample at a given strain is normally higher than that obtained from a die C sample.

2.2.6.7 Tear Resistance

The tear strength of polyurethane elastomer, as indicated previously, is related to their hard segment content. A polyurethane elastomer with a high hard segment content normally has a high tear strength. The tear strengths of ester-based polyurethane elastomer are usually higher than those of ether-based polyurethane elastomer of similar hardness. The die C (split or trouser tear, ASTM D 1938) and die D (ASTM D 1004) are two common methods of measuring tear strengths of polyurethane elastomer. Because the die D method creates stress concentration in a small area, the tear strengths will be affected by a slight variation of defect in the angle area of the test specimen.

2.2.6.8 Abrasion Resistance

Polyurethane elastomer are known to exhibit excellent resistance to abrasion. However, the abrasive wear of a polyurethane elastomer is considerably affected by the surface heat buildup during the test, which is believed to be related to coefficient of friction, stress loading, and contact areas. The abrasive wear of a lubricated polyurethane

elastomer is generally lower than that of an unlubricated one, probably because of a decrease in heat buildup from friction.

2.2.6.9 Hydrolytic Stability

Because polyurethane elastomer contain ester (or ether) and urethane linkages, some degree of hydrolysis will inevitably occur. Schollenberger and Stewart(1971) have determined that the hydrolytic stability of polyurethane elastomer based on three different long-chain diols, is as follows:

Polyether > Polycaprolactone > Polyester

Although the urethane linkage can be hydrolyzed, ester linkage cleavage is the primary route for hydrolytic degradation of the ester-based polyurethane elastomer. Acids present in the polyurethane elastomer will catalyze the cleavage reaction of carboxylic esters. The carbodiimides, which act as acid scavengers, are effective additives against hydrolysis for ester-based polyurethane elastomer. The hydrolysis of urethane linkages, on the other hand, is the major means of decomposition of ether-based polyurethane elastomer. The effect of hydrolysis on the mechanical properties of polyurethane elastomer is believed to be due to chain cleavages, with an accompanying reduction in average molecular weight. When the molecular weight of a polyurethane elastomer is reduced to a critical value, cracks will develop on the surface of polyurethane elastomer.

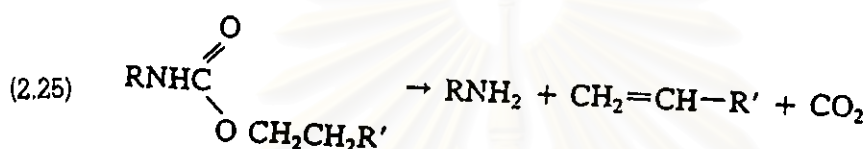
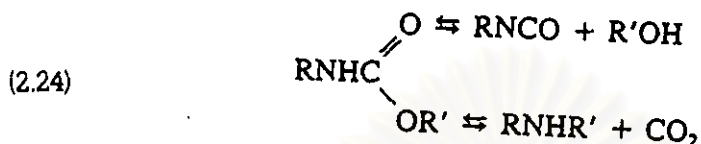
2.2.6.10 Thermal and Oxidative Stability

There are two types of property loss mechanisms for polyurethane elastomer at temperatures above ambient temperature.

1. The property loss is due to a morphology change. This process, which was described earlier, is related to the thermoplastic nature of a polyurethane elastomer and is reversible.
2. The other mechanism is chemical degradation destructive change in chemical structure.

Then thermal stability of polyurethane elastomer is strongly dependent on the structure of the isocyanates and chain extenders. Most polyurethane elastomer are decomposed slowly

at 150 to 200 °C. The following mechanisms have been proposed for the thermal degradation of polyurethane elastomer.



The thermal degradation of ester- and ether-based polyurethane elastomer has been performed under vacuum, air and nitrogen. Based on these studies, the significantly improved thermal stability of ether-based polyurethane elastomer under vacuum and nitrogen indicates that the oxidative process plays a major role in the decomposition of ether-based polyurethane elastomer. The ester-based polyurethane elastomer normally exhibit considerably better thermal and oxidative stability than the ether-based ones.

2.2.6.11 Ultraviolet Stability

The MDI-based polyurethane elastomer exhibit a loss of mechanical properties and discoloration upon exposure to sunlight. The formation of quinone-imide structures from the photo-oxidation of the aromatic diurethane bridges might be the cause of the discoloration of these polyurethane elastomer. The UV stability of polyurethane elastomer can be improved by the addition of UV stabilizers. Carbon black pigmented have also been found to exhibit better UV stability.

2.2.6.12 Electrical Properties

Although the hydrophilic characteristics of polyurethane elastomer have prevented their use of polyurethane elastomer as a protective covering for various cable applications has been increasing because of their flexibility and abrasion resistance.