CHAPTER 1

INTRODUCTION

1.1 EPOXY RESINS

Epoxy resins were introduced commercially in 1947 and their consumption increased by about 20% per year over the past four decades (Lee and Niville 1982). Epoxy resins are a family of thermosetting materials widely used as adhesives, coatings and matrices in polymer composites because of the low viscosity of their formulations, good insulating properties of the final material even at high temperatures and good chemical and thermal resistance, toughness, electrical and mechanical strength and good adhesion to many substrates.

Epoxy thermosets can be described as 3D polymer networks formed by the chemical reaction between monomers. The linear epoxy is cured into three dimensional crosslinked networks by curing agents, to give a hard and infusible thermoset resin. These cured polymers find applications in surface coatings, painting materials, composites, laminates, encapsulates for semiconductors and insulating materials for electrical devices. Currently more than 90% of the thermosetting resins are used as printed wiring laminates for epoxy boards (Young and Lovell 2002). Most of the composite applications utilize conventional bifunctional epoxy as a matrix.

Epoxy formulations usually include more than one component, although there are different crosslinking mechanisms involving either chemical reaction between one type of monomer or two kinds of monomers
with different functional groups. In both cases, a common constituent is always found: the epoxy monomer. The main feature of the epoxy monomer is the oxirane functional group, which is a three member ring formed between two carbon atoms and an oxygen as shown in Figure 1.1. The atomic arrangement shows enhanced reactivity when compared with common ethers

![Figure 1.1 Epoxy group](image)

because of its high strain. Due to the difference in the electronegativities of carbon and oxygen, the carbon atoms of the ring are electrophilic. These epoxies can undergo ring opening reactions towards nucleophiles.

There are mainly two families of epoxies: the glycidyl epoxies and non-glycidyl epoxies also called aliphatic or cycloaliphatic epoxy resins. The Figure 1.2 shows the structure of the most common epoxy monomers of each family, diglycidyl ether of bisphenol-A (DGEBA) and 3, 4-Epoxy cyclohexyl-3′4’-epoxy cyclohexane carboxylate (ECC) respectively,

![Figure 1.2 Structure of bisphenol-A epoxy (DGEBA) and 3, 4-Epoxy cyclohexyl-3′4’-epoxy cyclohexane carboxylate (ECC)](image)

Despite having the same main functional group, the reactivity of both families of epoxies is completely different as a consequence of the structure of the molecules. The linkage between the aromatic ring and the
oxygen (ether) in DGEBA has a strong electron-withdrawing effect that makes the oxirane group highly reactive towards nucleophilic compounds, unlike the cyclohexyl group in aliphatic epoxies which is reactive towards lewis acids like anhydrides. Barabanova et al (2008) reported that the best performance and the highest crosslinking degree for DGEBA-based resins is achieved when cured via an addition mechanism with diamines (either aliphatic or aromatic), whilst cycloaliphatic epoxies are commonly cured with anhydrides (Tao et al 2007a).

The use of epoxy resins are increasing in industries. Research and developments in this area are expanding significantly. Efforts are being made to develop epoxy resins with better toughness, lower viscosity, reduced shrinkage during cure and lower moisture absorption. Recent developments in epoxy resins include the synthesis of new epoxy resins with better structural properties.

1.2 TYPES OF EPOXY RESINS

Epoxy resins are compounds containing more than one epoxide group per molecule on average. Based on the epoxide content they are classified as diglycidyl resins, multifunctional epoxy resins and cycloaliphatic resins. Commercial epoxy resins contain aliphatic, cycloaliphatic or aromatic backbones.

1.2.1 Diglycidyl resins

These are difunctional epoxy resins containing two oxirane groups per molecule of resins. The most important commercial epoxide is based on bisphenol-A. They are prepared from either epichlorohydrin or by direct epoxidation of olefins with peroxides. The synthesis of diglycidyl resins involve reaction of bisphenol-A with excess of epichlorohydrin in the presence of a base is as shown in scheme 1.1.
Commercial liquid epoxy resins are prepared using different molar ratio’s of epichlorohydrin to bisphenol-A to afford different molecular weight products. High molecular weight solid epoxy resins with ‘n’ values ranging from 2 to 30 are prepared by two processes. Lower molecular weight solid resins with n values up to 3.7 are prepared directly from epichlorohydrin, bisphenol-A and a stoichiometric amount of NaOH. Higher molecular weight solid resins are prepared by chain extension reaction of liquid epoxy resin with bisphenol-A using basic inorganic reagents such as NaOH or Na$_2$CO$_3$ as catalyst (Lee and Niville 1982).

Scheme 1.1 Preparation of bisphenol A (DGEBA) epoxy resin

1.2.2 Multifunctional Epoxy resins

Multifunctional epoxy resins such as aromatic glycidyl ether resins and aromatic glycidyl amine resins are commercially available. The important epoxy phenol novolac resins (EPN) and epoxy cresol novolac resins are prepared from excess epichlorohydrin and phenol-formaldehyde or o-cresol-formaldehyde resins in presence of base as catalyst. Novolac epoxy resins generally contain multiple epoxide groups. The number of epoxide groups per molecule depends upon the number of phenolic hydroxyl group in the starting phenolic novolac resin, the extent to which they have reacted and the degree of low molecular species being polymerized during synthesis.
The high functionality of these Novolac resins increases crosslink density and improves thermal stability and chemical resistance. Epoxy resins derived from multifunctional aromatic glycidyl amine resins such as triglycidyl-p-aminophenol (ERL 0510, CIBA-GEICY) and tetraglycidyl-4, 4’-diaminodiphenyl methane (TGDDM, Araldite MY720, CIBA-GEIGY) have excellent elevated temperature properties.

1.2.3 Cycloaliphatic Epoxy resins

The epoxidation of unsaturated compounds with peracids is used in the manufacture of cycloaliphatic epoxy resins. Cycloaliphatic epoxy resins do not contain aromatic compounds and hence are more stable to ultra-violet exposure than bisphenol-A derived epoxy resins (Zhang et al 2008).

1.3 GENERAL PROPERTIES OF EPOXY NETWORKS

Epoxies exhibit outstanding properties that have placed them as the standard option for a variety of applications such as adhesives, coatings, composites for structural applications and so on.

Some of the reasons for this are:

(i) No emission of volatile products in the polymerization reaction.

(ii) Flexibility in the selection of monomers and co-monomers enabling one to obtain a variety of products from low –Tg rubbers to high –Tg materials.

(iii) Possibility to use and combine different polymerization chemistries appropriate for the particular processing needs.

(iv) Very low contraction during polymerization.
(v) Very high adhesion to a variety of surfaces due to the polar groups present in the structure.

(vi) Possibility of introducing different modifiers to generate optical properties (as in dispersions of droplets of liquid crystals in an epoxy matrix), or to increase toughness (rubber or thermoplastic-modified epoxies).

1.4 CURING AGENTS

Epoxy resins can be cured with a wide variety of curing agents. The addition of curing agents to epoxy depends on the required physical and chemical properties, processing methods and curing conditions. Epoxy resins can be cured with either catalytic or coreactive curing agents. Catalytic curing agents function as initiators for epoxy ring-opening homopolymerization. Epoxy resins can be catalytically cured by Lewis bases such as tertiary amines or Lewis acids such as boron trifluoride monoethylamine. These catalytic curing agents can be used for homopolymerization, as accelerators or supplemental curing agents for other curing agents such as amines or anhydrides. Photoinitiated cationic curing of epoxy resins has received great attention for the application of coatings from solvent-free or high solid systems.

The oxirane ring in the epoxy can react with the compounds containing activated hydrogen atoms such as alcohols, amines and carboxylic acids etc. Among them, primary and secondary amines are the most widely used curing agents for epoxy resins. A primary amine reacts with an epoxy group to produce a secondary amine and a secondary alcohol. The secondary amine can further react with an epoxy group to form a tertiary amine. The reaction involved between the epoxy ring and amine is shown in scheme 1.2. Aliphatic amines cure epoxy resins at room temperature; aromatic amines are
less basic and require elevated temperatures or accelerators to cure epoxy resins.

Other commercially important curing agents are formaldehyde resins and acid anhydrides. Melamine-formaldehyde, urea-formaldehyde and phenol-formaldehyde resins react with hydroxyl groups of high molecular weight epoxy resins to form crosslinked networks. Most commercial anhydride curing agents are based on cycloaliphatic structures. Epoxy-anhydride systems exhibit low viscosity, long pot life and low exothermic heats of reaction. The cured epoxy thermosets have good mechanical and electrical properties. Other curing agents including carboxylic acids, mercaptans, phenol Novolac resins and isocyanates are also commercially available.

![Scheme 1.2 Reaction between an amine and epoxy group](image)

**Scheme 1.2 Reaction between an amine and epoxy group**

### 1.5 PHOTOPOLYMERS

Photopolymers are imaging compositions based on polymers, oligomers or monomers which can be selectively polymerized and/or crosslinked upon image wise exposure by light radiation such as ultra-violet light (Fang and Yamamoto 2003). For final use, they are made into different forms including film/sheet, liquid, solution etc., which find outlets in printing plates, photoresists, stereolithography and imaging (Choi and Cha, 2002a).
Polymers containing photosensitive segments in the main or side chain have become attractive due to the photocrosslinking properties conferred by the presence of such units. Photoreactive polymers have unique characteristics which meet recent demands such as low polluting crosslinking reactions and high resolution for imaging, patterning and recording materials. Polymers containing the following groups either on the backbone or in the main chain are acting as photopolymers.

\[
\begin{align*}
\text{C} &= \text{C} \\
\text{C} &= \text{C} \\
\text{C} &= \text{C} \\
\text{C} &= \text{C} \\
\hline
\text{Unsaturated} & \quad \alpha, \beta-\text{Unsaturated} & \quad \text{Diazonaphthanone} \\
\hline
\text{Azide} & \quad \text{Azo} & \quad \text{Alkylazide} \\
\hline
\text{Benzoxazole} & \quad \text{Spiropyran} & \quad \\
\end{align*}
\]

Today photosensitive polymers are utilized in many technologies from photoresists to microelectronic components (Yakimansky 2002), miniature and integrated circuits, photo engraving, precision chemical milling and formation of protective and decorative coatings.

1.5.1 Photopolymerisation and Photocrosslinking

Photopolymerization is defined as the process whereby light is used to induce an increase in molecular weight, for example: photo polymerization of a vinyl monomer. Another type of photopolymerization is concerned with
the crosslinking of pre-existing high polymers. Following the common practice, however we refer to the former process as photopolymerization and the latter as photocrosslinking.

Any polymeric material undergoes physical changes when exposed to sunlight for prolonged periods. In more recent years, photopolymerization has proved to be of immense value in the understanding of the precise nature of polymerization processes. Photopolymerization techniques can be used in the production of photographic image (Crivello and Shim 1995). Photopolymerization at low temperature yields the low energy stereoregular configuration of the polymer. Indeed, photopolymerization is a practical means of carrying out the polymerization which cannot be carried out at high temperatures (Choi et al 2001).

Many photocrosslinkable ink and coating compositions in commercial use today consist of pre polymers or oligomers that are combined with polyfunctional monomers and photoinitiators.

Use of photosensitizers is often limited commercially to photocrosslinking some special coatings and a small number of special lithographic inks. UV light curing of most coatings and inks require greater crosslinking speeds than most photosensitivity can deliver. Currently industry uses many polymers that crosslink mostly by $2\pi + 2\pi$ type dimerizations with formations of cyclobutane rings. This is similar to the crosslinking reaction of the cinnamate group. These groups also include chalcone, urethane, acetal, polyester, polycarbonate etc. Such materials are used in photoresists, photolithography and in many ultraviolet light curable compositions intended for other uses. The photocrosslinking property has gained much importance as a photoresist for the production of printed circuits (Rehab 1998).
The UV-polymerization of multifunctional monomers is one of the more efficient methods available to generate three-dimensional polymeric networks. Among the advantages of this technology the high cure speed, the reduced energy consumption and the absence of VOC emissions are the most remarkable. It is well known that the UV curing can be performed either by a radical or a cationic photoinduced process presents some advantages compared to the radical one, in particular lack of inhibition by oxygen, lower shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates.

1.6 APPLICATIONS OF EPOXY RESINS

1.6.1 Bonding and Adhesives

Epoxy adhesives were originally developed for use in metal bonding in the aircraft industry. Recently, considerable interest has been developed for epoxy adhesives that cure at ambient with elevated temperature capability; such adhesives would aid industries like aerospace, automotive and electronics by facilitating low cost fabrication and rework.

1.6.2 Laminates and Composites

High performance materials are required for complex telecommunication equipment; epoxy resin based laminates fulfill the need. A polymer with a UV-sensitive group allowing photocrosslinking and an epoxy group for thermal crosslinking has been used as a photopolymerizable solder mask and in photoresists (Crivello and Shim 1995). Filament-wound epoxy components are used for rocket-motor castings, pressure vessels and tanks. In the aerospace industry, use of graphite fibre reinforced multifunctional epoxy resin composites is expected to increase rapidly because of their high strength to weight ratio.
Photopolymerizable epoxies using onium salt photoinitiators also show considerable promise for use in high performance composite applications. Traditional thermally cured epoxy resins are already well entrenched in these applications. However, the use of the recently developed photocurable epoxy materials offers considerable potential for rapid fabrication of fiber-reinforced composites without the need for cumbersome ovens and long cure times (Crivello and Lee 1989).

1.6.3 Tooling, Molding and Casting

Electrical equipment manufacturers have taken advantage of the design freedom afforded by epoxy casting techniques to produce transformers, insulators, high voltage cable accessories and switchgear components, etc. DGEBA and cycloaliphatic epoxy resins are used in casting systems, the cycloaliphatic resin systems exhibit good tracking properties and better resistance than DGEBA resins to UV radiation, which causes crazing and surface breakdown.

Transfer molding is used to encapsulate the solid state devices such as diodes, transistors and integrated circuits in epoxy molding powders. In manufacture of tools, epoxy casting resins are used as prototype and master models for product design, drilling and welding jigs, checking fixtures, injecting moulding, foundry patterns and stretch blocks. Epoxy resins prototype is less expensive than metals and can be modified quickly and cheaply.

1.6.4 Coatings

Epoxy resins provide durable coatings of high mechanical strength with good adhesion to variety of substrates. Epoxy resin based paints are widely employed for protection of steel structure in marine environment. The
bonding of epoxy coating to an uncontaminated steel substrate is due to the reaction between hydroxyl group and iron. Polyamidoamines and solvent-free epoxy coatings employing liquid resins and amine adduct are the most widely used systems. Solvent-free epoxy systems exhibit better resistance to chemicals and corrosion. Waterborne epoxy systems for baked finishes are used in electrodeposition and can coatings.

In recent years, there has been an increasing interest in the use of photosensitive epoxy resins for many industrial coating and printing processes. Because of their high cure and application speeds, essentially pollution-free operation, very low energy requirements, and generally excellent properties, coatings prepared by photopolymerization have made a substantial impact on the wood coating, metal decorating, and printing industries.

### 1.6.5 Construction

The epoxy resins are most commonly used in the construction field for concrete repair and rehabilitation. Epoxy resins are incorporated in flooring, where a covering is placed on a sub floor. In epoxy terrazzo floors, and epoxy binder replaces the cement matrix in marble aggregate flooring, providing impact resistance, mechanical strength and adhesion.

Epoxy resin systems for roads and bridges are effective barriers to moisture, chemicals, oils and greases, where liquid epoxy resin extended with coal tar and diethyltriamine curing agent (Hawary et al 2000).

### 1.6.6 Electronic applications

Owing to their excellent electrical properties, mechanical strength and processability as well, epoxy resins are widely adapted in the field of electronics. Novolac epoxy resins are widely used to formulate the moulding
compounds for microelectronics and packaging because of their superior performance at elevated temperature, excellent mould-ability, mechanical properties, superior electrical properties, heat and humidity resistance.

An electrical insulating compound having reduced viscosity, improved dielectric properties can be used for impregnation of high-voltage and low-voltage components of electronic devices, transformers and choke coils was produced by mixing bisphenol A epoxy resin having a molecular weight of 1,000-6,000 with phosphorous containing reactive modifier such as triglycidyl phosphate, diglycidyl methyl phosphate, or diglycidyl methylphosphonate and the aromatic diamine being selected from 4, 4’-diaminodiphenyl methane, 4,4’-diaminodiphenyl sulfone, and 4,4’-diaminodiphenyl ether.

1.7 REVIEW OF LITERATURE

1.7.1 Epoxy synthesis and their characterization

Oyanguren and Williams (1992) reported that there is no commercial epoxidised novolacs to convert phenolic hydroxyls into 100% of arylglycidyl ethers. The characterization of the epoxidised novolacs showed that the epoxidation efficiency was 84.3% and the fraction of –CH$_2$-CH(OH)-CH$_2$- bridges was 14.3%.

Carfagna et al (1997) demonstrated that liquid crystalline epoxy resins can be used as a matrix to encapsulate low molecular weight liquid crystalline droplets to produce polymer dispersed liquid crystal composites. They synthesized p-(2,3-epoxy propoxy)-a-methylstilbene(DOMS) and p-(2,3-epoxy propoxy)-diphenyl(DIF) as shown below. These were mixed with the liquid crystals and the curing kinetics of the resins was studied and the films from the resins were analyzed for optical and electro-optical properties.
Liu et al (1997) synthesized and studied a new phosphorus-containing oxirane bis-glycidyl phenylphosphate (BGPP), and a diamine, bis(4-aminophenyl)phenylphosphate (BAPP). They studied the curing kinetics of the BGPP with various curing agents, including BAPP. The introduction of electron withdrawing group into the compounds increased the BGPP and decreased the BAPP reactivity in the curing reaction. The thermal and the weight loss behavior of the cured epoxy resins studied by TGA showed the high char yields (32–52%) as well as high limiting oxygen index.
(LOI) values (34–49). These results showed the usefulness of these phosphorus-containing epoxy resins as flame retardants.

Chen-Yang et al (2000) synthesized a novel flame-retardant epoxy resin (4-diethoxyphosphoryloxyphenoxy)(4-glycidoxyphenoxy) cyclotriphosphazene (PPCTP). The curing of the synthesized epoxy resins were also studied with various commercially available curing agents. The flame retardant epoxy resins showed the higher reactivity of curing due to the presence of the electron withdrawing cyclotriphosphazene group in the PPCTP.

Kimura et al (2001) synthesized branched epoxy copolymers with oligo(benzoate) side chains carrying donor and acceptor functions in each end. They were synthesized to create unique second-order nonlinear optically active polymers. They reported that UV-Vis analysis of these polymer films have good optical quality and no absorption in visible region.

Lin et al (2002) synthesized novalac-based epoxy resins; tetramethyl stilbene-based novolac (II and IV) were synthesized from 2,6-dimethyl phenol and chloroacetaldehyde dimethylacetal or chloroacetone. They compared the thermal properties of synthesized stilbene-based epoxy resins with bisphenol epoxy system and observed that the degradation temperature is better than the bisphenol epoxy system. They also reported
that the methyl substituted synthesized epoxy resin has lower thermal stability than their counterparts.

Huang and Woo (2002) studied the physical miscibility at ambient temperature and chemical reactions between diglycidylether of bisphenol-A epoxy (DGEBA) and poly(4-vinyl phenol) (PVPh) by differential scanning calorimetry, fourier-transform infrared spectroscopy, scanning electron microscopy and solid-state $^{13}$C-NMR. They reported that, the blending of bisphenol-A and polyphenol took place above the temperature 80°C due to the reaction between the epoxide group of DGEBA and phenylhydroxyl group of PVPh.

He et al (2002) synthesized and characterized epoxy-based azopolymers with three kinds of backbone, containing different types of azochromophores and functionalized to different degrees. They studied the
structure-property relation of the polymers through photoinduced surface-relief grating (SRG) inscription experiments. They found that there was fastest inscription rate for 1,4-bis(2,3-epoxypropoxy)benzene-aniline-nitrosubstituted-bisphenol A epoxy resin.

Dinakaran et al (2003) prepared and characterized the modified epoxy matrix system which was made by using epoxy resin with 1,3-dicyanatobenzene or bismaleimide with diaminodiphenylmethane as a curing agent. By characterizing the epoxy matrix with FTIR and solid state $^{13}$C NMR techniques, they found that the mechanisms of reactions leading to a homogenous network between the DGEBA epoxy resin and poly(4-4-vinyl phenol).

Cascaval et al (2003) studied the thermal degradation of semi-interpenetrating polymer networks based on polyurethane and epoxy maleate of bisphenol-A using thermogravimetric analysis (TGA). The data was obtained from DTG-TGA curve. They studied the thermal behaviour of the polymers using Coats Redfern and Flynn-Wall-Ozawa and Reich Levi methods, which involve an approximate integration. They reported that the polymers containing high content of epoxy maleate of bisphenol-A showed higher thermal stability.

Dinakaran and Alagar (2003) studied the thermal and morphological properties of 1,1-bis(3-methyl-4-cyanatophenyl)cyclohexane-epoxy-bismaleimide matrices. They indicated that the introduction of cyanate ester and bismaleimide into epoxy resins improved the thermal properties, which was studied by TGA and DSC.

Xu et al (2004) synthesized and characterized epoxy resins bearing naphthyl and limonene moieties and its cured polymer. This epoxy monomer contains both naphthyl and cycloaliphatic group by chemical bonding in
molecule backbone and they are called as structural hybrid and named as NL epoxy resins. By structural characterization they inferred that the epoxy monomers were in mixtures of stereoisomers and geometric isomers. They reported that the cured NL epoxy resins exhibited much higher glass transition temperature, lower thermal expansion coefficient, lower water absorption, better resistance to thermally oxidative degradation and lower dielectric constants compared to that of diglycidyl ether of bisphenol A.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

The wide angle X-ray diffraction patterns showed an evidence for dense packing in molecules of the epoxy polymers when cured with dicyanodiamide (DICY) and bisphenol A-formaldehyde novolac resins. So they concluded that these epoxy polymers can be used as composite matrix and packaging material.

Wang and Lin (2005) prepared bis(3-hydroxy phenyl)phosphate (BHPP) monomer and synthesized phosphate based epoxy resins by reacting diglycidyl ether of bisphenol-A with BHPP. Further, these epoxy resins were cured with phenolic melamine, novolac and dicyanodiamide to prepare thermoset resins. They investigated thermal properties and thermal degradation behaviour of these thermoset resins by differential scanning calorimetry and thermogravimetric analysis. They reported that the thermoset resins cured with phenolic melamine exhibited higher glass transition temperatures than the other cured resins, owing to the high rigidity of their molecular chain. The decomposition temperatures of the thermoset resins cured with novolac were higher than those of the others. From the results they
revealed that the combination of phosphate based epoxy resins and the nitrogen containing curing agent can give improvement of flame retardance for their thermoset resins.

Ni and Zheng (2006) prepared epoxy containing Polyphenylsilsequioxane (PPSQ) and studied the morphological and thermomechanical properties of the synthesized composite system. They followed two strategies to prepare these epoxies. First, PPSQ was physically blended with epoxy and expected that polymerization induced phase separation would occur in the composite system. Second, an organometallic compound, aluminium triacetylacetone (Al(acac)$_3$), was used as a catalyst to promote the intercomponent reaction between epoxy and PPSQ to suppress the phase separation on a macroscopic scale. They reported that the organic-inorganic composites displayed improved thermal stability and flame retardancy.

Tao et al (2007b) synthesized a fluorinated epoxy resin, 1,1-bis(4-glycidylesterphenyl)-1-(3’-trifluoro methyl phenyl)-2,2,2-trifluoroethane (BGTF) cured with hexahydro-4-methylphthalic anhydride(HMPA) and 4,4’-diaminodiphenyl-methane(DDM) to study the thermal stability and reactivity of the fluorinated epoxy resins. To compare the reactivity and properties of synthesized resins, commercially available bisphenol-A diglycidyl ether (BADGE) was cured with HMPA and DDM. The synthesized fluorinated epoxy resins exhibited improved dielectric properties as compared with the BADGE epoxy resins. This is due to the low polarizability of the C-F bond and the large free volume of CF$_3$ groups in the polymer and also BGTF showed low water absorption because of the existence of hydrophobic fluorine atom.
Raghu et al (2007) synthesized polyurethanes containing 2,6-bis(4-hydroxy benzylidene)cyclohexanone hard segments with diisocyanate, 4,4'-diphenylmethane diisocyanate, toluene 2,4-diisocyanate isophore diisocyanate and hexamethylene diisocyanate. They characterized and studied the properties of the synthesized polymers by spectral methods, thermal analysis, X-ray diffraction methods and acoustic properties. They reported that these polymers contained domains of semicrystalline and amorphous structures and acoustic properties of the polyurethanes were in good range.

A new phosphazene based epoxy resin (PN-EP) through the reaction between diglycidylether of bisphenol-A (DGEBA) and Hexakis(4-hydroxyphenoxy)-cyclotriphosphazene (PN-OH) was synthesized by Liu and Wang (2009). The reactivity of PN-EP with the four curing agents 4,4'-diaminodiphenylmethane (DDM), dicyandiamide (DICY) and pyromellitic dianhydride (PMDA) was studied and reported that epoxy cured with DDM showed good flame retardancy. Their investigation on thermal properties shows that the synthesized epoxy resins showed higher glass transition temperature and decomposition temperatures in comparison with the corresponding DGEBA.

Morell et al (2010) studied the influence of hydroxyl-functionalized hyperbranched poly(ester-amide) in diglycidylether of bisphenol A. They used methyltetrahydrophthalic anhydride as curing agent to study the curing effect of the modified epoxy. The modified materials showed a higher thermal degradability than the neat diglycidylether of bisphenol A epoxy.
Ismail et al (2010) developed various biomass-based components, particularly lignin and glycerol, since they are abundantly produced as by-products in industrial processes. New types of crosslinked epoxy resins were synthesized from lignin and glycerol. Polymers were prepared through two-step reactions, ester-carboxylic acid derivative preparation followed by crosslinked epoxy resin preparation, in order to establish a crosslinked epoxy resin system in which glycerol units were included. The resins obtained were labeled as lignosulfonate-glycerol polyacid (LSGLYP A), and glycerol diglycidyl ether (GLYDGE). The glass transition temperature of the crosslinked epoxy resins increased with increasing LSGLYP A and GLYDGE contents for LSGLYP A and GLYDGE, respectively. The thermal degradation temperature for LSGLYP A and GLYDGE did not show significant change, suggesting that the crosslinked epoxy resins were thermally stable. The mass residue at 500°C was not affected by the changes of LSGLYP A and GLYDGE contents.

1.7.2 Flame retardant epoxy resins

For the enhancement of flame retardancy in epoxies, much research and development has been done. Modification of epoxy backbone by utilising monomers containing flame retardant elements (intrinsically flame retardant) such as halogen, nitrogen, phosphorous, boron, antimony etc is one approach, which is expensive, requires new monomers and affects the normal properties of the materials to a large extent.

Wu et al (2003) studied the thermal properties and flame retardancy of maleimide-epoxy resins. Maleimide epoxy compounds were prepared through reacting N-(4-hydroxylphenyl) maleimide with diglycidylether of bisphenol-A. The kinetics of the curing reactions of the maleimide-epoxy compounds with 4,4-diaminodiphenylenemethane (DDM) and dicyandiamide(DICY) showed that the incorporation of maleimide goups into
epoxy resins provided cyclic imide structure and high cross-linking density to the cured resins, increased the glass transition temperature and good thermal stability to the cured resins, high values of char yields and LOI values (25.5-29.5) of the cured resins showed good flame retardance.

Park and Shin (2006) showed the application of epoxy-based photosensitive polymers for optical MEMS. In their work, for the fabrication of the optical MEMS, they used epoxy-based negative photosensitive polymers such as commercially available SU-8 and SU-8-2000. They conducted subsequent reliability evaluation under the mechanical integrity and endurance tests. It was found that SU-8-2000 was better for uniformity than SU-8 and there are changes in the transmission and the peak wavelength.

Gao et al (2008) synthesized a novel reactive phosphorus containing flame retardant epoxy resin from 4-[(5, 5-dimethyl-2-oxide-1, 3, 2-dioxaphosphorinan-4-yl)oxy]-phenol and diglycidyl ether of bisphenol-A (DODPP-EP$_3$/LNPA). The glass transition temperatures and the thermal stabilities of cured epoxy resins decrease, while char yields increase with increasing phosphorous content. The analysis from cone calorimeter tests give the evidence that heat release rate, average mass loss rate and the fire growth rate index decrease significantly and inhibit the transmission of heat during combustion.

Hsin Ho Wu and Chu (2009) reported the physical characteristics of two modified novolac resins: carbonyl phenyl azo novolac resin and 4-(4-hydroxy phenyl azo) benzyl ester novolac resin. These modified novolac
resins give higher LOI and char yield due to the increase of the aromatic amounts and the cross-linking density and very good thermal stability.

Ding et al (2009) reported halogen free flame retardant epoxy resins with phosphorus containing siloxanes. It was prepared using 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with 1,2-divinyl-1,1,2,2-tetramethyldisiloxane (TMDS) and dichloromethylvinylsilane (DMDP). The phosphorus containing siloxanes showed good thermal stabilities, mechanical properties as well as flame retardancy of the epoxy resins. The cured epoxy resins exhibited improved mechanical properties and better thermal stabilities. The LOI values of 32-33 for cured epoxy resins with phosphorus confirmed their flame retardancy.

Toldy et al (2011) studied the effect of fibre retardancy of fibre-reinforced epoxy resin composites for aerospace applications. They studied the effect by comparing the flame retardancy and mechanical properties of aliphatic and aromatic epoxy resin matrices and composites flame retarded by phosphorous containing reactive amines.

1.7.3 Photosensitive epoxy resins

Everett et al (1995) modified simple cresol epoxy novolac resin with hydrophilic chain producing surfactant-modified epoxy resins. They were modified with photoacid generator and solvent, subsequently exposed to deep UV light. They behaved as a conventional chemically amplified negative resist material. Crivello and Shim (1995) synthesized the copolymer di-tert-butylfumarate with either allyltrimethyl silane or styrene which showed photosensitivity behaviour with poor dry etches resistant.
Decker et al (1996) synthesized different types of tridimensional polymer networks by photoinitiated polymerization of difunctional monomers (cycloepoxy, vinyl ether, and acrylate) blended to an epoxidised natural rubber. They studied the reactivity of photocurable epoxidised rubber, which can be substantially enhanced by the addition of a liquid difunctional monomer that acts as an efficient plasticizer, while at the same time contributing to the production of the three-dimensional network. By acting as a plasticizer, the monomer was found to markedly accelerate the ring-opening polymerization of the epoxy groups of the rubber chain. Cationic polymerization continues to proceed effectively after the UV-exposure, until total consumption of the epoxy groups. The nature of the comonomer has a strong influence on the properties of the crosslinked rubber. Low-modulus polymers were obtained with divinyl ether monomers, while hard but still flexible films were obtained with dicycloepoxy and diacrylate monomers.

So et al (2000) reported aryl cyclic sulphonium zwitterions which on ring opening photo polymerization gave non ionic polymers.

![Chemical structure](image)

Oyama et al (2001) prepared novel polystyrenes having various pendant epoxy groups by homopolymerization and copolymerization of the epoxide containing monomers with styrene and hydrosilation of polystyrenes having Si-H group with vinyl containing epoxides. He studied the photocrosslinking reactivity of the polymer in the presence of photoacid generator and concluded that the polymers having methyl group in the oxirane
ring had higher reactivity than the corresponding polymers without methyl groups and also the polymer having both silicon and cyclohexane oxide structure showed the highest crosslinking reactivity due to essentially high cationic polymerizability of cyclohexane oxide unit.

Choi and Oh (2002) synthesized photosensitive oligomer containing chalcone moiety in the main chain by end-capping reaction of diepoxide compound with methacrylic acid. The chalcone-epoxy oligomeric compound was synthesized with 4,4’-dihydroxychalcone and epichlorohydrin. They investigated the photosensitivity of the synthesized chalcone oligomer by using UV-Vis absorption and infrared spectroscopic techniques. Upon UV irradiation the synthesized epoxy undergo photodimerization and also photopolymerization with trace amount of dimethoxyphenylacetophenone.

Wang (2003) synthesized and characterized UV-curable polydimethylsiloxane epoxy acrylate (PSEA). It was synthesized by hydrosilylation of allyl glycidyl ether with hydrogen-containing polydimethylsiloxane to give poly dimethyl silozone-type epoxy resin which modified with acrylic acid. The curing speed and the double bond conversion
in the UV-cured film were found to be influenced by PSEA, as indicated by fourier transform infrared spectroscopy.

Acrylamide based photocrosslinkable polymers were prepared by polymerizing 4-acrylamidophenyl-2', 3'-benzostyryl ketone or 4-acrylamidophenyl-4'-N, N'-dimethylstyryl ketone in ethyl methyl ketone using benzoyl peroxide as the initiator (Selvam and Nanjundan 2005). Thermal stability, effect of different solvents and concentration of polymers on the rate of photocrosslinking were also assessed for using the polymers as negative photoresist materials.

Awaja and Pigram (2009) examined the surface molecular changes of epoxy composites with different reinforcements, in response to intense ultraviolet irradiation and high temperature. The surface degradation behavior is explored using X-ray photo electron spectroscopy and time-of-flight secondary ion mass spectrometry. They reported that the epoxy undergo surface crosslinking due to UV degradation.

A push-pull azo group containing epoxy polymer was synthesized by Fernandez et al (2009) and studied the photosensitivity of the epoxy. The results showed that the epoxy polymers with diverse chemical structure that contain azo groups could exhibit optical anisotropy when are excited with polarized laser light in the blue region.

Doring and Arnold (2009) studied metal complexes as initiators for the cationic polymerization of glycidyl-based epoxy resins. Among the metal complexes prepared, silver alkene complexes showed good thermal stability and high degree of crosslinking on thermal curing and electron beam induced curing.
Cindy et al (2010) studied the cationic photopolymerization of cycloaliphatic diepoxide coatings containing a monodisperse carbon black nano particles. They indicated that the long life times and reactive diffusion of cationic active centers may be used for effective curing of coatings carbon black nanoparticles.

Foix et al (2011) reported the effect of adding a hyperbranched polymer as chemical modifier of epoxy resins in UV cationic photocuring. They synthesized the hyperbranched polymer that contain a main structure of aromatic polyester with phenol chain ends, they modified the polymer with a linear polyethylene glycol in order to get an amphiphilic structure that can undergo supramolecular assembly during UV curing, leading to phase-separated thermosets.

1.7.4 Epoxies for liquid crystals

Choi and Cha (2002b) synthesized photocrosslinkable chalcone-epoxy compound comprising 1,3-bis-(4-hydroxy-phenyl)-propenone for fabricating photo-alignment layer of liquid crystals. Chalcone group was introduced into the main chain unit of the epoxy oligomer. They observed a photodimerization behavior and an optical anisotropy of this material by irradiation of a linearly polarized UV(LP-UV) light. With a trace amount of cationic photoinitiator, polymerization of epoxy groups leads to formation of photopolymerization. Linearly polarized UV irradiation on the chalcone-epoxy films with cationic photoinitiator induced optical anisotropy of the film and the resultant film can be used for alignment layers for low molecular weight nematic liquid crystals.
Murali et al (2007) reported the synthesis and characterization of epoxy terminated hyperbranched liquid crystalline benzylidene polyester with pendant hydroxyl groups. The polymers were synthesized by the polyaddition reaction of photoactive epoxidised bisbenzylidene cyclopentanone monomer with terephthalic acid and trimesic acid respectively. Both the polymers exhibited nematic mesophase. Upon UV irradiation the rate of photo-cycloaddition for hyperbranched polymers was found to be higher than that of linear one.

Gao et al (2007) synthesized a novel liquid crystalline epoxy monomer, 1,1’-bis[4-(2,3-epoxypropoxyphenylenevinomethyl)]-2,2’dimethyl biphenylene (BMPE) and studied the effect of BMPE content on the mechanical and thermal properties of its blends with diglycidyl ether of biphenol -A (DGEBA). BMPE presented a Schlieren texture in the range of 150 to 215°C as observed by differential scanning calorimeter (DSC) and polarizing optical microscope (POM). The improvement of mechanical properties of DGEBA modified with BMPE was achieved without sacrificing thermal resistance.

Srinivasa Rao and Samui (2008) studied the photoactive liquid crystalline hyperbranched polyester epoxies containing benzylidene moiety. The effect of linear and hyperbranched polymers and size of mesogenic unit on the physicochemical, thermal, mesogenic and photoactive properties of hyperbranched polymers were studied and compared. They found that the hyperbranched polymers containing acyclic alkanones moiety underwent faster photo cycloaddition reaction when compared to polymers containing cycloalkanone moieties.
1.7.5 Epoxy coatings for corrosion protection

Recently, there has been an upsurge of interest in the prevention of metallic corrosion using coating strategies. Epoxy is one of the most common coating materials used in severe corrosion environments moulding marine environment. Due to the hydrophilic chemical groups of used epoxy structure such as hydroxyl group (-OH), carboxyl group (C=O) and amino group (N-H) that have unpaired electrons and forms an adherent coatings consists mainly of resistance inhibition and the introduction of a barrier for the transport of corrosive species. The behaviour of a protective system depends mainly on a) the dielectric properties of the coating b) the adhesion of the coating to the substrate c) the water and oxygen uptake of the coating d) ion penetration through the coating e) pigments and inhibitive additives f) the surface characteristics of the metal substrates and surface pretreatment and g) various electrochemical corrosion reaction at the metal-coating interface after permeation of water and oxygen.

Miscokovic – Stankovic et al (1996) reported that the cathodic electrodeposition of an epoxy resin modified by an amine and isocyanate using a constant voltage method acts as protective coating for steel in different corrosive environments. The corrosion behaviour of these coatings was investigated using H$_2$O, 3%NaCl, 3%Na$_2$SO$_4$ and 3% sodium salt of 2-naphthol-3, 6 disulphonic acid using a.c. impedance measurements, gravimetric liquid sorption experiments and differential scanning calorimetry. They suggested that electrolyte penetration through an organic coating occurs in two steps; the first step is related to water uptake and second step is related to water in penetration through the macropores which leads to contact between the electrolyte and the metal surface and the beginning of the electrochemical processes.
Zhang et al (2002) studied the effect of polymeric structure on the corrosion protection of epoxy coatings. The two epoxy resin, phenol novolac resin and phenol novolac acetate was cured with o-cresol novolac epoxy resin and coated over aluminium substrate. The water sorption of the resin was determined by electrochemical impedance spectroscopy method (EIS). The narrowing of water passage at coating/metal interface is due to the hydrophobic layer can greatly improve the corrosion protection of the coating.

Brand et al (2004) studied two different methods by improving the adhesion between epoxy coating over aluminium substrates. An investigation of the interphasial region between the epoxy coating and the aluminium substrates in the final cured system showed that the polymeric layers were indeed unsolved in the curing reaction with the epoxy.

Muller and Fischer (2006) studied the corrosion inhibition action of epoxy ester resins for aluminium and zinc pigments in aqueous media at pH 10. An increase of resin addition effects a decreasing hydrogen evolution. Corrosion inhibition of aluminium and zinc pigments by the epoxy ester EPE is not significantly affected by other added paint resin such as saturated polyester or melamine resin.

Ji et al (2006) interestingly found that incorporation of silane monomer in epoxy coatings reduced the water absorption. Coating capacitance, measured by electrochemical impedance spectroscopy (EIS), was employed to calculate the amount of water uptake in epoxy coatings in aqueous solution. The water absorption in epoxy coatings was found to decrease drastically after incorporating silane component. EIS measurements were performed on coated aluminium alloys in 3.5% NaCl solution in the frequency range of 100KHz – 10mHz at 25°C.
Chen et al (2007) studied the anticorrosion performances of polyaniline emeraldine base / epoxy resin (EB/ER) coating on mild steel in 3.5% NaCl solution of various pH values were investigated by electrochemical impedance spectroscopy (EIS) for 150 days. In neutral solution (pH 6.1), EB/ER coating offered very efficient corrosion protection with respect to pure ER coating, especially when EB content was 5-10%. The impedance at 0.1Hz of the coating increased in the first 1-40 immersion days and the remained constant above $10^9 \Omega \text{cm}^2$ until 150 days, which in combination with the observation of a Fe$_3$O$_5$/Fe$_3$O$_4$ passive film formed on steel confirmed that the protection of EB was mainly anodic. In acidic or basic solution (pH 1 or 13), EB/ER coating also performed much better than pure ER coating. However, these media weakened the corrosion resistance due to breakdown of the passive film or deterioration of the ER binder.

Gonzalez-Garcia et al (2007) investigated the corrosion protection of steel substrates using polyurethane coating by electrochemical and structural properties. They used galvanised steel and mild steel for the study. Electrochemical impedance spectroscopy (EIS) was employed in the investigation of the corrosion characteristics of polyurethane polymeric film applied on metallic substrates during immersion in 0.5M NaCl aqueous solution. EIS measurements were carried out at the $E_{\text{corr}}$ potential of the samples in the frequency range 0.01 – 40,000 Hz. The spectra were fitted to model equivalent circuits by using the ZsimpWin 2.00 software. It has been found that polyurethane adheres more strongly to carbon steel than to galvanized steel.

Armelin et al (2008) carried out an investigation of polyaniline emeraldine salt and polypyrrole composite with carbon black as anticorrosive additives for epoxy paint coating. They studied the corrosion inhibition of
steel panels coated with paint modified with polyaniline emeraldine salt and polypyrrole composite after exposing to 3.5% NaCl solution for 720h. They indicated that polyaniline emeraldine salt presented the best protection.

Umoren et al (2008) studied the corrosion inhibition of mild steel in H₂SO₄ in the presence of gum arabic and polyethylene glycol. Among the two polymers, polyethylene glycol was found to be a better inhibitor for mild steel corrosion in acidic medium than gum arabic, a naturally occurring polymer. They also studied the effect of addition of halides such as KCl, KBr and KI to the medium, and found that there is increase in the inhibition efficiency (I%) and degree of surface coverage (Q).

Ahmetli et al (2011) synthesized copolymers of glycidyl ester of styrene with acrylic, methacrylic and itaconic acids by polymerization in toluene with benzoyl peroxide initiation and have been tested as anticorrosive films. Polarizing microscope images were employed to characterize the anti corrosive properties of the formed films and the copolymers showed strong adhesion to the substrate.

Bajat et al (2010) investigated the influence of aluminium surface pretreatment by vinyltriethoxysilane (VTES) film on the adhesion and corrosion stability of thin nonpigmented epoxy cataphoretic coating on exposure to 2% NaCl. The results from the adhesion strength by pull off test and coating expectance of epoxy coating by impedance measurements revealed the better adhesion of epoxy coating on aluminium pretreated by VTEs film.
1.8 SCOPE AND OBJECTIVES

The great efforts of many researchers have culminated in the development of epoxy resins having desired levels of flame retardant characteristics and thermal stability. A better knowledge on the network structure, physical properties and performance shall help to initiate widespread applications of these resins in electrical, electronic and aerospace industries.

Even though, the literature survey indicates a vast variety of epoxy resins being made globally for many different fields, there are very few reports regarding epoxies with photosensitive groups. Taking into consideration the preeminent importance assumed and the potential as futuristic materials, the present investigation focuses on the synthesis and characterization of photosensitive epoxy resins containing benzylidene and cycloalkanone moieties in the main chain. Cycloalkanone moiety is expected to be stable towards UV radiation and at the same time, benzylidene moiety is more prone to undergo crosslinking.

The objectives are:

1. Synthesis of following monomers and their epoxy resins:
   • 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone (BHMBCH)
   • 2,5-bis(4-hydroxy-3-methoxybenzylidene) cyclopentanone (BHMBCP)
   • 2,6-bis(4-hydroxybenzylidene)cyclohexanone (BHBCH)
   • 2,5-bis(4-hydroxybenzylidene)cyclopentanone (BHBCP)

2. Synthesis of bisphenol A epoxy
3. Synthesis of copolymers of epoxy resins by reacting either BHMBCH or BHMBCP or BHBCH or BHBCP with bisphenol–A and epichlorohydrin in presence of base catalyst by solution polycondensation method.

4. Characterization of monomers by elemental analyses, solubility, UV-Vis, FTIR, $^1$H and $^{13}$C-NMR spectroscopic techniques.

5. Characterization of synthesized epoxy resins by solubility, epoxy equivalent by pyridinium method, GPC, FTIR, $^1$H and $^{13}$C-NMR spectroscopic techniques and X-ray diffraction studies.

6. Examination of the thermal properties of the synthesized epoxy resins by TGA and DSC.

7. Determination of LOI of the epoxy resins using Van Krevelen’s equation.

8. Study of the photocrosslinking of the epoxy resins by UV-Vis spectroscopy

9. Study of the photopolymerization of the epoxy resins by UV-Vis, FTIR and DSC.

10. Investigation of the thermal degradation kinetics of UV exposed epoxy resin in presence and absence of photoacid generator.

11. Study of the corrosion inhibition behaviour of epoxy resins by electrochemical methods and SEM analysis.

The scheme of present study is represented in the following flow chart.
SYNTHESIS AND CHARACTERIZATION OF PHOTOSENSITIVE EPOXY RESINS CONTAINING BENZYLIDENE AND CYCLOALKANONE MOIETIES IN THE MAIN CHAIN

Synthesis of aromatic diol monomers

Monomer characterization: UV-Vis, FTIR, $^1$H-NMR, $^{13}$C-NMR, Elemental analysis

Synthesis of epoxy resins from diol monomers and copolymers of epoxy resins

EPOXY RESINS CHARACTERIZATION

Solubility

Spectral analysis

Thermal analysis

Photosensitivity study

Corrosion studies

FT IR, $^1$H-NMR, $^{13}$C-NMR

TGA & DSC

Photocrosslinking

Photopolymerization

Electrochemical methods

Thermal degradation kinetics by TGA

Monitored by UV

Monitored by FTIR DSC

SEM analysis