Chapter II
LITERATURE REVIEW
The chemistry of macromolecules is at present one of the most vigorously developing branches of the chemistry. The rapid rate of its development can be accounted for by the fact that the polymers can be prepared, both by chain growth polymerization like group transfer polymerization [6], template [7] and plasma polymerization [8] as well as by step growth polymerization e.g. synthesis of interpenetrating polymer network, liquid crystal polymers and epoxy resin. Out of which latter occupies an important role because of its endless applications in modern society. The present literature survey includes reviews [9-25] intending to gather the new results of the work done till early 1993 with particular emphasis on the synthesis and characterization of modified epoxy resins.

Epoxy resin in one form or another comprises significant fraction of the literature on step growth polymerization. Until mid 1970's, the synthetic epoxy resins were of considerable technological interest largely as material in their own rights. The synthesis of new epoxy resins and the detailed investigations of mechanism and characteristics had been directed towards the production of improved epoxy resins.

The first synthesis of epoxy resin was reported as back as 1927 when Scharade [26] cited the first commercial attempt to

* A part of this is under communication.
synthesise epoxy resin from bisphenol-A and epichlorohydrin. This was followed by few publications of *Caston* [27-30] by synthesising low melting amber coloured resin cured with phthalic anhydride to produce a thermoid compound.

However, systematic study of epoxy resins had begun only about 40 years ago and the first detailed publication in the open literature on such epoxy resin was that of *Wegler et al.* [31] in 1955 who gave more detailed discussion of historical and chemical background to the discovery of epoxy resins from epichlorohydrin synthetic route. It was followed by few publications of *Lee* and *Neville* [32], *Wallace* [33], etc.

Recently, increasing number of publications have been devoted to the synthesis and characterization of modified epoxy resins for various end applications. Such report was first described in the Polymer Journal only in the year 1970 by *Chakravarty* [34] who reported Synthesis of quinoxy resin by employing hydroquinone instead of bisphenol-A. The literature was further enriched by many researchers like *Kawamura et al.*[35], they used sodium-0 allyl phenolate in dioxane with phosphonitrile chloride followed by oxidation with benzoic acid to produce fire-resistant epoxy resin.

The pioneering work of *Sperling* and *Arnts* [36] in 1971 led to the synthesis of interpenetrating polymer network of cross-linked poly(ethyl acrylate) in an epoxy resin (Epon 828) by simultaneous heating and UV irradiation. This polymer was
prepared by sequential heating and UV irradiation or the reverse.

Prabhakar et al. [37] constructed high voltage chamber of Dobeckol 500 (cured by hardner 700) cylindrical section glued to metal rings by epoxy adhesive. It withstood a voltage of 225 KV d.c. without discharge for 30 min. and 450 KV pulses without flashover and did not have an altered field owing to the dielectric walls.

Filippenka et al. [38] used aromatic polyhydramide or poly(hydroxy methoxamide) to improve their heat resistance and adhesive properties of epoxy resin. However, the chemistry and properties of epoxy resin was studied by Garnish [39]. During the same period, Blyakhman et al. [40] synthesized self extinguishing epoxy resin having improved fire resistance and mechanical properties from 3-3' dichloro 4-4' diamino diphenyl methane polyglycidyl derivatives and 3-3' dichloro 4-4' diamino diphenyl methane.

Seller et al. [41] determined hydrolyzable chlorine in epoxy resin for liquid epoxy resin and the corresponding solid epoxy resin by carbitol and D.M.S.O. method, respectively which gave the same hydrolyzable chlorine content whereas for liquid epoxy resin, the values were greater than those by the ASTMD-1726 method. The 150°C gel temperature of the treated solution correlated poorly with the hydrolyzable chlorine content of the liquid epoxy resin determined by the ASTMD-1726 method but they
correlated well with the hydrolyzable chlorine content by Carbitol and D.M.S.O. method.

**Tadatomi et al.** [42] studied the synthesis and rates of photo cross-linking of epoxy acrylates and determined their average molecular weight, weight average molecular weight, polydispersity index value and hydroxyl number.

An important contribution to the development of epoxy resin including modification and characterization was made by **Fukami et al.** [43-44] who employed heterocyclic rings (I) and (II) instead of bisphenol-A.

\[
\begin{align*}
\text{HOOCRN} & \quad \text{CH}_2 \\
\text{O} & \\
\text{I} & \\
\text{HOOCRN} & \quad \text{CO} \\
\text{II} & 
\end{align*}
\]

The II, cured with phthalic anhydride had glass transition temperature \(T_g\) of 135°C and exhibited 50% ignition loss at 43°C in TGA (5°C min\(^{-1}\)). **Doi et al.** [45] synthesised alkali and water resistant epoxy resin with improved electrical properties by reacting formaldehyde-co-xylene, phenol, p-toluene sulphonic acid and epichlorohydrin. **Saida et al.** [46] deserve credit for reporting the significance of epoxy resin in the field of polymerization. They concentrated their attention on synthesis of cyanuric rings containing epoxy resin (epoxide equivalent-179) by
condensing phenol derivatives (I) \( (R' = H \text{ or } Me, R_2 = H, Me, Ph \text{ or tertiary octyl } n = 1-3) \) and optically dihydric phenols with cyanuric chloride in the presence of an acid acceptor and oxidizing the double bonds in the condensate.

\[
\begin{align*}
\left[ R' \text{CH:CH}_2 \right]_n \text{OH} \\
(1)
\end{align*}
\]

One the other hand Lin and Pearce [47] synthesised DGEBA (I, II, III, respectively) from epichlorohydrin and bisphenol-A, phenothalein and 99' bis (4 hydroxy phenyl) fluorine to study the relation between the title cured polymer structure and their properties. The reactivity of I-III towards IV (trimethoxybroxime) by DSC was in the order of I > III > II, order of crosslinked density was I > II > III. The \( T_g \) of the polymers was also determined.

The pioneering work of Kasotik et al. [48] in 1980, led to the synthesis of low molecular weight epoxy resin by addition of epichlorohydrin to phenolic compounds followed by subsequent dehydrohalogenation of the resulting chlorohydrin ethers in presence of catalyst consisting of a dispersion of alkali hydroxide in epichlorohydrin, is of great significance.

In an attempt to prepare phosphorous modified brominated epoxy resin Kim et al. [49] carried out the reaction of tetra bromo bisphenol-A and epichlorohydrin which on modification with Cl PO (OEt)_2 resin with different phosphorous content (0.48 to
2.48%). Thermogravimetric analysis (TGA) indicated that thermal stability decreased with increase in phosphorous content. Charmos and Podkoscieleńy [50] observed that when bis (mercaptomethyl) phenyl and epichlorohydrin or methyl epichlorohydrin were treated with isopropyl alcohol, bis(glycidyl thiomethyl) phenyl ether (epoxide equivalent 0.52 g eq/100g and 0.4% bound chlorine) was synthesized. In an attempt to prepare thioglycidyl resins [51], the condensation of $1-C_{10}H_6(CH_2SH)(I)$, $1,4-C_{10}H_6(CH_2SH)_2(II)$ or $1,5-C_{10}H_6(CH_2SH)_2(III)$ or II or III or mixtures of II & III with epichlorohydrin thioethers was done. The structure of the resins with the highest epoxide content was determined by element analysis, IR and $^1$HNMR spectroscopy. Thermal stability of the resins varied with thiols in the order $I < III < II$.

Soula and Locatelli [52] contributed significantly to our knowledge by synthesising modified epoxy resin from epichlorohydrin with sodium and potassium salt of bisphenol-A in an anhydrid aprotic medium in the presence of catalysts such as $[R(OCH_2CH_2)_n]_n$ [n=2 or 3, R=H, Me, Et] having viscosity 110 P, epoxy content 0.52 geq/100g and chlorine content 5%. Similarly, aromatic glycidyl thioether resins [53] were synthesised by reacting a mixture of one part mercaptane or mixture titraline or anthracene ring (n=1-3) and 1.1 part epichlorohydrin or methyl epichlorohydrin in 1-3 parts alcohol (epoxy content 0.53 geq/100g and organic chlorine 0.50%). One the other hand, Kakiuchi and Takei [54] synthesised epoxy resin from alkylene bis (p-hydroxy benzoate) and p-hydroxy sodium benzoate followed by reaction with epichlorohydrin. The cured resin had good adhesive properties.
Literature was further enriched by the pioneering work of Banthia et al. [55], they carried out interfacial synthesis of polyhydroxy polyether rapidly and efficiently by interfacial polycondensation of bisphenol-A with epichlorohydrin in aqueous alkali dioxane at 86° using quarternary ammonium salt as phase transfer catalyst. Colourless epoxy resin [56] with good resistance to thermal discoloration and increased gelation time was obtained by polymerizing bisphenol-A with epichlorohydrin in presence of 0.001-0.065 mol KOC1, NaOCl, CdCl or chloroamide/mol epichlorohydrin. Further, a wide range of liquid epoxy resins were synthesised and characterized [57-59] with slight modification or alteration of bisphenol-A.

Buxbaum and Seiz [60] synthesised and characterized the epoxy resin by interaction of tetrabromo benzimidazolene with epichlorohydrin which produced fire resistant 1-3 diglycidyl 4,5,6,7-tetrobromo benzimidazolene. The kinetics of the reaction of bisphenol-A and epichlorohydrin is studied by Enikolokyan et al. [61]. The results obtained are explained with the following postulates: all the alkali is bound as phenolate ions, all the phenolic groups are of equal reactivity, the reactivity of epichlorohydrin is higher than that of diglycidyl ethers. The factors leading to differences between the experimentally obtained parameters over the values of epoxide resins have been discussed.

There are very few publications in the literature on the possible use of fluorine as a modifier. Griffith [62] was successful in synthesising fluorine containing epoxy resin and
combatible curing agents for the system whose properties in the cured state provided many potential uses. Chen et al. [63] synthesised 4-4' isopropyldine diphenol diphenyl glycidyl ether(I) and a,a-bis(4-hydroxy phenyl) fluorene diglycidyl ether(II) and crosslinked the synthesised resin by trimethoxyboroxine(III), triethoxybromoxine(IV), tri-isoproxyboroxine(V) and triphenoxy-boroxine(VI). The glass transition temperature ($T_g$), degradation temperature ($T_d$) and gel fraction for I and II cured with various boroxines fell in the order: II cured epoxy $<$ IV cured epoxy $<$ V cured epoxy $<$ VI cured epoxy. II system usually had a higher $T_g$, $T_d$, gel fraction, 0-index and char yield than the related I system. Allard [64] concentrated his attention on studying the synthesis and properties of acrylic interpenetrating network.

A significant contribution was made by Hoffman et al. [65] who synthesised acrylic modified epoxy resin by the addition of 2-ethyl hexyl acrylate and glycidyl methylacrylate to hot epoxy resin (DER 383). No reduction in heat distortion temperature was observed when compared to the unmodified resin.

As revealed in the literature, Bellstedt et al. [66] synthesised interpenetrating polymer network by photopolymerization of triethylene glycol dimethacrylate in the presence of bisphenol-A diglycidyl ether and NN'-dibenzyl 3-6 dioxa octane-1,8-diamine. The $T_g$ of interpenetrating polymer network has been shown to depend on the concentration of the acrylic component or on which polymer formed first at acrylic component 40%. The $T_g$
was not altered indicating a multiple phase system, but at 50-80% acrylic component, T indicated single phase system. Soon Gao and coworkers [67] made a successful attempt for synthesising high molecular weight epoxy resin by polymerization of bisphenol-A and bisphenol S with epichlorohydrin in aqueous alkali dioxane system using poly oxyethylene as phase transfer catalyst. The molecular weight of the epoxy resin increased with increasing bisphenol(S) content and polymerization time. The melting point and decomposition temperature of epoxy resin was 40° higher than that without bisphenol S.

Increasing number of publications, devoted to the synthesis and characterisation of epoxy resins have recently appeared in various Journals around the globe. Chiang et al. [68] studied that epoxy and ionic conducting poly(ethylene oxide) salt complexes from interpenetrating polymer network. The co-continuity of the two phases tested independently by mechanical and electrical measurement. The size scale of the phase ranges from 0.1 to 0.5 μm. However, low hydrolyzable chlorine content containing epoxy resin was synthesised by Wang and Liao [69] by reacting compounds containing -OH/NH₂/COOH groups with excess epichlorohydrin in presence of alkali metal hydroxide and > polar aliphatic solvents (5-60% by total solvents). The resin had hydrolyzable chlorine 65 and bound chlorine 674 ppm. It is notable that even a series of epoxy derivatives of bis(azomethine) [70] was synthesised by reacting an aromatic diamine with 4-hydroxy benzaldehyde in a 1:2 mole ratio to afford the corresponding
bis(azomethines). The compound was analyzed by IR, NMR spectroscopy and thermally polymerized in presence of 4-4' sulfonyldianiline, and investigated by DTA. The polymer was stable upto 293-340°C and afforded an anaerobic char yield of 43-62% at 800°C. The results of polymerisation of bisphenol-A with epichlorohydrin in the presence of Bu₄NBr catalyst by ring opening followed by ring closure [71]. The first step was a second order reaction with activation energy 56.0 KJmole⁻¹ while the second step was a first order reaction with activation energy 48.84 KJmole⁻¹.

In another splendid publication Fukami and Moriwaki [72] prepared modified epoxy resin as per scheme given below. The mechanical and solubility behavior of the cured resins were evaluated. The resins had glass transition temperature $T_g > 200°C$ and excellent thermal stability, and $T_g$ increases in the order of $O > M > P$ substituted phenol groups.

Scheme-I

![Scheme-I](image-url)
In a significant communication, Hasegawa [73] reported the synthesis of seven tetra glycidyl ethers (Scheme II) from four nucleic novolacs in which the position of methyl linkages or number of kinds of substituents were different. These epoxy compounds were cured with diamine diphenyl methane. The characteristic properties such as glass transition temperature ($T_g$), average molecular weight between crosslinking points ($M_c$) and front factor ($\phi$) were obtained. It was concluded that higher linearity in the main chain of epoxy resins gave a cured resin with a higher $T_g$, a smaller $M_c$ and a large $\phi$. 
Scheme-II.1
In another pioneering contribution Hasegawa et al. [74] reported the synthesis and properties of a number of (1-4) epoxy resins having a hydroxy methyl group from phenolic alcohols. The resins were characterized by $^1$H NMR, glass transition temperature and epoxide equivalent.
Renner et al. [75] reported synthesis of resolved type epoxy resin and concluded that not only phenolic hydroxy group but all hydroxy methyl groups were glycidyl etherified with epichlorohydrin. Such resins have excellent performance such as rapid curing, high heat resistance and good adhesive properties.

Literature on modification of epoxy resins further became voluminous by Jain and Thangamathesvaran [76], they reported the synthesis and characterization of novel epoxy resin of thiocarbonohydrazones by reacting the aldehyde and ketone derivatives of thiocarbohydrazides with excess of epichlorohydrin (Scheme 4). The resins were characterized by elemental analysis, epoxy equivalent \(^{1}H\) NMR, and IR spectroscopy, thermal analysis and viscosity measurement. Curing of the resin had been done by mixing it with thiocarbohydrazide or ethylene diamine and heating at 80°C for 48h. A comparison of the thermal stability of the cured resin samples was done.
Scheme-4

\[
\begin{align*}
\text{HO - R - CH = N NH - C - NH N = CH - R - OH + 4Cl - CH}_2\text{- CH - CH}_2 \rightarrow \\
\text{H}_2\text{C - HC - H}_2 \\
\text{H}_2\text{C - CH - CH}_2 - O - R - CH = N - N - C - \\
\text{N - N = CH - R - O - CH}_2 - CH - CH_2 + 4\text{HCl} \\
\text{CH}_2\text{- CH - CH}_2
\end{align*}
\]

where,

\[
R = \bigcirc
\]

(TGm HBTCH) Tetracyglycidyl ether of m-hydroxy benzaldehyde thiocarbonohydrazone

\[
\bigcirc \text{OCH}_3
\]

(TGVTHC) Tetracyglycidyl ether of Vanillin thiocarbonohydrazone

\[
\bigcirc
\]

(TGO HBTCH) Tetracyglycidyl ether of O-hydroxy benzaldehyde thiocarbonohydrazone

\[
\begin{align*}
\text{R - C = N - NH - C - NH - N = C - R + 2Cl - CH}_2\text{- CH - CH}_2 \rightarrow \\
\text{R'} \text{ CH}_2\text{- CH - CH}_2 \\
\text{R - C = N - N - C - N - N = C - R = 2HCl} \\
\text{R'}
\end{align*}
\]

where \( R = R' = \text{CH}_3 \)

(DGATCH) Diglycidyl ether of acetone thiocarbonohydrazone
and

\[ R = H, R' = \bigcirc \]

**Resin 5**

(DGEBTCH) Diglycidyl ether of benzaldehyde thiocarbono-hydrazone

The field of modification of epoxy resin attracted a number of polymer chemist like Shen and Wang [77], they condensed xylenediamine instead of bisphenol-A with epichlorohydrin synthesis \( NN'N'N' \) tetra glycidyl xylylene. Structure was analysed by IR, NMR spectroscopy and chemical analysis (epoxide equivalent 0.8639–0.9889 g eq/100g). Wang et al. [78] studied modified epoxy resin system with poly(acryl ether ketone). Phenoiphthalien based poly(acryl ether ketone) was blended with epoxy resins based on \( NN'N' \) – diaminodi phenyl sulfone and either E-44 or E-51 DGEBA. Kinetics of curing, mechanical and thermal properties, miscibility and morphol of the blends were determined. Addition of poly(aryl ether ketone) did not effect the curing of the epoxy. It was observed that ultimate elongation of the composite increased with increasing amount of the poly(acryl ether ketone). Tensile modulus, glass transition temperature and tensile strength were not effected.

In early nineties a series of UV autocurable epoxy multi-acrylates poly ketone resins (EMAPKR) were synthesised by Chiang et al. [79]. The resins were cured rapidly when exposed to UV without the addition of photo initiator. Stress strain, DSC and dynamic mechanical analysis were used to characterize the
properties. Cured EMAPKR had glass transition temperature of 74–102°C. An interesting modification was made by Nakamura et al. [80] by modifying epoxy resin with poly(butyl acrylate)I and poly (ethyl acrylate)II produced by in situ UV radiation polymerization of their corresponding monomers, respectively. The glass transition temperature \(T_g\) of the epoxy matrix decreased in II system more than in I system and I modified resin was superior to the II modified resin in reducing the internal stress without decreasing the thermal resistance of epoxy resin.

Tamaresely et al. [81] in early 1990 carried out analytical studies using chemical, spectral and chromatographic methods for four commercial diglycidyl ether of bisphenol-A resins for synthesising 2,2-bis[4-(2 hydroxy-3-methacryloyloxy propoxy)] phenyl propane (Bis-GMA). Parameters such as epoxy equivalent weight hydroxyl value and hydrolyzable chlorine content had been estimated. The role of these parameters in determining the final purity of Bis-GMA had also been discussed.

Bisphenol-A diglycidyl ether-butanediol copolymer were prepared [82] using \(\text{Mg(ClO}_4\text{)}_2\) or \(\text{Ph CH}_2\text{NMR}_2\) accelerators and the viscoelastic properties of the network were compared. The glass transition temperature increased with increasing diol content especially retardation spectra and molecular weight between crosslinks were also compared.

Recently in 1992, o-cresol novolac type epoxy resin having hydroxy methyl group [83] were synthesised and cured with a
mixture of 4,4'-diaminodiphenyl methane and m-phenylene diamine and examined by DSC. Viscoelastic properties of the cured epoxy resins were studied by dynamic mechanical analyzer. It was found that the lower the average molecular weight of the epoxy resin, that is, the higher the concentration of hydroxy methyl group, the shorter the onset time of exothermal reaction, the higher the rate constant \( k \), and lower the activation energy \( E_a \) were. Toughening epoxy resin can be achieved by blending a low percentage of liquid crystalline polymer with the thermoset [84]. The processing technique consists of the spinning of blends of a thermoplastic (Ardel) with subsequently dissolved in the uncured epoxy resin (Epon 825). After curing, the LCP phase separates from the matrix in the form of microfibres with a very high aspect ratio, which acts as crack stoppers and improves fracture toughness of the material.

Chandra et al. [85] modified diglycidyl ether of bisphenol-A (DGEBA) by acrylic acid. The reaction between the active epoxy groups of DGEBA and the carboxylic group of acrylic acid was catalysed by triphenyl phosphine to prepare di(vinyl-2-hydroxypropanoate) ether of bisphenol-A (DEBA). The DEBA so formed was co-polymerised with 2-ethylhexylacrylate using benzophenone as the photoinitiator to yield a flexible polymer. The kinetics of the photo-initiated radical polymerization was studied by a new technique called differential photocalorimetry and the results thus obtained were analysed to determine the Arrhenius activation energy and pre-exponential factor.
**Spectroscopic studies of epoxy resin**

Spectroscopy has become one of the most important tools for the characterization of the chemical and physical nature of polymers. In principle IR and NMR spectroscopy provides, useful informations about chemical nature, steric order and conformational orientation of the polymers.

Gupta et al. [86] in 1972 were amongst very few scientists who gave the full IR and TGA data for epoxy resin prepared from bisphenol-A and epichlorohydrin.

However, in 1981 Stevens and Gary [87] made assignments of different epoxy resin-phthalic anhydride system and presented complete band assignment and their optical behaviour during the reaction in IR spectrum. Based on this, he also discussed the kinetics and mechanism of the reactions. According to him, the reaction followed consecutive step addition, esterification and simultaneous epoxide OH group and carboxylic dimer hydrogen bonding occurred.

Infra red spectroscopic analysis of cyclo aliphatic epoxy resins, cured with polyols and dicarboxylic anhydride, was presented by Eross and Klara [88]. A method was developed for estimation of the \(-\text{OH}\) group concentration in the crosslinked resins with the aid of model compounds and the absorbance ratio of the OH and CO stretching vibration bands calculated from the spectra of the samples.

IR data was utilized by Lin et al. [89] on benzylidimethylamine catalyzed dicyandiamine (II) DDA-poly(bis-A diglycidyl ether)
pre polymer system to investigate the influence of bisphenol-A on the curing mechanism. The authors observed that the reaction pathway of II varies with temperature, especially at lower temperature. The glass transition temperature is reported to be a complex function to different mechanism and it was observed that higher $T_g$ could be reached with an amine to epoxy ratio 0.6 and after a curing cycle including a precure at 100°C.

The pioneering work of Hu et al. [90] reveals the utilization of the principles and application of IR spectroscopy in the study of UV curable epoxy resin meth acrylate and gave the fast and simple method with good reproducibility.

Lin et al. [91] studied degradation of three cured epoxy resin systems under various degradation conditions by FTIR spectroscopy and concluded following order of thermal stability. Me group–total benzene ring > CH₂ > p-phenylene > other linkage > isopropylidene. The oxidative thermal and photo-degradation process were related to the classical autocatalytical oxidation of aliphatic hydrocarbon segments, Claisen type rearrangements and other possible degradation mechanisms are suggested by the data.

Roush [92] successfully presented FTIR spectroscopic analysis to study the changes occurring during the curing reactions and its application to curing of the epoxy resin, Epon 828 with hexahydrophthalic anhydride has been discussed.

One of the more recent contribution of Yang et al. [93] dealt with the FTIR spectroscopy for analysis of crosslinking of
E-51 epoxy resin with 2-ethyl 4-methyl imidazol. The average apparent energy for the first and second stage was 47 and 62 KJ/mol, respectively by DSC method.

However, pulsed NMR spectroscopy was used to measure glass transition temperature of cured epoxy resin [94]. The measurements allow monitoring of the cure and determination of the $T_g$ as a function of curing conditions and the concentration of the components.

In order to further explore the utility of spectroscopy in the field of epoxy resin, Ratov et al. [95] continued their studies and found that nuclear magnetic spectroscopic analysis of epoxy resin improved and revealed more information when epoxy resin modified with $\text{Ac}_2\text{O}$ at 137-8°C for 1 h was subjected to NMR spectroscopy. Similarly NMR spectroscopic analysis is utilized by Lind [96] to study the inhomogeneties in epoxy resin as well as it can be utilized to study the relaxation studies of two phase polymeric systems [97].

The literature using the spectroscopy as a tool was further strengthened by the use of NMR by Garroway et al. [98]. The authors studied the effects of strongly intracting $^1\text{H}$ spin system on the determination of $^{13}\text{C}$ NMR rotation frame study of DER 332 cross-linked by piperidene at 393°K. The $^{13}\text{C}$ shows a significant temperature dependence corresponding to activation energy of 11 KJ/mole.
Few reports are also available on the possible applications of $^{13}$C NMR spectroscopy [99] in which the content of primary, secondary and tertiary amines as a function of changes in epoxy concentration was determined for several reactivity ratios. Another milestone laid down by Attias and his Colleagues [100] by investigating the structure of NNN'N' tetra glycidyl 4 4' diamino diphenyl methane based epoxy resin crosslinked with 44' diaminodiphenyl sulfone by high resolution solid state $^{13}$C NMR spectroscopy.

The main structural features of all the system was the predominance of intramolecular reactions of N N' diglycidyl aniline groups.

In spite of long history of interest as described previously, NMR spectroscopy led to a long way to determine the structural evidences of epoxy resin. As Tanaka et al.[101] studied the curing of Epon 828 with N-(3-aminopropyl)-3 methyl(I), 3 propane diamine(II) or N-(3-amino propyl)-1,3 propane diamine (III). The structure of the reaction products was analysed and their relative contents were estimated by integration of the signals. The chemical conversion, determined by 'H NMR coincided well with those by the DSC method.

Similarly, two dimensional fourier-transform NMR spectroscopy was applied to the study of the epoxy resin, DGEBA [102]. The combination of the homonuclear shift correlated and J-resolved experiments permits the complete elucidation of the proton spectrum of the glycidyl ether moiety.
The important lead towards the application of gel permeable chromatography came into picture from the observation of Roger [103], Braun and Lee [104] and Zhang et al. [105] in 1987. The molecular weight and molecular mass distribution were determined by GPC and the average molecular weight of the resin was determined by vapour phase osmometry. However, high resolution gel permeable chromatography and HPLC were applied to commercially available bisphenol-A diglycidyl ether [106] to elucidate small but significant difference in the oligomer and impurity composition of these resin and DSC analysis was used to obtain the relative resin reactivity.

**Curing Literature**

The wide ranging applications of cured epoxy resins in fabrication of high performance polymers, have led to a high degree of research interest in the curing and properties of such resins. It is important to understand the mechanism and kinetics of various reactions involved. The curing of epoxy resin directly controls the final network structure and performance of the resin. The cured kinetics has been carried out by the changes in the concentration of amines, epoxy and hydroxy group, concentration at 160°C. These changes have been measured with the help of infrared spectroscopy. The different compounds like primary, secondary and tertiary amines have been used, the details are as follows:
Curing agents have been classified on the basis of their nature into two categories:

1. Acidic curing agents
2. Basic curing agents

1. **Acidic curing agent:**

The acidic curing agents normally used in the epoxy resins are carboxylic acid, anhydrides, dibasic acids, phenols and Lewis acids. The details have been summarized in Table-II. The mechanism is depicted in Scheme (1)

**Scheme-I**

Acid anhydride as curing agent: The anhydride ring may be opened by active hydrogen to produce one or two carboxyl groups.

Ring opening by water

Ring opening by hydroxyl group
Table-II.1

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Epoxy Resin</th>
<th>Name of curing agent</th>
<th>Curing properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Araldite CYC05</td>
<td>acid anhydride (tertiary amine accelerator)</td>
<td>0.5 order of reaction at 18-80% conversion with activation energy 13.9cal/mol. 1st order at 79.6cal/g with activation energy 13.4cal/mol was determined by DSC.</td>
<td>107</td>
</tr>
<tr>
<td>2.</td>
<td>ED-5 resin</td>
<td>maleic anhydride (I), methyl tetrahydrophthalic anhydride, succinic anhydride, phthalic anhydride (II).</td>
<td>1st order reaction, activation energy with (I) decreased from 50.4K/mole to 234cal/mole with (II), heat evaluation was determined by DTA</td>
<td>108</td>
</tr>
<tr>
<td>3.</td>
<td>Novolac resin DEN 431</td>
<td>succinic anhydride, maleic anhydride, hexa hydrophthalic anhydride, methyl tetra hydrophthalic anhydride and methylene tetra hydrophthalic anhydride</td>
<td>Flexural strength, tangent modulus, toughness, density, heat distortion temperature, solvent sensitivity</td>
<td>109</td>
</tr>
<tr>
<td>4.</td>
<td>Epon 828</td>
<td>dicarboxylic acid dihydrazide</td>
<td>3rd order kinetics studied by DSC, inhomogeneous system $\Delta E$ is 69.12Kcal/mol, in heterogeneous system $\Delta E$ is 32Kcal/mol</td>
<td>110</td>
</tr>
<tr>
<td>5.</td>
<td>Epoxy resin</td>
<td>acid anhydride</td>
<td>activation energy in the range 75-142 KJ/mol, order of reaction 1 studied by DSC.</td>
<td>111</td>
</tr>
<tr>
<td>6.</td>
<td>Epoxy resin Et 20</td>
<td>phthalic anhydride</td>
<td>zero order reaction in both epoxide and anhydride.</td>
<td>112</td>
</tr>
</tbody>
</table>
7. Epon 828 methyl tetra glass transition
or hydrophthalic temperature(T) increases with increasing staging temperature
Epon 826 anhydride

8. Glycidyl plasticizers compatibility, having good mechanical properties, resistance to weathering is discussed.
derivative 230

9. Epoxy resin Heat distortion temperature 320°C and exhibits long term storage at ambient temperature and cures rapidly at
1,3-di[5-(2.2')-bi cyclo hexyl-2,3-di carboxylic anhydride)
-1,1,3,3-tetra-methyl siloxane (I)

(2) Basic curing agents:

The basic curing agents employed in epoxy resin technology are lewis bases, inorganic bases, amines and amides. The details have been illustrated in Table-II.2 and the mechanism of curing by various amines is as follows:

(A) Mechanism of curing with Primary amine:

\[
\begin{align*}
\text{R-NH}_2 + & \quad \text{C--C} \\
& \rightarrow \text{R-NH--C} \quad \text{OH}
\end{align*}
\]
(B) Mechanism of curing with Secondary amine:

\[
\begin{align*}
\text{C} - \text{C} + \text{R}_2\text{NH} & \rightarrow \text{C} - \text{C} - \text{NR}_2 \\
\end{align*}
\]

(C) Mechanism of curing with Tertiary amine:

Table-II.2

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Epoxy resin</th>
<th>Name of curing agent</th>
<th>Curing properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2-2' bis(4-hydroxy aliphatic amine)</td>
<td>methametical relation between glass transition temperature (T_c) and crosslinked density</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Epon 828 (I) piperidine at 90°C, N-N' (II) dimethyl amine, pyridine at 50-90°C III</td>
<td>rate of crosslinking of I with II or III decreases with decrease in basicity of amines</td>
<td>117</td>
<td></td>
</tr>
</tbody>
</table>
3. Epoxy resin diamine

4. Epikote Ekikura 114
     828 (aliphatic amine)

5. bisphenol-A methylene
diglycidyl dianiline ether

6. phenyl glycidyl aniline ether

7. bisphenol-A triethylene
diglycidyl tetra amine ether

8. 3,3 2-araldite
     2,5 dimethyl
     2,5 hexa diamine
diamine

9. bifunctional aromatic
epoxy diamine
    (18-160°C)

10. DGEBA bis(m -amino
     phenyl)methyl
     phosphene oxide

11. Epoxy resin m-phenylene
     diamine

DSC, rheological data, \( \Delta E \) determined by isothermal gel time and isothermal reaction rate, 3rd order rate of reaction.

Glass transition temperature, relation between heat distortion temperature and chemical cure.

Glass transition temperature \( T_g \) by NMR \( (410^\circ K) \) in presence of absorbed water \( T_g \) reduced to \( 378^\circ K \)

Values of \( K_2/K_1 \), determination of crosslinking kinetics of epoxy resin

Mechanical properties tensile strength

IR, 45.9K/mol of activation energy, kinetics of steric hindered system

Rate of reaction, activation energy, frequency factor by DSC, cure kinetics

Resin stable upto \(<300^\circ C\), ageing 100H at 185°C did not effect the mechanical properties, significant decrease in interlaminar shear strength after boiling in \( H_2O \) for 100 and 200h.

Change in thermal tensile and dynamic mechanical properties
12. Bis methacryloxy styrene derivative of diglycidyl ether of bisphenol-A

- methyl heat of reaction and activation energy of reaction (8-333kJ/mol) by DSC, weight loss by TGA

13. Acrylic styrene/benzoyl peroxide diester styrene/methyl aniline

- kinetics of crosslinking thermal stability studied by DSC and TGA, ΔE 14.9Kcal/mol, Arrhenius constant 8.69x10⁹, shear strength increased with increasing time of crosslinking.

14. Epoxy resin tris(N,N'-dimethyl amino)methyl phenol, at room temperature and at 120°C
carboxyl terminated butadiene acrylonitrile were investigated, CTBN content increased lot sheer strength and T. peel strength increased

15. Diglycidyl ether of bisphenol-A, phenylglycidyl ether tertiary amino alcohol followed by IR & HPLC mass spectroscopy, soluble fraction and Crit conversion at gel point were determined. Three series of oligomers arise from 3 initiating centres, relative content of products depend on temperature and concentration of the initiator

16. Bifunctional primary and epoxy resin secondary amine effects of high reactivity of primary amine(1) increase extent of reaction to reach the gel point (2) Increased number of less branched species are generated during the reaction.

17. Bisphenol-A aromatic diglycidyl diamine ether resin has restricted conformational freedom owing to coulombic repulsion between O-N atoms. The segment was approximated by virtual bond ~9.5Å long.
18. Epoxy resin 4-4' and 3-3' diaminodiphenyl sulfone, bis(4-4'-amino phenox) phenyl sulfone

FTIR, reaction rate, $\Delta E$, frequency factor by DSC. A mechanism scheme for cure, mechanical and viscoelastic properties, density, flexibility and packing, density and molecular weight between crosslinks.

19. Epoxy resin piperidine DGEBA

variation of the molecular weight between crosslinks, MC, glass transition temperature versus 1/MC exhibits linear relationship, fracture toughness increases with increasing MC.

20. 1,1 bis(4-hydroxy phenyl) cyclohexane

activation energy 40-97 KJmol$^{-1}$ by DSC, TGA shows single step process with activation energy 30-50 mol$^{-1}$.

21. Difunctional m-phenylene epoxy resin diamine

crosslinked density volume expansion from room temperature to 180°C, effect of molecular packing on physical properties considered.

22. DGEBA diamino diphenyl sulfone

After 90 min. at a cure temperature all amine reaction stopped but epoxide group reaction continued, due to formation of ether linkage.

23. diglycidyl m-phenylene ether of bisphenol-A

glass transition temperatures were inversely proportional to the epoxy chain molecular weight, the average molecular weight between crosslinks agreed to within 15 to 18% with the values.
Other curing agents:— Besides acid anhydrides and amine curing agents other hardeners were also used for curing purposes. Some of which are given in Table-II.3.

### Table-II.3

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Epoxy resin</th>
<th>Name of curing agent</th>
<th>Curing properties</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Epoxy resin</td>
<td>2 ethyl 4 methyl imidazole</td>
<td>1st order reaction, activation energy (80-93KJ/mole) and pre-exponential factor (log A ≈ 9-10)</td>
<td>141</td>
</tr>
<tr>
<td>2.</td>
<td>bisphenol-A diglycidyl ether</td>
<td>carboxylic acid hydrazide</td>
<td>T increases with increase of crosslinked density.</td>
<td>142</td>
</tr>
<tr>
<td>3.</td>
<td>Epon 828 V 40 polyamide (115-165°C)</td>
<td></td>
<td>gelation time and temperature, tensile modulus, cure stress and shrinkage, thermal expansion coefficient, glass transition temperature, dynamic mechanical properties, tensile shrinkage $\approx 0.5%$</td>
<td>143</td>
</tr>
<tr>
<td>4.</td>
<td>Epoxy resin imidazole</td>
<td></td>
<td>curing rate of $\propto$ to imidazole and epoxide concentration, activation energy 70-79KJ/mole</td>
<td>144</td>
</tr>
<tr>
<td>5.</td>
<td>DGEBA</td>
<td></td>
<td>simultaneous measurement of viscosity, ionic conducting and glass temperature during isothermal curing using modified William Ferry-Landed equation</td>
<td>145</td>
</tr>
<tr>
<td>6.</td>
<td>Epitox A 1700</td>
<td>diols in presence of $\text{PhCH}_2\text{NM}_2$</td>
<td>lower crosslinked density, structure determined by DSC, HPLC</td>
<td>146</td>
</tr>
</tbody>
</table>
7. Tetra glycicyl DDS dy1-4-4' and diamino BF$_3$ Et NH$_2$ diphenyl methane

DSC shows complex nature of the reaction. Heat of reaction showed decreasing trend with increasing catalyst concentration.

8. Vinyl ester benzoyl resin peroxide at 30°C

Appreciable curing rate is obtained at lower temperature, acid value, activation energy, arrhenius factor and specific heat by DSC.