

CHAPTER II

THEORY AND LITERATURE REVIEW

The Chemistry of the Epoxy Group

The epoxy group is a three-membered cyclic ether (Figure 2.1). The bond angles are greatly strained, and the ring is under stress. By reacting with various other compounds, the ring will open to form a less strained molecule. The epoxy group is polarized by the different electronegativities of carbon and oxygen. Oxygen has a partial negative charge while that of carbon is partially positive.

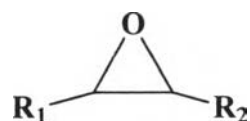


Figure 2.1 The epoxy compound.

The epoxy group reacts with a variety of reagents to produce chemicals of broad interest. To illustrate their potential as intermediates, a number of typical reactions are given in Table 2.1 [28]. Every epoxide, however, will not undergo all reactions as shown in the table. The course of any individual reaction depends upon the structure of the epoxide, a solvent and a catalyst used, the nature of other reactants presented in the reaction medium, and the reaction conditions.

Table 2.1 Various examples of the reactions of epoxy groups with various chemical groups.

Reactants (containing various chemical groups)	Reactions	References
Acid anhydrides	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + R-\overset{O}{\parallel}C-O-\overset{O}{\parallel}C-R \longrightarrow R-\overset{O}{\parallel}C-O-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-O-\overset{O}{\parallel}C-R$	[29]
Alcohols	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + ROH \longrightarrow RO-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-OH$	[30]
Amides	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + R-\overset{O}{\parallel}C-NH_2 \longrightarrow R-\overset{O}{\parallel}C-NH-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-OH$	[31]
1° Amines	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + RNH_2 \longrightarrow HO-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-NHR \longrightarrow$ $HO-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-N\begin{array}{c} R \\ \\ -C & -C- \\ & \end{array}-OH$	[32]
2° Amines	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + R_2NH \longrightarrow HO-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-NR_2$	[33]
3° Amines	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + R_1R_2R_3N \xrightarrow{H_2O} \left[HO-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-N\begin{array}{c} R_1 \\ \\ R_2 \\ \\ R_3 \end{array} \right]^{\oplus} OH^{\ominus}$	[34]
Carboxylic acids	$\begin{array}{c} & \\ -C & -C- \\ / & \backslash \\ & O \end{array} + R-\overset{O}{\parallel}C-OH \longrightarrow R-\overset{O}{\parallel}C-O-\begin{array}{c} & \\ -C & -C- \\ & \end{array}-OH$	[35]

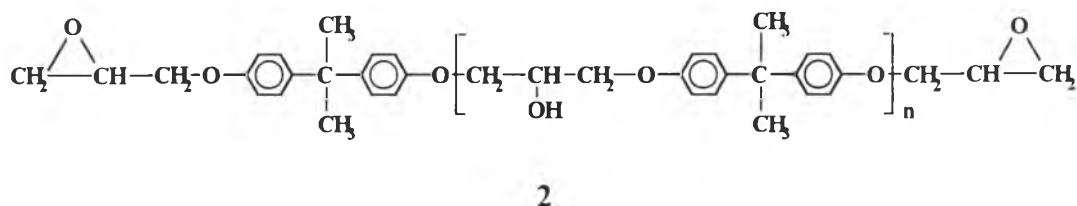


Table 2.1 (continued).

Reactants (containing various chemical groups)	Reactions	References
Grignard reagents	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{RMgX} \longrightarrow \begin{array}{l} \text{(a) } \text{HO---C---C---X} \\ \text{(b) } \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} \\ \text{(c) } \text{HO---C---C---R} \end{array}$ <p style="text-align: center;">depending on reaction conditions</p>	[36]
Halohydrins	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{HO---CH}_2\text{---CHR---X} \longrightarrow \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{OH} \quad \text{X} \end{array} + \begin{array}{c} \text{CH}_2 \quad \text{CH---R} \\ \quad \\ \text{O} \end{array}$	[37]
Hydrogen cyanide	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{HCN} \longrightarrow \text{HO---C---C---CN}$	[38]
Phenol	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{C}_6\text{H}_5\text{---OH} \longrightarrow \text{C}_6\text{H}_5\text{---O---C---C---OH}$	[39]
Thioacids	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{R---C(=O)---SH} \longrightarrow \text{HO---C---C---S---C(=O)---R}$	[40]
Thiols	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{RSH} \longrightarrow \text{HO---C---C---SR}$	[41]
Water	$\begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{O} \end{array} + \text{H}_2\text{O} \longrightarrow \text{HO---C---C---OH} \longrightarrow \begin{array}{c} \quad \quad \quad \\ \text{HO---C---C---O---C---C---OH} \\ \quad \quad \quad \end{array}$	[42]

Epoxy Resins

Bisphenol-A epoxy resins (2) are α,ω -epoxide end-functionalized prepolymers that react further with curing agents to yield high performance thermosetting plastics. They are characterized by the presence of a three-membered cyclic ether group commonly referred to as an epoxy group, 1,2-epoxide, or oxirane. Epoxy resins made their significant commercial debut around 1947. In the United States, the first product was made by the Devoe-Raynolds Company [43].



1 Characteristic Properties of Epoxy Resins

Some important properties of epoxy resins to be noted are the followings:

1. Very low shrinkage (caused by reaction), which makes epoxy resins suitable as encapsulating compounds.
2. Ease of processing by reaction casting at room temperature and atmospheric pressure without elimination of volatile compounds.
3. High adhesive strengths because of the presence of polar hydroxy and ether groups.

4. High mechanical properties (The strength of properly formulated epoxy resins usually surpasses that of other types of casting resins).

5. Good electrical insulation.

6. Good chemical resistance: The chemical resistance of the cured epoxy resin depends considerably on the curing agent used. Selectively outstanding chemical resistance can be obtained. Overall, most epoxy resins possess extremely high resistance of alkalines and good to excellent resistance to acids.

7. Versatility: The epoxy resins are probably the most versatile contemporary plastics. The basic properties may be modified in many ways, such as by blending of resin types, by selection of curing agents, and by the use of modifiers and fillers.

2 Classification of Epoxy Resins

Epoxy resins are usually classified into three groups as (a) Epoxy resins based on polyphenols, (b) Aliphatic and cycloaliphatic epoxy resins, and (c) Nitrogen-containing epoxy resins. The oldest (in volume of production) and the most important epoxy resins are the ones based on polyphenols. Aliphatic and cycloaliphatic epoxy resins have come recently on the market with smaller quantities in comparison to the polyphenol epoxy resins. Amines are used for the synthesis of epoxy resins containing nitrogen, however the effect of amines on the reactions of the epoxy group is very similar to that of phenols or olefins.

The polyphenols and The epoxy resins based on cycloaliphatics and amines as starting materials for the synthesis of epoxy resins are shown in Table 2.2 and 2.3, respectively.

Table 2.2 Polyphenols as starting materials for the synthesis of epoxy resins [44].

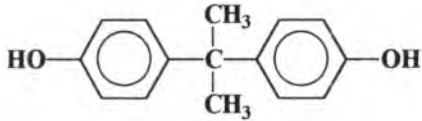
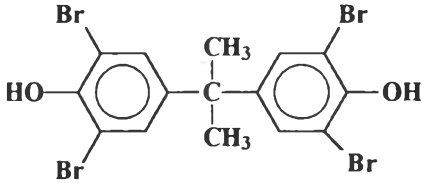
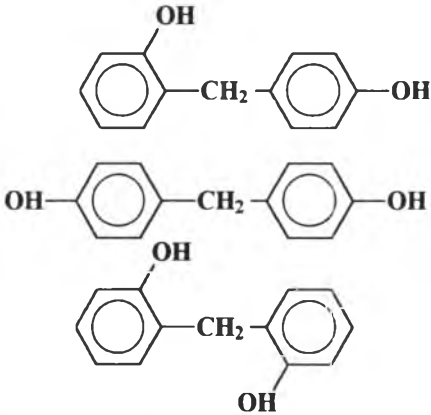
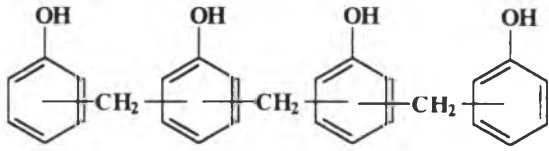
Chemical	Chemical structure
4,4'-Dihydroxydiphenyl- 2,2-propane (Bisphenol-A)	
Tetrabromobisphenol-A	
Dihydroxydiphenylmethane (Bisphenol-F)	
Novolak resins (intermediates for producing phenolplasts)	

Table 2.3 Epoxy resins based on cycloaliphatic compounds and amines [44].

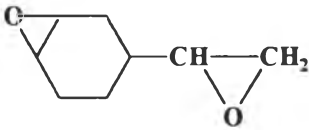
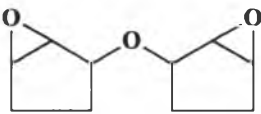
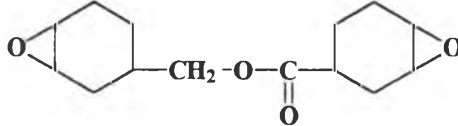
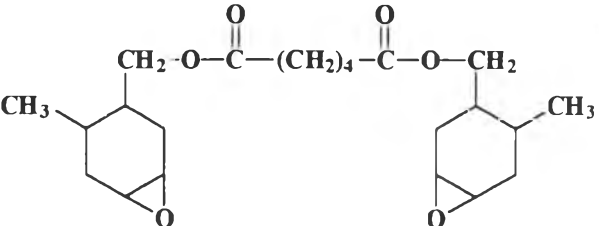
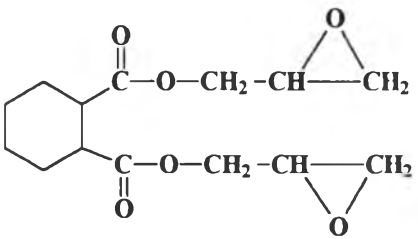
Chemical	Chemical structure
Vinylcyclohexenedioxide	
Bis-(2,3-epoxycyclopentyl)-ether	
3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate	
Bis-(3,4-epoxy-6-methyl cyclohexyl-methyl)-adipate	
Hexahydrophthalic acid diglycidylester	

Table 2.3 (continued).

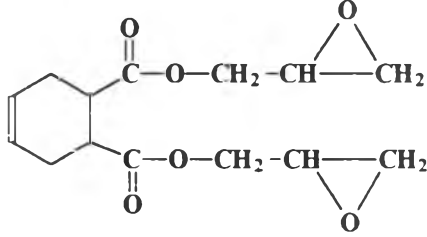
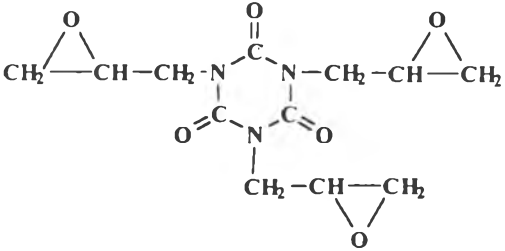
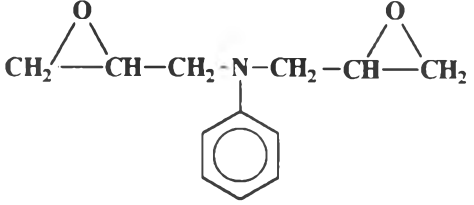
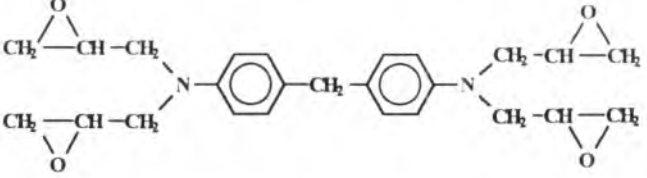
Chemical	Chemical structure
Trimethylpropane-tri-(2,3-epoxypropylhexahydro phthalate)	$\text{CH}_3\text{-CH}_2\text{-C}\left\{ \left(\text{CH}_2\text{-O-C}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{-C}_6\text{H}_4\text{-C}\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}\text{-O-CH}_2\text{-CH}\begin{array}{c} \text{O} \\ \diagup \diagdown \\ \text{CH}_2 \end{array} \right) \right\}_3$
Tetrahydrophthalic acid diglycidyl ester	
Triglycidylisocyanurate	
N,N-Diglycidylaniline	
N,N,N',N'-Tetraglycidyl-4,4'-diaminodiphenylmethane	



Table 2.3 (continued).

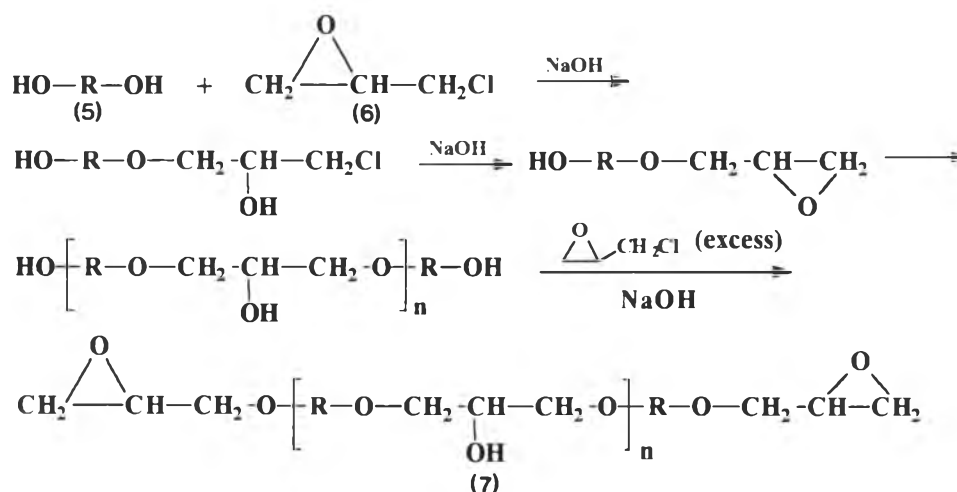
Chemical	Chemical structure
2,4-Diglycidyl-5,5-dimethylhydantoin	
2,4-Di-(2-glycidylpropyl)-5,5-dimethylhydantoin	

Epoxy resins can also be classified according to the technical process as (a) Cold setting resins (room temperature), (b) Thermosetting resins (less than 100°C), and (c) High temperature thermosetting resins (more than 100°C)

Usually, the curing conditions do not depend on the chemical structure of the epoxy resins but rather on types of hardeners and catalysts. The room-temperature curing systems generally use amine hardeners. In the case that anhydride hardeners are used, crosslinking reactions between anhydride with hydroxyl and with newly formed carboxyl and epoxy groups are occurred. Addition of catalysts will lower the curing temperature; these resins can be classified as moderate-temperature curing resins.

3 Synthesis of Epoxy Resins

Epoxy resins are most commonly synthesized by the base-induced condensation of a polyfunctional hydroxy compound (5), usually a bisphenol, with, in most case, epichlorohydrin (6) to give an intermediate having low molecular weight (MW), with essentially linear polymer (7) having terminal epoxide groups and pendant hydroxyls [45]. Scheme 2.1 are believed to occur in the one-step operation leading to the fusible prepolymer.



Scheme 2.1

MW of the prepolymer is varied by suitable adjustment of the mole ratios between epichlorohydrin and dihydroxy compounds. Depending on the number of repeating units (n) and on the structure of the dihydroxy compound, the product varies from a viscous liquid to a solid.

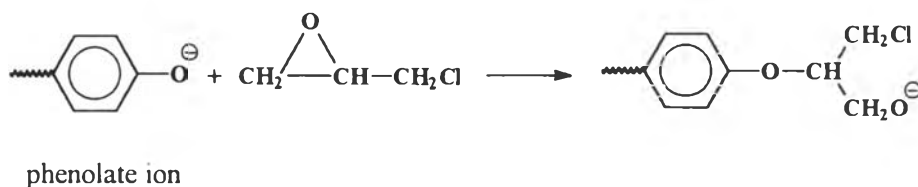
The mole ratio of epichlorohydrin to bisphenol-A in relation to the epoxy equivalent weight of the resin produced is shown in Table 2.4.

Table 2.4 The relationship between mole ratio of epichlorohydrin to bisphenol-A and epoxy equivalent weight [46].

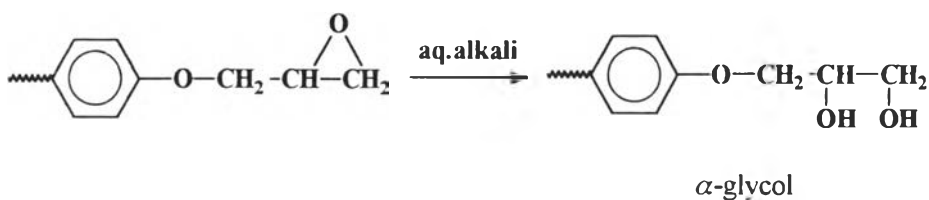
Mole ratio (Epichlorohydrin : Bisphenol-A)	Epoxy equivalent weight
2.60	249
2.15	345
1.57	516
1.40	582
1.33	730
1.25	862
1.20	1180

In practice, (7) is mixed together with small amounts of different structures formed by side-reactions and trace amounts of inorganic ions. Possible side reactions are:-

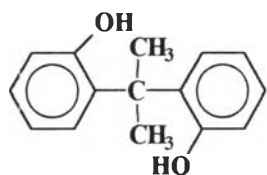
1. Abnormal addition of the phenolate anion to the epichlorohydrin epoxide group (addition to the more substituted carbon atom).



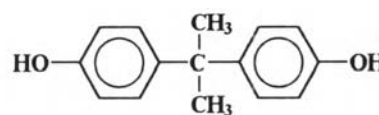
2. Hydrolysis of the epoxide group of the resin to form an α -glycol.



3. The *ortho*-Diphenylolpropane (Bisphenol A) isomer is less reactive than the *para*-isomer; therefore, a possible source of unreacted phenolic hydroxyl in the resin obtained.

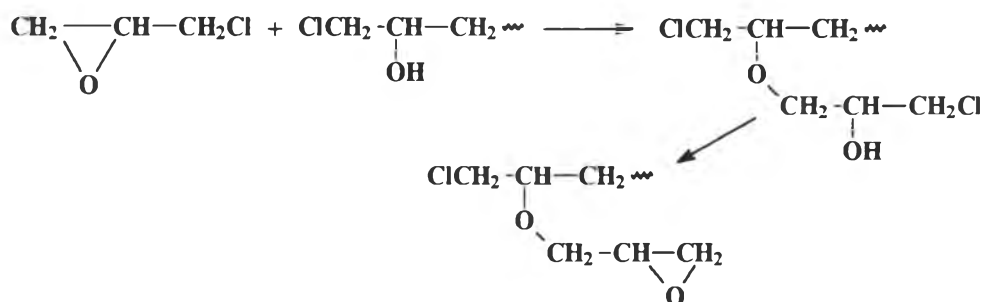


ortho-Diphenylolpropane



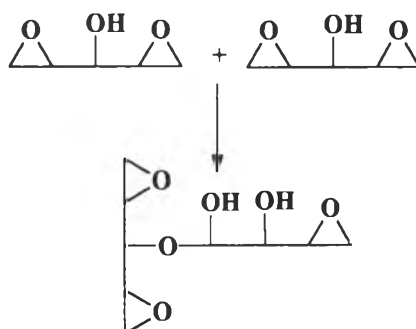
para-Diphenylolpropane

4. Formation of bound chlorine by reaction of epichlorohydrin with hydroxyl groups.



5. Incomplete dehydrochlorogenation resulting in a residual amount of sponifiable chlorine (hydrolyzable chlorine).

6. A possible cause of chain-branching (see the structure shown below) is the reaction between an epoxide group of a resin with a secondary hydroxyl groups, when reaction temperature used approaching 200°C and in the presence of base.



Curing Reactions [44,47-49]

Epoxy resins can react with various curing agents (also known as hardeners or curatives), or they can react with each in the presence of an appropriate catalyst to form infusible three-dimensional structures. Epoxies react by a ring opening mechanism. It is necessary to have a catalyst and a hydrogen donor. In the case of solid resins, they are composed of both epoxy and hydroxyl curing site so the crosslinking can also occur by the reaction between the hydroxyl groups of resin and curing agents.

The curing agents fall broadly into two types, i.e., catalytic and polyfunctional.

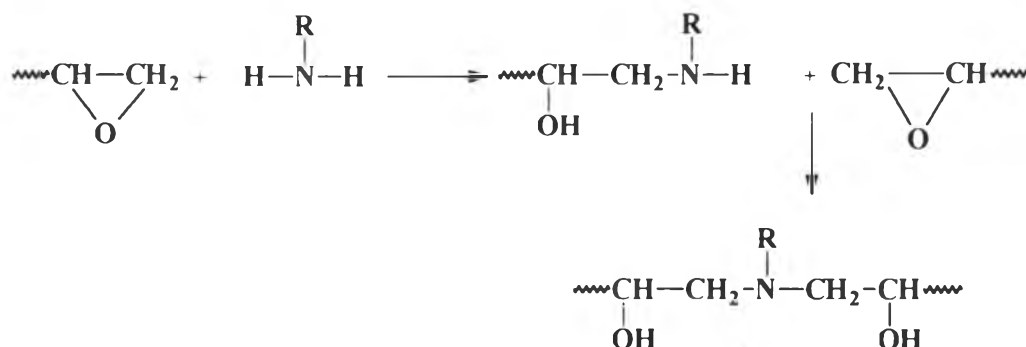
1 Curing of Epoxy Resins with Polyfunctional Curing Agents

1.1 Amines

1° and 2° amine hardeners react very quickly with epoxy resins at relatively low temperatures. The former are commonly used as curing agents in

greater number than the latter. It can be used for curing at room temperature, i.e., cold-temperature curing.

Primary aliphatic amines react at room temperature, with the epoxide ring forming a secondary amine, which, in turn, reacts with a further epoxide ring to form a tertiary amine link between the two epoxy resin molecules. (Scheme 2.2).



Scheme 2.2

The reaction of the hydroxyl groups, so formed, with epoxide groups is suppressed in the presence of secondary and primary amines. Monoamines act as bifunctional compounds (towards epoxy resins) and are able to convert diepoxy resins into high MW macromolecules through chain propagation. Diamines are tetrafunctional compounds and, therefore, yield highly crosslinked products.

In practice, primary aliphatic diamines are too volatile to be satisfactorily used as curing agents, but higher molecular weight polyamines, usually diamine dimer acid adducts, are used. Aromatic amines are not as



reactive as aliphatic amines. They usually require temperatures of about 200°C prior to significant reaction can occur.

Tertiary amines do not have any free hydrogen atoms and are therefore unable to react with epoxy resins. However, they are able to act as catalysts to reactions of epoxy groups with carboxyl, hydroxyl and amino groups.

Table 2.5 Reactive amines as curing agents [48].

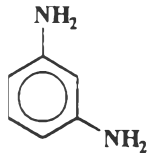
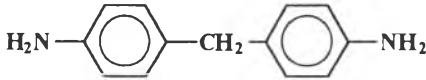
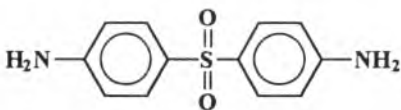
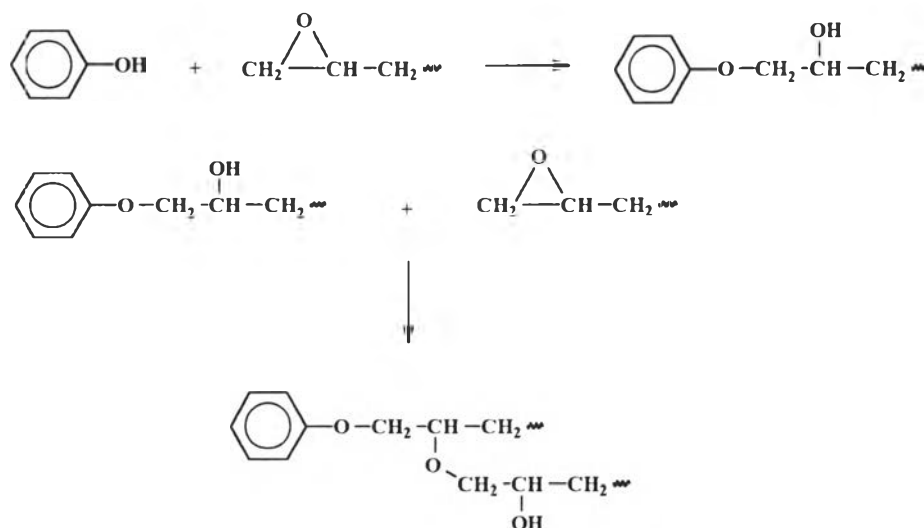
Compound	Structure	Equivalent weight	Mp. (°C)
Ethylenediamine	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	15	11
Diethylenetri-amine	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$	20.6	39
Triethylene-tetramine	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$	24.3	35
<i>meta</i> -Phenylene diamine		27	62-63
4,4'-Diamino diphenylmethane		49.5	90-92
4,4'-Diamino diphenylsulfone		62	177

Table 2.5 (Continued).

Compound	Structure	Equivalent weight	Mp. (°C)
Polyaminoamide	$\text{HO} \left(\overset{\text{O}}{\parallel} \text{C} - \text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - \text{R}' - \text{NH} \right)_n \text{H}$	Depending on types of R and R' and number of repeating unit	viscous

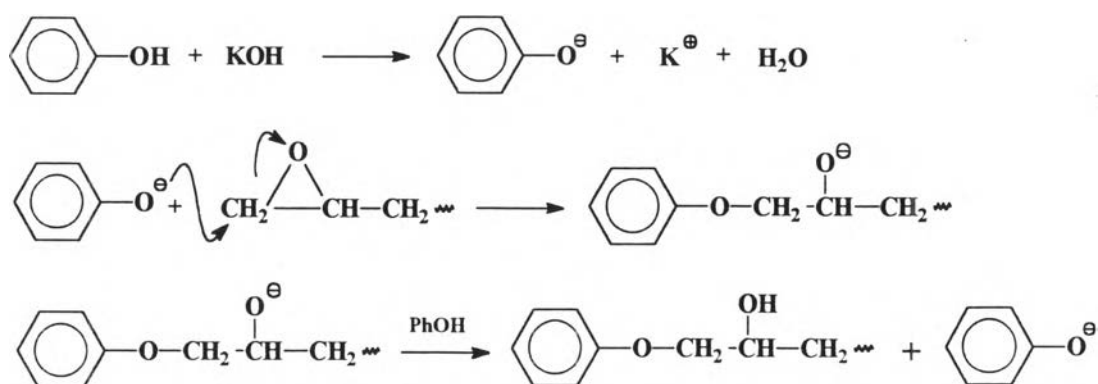
1.2 Phenols

The reaction between phenolic hydroxyl and epoxide, catalysed by alkalines, is used in the synthesis of the higher molecular weight epoxide resins. There are two possible reactions (Scheme 2.3), the phenol-epoxide followed by the alcohol-epoxide reaction. It was found that in the absence of catalysts, no reaction occurred between epoxide and phenol at 100°C. At 200°C reaction commenced, and epoxide was consumed at a faster rate than phenol. About 60% of the reaction was epoxide with phenol, and 40% epoxide with alcohol. Since alcohol was absent at the beginning of the reaction and appeared when phenol reacted with epoxide, it was concluded that the phenol preferred to catalyze the alcohol-epoxide reaction rather than self-reacted [47].



Scheme 2.3

The based-catalyzed reaction, however, proceeded at 100°C almost exclusively via the phenol-epoxide route to the virtual exclusion of the alcohol-epoxide reaction. Shechter and Wynstra [47] proposed the mechanism shown in Scheme 2.4 to fit the experimental facts.



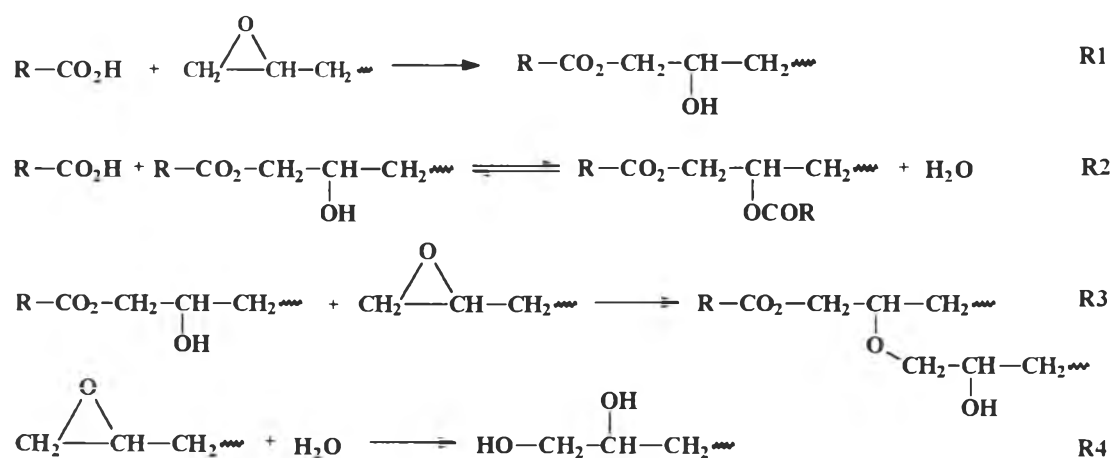
Scheme 2.4

In the same study, the rule of tertiary amines as catalysts for the reactions was also examined. It was observed that benzyldimethylamine was a

more effective catalyst than potassium hydroxide did. The quaternary compound benzyltrimethylammonium hydroxide was even more powerful catalyst. In each case, the epoxide-phenolic reaction was essentially the only reaction occurring following the first order kinetics.

1.3 Polybasic Acids

The reactions between epoxides and the acids can be expected to be of four types as shown in Scheme 2.5.

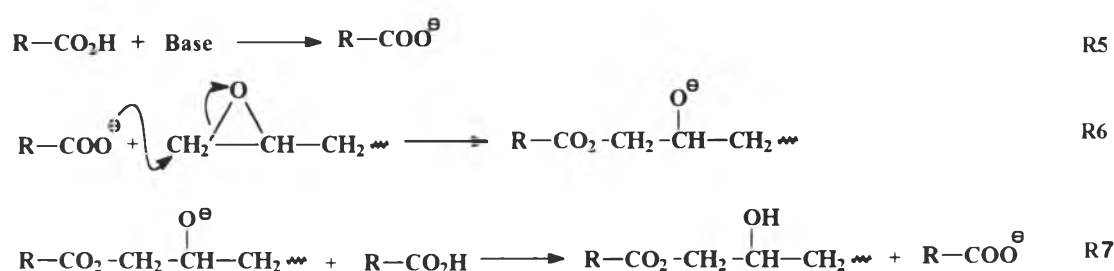


Scheme 2.5

Reaction R.1 leads to the formation of an hydroxy ester which, via Reaction R.2, can combine with a second molecule of acid to form a diester and water. The hydroxy ester can also serve to initiate polymerization via the epoxide-hydroxyl (Reaction R.3). Finally, the epoxide ring can undergo hydrolytic opening with water, forming the diol (Reaction R.4). It is probably that water is sensitive to the hydroxy ester in Reaction R.1 that is readiness to

undergo hydrolysis, coupled with the fact that water is formed in Reaction R.2, that has limited the wider use of acids as curing agents.

Reaction of a low molecular weight diglycidyl ether liquid resin with caprylic acid in the absence of base catalysts, Reactions R.5, R.6 and R.7 occur as shown in Scheme 2.6.



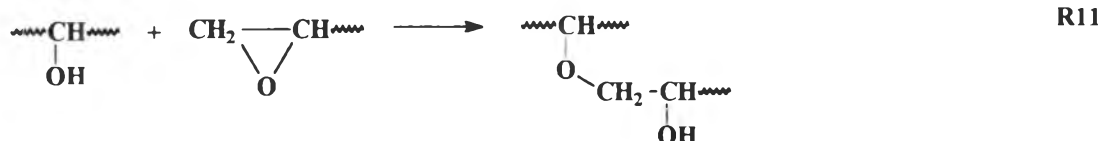
Scheme 2.6

The overall sequence becomes more specific, and the relative priorities of each depend on the stoichiometry. Thus in general, with a ratio of epoxide to acid of 1:1, Reactions R.1 and R.2 would occur, with formation of the hydroxy ester. This would virtually exclude any further reactions of the hydroxy ester, such as Reaction R.3. The formation of polyethers leading to resin homopolymerization. Where an excess of epoxide groups occurs, Reactions R.1 and R.2 proceed until all acid is consumed. Thereafter, the faster epoxide-alcohol (Reaction R.3) are commencing.

1.4 Anhydrides

Epoxy resins with no hydroxyl groups cannot be cured by carboxylic acid anhydrides. If anhydrides are to be used for the curing process, the resin has to contain secondary hydroxyl groups or small amounts of components with

or react with an epoxide group to form an ether linkage. The presence of the acid anhydride acts as a catalyst for the reaction shown below.



The uncatalyzed curing reactions between acid anhydrides and epoxy esters are slow, if uncatalysed, even at a temperature of 200°C. In the presence of basic or acid catalysts, the reaction proceeds readily. Basic catalysts, tertiary amines in particular, favour the formation of diester structures.

Table 2.6 Anhydride curing agents [44].

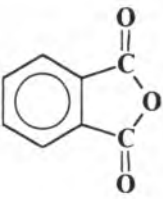
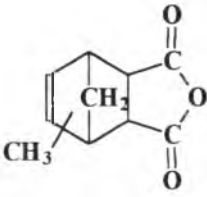
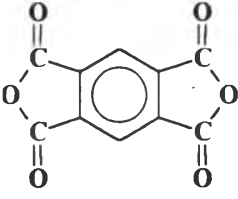
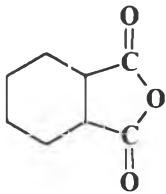
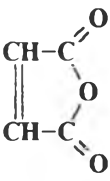
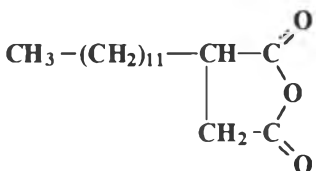
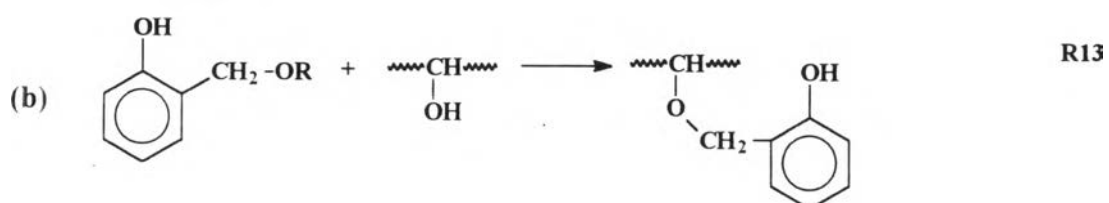
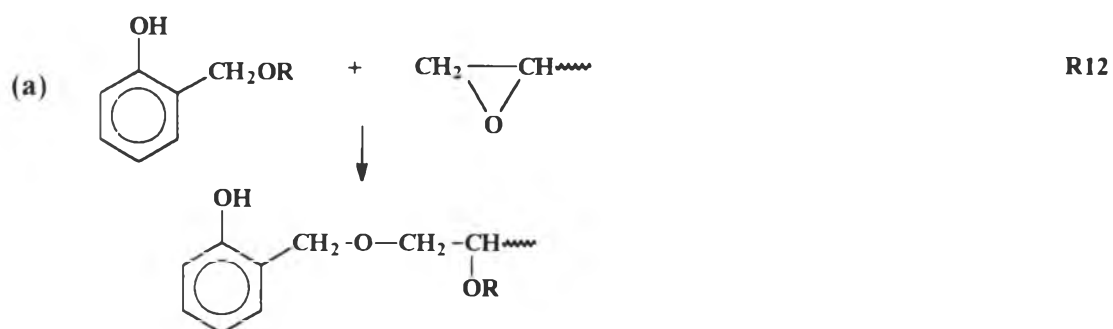
Chemical	Structure	Equivalent weight	Mp.(°C)
Phthalic anhydride		148	128-130
Nadic methyl anhydride		178	liquid
Pyromellithic acid dianhydride		109	284-286

Table 2.6 (continued).

Chemical	Structure	Equivalent weight	Mp. (°C)
Hexahydrophthalic anhydride		154	35-37
Maleic anhydride		98	52-53
Dodecenyl succinic anhydride		266	liquid

1.5 Methylol and Methylol Ether Groups

Methylol and methylol ether groups react with epoxy resins via (a) the epoxide group and (b) any hydroxyl groups presented in the epoxy resin molecule as shown in Reactions R.12 and R.13 (Scheme 2.7), respectively.



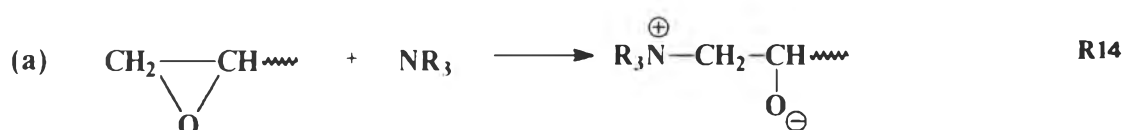
where R is H or an alkyl group.

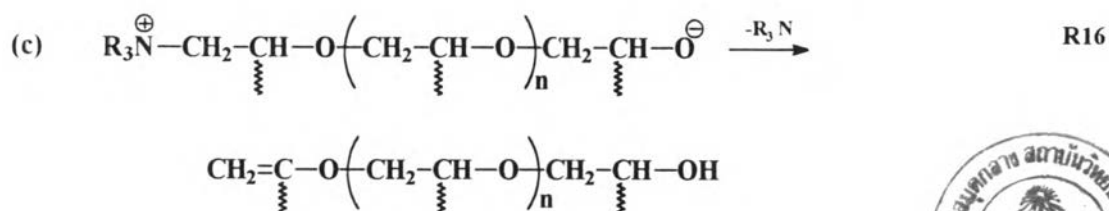
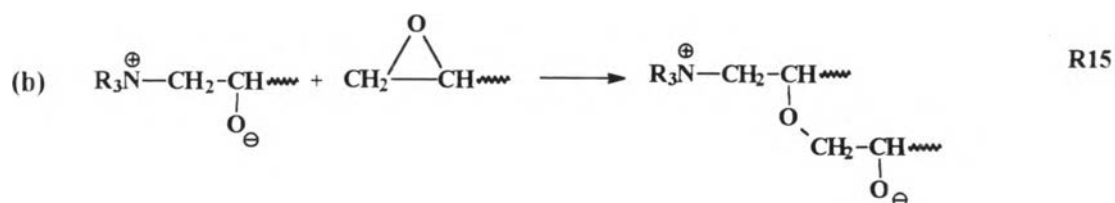
Scheme 2.7

2 Curing of Epoxy Resins by Catalytic Polymerization

2.1 Lewis Base

Lewis bases contain an unshared pair of electrons in an outer orbital, which are available for bond formation. They are therefore nucleophilic in character, seeking areas of low electron density. As catalytic curing agents they are used in small amount and primarily achieve homopolymerization of the resin. The most important compounds of this type are tertiary amines. The curing reactions of epoxy resin with the amine are shown in Scheme 2.8.





Scheme 2.8

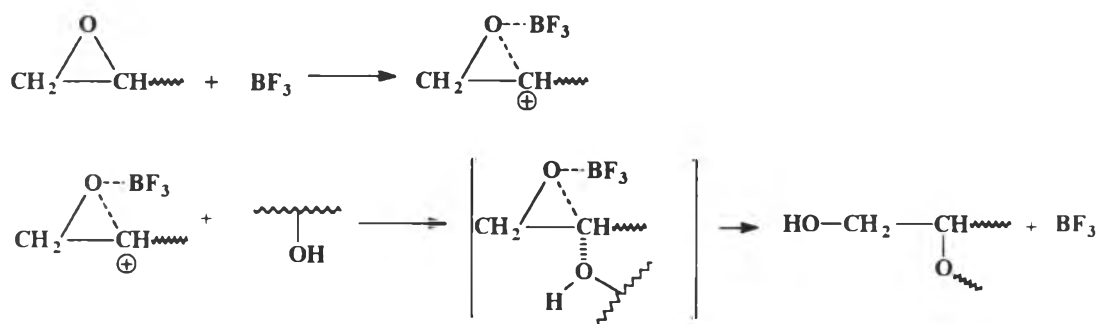
Addition of the catalysts onto the epoxy ring results in ring scission and formation of an amphoteric ion (Reaction R.14). Continuous addition of the epoxy group to the negative anion of oxygen results in polymerization of the epoxy resin (Reaction R.15).

Elimination of the activator R_3N group and proton transfer result in termination reaction as seen in Reaction R.16.

2.2 Lewis Acid

Lewis acids contain empty electron orbitals in the outer shell of an atom, i.e., BF_3 or $AlCl_3$, and are electrophilic in character (electron acceptors). They can be used in forming a bond by a donating atom.

Boron trifluoride (BF_3) has been major used for curing epoxy resins. Polymerization mechanisms of epoxy resins with BF_3 in the presence of hydroxy groups are shown in Scheme 2.9.



Scheme 2.9

Epoxide oxygen is attacked by the BF_3 forming a carbonium ion. This is followed by interaction of hydroxyl (presented in the molecule of resin) with the ion to form an alkoxide with the regeneration of BF_3 .