Literature Review
In 1907, first of all bakelite was prepared by Leo Backeland [8], is a phenolic resin produced from the reaction of formaldehyde and phenol. Although, Baeyer [45] discovered phenol-formaldehyde resins as early as 1872, their commercial significance was not apparent until Backeland developed an economical method using heat and pressure to covert the resins in hand, chemically resistant parts. Since first commercialized in 1909, Bakelite has been employed in numerous applications with several modifications in the conditions of the synthesis of phenolic resins.

Lee, et al. [30] and Meath [46] took a molar ratio of 1:0.5 between phenol and formaldehyde at about 80 to 95°C for the production of novolac-type phenolic resins. The basis of their work has led to optimize the molar ratios of one to up to slightly less than one by various workers till date [43-47]. They used acids, viz., sulfuric acid, p-toluene sulfonic acid, phosphoric acid, oxalic acid, etc. to synthesize the polymer.

Sandler and Karo [9] worked on the condensation reaction of phenol and formaldehyde and concluded that their did not occur reaction to any appreciable degree within days or weak at pH 3.0-3.1. On the either side of this pH, the reaction proceeded but the kinds of novolacs that resulted were different [1]. Fonrobert [49]
had already proposed the concept of pH the concluded in his work that under alkalins pH range, the condensation reaction between phenol and formaldehyde resulted in highly substituted novolacs.

Hashimoto et al. [3] have prepared the novolac resins by allowing to react a phenol with an aldehyde in the presence of an acidic catalyst, 0.1-2 mol of the acidic catalyst with 3 less than and pKa less than and 5 is used with respect to the phenol (1 mol) preferable the catalyst may be acetic acid or oxalic acid.

Epoxies have been of scientific interest for the last several decades, however phenol formaldehyde modified epoxies gained importance in early 60's for a number of high temperature applications. These polymers combine, the reactivity of the epoxy groups and thermal resistance of the phenolic backbone in the cured structure.

Epoxies were introduced commercially in 1940s, and can be considered as technological advances over the phenolic resins. Two pioneers-Pierre Caston[50] of Switzerland and Sylvan Greenlee [51] of the United States made especially important discoveries that achieved commercial significance of epoxy resins.

With the rapid development of technology for aerospace, electronic and telecommunications application, a large amount of work has been done in the development and production of high temperature polymers. Adhesives and composites that will withstand several thousand hours of usage over the temperature range of -54 to 230°C (and shorter time at higher temperatures)
are needed for advanced aerospace vehicles. In microelectronics, polymers are needed with will adhere to the substrate during processing cycles where the temperature may reach 400°C in an inert atmosphere.

In an attempt to develop better high temperature structural resins, recent work has been directed towards the modification of polyimides, polyphenyl-quinoxalines, polyacrylene ethers and polyepoxide resins. The chemistry, physical and mechanical properties of new high temperature polyimides, polyphenyl quinoxilines and polyarylene ethers have been discussed recently by Hergenrother [52].

An attempt has also been made by Kumar, Fohlen and Parker [53] to develop fire and heat resistant laminating resins based on maleimide substituted aromatic cyclotriphosphazenes. The polymer has good thermal stability and is noteworthy for its high char yield, viz., 82% at 800°C in nitrogen and 81% at 700°C in air. Further, such polymers do not form toxic products upon oxidative thermal decomposition. However, the industrial use of such polymers are limited because of their high cost.

Undoubtedly, the synthesis of high temperature polymers is a promising trend in modern material development. Modified epoxy polymers play an important role in this field. Higher heat-resistant and thermally resistant polymers are obtained if the polymer is modified by changing the aliphatic side groups of the chain backbone to highly aromatic ring content side groups (forms cardopolymers). The approach was originally practiced by Korshak, Soloveva and Kamenskh
They have prepared a series of epoxy resins with varying structural units. Thermo-analytical studies of the cured materials showed that the heat resistance and thermal stability of the polymers varied based on the varying structure of the elementary unit. The best thermal stability was obtained from polymers having a fluorine or anthrone group between the two phenyl groups using trimellitic anhydride and m-phenylenediarnine as curing agents.

Based upon these results; Chen, Bulkin and Pearce[55] prepared four new glycidyl ether-type epoxy resins from 9, 9-bis (4-hydroxy phenyl) fluorene (DGEBF), 3,6-dihydroxy spirofluorene-9, 9-xanthane (DGEFX), 10, 10-bis (4-hydroxy phenyl) anthrone (DGEA), and 9, 9, 10, 10-tetrakis (4-hydroxy phenyl) anthracene (TGETA). These resins were cured with trimethoxy-boroxine (TMB) and diaminodiphenyl sulfone (DDS). They studied structure - thermal stability-flame resistance property relationships of these resins and compared them with diglycidyl ether of bisphenol-A (DGEBA). They observed that the char yield at 700°C under a nitrogen atmosphere and the glass transition temperature (Tg) for the uncured resins decrease according to the sequence TGETA > DGEFX > DGEA > DGEBF > DGEBA. The Tg values for these cured epoxy resins are DGEBA < DGEBF < DGEFX < DCEA. They also found that the char yields at 700°C of these cured epoxy resins have the same trend as the uncured resins. DGEBF, DGEFX, DGEA and TGETA added to the DGEBA system show increase in the char yield, Tg and oxygen index with increasing concentration of these novel epoxy resins.
Martin and Price[56] have investigated the effects of epoxy resin composition, curing conditions, fillers and flame retardant additives on the flammability and have observed that the oxygen index of DGEBA cured with various curing agents is between 19.8 to 23.8. They have also found that fillers and flame-retardant additives can increase the oxygen index to a certain level dependent on the material and the amount used.

Factor and Orlando [57] have found that 1,1-dichloro-2,2-bis (4-hydroxyphenyl) ethylene (BPC) which does not contain aromatic side groups also have a very high oxygen index. Lin and Pearce[58-59] reported that the TMB-cured diglycidyl ether of phenolphthalein (DGEPP) has a char yield at 700°C of 47% compared to 26% for the TMB-cured diglycidyl ether of bisphenol-A (DCEBA). The oxygen index for these two materials varies in a similar manner from 43.0 to 20.5, respectively.

The cardo polymers have high heat resistance and thermal stability. Polymers which are classified as "Cardo" or "loop" polymers have groups which can be regarded as loops in relation to the main chain of the macromolecules [60].

Lopata and Riccitello [61] have investigated the TMB-cured bisphenol-A epoxy system by differential thermal analysis (DTA) and found that there are three exothermic peaks at approximately 390°C, 430°C and 470°C, with the major exotherm at 430°C. They have also studied the kinetics of TNB-induced thermal polymerization of phenyl glycidyl ether (PGE) by using
infrared absorption spectroscopy and gel permeation chromatography to follow the course of the polymerization and in addition, proton and boron-11 NMR spectroscopy are used to support the kinetic model developed. The mechanism that is proposed involves a fast initiated, non-stationary, cationic polymerization with five elementary steps, including spontaneous transfer and monomer transfer steps as well as a termination reaction. Chen et al. [62] proposed a modified mechanism for the polymerization of PGE with TMB. This mechanism does not account for the formation of small amounts of methanol. This study shows that CH$_2$OH, C$_2$H$_7$OH and C$_6$H$_5$OH appear to be volatile by products from the reaction of PGE and TMB. Based upon this they proposed an additional termination step to account for the formation of the respective hydroxyl compounds.

A polymer with high aromaticity and/or cyclic ring structured chain backbone usually has high heat, thermal, and flame resistance. The attempt has been made to modify epoxy polymers with phenol formaldehyde resins in order to further increase the range of properties and further extend their area of use especially in high temperature applications.

Ivinson et al. [63] discussed the differences in functionality of diepoxide (DGEBA) and polyepoxide (epoxidised novolac) resins with special reference to their behaviour with various types of amine used for hardening the resins. Meath [64] observed that because of multi-functionality, the epoxidised novolac resins, when cured with any of the conventional epoxy curing agents
produce a tightly cross-linked system with improved elevated temperature, performance, chemical resistance, and adhesion, than the bisphenol-A based epoxy resins (DGEBA). The authors reported that the thermal stability of a cured epoxidised novolac resin is affected markedly by the length of the cure cycle.

Ohara et al. [65] have prepared the novolac from o-cresol, 2, 4-di methylol-phenol, and phenols in the presence of acidic catalysts are reacted with epihalohydrins to give novolac epoxy resins containing greater than and equal 2 glycidyl group/mol. and average of 2.1-3.9 glycidyl group /mol.

Further, in the year 2003, Lin-Gribson et al. [66] studied the reaction conditions, viz., pH, molar ratio of phenol-to-formaldehyde (P/F) etc. in the production phenol-formaldehyde novolac resins they concluded that under neutral it acidic condition resulted novolacs having P/F ratio 1:(0.75-0.80) while under basic conditions resoles resulted with P/F ratio of 1:(1.0-3.0).

Martin [67], Malhotra and Kaur [68] reported. The rate of formation of dihydroxydiphenyl methane (condensation reaction) has been more than five times and 10-13 times as fast as the formation of hydroxy methyl phenol (substitution reaction).

Roezinak and Biemach [69] reported some physical and chemical properties of novolac and resole resin prepared with phenol and formaldehyde using various catalysts.

Born et al. [70] prepared pure novolacs, by using PHOH or alkyl or haloderivative with aldehyde in the molar ratio of 1.5:1 in
They also used the same constituents for synthesis of pure novolacs at atmospheric pressure. Shitooka and Yasuhara [71] synthesized low molecular weight novolac resin in high yield by refluxing phenol, formalin and oxalic acid as catalyst at 100°C at reduced pressure having number average molecular weight 520.

Stockinger and Haug [72] synthesized the modified novolacs using ortho or para substituted phenols with aldehydes or ketone and disubstituted anilene in specific ratios of pH 0.5-3.0 infrared spectra and aromatic structure of the resins are reported in these studies. The reactivity of various resin showed the gelation kinetics depends on the ratio of reagents and on the structure of resins.

Alma et al. [73] prepared calabrian pine novolac resin by condensation of barks of calabrian pine (Binus brutia) and Anatoua chest nut (Castenia sativa) with phenol in presence of sulphuric acid at 130°C for 1 hours. This product was cured with hexamethylenetetramine (HMTA) at 190°C for 5 minute. The thermal properties were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) method. The result showed that thermogravimetric weighted losses and glass (T_g) of the cured phenolated bark decreased with increasing catalyst concentration.

Seung-Hwan et al. [74] synthesized Corn Bran (CB)/phenol-formaldehyde condensed resins at high temperature
(200°C) under high pressure (> 1 atm) and obtained liquefied products. The obtained products were examined for their thermofluidity, thermo setting reactivity and flexural/properties of the thermosetting moldings prepared there form and these properties were compared were those obtained for the liquefied products before condensation. These C.B. products are used for manufacturing of biomass products including agriculture-production wastes, food industry waste, and other phenol formaldehyde novolacs have largely been epoxidized with epichlorohydrin (ECH) to obtain epoxies which have been referred to as epoxy novolacs in the remaining text of this thesis.

Union Carbide Corporation[75] proposed an infusible product having excellent physical, chemical and electric properties with good storage stability. The product was obtained by curing epoxidised novolac resin with phenol formaldehyde novolac resin and imidazole composition.

A finely divided heated solid chemical - inert material such as sand or heated glass beads were embedded with a high molecular weight epoxidised novolac resin to decrease the time required for complete curing at elevated temperature. This technique was developed by Schmitz[76]. The coated panels and molded articles were prepared by this technique successfully.

Kanekawa et al.[77] investigated heat resistant modified epoxy resins from primary condensates of phenol and formaldehyde in presence of basic catalyst which were treated with resorcinol
and further treated with epichlorohydrin in presence of basic compounds. The resin was cured with nadic methyl anhydride and benzylidimethylamine for 2 hrs at 120°C and 3 hrs at 150°C to give test pieces having heat distortion temperature of 179°C, barcol hardness 47, flexural strength and modulus 132 and 361 kg/mm² respectively, and water absorption after boiling in water of 0.59%.

Generally, the amount of char produced in controlled pyrolysis (TGA) and in some hyperthermal environments, is proportional to the crosslink density and the amount of aromaticity in the original structure. Fleming[78] investigated the mechanisms initiating the unusual thermal degradation of epoxidised novolac resin cured with methyl nadic anhydride (MNA). He observed that MNA lends no aromaticity to the polymer system and seems to give a low crosslink density. Therefore, it seems apparent that a constructive degradation mechanism is operative. He suggested two mechanisms each assuming greater importance than the other depending upon the severity of the thermal environment. One is an internal acid - initiated mechanism operating from 240 to 350°C under slow heating rates. The other is a reverse Diels-Alder reaction which operates above 350°C, usually under instantaneous pyrolysis conditions such as encountered in ablation. When reverse Diels-Alder reaction occurs, the backbone of the polymer is left virtually intact with a double bond at every prior MNA site. Further crosslinking and possible ring formation occur via free radicals formed in this
pyrolysis through the olefinic linkages. On this basis, Fleming explained the greater quantities of char are formed with MNA-cured systems than with similar systems such as tetrahydrophthalic anhydride-cured epoxies. These two mechanisms, working simultaneously, promote further crosslinking of the resin system giving rise to a greater amount of carbonaceous residue than would otherwise be expected.

Epoxidised novolacs contain phenolic hydroxyls along with epoxy groups, which on heating elevated temperatures oven in presence of curing agent result in crosslinking of epoxide molecules themselves due to hydroxyl-epoxy reactions similar to that in homopolymerisation. The curing reaction that lead to crosslinking in presence of a reactive/polyfunctional curing agent such as DDS, MNA etc. have been referred to as hetopolyaddition reactions[79]. The curing reactions of such epoxies involve chain mechanism and the product of a reaction becomes a reactant for the another reaction. Kumar and Mathur[80] studied the mechanism of curing reactions of polynuclear epoxidised novolac resins with DDS by differential scanning colorimetry. They observed that the cure kinetics may be much more complex than reflected by the Borchardt-Daniels equation [81], \( \frac{d\alpha}{dt} = K (1-\alpha)^n \) where 'n' is reaction order. Therefore the equation \( \frac{d\alpha}{dt} = K (1-\alpha)^m \propto m^{-1} \) where m and m' are empirical constants deduced by Zsako[82] has been considered a more general forth of the formal equation to elucidate the mechanism of cure. It was recognized
that the reaction rates of such epoxies were more linearly related to the fraction reacted ($\alpha$) than fraction unreacted ($1-\alpha$). From the mathematical signs of empirical constants of Zsako's equation, the $f(\alpha)$ appeared to have the form $\alpha/(1-\alpha)$. The dependence of reactions on $\alpha$ indicated that they were rather heterogeneous and perhaps affected by several factors like rate of diffusion of the components to or away from the reaction interface, rates of nucleation and growth of nuclei, geometry of the reaction interface etc. Furthermore, the term $\alpha$ in numerator in both the situations indicated that the kinetic model(s) applicable to curing reactions were perhaps exponential i.e. the curing process never be absolutely complete, whereas the term $(1-\alpha)$ in denominator indicated that perhaps the former reactions were diffusion controlled.

Partansky and Scharaner [83] and Howe et al. [84] were perhaps the first and second respectively. To synthesize epoxidized novolacs based on phenol and formaldehyde, they found to short-term high temperature stability and the chemical versatility of these resins.

The simplest novolacs are used for the synthesis of epoxy novolacs has been p:p dihydroxy di-phenyl methane or bisphenol-A. However higher novolacs containing more than two phenolic hydroxyls have also been used for the synthesis of epoxy novolacs. The number of phenolic hydroxyls in the base novolacs determine the functionality of the resin depending upon the
degree/extent of its epoxidation. Theoretically all the phenolic hydroxyls of a novolac/should get epoxidized by reaction with epichlorohydrin (ECH). However, it has not been practically observed to be so because of steric hindrances. As a consequence, several polymeric species differing in their chain lengths/molecular weights and functionality have often been encountered in epoxidized novolacs. The usual functionality of epoxy novolacs is more than 2.5 and up to 6.0 or even higher [85-86]. The most popular and versatile class of epoxies based on novolacs is glycidyl ether of novolacs prepared from phenol and formaldehyde. On the basis of commercial importance novolac based on substituted phenol (Cresol) and formaldehyde have been used extensively, captured second position, instead of their high prices.

Bauer [87] produced epoxy resins by void-free phenolic networks by reacting novolacs oligomers with an excess of epichlorohydrin (ECH). These epoxidized novolacs were of high strength, excellent dielectric properties and improved oxidative resistance. Meath [88] and Potter [89] found that the usual functionality of epoxy novolacs was more than 2.5 and up to 6.0 or even higher.

Lee and Neville [30], Potter (90), Lazzerine et al. [91], and Vasistha and Kaushal [92] carried out epoxidation of novolacs with epichlorohydrin (ECH) under alkaline conduction in the temperature, range 100-120°C, (usually at 112 ± 2°C). An excess of epichlorohydrin than the theoretically required stoichiometric amount in a ratio of 2:1 between epichlorohydrin and bisphenol-F
has been suggested by several researchers to get pure and low molecular weight epoxies in over 90% yields.

Goppel [31] reported the use of aqueous caustic solution in the epoxidation of novolacs as it does not occur under anhydrous condition to act as catalysts for the phenolics hydroxyl-epoxide reaction. The water content of the reaction mixture is required to be maintained between 0.3 and 2% by weight throughout the reaction. For obtaining desirable products in high yield (90-95%). He also suggested that if the water content of the reactions mixture exceeds 2%, undesired by products are formed.

The epoxidation of novolacs with epichlorohydrin is carried for a period of 3-4 hours under reflux condition at 112 ± 2°C, during which the aqueous caustic solution is added gradually. After the addition of alkali, the reaction is further continued for an additional period of ½ hours at the end of which the excess epichlorohydrin is recovered from the reaction mixture by distilling it under vacuum. The crude reaction mass is then dissolved in a suitable solvent (usually to keen) to separate salt sodium chloride (NaCl) by filtration. The resin from the filtrate is then recovered by distilling of the solvent under reduced pressure.

Chetan et al. [93] synthesized novolac with different mole rations varied in different reaction between1:0.5 and 1:0.8, oxalic acid was used to catalyst. The polycondensations were conducted in 500 ml three necked round flask at 90°C for 6 hours with constant stirring. The unreacted monomers were distilled out at
reduced pressure at elevated temperature to obtain the resin. The resin was dried in desiccator over phosphorus pentoxide. The softening temperature was estimated with sealed glass capillaries on a meting point apparatus.

Stanley et al. [94] developed a low molecular weight phenolic resin was made by drop wise addition of 600g (7.4 mol) of 37% formaldehyde into 3500g (37.2 mol) of phenol and 17 gm (0.2 mol) of oxalic acid at 100°C. The temperature was maintained at 100-110°C for 1 hours differ the addition. The reaction mixture was vacuum distilled and a fraction of Bisphenol-A was collected temperature 340-360°C. The resin is characterized by carbon 13 nuclear magnetic resonance $^{13}$C-NMR chemical spectroscopy. The $^{13}$C-NMR chemical shifts of positional isomer of Bisphenol and bismethanes are reported. The $^{13}$C-NMR chemical shifts of these oligomers are assigned and grouped into classes. These data are useful for understanding of more complete resin system.

Leonard [95] proposed a kinetic model for the acid base catalyzed condensation of m-and p-cresol with formaldehyde it differs from previous model in that, rather than considering the two reaction steps separately it describes them together using relative reactivities of reactive ring position. In a typical reaction, m-cresol (296.99-2.075 mol), oxalic acid dehydrates (299.9, 0.24 mol) and diglyme (290.1g) were mixed to dissolve and heated under nitrogen to 99°C. A solution of formation (1590 x 36.6% W/W HCHO = 57.72g, 1.92 mol) in diglyme (57.5g) were added at once. The solution was stirred under nitrogen at 99°C for 3 hours
and then the volatite components were distilled. During the distillation the temperatures maintained 215°C.

Nyquist [96] studied infra-red spectra of epoxy resins. The major bands arise from hydroxyl groups (2.9 µm), aromatic ether (8.1 µm), aliphatic ether (9.6 µm) and the p-substituted benzenes nucleus (12.0 µm). The most obvious band of the terminal epoxy group appears at 10.9 µm, with further less obvious bands at about 11.8 µm and 13.2 µm. He observed that the spectrum of epoxidised novolac resin has all the features of that of the epoxy resin based on epichlorohydrin and bisphenol-A but in addition the substitution pattern bands of phenol-formaldehyde resin appear at about 12.2 µm and 13.3 µm. This product may also be distinguished from a mixture of phenol formaldehyde resin and epoxy resin (Bisphenol-A epichlorohydrin) by the absence of a strong phenolic hydroxyl band near 3.0 µm. Infrared quantitative measurements of epoxy content have found their major application in estimating the degree of cure of epoxy resins. In the curing process the terminal epoxy groups disappear, and their disappearance may be conveniently followed by measurement of the intensity of the 10.9 µm band. A quantitative method is suggested by Burge and Geyer [97].

Gel Permeation Chromatography (GPC) is a useful tool for calibration of epoxy resins [98], kinetics of epoxy resin synthesis[99] application and characterization of epoxy resins [100].
The techniques of Differential Scanning Calorimetry (DSC) applied to polymerization studies have been investigated by Eava[101] using epoxy resin system. He described the cure behaviour and reaction kinetics of epoxy resins by DSC. He obtained three different methods of producing isothermal cure curves for epoxy resins. One of these methods yielded indirectly information related to the curing reaction during the first records of an idealised isothermal experiment and has important applications in fundamental studies of rate processes. The isothermal method of obtaining cure curves is suitable if very little happens to the resin during the first few minutes at the cure temperature. Otherwise the exotherm is distorted by heating effects. This method is therefore suitable for cure times of the order of hours. If the cure proceeds for longer than about six hours, the exotherm is generally too slight to be detectable accurately by this apparatus. For these cases, he suggested to use the third method in which the residual exotherm of partially cured samples is detected by a scanning technique. He considered the suitability of applying simple kinetic laws to the reaction from the cure curves. He examined that the Arrhenius equation appears to be applicable giving activation energy for the curing process. The relationship between glass transition and cure was also explored.

Nobel [102] synthesized epoxy novolac resin, which was produced from O-cresol, formaldehyde and epichlorohydrin. In the preparation of novolac 800 gms of a 30% aqueous solution of
formaldehyde was added drop wise with in 3 hours to a mixture of o-cresol 2500 gm, concentrated HCl 100 ml and water 200 ml at 90°C with stirring. The stirring was continued for 2 hours at 95-100°C and water distilled off. Excess cresol was removed in vacuum and for epoxy resin 200 ml of water added to a solution of 400 gm novolac in 400 gm epichlorohydrin at 55-60°C. Then 195 gm sodium hydroxide in 800 ml. Water was stirred for another 2 hours at 80-90°C and resin dried under vacuum.

Albert [103] synthesized epoxy resin from epichlorohydrin and 'monophenols', which were produced from formaldehyde and phenols (phenol, ortho and para cresols, and para tert butyl phenol) in the presence of alkali catalyst. The resin formed had better properties in comparison with bisphenol-A based epoxy, as they were self cured and also had a longer pot life with acid catalyst during storage.

Bradley and Newely [104], synthesized epoxidized novolac resin by condensing epichlorohydrin with a novolac resin of a monohydric mononuclear alkyl phenol containing at least four carbon atoms in the alkyl group. The novolac resin contained 3-12 phenolic hydroxyl group per average mole and was prepared by condensing a phenol and aldehyde in the presence of an acid catalyst with about 0.4-0.9 moles of aldehyde per mole of phenol. The epoxidized novolac resin was made by mixing the novolac resin with at least 3 moles of epichlorohydrin per phenolic hydroxyl equivalent of novolac resin and with the addition about 1 mole of alkali metal hydroxide per phenolic-hydroxyl equivalent.
The reaction mixture was kept at 60-150°C and when completed. The epoxidized novolac resin was removed and purified.

Hass et al. [105] developed epoxidized novolac resin from m-cresol 811, oxalic acid 11.8, 35% a aqueous formaldehyde 579 gm, and water 125 ml was refluxed for 2 hours. The solution was neutralized by 10% NaHCO₃, 2 ethoxy ethyl acetate 1.25 liters added and the water removed by distillation. The resultant mixture was mixed with para-formaldehyde 6.25 and oxalic acid 5.0 gm stirred 5 h at 110° neutralized with 100% aqueous NaHCO₃.

Ohara et al. [106] prepared nevolac resin from o-cresol, 2.4 dimethylol phenol and phenol in the presence of acidic catalyst are reacted with epichlorohydrin to give novolac epoxy resin contain ≥2 glycidal groups/mol and average of 2.1-3.9 glycidyl groups / mol.

Roth et al. [107] synthesized novolac epoxy resin acrylates by stirring solution of cresol novolac epoxy resin Me₄N⁺Cl and bisphenol-A at 130°C for 6 hours, they collected 68.4% solution of advanced resin with epoxy content 2.85 mol/mg and weight average molecular weight 16,050 esterification of which with acrylic acid gave 68% solution of resin with molecular weight 23,978 and epoxy content 0.05 mol/kg. A photo resist formulated with this resin had wedge sensitivity stage 11, Vs 2.3 with a conventional epoxy resin as acrylates.

Takao et al. [108] reported the synthesis of new o-cresol epoxy resin containing oxy ethylene units and were compared to a
conventional o-cresol novolac epoxy resin. New epoxy resin gives a cured resin with higher flexibility.

Clair [109] and Orobchenko et al. [110] worked on epoxidation reaction with epichlorohydrine (ECH). They infered that the water content of the reaction mixture is maintained in the desirable range either by controlling the rate of addition of aqueous alkali during the reaction alongwith distilling off the water as an azeotrope with epichlorohydrine and returning epichlorohydrine back to the reaction vessel after the separation of water, or by carrying out the epoxidation reaction in alcoholic mechanism.

Partansky and Scbrader [111] and Howe et al. [84] were perhaps the first and second, respectively, to synthesize epoxidized novolacs based on phenol and formaldehyde. These researchers also claimed the values of these resins for its short-term high temperature stability and the chemical versatility of the epoxide group. Since then several scientific reports on the properties and applications of epoxy novolacs have appeared in the literature.

Omura and Murakami [112], and Umeyama [113] have recommended a large number of applications of epoxy resins based on novolacs and their use either in as is form or in blends with other resins, particularly the halogenated ones, Parkinson [114] Sumida and Iida [115] have used for printing inks of epoxy resins based on novolacs, Fujiki et al. [116] water resistant coating, Yamakoshi et al. [117] water repellent coating, Bicart
stabilization of polyvinyl chloride (PVC), Maeda et al. [119] heat resistant adhesives, Yagon et al. [120] and Avrasin [121] glass fiber laminates, Hanrahan et al. [122] ultraviolet curable coatings and inks, Bialan et al.[123] absorbing coating composition, Livova and Shizorin [124] water thinned coatings for protective purpose, Tanaka and Suzuki [125], Kodama et al.[126] semi-conducting scaling compositions, Nikuchi et al. [127] insulating varnishes for coil winding, Mogurran [128], Horowitz and Mangaraj [129] binding abrasives sealants for semi conductor and electronic devices auto mobile coating, Balan et al. [130] heat resistant coatings for printed circuit boards, coating for edges and slots of motor parts, Aprasina et al. [131], Dyer et al. [132] and Inomata [133] chemical resistant coating, Kittamura et al. [134]. Nagata et al. [135] potting and sealing compositions, Hanmori et al. [136] electrical insulating coating, Nishii et al. [137] corrosion resistant coatings, Nakao Isato [138], Arita et al. [139] thermal shock resistant composition, Sirotal et al. [140] electrode position coatings, Bertram et al. [141], Naotomi et al. [142] general purpose curable compositions with improved mechanical electrical and thermal properties, Jandel et al. [143], Uno et al. [144], Bymark et al. [145] and Miyazawa et al. [146] improved mechanical properties coating compositions.

In phenol epoxy reactions, the reactions mechanism and the extent of side reactions are highly dependent on the reactions conditions and catalysts employed. The reaction between the phenolic hydroxyl groups of novolac oligomers and the epoxide
may be catalyzed with a wide variety of catalysts including acids, bases, tri aryl or tri-alkyl nucleophilic, of group 5a compounds [147], and quaternary ammonium complexes [148]. Typically, tertiary amine or phosphine catalysts are employed, with triphenylphosphine being the most commonly used reagent.

Romanchick et al. [149] proposed a mechanism for the triphenylphosphine catalyzed phenol-epoxy reaction. In the first step, the triphenyl phosphine catalyst ring-opens the epoxide ring and produces zwitterions. A rapid proton transfer follows this form the hydroxyl group of the phenol to the zwitterions. The third step of the mechanism shows two reactions pathways available for the phenoxide molecule. Phenoxide may react with the electrophilic carbon next to the phosphorus of the secondary alcohol, regenerating triphenyl phosphine, or it may react with another epoxide ring and abstract a proton from a phenol molecule, thus regenerating the nucleophilic.

Bortan [150] reviewed with 116 references on the use of DSC as a method of monitoring and investigating the kinetics of epoxy resin curing reactions, especially using carboxylic acid anhydrides, primary arid secondary amines, dicyandiamide and imidazoles as crosslinking agents.

Jaeqers and Gedemer[151] proposed a new approach for evaluating track resistance of certain epoxy compounds by TGA. They reported that the percent residue obtained by TGA correlates reasonably well with a calculated carbon-forming tendency
with results of a modified ASTM track test (D2303). Except systems cured with phthalic anhydride. They investigated that materials which have a low calculated carbon-forming tendency yield less than 25% residue by their TGA method and have a high degree of track resistance.

Epoxidised novolac resins have been reviewed for their use in different areas by Srinivasan and Kapur [152]. To add to this already rich field of epoxy functions, a new approach in recent research which features the thermal behaviour of epoxy phenol formaldehyde novolac block copolymer and have not as yet been widely exploited. The approach was originally reported by Russian scientists in 1968.

Dokhturishirli [153], suggested synthesis and curing of epoxy novolac block copolymer which was used as binders for glass fibres to give reinforced plastics having flexural strength of 3250-3550 kg/cm², impact strength of 105-120 kg/cm², specific volume electrical resistance 3.0-7.8 x 10¹³ ohm cm, sp. surface elect, resistance 2.0-2.7 x 10¹³ ohm and electrical strength 21-25 KV/min. It was observed that the heat resistance of epoxy novolac block copolymer was greater than that of epoxidised novolac resin.

The crosslinking kinetics of epoxy novolac block copolymer in the presence of seven amines was studied by Yartsev et al. [154]. It was found that products obtained in the presence of hexamethylene-tetramine (HMTA) acted as a catalyst had most
homogeneous structure with best physico-mechanical and processing properties and suffered smallest weight losses during the crosslinking.

Epoxy novolac block copolymer compositions were described for use as quick setting adhesives [155], with increased heat resistance and hardness [156], better heat resistance [157], foam composition [158], and suitability for commercial production [159].

Sumitomo Bakelite Co. Ltd. [160] developed a rapid setting epoxy resin prepared by epoxidising a condensate of phenol derivative, primary amines and formaldehyde and cured with novolac curing agent by using imidazole as a curing accelerator. They suggested that the mixture is especially useful in potting semiconductor devices.

An epoxidised novolac resin acrylate with good physico-mechanical properties and resistance to thermal aging was obtained by treating a novolac (as above R=H, R' = C_{1-10} alkyl) with epichlorohydrin to give the glycidyl ether, esterified with an unsaturated monocarboxylic acid (structure as shown above)

$$[R = \text{CH}_2 \text{CH (OH)} \text{CH}_2\text{O}_2 \text{CCH: CH}_2; R_1 = \text{C Me}_3]$$

and crosslinked with a compatible ethylenically unsaturated movement. The approach was suggested by Yasno and Toyoidi
They observed that the cured polymer had bending strength of 645 and 644 kg/cm², flexural modulus of 20, 900 and 30, 200 kg/cm², tensile strength of 431 and 558 kg/cm², elongation 3.8 and 1.7% and Barcol hardness 40 and 53 before and after 200 hr at 150°C respectively. Brewbaker and Sprenger [162] recognized that polyalkylene glycols are good low profile additives for such resins prepared by treating an epoxidised novolac resin with an unsaturated carboxylic acid. Marimichi et al. [163] investigated the use of hydroquinone and 0-nitro catechol to inhibit the generation of heat during the gelation of the resin which when added to the reaction products of epoxy resin with acrylic acid or methacrylic acid. It was observed that the composition were gelled at maximum temperature 30°C, compared with 72°C for a similar composition without hydroquinone.

Mitsubishi Petrochemical Co. Ltd., Japan [164-165] formulated a thermosetting resin with good heat and fire resistance by esterifying brominated novolac epoxy resins with methacrylic acid in the presence of tetramethyl ammonium bromide. This nonflammable plastic had heat distortion temperature of 140°C and had excellent solvent and alkaline resistance.

Felicia et al. [166] investigated the use of phenol-formaldehyde resins to improve the heat resistance of epoxy resins from bisphenol-A, halogenated bisphenol-A and epichlorohydrin. They prepared a glass fabric reinforced laminate containing the resin, dicyandiamide hardner and benzylidimethyl amine catalyst which exhibited static bending strength 150 N/mm²
at 150°C, compared with 75 N/mm² for a laminate from a similar resin prepared in the absence of phenol-formaldehyde resin.

A highly pure flame-retardant epoxy resin with excellent heat and moisture resistance were prepared by Keiichi and Minoru[167] by forming brominated novolac chlorohydrin from the addition reaction of brominated novolac with epichlorohydrin in presence of a catalyst.

Toho Beslon Co. Ltd., Japan[168] suggested prepreg for the production of heat and impact resistant composites which were prepared by impregnating carbon fibres with a resin composition containing a poly functional maleimide, epoxidized novolac resin and imidazole. Toray Industries, Inc., Japan[169] developed prepreg resins for preparing carbon fibre composites materials having excellent impact, heat and water resistance as well as high mechanical characteristics necessary for structural materials. These resins were composed of epoxidized novolac resin, bisphenol-A epoxy resin, tetraglycidyl diaminodiphenyl methane and diaminodiphenyl sulphone.

Hitachi Chemical Co Ltd., Japan [170] prepared good heat and water resistant resin composition by modifying bisphenol-A epoxy resin with novolac epoxy resin. It was observed that the cured composition had heat distortion temperature of 165°C Vs 109°C using a bisphenol-A epoxy resin instead of epoxy resin mixture.
Klans et al. [171] reported that chlorinated PVC Contq. 60-74% Cl is stabilized for processing at high temperature by the addition of a glycidyl ether of a phenol or cresol novolac resin 0.03-10, a metal compound like Ca stearate, Zn stearate etc. 0.1-5, and conventional additives of 05 phr. The approach as suggested earlier by Kunimara et al. [172] and Bicart[173].

High temperature properties are influenced strongly by incorporating aromaticity into a basic resin structure. Recently many investigators have synthesized high T_g epoxy system by epoxidation of polynuclear polyhydroxy phenols. Chan et al. [174] prepared high temperature epoxy polymers from the epoxidation of tris (hydroxyphenyl) methane and cured with 4,4' diaminodiphenyl sulphone. They have studied time-temperature transformation (TTT) diagram of such epoxy systems and compared its cure and thermal degradation behaviour with similar DGEBA system. They found char residue 46% at 470°C and 75% at 300°C for 20 hrs in high T_g epoxy system as compared to 18% at 470°C and 50% at 300°C for 20 hrs in DGEBA epoxy system. Shigeru et al. [175] also formulated polyhydric polynuclear phenol with structure as shown below and-
epoxidised it in the same fashion as DGEBA. The resin was cured with methylenedianiine. The resulting resin had glass transition temperature 330°C and heat distortion temperature 277°C.

A similar approach has been followed by researchers at Sumitomo Chemical Co.Ltd., Japan [176]. They prepared polynuclear phenols by reaction of phenols comprising I, II and III as shown below (R-R₅=H, alkyl, arom, halo; R₆-R₈=alkyl, aryl, halo) with unsaturated aldehydes CₙH₂n-₁CHO (n=2-6) and saturated aldehydes in the presence of acid catalysts. The resulting polynuclear phenols reacted with epichlorohydrin to produce heat resistant epoxy resin having softening point 69°C, epoxy equivalent weight 197, hydrolyzable chlorine 0.06 weight % and average number of phenyl rings 5.3.

![Chemical Structures](image)

The approach for preparing new phenol formaldehyde dimeric model compounds and isomeric trimeric model compounds were suggested earlier in 1967 by Peterson et al. [177]. They have synthesized such compounds and studied their structures in detail.

In an uncatalyzed reaction generated from the initial phenol- epoxy reaction can react with another epoxy to give a branched species. Branching is undesirable in the pursuit of high
molecular weight polyhydroxyether. The extent of the branching reaction may by limited with the use of satirically hindered catalysts such as those described above [178].

Gagnebien et al. [179] have commonly use to aliphatic amine catalyze phenol reactions. The melt reaction mechanism of tertiary aliphatic amine- catalyzed phenolic-epoxy reaction. In the first step, trialkylamine abstracts a protons from the phenol to from an ion pair. The ion pair complexes with the epoxide ring and the complex dissociates to from a β-hydroxy ether and trialkylamine.

Phenol-epoxy reaction exhibit three different side reactions: epoxy homopolymerization, a branching reaction through the secondary hydroxyl, and zwitterions catalyzed branching through the secondary hydroxyl. The branching reaction is the predominant side reaction. However, the extent of branching should decrease as the ratio of epoxy to phenol decreases because the phenolate amines are more nucleophilic than the competing aliphatic hydroxyl groups. Batzer and Zahir [180] also used NMR (Nuclear Magnetic Resonance) technique to obtain informati’n on extent of branching and structure of epoxy resins.

Lee and Vincent [181], Huang [182] have largely used IR (Infrared) spectroscopy to get molecular structural information on epoxy groups in uncured and cured epoxy resins. The characteristic bands for terminal, internal and substituted epoxy at different wave numbers. John and Goetzky [183] reported
epoxy resins of low molecular weight does not require much preparation for determining their IR-spectra, but in case of high molecular weight epoxies and cured epoxies.

The chemical methods of determining epoxide equivalent weight usually depend upon the reaction of an hydrogen halide with the epoxide, yielding the halohydrine. Amount of hydrogen halide consumed is a measure of the epoxide content, is obtained either directly or indirectly by using an excess of hydrogen halide followed by back titration. Lee and Neville [30], Lakiza et al. [184] have reported several hydrogen halides employed in different methods of quantitation of epoxide equivalent.

Bring and Kadlecek [185] have determined hydroxyl equivalent of epoxy resins which refers to weight of the resin containing one equivalent weight of hydroxyl group by near infrared spectroscopy or chemical methods. Chandros and Sharpe [186] have proposed typical anionic catalyst that are use us tertiary amines, metal alkoxides, tri-ethanol, amine, borate and imidazoles and their derivatives. Excepting imidazoles and their derivatives, the other anionic catalysts require long cure cycles and provide products with poor thermal properties. Landau [187] has used halides of Tin, Aluminum, Zinc, Borane, Silicon, Iron, Titanium, Magnesium and antimony as cationic catalyst. Among these, the commercially important catalysts are di-ethylether, tetrahydrofuran-, aliphatic amine-, and aromatic amine-, Borontrifulide (BF₃) complexes. Cationic catalyst are used either in conjunction with other curing agents such as acid anhydride or
laminating compositions. However these curing agents are problematic to us because of corrosion and gassing under high vacuum.

Takecuehi et al. [188] have used both aliphatic and aromatic type of polyamines for curing for epoxy resins. Aromatic polyamines usually require much higher and elevated temperatures than those required by aliphatic polyamines for epoxy cures. Certain commonly used aliphatic polyamines are triethylene, tetramine, dimethyl and diethyl-aminopropylamine, ethylene di- and tri-amine, and hexamethylene diamine, which cause epoxies to cure rapidly at moderate temperature the aromatic polyamines that have generally used m-phenylene diamine (MPDA), diaminodiphenyl methane (DDM), diaminodiphenyl, sulfone (DDS) and Methylene dianiline. Since aromatic polyamines are mostly solid, these require dissolution in resin at higher temperatures otherwise difficulties in their mixing with or dispensing in resin are encountered. A majority of polyamines are skin-sensitize and require special precaution in handling and use.

Kawakmi et al. [189] have used in coatings compositions of polybasic inorganic and organic acid such as phosphoric, oxalic, adipic citric, sebalic and maleic acids, carboxyl terminated polyester and polymeric dimer and trimer fatty acid. Ito et al. [190] proposed the polyamide used to cure epoxy resins are aminopolyamides or polyamidoamines. These are largely prepared from the reaction of di-, tri- and polymerized fatty acids and their products with polyamines, which have low viscosity and amber
colour. There are comparatively easy to handle and are used in costing, Sealing, coating, and Adhesives formulations for water-resistant.

Kawamoto et al. [191] have studied acid anhydrides constitute an important class of curing agents for epoxides, and include linear aliphatic, alicyclic, aromatic, halogenated polymeric, and di-anhydrides. Nadic, nadic methyl, phathalic, tetrachlorophathalic anhydrides, hexahydrophthalic, dodecenyl Succinic, trimellitic and polysebacic anhydrides are some of the commercially important members of this class of epoxide curing agents. Anhydrides have preferred for epoxy cures where long pot lives, good electrical properties, an better high temperature stability are desired in the cured products.

Shigeo et al. [192] synthesized and moisture resistant epoxy resin potting composition for electronic devices. The components contain epoxy resin bearing ≥ 2 epoxy group per mol. Compounds bearing ≥1 active ester group curing accelerator and 60-85% inorganic filters. A compound contains cresol novolac epoxy resin [ESC95] 80, phenolic novolac resin and brominated bisphenol-A epoxy resin 1.3 parts N-methyl imidazole and quaty powders and heated to give cured product showing good heat and moisture resistance.

Smith [193] used aliphatic and aromatic polyamines for curing reaction of epoxidized novolacs. Dannenberg [194] explained a primary amines are fastly reacts with an epoxide
group forming a secondary amine with secondary hydroxyl groups. The secondary amine produced from this reaction are used as a starting curative in epoxy cures react with another epoxy group to form a tertiary amine with a secondary hydroxyl groups.

Kumar and Mathur [195] studied the mechanism of curing reaction of polynuclear epoxidized novolac resin with diaminodiphenyl sulfone (DDS) by differential scanning calorimetry (DSC). The observed that the cure kinetics may be much more complex than reflected by the Borchardt-Danial's equation [139]: \( \frac{d\alpha}{dt} = K (1-\alpha)^n \) where 'n' is reaction order. Therefore the equation \( \frac{d\alpha}{dt} = K (1-\alpha)^m \propto m^1 \) where m and m^1 are empirical constants deduced by Danial has been considered a more general form of the formal equation to elucidate the mechanism of cure. It was recognized that the reaction rates of such epoxies were more linearly related to the fraction reacted (\( \alpha \)) than fraction unreacted (1-\( \alpha \)). Form the mathematical signs of empirical constants of Zsakoss equation, the f (\( \alpha \)) appeared to have the form \( \alpha/(1-\alpha) \). The dependence of reaction on indicated that they were rather heterogeneous and perhaps affected by several factors like rate of diffusion of the components to or away from the reaction interface, rates of nucleation and growth of nuclei, geometry of the reaction interface etc. further more the term is numerator in both the situations indicated that the kinetic model (s) applicable to curing reaction were perhaps exponential.
Nobel [196], cured epoxy resin with novolac catalyzed by triethyl amino and hexamethylenetetramine and it was observed that product was having good elasticity and improved resistance to alkali. Chen et al. [197] studied the DSC thermograms of Diamino diphenyl suiphone (DDS) and after mixing with various polynuclear epoxy resin. The curing onset, extrapolated onset and maximum exothermic temperature were reported by them. They found an interesting small endotherm at around 80°C in the DSC thermograms for the DDS curing epoxy system. Martin [67] explained a similar observation as the vaporization of a small amount of solvent in the epoxy formulation.

Tsujiku et al. [198] reported that the shelf life of an epoxy resin is predicted rapidly and accurately from the calibration curve of the temperatures at which the heat starts to evolve (measured by a differential calorimeter) and the shelf life of known epoxy resin.

The cured epoxidized novolacs have been largely characterized by its degree of cure of the extent of crosslinking which controls the properties of epoxidized novolacs for its and uses. The degree of cure has been assessed by either the chemical conversion or the physical, electrical, rheological and thermal properties of epoxies. Mika [199] reported the use of modifying reactive additives to amine and anhydride -catalysed epoxy cures at low temperatures for impact, flexibility and reduced shinkage. The polymercaptans are mercaptain terminated polysulfide polymer such as mercapto alkyl esters of poly carboxylic acid and
polytriglycolate ester. Park et al. [200] reported the use in curing epoxy compositions for surface coatings by polyphenols such as tetra brominated bisphenol novolacs based on phenol and formaldehyde resoles, coal-pitch, arid polybutadine.

Masahiro et al. [201] have largely used to assess the degree of cure and dielectric constant/dielectric strength, volume resistivity and power factor/loss factor for electrical properties. Weinmann et al. [202] have largely used to assess the degree of epoxy cures for the thermal properties such as thermal stability/decomposition. These properties have monitored by thermogravimetry (TG), thermo-mechanical analysis (TMA). Differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Besides the degree of cure, these techniques also provide information on kinetics and mechanism of epoxy cures.

Shkanov et al. [203] have assessed by sensitive dynamic mechanical test and used to follow the degree of cure in curing of epoxy resins for rheological properties, particularly the viscoelasticity which increase with time a temperature of cure.

Wang and Zang [204] and Huang et al. [205] have determined by quantitation of epoxy and/or hydroxyl group by infrared spectroscopy, FTIR and chemical analysis for the chemical conversion i.e. the disappearance of epoxy group. John and Goetzky [206] have often encountered in chemical analysis due to functional groups other than epoxies and hydroxyls. The IR spectra of cured products may also show unexpected shifts in
characterize peak due to insolubility of resins and interferences from the fillers.

A large number of available epoxy resins and curing agents etc. has made possible the preparation of cured epoxy resin compositions with varying properties. The epoxy resins based on novolacs have been largely used in surface coating due to their superiority in chemical resistance, thermal stability, mechanical and electrical properties over the conventional coating compositions. These resins have been cured with different curing agents and the films of coatings based on these cured compositions have been characterized for these properties and identified for specific uses by several researchers and are claimed in the literature.

The effect of heat treatment on the thermo-mechanical properties of filled epoxy novolac blend composition have been studied by Tsyba and Lakiya [207]. The heat resistance of mica filled blend composition increased significantly on thermal treatment at 150°C. Thermal stability of composition contg. 0, 25, 50 and 100 phr filler was observed at 130, 145, 175 and 177°C respectively and all samples showed a brittle thermal degradation. The thermomechanical curves of composition sample, indicated a transition from glass forming to low molecular weight amorphous state relaxation processes decreased the tension of polymer filler interface, which increased the impact and compression strength of highly filled composition.
Nishii et al. [137] have reported potting compositions for semiconductors and other electronic devices based on cresol novolac epoxy resins and phenolic novolac. Solder resistant ink for PCB based on epoxy resin has been found by Sugimoto and Kawaguchi [208].

Taguchi et al. [209] found that good crack and thermal shock resistant coatings for electrical devices by using bisphenol-A epoxy resins and Boron trifluoride (BF₃) amine complexes as catalyst (Epikote 825). Protective coaling for electrical insulation based on bisphenol-A and / or bisphenol-F and cresol novolacs epoxy resins have been studied by Hanamori et al. [210]. Toyama et al. [211] have studied the combination of flame retardance and heat resistant sealants could be identified in the brominated epoxy resins and epoxy silane couplers for electrical, electronic and semiconductor, Sato et al.[212] has obtained the photo curable and heat resistant coatings for PCB based on epoxy polyurethane. Good moisture and thermal shock resistant coatings for capacitors based on helogenated epoxy has been assessed by Akata et al. [213]. So and Kenichi [214] have reported heat resistant and improved moisture resistant moldable coatings compositions based on tetra functional epoxy resins for semiconductors and electronic devices based on o-cresol novolac epoxy has founded by Toyoto central research and development laboratories Inc. Japen [215], coatings for electrical insulation with thermal shock and moisture resistance based on epoxy resin and substituted phenolic novolacs has carried out by Sanuki
et al. [216]. They also studied low temperature and rapidly cured moisture resistance coating based on polymercaptans based epoxy resins. Thermal shock and moisture resistance coating based on substituted phenolic novolac and epoxy resins have also been elucidated by Sanuki et al. [216].

Good flame retardance and heat resistant molding materials for Sealants based on brominated epoxy and phenolie novolac has been carried out by Toyama et al. [217]. Costa et al. [218] have evaluated the thermal and flame retardant properties of phenol formaldehyde type resins crosslinked and non-crosslinked in mixture with triphenyl phosphate and styrene acrylonitrito resins.

Costa et al. [218] reported a combination of good mechanical properties and heat resistant could identified in the cresol novolac based epoxides. Novolac based epoxide for coating having good mechanical and thermal properties has been reported by Yamamoto et al. [219]. Bisphenol epoxy resins and phenolic resin as hardener based coating composition with good bending has been studied by Ogiwar et al. [220]. Holdereggere et al.[221] have reported bisphenol-A epoxy resins of multifunctional and solid crosslinking agent based coatings for good impact and solvent resistance and flexible. Good adhesion, good impact resistance and good heat resistance coatings for rotor slots in electric motors for insulating from bisphenol-A epoxy resin aria hardener have been reported Kitagawa et al. [222]. Sinohara et al. [223] have described the coatings for the food cans from bisphenol-A and / or bisphenol-F, based epoxy resins, cresol phenolic resins as
hardener having good adhesion, bendability and retort resistance, with out unpleasant flavour in water. Pasecky et al. [224] have elucidated the mechanical resistance coatings by UV irradiation for high-speed printings machines based on epoxy resin acrylate-polyol (meth) acrylate- unsaturated polyester in printing inks and paints.

Polyakova et al. [225] have studied the mechanical properties chemical resistance, dielectric strength and thermal stability coatings from epoxy rein and polyurethanes by cathodic deposition. Fukuka et al. [226] have investigated by coatings for metal procoatings based on epoxy resins and aliphatic and / or alicyclic diisocyanatcs.

Redforn [227] dealt with thermal analysis of polyimide resins, phenolic resins, polytetrafluoroethylene and poly butadiene. With this analytical method too he refers to the advantage of coupling with other methods, such as Ms or FTIR, which enables the volatile elimination products to be identified and quantified. A non-crosslinked polyimide resin was investigated using differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA). The DSC plot showed a glass transition at 55°C, an endothermic melting peak 121°C and an exothermic peak at 283°C. The latter should be attributed to crosslinking with the elimination of volatile compounds. Finally at 430°C decomposition takes place, which can be seen from the Thermogravimetric analysis (TGA) plot, analyzed by thermogravi-
metry and DTA, with the elimination products ammonia and formaldehyde being analysed by MS. The initial loss of water leads to a broad endothermic peak in the DTA plot, and covers a glass transition. Novolac hexamine complexes are formed at 140°C the TGA curve shows a sharp less in mass owing to the elimination of ammonia and formaldehyde and a little water. Subsequently, crosslinking continues until at 320°C.

Burmester [228] describes the advantage and limitations of differential scanning calorimetric (DSC) and DTA to applied coating system. Advantages are the small sample quantities required, the lack of dependency on the solubility of the system and the short duration of analysis. The limits of the method are imposed by the effect of pigment on the plots and by difficulties with interpretation if the resins contain waxes, oils or proteins.

Rai and Mathur [229] carried out differential scanning calorimetric (DSC) studies on epoxy novolacs. These were phenolformaldehyde resins in the M_n range from 300 to 900, which were epoxidized with epichlorohydrin. The study describes the influence of the epoxy equivalent and that of a crosslinking reagent based on a bicycle anhydride, and the effect of molecular mass on thermal stability. In the presence of the anhydride, crosslinking is accompanied by esterification takes place, and DSC plots with endothermic peaks in the region from 100 to 150°C are found, this finding being attributed to isomerization of the epoxide groups. The peak temperatures for the exothermic crosslinking reaction are at 218 to 235°C in the presence of
anhydride and at 345 to 360°C its absence for both cases the same is true: as the epoxy equivalent grow, the temperature range of the crosslinking peak also increases.

Vallo and co-workers [230] analysed the network structure of epoxy amine networks based on the diglycidyl ether of bisphenol-A. Using an empirical equation of Nielson for the glass (T_g) transition temperature and statistical calculations of the concentration of elastic chains, it is possible to make sensible predictions about the anticipated T_g values. In rigid networks, the concentration of the flexible chains has a direction in T_g where as in flexible networks the effect is less pronounced.

Stutz and co-workers [231] likewise concern them selves with the effect of, for example, and groups crosslinks and branching, and the distribution or functional group, in epoxy amine system.

Richardson [232] carried out DSC investigations in order to determine the glass transition temperature and crosslinking of epoxy coating materials. From the DSC diagram it is possible to make out the regions of the reactants which were initially mixed in powder from which undergo liquefaction at the glass transaction temperature, those of the pure liquid, and subsequently those of the exothermic cross linking reaction. From the latter peak it is possible to calculate the heat of reaction.

Schoff and Kamarchik [233] give an overview of the use of TMA with organic coatings the performance of a coating is
dependent on it physical and mechanical properties and on the way in which they can change with the temperature. For example, a coating for an exterior facade must not be too soft, so that dirt does not adhere, but at the same time must withstand the low temperature of winter without flaking off. The authors stress that the tests commonly used in the paint industry for determining these properties, such as pencil hardness, pendulum or buchnolz hardness, indentation testing, impact testing or even finger nail tests or tests former resistance, although giving rapid result, give result which are often also contradictory and difficult to interpret. The reason for this is the lacks of reference to a basic material property. TMA, on the other hand, is a method suitable for investigating the viscoelastic behavior, as well as physical transitions and relaxations. An advantage of TMA is its applications to coated substrates, since the production of free standing films, especially of multicoat systems, is not simple, typical measurements such as softening point (which in the case of TMA is similar to the glass transition temperature), degree of crosslinking, modules of elasticity and penetration hardness are described and discussed.

Yamada et al. [234] have study for metal sheet based on bisphenol-A epoxy resins and phenolic cresols with good resistance to methyl alcohol and salt water. A combination of methyl ethyl ketone resistance and crack resistant coatings could be identified in the bisphenol based epoxy resins and o-cresol formaldehyde based novolac for welded cans has been studied.
Uemura et al. [235]. Anticorrosive and ethyl alcohol resistant coatings based on bisphenol-A epoxy resin, melamine resin and phenolic hardener has been studied Urazuka et al. [236].

Morisono et al. [237] have described the manufacture of coating compositions based on diethanolamine as a hardener and bisphenol a based epoxy resin. Malichenko et al. [238] have suggested acid and heat resistance compositions for coating based on triethanolamine as hardener p-tert-butyl bisphenol a based epoxy resins.

McGarry and Wiliner [239] showed that low molecular weight carboxyl terminated butadiene-acryonitrile copolymer (CTBN) were the most effective agents for improving the fracture toughness of epoxy resin. The CTBN used in epoxy resins had a molecular weight in region of 2000-10,000, while the acryonitrile content which allowed the highest toughness of the resin was between 12 and 18 wt%.

Zhang et al. [240] synthesized moderate temperature curable two component epoxy resin adhesive with thick bondline. Epoxy resin (E44) was treated with liquid carboxyl-terminated butadiene nitrile rubber in the presence of tertiary amine catalyst to give component A. Heat treatment of diethylene glycol bis (aminopropyl) ether with mixed amine and catalyst gave component B. Epoxy resin structural adhesive with high shear strength under thick bond line was prepared by mixing a 100:23 (weight ratio) of component A and component B.
Kim and his co-workers [241] prepared carboxy terminated nitrile rubber toughened blend. The structure and properties of ternary blends of epoxy with poly(ether sulfone) PES and carboxyl-terminated butadiene-acrylonitrile rubber (CTBN) have been investigated.

Park and Shin [242] studied on the properties of CTBN modified epoxy resin. Unmodified DGEBA epoxy resin has substantially limited mechanical properties such as impact strength and elongation due to rigid chemical structure. Reactive liquid rubber, CTBN, is introduced in DGEBA epoxy resin to improve mechanical properties. Typical properties of CTBN-modified epoxy resin and film properties of CTBN-modified epoxy film were investigated.

Katiyar and Nagpal [243] studied the curing behavior and thermal properties of elastomer-modified bismaleimide resin, Bismaleimide resin (compimide 353) was modified with the liquid elastomer carboxyl terminated acrylonitrile butadiene rubber (CTBN). The pre-reaction synthesis and curing of the CTBN-bismaleimide resin was discussed. The structure of the modified resin was identified by IR and NMR spectroscopy. The basic curing mechanism is also discussed DSC and $T_g$ were used to study the curing behaviour and kinetic parameters viz. the order of reaction, energy of activation and pre exponential factor, adhesive properties such as lap shear strength and peel strength at room temperatures and elevated temperature were evaluated and are discussed.
Lee et al. [244] studied the effects of CTBN on the cure characteristics of DGEBA/MDA/PGE-AcAm-system. Effects of carboxyl terminated butadiene acrylonitrile rubber (CTBN) on the cure characteristics of diglycidyl ether of bisphenol-A (DGEBA)/4,4'-methylene dianiline (MDA)/phenol glycidyl ether (PGE) acetamide (AcAm) system were studied by autocatalytic cure-rate expression. Cure rate at initial rate stage increased with the increase in the content of the CTBN; however, at some high stage cure rate was inverted due to the diffusion control of formed CTBN domain. The total conversion was also decreased with the increase of the CTBN content.

Ochi et al. [245] modified the cured mesogenic epoxy resins with reactive elastomer (CTBN). Phenol-1,4-benzene dicarboxaldehyde novolac-cured bisphenol-type epoxy resin was modified with reactive elastomer of carboxy terminated butadiene acrylonitrile copolymer. The toughness of the cured epoxy resin was improved by the modification of the elastomer.

Lee et al. [246] studied the cure and thermal degradation kinetics of DGEBA/MDA/PGE-AcAm/CTBN system by Kissinger equation. The cure and thermal degradation kinetics of diglycidyl ether of bisphenol-A (DGEBA)/4,4'-methylenediane dianiline (MDA)/phenyl glycidyl ether (PGE)-acetamide (AcAm)/carboxyl terminated nitrile (CTBN) system were studied by Kissinger equation. The activation energy of the cure reaction is 11.15 K Cal/mole and the pre-exponential factor is 16.31x10^5 minute\(^{-1}\) reaction orders are varied from 1.42 to 1.68 depending upon cure
temperatures. The activation energy of the thermal degradation reaction is 34.89 KCal/mole and the pre-exponential factor is 2.04 x 10^{11} \text{ minutes}^{-1}. The reaction orders were ranged from 4.83 to 5.85 according to the decomposition temperature. The theoretical and experimental kinetics are well fitted, and it implies that Kissinger equation is applicable for studying the cure and thermal degradation kinetics.

Yuyama et al. [247] synthesized carbonyl- terminated nitrile rubber adhesive. Substrate for flexible printed circuit board using epoxy resin based adhesive. The flexible primed circuit board comprises (A) a polyimide film having flexural modulus 380-800 kg.mm^{2} comprising pyromellitic dianhydride and a 90/10-40/60 minutes of 4,4' diaminodiphenyl ether and p-phenylenediamine and (B) a metal foil laminated through (C) an adhesive comprising 100 parts epoxy resins 30-100 parts 95/5-55/45 mixture carboxyl terminated nitrile rubbers and non-functionalized 25:75-45:55 CTBN rubber. 1-30 parts crosslinking agents and 0.1-5 parts ≥1 crosslinking accelerators selected from imidazoles tetraborate salts, borofluorides and octylate salts. The circuit board showed improved dimensional stability and peeling resistance at high temperature.

Nigam et al. [248] characterized liquid carboxy-terminated copolymer of butadiene acrylonitrile modified epoxy resin. Toughening of epoxy cresol novolac (ECN) by carboxy terminated acrylonitrile-co-butadiene (CTBN) liquid functional rubber has
been studied, Wide Angle X-ray Scattering (WAXS) has been utilized to evaluate average molecular inter chain spacing ($< R >$) from the strong maximum in the diffraction scan using Bragg's equation. The half width ($< HW >$) of the maximum was used to qualitatively describe the distribution of ($< R >$). An increase in ($< R >$) value signifies formation of a separate packing order as well as increase in the free volume. Fourier transform infrared (FTIR) spectroscopy studies convincingly established that the interaction between oxirane group of epoxy and carboxyl group of CTBN are responsible for characteristic peak shifts in the blends compared to individual polymers. Physico mechanical properties of the blends e.g., the tensile, flexural and impact strengths showed an optimum concentration of CTBN (10 wt%) into ECN, which can offer maximum toughening. Cross sections of the composite specimens, failed during impact testing, have been critically studied through scanning electron microscopy (SEM) to gain insight into the mechanism of toughening and phase morphology.

Bilgin et al. [249] predicted the lifetime of carboxyl-terminated polybutadiene (CTPB). CTPB rubber was subjected to temperature and humidity aging in order to stabilize its useful lifetime as a solid propellant binder. Samples were aged from 1 week to 7 months at 50-100°C. At various stages of aging, viscosities of the samples were measured, end group analyses were performed and the samples, after being vulcanized were mechanically tested. The ultimate tensile stress of the samples
decreased and strain-at-break increased with temperature aging. End-group analyses indicated that the acid value of the samples decreased with aging. Viscosity increased with aging. The results of temperature aging were applied to an Arrhenius type temperature superposition relation and the useful lifetime of the rubber as binder at 20°C was predicted to be 10 year.

Kubota et al. [250] characterized CTPB as rocket propellant, in order to obtain high-energy fuel rich propellants used in gas generators, NH₄ClO₄ based composite propellants containing B particles were formulated.

Geetha and Prabhakaran [251] synthesized CTPB from HTPB. HTPB was synthesized by the free radical solution polymer using H₂O₂ as an initiator. The succinie anhydride (I) with >99.5% purity was prepared from sulfonic acid and acetic anhydride by the conventional procedure. HTPB and 1 at the molar ratio 1: 2 and butylated hydroxy PhMe (0.2%) were mixed and refluxed in PhMe with stirring. After cooling the reaction system and removing of the unreacted 1 and Ph Me the ester containing carboxyl-terminated polybutadiene (CTPB) was obtained.

Fujita and Hayashi [252] gave the blend composition of epoxy/CTPB for sealing semiconductor elements. Title composition giving low stress cured products with adhesion to metals. Cured insert molding of this composition showed flexural modulus of 1250 kg/mm² and no fracture at 15 kg when the bad frame was drawn off.
Saraf et al. [253] studied thermal characterization of CTPB/polyimide blends. In order to formulate a high temperature high fracture strength and easily moldable resin system, bismaleimide (RM1) and CTPB blends in various composition (1:1, 1:0.75 and 1:0.5) were studied by DSC and SEM. Diallyl bisphenol-A-BM1 adduct blends with CTPB were also studied for comparison. Even though both systems showed similar DSC patterns, BM1/CTPB blends seem to show better interaction amongst the constituents. DSC and SEM results support the above conclusions and suggest the formation of an interpenetrating network.

Amer et al. [254] studied the effect of thermal aging on some properties of (CTPB) rocket propellants. The effects of accelerated thermal aging at 80°C on the properties of two carboxy-terminated polybutadiene (CTPB) composite solid rocket propellant formulations were reported.

Niu and Wang [255] synthesized solution polymerized carboxy-terminated polybutadiene. Factors affecting the properties of carboxy-terminated liquid polybutadiene synthesized by free radical solution polymer with glutaric acid peroxide as initiator and anhydrous ethanol or acetone as solvent were studied. The microstructure was characterized by IR. The carboxy-terminated liquid polybutadiene for different demands could be prepared by controlling the reaction temperature and time adjusting the initial amount of initiator and the decrement rate of continuously adding initiator.
Kapadi and his co-workers [256] gave the viscoelastic properties of highly filled CTPB composites of the title rubbers are examined; these polymers are used as propellant binders.

Eroglu et al. [257] studied spectroscopic, thermal and mechanical characterization of carboxyl terminated polybutadiene based carbon black-filled networks. Carbon black-filled and unfilled CTPB networks were prepared using two types of reactive system at different reactive group ratios, to be applied to solid propellant of CTPB networks tris (2-methyl-1-aziridinyl) phosphine oxide (MAPO) and a mixture of liquid bisphenol A-epichlorohydrin (Epikote 828) and MAPO were used as two different reactive systems. The chemical and thermal stability of the CTPB networks were followed by Fourier transform IR spectroscopic (FTIR) and thermogravimetric (TG) techniques, where as mechanical and adhesive properties were tested by tensile measurements.

Nigam et al. [258] gave the cure characterization of rubber (CTPB) modified epoxy novolacs. A new type of toughened epoxy polymer based on epoxy cresol novolac resin (ECN) and carboxy-terminated polybutadiene (CTPB) liquid functional rubber and hardener e.g. diaminodiphenyl methane (DDM) has been studied. ECN has been synthesized in the laboratory and CTPB used was also of indigenous origin. Rubber modified epoxies were characterized with the help of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) techniques. Further, they reported wide-angle
x-ray scattering, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) studies on the influence of the addition of liquid functional rubber (CTPB) into epoxy thermoset.

Bittencourt et al. [259] studied the ionomer morphology of carboxy terminated butadiene rubber. The morphology of sodium-neutralized carboxy-terminated butadiene rubber sodium salt ionomer was characterized by small-angle x-ray scattering for varying degrees of neutralization between 20 and 100%.

Nigam et al. [260] studied the chemical interaction and phase morphology of CTPB/epoxy blend. Nature of chemical interaction of epoxy cresol novolac resin (ECN), CTPB and hardener e.g. diaminodiphenylmethane (DDM), at various stages of curing has been studied by Fourier transform IR spectroscopy (FTIR). Liquid blend samples were withdrawn at regular intervals and the recorded FTIR spectra showed intensity variation and back shifts of the oxirane group of epoxy and carboxy group of CTPB with the progress of curing at 150°C for two hours. A concomitant appearance of stretched peaks due to esterification between epoxy and CTPB, and curing of epoxy alone with amine hardener were also observed.

Akimoto et al. [261] prepared carboxyl containing rubber-modified epoxy resin for epoxy compositions with good storage stability, mechanical strength and toughness. Title epoxy resin is
prepared by reacting a carboxyl containing rubber with an epoxy resin in the presence of a phosphorous acid triester catalyst.

Verchere et al. [262] found that triphenylphosphine (TPP) was a very effective catalyst to promote the reaction between the carboxyl groups of the oligomer and epoxy groups of the resin, and it also assisted the nucleation of the toughening rubber particles from the original solution.

Bishopp [263] induced the rubbery phase to precipitate the epoxy network which remained essentially unchanged, thereby preserving its main properties, while the work of Chen and Shy [264] showed that the presence of fine precipitate rubbery particles, 1-5 µm, imparted an enhanced resistance to crack propagation and impact strength. Chen and Jan [265] used large amount of CTBN, which produces a simultaneous decrease in the glass transition temperature and modulus of the resins through plasticisation effect.

Yamanaka and Inove [266] studied the binary mixtures of bisphenol-A epoxy resin with either CTBN or ATBN (Amine-terminated butadieneacrylonitrile rubber) and showed that these systems exhibit an upper critical solution temperature (UCST) phase behavior mixtures of resin, telechelic oligomer and a curing agent, showing a single phase at the very early stage of curing, develop a two-phase structure via either a particle nucleation and growth (NG) or a spinodal decomposition (SD) as the cure process proceeds. During curing, in fact, the UCST is elevated by the
increase in the molecular weight of the epoxy and hence the system is moved into a two-phase region. This implies that one can control the two-phase morphology, by manipulating the kinetics of phase separation and curing reactions. It has been found that a high temperature cure (above 100°C) yields a dispersed-particle structure with fairly uniform particle size and that the particle size becomes smaller with increasing cure rate. Furthermore, a high temperature cure using a low reactivity-curing agent produces spherical particles having a bimodal size distribution. On the other hand, a co-continuous two-phase structure is obtained with a low temperature cure. The latter structure found to exhibit excellent damping characteristics and high peel strength.

Kunz and co-workers [267] investigated the toughness-morphology dependence, in terms of volume fraction, particle size distribution of the dispersed phase and the particle/matrix interface characteristics for two types of rubber-toughened/epoxies, i.e. CTBN and ATBN modified resins by using several techniques. The amount of rubber added to the bisphenol-A epoxy resin was varied in both cases between 5 and 15 parts by weight it was found that ATBN rubbers produce a diffuse interface between the dispersed rubber phase and the epoxy matrix, in contrast to the sharp boundaries at the interface of CTBN particles. The difference in interface structure has been attributed to ATBN particles having highly irregular shapes compared to the nearly spherical CTBN particles.
Yamanaka et al. [268] showed that the ATBN particles are somewhat interconnected owing to gelation of the matrix occurring before the spinodally decomposed rubbery phase fully develops into separate spherical particles. Bimodal particle size distribution, as well as a marked increase in the number of large particles (>200nm), were observed with both modifiers, unexpectedly from the difference in particle geometry, were found to have essentially identical toughness, which corresponded to greater than a five-fold increase over the pure epoxy. For both modifiers toughness seems not to increase with rubber content over the range 5-15 pph.

Butta et al. [269] studied the influence of curing temperature on morphology and mechanical properties of blends obtained by adding different amounts of ATBN to a bisphenol-A type epoxy resin and found that the final morphology of the toughened system is strongly dependent on cure temperature and rubber content. Curing at low temperature promoted the formation of optically clear materials, although DSC data and dynamic mechanical tests have revealed the presence of a two phase structure, albeit highly interdiffused. The temperature at which clear material were obtained was found to increase with increasing rubber content. Curing at high temperatures, on the other hand, gave rise to the formation of large spherical domains. With increasing ATBN content those domains become bigger and more closely packed, reaching phase inversion conditions above 20% rubber.
Reiw et al. [270] studied Infrared (IR) of oligomeric dicarboxylic acid prepared by salt with the amine, which is responsible for phase separation leading to particle precipitation. The carboxylate salt, in fact, will subsequently react very rapidly with the epoxy groups of resin. Since the latter is present in a large excess, reactions will take place also directly between the epoxy groups of the resin and the amine groups of hardener, but at a much lower rate, thereby allowing the reaction products containing the carboxylic acid component to reach gelation condition first and create the required fluctuations of concentration to induce phase separation by spinodal decomposition.

In addition to causing phase separation, the curing reactions leads to increase in viscosity and eventually to gelation of the entire resin mixture. The resulting reduction in molecular mobility lowers the rate of reactions. At 120°C, the epoxy resin piperidiene CTBN system de mixes during the first 60 min of the curing reactions, but shows no evidence of further phase separation thereafter. It therefore appears that phase separation is confined to the early stages of curing, and stops well before the matrix resin reaches the gel point.