

CHAPTER II

LITERATURE SURVEY

2.1 Polyurethane

Polyurethane can be called “polycarbamate” which is the ester amide derivative of carbonic acid. Polyurethane is synthesized by the chemical reaction between di- or polyisocyanate and di- or polyhydric alcohols (polyol). Various types of di- or polyisocyanate and di- or polyhydric alcohols can be used for manufacturing polyurethane. Also, a wide variety of additives may be added in order to control the reaction of polyurethane and modify the properties of the products.

2.1.1 Isocyanates

Types of isocyanates used can vary the properties of the polyurethanes. Although many types of isocyanates are available but most of polyurethanes are produced by using two kinds of aromatic diisocyanates which are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) and its derivatives [23]. TDI is used mostly in form of mixture of 2,4-TDI and 2,6-TDI in an 80:20 mixture. The chemical structures of these two isomers are shown in Figure 2.1.

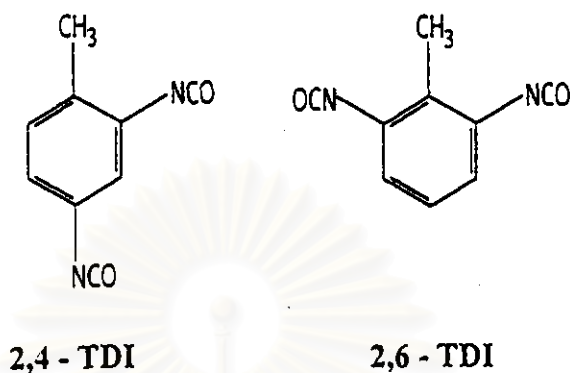
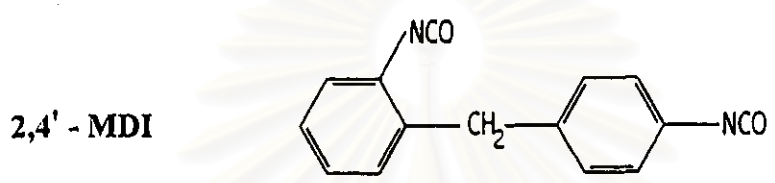
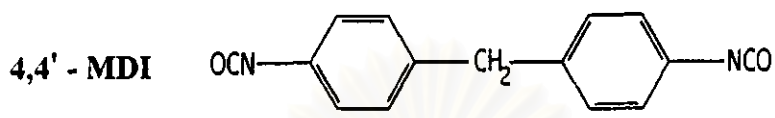
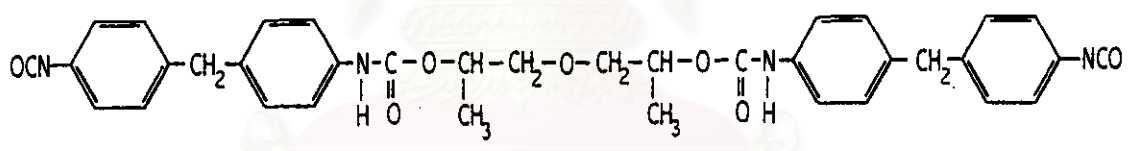


Figure 2.1 Chemical structures of 2,4-TDI and 2,6-TDI

Purified monomeric MDI and polymeric MDI are the two main types of MDI used in the production of polyurethane. Because of the difficulty of handling solid pure MDI and its instability when stored as a solution at over 40°C, modified pure MDI is developed. The modified pure MDI is liquid at ambient temperature. the chemical structure of pure MDI and two main modified MDI are shown in Figure 2.2.



Modified pure MDI



and

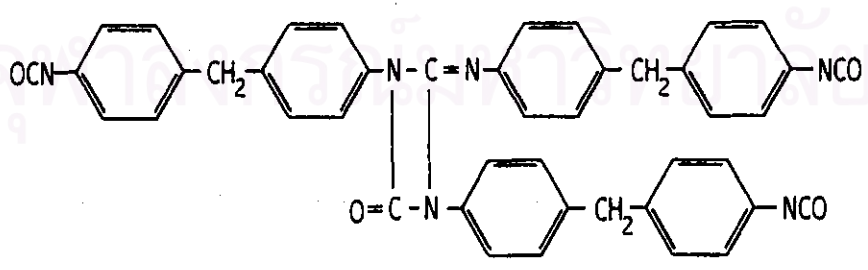


Figure 2.2 Chemical structures of different types of MDI

The reaction of isocyanates with amine results in urea as illustrated in Figure 2.5.

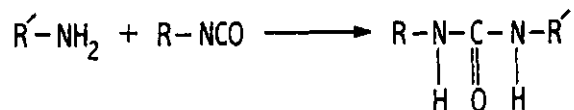


Figure 2.5 Reaction of isocyanates with amine

Because tertiary amines do not possess any active hydrogen atoms, they cannot react with isocyanates. However, they can catalyze many other isocyanate reactions efficiently.

The reaction of isocyanates with carboxylic acid yields an unstable product which is broken down into amide and carbon dioxide as shown in Figure 2.6.

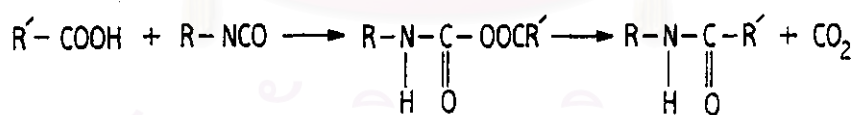


Figure 2.6 Reaction of isocyanates with carboxylic acid

In the case of excess isocyanate, under proper conditions, isocyanates may react with the urethane and urea linkages to form biuret and allophanate linkages, respectively.

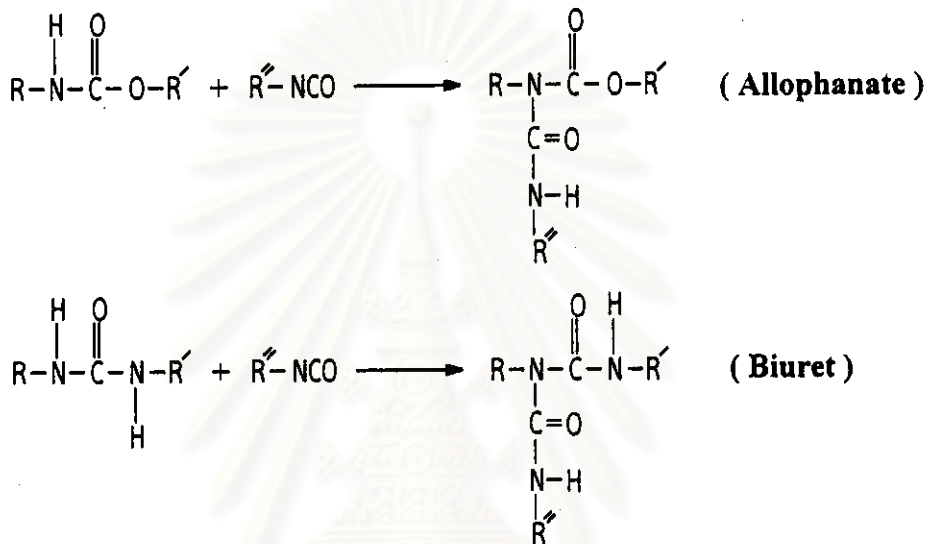


Figure 2.7 Reaction of isocyanates with urethane and urea

Isocyanates can also react with itself, especially in the acceleration of basic catalysts as illustrated by Figure 2.8.

Dimer can be formed only from aromatic isocyanates but trimer can be formed from both aliphatic and aromatic isocyanates. In the presence of special catalysts, carbodiimides can be formed by condensation of isocyanates, with the elimination of carbon dioxide. Further reaction between such carbodiimides and isocyanates can occur to form urethane as well.

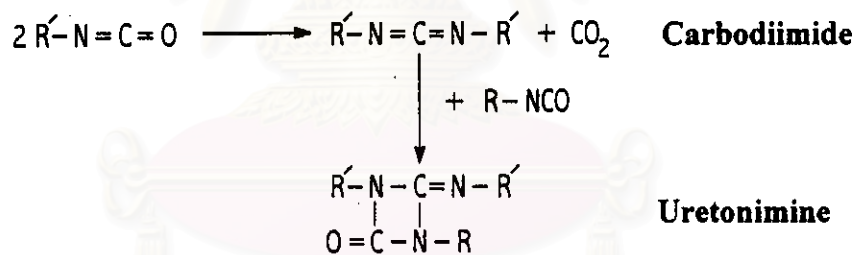
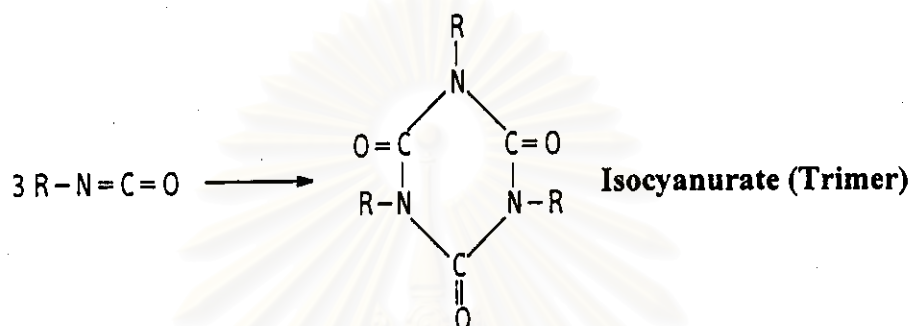
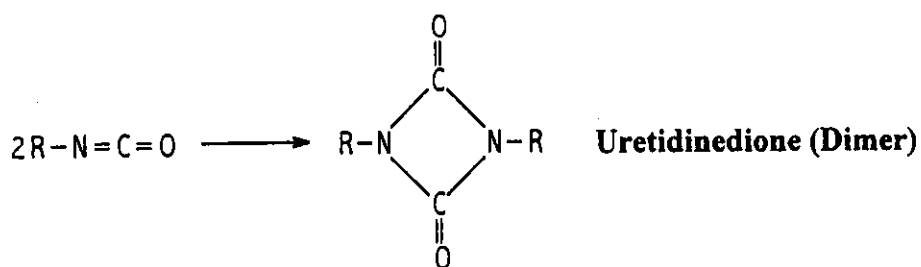


Figure 2.8 Homopolymerization of isocyanates

2.1.2 Polyols

A wide variety of polyols can be used in polyurethane manufacturing. But most of polyols used are based on polyester polyols and polyether polyols. The size, molecular weight, flexibility, functionality, and structure of the polyols have a significant effect on the characteristics and properties of the final urethane products. The higher molecular weight and lower functionality polyols are used in the production of flexible foams and elastomers. On the contrary, rigid foams, rigid plastics and stiff coatings need the lower molecular weight and higher functionality polyols in order to get the higher degree of crosslinking which contributes to the stiffness of the polymer. It is therefore necessary to utilize various polyols to produce polyurethane with desired properties.

- Polyether polyols

Polyether polyols are the main polyols used in the manufacture of polyurethane. These polyols are polyfunctional alcohols containing an ether linkage. The manufacture of these polyols is carried out by using the addition reaction of alkylene oxides with alcohols or amines. Alkylene oxide used may be pure propylene oxide or propylene oxide copolymerized with ethylene oxide. The addition reaction for commercial polyols production is usually catalyzed by base catalysts.

- Polyester polyols

Polyester polyols are only used to make polyurethane required the specific physical properties which can be obtained from polyester. This is because the cost of polyester polyols is higher than that of polyether polyol. Moreover, due to its higher viscosity, polyester polyols are more difficult to handle.

However, this type of polyols can provide many particular properties. Polyesters exhibit higher temperature resistance and less thermal oxidation than polyethers. Polyester-based polyurethane elastomers possess both good tensile properties and high abrasive and bending resistance. They also have good resistance to many types of oil. Polyester-based flexible foams combine high elongation with chemical resistance to dry cleaning solvents. Furthermore, in many rigid foams, the improved heat resistance can be obtained.

2.1.3 Types and Applications

Polyurethane are used in a variety of applications. Polyurethane can be divided roughly into two types, foams and non-foams.

- Foams

Foams are made by incorporating gas bubbles in the polymerizing mixtures. This method results in cellular structure instead of solid obtained by normal polymerization reactions. Gases used in the manufacturing of polyurethane foam can be carbon dioxide form in the reaction of water or carboxylic acid and diisocyanate. The gas can be used either as the sole blowing agent or as the principal blowing agent in association with the other blowing agents. However, the water-free systems are also employed. The heat of vaporization of the blowing agents is provided by the exothermic reaction occurred during the polymerization. Foaming by the carbon dioxide formed in the reaction is called chemical blowing. Foaming by the blowing agents, a chemically inert liquid having a low boiling point, vaporized by the heat from the polymerization is known as physical blowing.

Polyurethane foams can be separated into three types depending upon foam density, crosslinked density, and type of cell structure, e.g., closed cell or open cell.

- Low density flexible foams

Low density flexible foams are the most vastly used. They have densities about $10\text{-}80\text{ kg/m}^3$ and they are lightly crosslinked with an open-cell structure. Such foams possess a high tensile strength, elongation at break, and resilience.

Most flexible polyurethane foams are based on the reaction of diisocyanates with polyether or polyester diols or triols. The rate of polymerization and the rate of carbon dioxide evolution, which affect the particular properties, such as density, are controlled by using polyols and isocyanates with appropriate reactivity, by using catalysts and foam stabilizers and by controlling temperatures. Most of these materials are used in the furniture, bedding, and vehicle industries.

- High density flexible foams

These types of foams include semi-rigid foams, self-skinning foams and microcellular elastomers. They have densities above about 100 kg/m^3 . Almost of these foams are always manufactured as mould products and used mainly in the automotive and footwear industries.

Semi-rigid foams are mostly water-blown foams with higher stiffness and lower resilience than flexible foams. But, unlike rigid foams, semi-rigid foams are open cell foams and can be recovered completely. They can absorb high energy when subjected to shock loading since they recover from compression slowly. Thus, these foams are widely used for energy-absorbing padding in vehicles and in packaging.

Semi-rigid foams may be produced from both polyester and polyether polyols reacted with either TDI or MDI. However, the most popular systems are based on high molecular weight polyether polyols and polymeric MDI.

The structure of self-skinning or integral skin foams is composed of the cellular core and the skin. The skin has much higher density than the cellular core. This structure is resulted from a high temperature gradient across the reacting material adjacent to the relatively cool mould surface and the excess pressure, obtained by the reaction mixture, in the closed mould. Because of the pressure and the cooling of the surface layer, the blowing agent used still is liquid until the polymerization is substantially complete. So this type of foam is made by physical blowing agents instead of chemical blowing agents.

Self-skinning foams can be made from flexible, semi-rigid, or rigid foam. The structure of the core can be open or closed-cell foam. Usually the isocyanates used to produce the integral-skin foam are special polymeric MDI compositions or modified liquid forms of pure MDI. Low density self-skinning foams with an open cell core are used to make automotive interior trim, furniture, bicycle and motorcycle seats. The higher density self-skinning foams have a microcellular, closed-cell foamed core and are used to make shoe soles, bump stops and protective fenders.

Microcellular elastomers have a substantially uniform density which is about 400 to 800 kg/m³ and they have closed cells which are so small that these cells cannot be seen by the naked eye. The microcellular elastomers are mainly used for making moulded parts for upholstery, vehicle trim and shoesoles.

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such as, filling cavities in chips and boats, packaging of fragile objects and insulation materials for hot pipes and tanks.



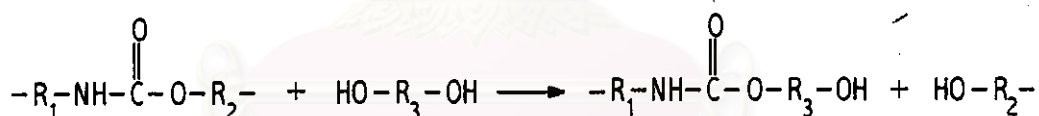
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2.2 Chemistry of Glycolysis

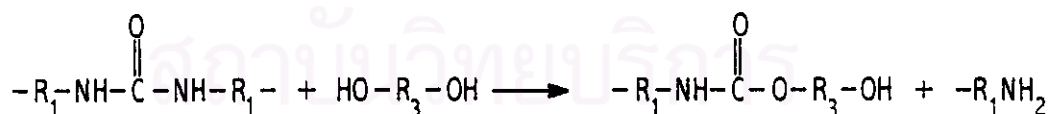
Glycolysis method for breaking down polyurethane foams can be carried out by various chemicals including glycol [2,21,18], dialkanolamine [19] and monoalkanolamine [17] under proper conditions.

Glycolysis of polyurethane by glycol yields a mixture of polyhydroxyl compound. The reactions become more complicated when urea linkage or isocyanurate linkage are involved. In both of these cases, not only polyhydroxyl compounds but also amines are produced. The chemical decomposition of polyurethane by glycol is shown by Figure 2.9.

Urethane linkage



Urea linkage



Isocyanurate linkage

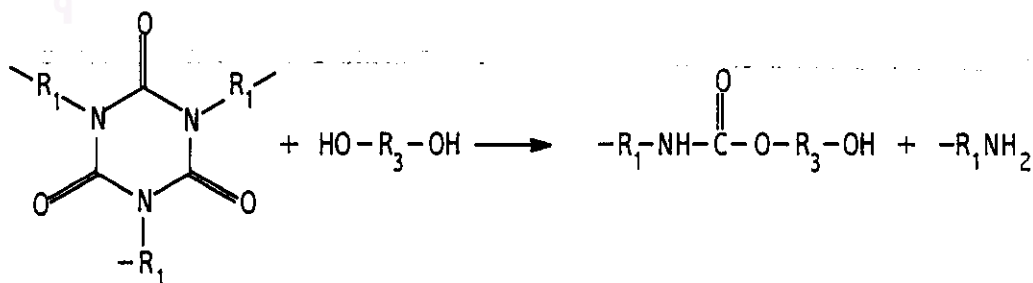


Figure 2.9 Chemical decomposition of polyurethane by glycol

The urethane bonds of the polyurethane foams are broken down by the hydroxyl group of monoalkanolamine as illustrated by Figure 2.10.

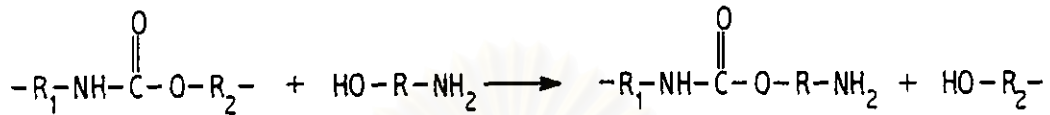
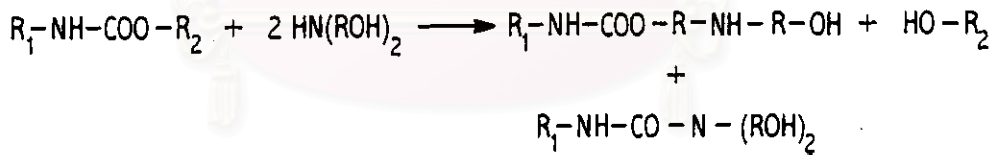


Figure 2.10 Chemical decomposition of polyurethane by monoalkanolamine

Dialkanolamine can react with polyurethane resulting in the decomposition of urethane and urea linkages as shown in Figure 2.11.

Urethane linkage



Urea linkage

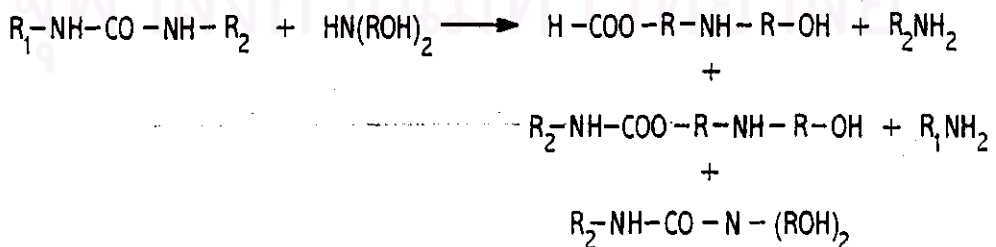


Figure 2.11 Chemical decomposition of polyurethane by dialkanolamine

2.3 Epoxy Resin and Its Curing Reaction

2.3.1 Epoxy Resin

Epoxy resins are fundamentally polyethers. Diglycidyl ether of bisphenol A (DGEBA) is the first commercial epoxy resins synthesized from bisphenol A and epichlorohydrin which is the principle epoxidizing agent. Other epihalohydrins or dihalohydrins can be used but they are not economically suitable. Epichlorohydrin is synthesized from propylene and chloride with dichlorohydrin as an intermediate [24].

Bisphenol A or diphenylol propane is synthesized from phenol and acetone as shown in Figure 2.12.

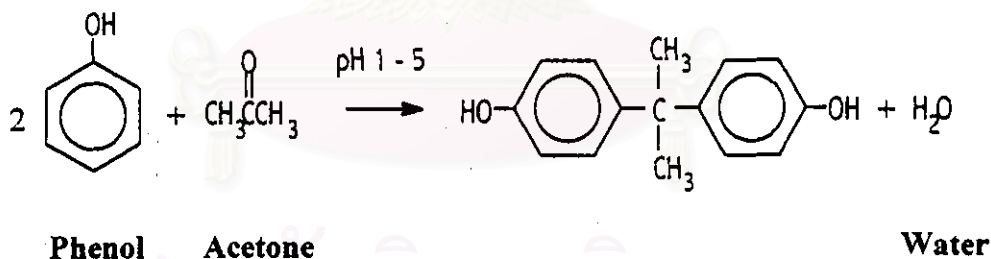


Figure 2.12 Synthesis of bisphenol A

Although other hydroxyl-containing molecules can be used to produce different glycidyl ethers, bisphenol A is the main dihydric phenol used in the synthesis of epoxy resin because of its ease of manufacture.

The structure of the diglycidyl ether of bisphenol A is shown in the Figure

2.13

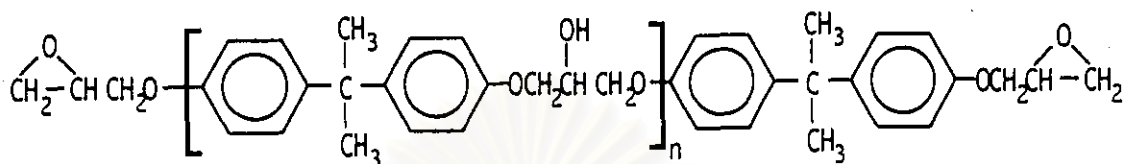


Figure 2.13 Chemical structure of the diglycidyl ether of bisphenol A

If an n value is up to 1 or about 1, the resins are low molecular weight liquid products. On the other hand, the resins are brittle solids when the n value is above 1.

Synthesis of monomeric DGEBA, is accomplished by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide as shown below.

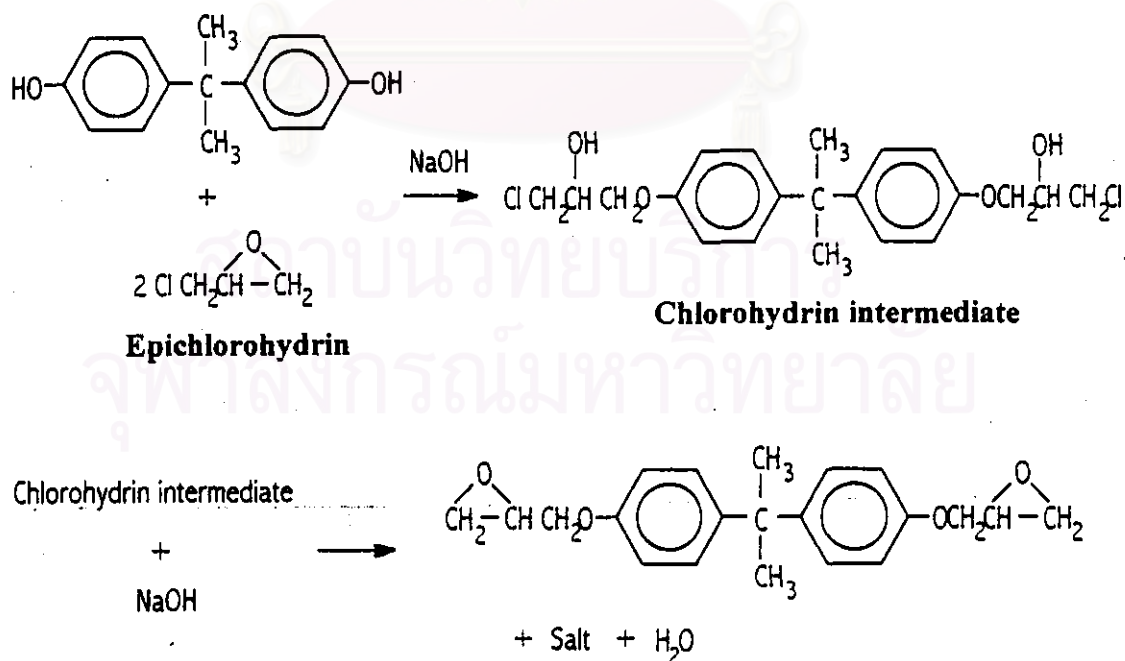


Figure 2.14 Synthesis of monomeric DGEBA

The reaction undergoes in two steps.

The first : A chlorohydrin intermediate is formed.

The second : This intermediate is dehydrohalogenated to be the glycidyl ether.

Sodium hydroxide in these reactions acts as the catalyst in the production of the chlorohydrin intermediate, as a neutralizer for the hydrochloric acid formed.

Theoretically, 1 mole of bisphenol A requires 2 moles of epichlorohydrin. But, actually, in order to obtain high yields of the monomeric product, about 2 to 10 times excess in epichlorohydrin is required. Otherwise, the monomeric yield is less than 10 percents, with the higher molecular weight polymerization products. However, the commercial liquid epoxy resin is the epoxy resin having an average molecular weight of approximately 380 g/mole.

The synthesis of the higher molecular weight epoxy resins can be carried out by reacting epichlorohydrin and bisphenol A in the presence of excess sodium hydroxide. In order to link the bisphenol A successfully, not only epoxy groups contained in the epichlorohydrin but also that formed by dehydrohalogenation should be consumed as illustrated by Figure 2.15 .

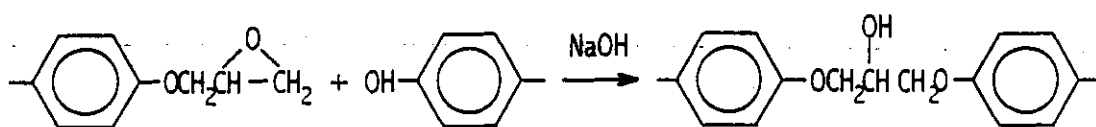
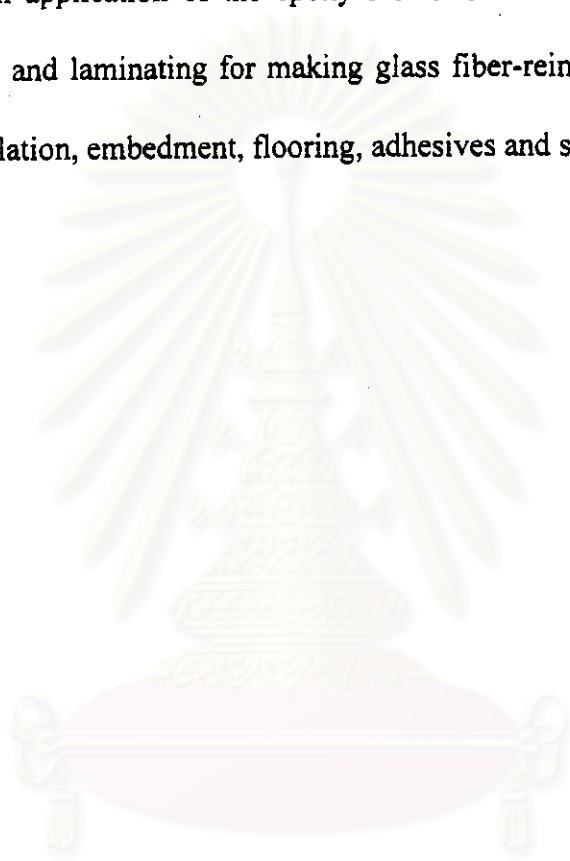


Figure 2.15 Reaction between bisphenol A and epoxy groups formed by dehydrohalogenation

Thus, the degree of polymerization can be controlled by regulating the ratio of epichlorohydrin and bisphenol A when employing the excess amount of sodium hydroxide.

The main application of the epoxy resins is in surface coating. Other uses include molding and laminating for making glass fiber-reinforced products, coating, potting, encapsulation, embedment, flooring, adhesives and solders.



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2.3.2 Curing Reaction

The curing of the epoxy resins bases on the reaction between the epoxide molecules themselves and the reaction between the epoxy group via other active-hydrogen compounds with or without a catalyst. The former is called homopolymerization and the latter is an addition reaction [25]. Polyaddition is the most commonly used reaction for curing epoxy resins. The most widely used curing agents are amines. Other curing agents, for examples, are amides, alcohols, ureas, urethanes, isocyanates, etc.

A. Polyaddition

- Amines

The only significant reaction between an epoxy resin and an amine is as illustrated by Figure 2.16 .

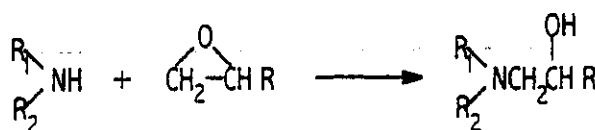


Figure 2.16 Reaction between an epoxy resin and amine

- Amides

Amides are rarely used alone as curing agents because the hydrogen of the amides is not very reactive with the epoxy group. Consequently, they are used with amines and acid anhydrides. They may require a catalyst like NaOH, KOH or NaOC_6H_5 .

- Alcohols

The reactions of epoxides with alcohols can undergo in various conditions. The reactions yield both primary ($\text{R}'\text{CHRCH}_2\text{OH}$) or secondary ($\text{R}'\text{CH}_2\text{RCHOH}$) alcohols and polyethers because of the reaction of the epoxide with the primary or secondary alcohols which are generated.

Acids or bases can catalyze the reaction of epoxides with alcohols. Without a catalyst this reaction requires a high reaction temperature. The reaction catalyzed by acid proceeds as shown in Figure 2.17 .

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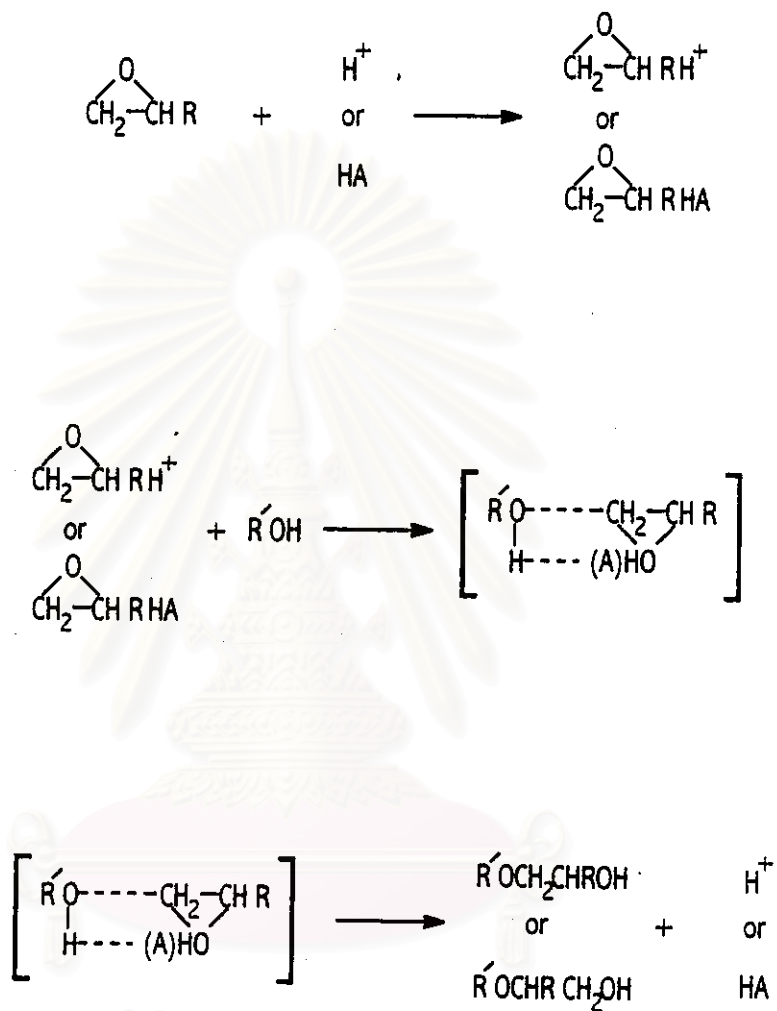


Figure 2.17 Reaction of epoxides with alcohols catalyzed by acid

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The possible mechanisms for a base-catalyzed reaction are shown by Figure

2.18.

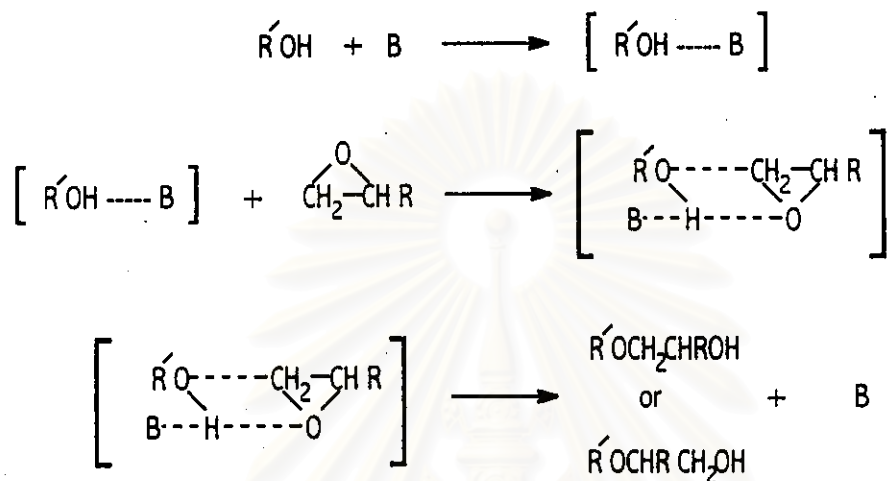


Figure 2.18 Reaction of epoxide with alcohols catalyzed by base

The other possible mechanism is illustrated by the following equations in Figure 2.19 which free ions play an important role.

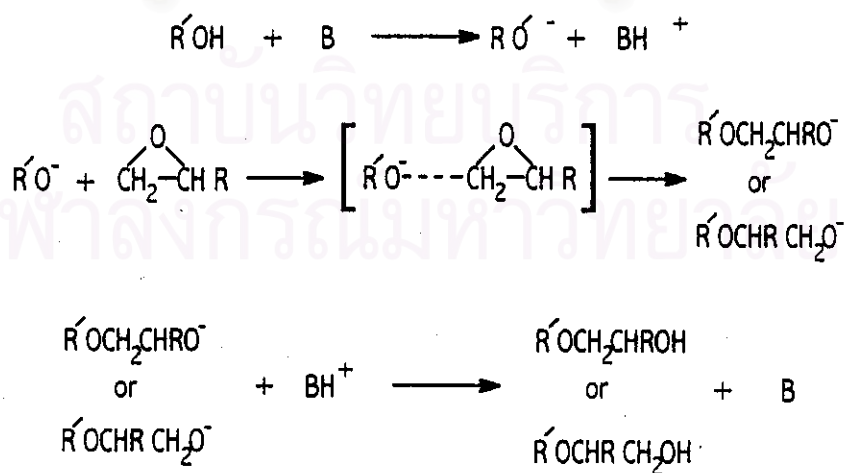


Figure 2.19 Reaction in which free ions play an important role

- Ureas

Ureas and its derivatives react with the epoxy resins at elevated temperatures to yield cured products. The following reaction mechanism (in Figure 2.20) has been suggested [26].



Figure 2.20 Reaction of epoxy resins and ureas

- Urethanes

The reaction between urethanes and epoxides results in 2-hydroxyethyl-urethanes and oxazolidones is shown in Figure 2.21.

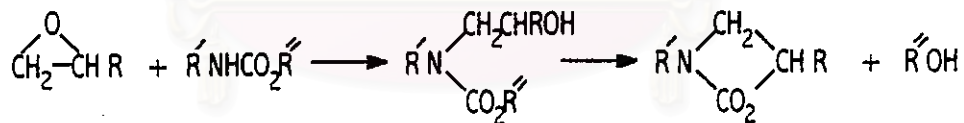


Figure 2.21 Reaction of epoxy resins and urethane

When the mole ratio of urethane to epoxide is less than 3, these products react further with the epoxide to yield adducts.

- Isocyanates

Isocyanates can be used as the curing agent for the epoxy resins in the presence of various catalysts such as quaternary ammonium halides, tertiary amines and some inorganic halides. The following reaction mechanism was proposed [27], where X is a halogen from the quaternary ammonium halide catalyst.

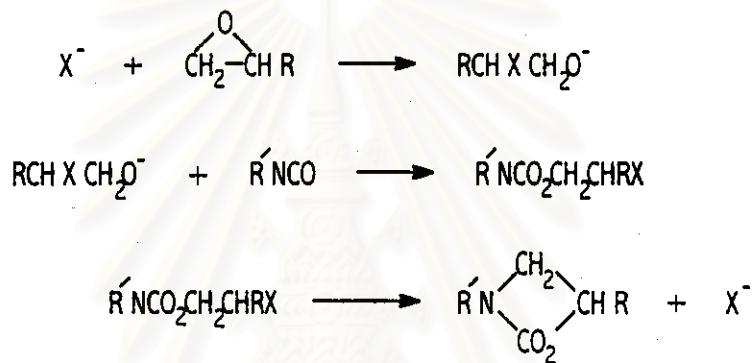


Figure 2.22 Reaction of epoxy resins and isocyanates

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2.4 Background and Outline of Thesis

Many techniques to recycle polyurethane foam have been investigated. Polyurethane foam scraps can be used for the production of rebonded carpet underlay [2,28], and compressing with the binder [2,3,29]. In addition, such scraps can be mixed in the new foam formulation, in thermoplastics or in thermoplastic elastomers as a filler [2,3,28,30]. Kadar and Zubonyai (1994) [3] reported that polyurethane foam grinded to particle sizes smaller than 200 microns can be added in amounts of 15 to 40% to virgin raw materials without deteriorating the properties of the foam.

In contrast to recycle by physical means, polyurethane foam can also be recycled chemically by various ways. Hydrolysis methods [2,5,8,11,12,14] can break down polyurethane foam into di- or polyamine, polyol and carbon dioxide gas by the action of high pressure steam at high temperature. Processes for recovery of polyether polyols from polyurethane foam by hydrolyzing in a water/dimethyl sulfoxide mixture have been described [12]. Hydrolysis methods are mainly applied to flexible and semi-rigid polyurethane foams. In order to carry out hydrolysis of polyurethane foam at a large scale, a continuous process has also been reported [8].

Furthermore, processes provided for the treatment of such waste by acidolysis have been discussed in the literature [10]. The ammonia decomposition process of polyurethane foam scrap by an addition of an inorganic or organic compound which can generate ammonia gas at the decomposition temperature have been described [14].

Another potential technique for the chemical reclaiming of polyurethane foam is aminolysis by the compound containing amino groups [17,20].

Glycolysis has been the most widely used method to decompose rigid polyurethane foam. In principle, this method involves treating such foam scraps by short-chained decomposers containing hydroxyl groups which can chemically break down the urethane linkage by transesterification. A number of papers related to glycolysis processes and a variety types of decomposer used for this reaction have been cited in the literature [2,3,6,7,13,8,19,21]. These works mainly concerned about recycling of polyol for manufacturing new PU foam.

Mixtures of dialkylene glycol/dialkanolamine have been employed to convert scrap polyurethane foam to polyols and amines [13]. Diethylene glycol mixed with different catalysts, which are KOH, CH_3COOK and diethanolamine have also been used for such a purpose [18]. Furthermore, the decomposition process of polyurethane foam by monoethanolamine has been disclosed. Kouji and Shizuo [17] examined monoethanolamine, which possess both a hydroxyl group and an amino group in the molecule, to prove that decomposition reaction is not aminolysis but alcoholysis. Instead of dialkanolamine, monoethanolamine has been added into glycol in order to promote the reactions [21].

A new chemical recycling process for polyurethane foam has been developed [22]. According to this process, the relatively high performance polyols can be produced by a two-step process. Polymer is broken down by dialkanolamine and a catalyst first. Subsequently, the alkoxylation is employed by using, for instance, propylene oxide in an effort to remove any amines and to obtain a relatively light-

colored multi-functional polyol. The liquid reaction products recovered were used to produce a variety of new polyurethane foams [7,13,17,19].

Xue et al. [20] decomposed rigid polyurethane and polyisocyanurate foams by aminolysis using aliphatic amines. Decomposition products were used as a hardener for epoxy resin. Aliphatic amines used in the decomposition process are diethylene triamine, triethylene tetramine, and tetraethylene pentamine.

Xue and He [21] prepared epoxy materials from the chemically reclaimed products of waste rigid polyurethane foams. Rigid polyurethane foams were decomposed by glycolysis reaction. Diethylene glycol with 5% by weight monoethanolamine was used as a decomposer. The decomposition reaction proceeded at 230 °C. The reclaimed products together with aliphatic amine and aromatic amine were then mixed with bisphenol A epoxy resin and a coupling agent at ambient temperature to make an adhesive system.

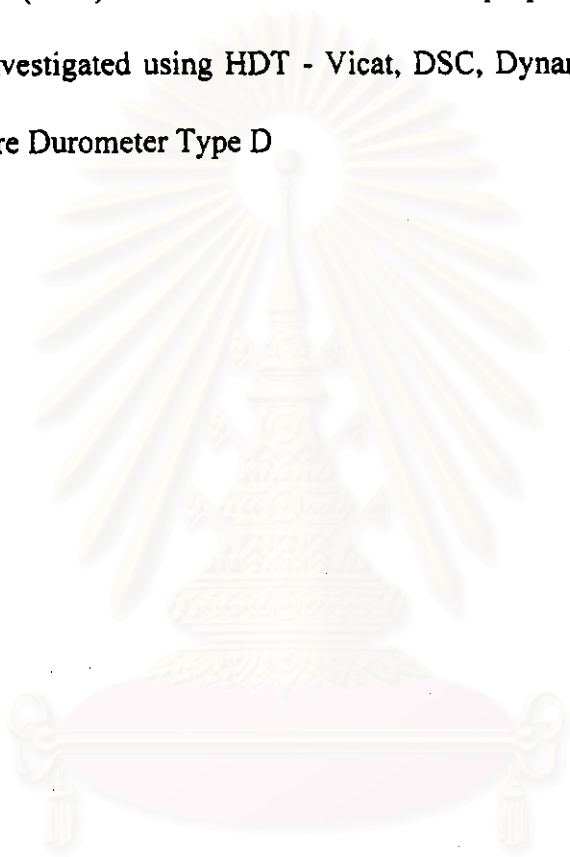
According to the work of Xue and He, the decomposition reaction was carried out at very high temperature. The preparation of epoxy material preparation needs the addition of aliphatic amine and aromatic amine as hardeners to achieve better material performance. From the work of Xue et al., decomposer used are expensive. In addition, there is no detail characterization and confirmation of chemical structures of the products presented in both works.

In this research, diethanolamine was chosen to be a decomposer because it can break down rigid polyurethane foam at relatively low temperature. Furthermore, diethanolamine is very cheap compared with the decomposer used in the work of Xue et al. Diethanolamine with sodium hydroxide, as a catalyst, can generate a large portion of amines which can be used as a hardener of epoxy resin. Like other methods, however, the decomposed products are mixtures including amines and polyols and they are difficult to be separated.

Sodium hydroxide has been reported in the literature[31, 32, 33] to be a catalyst for the reaction of epoxide ring and hydroxyl group. Therefore, the curing reaction of epoxy resin by the glycolyzed products with the presence of this catalyst is interesting. Otherwise, the remaining decomposer containing hydroxyl groups may have negative effects to mechanical strength of the cured epoxy resin.

In this work, the glycolysis of rigid polyurethane foam by diethanolamine with sodium hydroxide, as a catalyst, has been studied. Reaction products with various foam to decomposer ratios were prepared. Polyurethane foam was added portionwise into the decomposer at temperature of 130 to 150 °C under nitrogen atmosphere. The decomposed products were then mixed with epoxy resin in the presence of sodium hydroxide and cured at 150 °C for 100 minutes.

The crosslinking reaction was studied using Differential Scanning Calorimetry (DSC). The glycolized products were characterized by Infrared Spectroscopy (IR), Nuclear Magnetic Resonance Spectroscopy (NMR) and Gel Permeation Chromatography (GPC). Thermal and mechanical properties of the cured epoxy samples were investigated using HDT - Vicat, DSC, Dynamic Mechanical Analysis (DMA) and Shore Durometer Type D



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