2.1 Introduction

Epoxy resins are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin followed by dehydro halogenation [1]. The most important classes of epoxy resins are based on the glycidylation of bisphenol A, bisphenol F, phenol novolacs, diaminodiphenyl methane, p-aminophenol, aliphatic diols, aliphatic and cycloaliphatic carboxylic acids. Cycloaliphatic oxiranes, mostly formed by epoxidation of olefinic systems are also of commercial interest. A series of glycidylated resins based on the nitrogen heterocyclic system hydantoin was introduced in the 1970s. However, epoxy resins based on bisphenol A-epichlorohydrin are still the most widely used epoxies.

DGEBA resin is prepared by reacting bisphenol A with epichlorohydrin (ECH) in the presence of caustic soda [2]. The reaction occurs in two steps: i) the formation of a chlorohydrin intermediate and ii) dehydrohalogenation of chlorohydrin to the glycidyl ether. Many commercial liquid resins
consist essentially of the low molecular weight diglycidyl ether of bisphenol A together with small quantities of high molecular weight polymers. The HCl released during the reaction reacts with caustic soda to form NaCl.

Epoxy resin can be cured by several hardners. This chapter deals with optimization of weight percentage composition of hardener for curing, post curing time and post curing temperature, properties of epoxy resin used, sample preparation, modification of epoxy resin with epoxidised novolac resin from phenol, ortho cresol, p-cresol, phenol napthol mixture and epoxidised cardanol and measurement of various properties.

The reaction of an epoxy with a phenol has been studied extensively in the literature [3, 4]. This reaction has some importance in the epoxy industry in the preparation of high molecular weight epoxy resins and polyhydroxyethers, as well as for the crosslinking of epoxy resins with phenolic novolacs for microelectronics packaging applications. The reaction mechanism and extent of side reactions are highly dependent on the reaction conditions and the type of catalyst used [5]. The compatibility of phenolics with epoxy resin primarily arises from their almost similar polarities. At high temperatures, the phenolic hydroxyl groups react with epoxy groups and the methylol groups react with hydroxyl groups of the epoxy backbone (Scheme 2.2). The net result is a cross-linked polymer network which shows the best chemical and heat resistance of all epoxy coating systems [6].
Novolac resins are epoxidised through the phenolic hydroxyl groups by treatment with epichlorohydrin (Scheme 2.3).

A typical commercial epoxy novolac (EPN) resin has an average molecular weight of about 650 and contains about 3.6 epoxy groups per molecule. Branching in DGEBA epoxy resin is achieved by the incorporation of multifunctional epoxy systems like EPNs [7,8]. Branching takes place due to the reaction of the hydroxyl groups in the epoxy backbone and epoxy
functional group in EPN [9]. The epoxy groups in both epoxy novolac and epoxy resin are opened up by the same curing agent which triggers the cross-linking process. Likewise the addition of epoxidised cardanol into DGEBA will lead to chain extension of the epoxy backbone.

2.1.1 Ageing of epoxy resin

Epoxies and epoxy composites are often exposed to long-term sustained levels of elevated temperatures, moisture, electric fields, and other harsh environments. For extended periods of time, this exposure leads to the aging of the epoxy resin, that is, the possible degradation of its overall thermo-mechanical properties [10-17]. Traditionally, physical aging has been classified as one of the broad categories of glassy material aging mechanisms. Physical aging is usually associated with decrease in toughness, viscoelastic response, and permeability of polymers and other glassy materials. This is clearly a concern for the industries that use epoxy resins, as physical aging can compromise product durability, reliability, and safety.

2.2 Experimental

2.2.1 Materials

Commercial grade epoxy resin GY 250, and the room temperature amine hardener HY 951 (polyamine) were supplied by Petro Araldite Pvt. Ltd. in Chennai. Phenol, o-cresol, p-cresol, formaldehyde, epichlorohydrin, bezene, NaOH, oxalic acid, sodium sulphate were supplied by Merck India Ltd.
2.2.2 Characterisation methods

a) Spectroscopic studies

Fourier transform infrared (FTIR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm\(^{-1}\) by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indicative of the bond strengths and structural geometry in the molecule. FTIR spectra of the samples were taken in Bruker Tensor 27 FTIR spectrometer. NMR spectroscopy is also used for the characterization of epoxies.

b) Testing of liquid resin

The quality of the commercial epoxy resin was tested by determining the specific gravity, viscosity and the epoxide equivalent.

i. Specific gravity

The specific gravity of the resin was determined according to ASTM D 792 using a specific gravity bottle.

ii. Viscosity

The viscosity of the resin was measured at room temperature on a Brookfield viscometer model RVF as per ASTM D 2393. The appropriate spindle was allowed to rotate in the resin for 30 sec and the dial reading was taken. The procedure was repeated for constant dial reading.
iii. Epoxide equivalent (Weight per epoxide)

The epoxy content of liquid resins is frequently expressed as weight per epoxide (wpe) or epoxide equivalent which is defined as the weight of the resin containing one gram equivalent of epoxide. The epoxy content is also expressed as equivalent/Kg of the resin.

A common method of analysis of epoxide content of liquid resins involves the opening of the epoxy ring by hydrogen halides (hydrohalogenation)[18]. Weight per epoxide values of the synthesised and commercial epoxy resins samples were determined by the pyridinium chloride method as per ASTM D 1652-73.

0.1 to 0.2 g of the epoxy resin was mixed with 2ml HCl in 25 ml pyridine. The mixture was heated to reflux on a water bath for 45 minutes. The solution was cooled to room temperature and the un-reacted acid present in it was estimated by back titration with standard NaOH solution (0.1N) using phenolphthalein indicator. A blank was also carried out under the same reaction conditions.

Epoxide equivalent = \( N \times \frac{V}{w} \),

where \( N \) is the strength of alkali, \( V \) is the volume of alkali used up and \( w \) is the weight of the resin. Epoxide equivalent can be obtained as eq/Kg from which wpe value of the resin can be calculated.

c) Casting
i) Moulds
a. Tensile properties (ASTM D 638-99)

Dumbbell shaped multicavity moulds were fabricated from teflon for casting tensile specimens. Six sets of moulds were machined out of
Modification of DGEBA using Epoxidised phenolic Resin

teflon plates each set containing three dumb bell shaped mould cavities. Each mould consisted of a base plat (steel) and cavity plate. The dimensions of the tensile test specimens are shown in Fig. 2.1. The specimens were cast according to ASTM D 638.

![Fig. 2.1 The dimensions of the tensile test specimens](Image)

b. **Impact strength (ASTM D 256-97)**

The mould for impact specimens having sixteen cavities was fabricated out of Teflon according to dimensions specified in ASTM D 4812. It consisted of a base plate (steel) and cavity plate. The dimensions of each cavity are 49.5± 0.2 mm length, 5.3 ± 0.21 mm width and 4.1± 0.1 mm thickness.

c. **Surface hardness (ASTM D 2240-86)**

The mould was machined from mild steel plates containing four circular cavities having 50 mm diameter and 6 mm depth.

d. **Water absorption (ASTM D 570-98)**

A mould was fabricated for casting water absorption specimens according to ASTM D 647. The mould containing four circular mould cavities with a diameter of 50.8 mm and a thickness of 3.2 ± 0.3 mm was machined out of Teflon.
ii) Curing

Epoxy resin was cured at room temperature by adding 10 weight % of the amine hardener and stirring the mixture. The resin was then poured into appropriate moulds coated with a releasing agent. The releasing agent used was flooring wax. Curing was done at room temperature for 24 h, followed by post curing at 120°C for 4 hours.

d) Testing of cast samples

The samples after post curing were tested for tensile strength, modulus, elongation-at-break, flexural strength, toughness, impact strength, surface hardness and water absorption taking six trials in each case.

i. Tensile properties

The tensile properties were tested on a Shimadzu Autograph (AG-1 50 kN) Universal Testing Machine (ASTM D 638-99) at a constant rate of traverse of the moving grip of 5mm/min. The cast specimens were polished using emery paper prior to testing. One grip is attached to a fixed and the other to a movable (power-driven) member so that they will move freely into alignment as soon as any load is applied. The test specimen was held tight by the two grips, the lower grip being fixed. The output data in the form of stress-strain graph and elongation, modulus and energy absorbed at various stages of the test directly appear on the console of the microprocessor and as a print out. The area under the stress-strain curve provides an indication of the overall toughness of the material at the particular temperature and rate of loading. The energy absorbed by the sample to break is also a measure of the toughness.
Modification of DGEBA using Epoxidized phenolic Resin

ii. **Impact strength**

Izod impact strength was measured on a Zwick Impact Tester as per ASTM D 256-88 specifications. Impact strength is the energy absorbed by the specimen during the impact process and is given by the difference between the potential energy of the hammer or striker before and after impact.

The specimens were tested on the impact tester having a 4 Joules capacity hammer and striking velocity of 2.2 m/sec. A sample is clamped vertically in the base of the machine. The pendulum is released. The impact resistance or strength is evaluated from the impact values directly read from the tester.

iii. **Surface hardness**

Shore D Durometer was employed for measuring surface hardness (ASTM D 2240-86). The specimen was placed on a horizontal surface and the durometer held in a vertical position with the pointer of the indenter on the specimen. The pressure foot was applied on the specimen as rapidly as possible without shock and the foot is kept parallel to the surface of the specimen. The scale was read out within one second after the pressure foot was in firm contact with the specimen.

iv. **Water absorption**

Water absorption was tested as per ASTM D 570. The water absorption test samples were directly placed in a temperature-controlled oven. The temperature was kept constant at 50°C for 24 hours. The samples were taken out and cooled in a desiccator.
and weighed. The weighed samples were immersed in water for 24 hours at room temperature. The specimens were removed, wiped dry with a cloth and immediately weighed. The increase in weight was found out.

\[
\text{Water absorption (\%)} = \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 100
\]

v **Morphological studies- Scanning electron microscopy [19]**

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology [20]. Scanning electron microscope (Cambridge Instruments S 360 Stereoscan- version V02-01, England) was used to investigate the morphology of the fractured surfaces. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and photographed using black and white film. The SEM observations reported in the present study were made on the fracture surface of the tensile specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an E-101 ion-sputtering unit for gold coating of the sample to make it conducting. The gold-coated sample was subjected to SEM.
vi  Thermal studies [21]

a)  Thermogravimetric analysis (TGA)

A TA Instruments’ TGA Q 50 was used to investigate thermal degradation. A temperature ramp was run from room temperature to 600°C at 20°C/minute in air. Sample weights were between 5 and 10 mg.

b)  Dynamic mechanical analysis (DMA) [22]

The damping qualities were measured using fixed frequency dynamic analysis techniques. A dynamic analyser model TA Instruments DMA-Q 800, was made use of for this purpose. Rectangular specimens 127 mm length, 12.7 mm breadth and 3 mm height were used. DMA tests were conducted at a constant frequency of 1 Hz. A temperature ramp was run from room temperature to 200°C at 1°C/min to get an overview of the thermo mechanical behaviour of modified and unmodified samples.

vii  Soxhlet extraction and swelling studies of cured samples [23]

The samples were ground to particles of about 2 mm diameter and packets containing 2 grams of the sample in Whatman No.1 paper were extracted with toluene /benzene in a Soxhlet apparatus for 48 h. The difference in weights of packets gave the soluble matter and the percentage soluble matter was calculated.

The cross-link density was indirectly estimated from the equilibrium swelling data. Samples of approximately 10 mm diameter and 2 mm thickness are accurately weighed and allowed to swell in an excess of chloroform. The swollen samples were taken out of the solvent every 24 h, wiped dry with a tissue paper and immediately weighed. When
equilibrium is attained, the swollen samples were dried in vacuum and weighed. The volume fraction of polyester \( (V_p) \) in the swollen samples was calculated from the following equation [15].

\[
V_p = \frac{(D - FT)\rho_p^{-1}}{(D - FT)\rho_p^{-1} + A_o\rho_s^{-1}}
\]

where, \( D \)=deswollen weight of the specimen, \( F \)=weight fraction of insoluble components, \( T \) = weight of the specimen, \( \rho_p \) = density of polymer and \( \rho_s \) = density of solvent. \( V_p \) is linearly related to the cross-link density of the polymer samples.

### 2.2.3 Study of cure parameters of DGEBA

**a) Influence of hardener composition**

The optimization of hardener composition for hardening of epoxy resin was studied. The samples were post cured for 4 h. The samples were post cured at 100\(^\circ\)C. The Hardener composition was varied as 8 weight \%, 10 weight \% and 12 weight \%. The mechanical properties of the cured blends are compared to optimize the hardner composition.

**b) Influence of post curing temperature**

The effect of variation of post curing temperature for the commercial epoxy resin containing 10 weight \% R.T. hardener was studied. The post curing temperature was varied as 60, 80, 100 and 120\(^\circ\)C. The amount of hardener was kept constant. The samples were post cured for 4 h. The mechanical properties of the cured blends are compared to identify the ideal post curing temperature.
c) Influence of post curing time

The effect of variation of post curing time as 1, 2, 3, 4 and 5 hours for the commercial epoxy resin containing 10 weight % R.T. hardener was studied. The mechanical properties of the cured blends were compared to identify the optimal post curing time. The samples were post cured at 100°C.

2.2.4 Synthesis of modifier resins

a) Materials

Phenol (M.W=94.11, M.P.39.5-41°C), p-cresol, (MW=108.14, BP=202°C, 98% assay), o-cresol (MW=108.14, BP=191°C, 98% assay), formaldehyde (37-41% w/v, d²⁰=1.08), sodium hydroxide (M.W= 40, 97% assay) and oxalic acid (M.W=126.07, 99.8% assay) were L.R. grade supplied by Merk, India. Cardanol was recovered from cashew nut shell liquid by distillation.

Cardanol: Cashew nut shell liquid (CNSL) occurs as a viscous liquid in the soft honeycomb of the shell of the cashew nut. Cashew nut is a product of the cashew tree, Anacardium occidentale L native to Brazil. It is a naturally occurring substituted phenol which can take part in a variety of reactions [24]. As an agro-byproduct it has the advantages of low cost and renewable supply [25-28] and can replace phenol in many applications. Cardanol is obtained by vacuum distillation of commercial grade CNSL conforming to Indian Standard, I S: 841-1964. The structure of cardanol is given in Fig.2.2. The main constituents of CNSL are phenolic compounds with long side chain substitution at the meta position. Naturally occurring CNSL contains mainly four components: cardanol, cardol, anacardic acid, and 2-methyl cardol. The components of CNSL are themselves mixtures of four
constituents differing in side-chain unsaturation, namely saturated, monoene, diene, and triene. The structures of the side chains of varying degrees of unsaturation occurring in the four major components of CNSL are identical.

\[\text{Fig.2.2 Structure of cardanol}\]

For different values of \(n\), the following structures result for the side chain.

\[\begin{align*}
n&=0, (\text{CH}_2)_7-(\text{CH}_2)_7\text{CH}_3; \quad n=2, (\text{CH}_2)_7 \text{CH} = \text{CH}(\text{CH}_2)_5\text{CH}_3 \\
n&=4, (\text{CH}_2)_7 \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}(\text{CH}_2)_2\text{CH}_3 \\
n&=6, (\text{CH}_2)_7 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2
\end{align*}\]

Symes and Dawson[29] and Cornelius[30] identified the components of cardanol as 3-pentadeca-anisole, 1-methoxy 3-(8’,11’-pentadeca dienyl) benzene, and 1-methoxy 3-(8’,11’-pentadeca trienyl) benzene. Chemically it represents an interesting reactive substance thanks to double bonds in the alkyl chain and the phenolic character.

b) Synthesis of epoxidised phenol novolacs

i. Novolac resins

The novolacs were prepared by reacting phenol with formaldehyde in the molar ratio 1:0.8 in presence of oxalic acid catalyst in a 3-necked flask fitted with a mechanical stirrer, water condenser and thermometer.
Modification of DGEBA using Epoxidised phenolic Resin

The reaction mixture was heated and allowed to reflux at about 100°C for 2-3 hours. When the resin separated from the aqueous phase the reaction was stopped. The resin was neutralised with sodium hydroxide, filtered, washed with water and vacuum dried. The novolac resin contains 4-6 benzene rings per molecule. The same procedure was used to synthesise novolac resins from phenol, p-cresol, o-cresol and phenol/naphthol mixtures of varying molar compositions. Further, a series of novolac resins containing phenol and formaldehyde with varying molar ratios such as 1:0.6, 1:0.7 and 1:0.9 were also prepared using the same procedure.

ii. Epoxidised phenolic novolacs (EPNs)

1 mole of the novolac resin (1:0.8) was dissolved in 6 moles of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 16 hours while 3 moles of sodium hydroxide in the form of 30 % aqueous solution was added drop wise. The rate of addition was maintained such that the reaction mixture remains at a pH insufficient to colour phenolphthalein. The resulting organic layer was separated, dried with sodium sulphate and then fractionally distilled under vacuum. Epoxidised novolac resin was similarly prepared from p-cresol novolac (ECN) using the same procedure. Novolac resins containing phenol and formaldehyde in varying molar ratios such as 1:0.6, 1:0.7, 1.08 and 1:0.9 were also subjected to epoxidation by the same procedure to form EPNs of different compositions. These epoxy novolacs were designated as EPN-1, EPN-2, EPN-3 and EPN-4 respectively. The wpe values of the various epoxy novolacs were determined (Section 2.2.2b(iii)).
Chapter 2

c) **Epoxidised cardanol (EC)** [31]

Cardanol (1mole) was dissolved in a mixture of an excess of epichlorohydrin (2 moles) and 20 cc water in a one litre three necked flask. The flask was equipped with a mechanical stirrer, thermometer and a Liebig’s condenser. The mixture was heated gently over a water bath till the epichlorohydrin began to boil. Heating was stopped and caustic soda (1 mole) was added in portions of two pellets down the condenser. The reaction was allowed to subside before a new portion of alkali was added. When all the caustic soda pellets were added, the reaction mixture was refluxed for one hour. Heating was stopped as the reaction mixture turned viscous. The excess epichlorohydrin was removed by vacuum distillation. The remaining mixture was extracted with benzene to precipitate sodium chloride which was removed by filtration under vacuum. The filtrate was vacuum distilled to remove benzene. The dark brown epoxy cardanol resin was dried in vacuum for 3 hours. Using the same method cardanol resin was subjected to glycidylation at different reaction intervals (1, 3, 6 and 9h) to optimise the extent of reaction. These resins were designated as EC1, EC2, EC3 and EC 4 respectively. The epoxide equivalents of the resins were determined as described in Section 2.2.2.b(iii). The resin was characterised by spectroscopic methods.

![Fig. 2.3 Epoxidation of cardanol](image)

*Fig. 2.3 Epoxidation of cardanol*
Modification of DGEBA using Epoxidised phenolic Resin

d) Epoxidised novolac from phenol and naphthol mixture.

Novolac resin was prepared from phenol (95 wt%) and naphthol (5 wt%) using the procedure cited in Section 2.2.4 b(i). Then novolac resin was epoxidised by the procedure cited in section 2.2.4b(ii). The synthesis was repeated with phenol and naphthol in varying molar compositions such as 90/10 and 20/80. The epoxy equivalents of the resins were determined using the method described in Section 2.2.2(b(iii)).

2.2.5 Influence of P-F stoichiometry of epoxidised novolacs

Epoxidised novolac resins prepared using various stoichiometric ratios viz. 1:0.6, 1:0.7, 1:0.8 and 1:0.9 between phenol and formaldehyde (designated as EPN-1, EPN-2, EPN-3 and EPN-4) were used for blending with epoxy resin. Initially, unmodified resin was cured at room temperature using 10 wt% of the room temperature hardener. It was then degassed in vacuum and poured into a tensile mould with dumbbell shaped cavities coated with a releasing agent. Samples for water absorption and compression tests were cast separately in appropriate moulds. Curing was done at room temperature for 24 hours followed by post curing at 100°C for four hours. Subsequently, varying amounts of the epoxidised novolac resin (5 to 20 weight %) were added to the resin. The mixture was homogenized by gentle agitation using a stirrer and degassed in vacuum at 50°C. The blends were cured by the procedure employed for the neat resin.

The post-cured samples of modified and un-modified resins were subjected to all the tests outlined in Section 2.2.2(d), taking six trials in each case. Thermal properties of the blends were determined by TGA and DMA. Soxhlet extraction and swelling studies were carried out and the
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fractured surfaces (tensile samples) of the blends were subjected to morphological studies using SEM.

The epoxy equivalents (wpe) for these EPNs (EPN1, EPN2, EPN3 and epn4) were estimated as 188.8, 174.3, 170.5 and 200.3 respectively. The properties were compared with those of the un-modified sample.

2.2.6 Ageing studies on epoxy resin modified by epoxy phenol novolacs

Cured samples of neat epoxy resin and epoxy resins modified by EPN (15%) were prepared as described in Section 2.2.5. The samples were aged in a temperature controlled air oven kept at 100°C for 24, 48, 72, 96 and 120 hours successively. The aged samples were subjected to the tests outlined in Section 2.2.2(d). The properties of the cured samples were compared.

2.2.7 Modification with epoxidised cresol novolacs

Epoxidised novolac resins prepared (Section 2.2.4) from o-cresol (o-ECN) and p-cresol (p-ECN) were used for blending with commercial epoxy resin. The blends containing varying amounts of epoxy novolacs were prepared, cured and tested according to the procedures cited in Section 2.2.2(d). The properties were compared with those of the un-modified sample. The epoxy equivalents (wpe) for EPN, ECN and neat epoxy resin were found to be 170.5, 175.9 and 188 respectively.

2.2.8 Ageing studies on epoxy resin modified by epoxy cresol novolacs

Cured samples of neat epoxy resin and epoxy resins modified by o-ECN (15%) and p-ECN(15%) were prepared as described in Section 2.2.5. The samples were aged in a temperature controlled air oven kept at 100°C for 24, 48, 72, 96 and 120 hours successively. The aged samples were
subjected to the tests outlined in Section 2.2.2(d). The properties of the cured samples were compared.

2.2.9 Modification with epoxidised cardanol

Epoxidised cardanol (EC) samples synthesised (Section 2.2.4) for different reaction intervals such as 1h, 3h, 6h and 9h (designated as EC1, EC-2, EC-3 and EC-4) were used for blending with commercial epoxy resin. Blends were prepared by mixing the epoxy resin with varying amounts of epoxy cardanol and cured as per method given in 2.2.5. The mechanical and thermal properties of the cured blends were determined and compared with those of the neat resin.

2.2.10 Ageing studies on epoxy resin modified by epoxidised cardanol

Cured samples of neat epoxy resin and epoxy resins modified by EC-4 were prepared as described in Section 2.2.5. The samples were aged in a temperature controlled air oven kept at 100°C for 24, 48, 72, 96 and 120 hours successively. The aged samples were subjected to the tests outlined in Section 2.2.2(d). The properties of the cured samples were compared.

2.2.11 Modification with epoxidised novolac from phenol naphthol mixture

Epoxidised novolac from phenol naphthol mixture samples synthesised (Section 2.2.4) were used for blending with commercial epoxy resin. Blends were prepared by mixing the epoxy resin with varying amounts of epoxidised phenol naphthol mixture and cured as per method described in 2.2.5. The mechanical and thermal properties of the cured blends were determined and compared with those of the neat resin.
2.3. Results and discussion

2.3.1 Characterisation of DGEBA

i) Spectroscopic data [32]

i. FTIR: The FTIR spectrum of epoxy resin is given in Fig.2.4. The C-H stretching in epoxies is at 2860 -2999 cm\(^{-1}\). Symmetrical stretching or ring breathing frequency is observed at 1231 cm\(^{-1}\) and this is characteristic of the epoxy ring. The band at 915 cm\(^{-1}\) (asymmetric ring stretching in which C-C stretches during contraction of C-O bond), 826 cm\(^{-1}\) and 746 cm\(^{-1}\) are typical of the epoxy group [32].

![FTIR spectrum of commercial epoxy resin](image)

Fig.2.4 FTIR spectrum of commercial epoxy resin

ii) Epoxide equivalents and resin characteristics

The weight per epoxide (wpe) values of the commercial and the synthesised epoxy resin samples were determined using the procedure cited in Section 2.2.2(b). The commercial samples gave wpe values 188. These values correspond to epoxide equivalents 5.30 eq /Kg . Other properties like viscosity, gel time and density are given in the table 2.1
Modification of DGEBA using Epoxidised phenolic Resin

Table 2.1 Properties of commercial epoxy resins

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight per epoxide (wpe)</td>
<td>188</td>
</tr>
<tr>
<td>Epoxy equivalent. Eq/Kg</td>
<td>5.30</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.192</td>
</tr>
<tr>
<td>Viscosity (cp)</td>
<td>12095</td>
</tr>
</tbody>
</table>

iii) Mechanical properties

The mechanical properties of cured commercial epoxy resins are shown in Table 2.2

Table 2.2 Mechanical Properties of commercial epoxy resins

<table>
<thead>
<tr>
<th>Properties</th>
<th>Commercial DGEBA Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength.(MPa)</td>
<td>55.5</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>3.01</td>
</tr>
<tr>
<td>Modulus. ( MPa)</td>
<td>2425</td>
</tr>
<tr>
<td>Energy to break. (J/mm²)</td>
<td>4.01</td>
</tr>
<tr>
<td>Impact strength. Izod. (J/m)</td>
<td>111.04</td>
</tr>
<tr>
<td>Surface hardness. (Shore D)</td>
<td>88.15</td>
</tr>
<tr>
<td>Water absorption. (%)</td>
<td>0.2002</td>
</tr>
</tbody>
</table>

iv) Thermal Studies

TGA characteristics of cured NEAT DGEBA samples are given in Table 2.3

Table 2.3 TGA characteristics of DGEBA

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset temperature (°C)</td>
<td>343</td>
</tr>
<tr>
<td>Temperature of maximum rate (°C)</td>
<td>364</td>
</tr>
<tr>
<td>Temperature of half loss (°C)</td>
<td>378</td>
</tr>
<tr>
<td>Residue</td>
<td>6.68</td>
</tr>
</tbody>
</table>
v) Influence of hardener composition

The mechanical properties of the cured blends at different hardener composition are given in Table 2.4.

Table 2.4 Properties of commercial epoxy resins at different hardener compositions

<table>
<thead>
<tr>
<th>Property</th>
<th>Weight percentage of Hardener</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8%</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>45.6</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>2389</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>4.56</td>
</tr>
<tr>
<td>Energy absorbed to break. J.mm^2</td>
<td>2.05</td>
</tr>
<tr>
<td>Impact strength (J.m^-1)</td>
<td>52.80</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>99</td>
</tr>
<tr>
<td>Surface hardness. Shore D</td>
<td>85</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.275</td>
</tr>
</tbody>
</table>

Properties like tensile strength, modulus and elongation at break, energy absorbed to break and impact strength show maximum values at a hardener composition of 10wt%. Post curing was done for four hours at 100°C.

vi) Influence of post curing temperature

Properties of cured commercial resin at different post curing temperature are shown in Table 2.5.
Table 2.5 Properties of epoxy resin cured at different post curing temperatures *

<table>
<thead>
<tr>
<th>Property</th>
<th>Post curing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>52.6</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>2389</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>2.875</td>
</tr>
<tr>
<td>Energy absorbed to break. J.mm⁻²</td>
<td>2.76</td>
</tr>
<tr>
<td>Impact strength (J.m⁻¹)</td>
<td>106.80</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>99</td>
</tr>
<tr>
<td>Surface hardness. Shore D</td>
<td>86</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.2235</td>
</tr>
</tbody>
</table>

Properties like tensile strength, modulus and elongation at break, energy absorbed to break and impact strength show maximum values at a post curing temperature of 100°C. Post curing was done for four hours at 10 weight % hardener composition.

vi Influence of post curing time

The effect of variation of post curing time for the commercial epoxy resin containing 10 weight % of the RT hardener was studied. Properties of the cured resin at different post curing time are shown in Table 2.6.

Table 2.6 Properties of epoxy resin cured at different post curing time

<table>
<thead>
<tr>
<th>Property</th>
<th>Post curing time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>52.8</td>
</tr>
<tr>
<td>Tensile modulus (MPa)</td>
<td>2307</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>2.95</td>
</tr>
<tr>
<td>Energy absorbed to break. J.mm⁻²</td>
<td>3.76</td>
</tr>
<tr>
<td>Impact strength (J.m⁻¹)</td>
<td>107.36</td>
</tr>
<tr>
<td>Compressive strength MPa</td>
<td>98.65</td>
</tr>
<tr>
<td>Surface hardness. Shore D</td>
<td>85.5</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.229</td>
</tr>
</tbody>
</table>
Properties like tensile strength, modulus and elongation at break, toughness and impact strength show maximum values at a post curing time of 4 h.

2.3.2 Influence of P-F stoichiometry of epoxidised novolacs

Epoxy novolacs are highly compatible with DGEBA resin because both have almost similar polarity. The epoxy groups in both EPN and epoxy resin are opened up by the amine curing agent by the conventional mechanism involving replacement of the active hydrogen atoms in the amine. This triggers the cross-linking process. The simultaneous cross-linking of DGEBA and EPN leading to hybrid networks can take place via the following different possible pathways.

i). The hardener can give rise to –NH groups on opening the epoxy rings of both DGEBA and EPN. These can further initiate opening up of additional epoxy rings leading to a cross-linked network.

ii). The secondary hydroxyl groups generated from DGEBA by opening of the epoxy ring by the hardener can condense with the secondary hydroxyl groups generated from the opening of the epoxy rings in EPN.

iii). The EPN may contain un-epoxidised phenolic hydroxyl groups which may initiate opening of epoxy rings in DGEBA and those in EPN.

iv). The methylol groups that may be present in limited amounts in EPN may initiate opening of epoxy rings of DGEBA and EPN.

The identification of the exact cross-linking reactions has not been attempted because of the above complexities resulting from the extremely
reactive environment. It is possible that all the above reactions take place to some extent, the possibility of the fourth reaction being significantly less due to the very limited number of methylol groups.

Epoxidised novolac resins prepared using various stoichiometric ratios viz. 1:0.6, 1:0.7, 1:0.8 and 1:0.9 between phenol and formaldehyde (designated as EPN-1, EPN-2, EPN-3 and EPN-4) were used for blending with epoxy resin. The epoxy equivalents (wpe) for these EPNs (EPN1, EPN2, EPN3 and epn4) were estimated as 188.8(5.30 eq/kg), 174.3(5.73 eq/kg), 170.5(5.87 eq/kg) and 200.3(4.99 eq/kg) respectively. EPN-3 which contains phenol and formaldehyde in the ratio 1:0.8 was found to have greater epoxide content than the other epoxy novolacs.

i) **Spectroscopic data**

The FTIR spectrum of synthesised epoxidised novolac resin (EPN-3) is given in Fig 2.5.

![Fig. 2.5 FTIR spectrum of EPN](image-url)
The strong band at 1236.9 cm\(^{-1}\) denotes symmetrical C-O stretching (ring breathing frequency) in epoxides. The C-H stretching in epoxides occurs at 2929.85 cm\(^{-1}\). Further, the bands at 915 cm\(^{-1}\), 840 cm\(^{-1}\), and 760 cm\(^{-1}\) are also typical of epoxides.

**ii. Tensile properties.**

Referring to Fig. 2.6 tensile strength values obtained by blending epoxy resin with 5 to 20% epoxy novolacs are significantly higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 15 wt% for EPN-3 modified DGEBA beyond which the strength is found to decrease. The improvement in tensile strength over that of the base resin is due to a higher degree of cross-linking as well as chain extension. This can also be attributed to some amount of entanglement among the polymer chains.

![Graph showing tensile strength vs composition of EPN](image)

**Fig. 2.6. Tensile strength of modified resin Vs EPN concentration**
The modifying effect of EPN-3 is superior to that of the other EPNs due to its increased epoxy functionality as evident from the wpe value.

The effect on elongation at break is shown in Fig. 2.7. Compared to unmodified resin the blends show an increase in elongation. Epoxy-EPN blends show maximum elongation at 15 wt % of EPN. In this case also EPN-3 enjoys clear superiority over the other epoxy novolacs used. A higher elongation may be the result of straightening of the entangled chains. Fig. 2.8 gives the variation of energy absorbed (to break) by the blends of epoxy resin with epoxy novolacs. This can be taken as a measure of the toughness. At 15wt % of EPN-3, the energy absorbed (at break) is improved by about 52 % of that of the neat resin. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement.
Fig. 2.8. Energy absorbed (to break) of modified resin Vs EPN concentration

The superiority of EPN-3 is observed in the impact strength values also (Fig.2.9). At 15 weight% EPN-3 shows about 87% improvement in impact strength compared to the un-modified resin. This is the result of increased cross-linking and chain extension taking place in the blend by virtue of the relatively higher epoxy content in EPN-3.

Fig. 2.9. Impact strength of modified resin Vs EPN concentration
iii. Surface hardness and water absorption

Fig. 2.10 indicates a general improvement in surface hardness upon blending epoxy resin with epoxy novolac. However, the increase is only marginal. Water absorption of epoxy novolac-modified epoxy resins are given in Fig. 2.11.

![Graph of Surface Hardness vs EPN Concentration](image1)

**Fig. 2.10 Surface hardness of modified resin Vs EPN concentration**

![Graph of Water Absorption vs EPN Concentration](image2)

**Fig. 2.11 Water absorption of modified resin Vs EPN concentration**
The blends show increased water resistance. This is possibly due to a greater extent of methylene groups which are not amenable to hydrogen bonding. The highest resistance is shown by epoxy /EPN-1 blend. This can be due to a higher extent of aromatic rings arising from the higher phenol content (1:0.6).

Table 2.7 summarizes the mechanical properties of epoxy–EPN blends. The maximum improvement acquired in each property and the corresponding concentration are tabulated

**Table 2.7 Properties of DGEBA/epoxy phenol novolac blends**

<table>
<thead>
<tr>
<th>Property</th>
<th>DGEBA</th>
<th>% improvement / weight % EPN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EPN-1/ DGEBA</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>55.5</td>
<td>10.3/15</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>3.01</td>
<td>11.5/15</td>
</tr>
<tr>
<td>Energy absorbed (J/mm²)</td>
<td>4.05</td>
<td>20.2/10</td>
</tr>
<tr>
<td>Impact strength (J/m)</td>
<td>111.04</td>
<td>52.3/15</td>
</tr>
<tr>
<td>Surface hardness (Shore D)</td>
<td>88.1</td>
<td>2/20</td>
</tr>
</tbody>
</table>

**iv. Thermal properties**

1. **TGA**: The TGA curves of the neat resin and DGEBA / EPN-3(15wt%) blend (Fig 2.12) show marginally better thermal stability for the modified sample. An increased level of cross-linking as well as the presence of phenolic groups gives better thermal resistance to the blend. The EPN-3 modified sample gave 8.78 % residue at 600°C compared to 6.7 % by the un-modified resin. The higher functionality and phenolic content of novolac resins increase cross-link densities and improve thermal and chemical resistance.
Modification of DGEBA using Epoxidised phenolic Resin

Fig. 2.12 TGA curves for DGEBA and DGEBA/EPN-3

Table 2.8 Thermal properties of DGEBA/EPN blends

<table>
<thead>
<tr>
<th>Resin</th>
<th>Onset temperature (°C)</th>
<th>Temperature of maximum rate (°C)</th>
<th>Temperature of half loss (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>343</td>
<td>364</td>
<td>378</td>
<td>6.68</td>
</tr>
<tr>
<td>EPN</td>
<td>340</td>
<td>365</td>
<td>380</td>
<td>8.78</td>
</tr>
</tbody>
</table>

ii. DMA: The tan δ (loss factor) values are shown in Fig.2.13. The shape of the loss spectra can give additional information about the nature of the cross linked networks. The amplitude of the damping peak (tan δ\text{max}) becomes lower as the distance between the crosslink decreases. The tan δ\text{max} for neat DGEBA decreases on blending with EPN indicating increased crosslink density. The Tg of the epoxy rich phase increased with the addition of EPN. This is due to the increase in crosslink density of the blends with EPN.
Fig. 2.13. Tan delta curves for DGEBA and DGEBA/EPN blends

Fig. 2.14. DMA-storage modulus curves for DGEBA and DGEBA/EPN blends

The storage modulus decreases with increase in temperature (Fig 2.14). At room temperature EPN blends showed a higher value compared to the neat DGEBA. The storage modulus gradually drops off as the sample
is heated, due to the increasing molecular motions within the material, the main chain movements being seen at the glass transition temperature. A sharp decrease in storage modulus was observed for all blends near the glass transition of epoxy network. The EPN/DGEBA blends have higher crosslink density due to the cross linking of the epoxide groups of EPN resulting in higher values of storage modulus.

v. Soxhlet extraction and swelling studies

Among the different EPNs used, EPN-3 was found to give the least amount of soluble matter during soxhlet extraction (Table 2.9). This effect is in conformity with the higher level of cross-linking facilitated by EPN-3. The higher functionality and phenolic content of novolac resins increase cross-link density. This effect is the most in the case of EPN-3 due to its relatively higher epoxy content as evident from its lower wpe value.

Table 2.9 Soxhlet extraction and swelling data

<table>
<thead>
<tr>
<th>Samples</th>
<th>DGEBA</th>
<th>EPN-1</th>
<th>EPN-2</th>
<th>EPN-3</th>
<th>EPN-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble matter %</td>
<td>4.98</td>
<td>4.59</td>
<td>4.08</td>
<td>3.99</td>
<td>4.32</td>
</tr>
</tbody>
</table>

vi Morphological studies

Fig.2.15 (a) is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Fracture paths show river markings and are mostly straight.
(a)                                                        (b)

Fig. 2.15 SEM micrographs of a) DGEBA b) DGEBA/EPN3

The fracture surface is characterized by pin point crazes within the material. Fig.2.15 (b) shows the fractured surface of an epoxy-EPN blend. There are distinct signs of increased energy absorption in this case. Multilevel fracture paths indicate energy absorption on a large scale during failure.

2.3.3 Ageing studies on epoxy resin modified by epoxy novolacs

In this study, blends with the maximum improvement in properties have been subjected to ageing studies and the results compared with those of the neat resin. The post-cured samples of the neat DGEBA and DGEBA/EPN blend (15 wt %) were aged in a temperature controlled air oven kept at 100°C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties, water absorption and surface hardness.

i. Tensile properties

The effect of variation of ageing time with tensile strength is shown in Fig.2.16 Tensile strength decreases during ageing due to the stiffening and thermal degradation of polymer chains. After ageing for 120 hrs the
neat resin shows a reduction of 37% in tensile strength while the reduction is only 30% in the case of DGEBA/EPN.

![Graph of Tensile Strength vs Ageing Time](image1.png)

**Fig. 2.16** Tensile strength of modified resin Vs ageing time

![Graph of Elongation at Break vs Ageing Time](image2.png)

**Fig. 2.17.** Elongation at break of modified resin Vs ageing time

Fig. 2.17 depicts the decrease in elongation at break with ageing time, which is attributed to the reduction in flexibility due to increased stiffening.
of polymer chains. The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 2.18.

Fig. 2.18. Energy absorbed (to break) of modified resin Vs ageing time

The energy absorbed (to break) decreases with ageing time mainly due to reduced flexibility of the chains. While the neat resin shows a reduction of
40% in energy absorption at break, the EPN modified system shows a reduction of only 33%. This suggests the superiority of these phenolic resins in improving the ageing characteristics.

The variation in impact strength of the modified resin during ageing is given in Fig.2.19. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blend (EPN 28%) compared to the unmodified sample (32%). This confirms the ability of epoxy novolacs to improve the ageing properties.

ii. Surface hardness and water absorption

Ageing improves the surface hardness of the blends. Additional cross-linking is responsible for the improved hardness (Fig.2.20). Water absorption decreases steadily with ageing time (Fig 2.21). DGEBA/EPN blend show better water resistance than DGEBA resin. This is also due to additional cross-linking accompanying the ageing process.

![Graph showing surface hardness vs ageing time](image)

**Fig. 2.20. Surface hardness of modified resin Vs ageing time**
Chapter 2

The study reveals that modification using epoxy novolacs improves the ageing behaviour of the resin. The modified resin retains the mechanical properties to a greater extent than the unmodified resin.

![Water absorption of modified resin Vs ageing time](image)

**Fig. 2.21. Water absorption of modified resin Vs ageing time**

### 2.3.4 Modification with epoxidized cresol novolacs

Hybrid polymer networks of DGEBA with epoxidised cresol novolac resins (ECN) containing cresol and formaldehyde in 1:08 stoichiometric ratio was prepared. The modified epoxy resins were found to exhibit improved mechanical and thermal properties compared to the neat resin. O-cresol and p- cresol were used for the synthesis of ECN and they are represented as o-ECN and p-ECN. In the presence of the epoxy hardener, the epoxy groups in both the matrix resin and ECN are opened up resulting in chain extension and cross-linking. The mechanism of DGEBA/ECN reaction is expected to be similar to that of DGEBA/EPN reaction.

The epoxy equivalents (wpe) for these p-ECN and o-ECN were found to be 175.8 and 195 respectively.
i) Spectroscopic datas

The FTIR spectrum of synthesised epoxidised cresol novolac resin (o-ECN and p-ECN) is given in Fig. 2.22. The strong band at 1236.9 cm\(^{-1}\) denotes symmetrical C-O stretching (ring breathing frequency) in epoxides. The C-H stretching in epoxides occurs at 2929.85 cm\(^{-1}\). Further, the bands at 915 cm\(^{-1}\), 840 cm\(^{-1}\), and 760 cm\(^{-1}\) are also typical of epoxides.

![FTIR spectrum of o-ECN](image1)

**Fig.2.22a FTIR spectrum of o-ECN**

![FTIR spectrum of p-ECN](image2)

**Fig.2.22b FTIR spectrum of p-ECN**
i.  Tensile properties

Referring to Fig.2.23, tensile strength values obtained by blending epoxy resin with 5 to 20% epoxy novolacs are significantly higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 15 wt % for p-ECN beyond which the strength is found to decrease. For o-ECN tensile strength reaches a maximum at 10 wt % beyond which the strength is found to decrease. The improvement in tensile strength over that of the base resin is due to a higher degree of cross-linking as well as chain extension. This can also be attributed to some amount of entanglement among the polymer chains. It is likely that at about 15% p-ECN the cross-linking process reaches an optimum level. This results in increased tensile strength.

![Graph showing tensile strength vs ECN concentration]

**Fig. 2.23 Tensile strength of modified resin Vs ECN concentration**

The effect of addition of epoxy novolacs on elongation at break is shown in Fig.2.24. Compared to unmodified resin the blends show an increase in elongation. Epoxy /ECN blends show maximum elongation at 10 and 15 wt % of epoxy novolac. A higher elongation may be the result of straightening of the entangled chains. But as the ECN content goes up, it becomes increasingly difficult for the chains to disentangle and elongation falls.
Modification of DGEBA using Epoxidised phenolic Resin

Fig. 2.24 Elongation at break of modified resin Vs ECN concentration

Fig. 2.25 gives the variation of energy absorbed by blends of epoxy resin with epoxy novolacs. This can be taken as a measure of the toughness. At 15 wt % of p-ECN, the improvement in energy absorption (to break) is about 75%. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement. A profusion of epoxy novolac groups beyond 15 wt % is found to lower the energy absorption capacity.

Fig. 2.25 Energy absorbed (to break) of modified resin Vs ECN concentration
Chapter 2

Fig. 2.26 shows the variation of impact strength of modified resin with the concentration of epoxy novolac. DGEBA/p-ECN blend shows about 104% improvement in impact resistance. The improvement in impact strength of epoxy novolac modified resins is a direct consequence of compatibility, chain entanglement and enhanced cross-linking. P-ECN, with a more linear structure can produce blends with increased network flexibility and this result in the absorption of larger amounts of energy.

![Impact strength of modified resin Vs ECN concentration](image.png)

**Fig. 2.26 Impact strength of modified resin Vs ECN concentration**

ii. Surface hardness and water absorption

Fig. 2.27 indicates a general improvement in surface hardness upon blending epoxy resin with epoxy cresol novolacs. ECN from para-cresol shows better surface hardness than that from ortho-cresol.
Fig. 2.27 Surface hardness of modified resin Vs ECN concentration

Water absorption of various epoxy novolac - modified epoxy resins are given in Fig. 2.28. The blends show increased water resistance. This is possibly due to a greater extent of methylene groups and phenolics group which are not amenable to hydrogen bonding.

Fig. 2.28 Water absorption of modified resin versus ECN concentration.
Table 2.10 summarizes the effect of adding varying amounts of epoxy cresol novolac resins to the base resin. The maximum improvement acquired in each property and the corresponding concentrations are tabulated.

<table>
<thead>
<tr>
<th>Properties</th>
<th>% Improvement/ composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DGEBA</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>55.5</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>3.01</td>
</tr>
<tr>
<td>Energy absorbed (J/mm²)</td>
<td>4.05</td>
</tr>
<tr>
<td>Impact strength (J/m)</td>
<td>111.04</td>
</tr>
<tr>
<td>Hardness (Shore D)</td>
<td>88.1</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.2003</td>
</tr>
</tbody>
</table>

iii. Morphological studies

Fig. 2.29 (a) is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Fracture paths show river markings and are mostly straight.

![SEM micrographs](image-url)
Modification of DGEBA using Epoxidised phenolic Resin

Fig.2.29 (b) shows the fractured surface of an epoxy-p-ECN blend. There are distinct signs of increased energy absorption in this case. Multilevel fracture paths with feathery texture indicate energy absorption on a large scale during failure. The stretching taking place prior to fracture is evident from the pulled up wavy crests in the modified sample.

iv. Soxhlet extraction and swelling studies

The soxhlet extraction data are given in Table 2.11. The cured EPN/ECN modified samples yield very little soluble matter compared to the un-modified resin indicating effective cross-linking between the epoxy resin and the epoxy-novolacs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Neat Resin</th>
<th>p-ECN Blend 15%</th>
<th>o-ECN Blend 15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble matter %</td>
<td>4.98</td>
<td>3.78</td>
<td>4.73</td>
</tr>
</tbody>
</table>

v. Thermal properties

i. TGA: The TGA curves of the neat resin and DGEBA-ECN blend are shown in Fig.2.30. The modified resin has marginally better thermal stability as shown in Table 2.12. This may be due to an increased level of cross-linking as well as the presence of phenolic groups. The pECN modified sample gave 9.1 % residue at 600°C compared to 6.68% by the un-modified resin. The high functionality of novolac resins compared to DGEBA resin increases cross-link densities and improves thermal and chemical resistance.
Table 2.12 Thermal Properties of DGEBA and DGEBA/ECN blends

<table>
<thead>
<tr>
<th>Resin</th>
<th>Onset temperature (°C)</th>
<th>Temperature of maximum rate (°C)</th>
<th>Temperature of half loss (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>343</td>
<td>364</td>
<td>378</td>
<td>6.68</td>
</tr>
<tr>
<td>p-ECN</td>
<td>340</td>
<td>366</td>
<td>380</td>
<td>9.1</td>
</tr>
</tbody>
</table>

**Fig.2.30 TGA curves for DGEBA and DGEBA/ECN**

iii. **DMA:** Fig. 2.31(a) (b) and (c) illustrate the DMA-tanδ, storage modulus and loss modulus curves respectively. The glass transition of neat epoxy obtained from tanδ curves is $120^\circ$C corresponding to tan δ 0.680. Incorporation of p-ECN (15 wt %) and o-ECN (15 wt %) increases the glass transition temperature to $128^\circ$C and $126^\circ$C corresponding to tan δ values 0.5852 and 0.648 respectively. The shift of $T_g$ to a higher value is indicative of increased cross-linking in the modified samples.
Modification of DGEBA using Epoxidised phenolic Resin

Fig. 2.31a. Tan delta curves for DGEBA, DGEBA/p-ECN and DGEBA/o-ECN

Fig. 2.31b. Storage modulus curves for DGEBA, DGEBA/p-EPN and DGEBA/o-ECN
The blends have higher storage modulus than the neat resin which again points to a higher level of cross-linking in the blends. Storage modulus curve for the neat resin indicates a lowering of modulus from 2067 MPa to 837 MPa at the glass transition region while the modulus of o-ECN and p-ECN modified samples show a decrease from relatively higher modulus values; 2195 Mpa to 917 Mpa and 2565 MPa to 1297 MPa respectively at the glass transition region. Decrease in loss modulus of blends also indicates higher crosslink density.

2.3.5 Ageing studies on epoxy resin modified by epoxy cresol novolacs

In this study, two blends with the maximum improvement in properties have been subjected to ageing studies and the results compared with those of the neat resin. The post-cured samples of the neat DGEBA, DGEBA/p-ECN blend (15 wt %) and DGEBA/o-ECN blend (15 wt%) were aged in a temperature controlled air oven kept at 100 °C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties, water absorption and surface hardness.
i. **Tensile properties**

The effect of variation of ageing time with tensile strength is shown in Fig.2.32. Tensile strength decreases during ageing due to the stiffening and thermal degradation of polymer chains. After ageing for 120 hrs, the neat resin shows a reduction of 37% in tensile strength while the reduction is 32% in the case of DGEBA/o-ECN and 28% in DGEBA/p-ECN blends.

![Tensile Strength Graph](image)

**Fig. 2.32. Tensile strength of modified resin Vs ageing time**

Fig.2.33 depicts the decrease in elongation at break with ageing time, which is attributed to the reduction in flexibility due to increased stiffening of polymer chains. The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 2.34. The energy absorbed (to break) decreases with ageing time mainly due to reduced flexibility of the chains. While the neat resin shows a reduction of 41% in energy absorption at break, the o-ECN and p-ECN blends show a reduction of only 32-27%. This suggests the superiority of these phenolic resins in improving the ageing characteristics.
The variation in impact strength of the modified resin during ageing is given in Fig. 2.35. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However, the extent of decrease is less in the blends (p-ECN 27% and o-ECN 29%) compared to the unmodified sample (33%). This confirms the ability of epoxy novolacs to improve the ageing properties.
Modification of DGEBA using Epoxidised phenolic Resin

Fig. 2.35. Impact strength of modified resin Vs ageing time

ii. Water absorption

DGEBA/p-ECN and DGEBA/o-ECN blends show better water resistance (Fig.2.36) than DGEBA resin. This is also due to additional cross-linking accompanying the ageing process.

Fig. 2.36. Water absorption of modified resin Vs ageing time

The study reveals that modification using epoxy cresol novolacs improves the ageing behaviour of the resin. The modified resin retains the
Chapter 2

mechanical properties to a greater extent than the unmodified resin. p-ECN modified DGEBA shows better ageing behaviour than o-ECN modified DGEBA.

2.3.6 Modification with epoxidized cardanol.

Cardanol, the major constituent of cashew nut shell liquid, was epoxidised (Section 2.2.4) for different periods and used as an epoxy modifier. The extent of epoxidation was monitored by determining the epoxide equivalents (Section 2.2.2(b)). These resins are designated as EC-1, EC-2, EC-3 and EC-4 corresponding to reaction times 1h, 3h, 6h and 9h respectively. Epoxy cardanol shows good compatibility with the epoxy resin due to their similar polarities. In the presence of the epoxy hardener, the epoxy groups in both the matrix resin and EC are opened up resulting in chain extension and cross-linking. The mechanism of DGEBA/EC reaction is expected to be similar to that of DGEBA/EPN reaction.

i  Epoxy equivalent weight

The wpe value of epoxy cardanol (EC) obtained by epoxidation of cardanol for one hour (EC-1) was found to be 530.9 (1.89eq/Kg). As the epoxidation time was increased to 3h, 6h and 9h (EC-2, EC-3 and EC-4) the wpe values were found to be 504.8, 465.4 and 463.6 respectively. These values correspond to 1.98eq/Kg, 2.15 eq/Kg and 2.157eq/Kg of epoxide respectively. The epoxide equivalent increased sharply with time of epoxidation and reached almost a limiting value at 6-9hr.
Cardanol being less reactive undergoes epoxidation to a smaller extent than phenol. The wpe values for EC-3 and EC-4 did not vary much and hence maximum epoxidation might have taken place by about nine hours. Theoretically, complete epoxidation of cardanol would have given a wpe value of about 360. However, nine hours of reaction resulted in a wpe value of 463.6 which indicated incomplete epoxidation.

### ii Spectroscopic studies

Figure 2.37 shows the FTIR spectrum of cardanol (a) and the synthesised epoxy cardanol resin(EC-4) (b). The bands at 2924.37 cm\(^{-1}\) (C-H stretching of epoxide), 1265.28 cm\(^{-1}\) (symmetrical C-O str.) and 915.9 cm\(^{-1}\) are characteristic of epoxy group. The intensity of the broad band at 3343 cm\(^{-1}\) in (a) due to the phenolic hydroxyl group has decreased considerably in (2.37 b) indicating the involvement of that group in epoxidation.

<table>
<thead>
<tr>
<th>Reactionised cardanol</th>
<th>EC-1</th>
<th>EC-2</th>
<th>EC-3</th>
<th>EC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction time</td>
<td>1h</td>
<td>3h</td>
<td>6h</td>
<td>9h</td>
</tr>
<tr>
<td>Epoxy equi valent (eq/Kg)</td>
<td>1.88</td>
<td>1.98</td>
<td>2.15</td>
<td>2.157</td>
</tr>
<tr>
<td>Weight per epoxide</td>
<td>530.9</td>
<td>504.8</td>
<td>465.4</td>
<td>463.6</td>
</tr>
</tbody>
</table>
Fig. 2.37a. FTIR spectrum of cardanol

Fig. 2.37b. FTIR spectrum of epoxy cardanol (EC)
iii. Tensile properties

The variation in tensile strength obtained by adding varying amounts of EC into epoxy resin shows in Fig 2.38. Only a slight increase in tensile strength was observed at lower concentrations of EC. EC samples prepared at higher reaction times (EC-3, EC-4) are found to give improved tensile strength at still higher EC concentrations. These samples have relatively higher epoxy content as evidenced from their epoxy equivalents and the cross-linking/chain extension reaction will be more effective in such cases.

Figure 2.39 gives the variation of elongation at break of the modified resin. There is considerable improvement in elongation for DGEBA/EC blends. This is the striking feature of the blends containing cardanol based compounds. Blends containing EC-3 and EC-4 show increase in elongation at higher EC concentrations due to better compatibility arising from increased epoxy content.

![Fig. 2.38 Tensile strength of EC modified resin Vs EC concentration](image_url)
Figure 2.39 illustrates the effect of EC on the energy absorbed by the blends at break. DGEBA/EC blends absorb more energy at break than the unmodified resin. This can be taken as a measure of the toughness of EC modified epoxy resins. DGEBA/EC-4 sample exhibited almost 90% improvement in energy absorption. Cross-link density is found to have a great influence on toughening. Practically, toughness exhibits a maximum for intermediate cross-linking densities. The presence of mono functional EC can easily control the cross-link density to an optimum level necessary for imparting toughness.

![Figure 2.39 Elongation (at break) of EC modified resin Vs EC concentration](image1)

Fig. 2.39 Elongation (at break) of EC modified resin Vs EC concentration

Figure 2.40 illustrates the effect of EC on the energy absorbed by the blends at break. DGEBA/EC blends absorb more energy at break than the unmodified resin. This can be taken as a measure of the toughness of EC modified epoxy resins. DGEBA/EC-4 sample exhibited almost 90% improvement in energy absorption. Cross-link density is found to have a great influence on toughening. Practically, toughness exhibits a maximum for intermediate cross-linking densities. The presence of mono functional EC can easily control the cross-link density to an optimum level necessary for imparting toughness.

![Figure 2.40 Energy absorbed (to break) of EC modified resin Vs EC concentration](image2)

Fig. 2.40 Energy absorbed (to break) of EC modified resin Vs EC concentration
The variation in impact strength of EC-modified resin is given in Fig. 2.41. Impact strength shows maximum values at about 5-10 weight % for the different EC samples. EC-3 and EC-4 samples gave substantial improvement in impact strength due to better compatibility with the matrix resin.

![Graph showing impact strength vs EC concentration](image.png)

**Fig. 2.41 Impact strength of EC modified resin Vs EC concentration**

### iii. Surface hardness and water absorption.

Fig. 2.42 indicates a general lowering of surface hardness on addition of EC to epoxy resin. This can be due to a higher degree of flexibility and the creation of free volumes within the polymer. The variation in water absorption is given in Fig. 2.43. In general the blends show increased water absorption. The hydroxyl groups in unreacted cardanol can form hydrogen bonds with water and increase water absorption.
Table 2.14 summarises the overall effect of adding varying amounts of EC resins into epoxy resin. The maximum improvement achieved in each property and the corresponding compositions are tabulated.

iv. Morphological studies

Scanning electron micrographs of unmodified and EC modified epoxy resin fractured at low deformation are shown in Fig. 2.44. The
fracture surface of the blend is characterised by a morphology indicating extensive crazing. The micrograph (a) of the unmodified resin shows typical brittle fracture with pinpoint crazes.

![Fracture Surface Images](image)

**Fig. 2.44** Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/EC

Referring to the EC-4 modified sample (b), the fracture paths have a feathery texture with large breadth. Peaks and parallel fibril structures in pulled up wavy crests indicate the stretching that takes place prior to fracture. Stress whitening characteristic of crazing is also observed. All these features point to the improved toughness and load bearing characteristics of DGEBA/EC blend.

**Table 2.14 Properties of EC modified epoxy resins**

<table>
<thead>
<tr>
<th>Property</th>
<th>% maximum improvement / % composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DGEBA</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>55.5</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>3.01</td>
</tr>
<tr>
<td>Energy absorbed (J/mm²)</td>
<td>4.05</td>
</tr>
<tr>
<td>Impact strength (J/m)</td>
<td>111.04</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.2003</td>
</tr>
</tbody>
</table>
Chapter 2

Thermal properties

i. **TGA:** The TGA curves of the neat resin and DGEBA-EC blend are shown in Fig.2.45. The modified resin has marginally reduced thermal stability as shown in Table 2.15. This may be due to long aliphatic chains and lesser number of phenolic groups. The EC modified sample gave 7.4 % residue at 600°C compared to 6.68% by the un-modified resin.

![TGA curves for DGEBA and DGEBA/ECN](image)

**Fig.2.45 TGA curves for DGEBA and DGEBA/ECN**

**Table 2.15 TGA Characteristics of EC modified resin**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Onset temperature (°C)</th>
<th>Temperature of maximum rate (°C)</th>
<th>Temperature of half loss (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>343</td>
<td>364</td>
<td>378</td>
<td>6.68</td>
</tr>
<tr>
<td>EC/DGEBA</td>
<td>333</td>
<td>360</td>
<td>375</td>
<td>7.4</td>
</tr>
</tbody>
</table>
ii. **DMA**: Referring to tan δ curves (Fig 2.46) the peak occurs at 130 °C at tan δ 0.7263 for the modified sample compared to tan δ 0.684 for the neat resin. The increased height of tan δ peak of the blend indicates effective plasticizing.

![Fig.2.46. Tan δ curves for EC-modified and unmodified epoxy resins](image1)

![Fig.2.47. Storage modulus curves for EC-modified and unmodified epoxy resins](image2)
The DGEBA/EC blend has lesser storage modulus (Fig 2.47) showing a lesser extent of cross-linking and greater interaction of EC with DGEBA in the blend. Cross-linking between the shorter polymer chains gives flexibility to the cured matrix which in turn lowers the glass transition temperature.

vi. Soxhlet extraction and swelling studies

The Soxhlet extraction and swelling data are given in Table 2.16. The cured modified samples yielded somewhat smaller amounts of soluble matter compared to the unmodified sample.

<table>
<thead>
<tr>
<th>Samples</th>
<th>DGEBA</th>
<th>EC-3</th>
<th>EC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble matter %</td>
<td>4.98</td>
<td>4.3109</td>
<td>3.957</td>
</tr>
</tbody>
</table>

2.3.7 Ageing studies on epoxy resin modified by epoxy cardanol

In this study, blend with the maximum improvement in properties have been subjected to ageing studies and the results compared with those of the neat resin. The post-cured samples of the neat DGEBA and DGEBA/EC blend (10 wt %) were aged in a temperature controlled air oven kept at 100 °C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties, water absorption and surface hardness.

i. Tensile properties

The effect of variation of ageing time with tensile strength is shown in Fig.2.48. Tensile strength decreases during ageing due to the stiffening
and thermal degradation of polymer chains. After ageing for 120 hrs the neat resin shows a reduction of 37% in tensile strength while the reduction is only 35.6% in the case of DGEBA/EC

![Tensile Strength vs Ageing Time](image)

**Fig. 2.48 Tensile strength of modified resin Vs ageing time**

Fig. 2.49 depicts the decrease in elongation at break with ageing time, which is attributed to the reduction in flexibility due to increased stiffening of polymer chains. The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 2.50. The energy absorbed (to break) decreases with ageing time mainly due to reduced flexibility of the chains. While the neat resin shows a reduction of 40% in energy absorption at break, the EC modified shows a reduction of only 36%. This shows marginally improved ageing characteristics of EC modified DGEBA resin
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Fig. 2.49. Elongation at break of modified resin Vs ageing time

Fig. 2.50. Energy absorbed (to break) of modified resin Vs ageing time

The variation in impact strength of the modified resin during ageing is given in Fig.2.51. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blend (EC 29%) compared to the unmodified sample (32%). This confirms the ability of epoxy cardanol to improve the ageing properties.
Modification of DGEBA using Epoxidised phenolic Resin

Fig 2.51. Impact strength of modified resin Vs ageing time

ii. Surface hardness and water absorption

Ageing improves the surface hardness of the blends. Additional cross-linking is responsible for the improved hardness (Fig. 2.52). Water absorption decreases steadily with ageing time (Fig 2.53)
Fig. 2.53. Water absorption of modified resin Vs ageing time

The study reveals that modification using epoxy cardanol marginally improves the ageing behaviour of the resin. The modified resin retains the mechanical properties to a greater extent than the unmodified resin.

2.3.8 Modification with epoxidized novolac synthesized from phenol naphthol mixture.

Novolac resin was prepared from phenol (95 wt%) and naphthol (5 wt%) mixture. Then novolac resin is epoxidised by the procedure cited in Section 2.2.4. The synthesis was repeated with phenol and naphthol in varying molar compositions such as 90/10 and 80/20. These were designated by 5% naphthol EPN, 10% naphthol EPN and 20% naphthol EPN. The epoxy equivalent weight values obtained were 322, 378 and 450 respectively. In the presence of the epoxy hardener, the epoxy groups in both the matrix resin and naphthol resin are opened up resulting in chain extension and cross-linking. The mechanism of DGEBA/naphthol EPN reaction is expected to be similar to that of DGEBA/EPN reaction.
Modification of DGEBA using Epoxidised phenolic Resin

i  Spectroscopic Studies

![FTIR spectrum of epoxy phenol naphthol mixtures](image)

**Fig. 2.54 FTIR spectrum of epoxy phenol naphthol mixtures**

Fig 2.54 shows FTIR spectrum of 5% naphthol EPN. The bands at 2924.37 cm\(^{-1}\) (C-H stretching of epoxide), 1265.28 cm\(^{-1}\) (symmetrical C-O str.) and 915.9 cm\(^{-1}\) are characteristic of epoxy group. This confirms epoxidation.

ii  Tensile properties

The variation in tensile strength obtained by adding varying amounts of modifier into epoxy resin is shown in Fig 2.55. Only a slight increase in tensile strength was observed at a lower concentration of 5% naphthol EPN. This sample is found to give improved tensile strength compared to others. 5% naphthol has relatively higher epoxy content as evidenced from their epoxy equivalents and the cross-linking/chain extension reaction will be more effective in this cases. At higher naphthol loading the polymer chains might become less flexible due to bulky naphthol group and so tensile strength decreases.

Figure 2.56 gives the variation of elongation at break of the modified resin. There is only marginal improvement in elongation for DGEBA/5%
naphthol EPN blends. This may be due to straightening of the entangled chains. At higher naphthol loading the polymer chains might becomes less flexible due to bulky naphthol group and so elongation decreases.

Fig. 2.55 Tensile strength of EC modified resin Vs EC concentration

Fig. 2.56 Elongation (at break) of EC modified resin Vs EC concentration

Figure 2.57 illustrates the effect of naphthol EPN on the energy absorbed by the blends at break. DGEBA/5% naphthol EPN blends absorb
Modification of DGEBA using Epoxidised phenolic Resin

slightly more energy at break than the un-modified resin. This can be taken as a measure of slight improvement in the toughness of modified epoxy resins. At higher naphthol loading the polymer chains might becomes less flexible due to bulky naphthol group and so tensile strength decreases.

![Graph showing energy absorbed vs modifier concentration](image1)

**Fig. 2.57. Energy absorbed (to break) of modified resin Vs modifier concentration**

The variation in impact strength of modified resin is given in Fig.2.58. Impact strength shows maximum values at about 5-10 weight % for the different samples. 5% naphthol EPN samples gave substantial improvement in impact strength due to better compatibility with the matrix resin.

![Graph showing impact strength vs modifier concentration](image2)

**Fig. 2.58. Impact strength of modified resin Vs modifier concentration**
iii Water Absorption

Modified sample shows better water resistance (Fig 2.59) may due to the presence of hydrophobic aromatic rings present in naphthol EPN. Naphthol EPN shows better water resistance than EPN.

![Graph showing water absorption of modified resin vs ageing time]

**Fig. 2.59. Water absorption of modified resin Vs ageing time**

iv Thermal properties

*TGA*: The TGA curves of the neat resin and DGEBA /5% naphthol EPN(10wt%) blend (Fig 2.60) show marginally better thermal stability for the modified sample. An increased level of cross-linking as well as the presence of phenolic groups gives better thermal resistance to the blends. The modified resin has marginally increased thermal stability as shown in Table 2.17. The EPN modified sample gave 10.17% residue at 600°C compared to 6.7% by the un-modified resin.
Table 2.17 Thermal properties of DGEBA/EPN naphthol blends

<table>
<thead>
<tr>
<th>Resin</th>
<th>Onset temperature (°C)</th>
<th>Temperature of maximum rate (°C)</th>
<th>Temperature of half loss (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>343</td>
<td>364</td>
<td>378</td>
<td>6.68</td>
</tr>
<tr>
<td>5% Naphthol EPN/DGEBA</td>
<td>355</td>
<td>370</td>
<td>385</td>
<td>10.17</td>
</tr>
</tbody>
</table>

Fig.2.60 TGA curves for DGEBA and DGEBA/5% Naphthol EPN

iv. Morphological studies

Scanning electron micrographs of unmodified and 5% naphthol EPN modified epoxy resin fractured at low deformation are shown in Fig. 2.61. The fracture surface of the blend is characterised by a morphology indicating extensive crazing. The micrograph (a) of the unmodified resin shows typical brittle fracture with pinpoint crazes. Naphthol EPN modified sample (b) shows multiple fracture paths. Stress whitening
characteristic of crazing is also observed. All these features point to the improved toughness and load bearing characteristics of DGEBA/ Naphthol EPN blend.

![Fig. 2.61 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/Naphthol EPN](image)

2.4 Conclusions

Commercial DGEBA showed optimum mechanical properties by curing with 10wt % amine hardener and post curing at 100°C for four hours. Studying hybrid polymer networks of commercial epoxy resin with epoxy compounds were prepared and their properties studied.

Among the different EPNs, the one with a phenol/formaldehyde ratio 1:0.8 (EPN-3) was found to be superior to all other EPNs in improving mechanical and thermal properties. Compared to epoxy phenol novolac (EPN) and epoxy ortho cresol novolac(o-ECN), the one derived from p-cresol (p-ECN) gave significant improvement in mechanical and thermal properties. 15 wt% DGEBA/p-ECN system exhibited 90% improvement in toughness compared to the neat resin. Napthol EPN shows improvement in water resistance and thermal properties but shows only marginal improvement in mechanical properties compared to other EPNs.
Incorporation of cardanol reduced the brittle nature of epoxy resin considerably. An increase in the amount of cardanol resulted in decrease of tensile and compressive strengths and a sharp increase in elongation without appreciable lowering of the energy absorbed to break.

Further, the epoxy novolacs were found to considerably improve the ageing behaviour of the epoxy matrix

References


Chapter 2


Modification of DGEBA using Epoxidised Phenolic Resin


