MODIFICATIONS OF DGEBA USING EPOXIDISED RESINS

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Modifications of DGEBA Using Epoxidised Resins

Ph. D Thesis

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Certificate

This is to certify that the thesis entitled **"Modifications of DGEBA using Epoxidised Resins"** which is being submitted by Mr. Jenish Paul in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22 is a record of the bonafide research work carried out by him under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Cochin-682 022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

Dr. Eby Thomas Thachil
(Supervising Teacher)

Declaration

I hereby declare that the work presented in this thesis entitled "**Modifications of DGEBA using Epoxidised Resins**" is based on the original research work carried out by me under the guidance and supervision of **Dr. Eby Thomas Thachil**, professor, Department of Polymer Science And Rubber Technology, Cochin University of Science and Technology, Cochin-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

Cochin-22
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Jenish Paul

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Jenish Paul

Dedicated to

Parents, Teachers, Wife Bini

&

Daughter Jovina

Preface

The most widely used epoxies are the glycidyl ether derivatives of bisphenol A (DGEBA). High chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, flexibility, good electrical properties and ability to be processed under a variety of conditions are characteristics of DGEBA resins. However one major drawback is their poor resistance to impact and crack initiation. Consequently, there is a need to improve the fracture toughness and impact resistance while maintaining desirable properties. Various approaches to toughening include the addition of a second phase consisting of polymeric materials like rubbers and thermoplastics and reinforcement using high strength fibres.

This study broadly aims at investigating and optimising new as well as reported techniques for modifying epoxy resins. Consisting of six chapters, the thesis gives an introduction and literature survey in the first chapter.

Modification of DGEBA with epoxidised novolac resin from phenol, ortho cresol, p-cresol, phenol naphthol mixture and epoxidised cardanol and measurement of various properties are dealt with in the second chapter. The effect of ageing on DGEBA resin modified by epoxy novolacs and unmodified resin is also investigated.

Synthesis of epoxy functional polydimethyl siloxanes and modification of DGEBA with synthesised siloxanes are given in Chapter three. Synthesised resins are characterised by spectroscopic methods. The physical properties of the cured blends are compared with those of the neat resin. The effect of ageing on DGEBA resin modified by siloxanes as well as unmodified resin is also investigated.

Modification of commercial DGEBA resin by physical blending using two component systems is dealt with in Chapter 4. The two components used are EEN (mixture of EC and pECN), TPN (mixture of TEF PDMS and pECN) and PEN(mixture of PEF PDMS50 and pECN). The effect of ageing on DGEBA resin modified by two component as well as unmodified resin is also investigated.

The effects of matrix toughening on the properties of glass reinforced composites and on the properties of epoxy resin are studied in Chapter 5.

The major findings of the study along with scope for future research are summarised in the last chapter. Relevant references are given at the end of each chapter and a list of abbreviations and symbols is given at the end of the thesis.

Contents

Chapter 1
INTRODUCTION AND LITERATURE SURVEY -----------------01 - 75

Chapter 2
MODIFICATION OF DGEBA USING EPOXIDISED PHENOLIC RESIN--77 - 151

Chapter 3

Chapter 4
MODIFICATION BY TWO COMPONENT SYSTEMS -------- 199 - 238

Chapter 5
GLASS REINFORCED EPOXY RESIN --------------------------239 - 267

Chapter **6**

……

Chapter 1

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

Plastics are used on a daily basis throughout the world. The word plastic is a common term that is used for many materials of synthetic or semi-synthetic nature. The term was derived from the Greek ‘plastikos’, which means “fit for molding.” Plastics possess a wide variety of combinations of properties when viewed as a whole. We synthetically manufacture innumerable plastic items relating to clothing, packaging, automobiles, electronics, aircrafts, medical supplies, recreation etc. The list could go on and on and it is obvious that much of our comforts, appliances and technological advancements today would not be possible without plastics. According to their structure and behaviour, plastics can be classified as thermoplastics and thermosetting plastics or thermosets [1]

Thermoplastics soften or melt on heating and can be converted into any shape before they cool down to a solid. Solidification of these polymers is reversible and they can be reshaped by the application of heat and pressure, each cycle causing some deterioration in properties. Their polymer chains consist of linear or branched chain molecules having strong intramolecular bonds but weak intermolecular bonds. They are semi-crystalline or amorphous in structure and the chains can move freely each time the plastics are melted or softened. They generally require less time to solidify compared to thermosets which undergo a cross-linking reaction before solidification. Important commercial examples include polyethylene, polyvinyl chloride, polystyrene, polypropylene, polyamides, polycarbonate, polyacetals and polyesters.

Thermosetting plastics have cross-linked or network structures with covalent bonds between molecules. Once solidified by the cross-linking process, they cannot be remelted or reshaped. Since thermosets cannot be remelted, engineers use them in applications that require high resistance to heat. Common examples include epoxy resins, phenolics, aminoplastics, silicones, and unsaturated polyester resins.

Thermosetting plastics are brittle materials whose load-bearing qualities can be improved by reinforcing with fibres. Such fibre-reinforced plastics have replaced conventional structural materials, such as wood and steel, in innumerable engineering applications because of high strength-to-weight ratios, excellent chemical resistance, weatherability, and versatility of product design.

Epoxy resins constitute a class of thermosets containing more than one epoxide groups per molecule which are very reactive to many substrates [2]. They are used extensively as reinforced composites, adhesives, high performance coatings and potting and encapsulating materials.

1.2 Thermoset resins

Thermosetting resins change irreversibly under the influence of heat and/or catalysts into an infusible and insoluble material by the formation of covalently cross-linked, thermally stable networks. Such polymers are prepared in two stages. The first step is the formation of long chain molecules which are capable of further reaction with each other. The second stage is the application of heat and/or the addition of curatives/catalysts which cause a reaction to occur between the chains, thus producing a complex cross-linked polymer. Sometimes irradiation is employed to achieve cross-linking [3]. Important thermosetting resins are epoxy resins, unsaturated polyesters, alkyds, vinyl esters and allyl resins, phenolics, amino plastics, urethanes, silicones, furfural etc.[4].

1.2.1 Epoxy resins

Epoxy resins are characterised by the presence of more than one 1, 2 epoxide groups per molecule. The first and still the most important class of commercial epoxy resins is the reaction product of bis-phenol A (BPA) and epichlorohydrin in the presence of sodium hydroxide. It is called the diglycidyl ether of bis-phenol A (DGEBA). It has the general structure shown in Fig.1.1.

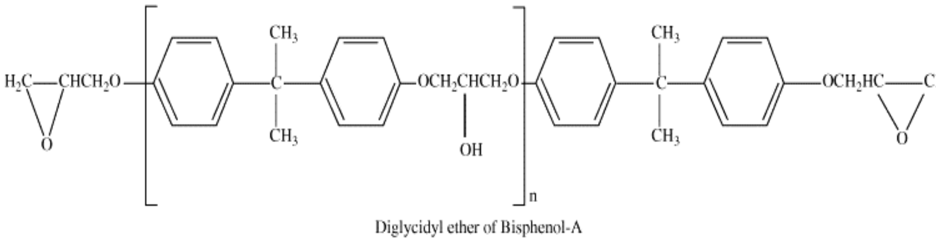


Fig. 1.1 Structure of DGEBA

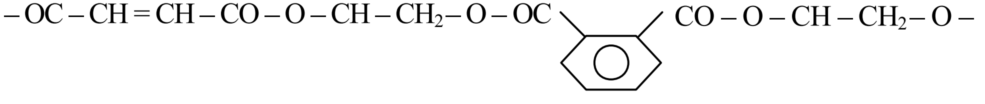
There are a large number of epoxy resins in use. High molecular weight resins are prepared by reducing the excess of epichlorohydrin and reacting under strongly alkaline conditions. The nonepoxy part of the molecule may be aliphatic, cyclo-aliphatic or aromatic hydrocarbon. It may be non-hydrocarbon and polar also. Treatment with curing agents gives insoluble and intractable thermosets. To facilitate processing and modify resin properties other constituents may be included in the compositions; e.g., solvents, diluents, plasticizers, flexibilizers and accelerators. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Hardeners include anhydrides (acids), amines, polyamides, dicyandiamide etc.

1.2.2 Polyester resins

A large number of thermoset polyester resins are commercially available and these can be conveniently classified into alkyds, unsaturated polyesters, vinyl esters, allyl resins etc.

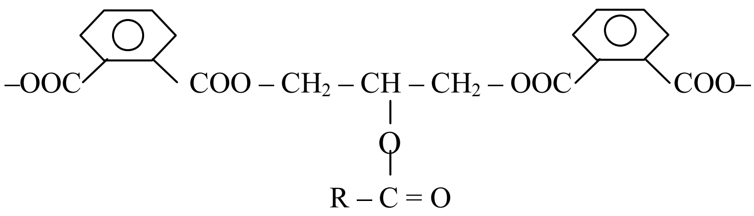
a) Unsaturated polyesters

Unsaturated polyesters(UP) are prepared by reacting a mixture of unsaturated and saturated dicarboxylic acids with diols. General purpose (GP) grade UP resin is prepared by the condensation of propylene glycol (PG) with a mixture of maleic anhydride (MA) and phthalic anhydride (PA). When cross-linking is initiated with the help of a catalyst and an accelerator styrene the co-reactive diluent facilitates cross-linking at the sites of unsaturation in the polyester chains.



b) Akyd resins

Alkyd resins are produced by reacting a polyhydric alcohol, usually glycerol, with a polybasic acid, usually phthalic acid and the fatty acids of various oils such as linseed oil, soyabean oil and tung oil. They are nowadays employed mostly in the surface coatings field.

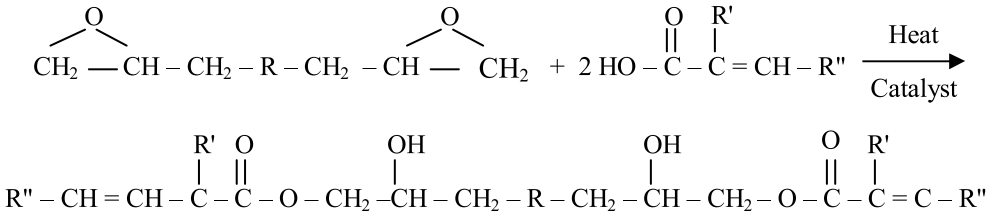


R represents the long chain alkyl radical characteristic of the oil.

c) Vinyl esters

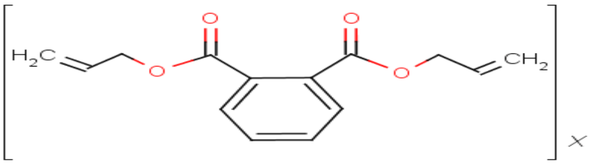
Vinyl esters [5] are chemically the reaction products of epoxy resin and ethylenically unsaturated monocarboxylic acids like methacrylic acid with styrene added as a coreactant.

Typical reactions are as follows:



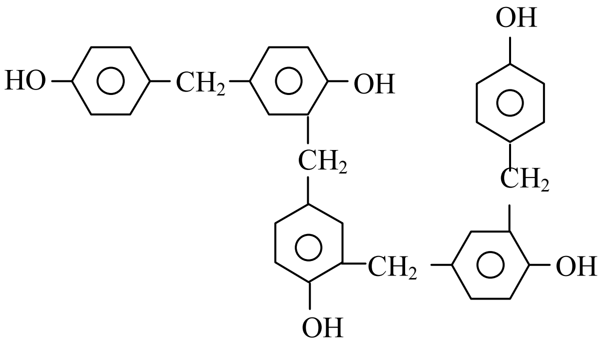
(d) Allyl resins

Allyl resins [1] retain their desirable physical and electrical properties on prolonged exposure to severe environmental conditions. Their monomers are employed widely as cross-linking agents in other polyester systems. The principal allylics are the reaction products of allyl alcohol and phthalic acid or isophthalic acid. They are used as monomers and partially polymerised prepolymers. They are cured by heat and /or free radical catalysts.

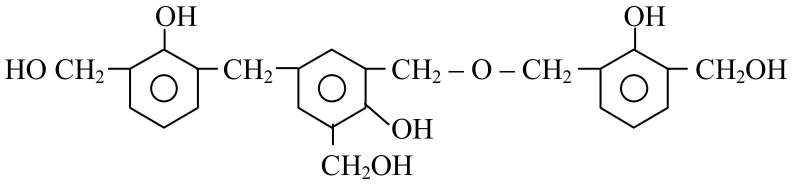


1.2.3 Phenolics [1]

Phenolic resins were the first polymeric resins produced commercially from simple low molecular weight compounds. Phenol formaldehyde (PF) resins are prepared by the polycondensation between phenol and formaldehyde in the presence of either an acid or a base catalyst. The initial phenol-formaldehyde reaction products may be of two types, novolacs and resols. Novolacs are prepared by reacting formaldehyde and a molar excess of phenol under acidic conditions. These resins are linear molecules containing 5-6 benzene rings. A typical example of the many possible structures is shown below.



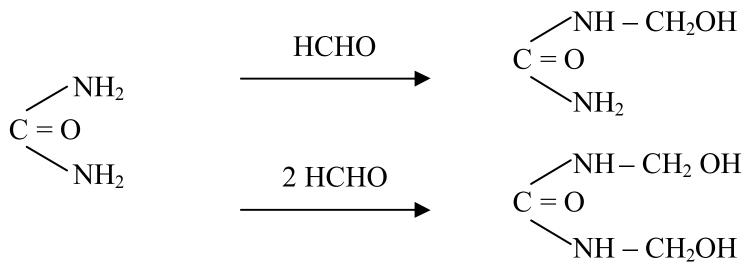
A resol is prepared by reacting phenol with an excess of formaldehyde under basic conditions. Although methylol formation is rapid subsequent condensation is slow. Hence low molecular weight liquid resols containing 2-3 benzene rings are formed. When the resol is heated cross-linking via the uncondensed methylol groups. A possible resol structure is as follows.



Phenolic resins are mainly used for moulding, bonding, surface coating, adhesive and laminating applications. Controlled synthesis of ortho substituted phenol-formaldehyde resin has been reported recently [6].

1.2.4 Aminoplasts

Aminoplastics [1] are a range of resinous polymers produced by the interaction of amines and amides with aldehydes. The important polymers belonging to this class are urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins. UF resins are prepared by a two-stage reaction. The first stage involves the reaction of urea and formaldehyde under neutral or mildly basic conditions to form mono and dimethylol ureas. Their ratio depends on the urea to formaldehyde ratio.

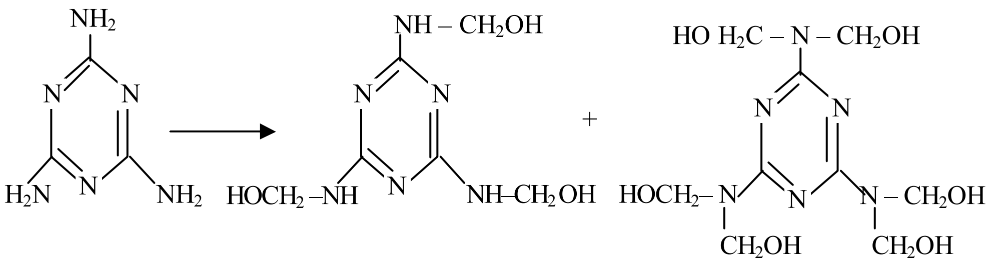


In the second stage these are subjected to acid conditions at elevated temperatures and the following reactions occur.

Methylol ureas condense with each other by the reaction between the $–CH_2$ group of one molecule and the $–NH_2$ group of another to form linear chains.

$$H_2N-CO-NH-CH_2OH + H_2N-CO-NH-CH_2OH \rightarrow \sim\sim HN-CO-NH-CH_2 \sim\sim$$

Melamine reacts with neutralised formaldehyde at about 80-100°C to form a mixture of water soluble tri and hexamethylol amines. The number of methylol groups depends on the melamine to formaldehyde ratio and the reaction conditions. The methylols formed enter into reactions similar to UF resins and give a cross-linked polymer. The main resinification reaction involves methylol- methylol condensation.



$$\sim\sim NH-CH_2-OH+HO-H_2C-HN\sim\sim\rightarrow\sim\sim NH-CH_2O-H_2C-HN\sim\sim+H_2O$$

The tensile strength and hardness of UF resins are better than that of phenolics. MF resins have better hardness, heat resistance and moisture resistance than UF resins. Amino resins are used as moulding and laminating resins apart from adhesive formulations.

1.2.5 Polyurethanes

Polyurethanes (PU) [1] are polymers which contain urethane groups (-NH-COO-) in the main chain formed by the reaction of a polyfunctional isocyanate and a polyol.

$$n\ HO\text{-}R\text{-}OH + n\ OCN\text{-}R'\text{-}NCO + \longrightarrow H\ \text{-}(OR\text{-}OOCNH\text{-}R')_n\text{-}NCO\text{-}$$

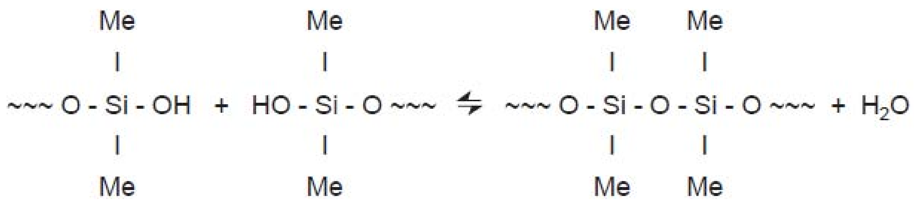
Polyurethanes are extremely versatile polymers. They occur in the liquid, gum or thermoplastic resin states. Depending on the raw materials used, either linear or crosslinked polyurethanes can be produced. Common isocyanates used are 4, 4’diphenyl methane diisocyanate (MDI) and toluene diisocyanate (TDI).

Polyurethane elastomers find a wide number of applications due to their unique property of combining high strength with high hardness and high modulus plus high elongation at break. This combination of properties is not possessed by any other commercial rubber or plastic. Urethane elastomers also have greater energy absorption properties than other similar rubbers and plastics.

1.2.6 Silicones

Silicone polymers are inorganic polymers having thermal stability, good electrical insulation, water repellancy, and anti-adhesive properties.

The polymers are available as fluids, greases, rubbers and resins. Silicon forms polymers mainly through silicone bonds represented as –Si–O–Si–. Silicone polymers are produced by intermolecular condensation of silanols formed by hydrolysis of alkyl chlorosilanes and aryl chlorosilanes.



$$\sim\sim\sim O-\underset{Me}{\overset{Me}{Si}}-OH + HO-\underset{Me}{\overset{Me}{Si}}-O\sim\sim\sim \rightleftharpoons \sim\sim\sim O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O\sim\sim\sim + H_2O$$

Silicone polymers are thermally stable and are available in liquid, waxy and rubbery forms. These polymers are used in surface coatings and adhesives where chemical resistance and water repellence are important. Silicone polymers are also used for laminates which can withstand high temperatures without degradation. Silicone foams are used in aeroplanes and missiles. Silicone elastomers can be vulcanised with peroxide initiators.

1.2.7 Furans

Furan resins have greater chemical and heat resistance than polyester, epoxide, phenolic or aminoplastic resins. Furfural and furfuryl alcohol are starting materials for these polymers. They undergo polymerisation to form resins. The important applications are lining of tanks and piping, manufacture of alkali resistant cements and preparation of laminates for chemical plants.

1.3 Epoxy Resins

1.3.1 Introduction.

Epoxy resins, also known as polyepoxides are a class of reactive prepolymers and polymers which contain epoxide groups.The three membered ring structure is also known as the epoxide, oxirane, or ethoxyline group (Fig.1.2).This group may lie within the body of the molecule but is usually terminal. The three membered epoxy ring is highly strained and is reactive to many substances, particularly proton donors.

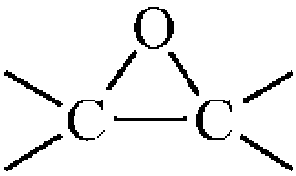


Fig.1.2 Epoxy ring

In 1936, De Trey Freres produced a low melting bisphenol A based epoxy resin which gave a thermoset composition with phthalic anhydride [7]**.** In 1939, a high molecular weight resin was produced in the US from bisphenol A and epichlorohydrin and esterification with unsaturated fatty acids provided an air dried coating**.** The commercial interest in epoxy resins became apparent with the publication of a German Patent [8] in 1939 which described liquid polyepoxides. In the early stages of development, epoxy resins were used almost entirely for surface coatings and developments in this field are to a large extent due to the work of S.O. Greenlee, described in a number of patents [9]. Epoxy resins were first offered commercially in 1946 and are now used in a wide variety of industries.

1.3.2 Types of epoxy resins

Epoxy resins fall into different types based on their structure and applications. In addition to DGEBA type resins; there are various other types of resins with epoxy functionality.

a. Phenoxy resins:

They are thermoplastic polymers derived from bisphenols and epichlorohydrin. Their molecular weights are higher than those of conventional epoxy resins. They do not have terminal epoxy groups and are therefore thermally stable. They have the same repeating units as advanced epoxy resins and are classified as polyols or polyhydric ethers. Phenoxy resins are prepared by reaction of pure bisphenol A with epichlorohydrin in a 1:1 mole ratio or from high purity DGEBA and bisphenol A in a 1:1 mole ratio. These resins are offered in the form of solutions for coating applications and as granular moulding compounds. Solution polymerisation is employed to achieve molecular weight and processibility [4].

b. Multifunctional epoxy resins

Aromatic glycidyl ether resins: Epoxidised phenol novolac resins (EPN) and cresol novolac resins (ECN) are made by glycidylation of phenol/cresol-formaldehyde condensates (novolacs) obtained from acid catalysed condensation of phenol/cresol and formaldehyde. This gives random ortho and para methylene bridges (see Fig.1.3). Epoxidation of novolacs with an excess of epichlorohydrin minimizes the reaction of phenolic hydroxyl groups with glycidylated phenol groups and prevents branching. A wide variety of novolac resins based on a range of phenols including cresols, ethyl phenols, t-butyl phenols, resorcinol, hydroquinone and catechol may be used to prepare epoxy novolac resins. An increase in the molecular weight of the novolac increases the functionality of the resin. EPN resins range from a high viscosity liquid to solids. The epoxy functionality is between 2.2 and 3.8. ECN resins derived from o-cresol novolacs have even higher functionalities (2.5 to 6). The major applications of epoxy novolac resins have been in heat resistant structural laminates, electrical laminates; chemical resistant filament wound pipes and high temperature adhesives. Epoxy phenol novolacs cured by hyper branched (3-hydroxy phenyl) phosphate exhibits improved thermal properties [10]. EPNs can be modified by different methods of which the one using poly siloxane is found to give a tough resin with enhanced thermal resistance [11].

The lowest member of the series of phenolic novolacs is bisphenol F which is prepared with a large excess of phenol to formaldehyde. Epoxidation of the product (a mixture of o,o', o,p' and p,p' isomers) yields a liquid bisphenol F resin which shows higher functionality than unmodified BPA liquid resins.

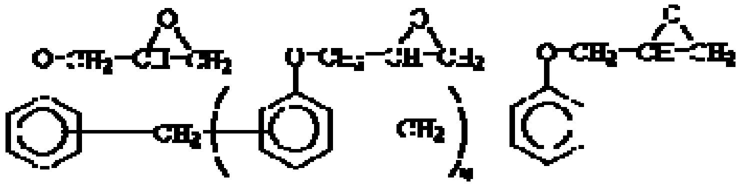


Fig. 1.3 Typical structure of EPN

Aromatic glycidyl amine resins: Among the multifunctional epoxies wth aromatic amine backbone, only a few have gained commercial importance. The triglycidyl derivative of p-amino phenol is formed by glycidilation of p-aminophenol with large excess of epichlorohydrin under controlled conditions. The resin has low viscosity, 2500-5000 mPa.s at 25^0C and weight per epoxy value (wpe) 105-115. The trifunctional resin can be cured at 70^0C and it possesses excellent elevated temperature properties. Tetraglycidyl methylene dianiline (MDA) resins are used as binders in graphite reinforced composites. They have viscosity in the range 5000-25000 mPa.s at 50^0C and wpe values in the range 117-133. Commercially these are available as Araldite MY 720. Glycidylation of cyanuric acid with epichlorohydrin gives triglycidyl isocyanurate marketed as PT 810 (Ciba Geigy). This crystalline compound (wpe 108) acts as a cross-linking agent for carboxylated polyesters. In addition, many glycidyl esters such as diglycidyl ester of hexahydrophthalic acid are also commercially available. They have low viscosities of the order of 500 mPa.s.[4]

c. ***Non-glycidyl ether epoxides***: [4]

Non-glycidyl ether epoxides are of two types: those with ring structures as well as epoxide group in the molecule (called cyclic aliphatic resins) and those having linear structure on to which are attached epoxide groups (called acyclic aliphatic epoxy resins). Vinyl cyclohexene dioxide, dicyclopentadiene dioxide etc. are commercially available cyclic aliphatic epoxy resins. Because of compact structure, density of cross-linking after cure is greater for cycloaliphatic resins compared to standard diglycidyl ether resins. ERL-4229(wpe131-143), ERL-4206 (wpe70-76) and ERL-4299 (wpe180-210) are commercial grades of cycloaliphatic epoxy resins.

Among acyclic aliphatic resins, three types of resins can be identified; epoxidised diene polymers, epoxidised oils and polyglycol diepoxides.

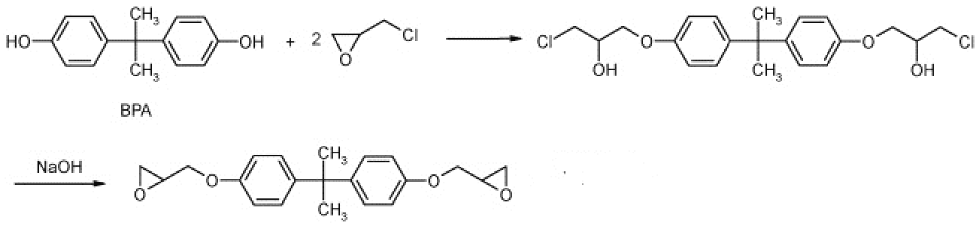
Epoxidation of unsaturated fatty acids and their glycerol esters is effected by peracids. Epoxidised soybean and linseed oils have been available for many years as stabilisers for polyvinyl chloride. Cationic polymerisation of a bio-based epoxy, epoxidised castor oil, initiated by N-benzyl pyrazinium and quinoxalinium hexafluroantimonates (BPH and BQH respectively) as catalyst has been reported [12]. Polyglycol diepoxides are used as flexibilisers in commercial epoxy resins.

Commercially epoxy resins are marketed under the trade names Araldite, DER, Epi-Cure, Epi-Res, Epikote, Epon, Epotuf etc.

1.3.3 Epoxy resin Chemistry

1.3.3.1 Synthesis of epoxy resin

DGEBA resin is prepared by reacting bisphenol A with epichlorohydrin (ECH) in the presence of caustic soda [7]. The reaction occurs in two steps: i) the formation of a chlorohydrin intermediate and ii) dehydrohalogenation of chlorohydrin to the glycidyl ether (Scheme 1.1). 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.



Scheme.1.1 Synthesis of DGEBA

Experimentally, when epichlorohydrin and bisphenol A are used in the ratio 2:1 some high molecular weight species are also formed. Therefore in practice two to three times the stoichiometric amount of epichlorohydrin is used to minimise polymerisation of reactants to high molecular weight species [13]. The typical commercial grade liquid epoxy resin has an average molecular weight of about 370, a viscosity of 11,000-15,000 mPa.s at 25^0C and weight per epoxide 188.

Epoxy resins with varying molecular weights are commercially made by two processes namely the Taffy process and the Advancement Process

i. The Taffy Process **[14]**

A mixture of bisphenol A (228 parts by weight) and 10% aqueous sodium hydroxide solution (75 parts by weight) is introduced into a reactor equipped with a stirrer. The mixture is heated to about 45^0C and epichlorohydrin (145 parts by weight) is added rapidly with agitation, giving off heat. The temperature rises to 95^0C where it is maintained for about 80 minutes for completion of reaction. Agitation is stopped and the reaction mixture is separated into two layers. The heavier aqueous layer is drawn off and the molten resin is washed with water until it becomes neutral. This taffy like product is dried at 130^0C to get a solid resin with a softening point of 70 ^{0}C and a wpe of about 500. Resins produced this way exhibit high α-glycol values (due to hydrolysis of epoxy groups) and n values 0,1,2,3 etc. The degree of polymerisation is decided by the ratio of liquid resin (crude DGEBA) to bisphenol A. The diglycidyl ether of bisphenol A has a molecular weight of 340 (n=0). Many of the commercial liquid DGEBA resins have average molecular weights in the range

340-400. High molecular weight solid products can be obtained by reducing the amount of epichlorohydrin and reacting under strongly alkaline conditions. They are characterised by a repeat unit containing a secondary hydroxyl group with degrees of polymerisation values ranging from 2 to 30 in commercial resins. Two terminal epoxy groups are theoretically present. Pure DGEBA is a solid melting at 43^0C. The unmodified resin can crystallise depending on the storage conditions

ii. The Advancement Process

This method involves chain extension reaction of liquid epoxy resin with bisphenol A and is widely used in commercial practice. This is also referred to as the ‘fusion process’. Resins produced this way exhibit mostly even numbered n values because a difunctional phenol is added to a diglycidyl ether of a difunctional phenol. Isolation of the polymerized product is simpler, since removal of NaCl is unnecessary. High molecular weight epoxy resin can be obtained from low molecular weight resin by reacting with bisphenol A in the presence of a basic catalyst [15]. An immediate molecular weight increase can be achieved by mixing low molecular weight resin with bisphenol A and curing with polyamines. Two competitive processes have been shown to take place namely chain extension and cross-linking [16]. Products of rather high molecular weight (>4000) can be formed before cross-linking starts.

Advancement reaction catalysts facilitate the rapid formation of medium and high molecular weight linear resins and control side reactions. The most prominent side reaction is chain branching due to addition of the epoxy group to the secondary alcohol group generated in the chain extenting process [17]. The extent of branching can be determined by spectroscopic methods [18]. Branched epoxy resins are also prepared by advancing a liquid epoxy resin with bisphenol A in the presence of an epoxy novolac having a functionality of about 3.6 epoxy groups per molecule. Conventional advancement catalysts include basic inorganic reagents such as caustic soda, sodium carbonate, KOH or LiOH and amines and quaternary ammonium salts. The selectivity of the catalyst is important i.e., the ability to direct the reaction of phenolic hydroxyl group to the epoxy ring in preference to the addition of the secondary hydroxyl groups. Regeneration of the phenoxide ion repeats the cycle and eliminates side reactions.

Excellent selectivity is obtained from amines containing β-hydroxy groups, particularly triethanolamine. Imidazole and substituted imidazoles have been used as advancement catalysts in low concentrations. A broad class of catalysts based on aryl or alkyl phosphonium salts are also used for this purpose. The role of triphenyl phosphine in advancement catalysis has also been investigated [19]. More recently epoxy resin has been synthesised by microwave irradiation technique [20]. Novel nitrogen containing epoxies [21] have been prepared by the condensation of xylene-formaldehyde-phenol (XPF) resin with triglycidyl isocyanurate (TGIC).

1.3.4 Characterisation

The epoxy resins of glycidyl ether type are characterised by six parameters namely resin viscosity, epoxide equivalent, hydroxyl equivalent, average molecular weight and molecular weight distribution, heat distortion temperature of cured resin and melting point (of solid resin) [1]. Colour, density, hydrolysable chlorine, esterification equivalent and volatile content are also important parameters used for epoxy characterisation.

Resin viscosity**:** Viscosities of liquid resins are determined with a Cannon-Fenske capillary viscometer at 25^0C or a Brookfield viscometer. Viscosities of epoxy resins are determined in butyl carbitol solutions (40% solids content) and by comparison with standard bubble tubes (Gardner–Holdt bubble viscosity). Typical commercial grade liquid epoxy resins have an average molecular weight of about 370, viscosity is 11,000-15,000 mPa. s at 25°C.

Epoxide equivalent: The epoxy content of liquid resins is expressed in epoxide equivalent or weight per epoxy (wpe) which is defined as the weight of the resin containing one gram equivalent of epoxide. For pure diglycidyl ether with two epoxy groups per molecule, the epoxide equivalent will be half the molecular weight. Quantitative determination of epoxy groups can be performed by a hydrohalogenation reaction. Hydrobromation of epoxies using HBr in acetic acid solution using crystal violet as indicator is a simple procedure. Many other methods for quantitative analysis of epoxy groups have been described in the literature [22]. Epoxy group determination by direct hydrohalogenation in pyridine medium is a popular method [ASTM D 1652-73].

Hydroxyl equivalent: It is the weight of the resin containing one equivalent weight of hydroxyl groups. The determination of hydroxyl groups in advanced bisphenol based resins is done using lithium aluminium hydride. Normally hydroxyl equivalent is determined by reacting the resin with acetyl chloride.

As the molecular weight of bisphenol A based epoxy resins increases the epoxy content decreases, whereas the hydroxyl content increases.

Molecular weight: The molecular weight and molecular weight distribution may be determined by gel permeation chromatography, HPLC and vapour phase osmometry. As the resins are of low molecular weight, it is possible to measure this by ebullioscopy and end-group analysis methods. Quantitative determination of oligomer distribution [23] can be done by different chromatographic methods such as HPLC, size exclusion chromatography (SEC) and thin layer chromatography (TLC). Determination of the number average molecular weight of fractions of epoxy resin by vapour phase osmometry and SEC coupled with multiple angle light scattering is a rather new technique [24]. HPLC analysis of liquid and solid epoxy resins has been studied in detail using normal phase and reversed phase columns respectively [25].

Hydrolysable chlorine content: Hydrolysable chlorine content of liquid and solid epoxy resins is determined by dehydrohalogenation with KOH solution and potentiometric titration of the chloride liberated by silver nitrate solution. The solvent in which KOH is dissolved can influence the extent of dehydrohalogenation when reflux conditions are used. In general the higher the reflux temperature, the higher the value of hydrolysable chlorine content.

Esterification equivalent: In the case of solid resins it is defined as the weight in grams of the resin esterified by one mole of monobasic acid. This includes both the epoxy and hydroxyl groups of the solid resin. The solid resin is esterified using acetic anhydride in the presence of pyridinium chloride, followed by titration with sodium methoxide using thymol blue-phenolphthalein indicator.

Conventional IR and FTIR spectroscopy can be used for quantitative analysis of epoxides and for studying the curing process [26]. The usefulness of high resolution NMR for the study of thermosetting polymers has been reported in the literature [2, 27]. High resolution liquid state ^{13}C NMR and solid state ^{13}C-CP-MAS NMR have also been employed for epoxy characterisation [28].

1.3.5 Cross-linking

The resin is mixed with a curing agent or hardener its choice depending upon the processing methods, conditions and the properties required. The reactivity of the epoxy ring is enhanced by the presence of the ether linkage separated from it by a methylene unit.

Two types of curing agents are widely used: catalytic systems and co-reactive systems (poly functional cross- linking agents that link the epoxide resin molecules together) [29]. Some systems may involve both catalytic and condensation systems. A catalytic curing agent functions as an initiator for the resin homopolymerisation process whereas a co-reactive curing agent acts as a co-monomer in the polymerisation reaction.

i) Catalytic cure:

Lewis bases contain unshared electron pairs by virtue of which they attack sites of low electron density. Tertiary amine systems are often used in practice. Lewis acids such as BF_3 are electron deficient and hence they attack sites of high electron density. BF_3 reacts with epoxy resins causing gelation within a few minutes. Complexing boron trihalides with amines is found to enhance the reaction rate [30].

Photo initiated cationic curing of epoxies is a fast developing technique. Photo initiators include aryl diazonium salts ($ArN_2^+X^-$), diaryl iodonium salts and salts of positively charged sulphur ($Ar3S^+X^-$). Electron beam curing of epoxy resins and its exothermic effect have been reported recently [3]. This method reduces the cure time and cure temperature and the cured resin attains good dimensional stability. Curing of solid and liquid epoxy resins by treating them with microwave oxygen plasma has been studied [19,31]. Frontal polymerisation - a process in which a spatially localized reaction zone propagates through a monomer converting it into a polymer- has been studied in a DGEBA/DETA model system using DSC [32].

ii) Co-reactive cure:

Primary and secondary amines are widely used as curing agents for epoxy resins. The reaction of an epoxy group with a primary amine initially produces a secondary alcohol and secondary amine. The secondary amine in turn reacts with epoxy group to give a tertiary amine and two secondary hydroxyl groups. Curing with secondary amine affords a tertiary amine and a secondary hydroxyl group. Primary amines react twice as fast as secondary amines [33].

1.3.6 Curing Agents

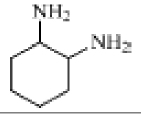
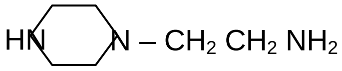
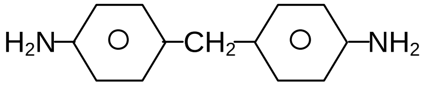
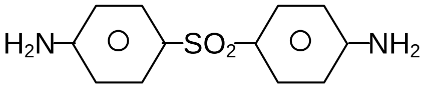
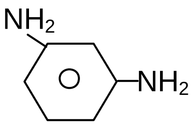
The choice of the resin and the curing agent (or hardener) depends on a variety of parameters such as type of application, viscosity, pot life, gel time, curing temperature, ultimate mechanical, thermal, chemical and electrical properties, toxicological and environmental limitations and cost.

I) ***Amine hardeners***:

In general, primary and secondary amines act as reactive hardeners whereas tertiary amines are catalytic [4]. The more common commercial amine hardeners are listed in Table 1.1.

Diethylene triamine (DETA) and triethylene tetramine (TETA) are highly reactive primary aliphatic amines used for room temperature cure of epoxy resins.

Table 1.1 Some commercial amine curing agents [4]

Formula	Name
$NH_2CH_2CH_2NHCH_2CH_2NH_2$ DETA,	Diethylenetriamine
$NH_2CH_2CH_2NHCH_2CH_2NH_2NHCH_2CH_2NH_2$ TETA,	Triethylenetetramine
 $NH_2\overset{CH3}{\overset{\mid}{C}}HCH_2(OCH_2\overset{CH_3}{\overset{\mid}{C}}H)_n\ NH_2$	Poly (oxypropylene) diamine
DAC, 	1,2–diamino cyclohexane
AEP, 	N-amino ethyl piperazine
MDA, 	Methylene di aniline
DDS, 	4,4’diaminodiphenylsulfone
MPDA, 	m – phenylene diamine

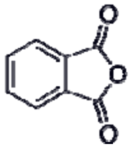
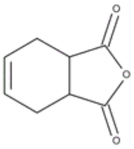
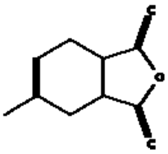
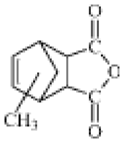
They contain respectively five and six active hydrogen atoms available for cross-linking. DETA is found to give a room temperature pot life of less than an hour at 10 phr concentration. With TETA, 12 to 13 phr concentration is required. However, they are highly volatile, pungent and skin sensitisers. In general, amine cured systems give high exotherms on cure. Modified aliphatic polyamines are better curing agents to achieve properties such as lower toxicity, lower exotherms in large castings, improved flexibility and longer pot life. Cycloaliphatic amines are found to increase pot life. Piperidine is shown to be fast reacting and effective in rubber modification of epoxy resins. N-aminoethyl piperazine is fast curing and gives flexibility and longer pot life. Aromatic amines react slowly with epoxy resin at room temperature and require high temperatures for cure. They give better chemical and thermal resistance properties than aliphatic amines. Methylenedianiline (MDA or 4,4'-diaminodiphenyl methane, DDM), 4,4'-diaminodiphenyl sulfone (DDS), meta xylenediamine (MXDA) and meta-phenylenediamine are important commercial solid aromatic amines used as epoxy curing agents. Recent studies show that 4,4-dithiodianiline (DTDA)- a disulphide cross-linking agent- is an effective hardener for epoxies [34]. Relaxation kinetics of DGEBA/MXDA system has been studied using differential scanning calorimetry [35].

A number of modified amines have been marketed commercially. The reaction product of the amine with a mono or poly-functional glycidyl material is used in larger doses so that errors in metering the hardener are reduced considerably. Resinous adducts are prepared by reacting excess of diamine with epoxy resin. The high molecular weight of the adduct affords a more desirable resin to hardener ratio and improves processibility of an epoxy composite system. For example, diaminodiphenyl sufone (DDS) is sparingly soluble in multifunctional epoxy resins, but, its epoxy adduct improves the solubility of the hardener in the epoxy resin thereby minimizing processing difficulties [36].

ii) Acid /anhydride hardeners:

Compared to amine cured systems, acid hardening systems give lower exotherms on cure and are less skin sensitive. In practice anhydrides are preferred to acids since the latter release more water on curing leading to foaming of the product. Numerous structurally different anhydrides can be used as epoxy curing agents. The most important commercial anhydrides are based on a cycloaliphatic structure (Table 1.2).The anhydrides are usually used at ratios of 0.85:1.1 moles anhydride carboxyl group per epoxy equivalent.

Table 1.2 Some commercial anhydride curing agents [4]

Phthalic anhydride	
Tetrahydrophthalic anhydride	
Methyl tetrahydrophthalic anhydride	
Nadic methyl anhydride	

Phthalic anhydride affords slow curing of epoxies (4-8hours, 150^0 C) and about 0.6-0.9 equivalent is used per epoxy group. For low molecular weight DGEBA resins, 35-40 phr hardener is employed at 120-140^{o}C. Hexahydrophthalic anhydride is soluble in epoxy resin at room temperature and gives higher heat distortion temperatures than phthalic anhydride. Anhydride hardeners with higher functionalities such as pyromellitic dianhydride and trimellitic anhydride have been used to improve the degree of cross-linking and to obtain higher heat distortion temperatures. Methyl nadic anhydride is found to give heat distortion temperatures as high as 202^0C with bisphenol epoxies and impart good heat stability to the cured system. Epoxy anhydride systems show long pot life, low exotherms and little shrinkage when cured at elevated temperatures. They exhibit good mechanical and electrical properties. Epoxy-anhydride systems have better thermal stabilities than similar amine-cured systems. Anhydrides are the principal curing agents for cycloaliphatic resins [37]. The mechanical and dynamic characteristics of microwave cured epoxy/anhydride system have been investigated in detail [38]. Modification of epoxy resin with optically active carboxylic acids has been reported [39].

iii) Other hardener systems:

In addition to amines and anhydrides, many other curing agents are also in use. These include several amides containing amine groups. Polyamides are non-irritating amine hardeners which act as flexibilizers also. Epoxy resins for adhesives make use of dicyanodiamide as curing agent [21]. Dicyanodiamide (DICY) is insoluble in common resins at room temperature, but dissolves at higher temperatures forming the basis of a one-pack system. Complexes of boron trifluoride and amines (e.g., monoethyl amine) are found to give long pot lives. Very high cure rates can be achieved by using mercaptans. Isocyanates act on epoxy group to form oxazolidone structure or on hydroxyl group to form urethane linkages.

1.3.7 Cured resin structure [4]

The ratio of resin to hardener has a strong effect on the structure of the cured resin and its properties. A variety of products are formed from different resin-hardener ratios. Between a difunctional epoxy resin and a tetra functional hardener such as a diamine, the products range from an epoxy-amine adduct with excess epoxy to an amine- epoxy adduct with excess amine (Fig.1.4). Theoretically, a cross-linked thermoset network structure is formed with equilibrium quantities of resin and hardener.

The extent of cross-linking is a measure of the degree of cure**.** The most important properties are obtained at maximum cross-linking. The curing temperature largely influences the ultimate cross-link density. Heating increases molecular mobility resulting in higher cross-link density which in turn affects the chemical resistance of the cured matrix positively. The increase in chemical resistance properties after post-cure demonstrates increased cross-link density. The reactivity of epoxy resin- hardener systems are determined by DSC. The structure of the hardener has a profound effect on the reactivity and heat resistance of cross-linked DGEBA. Aliphatic amines show a maximum reaction rate at 90^0C while the same epoxy resin is less reactive (125^0C) when homopolymerised by initiators. Aromatic amines and phenols react very slowly requiring very high cure temperatures. The highest temperatures are required for dicyandiamide cure which can be accelerated by basic compounds. The thermal properties reflect the degree of cure and thermal analysis is important in studies of epoxy resins [40].

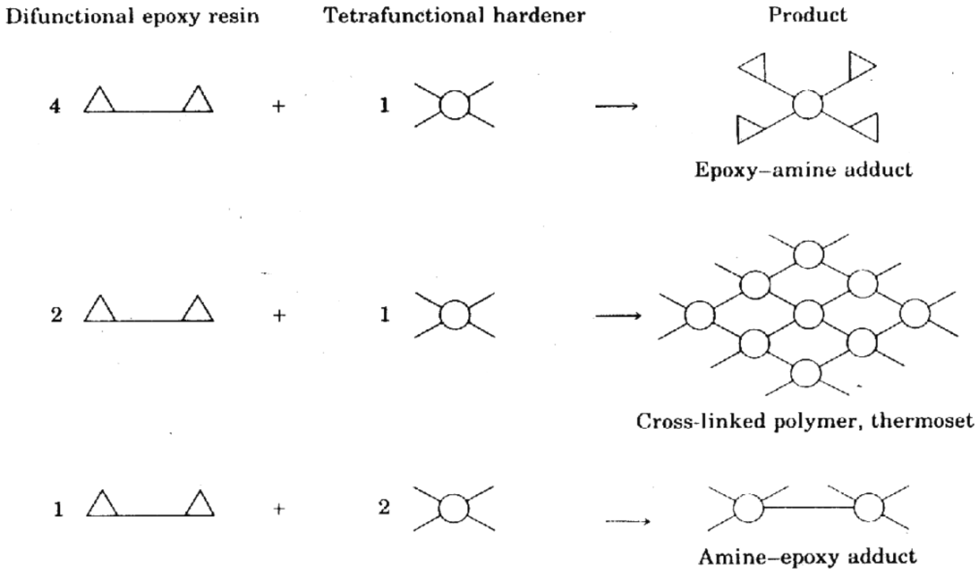


Fig.1.4 Formation of resin-hardener networks

The curing process is monitored by methods such as solvent swell and titration of functional groups. Disappearance of epoxy functionality (peak at 915nm) during cure can be followed by IR spectroscopy. HPLC is also a reliable tool for epoxy resin analysis [41]. Dielectric measurements are increasingly applied to monitor curing of epoxies [42]. Microdielectrometry is a new method which employs integrated circuit technology to develop a miniaturized dielectric probe [43].

1.3.8 Cured resin properties [44]

The properties of cured epoxy resins vary in importance depending on the use of the cured material.The main properties of interest from an application point of view are mechanical properties, chemical resistance, thermal resistance, electrical properties, flame resistance and weathering resistance (Table 1.3). Epoxies have excellent mechanical properties compared to other thermosets. They show high tensile strength, modulus, flexural and impact strength.

Chemical resistance**:** Epoxies are versatile from the view point of chemical resistance as well as physical and mechanical properties. Chemical resistance of the resin is determined as per ASTM D543-52. Three dimensional cross-link networks possess resistance to attack by corrosive chemicals, including weak alkalies, strong acids, and non-polar solvents. Cured epoxies are generally resistant to organic solvents. They are attacked by some strong acids, but are resistant to strong alkalies. The chemical resistance of a completely cured resin is a function of its chemical composition, molecular weight and the degree of cross-linking.

Electrical properties: The electrical properties of epoxies are good compared to other dielectric materials. Low dipolar nature contributes to the dielectric strength (ASTM D 150) and surface resistivity characteristics of these resins. Epoxies have short time dielectric strength of 300 to 500 v/mil. Epoxy resins are widely used for electrical encapsulation and reinforced laminates for various dielectric applications requiring structural properties.

Table 1.3 Properties of casting and glass-reinforced epoxy resin [34]

Property	**ASTM Test method**	**Cast resins**		**Glass filled resin**
		Rigid	**Flexible**	
Processing				
Compression molding temp.°K	----	----	----	420-440
Compression molding pr. MPa	----	----	----	2.07-35
Linear mold shrinkage ratio	----	0.0005-0.01	0.001-0.01	0.001-0.005
Specific gravity	D-792	1.11-1.4	1.05--1.35	1.6-2
Mechanical				
Tensile strength MPa	D-638	28-90	14 -70	69-140
Tensile modulus MPa	D-638	2400	----	21000
Elongation at break %	D-638	3-6	20-85	4
Flexural strength MPa	D.790	55-170	----	90-320
Flexural modulus MPa	D.790	3400-5000	----	7000-21000
Compressive strength MPa	D-695	100-170	7 -97	140-210
Hardness Rockwell	D-785	M80-110	---	M100-110
Impact strength Izod .Jm^{-1}	D-256	10 -50	120-270	1600-2100
Thermal				
Thermal conductivity $Wm^{-1}K^{1}$	C-177	0.19/293K	---	1.77
Specific heat cal / ^{0}C/g	----	0.25	0.20-0.27	0.19
Thermal expansion 10^{-5}in/^{0} C	D-696	4.5-6.5	2-10	1.1-3.5
Resistance to heat ^{0} K	----	400-750	400-420	420-770
Deflection temperature°K	D-648	115-150	298-350	350-750
Electrical				
Volume resistivity ohm-cm	D-257	10^{12}-10^{17}	1.3-15x10^{14}	>10^{14}
Dielectric constant at 1 MHz	D-150	3.5 –5.0	3-6	3.5-5.0
Dissipation factor at 1 MHz	D-150	0.003-0.028	0.010-0.040	0.01
Arc resistance sec	D-495	45-120	50-180	120-180
Optical				
Refractive index	D-542	1.55-1.61	---	----
Clarity	----	Transparent	Transparent	Opaque
Resistance characteristics				
Water absorption %	D-570	0.08-0.15	0.27-0.50	0.05-0.20
Effect of weak acid	D543	None		
Effect of strong acid	D543	Attacked by some		
Effect of weak alkali	D543	None		
Effect of strong alkali	D543	Slight		
Effect of organic solvents	D543	Generally resistant		

Thermal resistance: Heat resistance is directly related to resin composition. Molecular weight and frequency of cross-linking have direct effects on hot strength and rigidity at elevated temperatures. Cross-linked nature enhances the resistance to softening and deformation at high temperature. The structural transitions of these cross-linked networks are characterised by DSC or measuring heat distortion temperature. These studies give the transition temperature at which rigid crystalline network and amorphous boundaries transform to a rubbery state. The heat distortion temperature (HDT) is a measure of the heat resistance of the resin (ASTM D 648). HDT of epoxies varies in the range 115 – 150^0 C at 1.8 MPa fibre stress. Reinforcements improve the thermal properties.

Flame resistance: Flame resistance or fire retardancy *(ASTM D 635-56 T & ASTM D 757-49)* is defined as a slow rate of burning while in contact with a source of heat or the ability to extinguish itself when the source of fire is removed. Flame resistance is generally achieved by incorporation of chlorine, phosphorous, bromine or fluorine in the form of compounds which remain stable on both interior and exterior exposure. In epoxies, flame retardance is achieved by advancing the liquid DGEBA resin with tetrabromo bisphenol A [4]. Flame retardance can be improved by incorporating dialkyl (or aryl) phosphate in epoxy/DDS system [45]. Eventhough free of halogens, blends of epoxy resin and unsaturated polyester resin are found to have improved flame retardance [46].

1.3.9. Diluents and flexibilisers

The major disadvantages of un-modified epoxy resins include high viscosity, high cost and too great a rigidity for specific applications. Hence these resins have to be modified by incorporating diluents, fillers, flexibilizers and other additives. Diluents reduce the resin viscosity and simplify handling. Xylene and dibutyl phthalate are used as non-reactive diluents whereas phenyl glycidyl ether, butyl glycidyl ether and octylene oxide are used as reactive diluents in epoxy resins. Since diluents affect the physical properties of the resin and retard cure, they are used in small doses (less than 10 phr).

Fillers are used for tooling and casting applications [21]. They reduce the cost of the resin at the same time reducing the cure shrinkage. Sand is used in inner cores whereas metal powders and metal oxides are used as fillers in surface layers. Powdered metal oxides reduce the ultimate tensile and compressive strength of the resin, but have little effect on impact strength. However, asbestos and wire wool are shown to improve impact strength.

Un-modified DGEBA resins exhibit brittleness and low elongation after cure. Flexibilisers and plastisizers are added to improve the flexibility and as a result, the toughness of the resin. Aliphatic diepoxides enhance the flexibility providing chain segments with greater free rotation between cross-links. Low molecular weight polyamides from dimer acids, low molecular weight poly sulphides, polyamines and poly glycol diepoxides have been used as flexibilizers in epoxy resins. The low molecular weight polyamides are not only flexibilizers but they also act as amine hardeners.

Liquid polysulphide polymers with terminal mercaptan functionality improve impact properties when used along with polyamine hardeners. Oligomeric aliphatic polyesters containing carboxyl end groups are used to incorporate flexible chain segments in epoxy resins. Flexibilization is accompanied by reduction of T_g, elastic modulus and hardness properties.

1.3.10. Applications and processing techniques

Epoxy resins are commercially used in coating and structural applications. With proper selection of the resin, modifier and curing agent, the cured epoxy system can be tailored to specific performance requirements. Epoxy resins have excellent adhesion to various substrates; outstanding chemical and corrosion resistance; very good electrical insulation; high tensile, flexural and compressive strengths; thermal stability; a wide range of curing temperatures and low shrinkage upon cure. The largest single use of epoxies is in coatings where high chemical and corrosion resistance and adhesion are important.

i) Coatings:

Epoxy resins provide durable coatings of high mechanical strength coupled with good adhesion to many substrates. Their main applications include primers and paints for vehicles, chemical tank linings, and the inner coatings in beer cans. The modified resin is used in containers of beverages, meat and fish cans and aerosols. Considerable work has been carried out to develop water-thinnable systems which find use as primers for aircraft and automobile applications. Epoxy systems modified with 60% coal tar protect against corrosion caused by hydrochloric acid, sodium hydroxide and saline water [4].

In the field of water borne coatings, epoxy resins have provided versatility and inherent properties needed to solve difficult industrial problems [47]. Water borne coatings are made by dispersing or emulsifying the resin with surfactants. Waterborne epoxy systems for baking finishes are used in electro-deposition. The use of epoxies is fast developing in the field of powder coatings[48]. For powder coatings, solid epoxy resins are applied by an electrostatic spray gun. Epoxy powder coatings based on bisphenol A are generally used for interior use or limited outdoor exposure.

ii) Adhesives:

Upon curing epoxy resins possess excellent bonding characteristics. The reaction takes place without the evolution of volatiles and, often, without heat or pressure. They may be used to bond various metals, rubbers, wood, ceramics and glass with satisfactory results [49,50]. Higher molecular weight epoxies improve the bonding properties of the adhesive. Where enhanced high temperature and chemical resistance is required, multifunctional resins like EPN are used. Adhesives based on DGEBA resin cured by DICY have significantly improved mechanical properties when formulated as hybrid materials [51]. Metal-metal bonding is very successful with epoxy systems, which are now used extensively in the aircraft and automotive industry [52]. Epoxy resins are also used as adhesives in the bonding of microscopic hollow spheres of phenol-formaldehyde resin which gives syntactic foams.

iii). Laminates and composites:

Epoxy resins are excellent matrix for composites materials because they show good adhesion to reinforcement, cure with low shrinkage and provide mechanical, electrical, chemical, thermal and moisture resistance properties [53]. As laminating resins they are used with a variety of reinforcements such as glass fibres, asbestos and certain synthetic fibres. Glass cloth is usually the reinforcing material in electric laminates. Epoxies are also used in combination with graphite, boron and Kevlar fibres. Typical applications of epoxy laminates include structural components for aircrafts and missiles, chemical resistant tanks and laminated tubes and pipes for conveying oil. The space shuttle has some parts made of carbon fibre reinforced epoxy resins[4]. Some of the inner parts of aircrafts are increasingly replaced by advanced epoxy toughened carbon composites, for example the column supporting the floor and the seats of the passengers.

iv). Casting and tooling:

Casting techniques [4] are widely used with epoxy resins in the electronics industry for potting, encapsulating transformers, valves, capacitors and many other electronic components. Switchgear components, insulators and high voltage cable accessories are produced by epoxy casting techniques. Epoxy foams are suitable for use in encapsulation of electronic compounds where strength to weight ratio is critical. Epoxy cast tools are used mainly for making dies, jigs, foundry patterns and plastic processing models. In the manufacture of tools, epoxy casting resins are used as prototype models for product design, drilling and welding jigs, checking fixtures, stretch blocks and injection moulding. They are less expensive than metals and can be modified quickly and cheaply.

v). Construction:

Epoxy resins are used to improve the performance of traditional materials in the construction industry and are incorporated in flooring, concrete, metal or wood. Epoxy terrazzo floors provide adhesion, impact resistance and strength. Epoxy formulations for roads and bridges are effective barriers to moisture. Epoxies are used to repair concrete cracks and in adhesive and grouting systems[50]. Concrete to concrete bonding can be done with epoxy-polysulphide formulations in conjunction with polyamine hardeners. Epoxies are used as binders for swimming-pool decks and walks and to consolidate the soil around oil-well drills.

1.4 Modification of epoxy resins

Un-modified epoxy resins based on bisphenol A-epichlorohydrin exhibit brittleness and low elongation after cure. These polymers usually craze on their free surface and the crazed areas are converted into cracks which propagate with brittle energy absorption resulting in fracture. The high glass transition temperatures of epoxy thermosets are the result of cross-linked structures and this is achieved at the expense of reduced toughness and damage tolerance.

A polymer whose failure requires the application of large stress and the absorption of more energy will be more useful than a polymer that fails under less rigorous conditions [54]. Within the context of failure mechanics [55] toughness of a specimen refers to the total energy required to cause failure, i.e., the total area under the stress-strain curve. Toughening of the resin by the addition of suitable toughening agents or chemical modification is a means to improve the energy absorption capacity. Apart from toughness, this results in enhancement of impact resistance, elongation and resistance to crack propagation. Since high strength and modulus are required for engineering polymers, the toughening process must not lead to any serious deterioration in these properties.

There are several approaches to enhance the toughness of epoxy resins which include: (a) chemical modification of the epoxy backbone to make it more flexible (b) increasing the molecular weight of the epoxy (c) lowering the cross-link density of the matrix (d) incorporation of a dispersed toughener phase in the cured polymer matrix and (e) incorporation of inorganic fillers/reinforcements into the neat resin. Quite recently, it has been reported that fracture toughness of epoxy resin can be improved by blending the resin with resins of different molecular weights. In this method, high molecular weight DGEBA oligomer is converted into DGEBA monomers and the system is cured by aromatic amines [56].

1.4.1 Types of modification

On the basis of the choice of modifying agent, toughness modification of epoxy resins can be classified into (a) elastomer modification (b) polysiloxane modification (c) particulate/fibre modification (d) thermoplastic modification and (e) miscellaneous methods. The most successful toughening method has been found to be the incorporation of a second elastomeric phase into the glassy epoxy matrix through in situ phase separation [57].

(a) *Elastomer modification*

The most common approach to toughen thermosets is by dispersing a rubbery phase in it. Sultan et al. [58] were the first to show that the fracture toughness of epoxies can be improved by the introduction of a dispersed rubber phase. Following that a number of studies were reported concerning the application of butadiene-acrylonitrile liquid rubbers with various end groups such as carboxyl (CTBN)[59-66], amine (ATBN) [67-71], epoxy (ETBN) [72-74] and hydroxyl (HTBN) [63,75] as toughening agents. These liquid rubber modifiers are initially miscible with epoxy resin but will phase separate upon curing. These studies show that rubber modified epoxy resin shows improvement in fracture toughness and deterioration in some other important properties like glass transition temperature (Tg), Young's modulus and yield strength compared to the unmodified resin. The CTBN-modified thermosets are less resistant to oxidation, due to greater degree of unsaturation in the CTBN backbone. This deteriorates the chemical and physical properties of the resin, especially at elevated temperature [76].

In an attempt to solve this problem, different kinds of liquid rubbers based on functionalized acrylic oligomers were chosen as toughening modifiers. These rubber modifiers do not contain unsaturated bonds in the backbone and can provide good resistance against oxidation processes [77-80].

Toughness enhancement of epoxy matrix with elastomers demands a reaction (e.g., esterification) between the elastomer and the resin to provide adequate bonding between the elastomeric and epoxy phases. Attempts to employ hydroxyl terminated elastomers for toughness improvement have encountered difficulties because the conditions required to promote the necessary hydroxyl-epoxy reaction generally lead to self polymerisation of the epoxy, the latter occurring at the expense of the former and thus limiting the extent of elastomer-epoxy reaction. A recent approach to this problem is to employ a co-reactant such as toluene diisocyanate (TDI) capable of reacting with both epoxide and hydroxyl functionalities resulting in the formation of both urethane and oxazolidone groups between the elastomeric and epoxide components [81].

Another method is to incorporate rubbery epoxy particles into the glassy epoxy system [82]. These particles were prepared by curing droplets of an aliphatic epoxy in an aqueous medium. The particles were then transferred to an aromatic epoxy which was, subsequently, cured. Almost similar characteristics of that of CTBN-modified epoxy resin were obtained this way. Recently it was found that the impact strength of epoxy resin can be improved by blending with epoxidized natural rubber (ENR) [83].

(b) Polyorganic siloxane modifiers

Another type of elastomeric modification is by using poly dimethylsiloxanes. Organosiloxanes exhibit important characteristics such as very low glass transition temperature (-120^{0}C), moisture resistance, good electric properties, low stress, high flexibility, good weatherability and good thermal and oxidative stabilities. In addition, because of their low surface energy and nonpolar structure polysiloxanes tend to migrate to the air-polymer interface and provide a very hydrophobic surface for the substrate. Therefore, the presence of siloxane should strongly influence the friction and wear behavior of the modified epoxy resins [84]. Among the different elastomeric materials used for toughening of epoxy resin, hydroxyl terminated polydimethylsiloxane is the most suitable because of it's versatile properties like flexibility due to-Si-O-Si- linkage, high thermal and thermo oxidative stability, high moisture resistance, good dielectrical properties, excellent UV and chemical resistance [85-93]. Recently, the use of liquid functional polysiloxanes as modifiers for epoxy resins has attracted great interest. [94-102]. The solubility parameter of polydimethyl siloxane (≈ 7.5) is much lower than that of bisphenol A epoxy resin (≈ 9.4). Ideally one would like to control the solubility parameter in such a way that the siloxane oligomer is miscible with the epoxy resin in the initial stages of cure but phase separates during the later stage. It has been shown that by incorporating siloxane oligomers with reactive organofunctional terminal groups such as amine, epoxy or carboxyl into the epoxy networks improvements in the fracture toughness, water absorption, and surface properties can be achieved [98].

Yorkgitis et al. [84] blended functionally terminated polydimethylsiloxane and its statistical copolymers with either methyltrifluoropropyl(TFP)-siloxane or diphenyl siloxane with a chemically modified bisphenol-A-based epoxy resins. They found that the compatibility between the epoxy resin and the siloxane modifiers was enhanced by increasing the percentage of TFP or diphenyl units relative to the dimethylsiloxane content. Also, improved fracture toughness was achieved in epoxy resins modified with polysiloxane copolymers containing 40% or more TFP content or 20% diphenylsiloxane. A morphological study showed that improvement in fracture toughness may be attributed to the smaller rubber particle sizes and the altered particle morphology due to the enhanced compatibility of the resin and the modifier. For polysiloxane modifiers in general, the flexural moduli of the modified resins decrease with increasing modifier content. The decrease in Tg values of the siloxane-modified epoxy networks indicate either partial miscibility between the siloxane and epoxy phases or phase separation in these siloxane-modified epoxy networks.

Kasemura et al [94] showed that aminopropyl-terminated poly dimethylsiloxanes (ATPS) were good surface modifiers for epoxy resins because the oil and water repellency could be enhanced by blending the modifiers with epoxy resins. Also, the peel strength for pressure-sensitive adhesives affixed to a modified epoxy resin decreases with an increase in the modifier. Therefore these siloxane modifiers could be used as release agents for pressure-sensitive adhesives. Tsung-Han et al [95-97] extensively studied the reduction of stress in thermosetting resins by incorporating organosiloxane moiety into the uncured thermosetting resins and inducing phase separation before curing to form small discontinuous rubber particles in the resin matrix. Some important results have been achieved: (i) Using vinyl or hydrid terminated polydimethyl siloxanes effectively reduced the stress of cured epoxy resins by reducing the flexural modulus and the coefficient of thermal expansion. However, the Tgs were suppressed slightly [97]. (ii) A stable dispersion of polysiloxane thermoplastic polyurethane (TPU) particles in an epoxy resin matrix was achieved when the epoxy ring reacts with the isocyanate groups of urethane prepolymer to form an oxazolidone. The dispersed polysiloxane TPU rubbers also effectively reduce the stress of cured epoxy resins by reducing the flexural modulus_and the coefficient of thermal expansion, while the increase in Tg is due to the formation of the rigid oxazolidone structure [96]. (iii) Electronic devices encapsulated with the dispersed siloxane modified epoxy molding compounds have exhibited excellent resistance to the thermal shock cycling test and have resulted in an extended life for the devices [95-97].

Emel and İskender [98] investigated the modification of epoxy networks with reactive polydimethylsiloxane (PDMS) oligomers. They found that even at fairly low molecular weights such as Mn=500g/mol [or at a. $(CH3)_2$Si-O- repeat units of about 5], PDMS oligomers are incompatible with epoxy resins for a successful kinetic investigation in bulk. So they used 1, 3-bis (-aminopropyl) tetramethyldisiloxane (DSX) as a model curing agent and a modifier in epoxy resins and attained the expected improvements in tensile and impact strengths of the modified products. But the glass transition temperatures of these materials showed a decrease with an increase in DSX content. Yayun [99] and Menghuo [100] studied the thermal and mechanical properties of methoxyl-terminated polymethylphenylsiloxane-modified epoxy resins. The thermal stability and the fracture toughness of the modified products were improved. The Tg and the flexural modulus of the cross-linked epoxy network were not significantly lowered. Murias and co-workers studied epoxy resins modified with reactive low molecular weight siloxanes [85]. They showed that this modification can improve thermal and mechanical properties

(c) Thermoplastic modification

Thermoplastic modification is an alternative approach to toughen epoxy materials. This approach has been based upon blending the thermosetting resin with a thermoplastic polymer that phase separates upon curing of the resin, but where the thermoplastic phase has a relatively good thermal stability and lower water uptake compared to the rubbery phase in rubber-toughened thermosetting polymers. The thermoplastics used as modifiers include polysulfone[102-104] poly(ether sulfone) (PES)[105-111] poly(ether imides) (PEI)[112-141], poly (ether ketone) (PEK) [122], polyaryletherketones (PAEK) [121,122], amine terminated polysulfone (PSF) [120,123], hydroxyl-terminated polysulfone[124-127] poly(dimethylphenylene ether) [128] and hydroxyl terminated polyester [129]. Also, various amorphous thermoplastic polymers [130] and semi crystalline thermoplastic polymers [131], have been used to modify the epoxy system.

Raghava (1983) and Bucknall and Partridge (1983) were the earliest researchers to study the thermoplastic-toughened epoxy resins. They found that morphology was dependent on both the type and concentration of the resin and the curing agent employed. Unfortunately polyethersulphone addition was found to have only minor advantages in fracture energy; addition of up to 40 phr of resin in epoxy resulted in less than 100% increase in fracture energy. Raghava attributed this to poor adhesion between the phase-separated components. McGrath et.al used hydroxyl and amine terminated polysulphones as modifiers for DGEBA type resins [132]. Later researchers realized that it is important to increase the compatibility and interfacial adhesion of a thermoplastic modifier and the epoxy resin, in order to increase the fracture toughness. Therefore, different types of thermoplastic oligomers or polymers have been tried for toughening epoxy resins through physical blending or chemical reaction. Among them, PEK, PEI and PSF seemed to give better improvement in toughness (ΔKIC=1.4 Mpa-m1/2) [132], ΔKIC=0.9~1.0 Mpa-m1/2 [130, 131], and ΔKIC=0.7~0.9 Mpa-m1/2 [124- 126], respectively. Other thermoplastic toughening agents, which are found in the currently available literature, only modestly improve the fracture toughness (ΔKIC=0.4~0.8 Mpa-m1/2). The problem of poor processability in the use of such engineering thermoplastic modifiers, which is due to poor compatibility with the uncured epoxy resin, still remains unresolved [133, 134]. In comparison with rubber modification the level of toughness improvement achieved by thermoplastic modification is generally poor especially with relatively low T_g systems based on difunctional resins.

(d) Particulate modification

In addition to the above methods, other approaches to toughness improvement in epoxies have been investigated such as modification by high modulus particulates. Particulates contribute to a greatly enhanced modulus which is a significant advantage over elastomeric modification where a reduction in modulus is observed [135-137]. Glass beads [138, 139], fly ash [63,140-142], alumina trihydrate [143], silica [144-148] and kaolin [149,150] are generally used to modify epoxies.

A recent trend is to modify epoxy resin with nano particles [151-156] and carbon nano tube [157-159] for improved properties. Several studies have demonstrated that the fracture energy of filled epoxies reaches a maximum at a specific filler content [136, 138-145, 160]. The mechanism of particulate toughening is somewhat different from that of elastomeric modification. Some modest improvements in toughness have been achieved with particulate reinforcement. In recent years preformed particles such as thermoplastic powders or core-shell polymers made from latexes are increasingly being used as modifiers to improve the mechanical properties and thermal stability of thermosets and thermoplastics [161, 162].

(e) Other methods of modification

Modifications of epoxy resins by other methods of are also reported. Modification of epoxies by polyurethane pre-polymer based on hydroxyl terminated polyesters [163,164] and toughness modification by polycarbonate polyurethane [165] have been reported. Epoxy resin modified by bismaliemide resin shows improved thermal stability[166-168]. Further, studies on chain extended ureas as curing agents and toughness modifiers for epoxies have been conducted with reasonable success [169]. Modification of epoxies with cresol novolacs catalysed by triphenyl phosphine [170] has been reported. Blends of methylene dianiline (MDA)-cured DGEBA epoxy oligomer and ethylene-vinylacetate co-polymer rubber (EVA) [171] have been shown to have good tensile, flexural, thermal, and hardness properties. A series of poly (butyl acrylate)-poly (methyl methacrylate) core-shell elastomer particles (CSEP) were used as toughening modifiers for the general epoxy resin (E44) and the impact and shear strengths of the modified epoxy resin were apparently enhanced [172]. Talc powder with low strength and silica with high strength have been used to fill and toughen epoxy resins [173]. Toughening of epoxy resin by blending with thermotropic hydroxyl ethyl cellulose has been reported [174]. Plastisols based on PVC and diethyl hexyl phthalate have been used as modifiers for epoxy resins [175]. Schroder.N et al. have used telichelic methacrylates as toughening agents for epoxy resins [176]. High performance epoxy modified by poly etherimide was found to have increased fracture toughness [177]. Toughening of epoxies by aromatic polyesters has been achieved by Shin S.M. et. al.[178]. Isocyanate terminated poly buta diene has been employed as an effective modifier in epoxy resins [179]. Epoxidised soyabean oil [180] has been used to toughen epoxy resins cured with ambient temperature hardener. Strengthening of epoxy resins using liquid crystalline epoxies [181] has been studied extensively with reference to reinforcement of DGEBF by liquid crystalline diglycidyl ether of 4,4-dihydroxybiphenol (DGE-DHBP). Polyesters prepared by direct poly condensation from bisphenol A and alphatic dicarboxylic acids (adipic acid, sebacic acid and dodecanoic acid) have been used to improve toughness of DGEBA and diamino diphenyl methane epoxies [178].

1.4.2 Mechanisms of toughening

In recent years theoretical understanding regarding toughening mechanisms has advanced for both rubber and thermoplastic toughened epoxy resins. These mechanisms explain the improved fracture energy or fracture toughness which may result when a thermosetting polymer possesses a multiphase microstructure of dispersed particles. Several reviews [182, 183] have given detailed descriptions of the toughening mechanisms proposed to explain the improved toughness for rubber and thermoplastic toughened epoxy resins, respectively. It will be relevant to consider each of these mechanisms and to assess their application to modified epoxies.

a) Crack pinning

This mechanism was proposed by Lange and Radford [184] to explain modification by particulate fillers. . This theory states that as the crack begins to propagate through the resin, the crack front bows out between the filler particles but remains pinned at the particles. This mechanism is based on small particles as toughening agents. Because this mechanism operates mainly with inorganic fillers [185, 186] that resist fracture during failure of the epoxy matrix resin, it is generally less important in ductile matrix materials. A schematic diagram of the crack-pinning mechanism is shown in Fig. 1.5 [187].

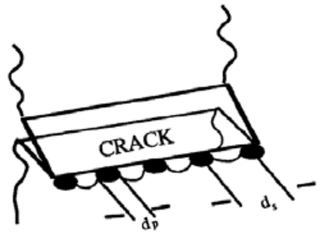


Fig. 1.5 A schematic diagram of the crack-pinning mechanism (Pearson, 1993)

b) Rubber tear

A mechanism devoted solely to the deformation and tearing of rubber particles present in two phase system was proposed initially by Mertz, Claver and Baer in 1956 [188]. According to this mechanism, rubber particles simply hold the opposite faces of a propagating crack together and the toughness of such a system is dependent on the energy required to rupture the particles together with that required to fracture the glassy matrix. Although this mechanism has been regarded as irrelevant to toughened thermoplastics, a number of microscopic investigations have proved its validity in the case of rubber modified epoxies by providing evidence of stretched rubber particles spanning loaded cracks. From such observations, Kunz-Douglas, Beaumont and Ashby proposed that the toughness enhancement provided by rubber particle inclusion was dependent primarily on the degree of elastic energy stored in the rubber particles during loading of the two-phase system [189]. According to them it is principally deformation mechanism in the matrix, enhanced by the presence of the second phase which improves toughness.

c) Multiple crazing

The multiple crazing theory, due to Bucknall and Smith proposes that toughness improvement is attributed to the generation and efficient termination of crazes by rubber particles [190]. This process has been demonstrated with thermoplastics such as high impact poly styrene through optical microscopic studies. Craze initiation has been shown to occur at regions of high stress concentration which, with rubber particle embedded in a brittle matrix, is the equatorial region normal to the applied stress direction. Craze termination occurs when the craze encounters another rubber particle. This stabilises the craze and prevents it from growing into a large crack like structure. Thus a greater amount of energy can be absorbed by the system prior to failure thereby leading to an effective improvement in the toughness of the polymer. Crazing has been shown to be the dominant toughening mechanism in rubber modified epoxies as is evident from the early work of Sultan and McGarry [58].

The detailed mechanism of craze initiation, growth and break down around rubber particles have been studied by Donald and Kramer [191,192]. According to them an optimum particle size of about 2-5 µm is responsible for maximum toughness and crazes are rarely mediated from particles smaller than 1 µm . Craze initiation from rubber particles follows the condition that the initial elastic stress concentration at the particle must exceed the stress concentration at a static craze tip and the spatial extent of stress enhancement scales with the particle diameter. This explains the inability of smaller rubber particles to initiate crazes. The possibility of crazing as a toughening mechanism in rubber modified epoxies has been suggested by Bucknall and Yoshi [193] in addition to shear deformation.

They observed increases in specimen volume in addition to longitudinal extension during tensile creep tests on rubber modified epoxies. This volume increase could be associated with a massive crazing within the specimen. However studies on thermoplastics have indicated an apparent transition from a crazing to a shear yielding mechanism as the length of polymer chain decreases. Thus, with thermosets where crosslink density is high and hence chain length between crosslinks is short, crazing would be suppressed. The frequently observed stress whitening phenomenon was attributed to the generation of crazes [58].

d) Shear yielding

This theory was proposed by Newman and Strella in 1965 following work on acrylonitrile-butadiene-styrene thermoplastics [194]. The main proposal of this theory is that shear deformation taking place either as shear bands or as diffuse form of shear yielding is initiated at stress concentrations resulting from the presence of rubber particles. This serves as the main source of energy absorption and hence toughness improvement. The function of the rubber particles is to produce sufficient triaxial tension in the matrix so as to increase the local free volume and hence enable shear yielding and drawing to initiate. According to Donald and Cramer the dispersed rubber phase initiates micro shear bands at an angle of 55 to 64 degrees to the direction of the applied stress [195]. A major drawback of this mechanism is its inability to account for stress whitening since shear yielding is a constant volume deformation. Therefore it has been suggested that crazing and shear yielding occur simultaneously in many polymers with the former accounting for the stress whitening effect. It is generally recognised that crazing rarely occurs in epoxies and the toughening mechanism now regarded by many workers as being the most applicable to rubber modified epoxies can be a dual-mode mechanism based on rubber particle cavitation and matrix shear yielding. A schematic diagram of the shear-yielding mechanism is shown in Fig 1.6[196].

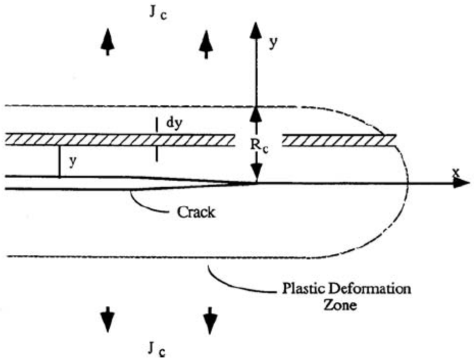


Fig. 1.6 A schematic diagram of the shear-yielding mechanism (Argon, 1989)

e) Cavitation -shear yielding

This toughening mechanism, developed independently by Kinloch, Shaw and Hunston [197] and by Pearson and Yee [198] is regarded as the most consistent in terms of experimental data generated in recent years. Kinloch et al. suggested that the rubber-tear mechanism only makes a secondary contribution to toughening, but it does not represent the major toughening mechanism. They proposed a mechanism that involves dilatational deformation of the matrix and cavitation of the rubber particles in response to the triaxial stresses near the crack tip, combined with shear yielding between the holes formed by the cavitated rubber particles. The stress-whitening was attributed to light scattering by these holes, and the major energy absorption mechanism was suggested to be the plastic deformation of the matrix. Plastic deformation blunts the crack tip which reduces the local stress concentration and allows the material to support higher loads before failure occurs.

f) Particle bridging (Rigid particles) mechanism

This mechanism was proposed by Sigl and coworkers [199]. In this toughening mechanism, the authors proposed that a rigid or ductile particle plays two roles: (1) It acts as a bridging particle that applies compressive traction in the crack wake. (2) The ductile particle deforms plastically in the material surrounding the crack tip, which provides additional crack shielding. Sigl et al. also pointed out that the shielding resulted from yielded particles is negligible, and that the particle bridging provides most of the improvement in toughness. In contrast to the crack-pinning mechanism, the particle bridging mechanism favors large particles and emphasizes the energy-to-rupture needed of the ductile phase. Fig. 1.7 shows a schematic diagram of the particle-bridging mechanism [187]

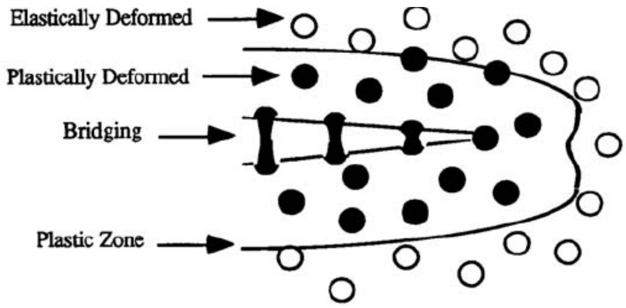


Fig. 1.7 A schematic diagram of the particle-bridging mechanism (Pearson, 1993)

g) Crack-path deflection mechanism

This mechanism was proposed by Faber and Evans in 1984 [200]. The crack-path deflection may explain the increase in toughness by a stress intensity approach. There are both Mode I and Mode II characters of the crack opening. Most materials are more resistant to Mode II crack opening. The deflection of the crack path decreases the Mode I crack opening, but increases the Mode II crack opening. Therefore, the materials exhibit a higher apparent toughness. This mechanism does not need to consider the particle size of modifiers, but it is thought that uneven spacing provides better results than uniform spacing. Fig. 1.8 shows a schematic diagram of the crack-deflection mechanism [187]

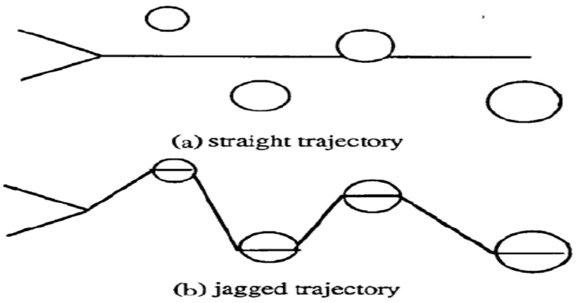


Fig. 1.8 A schematic diagram of the crack-deflection mechanism (Pearson, 1993)

h) Massive shear-banding mechanism

Argon proposed this mechanism [196] and suggested that additional crack-tip shielding in rubber-modified epoxy resins occurs due to the reduction in yield stress by the stress concentration of the compliant rubber particles that facilitate shear yielding.

Even though there are various toughening mechanisms proposed by different researchers, it seems that a single theory can not explain every experimental result and phenomenon of toughening. One reason may be the discrepancy of the raw materials chosen by different researchers, because the initial properties of raw materials have significant influence on the final fracture properties of epoxy materials. Another reason lies in the fact that fracture itself is a complex phenomenon and a single theory cannot represent every detail. So the toughening mechanism of epoxy resins may be a combination of the above two or several more mechanisms.

1.5 Fibre reinforced plastics (FRP)

A composite is a heterogeneous material created by the assembly of two or more components, filler or reinforcing agent and a compatible matrix binder in order to obtain specific characteristics and properties [201]. Fibre reinforced plastics are typical composite materials. Fibres are the load-carrying members, while the surrounding matrix keeps them in the desired location and orientation. Further, the matrix acts as a load transfer medium and protects the fibres from environmental damage due to elevated temperature and humidity. Epoxies are employed as matrix for the fabrication of numerous FRP products for high technology applications.

Composites, with light weight, high strength-to-weight ratio and stiffness properties, have come a long way in replacing conventional materials like metals, wood etc [202]. Fibre reinforced composites have a low specific gravity, high strength-weight and modulus-weight ratios, excellent chemical resistance, weatherability, versatility of product design and ease of fabrication and consequently possess a distinct advantage over conventional materials. Today, fibre reinforced composites have emerged as a major class of structural materials with increasing applications in weight-critical components for industry, particularly the aerospace, marine, and automotive sectors. Epoxy resins and unsaturated polyesters are the most widely used matrix materials in the FRP industry.The load bearing qualities of the cured resin are improved by reinforcing with fibres.The properties of composites and factors influencing the properties have been studied extensively [203,204].

1.5.1 Reinforcement fibres

The reinforcing agents used most widely are glass fibres although for advanced work carbon (and graphite), aramid or boron fibres are employed. Natural and synthetic polymer fibres are also used to a limited extent. Fibres are very effective and attractive reinforcement materials. A great majority of materials are stronger and stiffer in the fibrous form than as bulk material. A high fibre aspect ratio permits a very effective transfer of load via the matrix material to the fibres, thus taking advantage of their excellent properties.

a) Glass fibres:

Glass fibres are the most common of all reinforcing fibres for polymer matrix composites. Glass fibres are amorphous solids. Chemically, glass is primarily composed of silica (SiO_2) backbone in the form of $(-SiO_4-)_n$ tetrahedral. Modifier ions are added for their contribution to glass properties and manufacturing capability.

b) Carbon and graphite fibres:

Graphite fibres are the predominant high-strength, high-modulus reinforcement used in the fabrication of high-performance resin-matrix composites. The term ‘graphite fibre’ is used to describe fibres that have a carbon content in excess of 99% whereas the term ‘carbon fibre’ describes fibres that have a carbon content of 80-95%. The carbon content is a function of the heat treatment temperature.

c) *Aramid fibres:*

The Aramid polymers are aromatic polyamides made by solution polycondensation of diamines and diacid halides at low temperatures. Tensile strength and modulus are substantially higher and fibre elongation is significantly lower for Kevlar fibres than for other organic fibres. Kevlar fibres have poor characteristics in compression, with compressive strength being only one-eighth of the tensile strength. This is a result of the anisotropic structure, which permits local yielding, buckling and kinking of the fibre in compression.

d) *Boron fibres:*

Boron filaments are produced by chemical vapour deposition, by reduction of boron trichloride with hydrogen, on a tungsten or carbon monofilament substrate. Currently boron filaments are produced with diameters of 100, 140 and 200µm, in descending order of production quantity; however, both smaller and larger diameter fibres have been produced in experimental quantities.

e) *Other high-performance fibres:*

The need for reinforcing fibres in high temperature applications has led to the development of ceramic fibres. The ceramic fibres combine high strength and elastic modulus with high-temperature capability and, in general, freedom from environmental attack. Alumina fibres and silicon carbide fibres are among the important ceramic fibres. Alumina and SiC fibres are suitable for reinforcing metal matrices in which carbon and boron fibres exhibit adverse reactivity. In addition, alumina has an inherent resistance to oxidation that is desirable in applications such as gas turbine blades.

f) Plant Fibres:

With the exception of synthetic polymers, most economically important products, such as paper, cordage (cords and rope) and textiles are derived from plant fibres. Many varieties of plant fibre exist, such as fur (cotton, kapok), fibre sheaf of dicotylic plants or vessel sheaf of monocotylic plants (flax, hemp, jute and ramie) and hard fibres (sisal, henequen and coir). Based on the part of the plant from which they are obtained, plant fibres are classified as seed fibres (e.g., cotton), bast fibres (e.g., ramie, jute, banana and flax) and leaf fibres (e.g., abaca and pineapple).

1.5.2 Fabrication of composites

The fabrication and shaping of composites into finished products are often combined with the formation of the material itself. The formation of the composite involves the combination of the matrix and fibre such that the matrix impregnates, surrounds, and wets the fibres. The important processing methods for thermosetting polymers include hand lay-up, bag moulding process; filament winding, pultrusion, bulk moulding, sheet moulding, resin transfer moulding etc.

a) Hand lay-up

The hand lay-up technique (Fig.1.9) is the oldest, simplest and most commonly used method for the manufacture of both small and large fibre reinforced plastic products. The random chopped strand glass mat or woven roving is cut to fit the open mould contour and impregnated with the catalysed resin using a brush in successive plies. The quality of the product depends on the skill of the personnel in removing air bubbles and voids. The hand lay-up method is labour intensive and is suitable for low rate of production

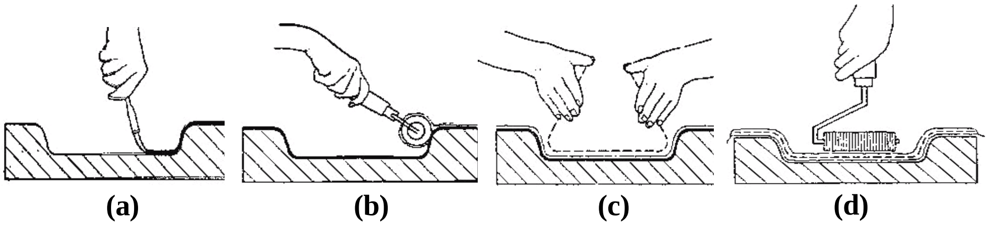


Fig.1.9 Hand lay up (a) apply gel-coat with brush (b) apply laminatin gresin with roller (c) cut and fit reinforcement layer (d) consolidate with ribbed roller

b) Spray-up technique

Spray-up technique is the principal fabrication process used by the FRP industry in developed counties. The catalysed resin and chopped glass fibre are laid down simultaneously on the mould surface with specialised spray equipment. The chopped fibre, 3.8-5.0cm long is produced by feeding continuous glass fibre roving into a rotating chopper at the head of the spray gun. The technique requires skilled operators to get uniform products and to prevent excessive scrap by over spraying

c) Bag moulding process:

Bag moulding is one of the oldest and most versatile of the processes used in manufacturing composite parts. The lamina is laid up in a mould and resin is spread or coated, covered with a flexible diaphragm or bag and cured with heat and pressure. After the required curing cycle, the materials become an integrated moulded part shaped to the desired configuration. The general process of bag moulding can be divided into three basic moulding methods: pressure bag, vacuum bag, and autoclave. Vacuum bag and autoclave methods are used to produce most bag-moulded parts.

d) Filament winding:

The strength of FRP products is enhanced by the concentration and length of the glass fibre reinforcement. The winding of continuous glass roving that have been impregnated with catalysed resin over a rotating mandrel gives maximum structural performance. However this technique is limited to articles with axial symmetry such as cylindrical products. The winding of the glass roving follows a reciprocating helical pattern using a bias angle suitable for the structural requirement. Polar winding is yet another winding method employed for the fabrication of bottles and spherical products. Filament winding is used for the manufacture of pipes, tubes, cylinders, and spheres and is frequently used for the construction of large tanks and pipe work for the chemical industry.

e) Pultrusion:

Pultrusion is an automated process using preimpregnated glass roving which is formed and cured as it is drawn through a heated steel die [202].Continuous glass fibre rovings, continuous filament mat, Kevlar or carbon fibres are used to produce articles of linear uniform cross section on a large scale. In pultrusion the product is pulled from the die rather than forced out by pressure. A large number of profiles such as rods, tubes and various structural shapes can be produced using appropriate dies. Profiles may have high strength and stiffness in the length direction, with fibre content as high as 60-65% by volume.

f) ***Compression moulding:***

Compression moulding offers a method for large volume production of components with excellent dimensional accuracy and good finish on both surfaces. Compression moulding is done by pressing and shaping the moulding charge in a matched die and curing the products by fast curing methods. The products take the shape of the cavity.

It is most convenient to use a preformed thermosetting moulding compound or premix to which all necessary ingredients are added. Moulding compounds can be divided into three broad categories: bulk or dough moulding (BMC or DMC), sheet moulding (SMC) and prepregs. In DMC, chopped fibres are employed while SMC employs woven or chopped strand mats. Prepregs consist of roving, woven fabric, and continuous unidirectional fibre reinforcement sheets or random chopped-fibre sheets impregnated with a partially cured resin system.

g) Resin transfer moulding (RTM):

Resin transfer moulding [205] is unique in that it permits the manufacture of high performance composite parts of essentially unrestricted geometry with fast cycle times. A dry reinforcement preform is placed in the mould and the mould is closed. The preform is impregnated with a thermoset liquid resin which is injected into the mould. During the infiltration process, the resin wets out the reinforcement and polymerises.

h) *Liquid composite moulding;*

A series of processes has emerged in which the reinforcement is placed in the mould and the resin matrix is injected. These are called collectively Liquid Composite Moulding (LCM). At its simplest, this involves placing the glass in the mould in a prescribed pattern, followed by injection of resin. Manual placement of glass is slow and skill-dependent, and preforms are widely used.

Variations also exist on basic resin transfer injection process. Resin transfer moulding (RTM), uses premixed resin, rather like a development of hand-lay-up with a closed mould. In vacuum assisted resin injection (VARI) vacuum helps to speed up the fill rate. This resembles vacuum injection, but it is quicker and less sophisticated. Structural resin injection moulding (SRIM) uses a pre-placed reinforcement or preform and injects a resin system which mixes in a mixing head on the way into the mould. Reinforced reaction injection moulding (RRIM) employs a reactive mixture which completes the polymerization and/or crosslinking step inside the mould in the presence of fibres.

1.6 Scope and objectives of the present work

The objective of this investigation is to develop modified polymer systems for DGEBA resin via reactive blending methods. The strategy for modification will be four fold;

i *Epoxy Novolacs modification*:

Epoxy novolac can be used as a modifier for epoxy resin in suitable proportions to obtain improved properties. These resins include epoxidised novolac resins, epoxidised cardanol and epoxidised novolac based on phenol naphthol mixture. Study of the physical ageing of epoxy novolac modified epoxy resin and comparison with neat DGEBA is also part of this section.

ii. *Siloxane modification*:

Epoxy resin can be modified by physical blending with siloxane and study its properties. Siloxanes are functionalised by hydrosilylation using platinum catalyst. Modify epoxy resin with functionalized siloxane, study the properties and compare it with unfunctionalised siloxane modified epoxy resin. To make a comparative study of the physical ageing of siloxane modified epoxy resin and neat DGEBA

iii. *Three component systems*:

Modification of commercial DGEBA resin by physical blending using two component systems is dealt in this section. The two components used are mixture of epoxy cardanol and epoxy novolac and mixture of epoxy siloxane and apoxy novolacs. The effects of ageing on DGEBA resin modified by the two components as well as unmodified resin are also investigated.

iv. *FRP modification*:

The effects of matrix toughening on the properties of glass reinforced composites and on the properties of epoxy resin are dealt in this section

The specific objectives of the work can be summarised as follows.

- To synthesise various modifier resins such as novolacs, epoxy novolacs, epoxy cardanol and siloxane based epoxides.

- To modify DGEBA using siloxane by physical blending and study its properties
- To synthesise epoxidised siloxane and used as modifier for DGEBA resin and study the properties
- To study the properties of a three component system consisting of epoxy novolacs, epoxy siloxane and DGEBA
- To study the physical ageing of epoxy and modified epoxy resins
- To study the effect of matrix toughening on the mechanical properties of glass reinforced composites.

References

[1] J. A. Brydson, Plastic materials 6th edition, Butterworths Heinemann, Oxford (1995).

[2] A. A. Collyer, Ed. *Rubber Toughened Engineering Plastics*, Chapter 6, Chapman & Hall, London (1994).

[3] Sabina Alessi, Alberto Spinella, Eugenio Caponetti, Clelia Dispenza, Giuseppe Spadaro Radiation Physics and Chemistry, 81(9),1328-1331 (2012)

[4] Herman F. Mark, Norbert M. Bikales, Charles G. Overberger and Georg Menges, Eds.,In Encyclopedia of Polymers Science and Engineering, 3rd ed., John Wiley, NewYork (1988).

[5] US patent 4996270.

[6] Jiyanying Huang, Meaquing Xu, Quang Ge, Minghuua Lin, Yihong Chen, Jiayan Chu, Lizong Dai, Yousi Zou. ,J.Appl. Polym. Sci, **97** (2), 652 (2005).

[7] Castan, Process for the Manufacture of Thermosetting Synthetic Resins by the Polymerisation of Alkylene oxide Derivatives, U.S. 2,444,333 (1948)

[8] German Patent 676,117

[9] U.S Patent 2,456,408 and U. S Patent 2,521,911

[10] Jiang Ding and Wanfang Shi, Eu. Polym. J., **40** (6),1137-1143 (2004)

[11] Metha Rutnakornpituk, Eu. Polym. J., **41**(5), 1043-1052 (2005)

[12] Soo-Jin Park, Fan-Long Jin, Jae-Rock Lu and Jay-Sup Shin., Eu. Polym. J., **41** (2),231-237 (2005)

[13] Applegath. et.al., Epoxy Novolacs., SPEJ, January, 1959

[14] U.S. Pat. 2643239 (June 23, 1953),

[15] N. Hata, J. Kumanotani., J. Appl. Polym. Sci., 17, 3545 (1973)

[16] P.N. Son and C.D. Weber., J. Appl. Polym. Sci 17, 2415 (1973)

[17] S.A. Zahir and S. Bantle., ACS Symp. Ser., 221, 245 (1983)

[18] J.F. Giebel, Org. Coat. Plast. Chem., **43**, 545 (1980).

[19] W.A.Romanchick and J.F. Giebel., Org. Coat. Appl. Polym. Sci. Proc., **46**, 410 (1982).

[20] Driusz Bodgal Polymer Science: A Comprehensive Reference, 4, 981-1027 (2012)

[21] Xing Hong Zhang, Hing Mei Wan, Yu Qin Min and Guo Rong Qi., J. Appl. Polym. Sci., **96** (3), 723-731(2005).

[22] H. Jahn and P. Goetzky in Epoxy Resin Chemistry & Technology, 2nd Ed. C.A. May Ed. Marcel Dekker, NY, p-1049 (1988).

[23] D. K. Hadad in Epoxy Resin Chemistry &Technology, 2nd Ed. C.A.May ed. Marcel Dekker, NY, p-1049 (1988).

[24] A. Kastaneck, M. Bohdanecky and S. Podzimek, Eu. Polym. J., 41(2), 319-28(2005).

[25] A. Schenk and A. Kayen., 'The Use of High Performance Chromatography in Epoxy Resin Analysis' 15th FATIPEC Congress, Amsterdam, FATIPEC, Liege, Belgium p-345-360 (1980).

[26] Monoj Pramanik, Sharathkumar K. Mendon, James W. Rawlins Polymer Testing, 31(5) , 716-721 (2012)

[27] W.B. Moniz, Org. Coat. Plast. 39, 99 (1981)

[28] D. Wolff, K, Schlothauer, M. Fedtke and J. Spracek., Polymer ,32, **(1990)**

[29] C.A. May, Epoxy Resins; Chemistry and Technology, 2nd Edn. Marcel Decker Inc. New York, Page ,551-718 (1988)

[30] M. Ghaemy, Eu. Polym. J., 34(8) 1151-1156(1998)

[31] A. Kondyurin and B. Lauke, Eu. Polym. J., 40(8) , 1915- 1923 (2005).

[32] E. Frulloni, M. M. Salinas, L. Torre, A. Hariani and J.M. Kenny, J. Appl. Polym. Sci., 96 (5), 1756-1766 (2005).

[33] J. Charlesworth, J. Polym. Sci., 18, 621 (1980)

[34] P. I. Engelberg and G. C. Tesoro., Polym. Eng. Sci., 30 (5), 303-307 (2004).

[35] F. Fraga, C. Castro Diaz, E. Rodriguez Nures and Martinez Ageitos, J. Appl. Polym. Sci., 96 (5), 1591-1598 (2005).

[36] J. King , R. Sellers and R. Castonguay., U S patent 4,330,659, (1982)

[37] W.A. Romanchick and J. F. Giebel., Org. Coat. Appl. Polym. Sci. Proc. 46, 410 (1982)

[38] V. Tanratanakul and K. Sae Traw., J. Appl. Polym. Sci., 97 (4), 1442-1461(2005)

[39] A.B. Samui, D. Ratna, J.G. Chavan and P.C. Deb., J. Appl. Polym. Sci., 86 (10), 2523-2529 (2002)

[40] J. Sickfield, and W. Mielke., Prog. Org. Coat.,12, 27 (1984)

[41] S.A. Mestan and C. E. M. Morris, J. Macromol. Sci. Rev. Macromol. Chem. Phys., 24(1), 117 (1984)

[42] A. Wereta Jr. and C.A. May, J. Adhes. 12, 317 (1981)

[43] S.D. Senturia, N.F. Sheppard, Jr. H.L. Lee and D.R. Day , J. Adhes., 15, 69 (1982)

[44] James E. Mark, Polymer Data Handbook, Oxford University Press, New York (1999).

[45] D. Derouet, F. Morvan, and J.C. Bross., J. Appl. Polym. Sci., 62 (11), 1855-1868 (1996).

[46] A.D. La Rossa, A. Recca, J.T. Carter and P.T. McGrail., Polymer, 40 (14), 4093-4098 (1999).

[47] A. Klippstein, M. Cook,S. Monaghan Polymer Science: A Comprehensive Reference 2012, Pages 519–539

[48] S. Radhakrishnan, N. Sonawane, C.R. Siju,Progress in rganic coatings, 64,(4), 2009, Pages 383-386

[49] H Jin, G. M. Miller, N. R. Sottos, Scott, R. White Polymer, 52(7) 2011, Pages 1628-1634

[50] F. Djouani, C Connan, M Delamar, M. M. Chehimi, K. Benzarti Construction and Building Materials, 25(2), 2011, Pages 411-423.

[51] A. Maazouz, H. Sautereau and J.F. Gerard., J, Appl. Polym Sci., 50, 615 (1993).

[52] W.D. Bascom, R.Y. Tinoy, C.K. Riew and A. R. Siebert., J. Mater. Sci., 16, 2657 (1981).

[53] M.M. Raj, L.M. Raj, P.N. Dave Journal of Saudi Chemical Society, 16(3) 2012, Pages 241-246

[54] M.F. Ashby, Materials Selection in Mechanical Design, Pergamon Press, New York (1992).

[55] A.J. Kinloch and R.J. Young, Fracture Behavior of Polymers, Elsevier Applied Science Publishers. London (1983).

[56] A. Zudeldia, M. Larranga, P. Remiro and I. Mondragon, J. Appl. Polym. Sci., Part B, polym. Phys., 42 (21), 3920-3933 (2004).

[57] A.J. Kinloch, In Rubber Toughened Plastics: C.K. Riew, Ed. Advances in Chemistry, 222, American Chemical Society: Washington DC., p 67 (1989).

[58] Sultan JN, McGarry FJ. Polym Eng Sci;13:29 (1973)

[59] Kalfoglou, N.K., and Williams, H.L., J. Appl. Polym. Sci., 17,1377, (1973)

[60] Kunz-Douglass, S., Beaumont, P.W.R., and Ashby, M.F. , J. Mater. Sci., 15,1109 (1980)

[61] Manzione, L.T., and Gillham, J.K., J. Appl. Poly. Sci., 26, 889(1981)

[62] Bartlet, P., Pascault, J.P., and Sautereau, H., J. Appl. Polym. Sci., 30, 2955 (1985)

[63] Valéria D. R, ,H M. da Costa,Vera L.P. S,Regina S.V. N ; Polymer Testing,Volume 24, Issue 3, May 2005, Pages 387–394

[64] Pearson, R.A., and Yee, A.F., J. Mater. Sci., 26, 3828 (1991).

[65] Garima T and Deepak S Materials Science and Engineering: A, 443, 2007, Pages 262-269

[66] Raju T, Ding Y,He Y,Yang L,Paula M,Yang W,Tibor C and Sabu T; Polymer, 49, 2008, 278–294

[67] Kunz, S.C., Sayre, J.A., and Assink, R.A., Polymer, 23, 1897 (1982).

[68] Dan H,Xiaodong D,Pengshan C,and Qingmin C; International Journal of Adhesion and Adhesives 38, 2012, Pages 11–16

[69] Butta, E., Levita, G., Marchetti, A., and Lazzeri, A., Polym. Eng. Sci., 26, 63 (1986)

[70] N Chikhi,S Fellahi, and M Bakar; European Polymer Journal Volume 38, Issue 2, February 2002, Pages 251–264

[71] Shaw, S.J., in .Chemistry and Technology of Epoxy Resins., edited by Ellis, B., Blackie, Glasgow, 1993

[72] Montarnal, S., Pascault, J.P., and Sautereau, H., in .Rubber-Toughened Plastics., edited by Riew, C.K.,Advances in Chemistry Series, 222, American Chemical Society, Washington, D.C., 193 (1989)

[73] Verchere, D., Sautereau, H., and Pascault, J.P., J. Appl. Polym. Sci., 41, 467 (1990)

[74] Verchere, D., Pascault, J.P., Sautereau, H., Moschiar, S.M., Riccardi, C.C., and Williams, R.J.J., J. Appl.Polym. Sci., 43, 293 (1991)

[75] Sankaran, S., J. Appl. Polym. Sci., 39, 1635 (1990)

[76] Kirshenbaum, S.L., Gazit, S., and Bell, J.P., in .Rubber Modified Thermoset Resins., edited by Riew.C.K., and Gillham, J.K., Advances in Chemistry Series, 208, Amer. Chem. Soc., Washington DC, 1984

[77] Bell, J.p., and Ochi, M., Polym. Mater. Sci., Eng., 49, 393 (1983)

[78] Ochi, M., and Bell, J.P., J. Appl. Polym. Sci., 29, 1381 (1984)

[79] Kirshenbaum, S.L., and Bell, J.P., J. Appl. Polym. Sci., 30, 1875 (1985)

[80] Schröder, N., Könczöl, L., Döll, W., and Mülhaupt, R., J. Appl. Polym. Sci., 70, 785 (1998)

[81] Sankaran , S ., and Chanda,M., J.Appl. Polym.Sci., 39 , 1459 (1990)

[82] B.J.P. Jansen, K.Y. Tamminga, H.E.H. Meijer*, P.J. Lemstra, Polymer, 40 5601–5607, (1999).

[83] Chuayjuljit, S; Soatthiyanon, N; Potiyaraj, P J. Appl. Polym. Sci. 102(1), 452-459 2006

[84] Yorkgitis, E.M., Tran, C., Eiss, N.S., Hu, T.Y., Yilgor, I., Wilkes, G.L., and McGrath, J.E., in .Rubber-Modified Thermoset Resins., edited by Riew, C.K., and Gillham, J.K., Advances in Chemistry Series,208, American Chemical Society, Washington, D.C., 1984

[85] Matsukwa k,Hasegawa k,Inoue h, Fukuda A, Arita y. J Polym Sci Polym Chem;30:2045-48 (1992)

[86] P Murias, H Maciejewski, H Galina European Polymer Journal, 48(4) 2012, Pages 769-773

[87] Lin S T, Hung SK. Eur Polym J;33:365-73(1997)

[88] Sung P H , Lin C Y. Eur Polym J;33:903-06 (1997)

[89] Lee SS, Kim SC, J Appl Polym Sci; 69:1291-1300 (1998).

[90] Agrawal JP, Venugopalan S, Athar J, Sobane J V, Muralidharan M. J Appl Polym Sci 1998;69:7-12

[91] Zhang, H., Zhang , J ., Yang, Y., Macromol Theory Simul 4, 1001, (1995)

[92] Burhans, A.S., Soldatos, A..C., in Multicomponent Polymer Systems. N.A.J. Platzer Ed: ACS, Advances in Chemistry Series , No. 99; ACS, Washington DC, pp-531-46

[93] Piotr M, Hieronim M, Henryk ,European Polymer Journal,48, (4) 2012, 769-773

[94] Kasemura, T., Takahashi, S., Nishihara, K., and Komatu, C., Polymer, 34, 16 (1993).

[95] Tsung-Han Ho, and Chun-Shan Wang, Polymer, 37, 2733 (1994).

[96] Tsung-Han Ho, Jenn-Hwa Wang, and Chun-Shan Wang, J. Appl. Polym. Sci., 60, 1097 (1996).

[97] Tsung-Han Ho, 1 Egan, D., and Weber, C.D., Adhesives Age, 43(1), 24 (2000).

[98] Emel Y and Iskender Y, Polymer, 39, 1691 (1998).

[99] Yayun L., Master thesis, Syracuse University, Syracuse, NY, 1999

[100] Meng-huo C., Master thesis, Syracuse University, Syracuse, NY, 2001.

[101] Zhiqiang Tao, Shiyong Yang, Jiansheng Chen, Lin Fan European Polymer Journal, 43(4)l 2007, Pages 1470-1479

[102] Min BG, Hodgkin JH, Stachurski ZH. J Appl Polym Sci.;50:1065 (1993)

[103] Soo-Jin Park*, Hyun-Chel Kim, J Polym Sci B: Polym Phys 39: 121-128, 2001

[104] Hendrick, L.; Yilgor, I.; Wilkes, G. L.; McGrath, J. E. Polymer Bull., 13, 201 (1985)

[105] Akay M, Cracknell JG. J Appl Polym Sci;52:663(1994)

[106] Yamanaka K, Inoue T. Polymer;30:662 (1989)

[107] Bucknall CB, Partridge IK. Polymer;24:639 (1983)

[108] Raghava, R. S., Soc. Adv. Mater. Proc. Eng, 28th Nat. Symp., 367 (1983)

[109] Raghava, R. S, J. Polym. Sci., Polym. Phys. Ed., 26, 65 (1988)

[110] Fu, Z., and Sun, Y., Polym. Prepr., 29(2), 177 (1988)

[111] Kim, B. S.; Chiba, T.; Inoue, T. Polymer, 36, 67 (1995)

[112] Park JW, Kim SC. IPNs around the world. Chichester: Wiley ,:27(1997)

[113] Chean CS, Eamor MW. Polymer;36(15):2883 (1995)

[114] Bucknall, C.B., and Gilbert, A.H., Polymer, 30, 213 (1989)

[115] Gilbert, A. H.; Bucknall, C. B. Makromol. Chem., Macromol Symp., 45, 289. (1991)

[116] Recker, H.G., Allspath, T., Altstadt, V., Folda, T., Heckmann, W., Ittemann, P., Tesch, H., and Weber T., Int. SAMPE Symp., 34, 747(1989)

[117] Recker, H.G., Altstaedt, V., Eberle, W., Folda, T., Gerth, D., Heckman, W., Itteman, P., Tesch, H., and Weber, T., Sampe J., 26 (2), 73 (1990)

[118] Hurston, D. J.; Lane, J. M.; McBeath, N. A. Polym. Int., 26, 17.(1991)

[119] Hourston, D. J.; Lane, J. M. Polymer, 33, 1379 (1992)

[120] Cecere, A.; McGrath, J. E. Polym. Prepr. (Am. Chem. Soc., Div. Poly. Chem.), 27(1), 299.(1986)

[121] Bennet, G. S.; Farris, R. J.; Thompson, S. A. Polymer, 32, 1633(1991)

[122] Iijima, T., Tochimito, T., and Masao, T., J. Appl. Polym. Sci., 43, 1685 (1991)

[123] Jabloner, H., Swetlin, B.J., Chu, S.G., U.S. Patent 4,656,207 (1987)

[124] Hedrick, J.L., Yilgor, I., Wilkes, G.L., and McGrath, J.E., Polym. Bull., 13, 201 (1985)

[125] Hedrick, J.L., Yilgor, I., Jurek, M., Hedrick, J.C., Wilkes, G.L., and McGrath, J.E., Polymer, 32, 2020 (1991)

[126] Chu, S.G., Swetlin, B.J., and Jabloner, H., U.S. Patent 4,656,208 (1987)

[127] Min, B.-G., and Stachurski, Z.H., Polymer, 34, 3620 (1993)

[128] Pearson RA, Yee AF. J Appl Polym Sci; 48:1051(1993)

[129] Harani.H. ; Fellahi S. ; BakarM. ; J. appl. polym. Sci., vol. 71, 29-38 (1999)

[130] Pearson, R.A., and Yee, A.F., Polym. Mater. Sci. Eng., 63, 311 (1990)

[131] Kim, J., and Robertson, R., Polym. Mater. Sci. Eng., 63, 301 (1990)

[132] Cecere, J.A., McGrath, J.E., Polym. Prepr. Amer. Chem. Soc. Div. Polym. Chem., 27(1), 299 (1986)

[133] Liello, V.D., Martuscelli, E., Musto, P., J. Polym. Sci. (Polym Phys Ed), 32, 409 (1994)

[134] Jang, J., Shin, S., Polymer, 36, 1199 (1995)

[135] G. Ragosta, M. Abbate, P. Musto, G. Scarinzi, L. Mascia, Polymer, (46) 23, 2005, Pages 10506-10516

[136] Moloney , A.C ., Kausch , H.H ., and Stieger , H.R., J. Mater. Sci. 18, 208 (1983)

[137] Moloney , A.C ., Kausch , H.H ., Kaiser , T., and Beer , H.R ., J.Mater.Sci., 22 , 381 (1987)

[138] Spanoudakis, J., and Young, R.J., J. Mater. Sci., 19, 473 (1984)

[139] Amdouni, N., Sautereau, H., Gerard, J.F., J. Appl. Polym. Sci., 46, 1723 (1992)

[140] Srivastava, V.K., Shembekar, P.S., J. Mater. Sci., 25, 3513 (1990)

[141] M.Sarojadevi,V.Murugesan,K.Rengaraj,PAnand,Appl.Polym.Sci,69,1385 (1998)

[142] Gaohui Wu, Jian Gu*,Xiao Zhao,j. App. Polym.Sci 105(3),2007,1118

[143] Phipps, Mark Anthony (1995) *The strength of alumina trihydrate filled epoxy resins.* (PhD thesis), Kingston University.

[144] Nakamura, Y., Yamaguchi, M., Kitayama, A., Okubo, M., and Matsumoto, T., Polymer, 32, 2976 (1991)

[145] Nakamura, Y., Yamaguchi, M., Okubo, M., and Matsumoto, T., J. Appl. Polym. Sci., 45, 1281 (1992)

[146] Chenggang Chen, Alexander B. Morgan Polymer, Volume 50, Issue 26, 10 December 2009, Pages 6265-6273

[147] Makoto Imanaka, Yoshihiro Takeuchi, Yoshinobu Nakamura, Atushi Nishimura, Takeo Iida International Journal of Adhesion and Adhesives, Volume 21, Issue 5, 2001, Pages 389-396

[148] Ying-Ling Liu, Wen-Lung Wei, Keh-Ying Hsu, Wen-Hsuan Ho Thermochimica Acta, Volume 412, Issues 1–2, 23 March 2004, Pages 139-147

[149] S. Fellahi *, N. Chikhi, M. Bakar, J. Appl. Polym. Sci., 82, 861-878 (2001)

[150] A. Astruc, E. Joliff, J.-F. Chailan, E. Aragon, C.O. Petter, C.H. Sampaio Progress in Organic Coatings, Volume 65, Issue 1, April 2009, Pages 158-168

[151] Byung Chul Kim, Sang Wook Park, Dai Gil Lee, Composite Structures, 86, 69-77, (2008)

[152] Wei Jiang, Fan-Long Jin, Soo-Jin Park, Journal of Industrial and Engineering Chemistry, 18(2),594-596(2012)

[153] H.J. Yu, L. Wang, Q. Shi, G.H. Jiang, Z.R. Zhao, X.C. Dong Progress in Organic Coatings, 55(3),296-300(2006)

[154] Hamad A. Al-Turaif ,Progress in Organic Coatings, 69(3),241-246(2010)

[155] Rongguo Zhao,Wenbo Luo Materials Science and Engineering: A, 483–484, 313-315, (2008).

[156] H. Alamri, I.M. Low Materials & Design, 42, 214-222(2012)

[157] A. Hernández-Pérez, F. Avilés, A. May-Pat, A. Valadez-González, P.J. Herrera-Franco, P. Bartolo-Pérez Composites Science and Technology, 68(6),1422-1431 (2008)

[158] A. Martone, C. Formicola, M. Giordano, M. Zarrelli Composites Science and Technology, 70,1154-1160, (2010)

[159] V. Leon, R. Parret, R. Almairac, L. Alvarez, M.-R. Babaa, B.P. Doyle, P. Ienny, P. Parent, A. Zahab, J-L. Bantignies ,Carbon, 50(14),4987-4994 (2012)

[160] Young, R.J., and Beaumont, P.W.R., J. Mater. Sci., 12, 684 (1977).

[161] Riew, C.K., Siebert, A.R., Smith, R.W., Fernando, M., and Kinloch, A.J., in .Toughened Plastics II.Novel Approaches in Science and Engineering., edited by Riew, C.K., and Kinloch, A.J., Advances in Chemistry Series, 252, American Chemical Society, Washington, D.C. (1996)

[162] Libor Matějka, Karel Du.ek, Josef Ple.til, Jaroslav Křĺ., Franti.ek, Lednický, Polymer, 40, 171 (1999).

[163] Harani H., Fellahi , S., Baker, M., J. Appl. Polym.Sci.,70 , n-13,2603 (1998)

[164] Harani H., Fellahi, S., Baker, M ., J. Appl. Polym. Sci., 71 (1), 29 (1999)

[165] Chen Tonghui, Li Hanshing, Gao-Yue, Zhang Minlian., J.Appl.Polym.Sci., 69, n-5 , 887 (1998)

[166] Dae Su Kim*,Mi Jeong Han, Jae Rock Lee Polymer Engineering & Science Volume 35, Issue 17, pages 1353–1358, September 1995

[167] S. Premkumar, C. Karikal Chozhan, M. Alagar, European Polymer Journal, 44(8), 2599-2607 (2008)

[168] Guanglei Wu, Kaichang Kou, Min Chao, Longhai Zhuo, Jiaoqiang Zhang, Ning Li , Thermochimica Acta, 537, 44-50 (2012),

[169] Zhang Baolong , Zhang Hui Qi ., You Ying Cai., Du Zongjie Ding ., peiyuan Wang Tao and Huang Ji Fu ., J. Appl. Polym.Sci ., 69 (2), 339 (1998)

[170] Lin-Gibson ,Sheng ., Cresol Novolac-Epoxy Networks .,Dissertation. ETD-etd-04262001-142525 .(2001)

[171] Siddhamali Sridhar K., J. Vinyl.Addit. Technol., 6 (4) ,211-220. (2000)

[172] Fan Hong ., Wang Jinali and Chen Zhuo ., Journal CA, Sec;37 (Plastic Manufacturing and Processing) (2000)

[173] Zhao Shiqi ., Yun Huiming ., Journal CA , Sec; 37 (Plastic Manufacture and Processing) (1999)

[174] Qizhou Dai ., Jinming Chen ., Yong Huang ., J, Appl. Polym. Sci., 70,1159 (1998)

[175] Lopez, J ., Gisbert , S ., Ferrandiz , S .,Vilaplana, J and Jemenez , A., J. Appl. Polym. Sci , 67 , 10 (1998)

[176] Schroder , N ., Koenczoel , L ., Doell, W ., Muelhaupt , R ., J. Appl . Polym. Sci., 70, n-4, 785 (1998)

[177] Shin Seungham and Jang Jyongsik ., J. Appl. Polym. Sci., 65 (11), 2237 (1997)

[178] Shin, S. M ., Shin , D. K., Lee, D.C., J. Appl. Polym. Sci , 78 ,(14), 2464 (2000)

[179] Barcia F.L., Abrahao, M.A ., Soares , B.G., J. Appl. Polym. Sci ., 83 (4), 838-849 (2002)

[180] Ratna, D., Polym. Int., 50 , (2) , 179 -184 (2001)

[181] Punchaipetch Prakaipetch., Brostow Witold., D'Souza N.A., Soc.Plast. Eng., 58 (2) , 2147 -2151 (2000)

[182] Garg, A.C., and Mai, Y.W., Composite. Sci. and Tech., 31, 179 (1988)

[183] Huang, Y., Hunston, D.L., Kinloch, A.J., and Riew, C.K., in .Toughened Plastics I., edited by Riew, C.K., and Kinloch, A.J., Advances in Chemistry Series, 233, Amer. Chem. Soc., Washington DC, 1993

[184] Lange, F.F., Radford, K.C., J. Mater. Sci., 6, 1197 (1970).

[185] Evans, A.G., Philos. Mag., 26, 1327 (1972).

[186] Rose, L.R.F., Mech. Mate., 8, 11 (1987)

[187] Raymond A Pearson, Albert F Yee ,Polymer, Volume 34, 17, September 1993, Pages 3658–3670

[188] Mertz ,E. H., Claver , G. C. and Baer , M., J. Polym. Sci. 22 , 325 (1956)

[189] Kunz-Douglas ,S ., Beaumont , P.W.R and Ashby , M.. F., J. Mater. Sci., 15, 1109 (1980)

[190] C. B. Bucknall, , Toughened Plastics, Appl. Sci. Publ., London (1977).

[191] Donald , A.M., and Kramer E.J., J. Appl. Polym. Sci., (1982)

[192] Donald , A.M., and Kramer E.J., J . Mater. Sci., 17 , 2351 (1982)

[193] Bucknall ,C.B. and Yoshii , T., Br. Polym. J., 10 , 53 (1978)

[194] Newman ,S. and Strella, S., J. Appl. Polym. Sci. , 9 , 2297 (1965)

[195] Donald , A.M., and Kramer E.J., J . Mater. Sci., 17 , 1765 (1982)

[196] Argon, A.S., in ICF7, .Advances in Fracture Research., Samala, K., Ravi-Chander, K., Taplin, D.M.R., Rama Rao, P., Eds, Pergamon Pregress, New York, 4 (1989).

[197] Kinloch , A.J., Shaw , S.J ., and Hunston , D.L., Polymer, 24 , 1355 (1983)

[198] Pearson , R.A. and Yee , A.F., Polym.Mater.Sci.Eng., 49 , 316 (1983)

[199] Sigl. L.S., Mataga, P.A., Dageleidsh, B.I., McMeeking, R.M., and Evans, A.G., Acta. Metall., 36, 1945 (1988).

[200] Faber, K.T., and Evans, A.G., J. Am., Cerom. Soc., 67, 255 (1984).

[201] G. Lubin, Ed., Handbook of Composites, Van Nostrand Rheinhold Company, NewYork (1982).

[202] Z.G. Shaker, R.M. browne, H.A. Stretz, P.E. Cassidy and M.T. Blanda, J. Appl. Polym. Sci ., 84, 2283-2286 (2002) .

[203] A.B.Pereira, A.B. de Morais, A.T Marques, P.T. de Castro., Compos. Sci. Technol.,64, 1653 (2004).

[204] J.A. Hough, S.K. Karad and F.R. Jones., Compos. Sci. Technol.,65, 1229 (2005)

[205] K. Potter, Resin Transfer Moulding. Chapman and Hall, London,(1997).

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Chapter 2

MODIFICATION OF DGEBA USING EPOXIDISED PHENOLIC RESIN

Contents

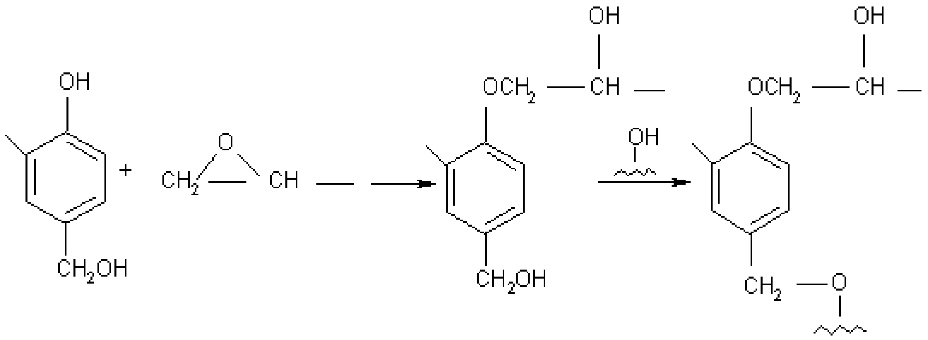
2.1 Introduction

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.

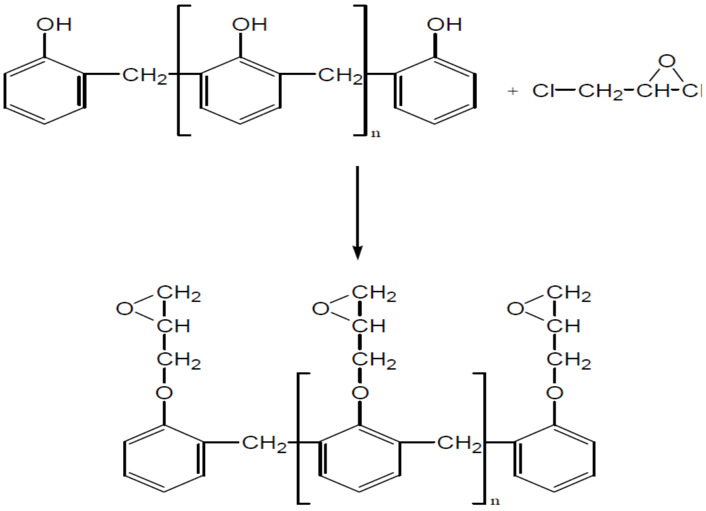
Epoxy resin can be cured by several hardners. This chapter deals with optimization of weight percentage composition of hardener for curing, post curing time and post curing temperature, properties of epoxy resin used, sample preparation, modification of epoxy resin with epoxidised novolac resin from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



Scheme. 2.2

Novolac resins are epoxidised through the phenolic hydroxyl groups by treatment with epichlorohydrin (Scheme. 2.3) .



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 back bone.

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 onegram 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 $= N \times V/w$,

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 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.

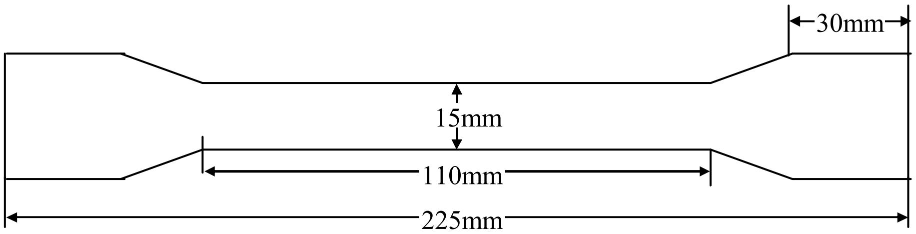


Fig. 2.1 The dimensions of the tensile test specimens

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.

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.

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

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 Stereoscanner- 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 3mm 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].

$$V_p = \frac{(D - FT)\rho_p^{-1}}{(D - FT)\rho_p^{-1} + A_0\rho_s^{-1}}$$

where, D=deswollen weight of the specimen, F=weight fraction of insoluble components, T = weight of the specimen, ρ_p = density of polymer and ρ_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^{0}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^{0}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 10weight % 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 100^0C.

2.2.4 Synthesis of modifier resins

a) Materials

Phenol (M.W=94.11,M.P.39.5-41^0C), p-cresol, (MW=108.14, BP=202^0C, 98% assay), o-cresol (MW=108.14, BP=191^0C, 98% assay), formaldehyde (37-41% w/v, d^{20}=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.

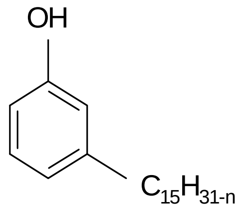


Fig.2.2 Structure of cardanol

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

n=0, $(CH_2)_7$-$(CH_2)_7CH_3$; n=2, $(CH_2)_7$ CH =CH $(CH_2)_5CH_3$

n=4, $(CH_2)_7$ CH =CH - CH_2 - CH =CH $(CH_2)_2CH_3$

n=6, $(CH_2)_7$ - CH =CH - CH_2 - CH =CH - CH_2 - CH =CH_2

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.

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)).

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 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.

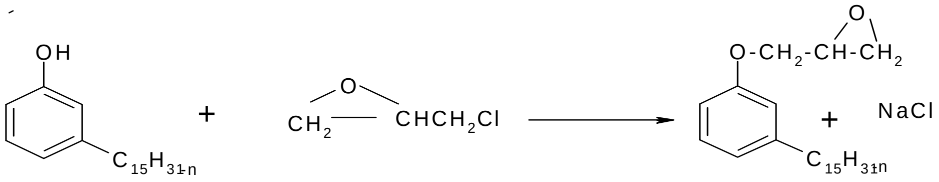


Fig. 2.3 Epoxidation of cardanol

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 dumb bell 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 at100^{o}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^{o} 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 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 100^0C 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 100^0C 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 100^0C 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].

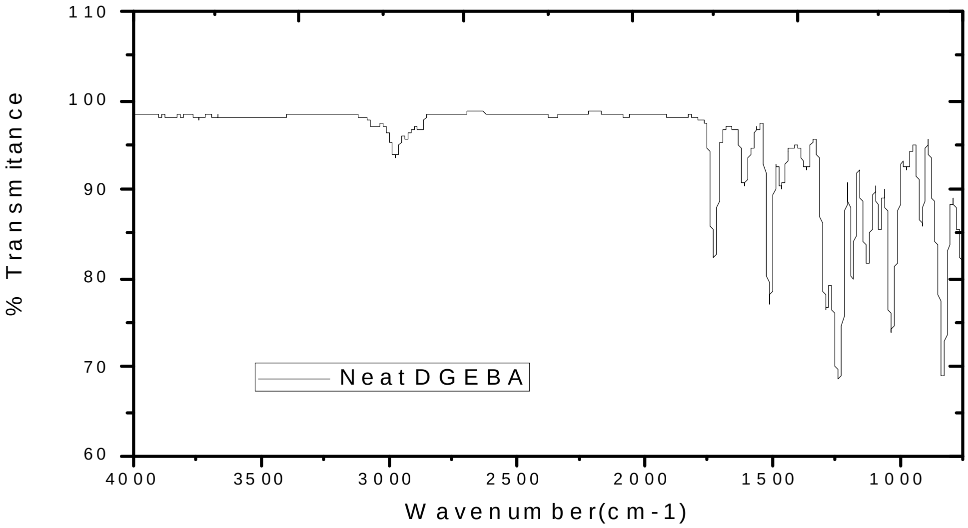


Fig.2.4 FTIR spectrum of commercial epoxy resin

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

Table 2.1 Properties of commercial epoxy resins

Properties	**Value**
Weight per epoxide (wpe)	188
Epoxy equivalent. Eq/Kg	5.30
Density (g/cm^3)	1.192
Viscosity (cp)	12095

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

Properties	**Commercial DGEBA Values**
Tensile strength.(MPa)	55.5
Elongation at break (%)	3.01
Modulus. (MPa)	2425
Energy to break. (J/mm^2)	4.01
Impact strength. Izod. (J/m)	111.04
Surface hardness. (Shore D)	88.15
Water absorption. (%)	0.2002

iv Thermal Studies

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

Table 2.3 TGA characteristics of DGEBA

Property	**Value**
Onset temperature (°C)	343
Temperature of maximum rate (°C)	364
Temperature of half loss (°C)	378
Residue	6.68

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

Property	Weight percentage of Hardener		
	8%	10%	12 %
Tensile strength (MPa)	45.6	55.5	50.9
Tensile modulus (MPa)	2389	2425	2393
Elongation at break (%)	4.56	3.01	2.89
Energy absorbed to break. J.mm^{-2}	2.05	4.01	2.915
Impact strength (J.m^{-1})	52.80	111.04	78.35
Compressive strength (MPa)	99	108	106.45
Surface hardness. Shore D	85	88.15	89.9
Water absorption (%)	0.275	0.2021	0.2018

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^{o}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 *

Property	Post curing temperature (°C)			
	60	80	100	120
Tensile strength (MPa)	52.6	54.05	55.5	54.2
Tensile modulus (MPa)	2389	2408	2425	2420
Elongation at break (%)	2.875	2.90	3.01	3.03
Energy absorbed to break. J.mm^{-2}	2.76	2.822	4.01	3.94
Impact strength (J.m^{-1})	106.80	107.25	111.04	110.50
Compressive strength (MPa)	99	104.5	108	108
Surface hardness. Shore D	86	87.5	88.15	88.20
Water absorption (%)	0.2235	0.2105	0.2002	0.2005

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.

vii 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

Property	Post curing time (hrs)				
	1	2	3	4	5
Tensile strength (MPa)	52.8	53.25	54.8	55.5	55.35
Tensile modulus (MPa)	2307	2327.8	2358	2425	2417.7
Elongation at break (%)	2.95	2.9822	3.075	3.01	3.04
Energy absorbed to break. J.mm^{-2}	3.76	3.848	3.914	4.01	3.937
Impact strength (J.m^{-1})	107.36	107.7	108.20	111.04	109.55
Compressive strength MPa	98.65	100.5	103	108	106.5
Surface hardness. Shore D	85.5	85.5	86	88.15	88.5
Water absorption (%)	0.229	0.224	0.2164	0.2002	0.2006

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 datas

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

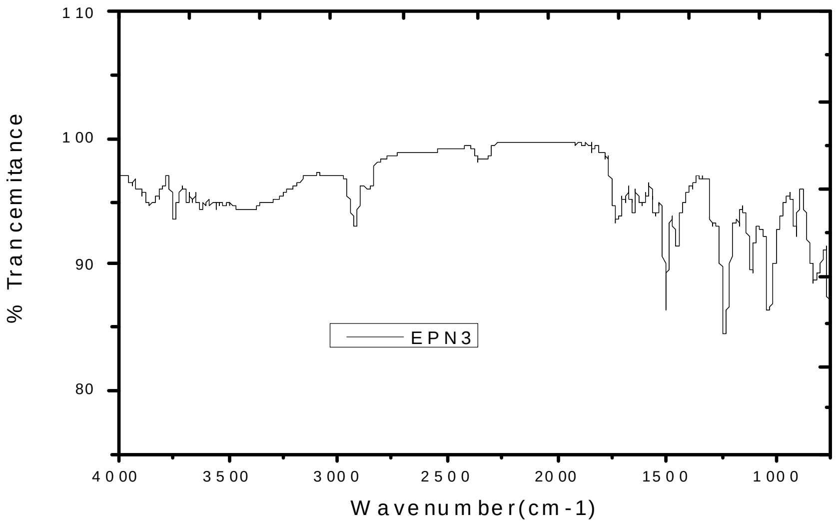


Fig. 2.5 FTIR spectrum of EPN

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 2929.85cm^{-1}.Further, the bands at 915cm^{-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 15wt % 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.

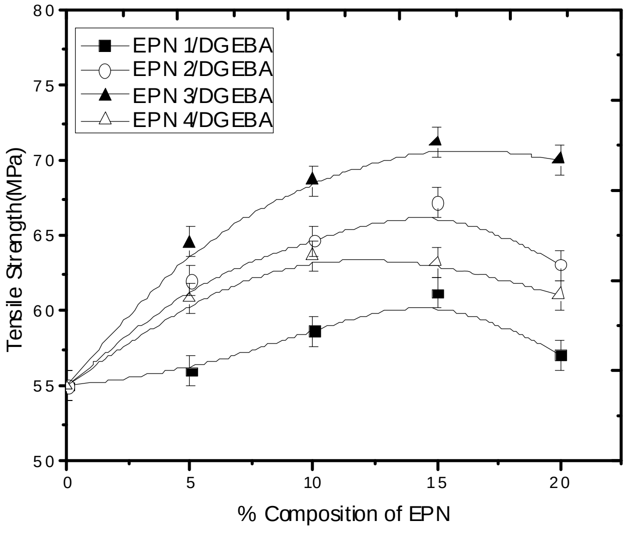


Fig. 2.6. Tensile strength of modified resin Vs EPN concentration

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.

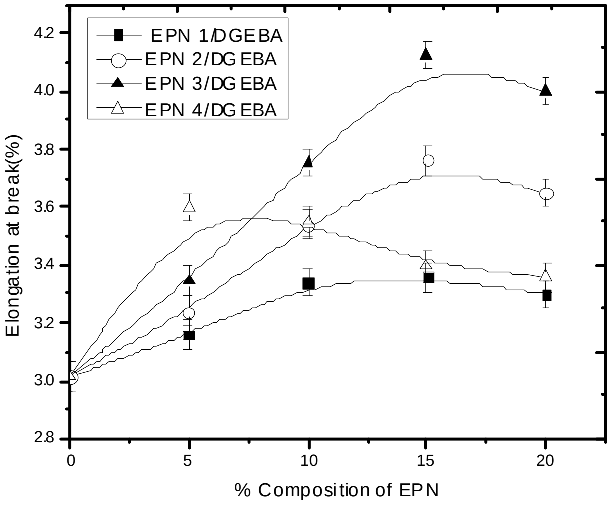


Fig. 2.7. Elongation (at break) of modified resin Vs EPN concentration.

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.

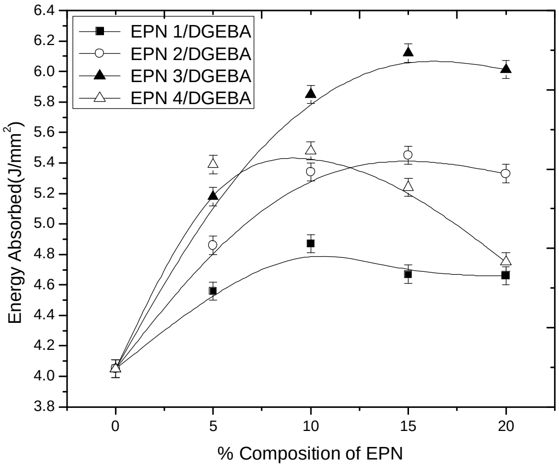


Fig. 2.8. Energy absorbed (to break) of modified resin Vs EPN concentration

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.

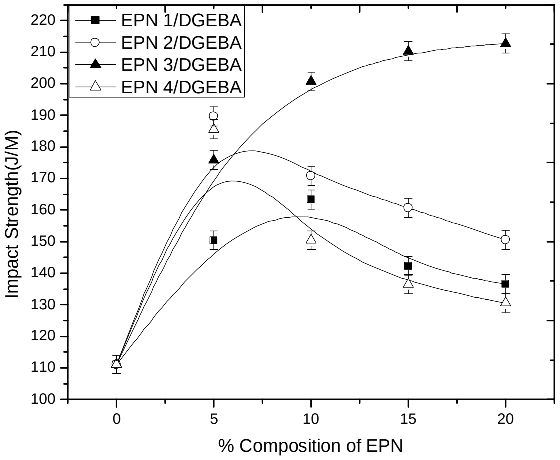


Fig. 2.9. Impact strength of modified resin Vs EPN concentration

iii. Surface hardness and water absorption

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

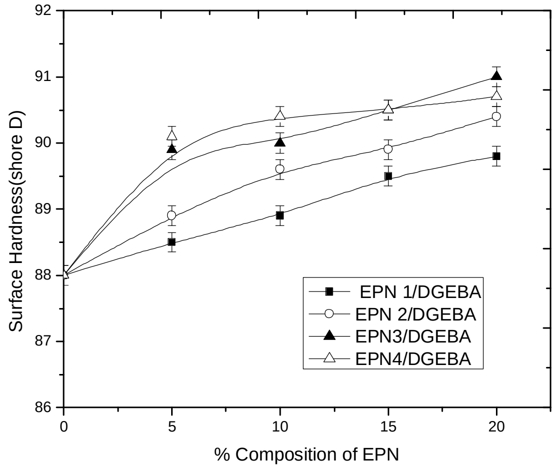


Fig. 2.10 Surface hardness of modified resin Vs EPN concentration

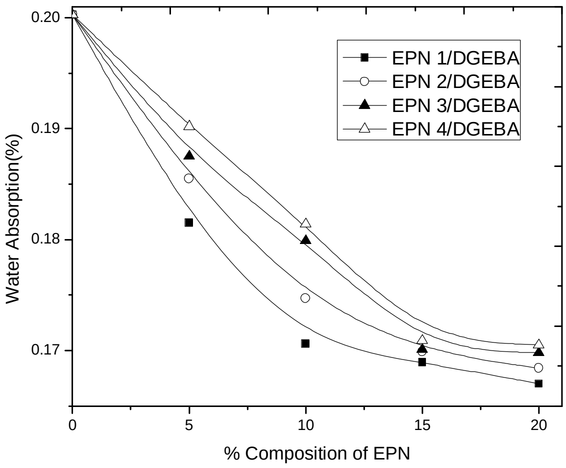


Fig. 2.11 Water absorption of modified resin Vs EPN concentration

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

Property	DGEBA	% improvement / weight % EPN			
		EPN-1/ DGEBA	EPN-2/ DGEBA	EPN-3/ DGEBA	EPN-4/ DGEBA
Tensile strength (MPa)	55.5	10.3/15	21.1 /15.	28.3/15	15.6/10
Elongation at break (%)	3.01	11.5/15	24.9/15.	36.9/15	19.6/5
Energy absorbed (J/mm^2)	4.05	20.2/10	34.6/15	51.1/10	35.3/10
Impact strength .(J/m)	111.04	52.3/15	61.9/5	89.5/15	58.2/10
Surface hardness (Shore D)	88.1	2/20	2.7/20.	3.4/20	3.1/20
Water absorption %	0.2003	-16.6/20	-15.9/20	-15.2/20	-14.9/20

iv. Thermal properties

i. *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^{0}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.

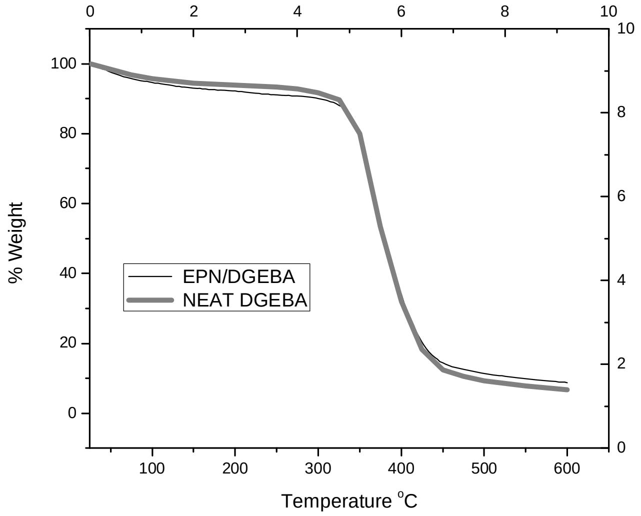


Fig. 2.12 TGA curves for DGEBA and DGEBA/EPN-3

Table 2.8 Thermal properties of DGEBA/EPN blends

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
EPN	340	365	380	8.78

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_{max}) becomes lower as the distance between the crosslink decreases. The tan δ_{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.

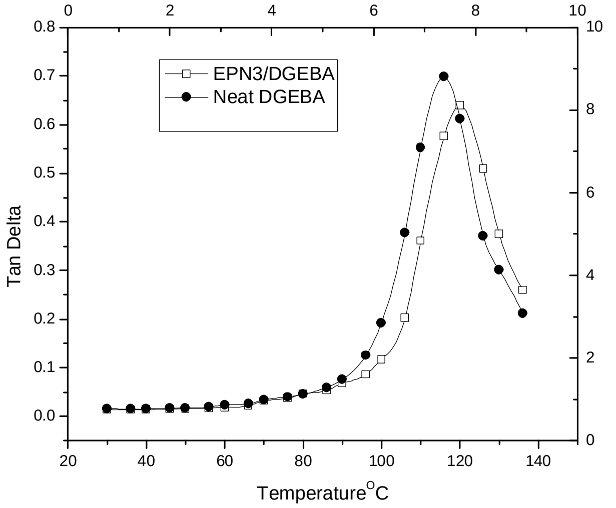


Fig.2.13.Tan delta curves for DGEBA and DGEBA/EPN blends

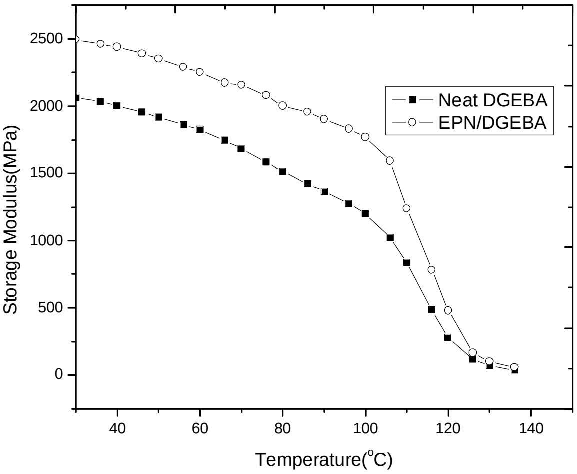


Fig. 2.14. DMA-storage modulus curves for DGEBA and DGEBA/EPN blends

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

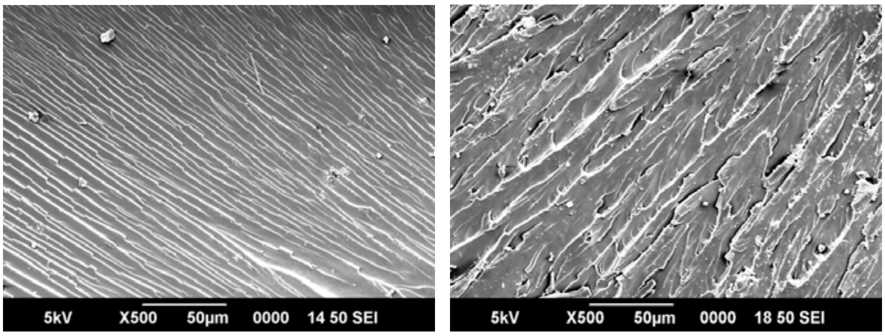
Among the different EPNs used, EPN-3 was found to give the least amount of soluble matter during soxhlet extraction (Table 2.9). This effect is in conformity with the higher level of cross-linking facilitated by EPN-3. The higher functionality and phenolic content of novolac resins increase cross-link 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

Samples	DGEBA	EPN-1	EPN- 2	EPN-3	EPN-4
Soluble matter %	4.98	4.59	4.08	3.99	4.32

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 ^{0}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

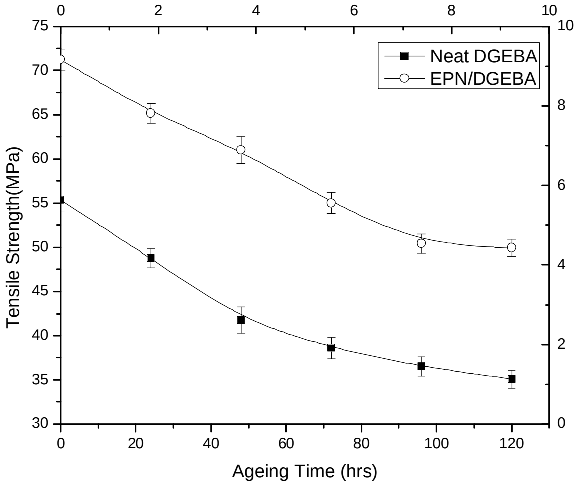


Fig. 2.16 Tensile strength of modified resin Vs ageing time

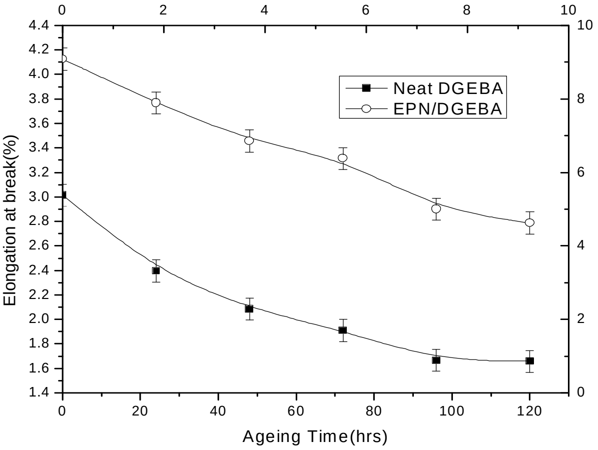


Fig. 2.17. Elongation at break of modified resin Vs ageing time

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.

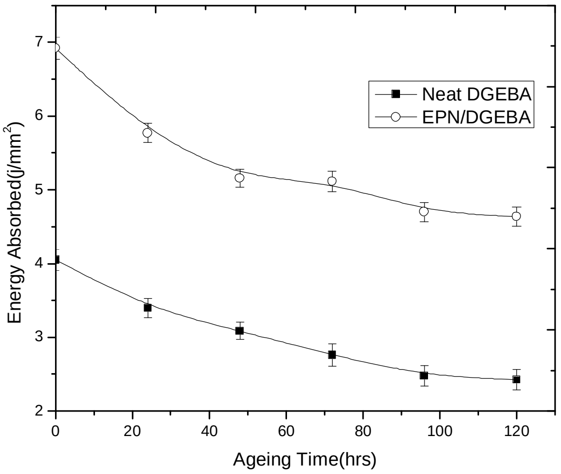


Fig. 2.18. Energy absorbed (to break) of modified resin Vs ageing time

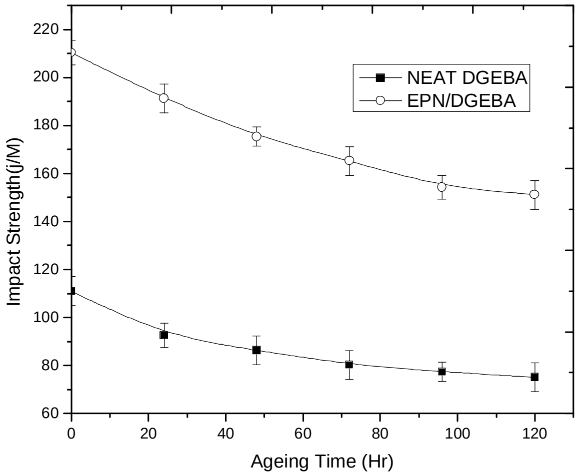


Fig2.19. Impact strength of modified resin Vs ageing time

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.

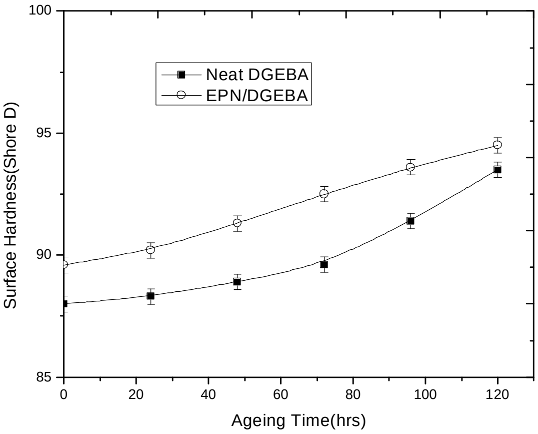


Fig. 2.20. Surface hardness of modified resin Vs ageing time

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.

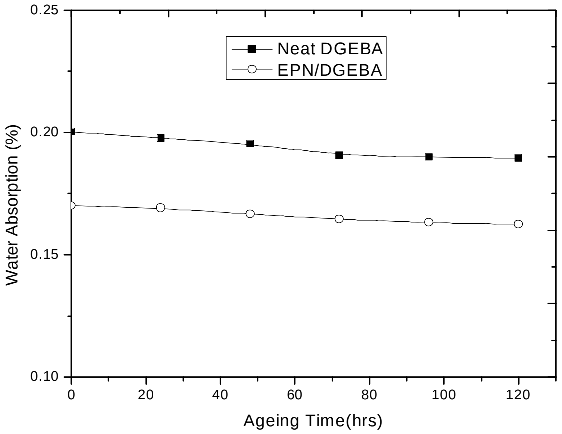


Fig. 2.21. Water absorption of modified resin Vs ageing time

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 2929.85cm^{-1}.Further, the bands at 915cm^{-1} 840 cm^{-1}and 760 cm^{-1} are also typical of epoxides.

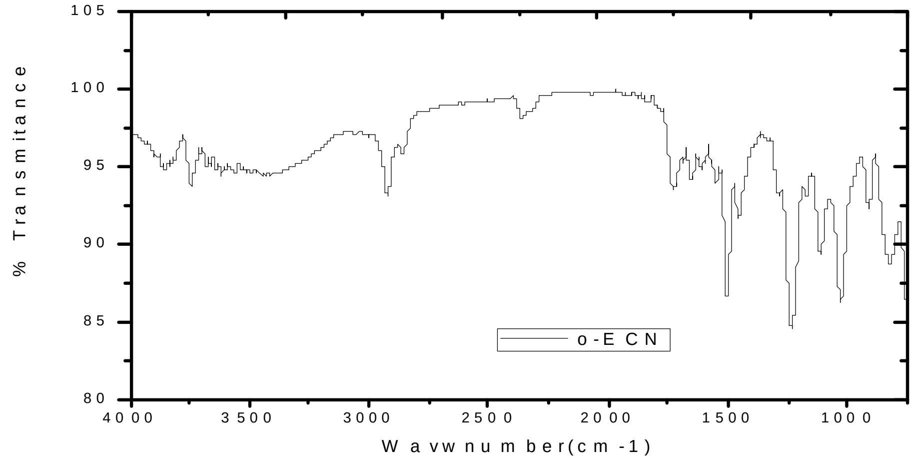


Fig.2.22a FTIR spectrum of o-ECN

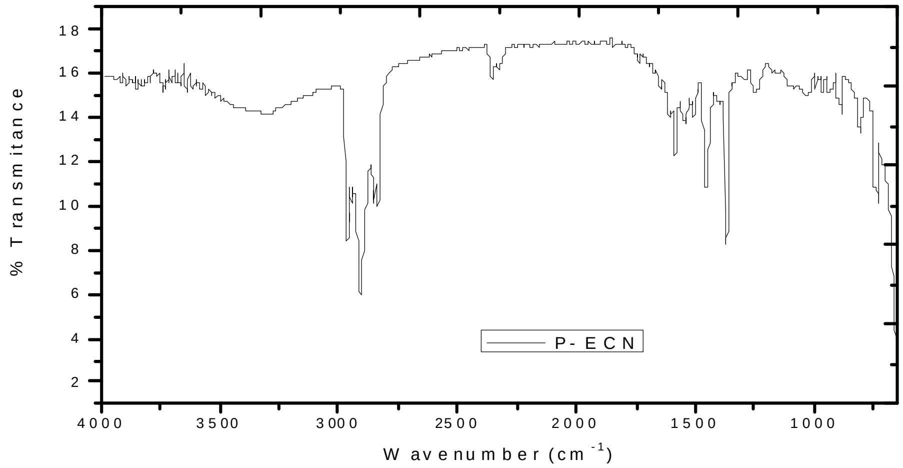


Fig.2.22b FTIR spectrum of p-ECN

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.

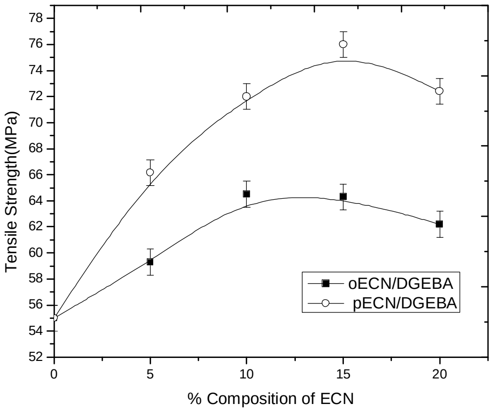


Fig. 2.23 Tensile strength of modified resin Vs ECN concentration

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.

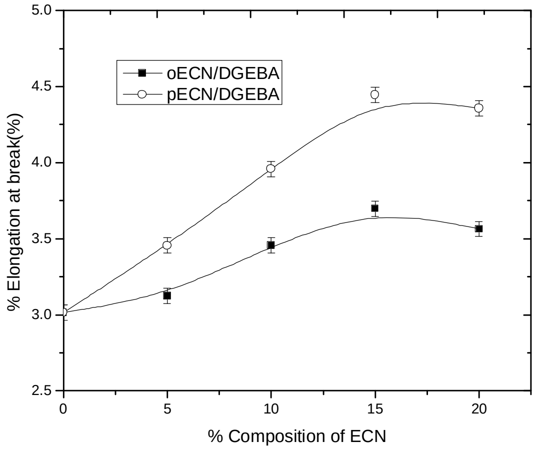


Fig.2.24 Elongation at break of modified resin Vs ECN concentration

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.

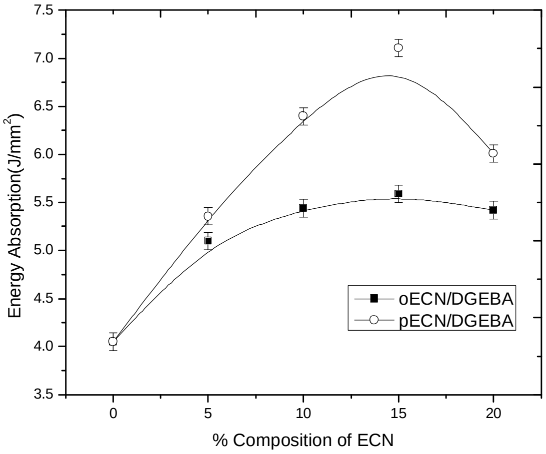


Fig. 2.25 Energy absorbed (to break) of modified resin Vs ECN concentration

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 .

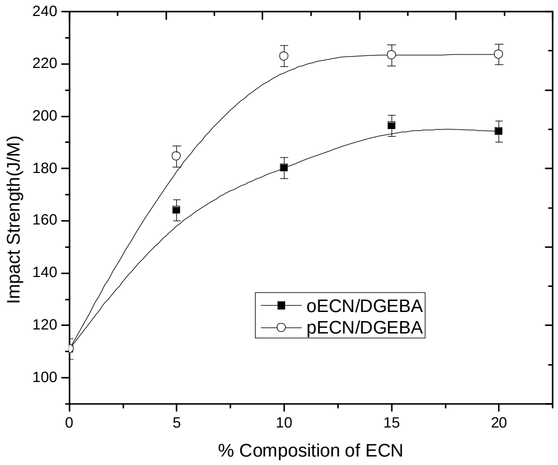


Fig. 2.26 Impact strength of modified resin Vs ECN concentration

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.

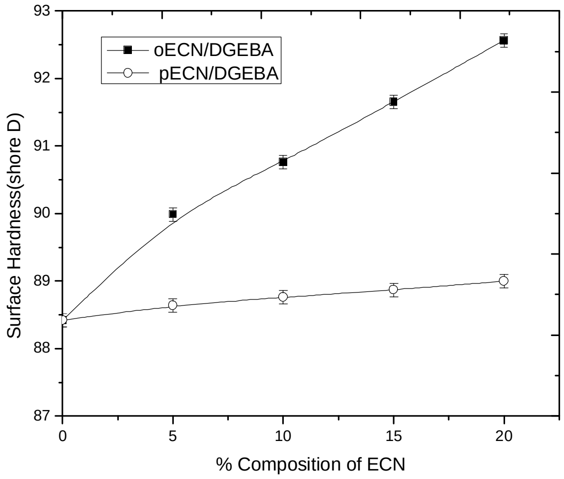


Fig. 2.27 Surface hardness of modified resin Vs ECN concentration

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.

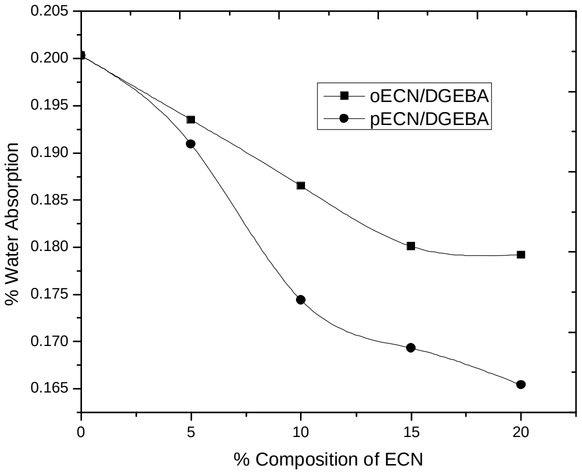


Fig.2.28 Water absorption of modified resin versus ECN concentration.

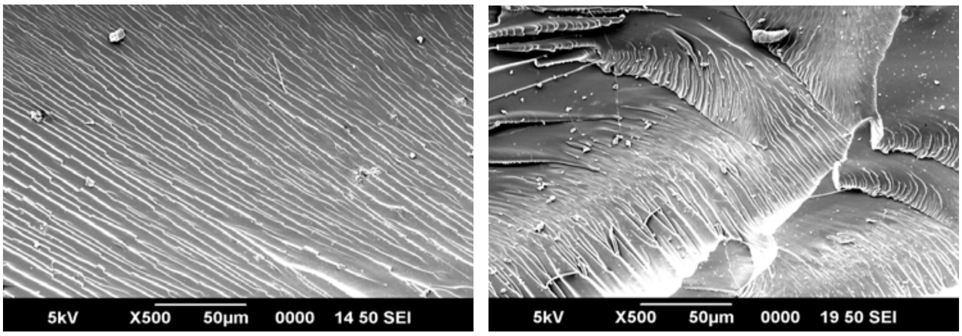
Table 2.10. summarizes the effect of adding varying amounts of epoxy cresol novolac resins to the base resin. The maximum improvement acquired in each property and the corresponding concentrations are tabulated.

Table 2.10. Properties of epoxy ECN blends

Properties	**% Improvement/ composition (wt %)**		
	DGEBA	**p-ECN/DGEBA**	**O-ECN/DGEBA**
Tensile Strength (MPa)	55.5	36/15	13.5/10
Elongation at break (%)	3.01	46/15	16.6/15
Energy absorbed (.J/mm^2)	4.05	75.5/15	38/15
Impact strength (J/m)	111.04	98/15	67/15
Hardness (Shore D)	88.1	4.5/20	0.5/20
Water absorption (%)	0.2003	-17.5/20	-10.08/20

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.



(a) (b)

Fig. 2.29 SEM micrographs of a) DGEBA b) DGEBA/p-ECN

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 2.11 Soxhlet extraction and swelling data

Samples	Neat Resin	p-ECN Blend 15%	o-ECN Blend 15%
Soluble matter %	4.98	3.78	4.73

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 600^0C 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

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
p-ECN	340	366	380	9.1

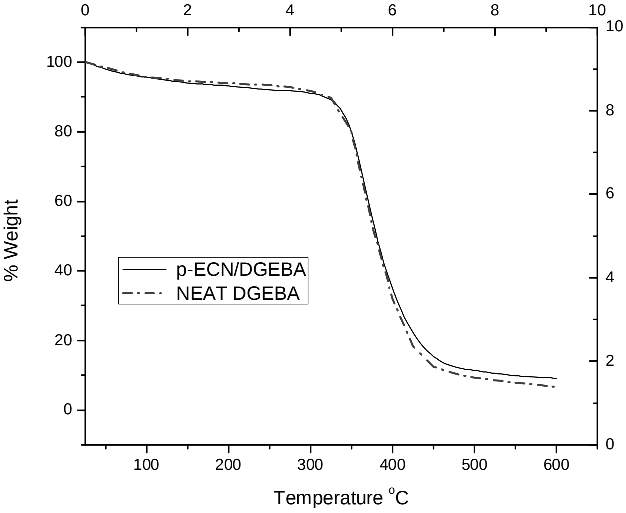


Fig.2.30 TGA curves for DGEBA and DGEBA/ECN

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 120^0C corresponding to tan δ 0.680. Incorporation of p-ECN (15 wt %) and o-ECN (15 wt %) increases the glass transition temperature to 128 ^{0}C and 126^0C 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.

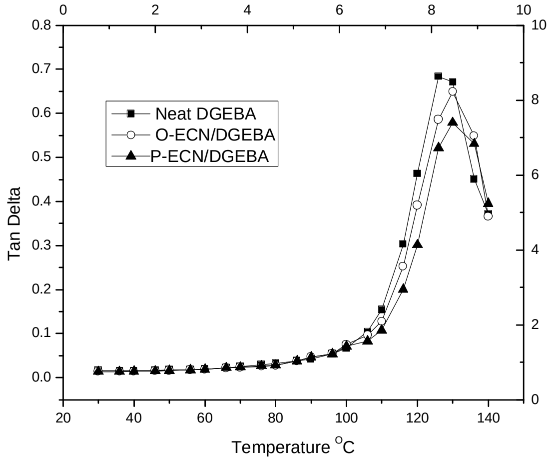


Fig.2.31 a. **Tan delta curves for DGEBA, DGEBA/p-ECN and DGEBA/o-ECN**

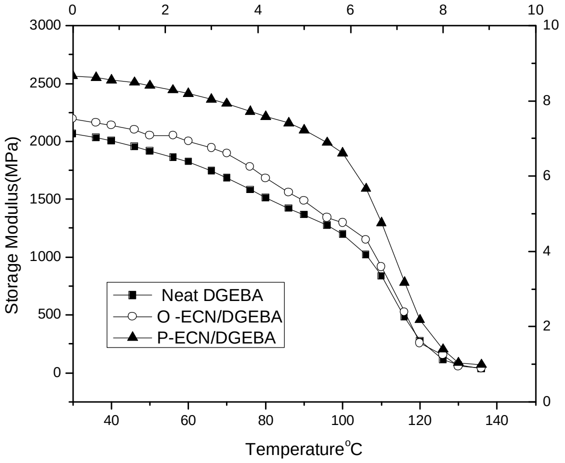


Fig.2.31 b. **Storage modulus curves for DGEBA, DGEBA/ p-EPN and DGEBA/o-ECN**

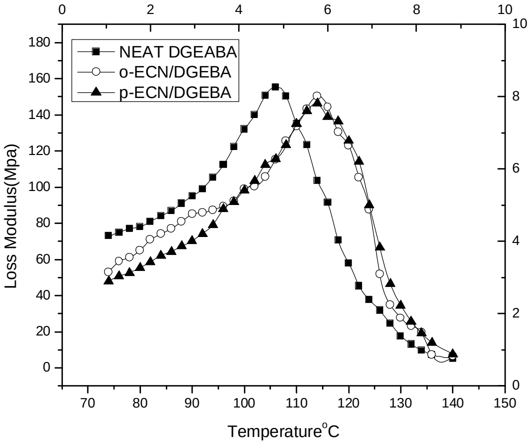


Fig. 2.31 c. Loss modulus curves for DGEBA, DGEBA/p-EPN and DGEBA/o-ECN

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 ^{0}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.

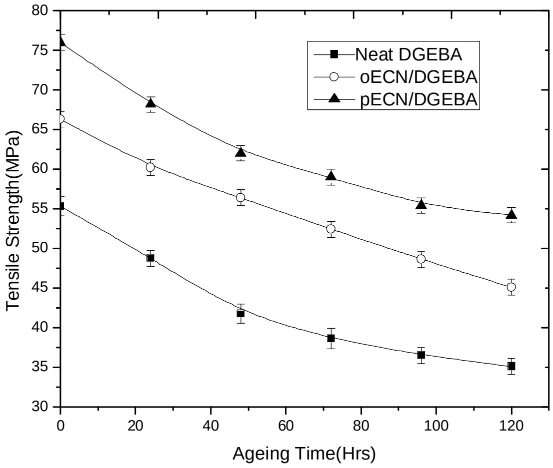


Fig. 2.32. Tensile strength of modified resin Vs ageing time

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.

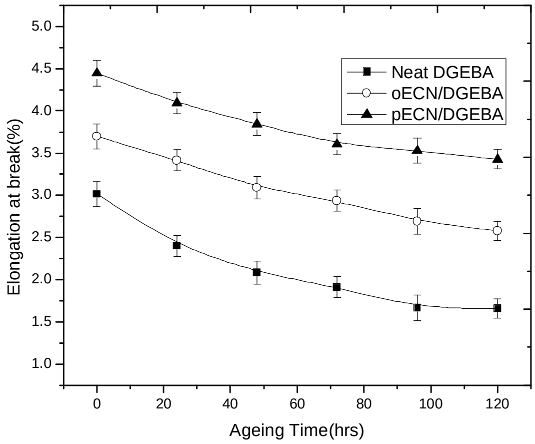


Fig. 2.33. Elongation at break of modified resin Vs ageing time

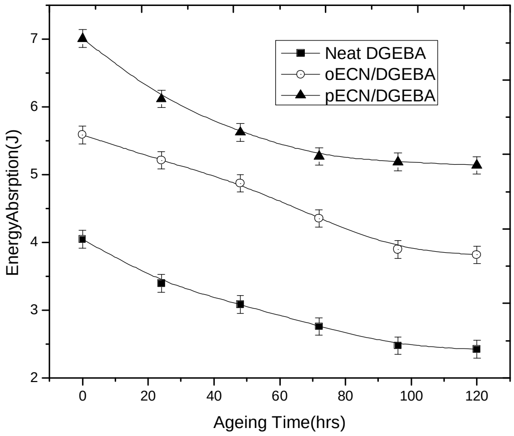


Fig. 2.34. Energy absorbed (to break) of modified resin Vs ageing time

The variation in impact strength of the modified resin during ageing is given in Fig.2.35. 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.

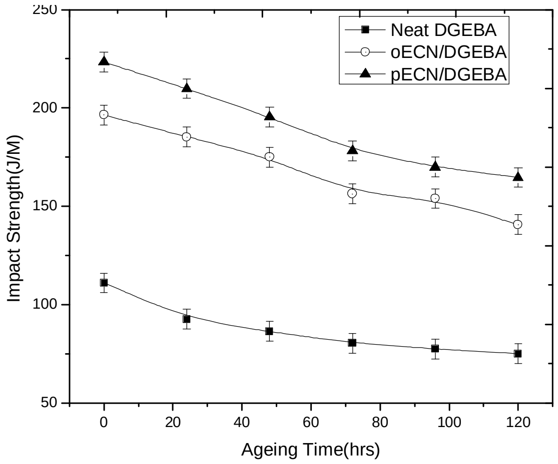


Fig. 2.35. Impact strength of modified resin Vs ageing time

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.

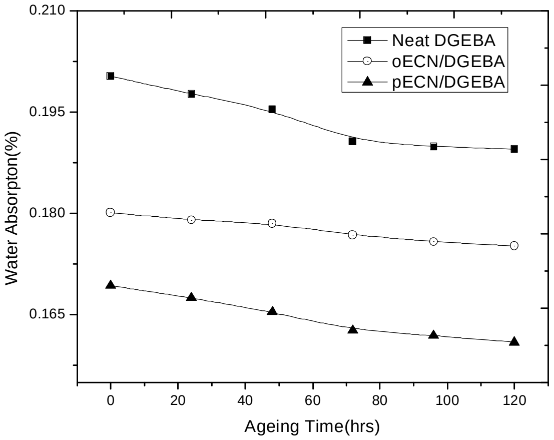


Fig. 2.36. Water absorption of modified resin Vs ageing time

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

Table 2.13. Epoxy equivalents of epoxidised cardanol at different reaction times

Epoxidised cardanol	**EC-1**	**EC-2**	**EC-3**	**EC-4**
Reaction time	1h	3h	6h	9h
Epoxy equi valent (eq/Kg)	1.88	1.98	2.15	2.157
Weight per epoxide	530.9	504.8	465.4	463.6

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), 1265.28cm^{-1}(symmetrical C-O str.) and 915.9cm^{-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

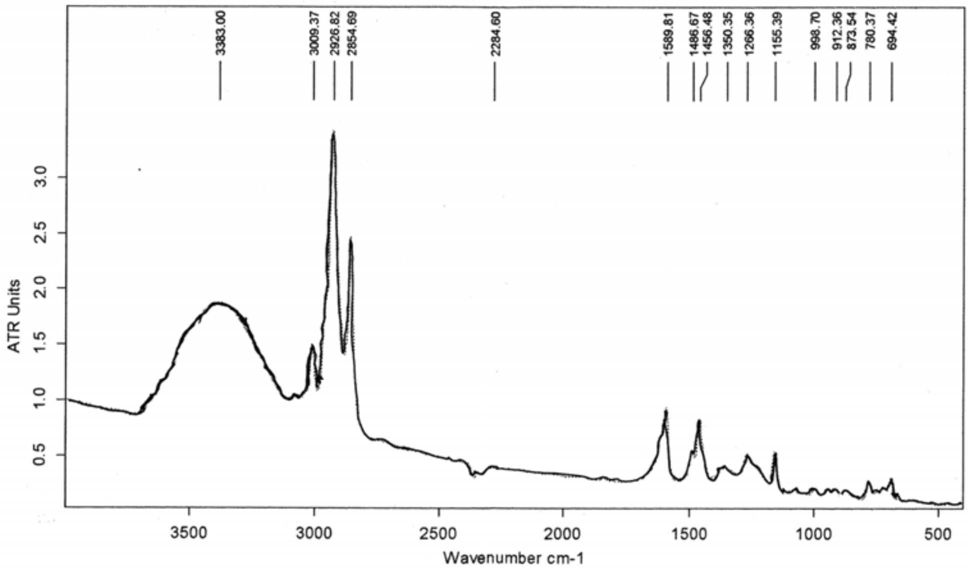


Fig.2.37a. FTIR spectrum of cardanol

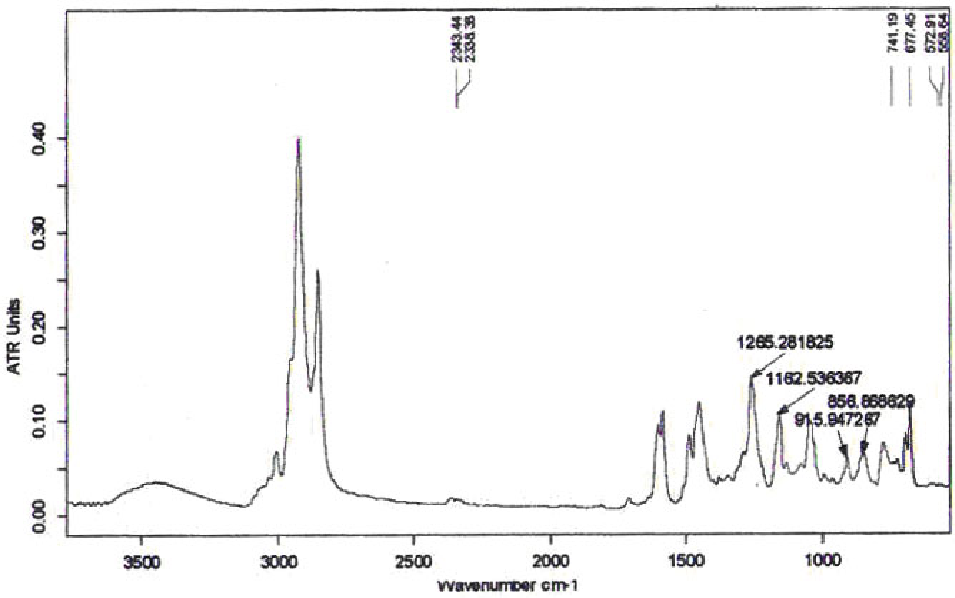


Fig.2.37b. FTIR spectrum of epoxy cardanol (EC)

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.

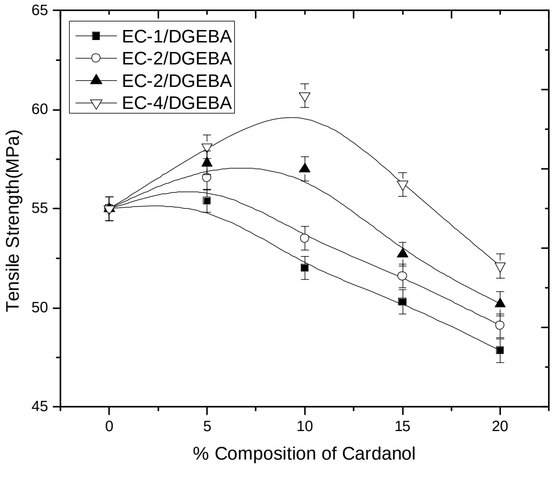


Fig. 2.38 Tensile strength of EC modified resin Vs EC concentration

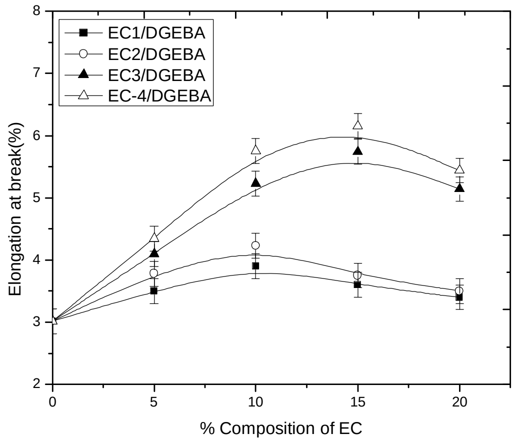


Fig. 2.39 Elongation (at break) of EC modified resin Vs EC concentration

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 un-modified 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.

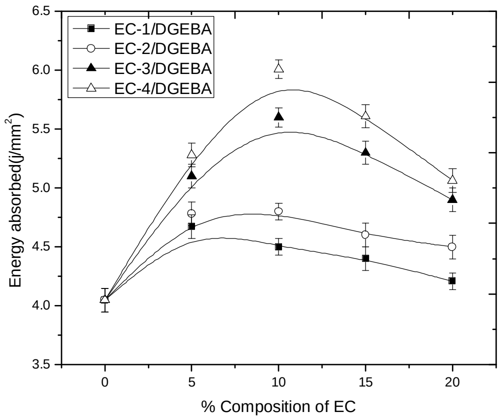


Fig. 2.40 Energy absorbed (to break) of EC modified resin Vs EC concentration

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.

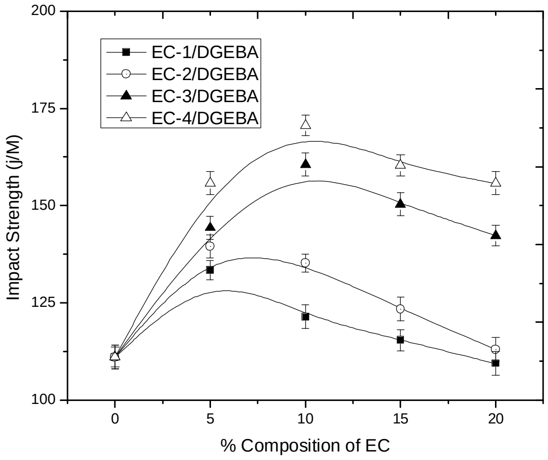


Fig. 2.41 Impact strength of EC modified resin Vs EC concentration

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.

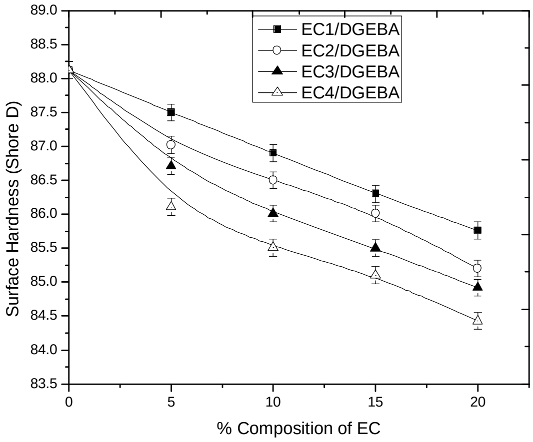


Fig. 2.42 Surface hardness of EC modified resin Vs EC concentration

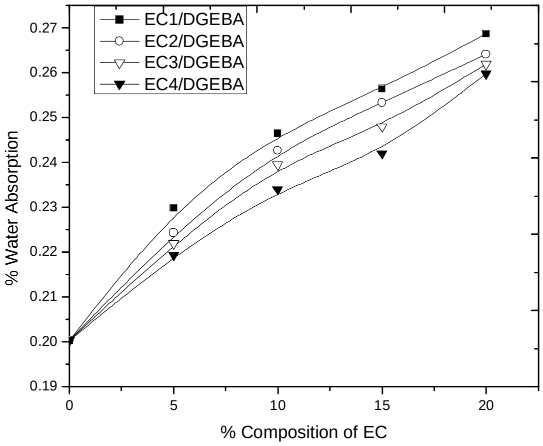
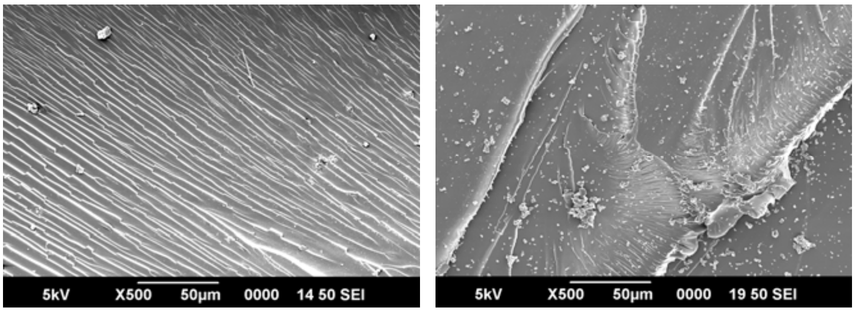


Fig. 2.43 Water absorption of EC modified resin Vs EC concentration

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.



(a) **(b)**

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

Property	% maximum improvement / % composition				
	DGEBA	EC-1	EC-2	EC-3	EC-4
Tensile strength (MPa)	55.5	0.7/5	2.8/5	4.2/5	10.38/10
Elongation at break (%)	3.01	29/10	41/10	91/15	105./15
Energy absorbed (.J/mm^2)	4.05	16.75/5	20/10	40/10	50/10
Impact strength (J/m)	111.04	9/10	25.2/5	44/10	53/10
Surface hardness. Shore D	88.1	-2.7/20	-3.3/20	-3.6/20	-4.2/20
Water absorption (%)	0.2003	34.1/20	32/20	30.9/20	29.9/20

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 600^0C compared to 6.68% by the un-modified resin.

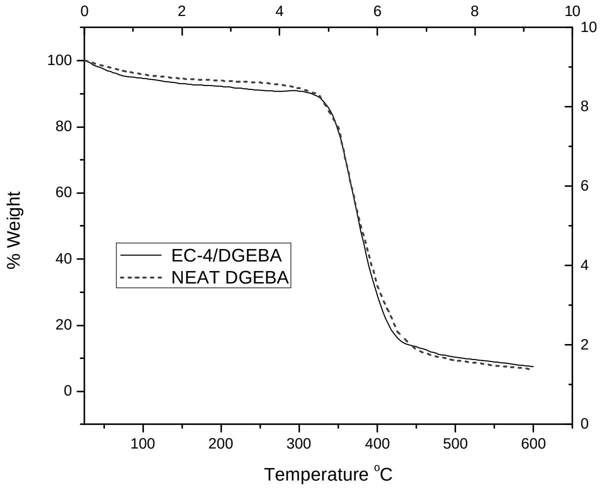


Fig.2.45 TGA curves for DGEBA and DGEBA/ECN

Table 2.15 TGA Characteristics of EC modified resin

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
EC/DGEBA	333	360	375	7.4

ii. *DMA*: Referring to tan δ curves (Fig 2.46) the peak occurs at 130 ^{0}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.

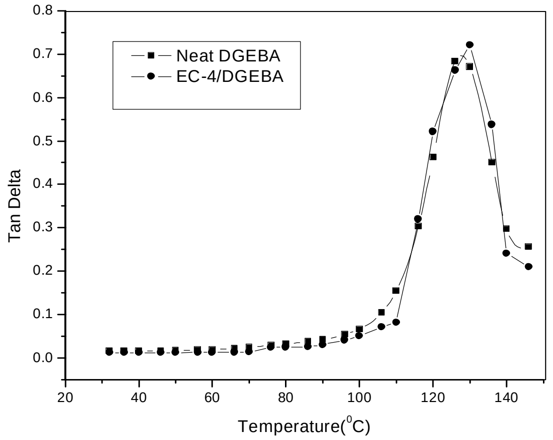


Fig.2.46. Tan δ curves for EC-modified and unmodified epoxy resins

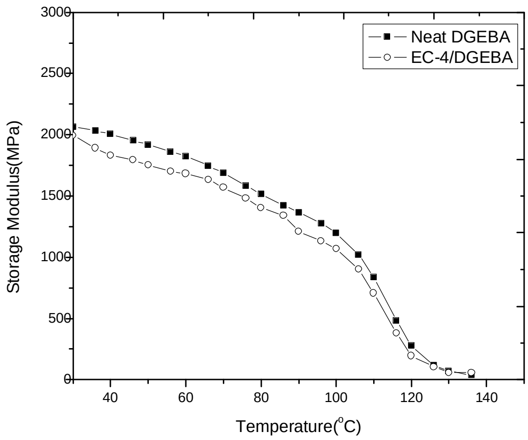


Fig.2.47. Storage modulus curves for EC-modified and unmodified epoxy resins

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 2.16 Soxhlet extraction and swelling data

Samples	DGEBA	EC-3	EC-4
Soluble matter %	4.98	4.3109	3.957

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 ^{0}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

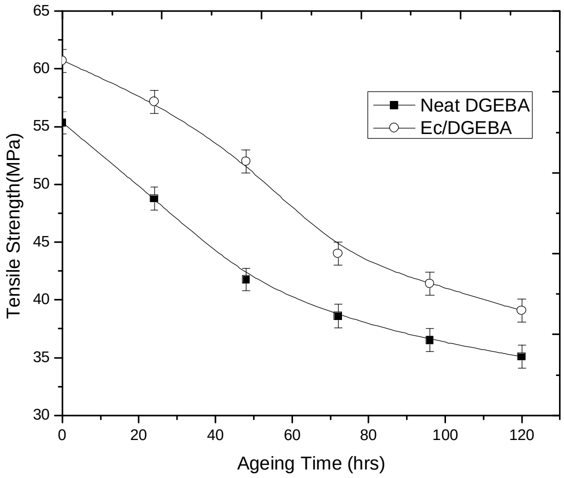


Fig. 2.48 Tensile strength of modified resin Vs ageing time

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

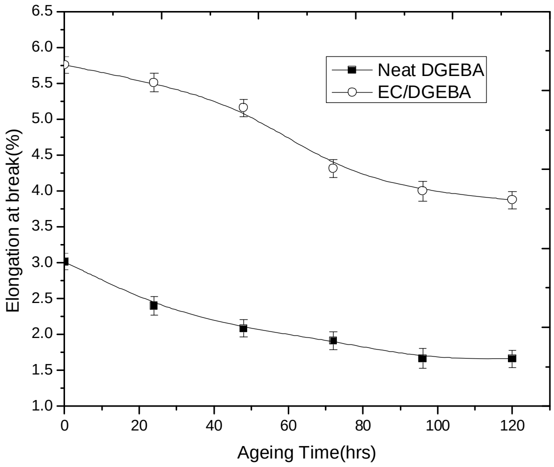


Fig. 2.49. Elongation at break of modified resin Vs ageing time

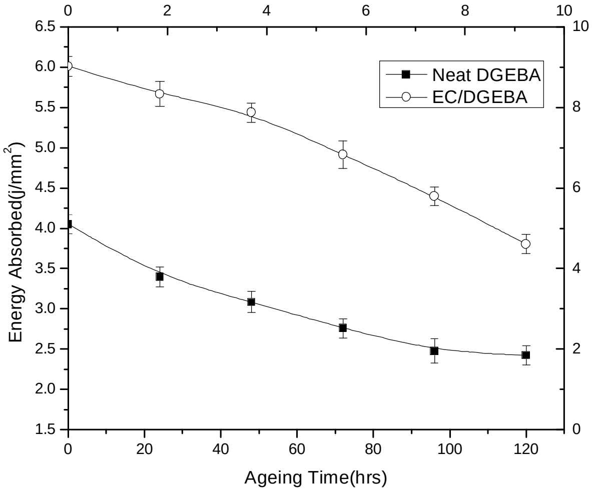


Fig. 2.50. Energy absorbed (to break) of modified resin Vs ageing time

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.

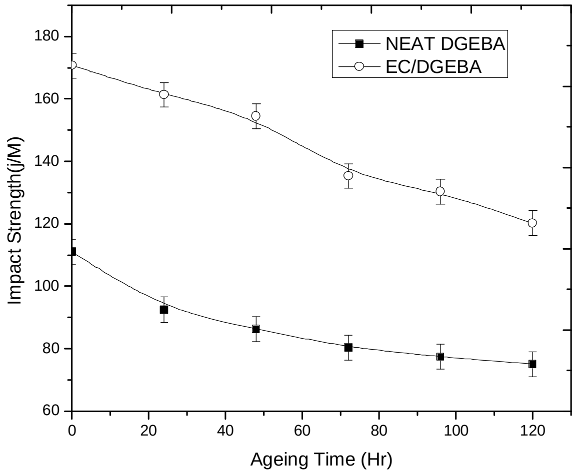


Fig2.51. Impact strength of modified resin Vs ageing time

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)

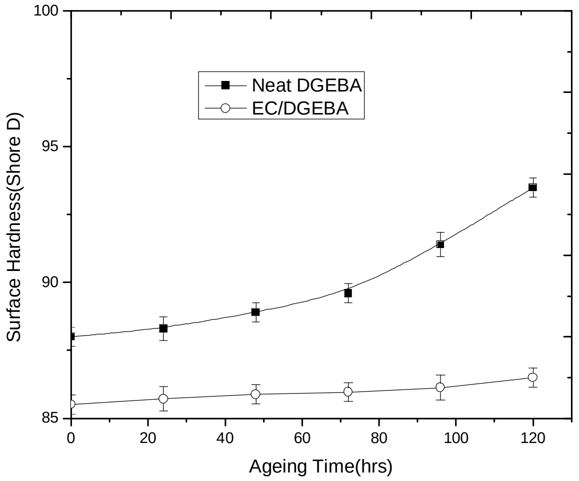


Fig. 2.52. Surface hardness of modified resin Vs ageing time

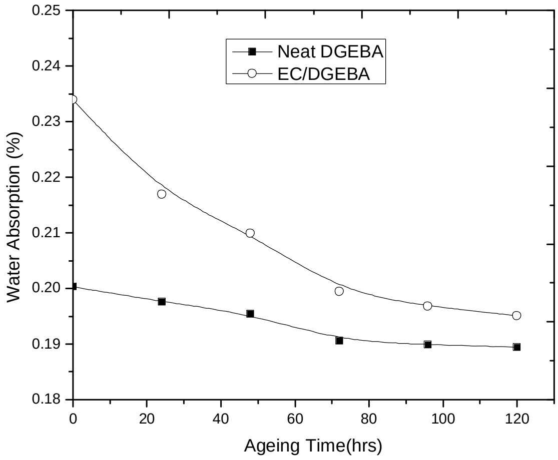


Fig. 2.53. Water absorption of modified resin Vs ageing time

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.

i Spectroscopic Studies

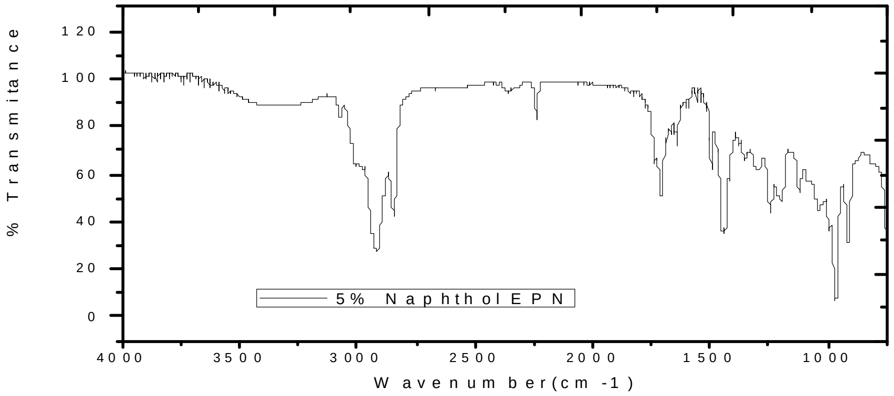


Fig.2.54 FTIR spectrum of epoxy phenol naphthol mixtures

Fig 2.54 shows FIIR spectrum of 5% naphthol EPN. The bands at 2924.37 cm^{-1} (C-H stretching of epoxide), 1265.28cm^{-1}(symmetrical C-O str.) and 915.9cm^{-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 shows in Fig 2.55. Only a slight increase in tensile strength was observed at a lower concentrations 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 becomes 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.

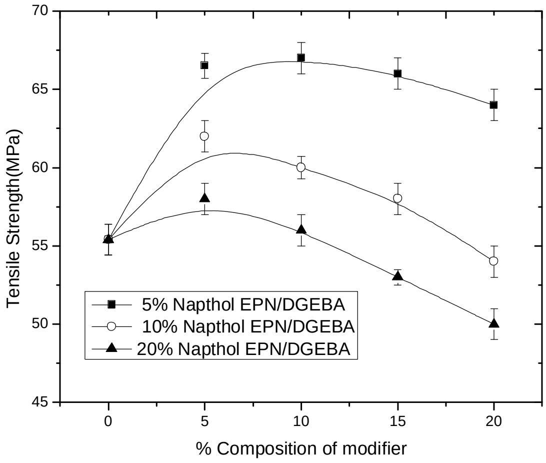


Fig. 2.55 Tensile strength of EC modified resin Vs EC concentration

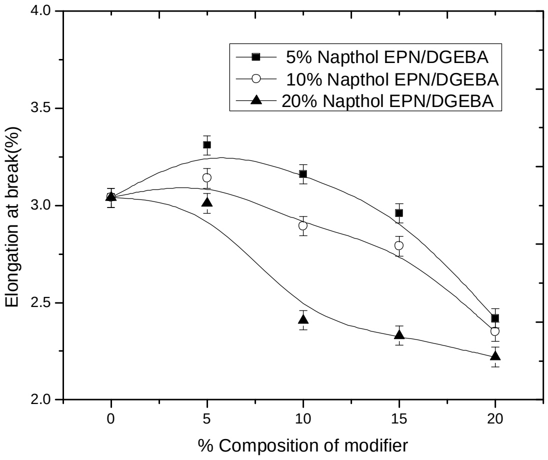


Fig. 2.56 Elongation (at break) of EC modified resin Vs EC concentration

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

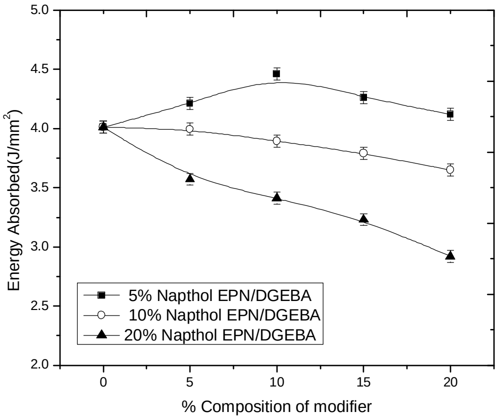


Fig. 2.57. Energy absorbed (to break) of modified resin Vs modifier concentration

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.

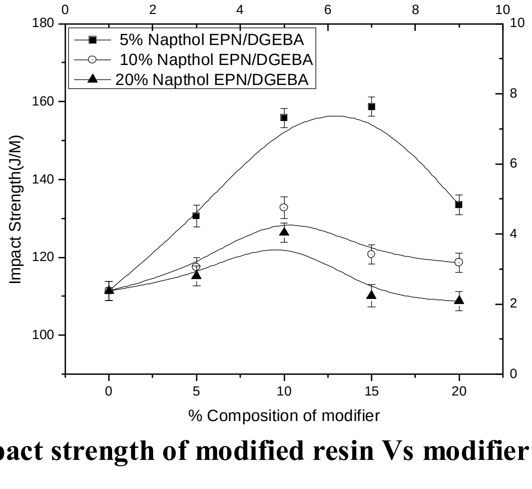


Fig. 2.58. Impact strength of modified resin Vs modifier concentration

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.

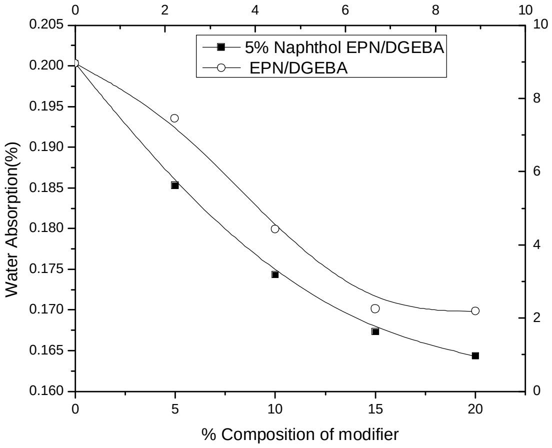


Fig. 2.59. Water absorption of modified resin Vs ageing time

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 600^0C compared to 6.7 % by the un-modified resin.

Table 2.17 Thermal properties of DGEBA/EPN naphthol blends

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
5% Naphthol EPN/DGEBA	355	370	385	10.17

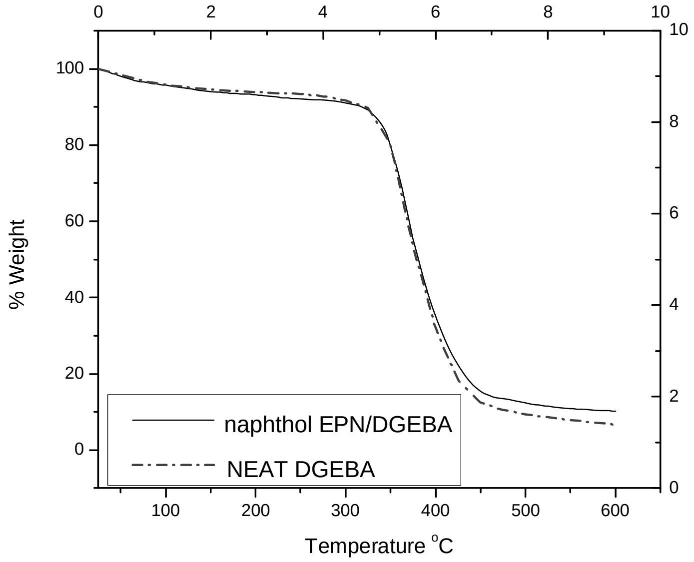
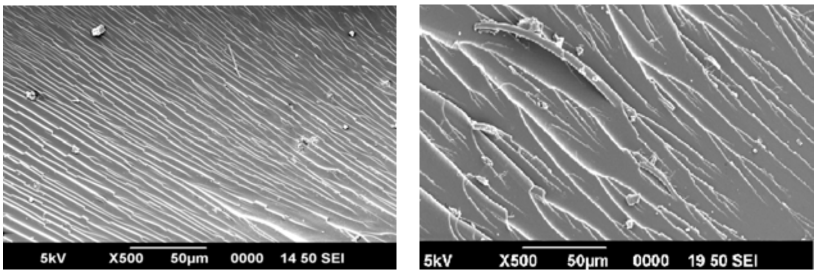


Fig.2.60 TGA curves for DGEBA and DGEBA/5% Naphthol EPN

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.



(a) (b)

Fig. 2.61 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/Naphthol EPN

2.4 Conclusions

Commercial DGEBA showed optimum mechanical properties by curing with 10wt % amine hardener and post curing at 100^0C 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

[1] J. A. Brydson, Plastic Materials, Butterworths Heinemann, Oxford, Ch.26, 667-669, (1999).

[2] Castan, Process for the Manufacture of Thermosetting Synthetic Resins by the Polymerisation of Alkylene oxide Derivatives, U.S.Patent. 2,444,333 (1948)

[3] C.P. Reghunadhan Nair , Prog. Polym. Sci. 29 ,401–498, (2004)

[4] T. Takeichi, N. Furukawa; Polym. Sci: A,5,723-751, (2012).

[5] R. W. Biernath, D. S. Soane,"Cure Kinetics of Epoxy Cresol Novolac Encapsulants for Microelectronics Packaging" Contemporary Topics in Polymer Science, J. C. Salamone and J. S. Riffle Eds., 7, 130-159 (1992)

[6] K.J. Saunders., Organic Polymer Chemistry, Chapter 16, p-380-390 Chapman and Hall, London (1976).

[7] J.F. Gabriel, Org.Coat.Plast.Chem.,43, 545(1980)

[8] K. P. Unnikrishnan and Eby Thomas Thachil,. Journal of Elastomers and Plastics, .37(4), 347-359 (2005).

[9] W. Burchard, S.Bantle and S. A. Zahir., Makromol.Chem.,182, 145 (1981)

[10] H. Berahim, H. Prabowo, Tumiran, Proceedings of the International Conference on Electrical Engineering and Informatics Institut Teknologi Bandung, Indonesia June 17-19,(2007)

[11] V. Bellenger, J. Decelle, N. Huet Composites Part B: Engineering, 36 (3),189-194(2005).

[12] G.Doyle, R.A.Pethrick, International Journal of Adhesion and Adhesives, 29(1),77-90,(2009)

[13] N.V. Datla, A. Ameli, S. Azari, M. Papini, J.K. Spelt, Engineering Fracture Mechanics, 79,61-77,(2012).

[14] F. Delor-Jestin, D. Drouin, P.-Y. Cheval, J. Lacoste Polymer Degradation and Stability, 91(6),1247-1255,(2006).

[15] H. Mokhtar, O. Sicot, J. Rousseau, Y. Aminanda, S. Aivazzadeh; Procedia Engineering, 10,2615-2620, (2011).

[16] F. Ravari, A .Omrani, A. A. Rostami, M. Ehsani ;Polymer Degradation and Stability,97(6),929-935(2012).

[17] S. Marouani, L. Curtil, P. Hamelin ;Composites Part B: Engineering, 43(4), Pages2020-2030(*2012).*

[18] Hans R Kricheldorf., Ed. Handbook of Polymer Synthesis, 1496-1498

[19] Arthur E Woodward, Atlas of Polymer Morphology, Hanser Publishers, New York, (1988)

[20] Lothar Engel, Hermann Klinglee, Gottfried W Ehrenstein and Helmut Schaper, An Atlas of Polymer Damage, Wollfe Science Books, Munich (1981)

[21] E.A. Turi, Thermal Characterisation of Polymeric Materials, Academic Press, New York (1981)

[22] T. Murayama, Dynamic Mechanical analysis of Polymer Materials., Elsevier Scientific Publishing Company, Amsterdam (1982)

[23] R. Brown., Ed. Handbook of Polymer Testing, Marcel Decker Inc., New York (1999).

[24] Mary C. Lubi and Eby Thomas Thachil. Designed Monomers and Polymers, 3(2): 123-153. (2000)

[25] Wassermann, and Dawson, C.R. Ind. Eng.Chem., 37: 396, (1945).

[26] Carraher, C.E and Sperling, l.H. Polymer applications of Renewable Resource Materials, Plenum press, NewYork. (1981).

[27] Roy, S.S Kundu, A.K. MaMaili, S.. J.Applied Polymer Sci., 36: 1283. (1988)

[28] Manjula, S. Sudha, J.D Bera, S.C. Pillai, C.K.S; J. Applied polymer Sci., 30: 1767(1985).

[29] W.F. Symes and C.R Dawson, Nature 171,841, (1953)

[30] J.A. Cornelius, Trop.Sci. 8 (2) 79 (1976)

[31] D. Narayana Murthy., Res. Ind., 13 (3), 134-136 (1968).

[32] R.M. Silverstein and F.X. Webster., Spectrometric Identification of Organic Compounds, 6th Edn. Ch. 3, p-71-143, John Wiley & Sons Inc., New York (2002).

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Chapter 3

MODIFICATION BY EPOXIDISED SILOXANES

Contents

3.1 Introduction

A siloxane is any chemical compound composed of units of the form R_2SiO, where R is a hydrogen atom or a hydrocarbon group. They belong to the wider class of organosilicon compounds. The introduction of incompatible materials such as siloxanes to epoxy resins[1-5] is attracting more and more attention because siloxanes possess many unique properties, such as low glass transition temperature, low surface tension, good flexibility, non-flammability and high resistance to thermal oxidation. In rubber modification of epoxies using silicone resins, the phase separation of the siloxane component from the epoxy matrix triggers an extrinsic toughening mechanism that effectively shields the growing crack tip, thus improving the fracture toughness [6– 8]. Incorporation of PDMS into the epoxy matrix is generally difficult because of the poor compatibility between soft segments of PDMS and polar hard segments in epoxy, which largely results from the lack of hydrogen bonding. These materials generally exhibit a high degree of phase separation resulting in poor thermo-mechanical properties and compositional heterogeneity resulting from poor segmental compatibility [9,10]. So for the incorporation of polysiloxane in epoxy matrix we have to functionalise them. One of the major processes used to functionalize polysiloxanes is hydrosilylation of polyhydridosiloxanes[11].

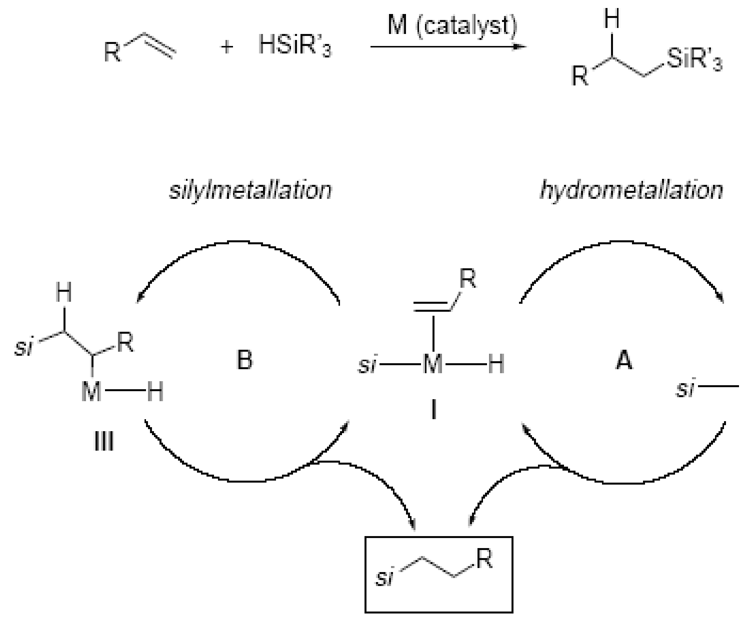
3.1.1 *Hydrosilylation*

Hydrosilanes undergo addition across the carbon-carbon multiple bonds under catalysis by transition metal complexes and the reaction is referred to as the hydrosilylation [12-15]. In this, the key step is the addition of hydridosilanes to unsaturated bonds, a topic that has been extensively reviewed [16-18]. The general sequence for hydrosilylation is as follows.

R_1, R_2 = alkyl
R_3 = $-NH_2$, $-NHR$, $-NR_2$, $-CN$, $-COOR$, $-COOH$, $-COR$, $-OR$, -epoxide...

3.1.2 Mechanism of hydrosilylation of olefins catalysed by transition-metal complexes

A transition metal complex, MLn (L=ligand), especially an electron-rich complex of a late transition metal such as Co(I), Rh(I), Ni(0), Pd(0), or Pt(0) as a pre -catalyst, activates both hydrosilanes, $HSiR_3$, and a variety of substrates, typically alkenes. A catalytic cycle is considered to involve further two steps as depicted in Scheme 1.



Scheme 1: Catalytic Cycle of Hydrosililation Mechanism

The conventional hydrosilylation of alkenes catalyzed by $H_2PtCl_6\cdot 6H_2O$/*i*PrOH (called the Speier catalyst [19]) is generally assumed to proceed by the Chalk-Harrod mechanism (Scheme 1, cycle A) [20, 21]. Oxidative addition of a hydrosilane gives a hydrido-silyl complex (**I**), which is coordinated with the substrate alkene (extremely rarely isolated at this stage). The complex **I** undergoes migratory insertion of the alkene into the M-H bond *(hydrometallation*) to give the alkyl-silyl species (**II**). Reductive elimination of the alkyl and silyl ligands from **II** forms the hydrosilylation product. The Chalk-Harrod mechanism accounts for an alkene isomerization, an H-D exchange between deuterio silanes and alkenes, as well as the observed regioselectivity always associated with the catalytic hydrosilylation. This demands an alternative mechanism which involves preferentially an alkene insertion into the M-Si bond (*silylmetallation*) by using Rh(I) or Co(III) catalyst precursor to form the β -silylalkyl-hydrido intermediate (**III**), followed by reductive elimination to complete the hydrosilylation process [22-24] (Scheme 1, Cycle B). It is worthy of note that hydrosilanes exhibit a wide spectrum of reactivities in the oxidative addition depending on the substituents on the silicon atom and the nature of the metal catalyst. Thus, Pt complexes tolerate hydrosilanes, such as $HSiClnMe_{3-n}$ (n=1~3), $HSi(OR)_3$, or $HnSiR_{4-n}$ (n=1~3; R = alkyl or Ph) in the hydrosilylation, while, Pd complexes are applicable mostly to $HSiClnR_{3-n}$(n=2, 3) and Rh complexes to preferably $HSiR_3$[15].

A large variety of catalysts are available for the synthesis of silanes and siloxanes via hydrosilylation. Although radical [24-27] and Lewis acid [28-30] induced procedures have been reported, the transition-metal-catalyzed reaction continues to play a dominant role [31-43]. Among all metal catalysts (Pd, Pt, Rh), platinum-based catalysts are the most widely used.

In this study, hydrosilylation of allyl glycidyl ether has been carried out using polydimethyl siloxane (PDMS) and a complex catalyst, platinum (0)-1, 3 -divinyl-1, 1, 3, 3-tetramethyl disiloxane. The PDMS selected are TSHF PDMS (Terminal Silyl Hydride Functional PDMS) PSHF PDMS [Poly (dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated containing 4% methylhydrosiloxane] and PSHF PDMS 50 [Poly (dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated containing 50 % methylhydrosiloxane]. The hydrosilylation reactions are shown in Scheme 2

Scheme 2: Hydrosilylation of allyl glycidyl ether by terminal silyl hydride functional PDMS(TSHF PDMS)

The strategy adopted is to mix varying amount of these functionalised siloxanes with DGEBA to modify the characteristics of the latter. Their damping, thermal, tensile and impact properties were studied.

3.2 Experimental

3.2.1 Materials

Epoxy resin GY 250(WPE 188) and amine hardener HY951 were procured from Petro Araldite Pvt. Ltd. Chennai. TSHF PDMS [Poly(dimethyl siloxane) hydride terminated] (M_W 3363,], PSHF PDMS [Poly (dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated containing 4% methylhydrosiloxane (M_W 5364)], PSHF PDMS 50 [Poly (dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated containing 50 % methylhydrosiloxane (M_W 18060), platinum(0)-1,3 -divinyl-1,1,3,3-tetramethyl disiloxane complex catalyst and allyl glycidyl ether (99% assay) were supplied by Aldrich.

3.2.2 Synthesis of terminal epoxy functional polydimethy siloxane (TEF PDMS)

TSHF PDMS was functionalised by hyrosilylation reaction using allyl glycidyl ether.

1 equivalent of PDMS was mixed with 2 equivalents of allyl glycidyl ether and stirred in a stoppered conical flask using a magnetic stirrer.

Platinum catalyst (approximately 100 ppm equivalent) was added and stirred for 20 hrs at a constant temperature of 85^0C. The crude product was cooled to room temperature, washed with methanol-water mixture to separate TEF PDMS (Terminal epoxy functional PDMS) from the unreacted allyl glycidyl ether and dried in vacuum.

3.2.3 Synthesis of pendant epoxy functional polydimethy siloxane (PEF PDMS)

PSHF PDMS was functionalised by hyrosilylation reaction using allyl glycidyl ether.

1 equivalent of PDMS was mixed with 5 equivalents of allyl glycidyl ether and stirred in a stoppered conical flask using a magnetic stirrer. Platinum catalyst (approximately 100 ppm equivalent) was added and stirred for 20 hrs at a constant temperature of 85^0C. The crude product was cooled to room temperature, washed with methanol-water mixture to separate PEF PDMS (Pendant epoxy functional PDMS) from the unreacted allyl glycidyl ether and dried in vacuum.

PSHF PDMS50 was fuctionalised by the above procedure to prepare pendant epoxy fuctional PDMS containing 50% pendant epoxies (PEF PDMS 50).

3.2.4 Characterisation methods

a) Spectroscopic studies

Fourier transform infra red (FTIR) spectra were 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 of the molecule. FTIR spectra of the samples were taken in a Bruker Tensor 27 FTIR spectrometer. NMR spectroscopy was also used for the characterization of epoxies.

b) Epoxy equivalent weight determination

Epoxy equivalent weight of the synthesised resin was determined by the method outlined in Section 2.2.2.b

3.2.5 Curing of neat resin

Epoxy resin was mixed with 10wt% hardener and stirred well to make the mixture homogeneous. The resin was degassed in vacuum, poured into Teflon moulds and allowed to cure for 24 hrs at room temperature. Post curing was done at 100^{o}C for 4 hours. 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

3.2.6 Curing of epoxy resin modified by siloxane

Epoxy resin was mixed with 2.5-10 wt % TSHF PDMS and the mixture was stirred well. 10wt % hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 100^{0}C for 4 hours.

Epoxy resin PSHF PDMS blends were also prepared by the procedure as described above. 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

3.2.7 Modification of epoxy resin with synthesized TEF PDMS

Epoxy resin was mixed with 2.5-10 wt% functionalized PDMS (TEF PDMS) and stirred well. The rest of the procedure was that given above in Section 3.2.6

3.2.8 Modification of epoxy resin with synthesized PEF PDMS

Epoxy resin was mixed with 2.5-10 wt% functionalized PDMS (PEF PDMS) and stirred well. The rest of the procedure was that given in Section 3.2.6

3.2.9 Modification of epoxy resin with synthesized PEF PDMS50

Epoxy resin was mixed with 5-20 wt% functionalized PDMS (PEF PDMS50) and stirred well. The rest of the procedure was that given in Section 3.2.6

3.2.10 Ageing studies on epoxy resin modified by epoxy functional siloxanes

Cured samples of neat epoxy resin and epoxy resins modified by TEF PDMS (5%) and PEF PDMS (5%) were prepared as described in Section 2.2.5. The samples were aged in a temperature-controlled air oven kept at 100^0C for 24,48,72,96 and 120 hours successively. The aged samples were subjected to the tests outlined in Section 2.2.2(d).

3.3 Results and discussion

3.3.1 Modification with terminal epoxy functional PDMS (TEF PDMS)

i. Epoxy equivalent weight determination

The wpe of TEF PDMS was found to be 1622.89 which is roughly half of the molecular weight of the starting material. This shows almost complete epoxidation of PDMS. This can be confirmed from spectral data also.

ii Spectral studies

The FTIR spectra of PDMS (TSHF PDMS) and functionalised PDMS (TEF PDMS) were analysed to assess the extent of hydrosilylation reaction. The peak corresponding to Si-H stretching was observed around 2150 cm^{-1} in TSHF PDMS (Fig.3.1). This Si-H stretching peak almost disappeared in the TEF PDMS spectrum (Fig3.2) indicating hydrosilylation. However the residual peak intensities in the fuctionalised samples indicate that the reaction is not 100% complete.

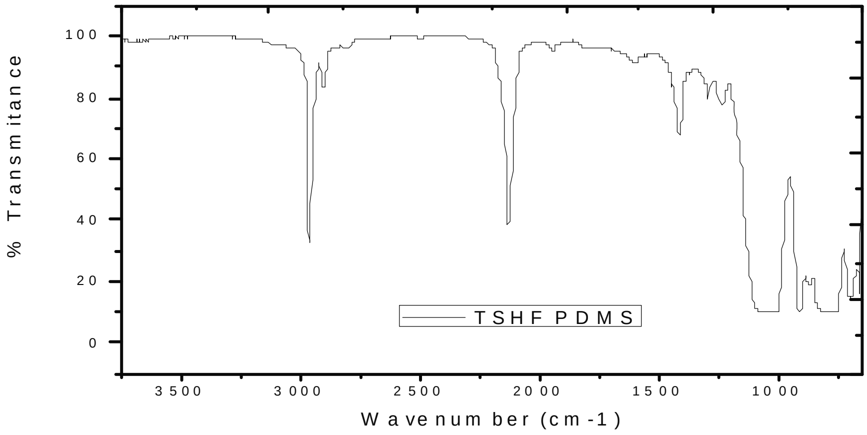


Fig. 3.1 FTIR spectrum of TSHF PDMS (Terminal silyl hydride functional PDMS)

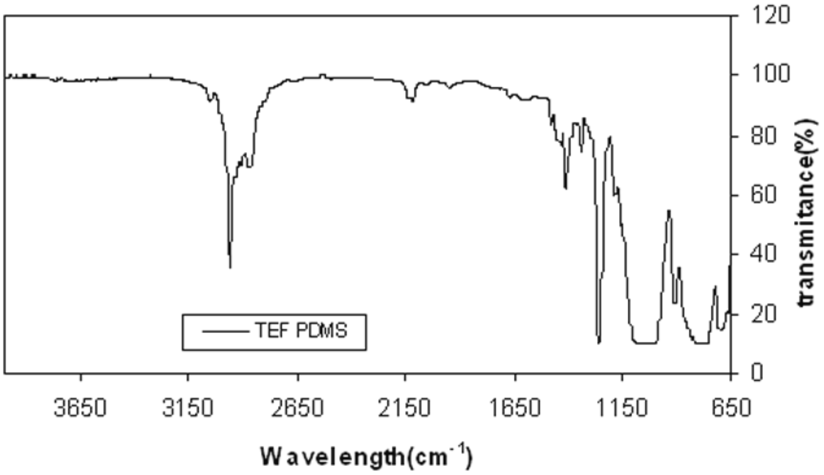


Fig 3.2 FTIR spectrum of TEF PDMS (Terminal epoxy functional PDMS)

The The ^{1}H NMR spectra of TSHF PDMS and TEF PDMS are shown in Fig.3.3 and 3.4. The Si – H resonance at δˆ 4:7 ppm in TSHF PDMS is almost absent in the spectrum of TEF PDMS. In addition, the peaks at δ 0.5; 1.6 and 3.4 ppm are the resonance peaks of the silylpropyl group, while those at δ 2.5; 2.7 and 3.1 ppm represent the resonance peaks of the epoxide group. These results clearly indicate that the hydrosilyation was successful.

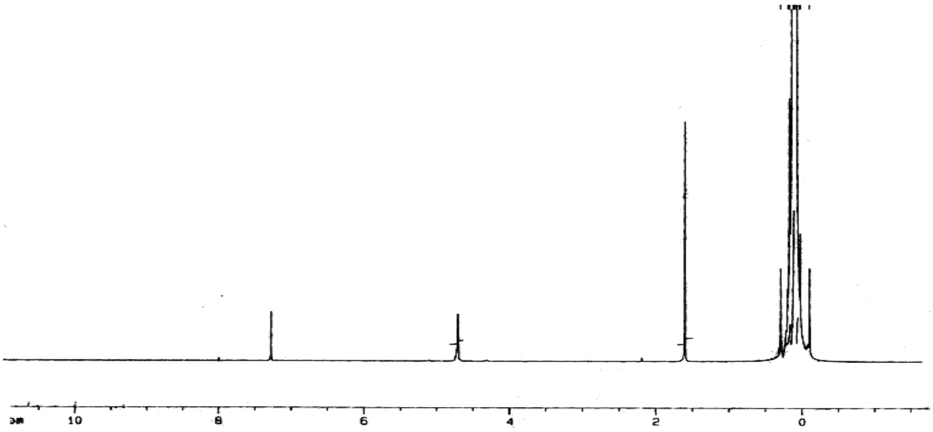


Fig.3.3 NMR spectrum of TSHF PDMS (Terminal silyl hydride functional PDMS)

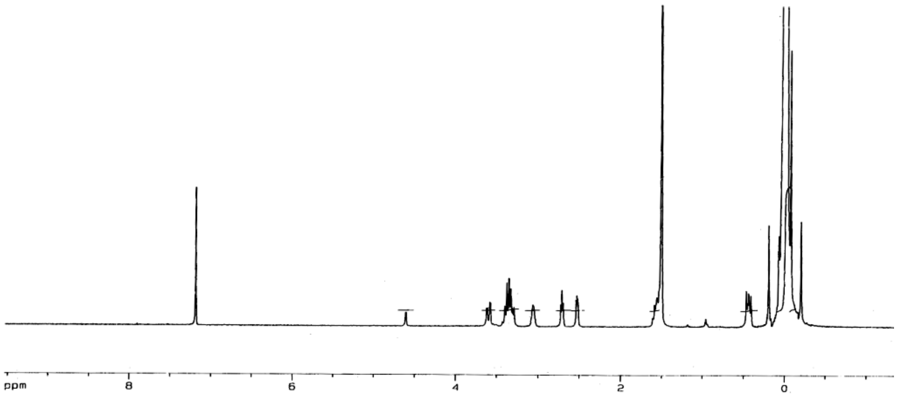


Fig.3.4 NMR spectrum of TEF PDMS (Terminal epoxy functional PDMS)

iii Thermal studies

TGA: The thermal stability of the cured blends was investigated by TGA. Comparative values of the onset temperature, temperature at maximum rate and temperature of half loss and residue (%) on using TSHF PDMS and TEF PDMS for modification along with corresponding values for the neat resin are given in Table 3.1. The thermal properties of cured blends having different concentrations of functionalised PDMS are given in Table 3.2 Functionalised PDMS/DGEBA blends have marginally better thermal stability.

The thermograms show that there is only one decomposition stage in the heating process. The siloxane segments improve thermal stability due to strong -Si-O-Si- linkage and better heat dissipation by the siloxane chains, thus reduces the temperature at the epoxy networks. The thermal stability and the residual weight are improved when a greater amount of siloxane segments are incorporated into the cured epoxy networks.

Table 3.1 TGA characteristics of blends of DGEBA, PDMS and functionalised PDMS

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343.	364	378	6.68
5% TSHF PDMS/ DGEBA	345	366|	379	8.89
5% TEF PDMS/ DGEBA	349	372	385	9.96

Table 3.2 TGA characteristics of blends having different concentrations of functionalised PDMS

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
5% TEF PDMS/ DGEBA	349	372	385	9.96
10% TEF PDMS/ DGEBA	353	376	389	11.55

iv Dynamic mechanical analysis

The storage modulus values of blends containing the TEF PDMS and neat DGEBA are shown in Fig.3.5. The storage modulus decreases with increase in temperature. At room temperature neat epoxy showed a higher value compared to the blends. The decrease in the storage modulus for blend is due to the reduced crosslink density and plasticization effect of siloxane in the epoxy matrix. The decrease in Tg of epoxy rich phase by addition of siloxane is due to the decrease in cross-link density of the cured blends.

The tan δ (loss factor) values are shown in Fig.3.6. 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_{max}) becomes lower as the distance between the crosslink decreases [6]. The tan δ_{max} for neat DGEBA increases on blending with siloxane indicating reduced crosslink density.

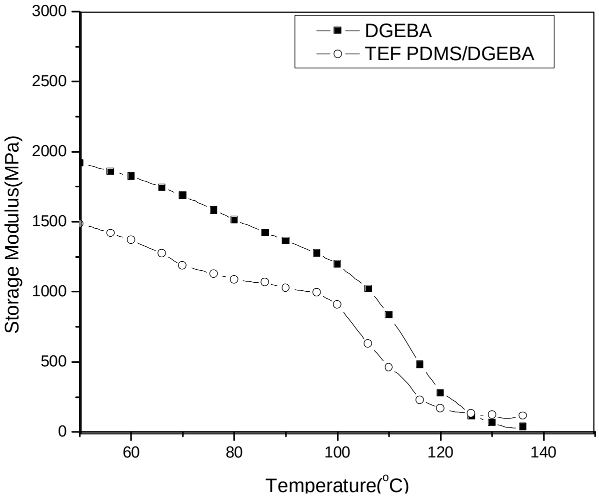


Fig. 3.5 Storage modulus of (a) DGEBA (b) TEF PDMS/DGEBA

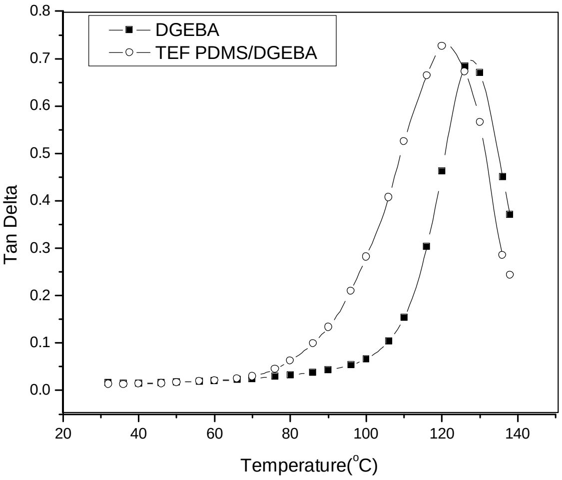


Fig.3.6 Tan δ relaxations of (a) DGEBA (b) TEF PDMS/ DGEBA

The glass transition temperature T_g corresponding to tan δ peak of neat DGEBA decreases when functionalized siloxanes are incorporated. The lowering of T_g is due to the flexible siloxane segments in the co- polymer.

v Mechanical properties

The impact strength increases with increase in concentration as shown in Fig.3.7. The increase in impact strength is due to the energy dissipation by the soft siloxane segments during the propagation of the fracture.

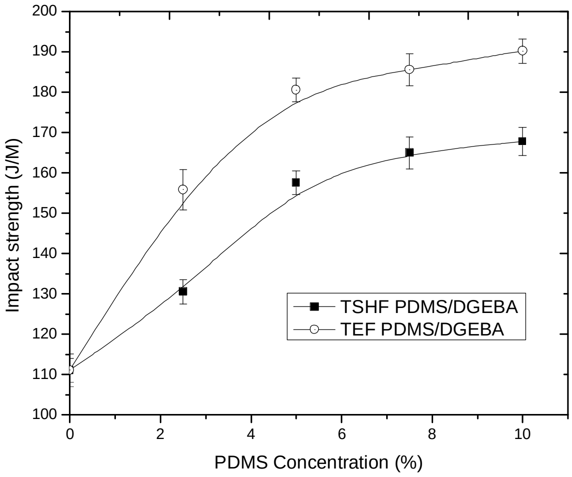


Fig. 3.7 Impact strength of modified resin Vs PDMS concentration

Tensile strength decreases with increase in concentration of PDMS (Fig. 3.8). This is due to the presence of flexible siloxane segments in the cross linked networks of the epoxy resin blend. The decrease in tensile strength is less pronounced in the case of TEF PDMS/ epoxy blends due hydrosilylation which enhances the compatibility with the neat resin.

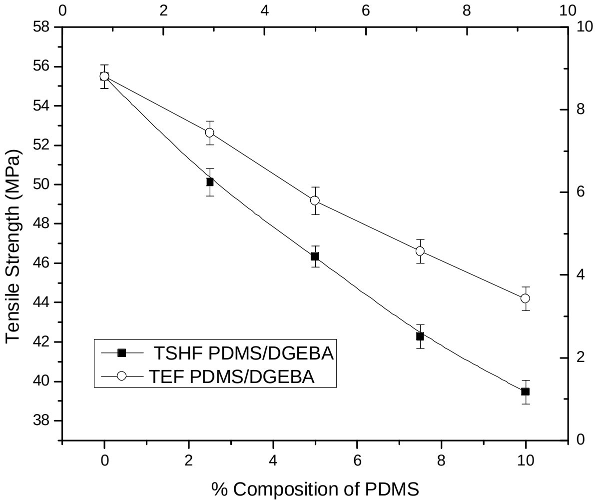


Fig.3.8 Tensile strength of modified resin Vs PDMS concentration

Fig.3.9 shows the variation of modulus with concentration of PDMS. The modulus decreases with increase in concentration of PDMS due to the presence of the soft segments of siloxane. The decrease in modulus is marginal in the case of functionalised siloxane(TEF PDMS) epoxy blends due to the presence of epoxy group which can participate in curing reaction.

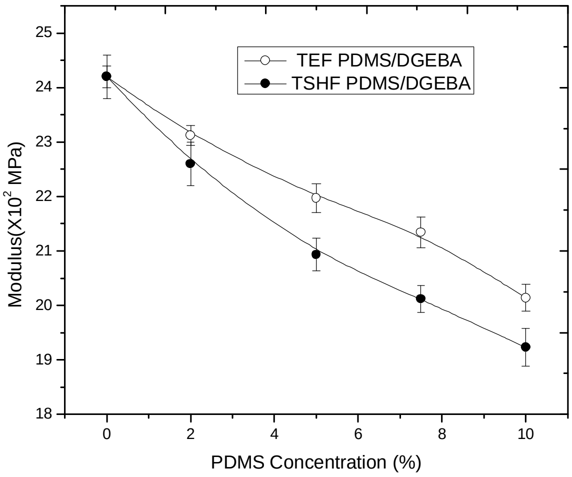


Fig.3.9 Modulus of modified resin Vs PDMS concentration

The variation of energy absorption with PDMS concentration is shown in Fig. 3.10. At 5% PDMS concentration, the energy absorption of the blend is at a maximum. The increase is due to greater energy dissipation by the soft siloxane segments. Energy absorption decreases due to lack of compatibilisation at higher concentrations of PDMS. The increase in energy absorption of functionalised PDMS (TEF PDMS) is due to compatibilisation resulting from functionalisation.

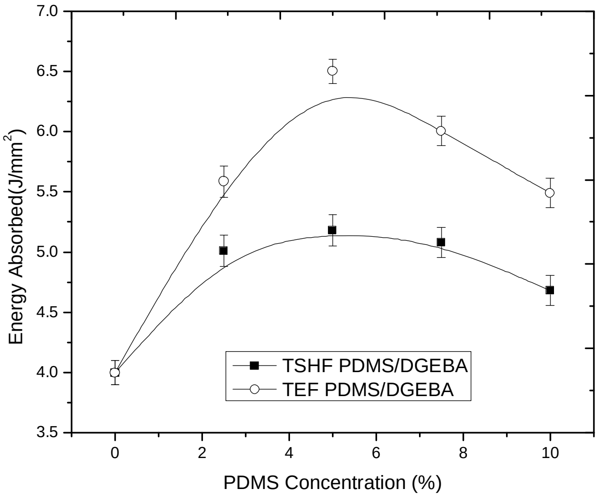


Fig. 3.10 Energy absorbed of modified resin Vs PDMS concentration

At 5% PDMS concentration, the elongation at break of the blend (Fig. 3.11) is at maximum. The increase is due to the presence of flexible siloxane segments. Elongation decreases due to lack of compatibilisation at higher concentration of PDMS.

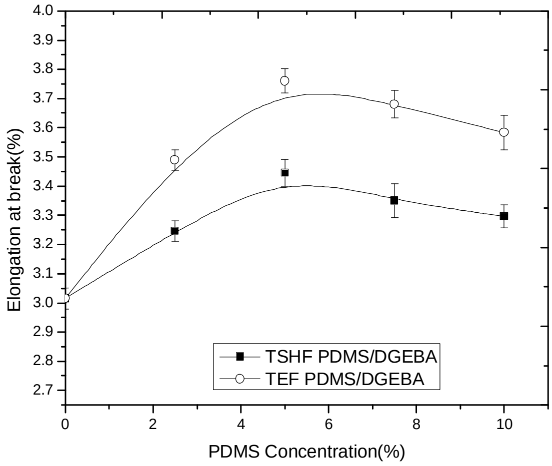


Fig.3.11 Elongation at break of modified resin Vs PDMS concentration

Vi Water absorption

The percentage water absorption of the various PDMS/DGEBA blends is given in Fig.3.12. Siloxanes lowered the water absorption of epoxy resin due to the hydrophobic nature of silicon molecule and its surface enrichment character thereby exhibiting lower permeability towards water molecules. The functionalised PDMS blend shows increased water resistance.

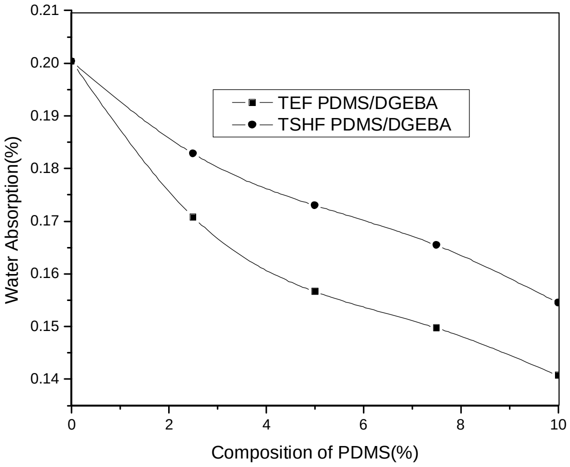
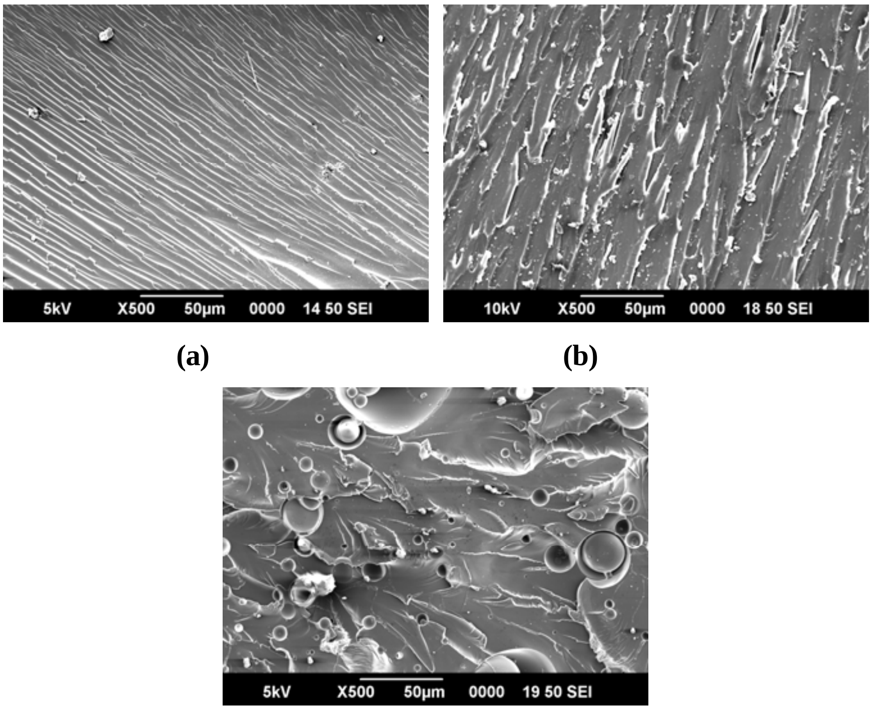


Fig. 3.12 Water absorption versus concentration of PDMS

vii Morphological studies

SEM micrograph of the unmodified epoxy resin and modified epoxy resin are given in Fig.3.13. Fracture SEM micrograph of the unmodified epoxy resin (Fig. 3.13 a) paths are mostly straight and constitute failure bands. It is a typical case of brittle fracture. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure in the case of terminal silyl hydride functional PDMS (TSHF PDMS/DGEBA) modified epoxy resin (Fig.3. 13 b). The fracture surface shows furrows and cavitation in the case of terminal epoxy functional PDMS (TEF PDMS/DGEBA) modified epoxy resin. (Fig.3.13 c).



(a) (b)

(c)

Fig 3.13 Scanning electron micrographs of the fracture surface of a) Neat DGEBA (b) TSHS-PDMS/DGEBA (c) TEF-PDMS/DGEBA

The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. The rubber particles dissipate the bulk strain energy by cavitation leading to reduction of yield stress of the blend. As a result, shear band formation is enhanced by the voids in the matrix caused by cavitated rubber particles. The superior energy absorption characteristics of the TEF PDMS modified epoxy are evident from the comparison of micrographs.

3.3.2 Modification with pendant functional PDMS

i Weight per epoxy (WPE) determination

The WPE of PEF PDMS was found to be 1274.31 which is roughly one by fifth of the molecular weight of the starting material. This indicates that 4 to 5 epoxy groups are introduced into PSHF PDMS. This can be confirmed from spectral data also.

ii Spectral studies

The FTIR spectra of unmodified PDMS (PSHF PDMS) and functionalised PDMS (PEF PDMS) were analysed to assess the extent of hydrosilylation reaction. The peak corresponding to Si-H stretching was observed around 2150 cm^{-1} in PSHF PDMS (Fig.3.14). This Si-H stretching peak almost disappeared in the PEF PDMS spectrum (Fig.3.15) indicating hydrosilylation. However the residual peak intensities in the fuctionalised samples indicate that the reaction is not 100% complete.

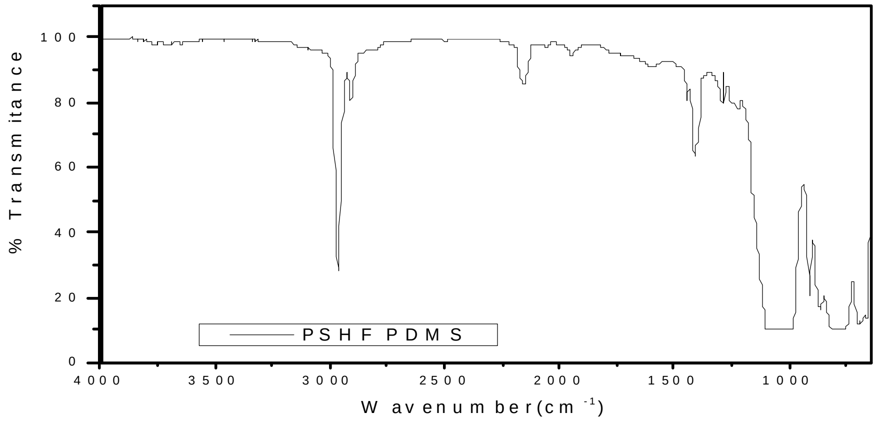


Fig.3.14 FTIR spectrum of PSHF PDMS (pendant silyl hydride functional PDMS)

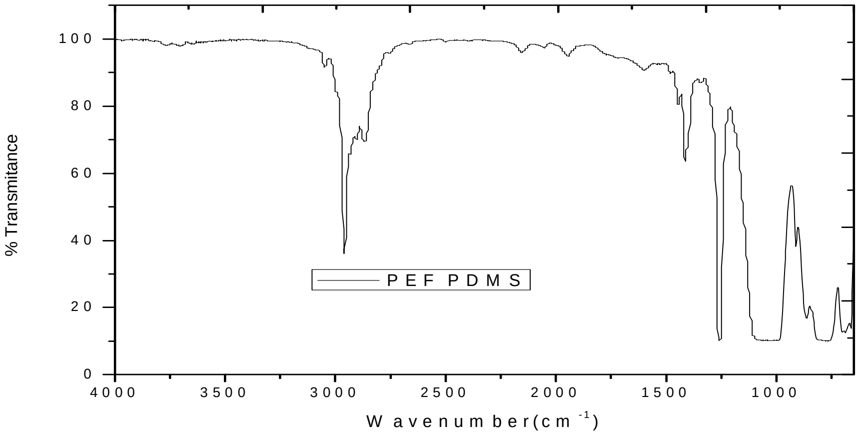


Fig.3.15 FTIR spectrum of PEF PDMS (Pendant epoxy functional PDMS)

The The ^{1}H NMR spectrum of PSHF PDMS and PEF PDMS are shown in Fig.3.16 and Fig.3.17. The Si – H resonance at δˆ 4:7 ppm in PSHF PDMS is almost absent in the spectrum of PEF PDMS. In addition, the peaks at δ ˆ 0.4; 1.5 and 3.4 ppm are the resonance peaks of the silylpropyl group, while those at δ ˆ 2.5; 2.7 and 3.1 ppm represent the resonance peaks of the epoxide group. These results clearly indicate that the hydrosilyation was successful.

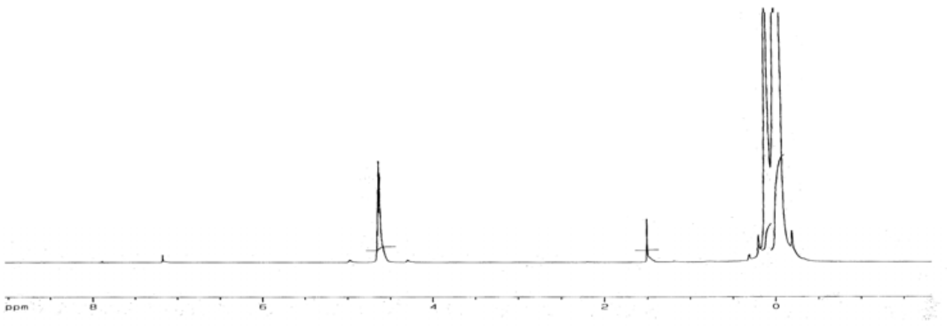


Fig.3.16 NMR spectrum of PSHF PDMS (pendant silyl hydride functional PDMS)

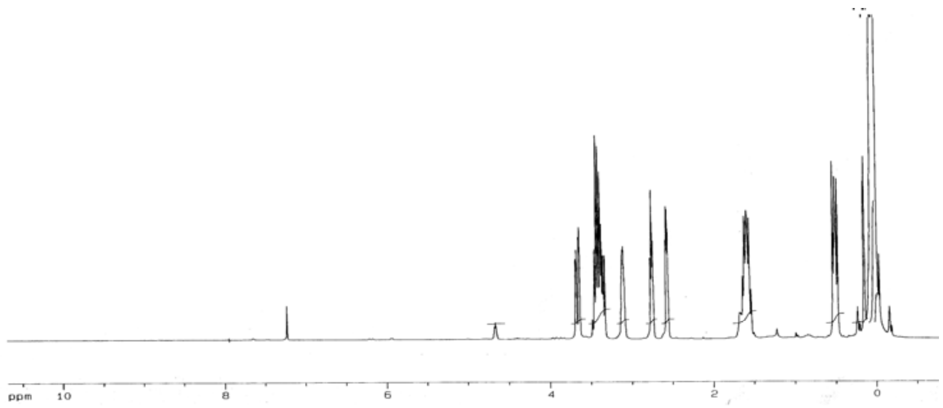


Fig.3.17 NMR spectrum of PEF PDMS (pendant epoxy functional PDMS)

iii Thermal studies

The thermal stability of the cured neat DGEBA and blends were investigated by TGA. Comparative values of the onset temperature, temperature at maximum rate and temperature of half loss and residue (%) on using PSHF PDMS and PEF PDMS for modification along with corresponding values for the neat resin are given in Table 3.3**.** The thermal properties of cured blends having different concentrations of functionalised

PDMS are given in Table 3.4. Functionalised PDMS/DGEBA blends have marginally better thermal stability.

Table 3.3 TGA characteristics of blends of DGEBA, PSHF PDMS and PEF PDMS

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364.65	378.76	6.68
5%PSHF PDMS / DGEBA	345	366|	380	8.98
5% PEF PDMS / DGEBA	351	375	387	10.01

Table 3.4 TGA characteristics of blends having different concentrations of PEF PDMS

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
2.5% PEF PDMS / DGEBA	343.55	365.21	386.22	7.65
5% PEF PDMS / DGEBA	351	375	387	10.01
7.5% PEF PDMS / DGEBA	353.43	375.35	388.63	10.5
10% PEF PDMS / DGEBA	355.46	378.18	394.43	11.93

The siloxane segments improve thermal stability possibly due to better heat dissipation by the siloxane chains, thus reducing the temperature at the epoxy networks. The thermal stability and the residual weight are improved when greater amounts of siloxane segments are incorporated into the cured epoxy networks.

iv Dynamic mechanical analysis

The storage modulus values of blends containing the PEF PDMS and neat DGEBA are shown in Fig.3.18. The storage modulus decreases with increase in temperature. At room temperature neat epoxy showed a higher value compared to the blends. The decrease in the storage modulus for blend is due to the reduced crosslink density and plasticization effect of siloxane in the epoxy matrix.

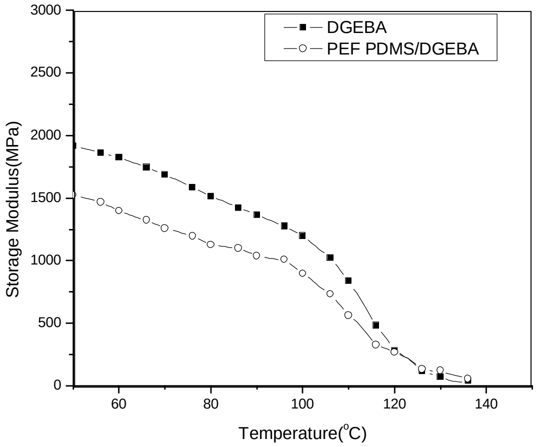


Fig.3.18 Storage modulus of (a) DGEBA (b) PEF PDMS/ DGEBA

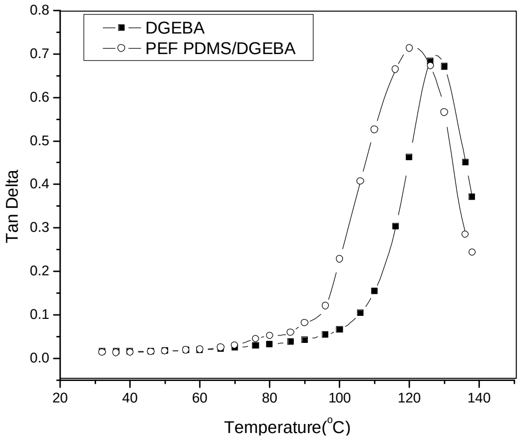


Fig 3.19 Tan δ relaxations of (a) DGEBA (bPEF PDMS/ DGEBA

The tan δ (loss factor) values are shown in Fig.3.19. 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_{max}) becomes lower as the distance between the crosslink decreases. The tan δ_{max} for neat DGEBA increases on blending with siloxane indicating reduced crosslink density. The glass transition temperature T_g corresponding to tan δ peak of neat DGEBA decreases when functionalized siloxanes are incorporated. The lowering of T_g is due to the flexible siloxane segments in the co- polymer.

v Mechanical properties

Fig.3.20 shows the variation of impact strength with the addition of siloxanes**.** The impact strength increases with increase in concentration of PDMS. The increase in impact strength is due to the energy dissipation by the soft siloxane segments occurring during the propagation of the fracture.

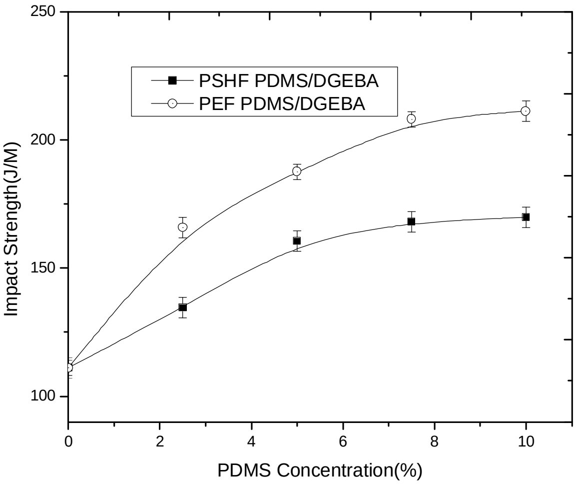


Fig. 3.20 Impact strength of modified resin Vs PDMS concentration

Tensile strength decreases with increase in concentration of PDMS (Fig.3.21). This is due to the presence of flexible siloxane segments in the cross linked networks of the epoxy resin blend. The decrease in tensile strength is less pronounced in the case of PEF PDMS/ epoxy blends due hydrosilylation which enhances the compatibility with the neat resin

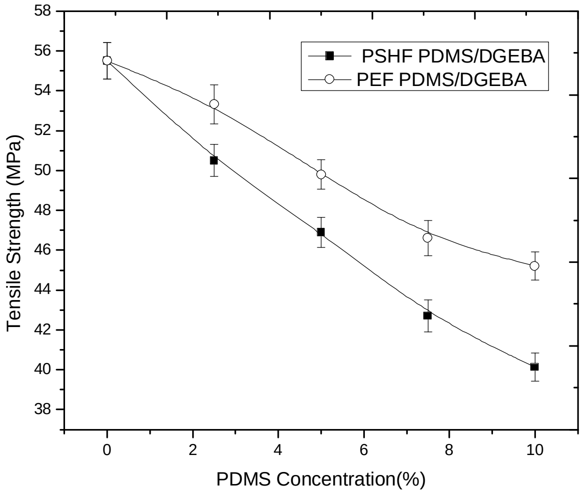


Fig.3.21 Tensile strength of modified resin Vs PDMS concentration

Fig.3.22 shows the variation of modulus with concentration of PDMS. The modulus decreases with increase in concentration of PDMS due to the presence of the soft segments of siloxane. The decrease in modulus is marginal in the case of functionalised siloxane epoxy blends due to hydrosilylation which enhances the compatibility with the neat resin

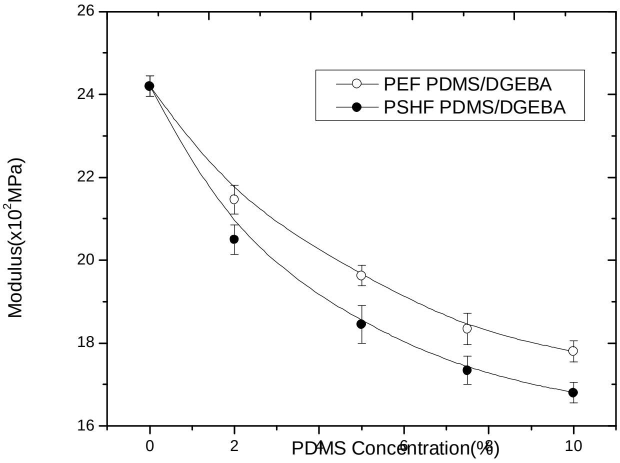


Fig.3.22 Modulus of modified resin Vs PDMS concentration

The variation of energy absorption with PDMS concentration is shown in Fig. 3.23. At 5% PDMS concentration, the energy absorption of the blend is at a maximum. The increase is due to greater energy dissipation by the soft siloxane segments. Energy absorption decreases due to lack of compatibilisation at higher concentrations of PDMS. The increase in energy absorption of functionalised PDMS is due to better compatibilisation resulting from functionalisation.

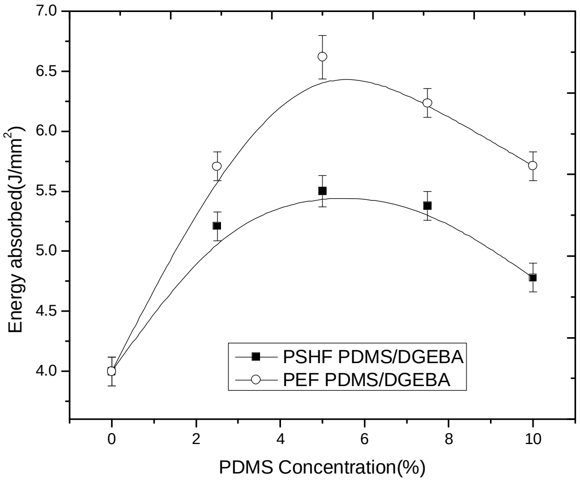


Fig.3.23 Energy absorbed of modified resin Vs PDMS concentration

At 5% PDMS concentration, the elongation at break of the blend (Fig. 3.24) is at maximum. The increase is due to the presence of flexible siloxane segments. Elongation decreases due to lack of compatibilisation at higher concentration of PDMS.

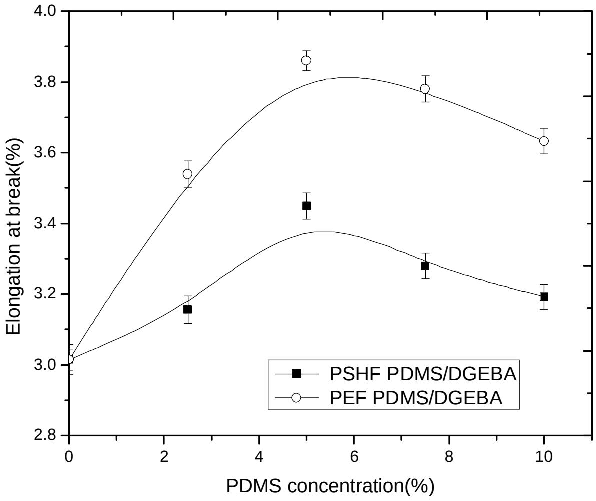


Fig.3.24 Elongation at break of modified resin Vs PDMS concentration

vi Water absorption

The percentage water absorption of the various PDMS/DGEBA blends is given in Fig.3.25. Siloxanes lowered the water absorption of epoxy resin due to the hydrophobic nature of silicon molecule and its surface enrichment character thereby exhibiting lower permeability towards water molecules. The functionalised PDMS blend shows maximum increase in water resistance.

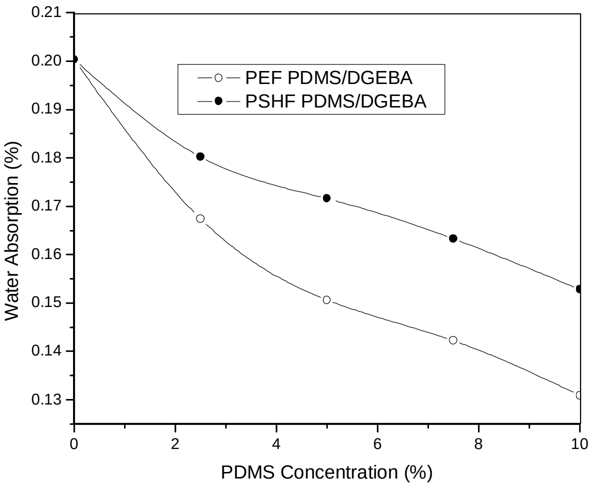


Fig.3.25 Water absorption versus concentration of PDMS

vii Morphological studies

SEM micrograph of the unmodified epoxy resin and modified epoxy resin are given in Fig.3.26 . Fracture SEM micrograph of the unmodified epoxy resin (Fig. 3.26 a) shows that paths are mostly straight and constitute failure bands. It is a typical case of brittle fracture. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure in the case of terminal silyl hydride functional PDMS (PSHF PDMS/DGEBA) modified epoxy resin (Fig. 3.26 b). The fracture surface shows furrows and cavitations in the case of terminal epoxy functional PDMS (PEF PDMS/DGEBA) modified epoxy resin. (Fig.3.26 c). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. The rubber particles dissipate the bulk strain energy by cavitation leading to reduction of yield stress of the blend. As a result, shear band formation is enhanced by the voids in the matrix caused by cavitated rubber particles. The superior energy absorption characteristics of the PEF PDMS modified epoxy are evident from a comparison of the micrographs.

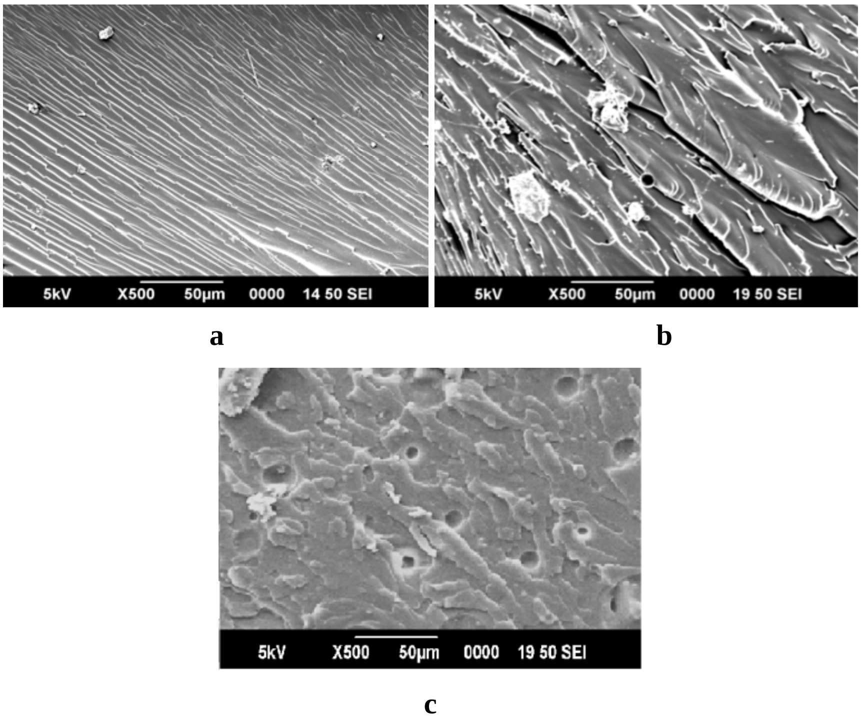


Fig 3.26 Scanning electron micrographs of the fracture surface of a) Neat DGEBA (b) PSHS-PDMS/DGEBA (c) PEF-PDMS/DGEBA

3.3.3 Modification with pendant functional PDMS(50%)

i. Epoxy equivalent weight determination

The wpe of PEF PDMS was found to be 602.06 which is roughly 1/30 th of the molecular weight of the starting material. This points to incomplete epoxidation of PDMS. This can be confirmed from spectral data.

ii Spectral studies

The FTIR spectra of unmodified PDMS (PSHF PDMS 50) and functionalised PDMS (PEF PDMS 50) were analysed to assess the extent of hydrosilylation reaction. The peak corresponding to Si-H stretching was observed around 2150 cm^{-1} in PSHF PDMS (Fig.3.27). This Si-H stretching peak has almost disappeared in the PEF PDMS spectrum (Fig.3.28) indicating hydrosilylation. However the residual peak intensities in the fuctionalised samples indicate that the reaction is not 100% complete.

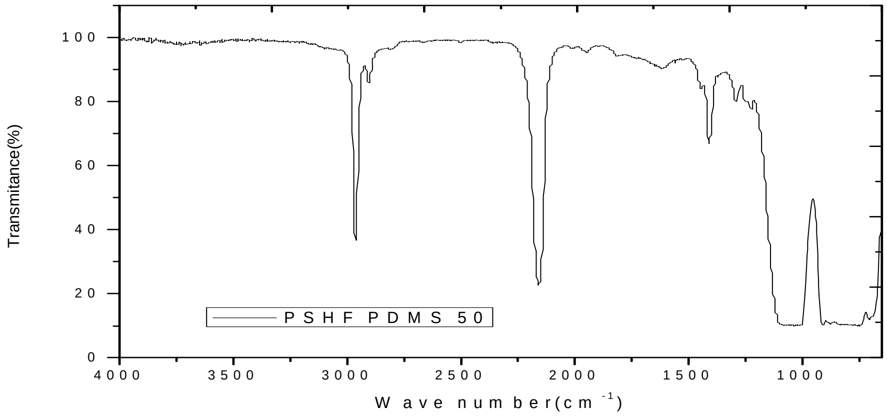


Fig 3.27 FTIR spectrum of PSHF PDMS 50

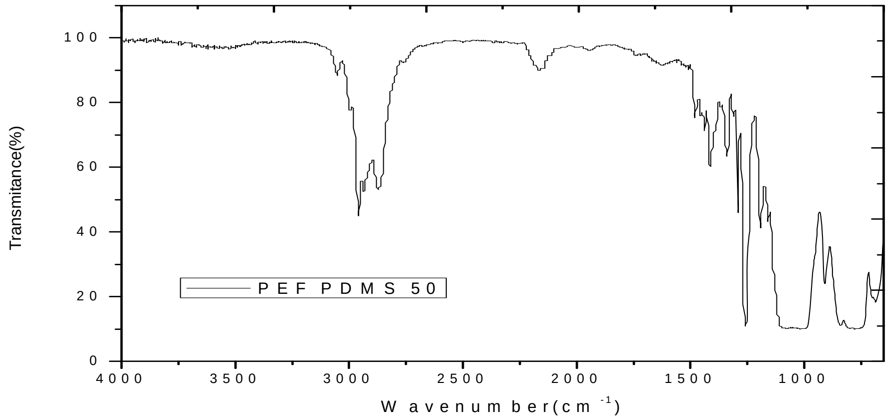


Fig.3.28 FTIR spectrum of PEF PDMS 50

iii Thermal studies

The thermal stability of the cured neat DGEBA and blends were investigated by TGA. Comparative values of the onset temperature, temperature at maximum rate and temperature of half loss and residue (%) on using PEF PDMS 50 for modification along with corresponding values for the neat resin are given in Table 3.5.

Table 3.5 TGA characteristics of blends having different concentrations of PEF PDMS50

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364.65	378.76	6.68
10% PEF/DGEBA	347.28	372.79	392.36	13.71
20% PEF/DGEBA	355.61	377.65	394.37	22.04

The siloxane segments improve thermal stability probably due to better heat dissipation by the siloxane chains, thus reducing the temperature at the epoxy networks. The thermal stability and the residual weight are improved when greater amount of siloxane segments are incorporated into the cured epoxy networks.

iv Dynamic mechanical analysis

The storage modulus values of blends containing the PEF PDMS50 and neat DGEBA are shown in Fig.3.29. The storage modulus decreases with increase in temperature. At room temperature neat epoxy showed a higher value compared to the blends. The decrease in the storage modulus for blend is due to the reduced crosslink density and plasticization effect of siloxane in the epoxy matrix. The Tg of epoxy rich phase slightly shifts towards the low temperature side with the addition of siloxane. The decrease in Tg of epoxy rich phase due to the decrease in cross-link density of the cured blends.

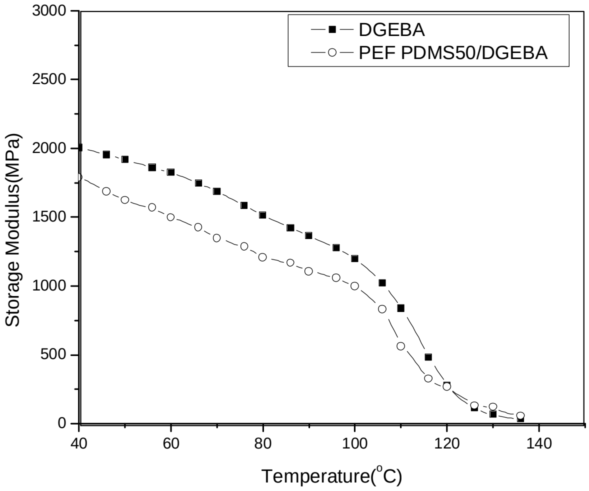


Fig.3.29 Storage modulus of (a) DGEBA and (b) PEF PDMS50/DGEBA

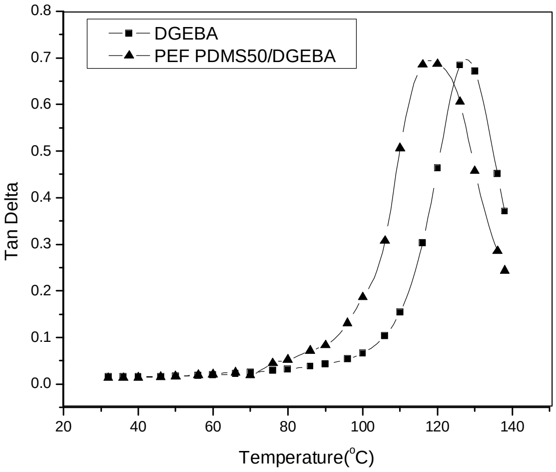


Fig.3.30 Tan δ relaxations of (a) DGEBA and (b) PEF PDMS50/DGEBA

The tan δ (loss factor) values are shown in Fig.3.30. The shape of the loss spectra can give additional information about the nature of the cross linked networks.. The glass transition temperature T_g corresponding to tan δ peak of neat DGEBA decreases when PEF PDMS50 are incorporated. The lowering of T_g is due to the flexible siloxane segments in the co- polymer.

v Mechanical properties

Fig.3.31shows the variation of impact strength with the addition of siloxanes**.** The impact strength increases with increase in concentration of PDMS. The increase in impact strength is due to the energy dissipation by the soft siloxane segments during the propagation of the fracture.

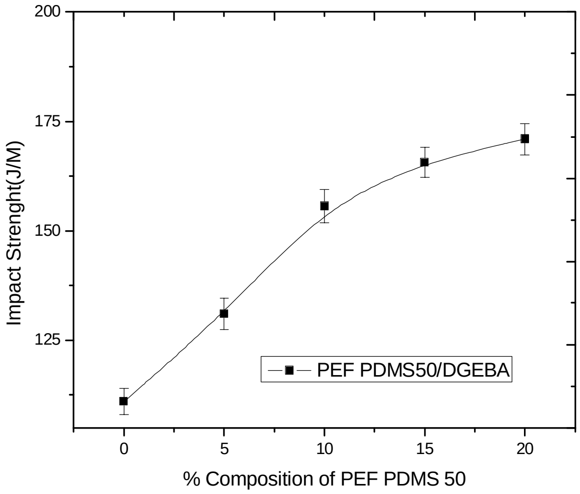


Fig.3.31 Impact strength of modified resin Vs PDMS concentration

Tensile strength decreases with increase in concentration of PDMS (Fig.3.32). This is due to the presence of flexible siloxane segments in the cross linked networks of the epoxy resin blend

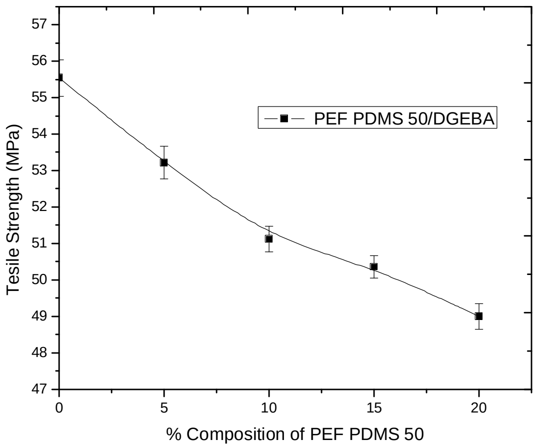


Fig.3.32 Tensile strength of modified resin Vs PDMS concentration

Fig.3.33 shows the variation of modulus with concentration of PDMS. The modulus decreases with increase in concentration of PDMS due to the presence of the soft segments of siloxane. The decrease in modulus is marginal compared to TEF PDMS and PEF PDMS modified DGEBA .

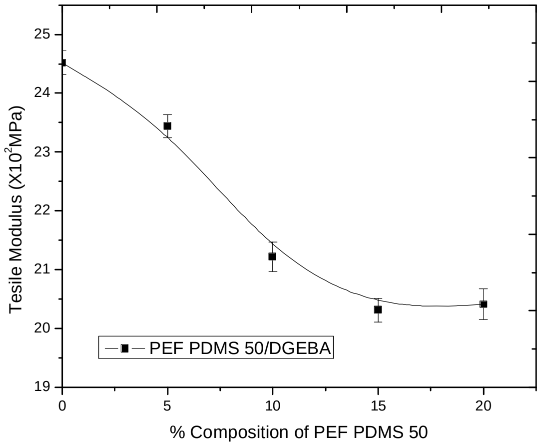


Fig.3.33 Modulus of modified resin Vs PDMS concentration

The variation of energy absorption with PDMS concentration is shown in Fig. 3.34. At 10% PDMS concentration, the energy absorption of the blend is at a maximum. The increase is due to greater energy dissipation by the soft siloxane segments. Energy absorption decreases due to lack of compatibilisation at higher concentrations of PDMS.

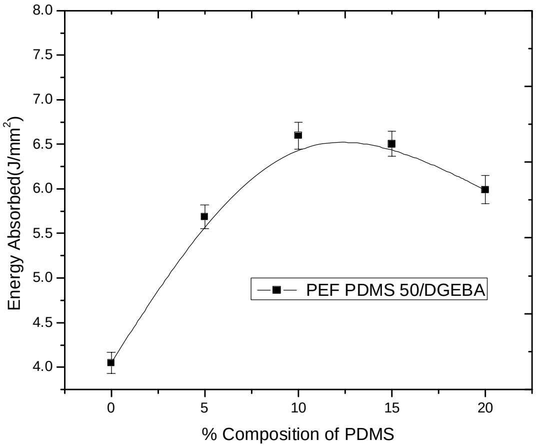


Fig.3.34 Energy absorbed by modified resin Vs PDMS concentration

At 10% PDMS concentration, the elongation at break of the blend (Fig. 3.35) is at maximum. The increase is due to the presence of flexible siloxane segments. Elongation decreases due to lack of compatibilisation at higher concentration of PDMS.

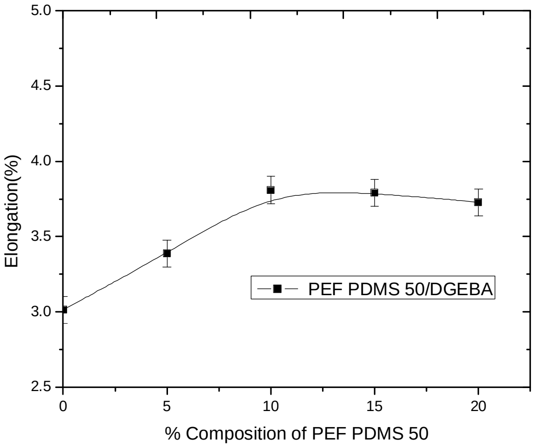


Fig.3.35 Elongation at break of modified resin Vs PDMS concentration

vi Water absorption

The percentage water absorption of the PDMS/DGEBA is given in Fig.3.36. Siloxanes lowered the water absorption of epoxy resin due to the hydrophobic nature of silicon molecule and its surface enrichment character thereby exhibiting lower permeability towards water molecules.

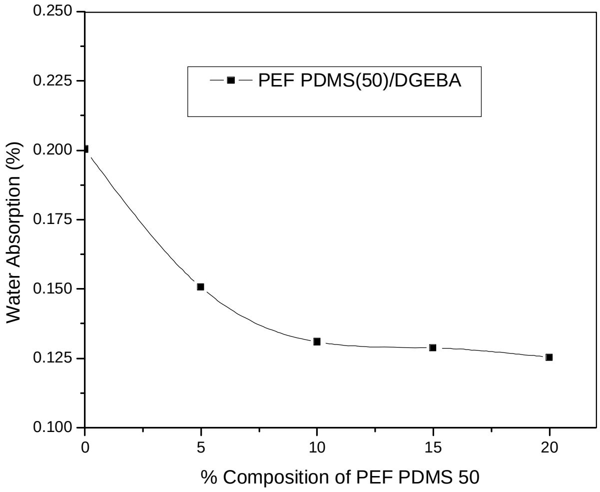
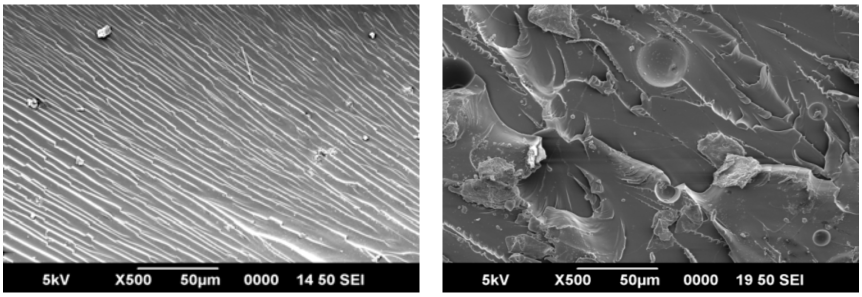


Fig.3.36 Water absorption versus concentration of PDMS

vii Morphological studies

SEM micrograph of the unmodified epoxy resin and modified epoxy resin are given in Fig.3.37. Fracture SEM micrograph of the unmodified epoxy resin (Fig. 3.37 a) paths are mostly straight and constitute failure bands. It is a typical case of brittle fracture. The fracture surface shows furrows and cavitations in the case of epoxy functional PDMS (PEF PDMS50/DGEBA) modified epoxy resin. (Fig.3.37 b). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. The rubber particles dissipate the bulk strain energy by cavitation leading to reduction of yield stress of the blend. As a result, shear band formation is enhanced by the voids in the matrix caused by cavitated rubber particles. The superior energy absorption characteristics of the PEF PDMS modified epoxy are evident from the comparison of micrographs.



a **b**

Fig 3.37 Scanning electron micrographs of the fracture surface of a) Neat DGEBA (b) PEF-PDMS 50/DGEBA

Table 3.6 shows a comparison of properties of siloxane modified epoxy resin

Table 3.6 Properties of siloxane modified epoxy resins

Property	% maximum improvement / % composition					
	DGEBA	TSHF PDMS	TEF PDMS	PSHF PDMS	PEF PDMS	PEF PDMS50
Tensile strength (MPa)	55	-29.1/10	-18.2/10	-27.3/10	-16.4/10	-10.9/20
Elongation at break (%)	3.01	10.5/5	25/5	13.3/5	25/5	26.7/10
Energy absorbed (.J/mm^2)	4.05	20/5	62.5/5	30.5/5	65/5	50/10
Impact strength (J/m)	111.04	44.1/10	79.2/10	45.2/10	89.2/10	54.9/20
Water absorption (%)	0.2003	-21.5/10	-29/10	-22.5/10	-34/10	-37.5/20

3.3.4 Ageing studies on epoxy resin modified by epoxidised siloxanes

The post-cured samples of the neat DGEBA, DGEBA/TEF PDMS blend (5 wt %) and DGEBA/PEF PDMS blend (5 wt%) were aged in a temperature controlled air oven kept at 100 ^{0}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.3.38 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 36.6 % in tensile strength while the reduction is 25.4% in the case of DGEBA/TEF PDMS and 24.7% in DGEBA/PEF PDMS blends.

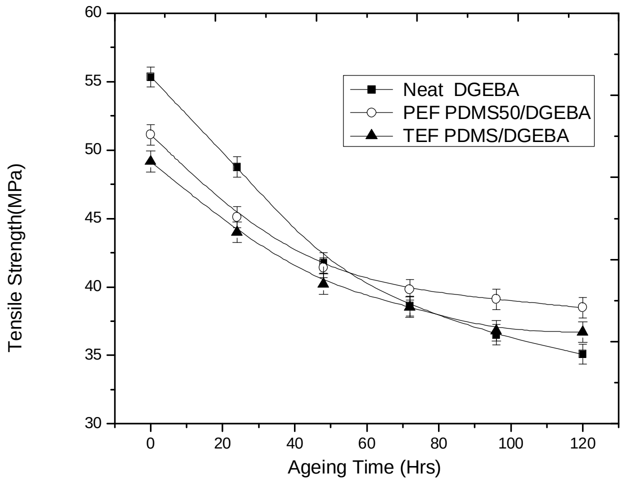


Fig. 3.38. Tensile strength of modified resin Vs ageing time

Fig.3.39 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.

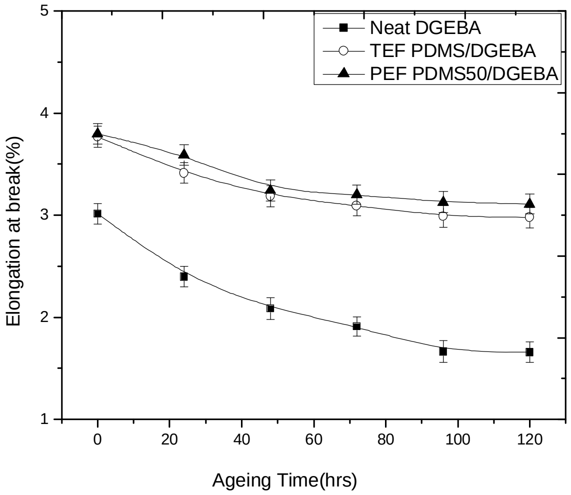


Fig. 3.39. Elongation at break of modified resin Vs ageing time

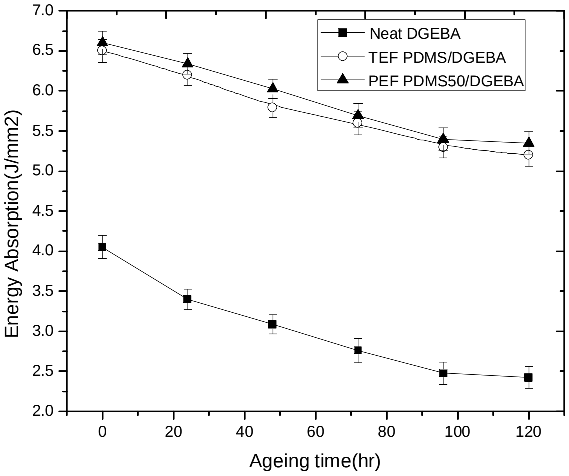


Fig. 3.40. Energy absorption of modified resin Vs ageing time

The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 3.40.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 PEF PDMS and TEF PDMS blends show a reduction of only 19-20%. This suggests the superiority of these siloxanes in improving the ageing characteristics.

ii Impact Strength

The variation in impact strength of the resins during ageing is given in Fig.3.41. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blends (PEF PDMS 22% and TEF PDMS 21%) compared to the unmodified sample (32.5%). This confirms the ability of siloxanes to improve the ageing properties.

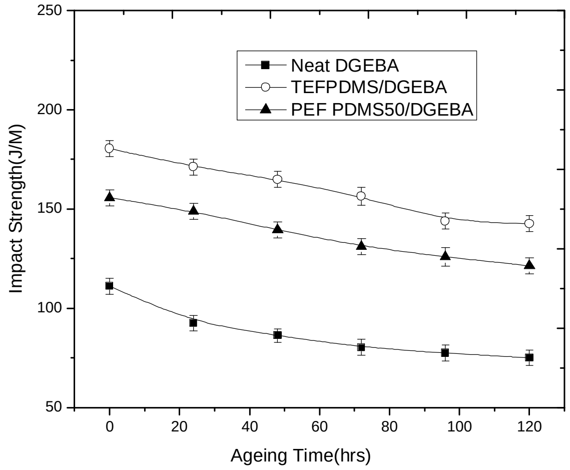


Fig. 3.40. Impact strength of modified resin Vs ageing time

iii. Water absorption

Water absorption decreases steadily with ageing time (Fig 3.41). This is due to additional cross-linking accompanying the ageing process. DGEBA/TEF PDMS and DGEBA/PEF PDMS blends show better water resistance than DGEBA resin.

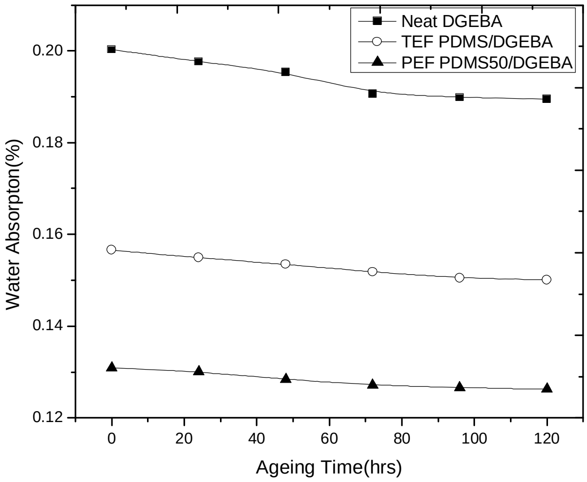


Fig. 3.41. Water absorption of modified resin Vs ageing time

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

3.4 Conclusion

Fuctionalised siloxane epoxy blends show considerable improvement in properties compared to nonfunctionalised siloxane epoxy blends. The poor compatibility of PDMS with epoxy can be improved by hydrosilylation.

The epoxy functionalised PDMS blends show substantial improvement in thermal stability as evident from TGA and damping data. The thermal stability of the blends improves as greater amounts of siloxane components are incorporated into the epoxy networks.

The impact strength increases with the concentration of PDMS. DGEBA/PEF-PDMS blends and DGEBA /TEF PDMS showed improved thermal and impact properties with marginal lowering in tensile strength and modulus. The functionalised siloxane/DGEBA blends show appreciable water resistance also.

Although PEF PDMS with 50% pendant hydride groups have improved compatibility with commercial epoxy resin and slightly higher tensile properties, the toughness properties are inferior to PEF PDMS with 4% pendant hydride groups at lower concentrations.

Siloxanes can marginally decrease the tensile properties but after ageing for 120 hrs the neat resin shows a reduction of 36.6 % in tensile strength while the reduction is only 25.4% in the case of DGEBA/TEF PDMS and 24.7% in DGEBA/PEF PDMS blends. After ageing the tensile strength values of modified resins are slightly better than that of the aged neat DGEBA. The modified resin retains the mechanical properties to a greater extent than the unmodified resin after ageing.

References

[1] Crespy A, Caze C, Loucheux C. Synthesis of macromolecular coupling agents and binders J Appl Polym Sci 1992;44:2061.

[2] Le Huy HM, Bellenger V, Verdu J. Polym Degrad Stab 1993;41:149.

[3] Crivello JV, Bi DS. J Polym Sci: Polym Chem 1993;31:3109.

[4] Crivello JV, Bi DS. J Polym Sci: Polym Chem 1993;31:3121.

[5] Epoxy resins modified with reactive low molecular weight siloxanes *European Polymer Journal*, *Volume 48, Issue 4*, *April 2012*, *Pages 769-773*Piotr Murias, Hieronim Maciejewski, Henryk Galina.

[6] Nograro FF, Liano-Ponte R, Mondragon I. Polymer 1996;37:1589. Nograro, F. F. ,Liano-Ponte, R.; Mondragon, I. Dynamic and mechanical properties of epoxy networks obtained with PPO based amines/mPDA mixed curing agents . Polymer 1996,37,1589.

[7] Jayle L, Bucknall CB, Partridge IK, Hay JN, Fernyhough A, Nozue I. Polymer 1996;37:1897.

[8] Yilgor E, Yigor I. Polymer 1998;39:1691.

[9] Gunatillake, P.A.; Meijs, G.F.; McCarthy, S.J.; Adhikari, R. Poly(dimethylsiloxane)/ poly(hexamethylene oxide) mixed macrodiol based polyurethane elastomers–I. Synthesis and properties. J. Appl. Polym. Sci. 2000, 76, 2026–2040.

[10] A. Anand Prabu, M. Alagar, Journal of Macromolecular Science Part A—Pure and Applied Chemistry, 42:175–188, 2005.

[11] Nicolas Sabourault, Ge´rard Mignani, Alain Wagner, and Charles Mioskowski. Organic Letters , Vol.4, No.13,2117-2119, 2002

[12] Hiyama T, Kusumoto T (1991) In: Trost BM, Fleming I (eds) Comprehensive organic synthesis. Pergamon, Oxford, vol 8, Sect. 3.12.

[13] Ojima I (1989) In: Patai S, Rappoport Z (eds) The chemistry of organic silicon compounds. John Wiley, Chichester, chap 25.

[14] Eaborn C, Bott BW (1968) In: MacDiarmid AG (ed) Organometallic compounds of the group IV elements. Marcel Dekker, New York, vol 1, chap 2.

[15] Marciniec B (ed) (1992) Comprehensive handbook on hydrosilylation. Pergamon, Oxford.

[16] Brook, M. A. Silicon in Organic, Organometallic, and Polymer chemistry; Wiley: New York, 1999.

[17] Marciniec, B.; Gulinski, J.; Urbaniak, W.; Kornetka, Z. W. ComprehensiVe Handbook on Hydrosilylation; Pergamon: Oxford, 1992.

[18] Ojima, I. The Hydrosilylation Reaction. In The Chemistry of Organic Silicon Compounds; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1, Chapter 25, p 1479.

[19] Speier JL (1979) Adv Organomet Chem 17:407.

[20] Chalk AJ, Harrod JF (1965) J Am Chem Soc 87:16.

[21] Tilley TD (1989) In: Patai S, Rappoport Z (eds) The chemistry of organic silicon chemistry.John Wiley, Chichester, p 1415.

[22] Bergens SH, Noheda P, Whelan J, Bosnich B (1992) J Am Chem Soc 114:2128.

[23] Duckett S, Perutz RN (1992) Organometallics 11:90.

[24] Brookhart M, Grant BE (1993) J Am Chem Soc 115: 2151.

[25] Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. J. Am. Chem. Soc. 1961, 83, 4385-4389.

[26] Benkeser, R. A. Pure Appl.Chem. 1966, 13, 133-140.

[27] Amrein, S.; Timmermann, A.; Studer, A. Org. Lett. 2001, 3, 2357-2360.

[28] Asao, N.; Sudo, T.; Yamamoto, Y. J. Org. Chem. 1996, 61, 7654-7655.

[29] Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. J. Org. Chem.1999, 64, 2494-2499.

[30] Jillian M. Buriak, , Michael P. Stewart, Todd W. Geders, Matthew J. Allen,Hee Cheul Choi, Jay Smith, Daniel Raftery, , and Leigh T. Canham, J. Am. Chem. Soc. 1999, 121, 11491-11502.

[31] Arico, C. S.; Cox, L. R. Org. Biomol. Chem. 2004, 2, 2558-2562.

[32] Trost, B. M.; Ball, Z. T. J. Am. Chem. Soc. 2001, 123, 12726-12727.

[33] Kawanami, Y.; Sonoda, Y.; Mori, T.; Yamamoto, K. Org. Lett. 2002, 4, 2825-2827.

[34] Maifeld, S. V.; Tran, M. N.; Lee, D. Tetrahedron Lett 2005, 46, 105-108.

[35] Faller, J. W.; D'Alliessi, D. G. Organometallics 2002, 21, 1743-1746.

[36] Kawanami, Y.; Yamamoto, K. Synlett 1995, 1232-1234.

[37] Uno, T.; Wakayanagi, S.; Sonoda, Y.; Yamamoto, K. Synlett 2003, 1997-2000.

[38] Denmark, S. E.; Wang, Z. Org. Lett. 2001, 3, 1073-1076.

[39] Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. J. Organomet. Chem. 2002, 645, 192-200.

[40] James W. Madine , Xiang Wang , and Ross A. Widenhoefer. Org. Lett. 2001, 3, 385-388.

[41] Chunxin Zhang and Richard M. Laine , J. Am. Chem. Soc.2000, 122,6979-6988.

[42] Youngim Na and Sukbok Chang , Org. Lett. 2000, 2, 1887-1889.

[43] Abdallah Hamze, Olivier Provot, Mouaˆd Alami,* and Jean-Daniel Brion, Org. Lett. 2005, 7, 5625-5628.

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Chapter 4

MODIFICATION BY TWO COMPONENT SYSTEMS

Contents

4.1 Introduction

This chapter deals with modification of epoxy resin with a two component system. Branching in DGEBA epoxy resin is achieved by the incorporation of multifunctional epoxy systems like EPNs [1,2]. Branching takes place due to the reaction of the hydroxyl groups in the epoxy back bone with the epoxy functional group in EPN [3]. 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 back bone. Cardanol, an agro-byproduct, has the advantages of low cost and renewable supply [4-7].The introduction of incompatible materials such as siloxanes to epoxy resins [8-12] is attracting more and more attention. Due to strong -Si-O-Si- linkage, siloxanes have high thermal and thermo oxidative stability, high moisture resistance, good dielectrical properties, excellent UV and chemical resistance The two component system is prepared by mixing two different modifiers in different proportions. The mixtures in different proportions were blended with DGEBA and the cured resins were tested for optimum properties. The mixture of p-ECN (epoxidised para cresol novolac) and EC (epoxidised cardanol) is represented as EEN and that of TEF PDMS [Terminal epoxy functional PDMS] and p-ECN as TPN and that of PEF PDMS 50 [pendant epoxy functional PDMS] and p-ECN as PEN .

4.2 Experimental

4.2.1 Materials

Epoxy resin GY 250(WPE 188) and amine hardener HY951 were procured from Petro Araldite Pvt. Ltd. Chennai. TEF PDMS [Terminal epoxy functional PDMS] (section 3.2.2), PEF PDMS [Pendant epoxy functional PDMS] (section 3.2.3), epoxidized cardanol(EC)(section 2.2.4), epoxidized p-cresol novolac(p-ECN)(section 2.2.4) were synthesized in the laboratory.

4.2.2 Modification of DGEBA using a mixture of p-ECN and EC

Epoxy resin was mixed with 0-20 wt% of a mixture of p-ECN and EC in different proportions viz. 0/100, 25/75, 50/50, 75/25 and 100/0 (designated as EC, EEN1, EEN2, EEN3 and P-ECN). 10w% hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Postcuring was done at 100^0C for four hours.

4.2.3 Ageing studies on epoxy resin modified by a mixture of p-ECN and EC

Cured samples of neat epoxy resin, epoxy resins modified by EC, epoxy resin modified by p-ECN and epoxy resins modified by EEN-3 (15%) were prepared. The samples were aged in a temperature controlled air oven kept at 100^0C 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.

4.2.4 Modification of DGEBA using a mixture of p-ECN and Terminal Epoxy functional PDMS

Epoxy resin was mixed with 0-20 wt% of a mixture of p-ECN and TEF PDMS in different proportions viz. 0/100, 25/75, 50/50, 75/25 and 100/0(designated as TEF PDMS, TPN1, TPN2, TPN3 and p-ECN). 10w% hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 100^0C for four hours.

4.2.5 Ageing studies on epoxy resin modified by a mixture of p-ECN and TEF PDMS

Cured samples of neat epoxy resin ,epoxy resins modified by TEF PDMS and epoxy resins modified by TPN-3 (15%) were prepared. The samples were aged in a temperature controlled air oven kept at 100^0C 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.

4.2.6 Modification of DGEBA using a mixture of p-ECN and pendant epoxy functional PDMS (PEF PDMS50)

Epoxy resin was mixed with 0-20 wt% of a mixture of p-ECN and PEF PDMS50 in different proportions viz. 0/100, 25/75, 50/50, 75/25 and 100/0 (designated as PEF PDMS50, PEN1, PEN2, PEN3 and p-ECN). 10w% hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 100^0C for four hours.

4.2.7 Ageing studies on epoxy resin modified by a mixture of p-ECN and PEF PDMS

Cured samples of neat epoxy resin, epoxy resins modified by PEF PDMS50 and epoxy resins modified by PEN-3 (15%) were prepared. The samples were aged in a temperature controlled air oven kept at 100^0C 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.

4.3. Results and discussion

4.3.1 Modification of DGEBA using a mixture of p-ECN and EC

i) Tensile properties

Referring to Fig.4.1 tensile strength values obtained on blending epoxy resin with 5 to 20% modifiers are significantly higher compared to that of the unmodified resin. While P-ECN/DGEBA shows a maximum improvement of 36% the EC/DGEBA shows only 10% improvement. Among the three components EEN-3 modified shows better tensile properties and its maximum improvement is about 20%**.**The improvement in tensile strength over that of the neat DGEBA 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. Three component systems show improved properties but to a lesser extend compared to pECN modified DGEBA.

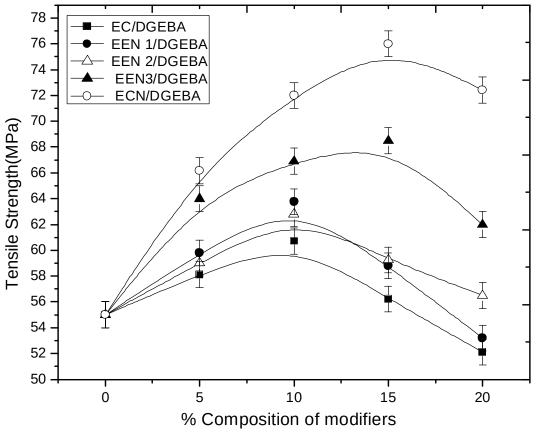


Fig. 4.1.Tensile strength of modified resin Vs Modifier concentration

The effect on elongation at break is shown in Fig.4.2. Compared to unmodified resin the blends show an increase in elongation. While EC modified resin shows an elongation of 105%, the ECN modified resin shows only 40%. Three component systems show improved properties. In this case EEN-1 enjoys clear superiority over the other three component systems. A higher elongation may be the result of straightening of the entangled chains.

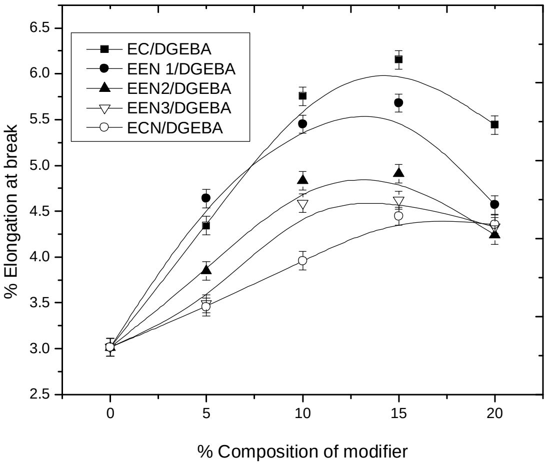


Fig. 4.2 Elongation (at break) of modified resin Vs modifier concentration

Fig. 4.3 gives the variation of energy absorbed (to break) by the blends of epoxy resin with modifiers. This can be taken as a measure of the toughness. By the addition of EC energy absorption is increased by 50 % and maximum improvement is 75.5% in the case of p-ECN modified DGEBA. In the case of the mixture we can see that the energy absorption can be improved by increasing the concentration of p-ECN. In the case of ECN enhanced compatibility and greater cross-linking are responsible for greater strengthening of the matrix. In the case of EC modified resin, the matrix resin contains relatively shorter chains due to the presence of mono functional EC.

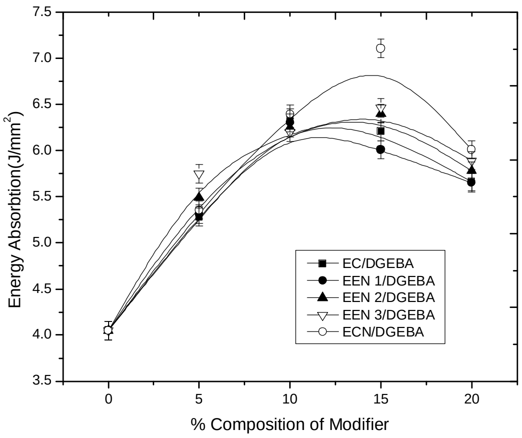


Fig. 4.3. Energy absorbed (to break) of modified resin Vs EPN concentration

ii Impact strength

Impact strength values obtained by blending epoxy resin with 5 to 20% modifiers are shown in (Fig.4.4). P-ECN modified epoxy resin shows a maximum improvement of 98% .The improvement in impact strength of epoxy novolac modified resins is a direct consequence of compatibility, chain entanglement and enhanced cross-linking. Since the polymer chains are smaller, by EC addition the improvement of impact strength over neat resin is only up to 50%. The impact strength can be further increased by the addition of mixture of ECN and EC to DGEBA.

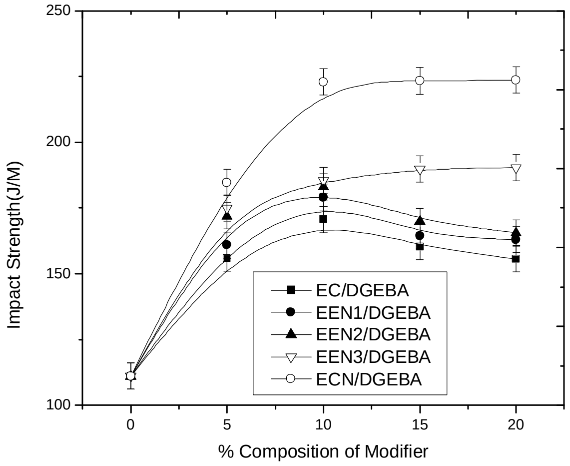


Fig. 4.4. Impact strength of modified resin Vs EEN concentration

iii. Thermal properties

The TGA values of the neat resin, EC/DGEBA, EEN-3/DGEBA and ECN/DGEBA are given in Table 4.1. There is not much deterioration in thermal properties of DGEBA by addition of the mixture (EEN) to the neat DGEBA. The EEN modified sample gave 8.1 % residue at 600^{0}C compared to 6.7 % by the un-modified resin which indicates some improvement in the charring properties.

Table 4.1 TGA characteristics of DGEBA, EC/DGEBA, p ECN/ DGEBA and EEN/DGEBA

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
p-ECN	340	366	380	8.4
EC/DGEBA	333	360	375	7.4
EEN /DGEBA	339	365	379	8.1

iv Water absorption

The variation in water absorption is given in Fig. 4.5.The hydroxyl groups in unreacted cardanol can form hydrogen bonds with water. So EC modified blends show increased water absorption. The water absorption can be reduced by adding p-ECN. This is possibly due to a greater extent of methylene groups and phenolic groups which are not amenable to hydrogen bonding. So by using a mixture of ECN and EC we can reduce the water absorption.

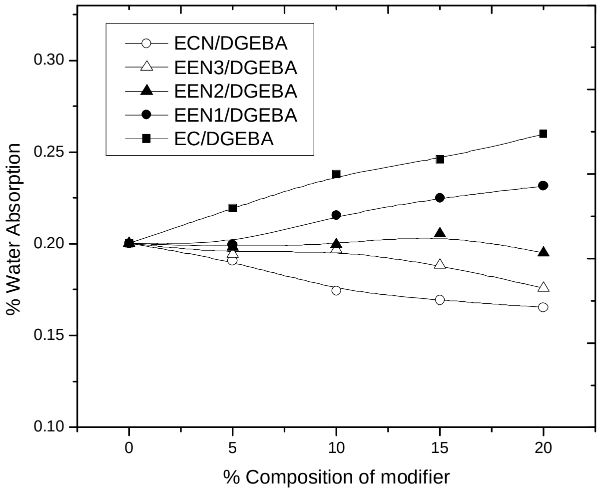
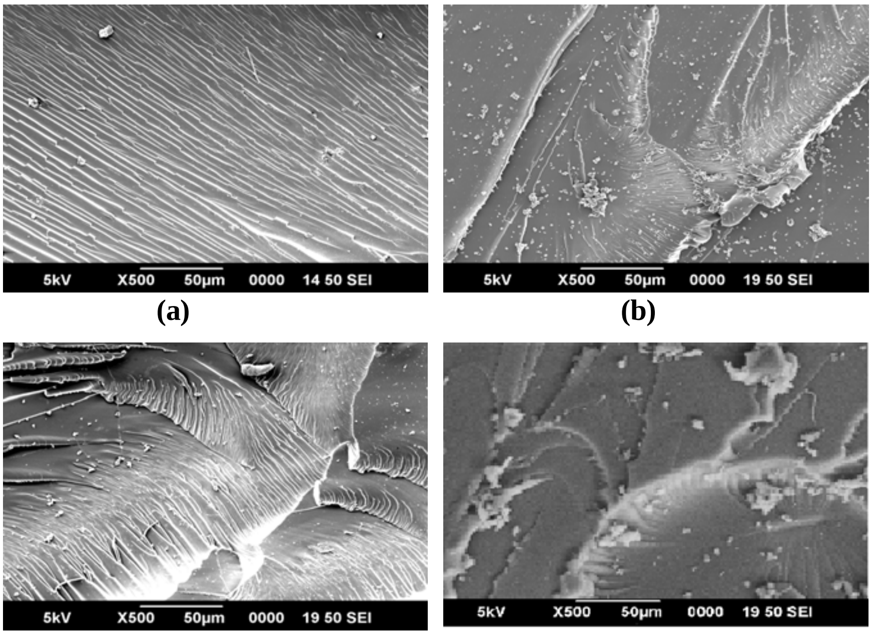


Fig. 4.5. Water absorption of modified resin Vs EEN concentration

iv. Morphological studies

Scanning electron micrographs of unmodified, EC modified, p-ECN modified and EEN modified epoxy resins fractured at low deformation are shown in Fig. 4.6. 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.



(a) (b)

(c) (d)

Fig. 4.6 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/EC c)DGEBA/pECN d) DGEBA/EEN

Referring to the EC modified, pECN modified, and EEN modified samples (b, c and d), 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 the modified resin.

From this study we can conclude that the addition of EEN (a mixture of EC and p-ECN) to DGEBA resin does not show much deterioration in mechanical and thermal properties. Epoxidised cardanol can be used as a good low cost modifier for laminates,but the improvements in properties are marginal.But this can be further improved if we use a mixture of EC and ECN.

4.3.2 Ageing studies on epoxy resin modified by a mixture of p-ECN and EC

In this study, three 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 %), DGEBA/EC blend (10 wt %) and DGEBA/EEN3 blend (15 wt%) were aged in a temperature controlled air oven kept at 100 ^{0}C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties and water absorption

i. Tensile properties

The effect of variation of ageing time with tensile strength is shown in Fig.4.7. 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 35% in the case of DGEBA/EC, 28% in DGEBA/p-ECN and 30% in DGEBA/EEN blends.

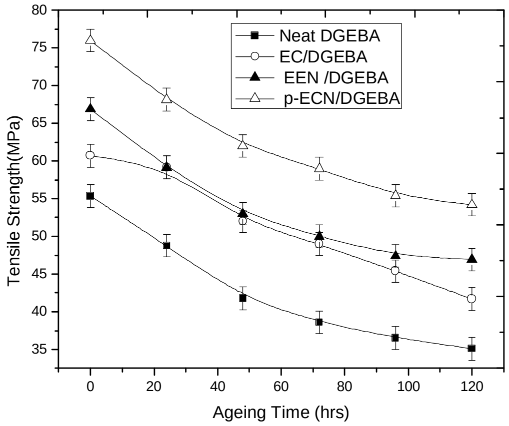


Fig. 4.7. Tensile strength of modified resin Vs ageing time

Fig.4.8 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. After ageing for 120 hrs the neat resin shows a reduction of 45.5 % in elongation while the reduction is 35% in the case of DGEBA/EC, 23% in DGEBA/p-ECN and 23% in DGEBA/ EEN blends.

The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 4.9. 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 and DGEBA/EC shows a reduction of 37%, the p-ECN and EEN blends show a reduction of only 27-30%. This suggests the superiority of these p-ECN resins in improving the ageing characteristics.

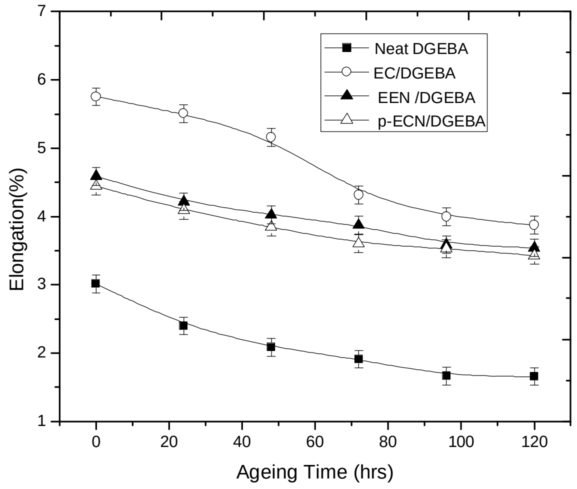


Fig. 4.8 Elongation at break of modified resin Vs ageing time

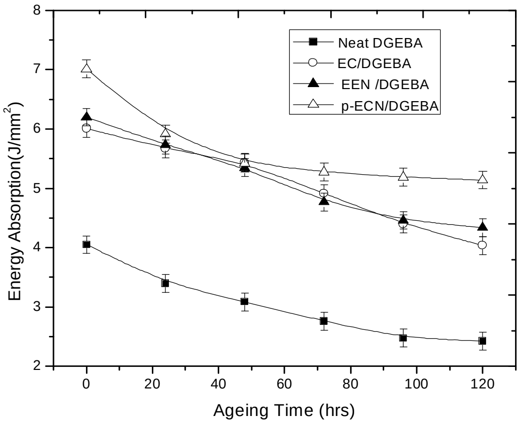


Fig. 4.9. Energy absorbed (to break) of modified resin Vs ageing time

ii) Impact strength

The variation in impact strength of the modified resin during ageing is given in Fig.4.10. 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 26.5% and EEN 26.4%) compared to the unmodified (33%) and EC modified DGEBA (29.4%) samples. This confirms the ability of p-ECN to improve the ageing properties.

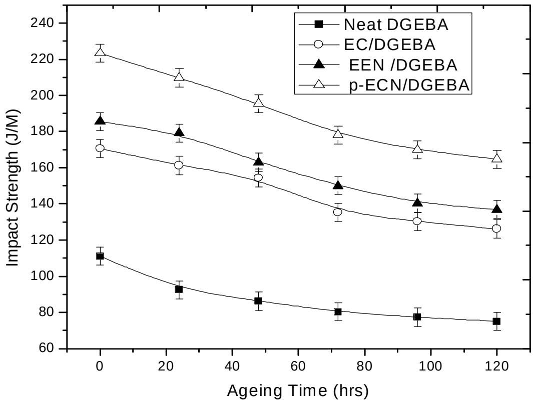


Fig. 4.10. Impact strength of modified resin Vs ageing time

ii. Water absorption

DGEBA/p-ECN and DGEBA/EEN blends show better water resistance (Fig.4.11) than neat DGEBA resin and EC modified DGEBA after ageing. This is also due to additional cross-linking accompanying the ageing process.

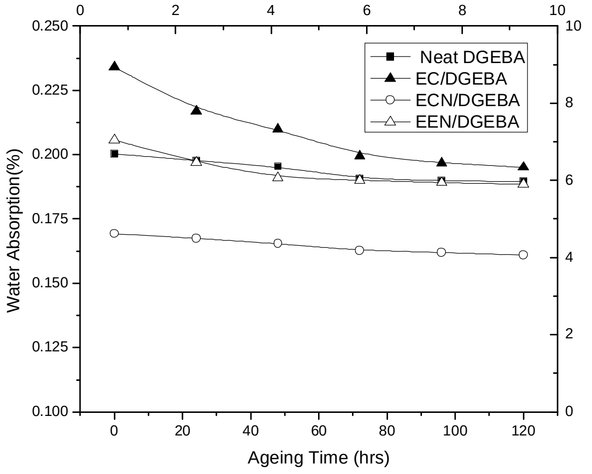


Fig. 4.11. Water absorption of modified resin Vs ageing time

The study reveals that modification using p-ECN and EEN improves the ageing behaviour of the neat resin. The modified resin retains the mechanical properties to a greater extent than the unmodified resin**.**

4.3.3 Modification of DGEBA using a mixture of p-ECN and TEF PDMS

i) Tensile Properties

Tensile strength decreases with increase in concentration of TEF PDMS (Fig. 4.12). This is due to the presence of flexible siloxane segments in the cross linked networks of the epoxy resin blend .Referring to Fig.4.12, tensile strength values obtained by blending epoxy resin with

5 to 20% modifiers show that a mixture of p-ECN and TEF PDMS considerably improves the tensile properties. The improvement in tensile strength over that of the neat DGEBA 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. Three component systems show improved properties but they are still less than that of pECN modified DGEBA. Among three components TPN3/DGEBA shows superior properties. TPN3 shows a maximum improvement of 13% in tensile strength.

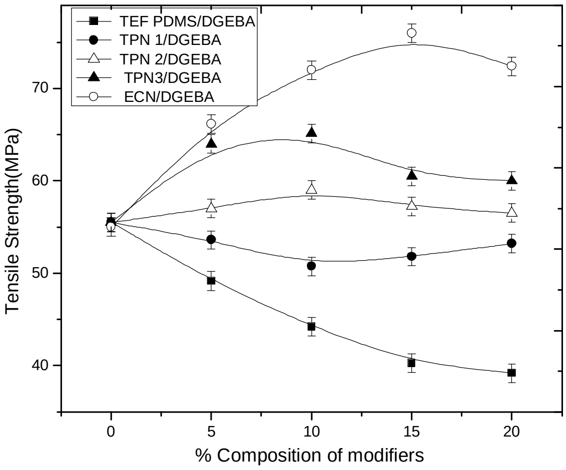


Fig. 4.12. Tensile strength of modified resin Vs modifier concentration

The effect on elongation at break is shown in Fig.4.13. Compared to unmodified resin all the blends show an increase in elongation. At 5% concentration of modifier TEF PDMS modified system shows maximum elongation. But after 5%, elongation decreases for TEF PDMS modified DGEBA due to lower compatibility. At 15% concentration of modifier ECN modified sample shows a maximum improvement of 41%. Three component systems show improved elongation than neat resin. In this case TPN-3 enjoys clear superiority over the other three component system. TPN-3 modified DGEBA shows a maximum improvement of 36% in elongation.

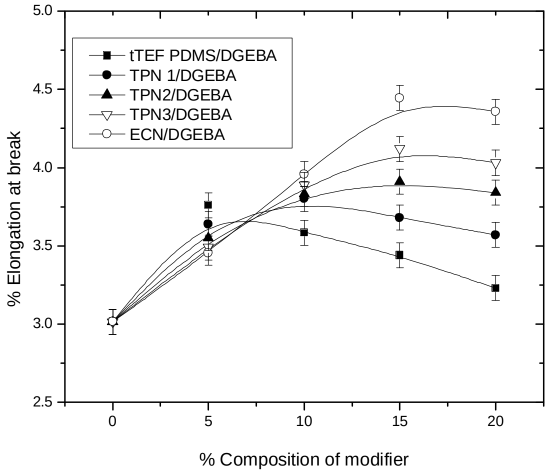


Fig. 4.13 Elongation (at break) of modified resin Vs modifier concentration

Fig. 4.14 gives the variation of energy absorbed (to break) by the blends of epoxy resin with modifiers. This can be taken as a measure of the toughness. While TEF PDMS/DGEBA shows a maximum improvement of 56% the ECN/DGEBA shows only 30% improvement at 5% loading of the modifier. The increase is due to greater energy dissipation by the soft siloxane segments. At higher concentrations of TEF PDMS energy absorption decreases due to lack of compatibilisation. The maximum improvement in energy absorption by the p-ECN modified DGEBA is 75.5% at 15% p-ECN concentration. The improvement in energy over that of the neat DGEBA is due to the formation of hyper branched network structure. This can also be attributed to some amount of entanglement among the polymer chains. Among the mixtures, TPN-3 modified DGEBA shows maximum improvement in energy. TPN-3/DGEBA shows an improvement of 68.5% in energy absorption.

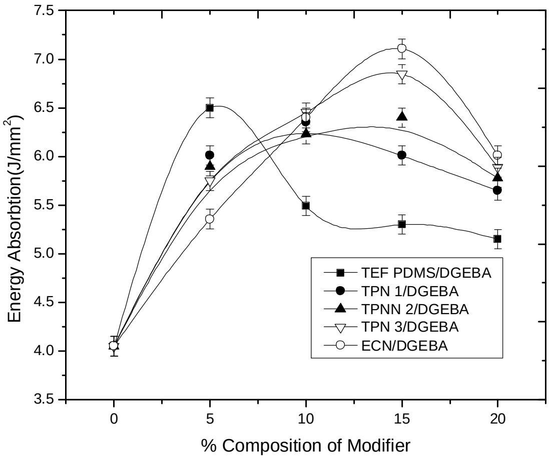


Fig. 4.14. Energy absorbed (to break) of modified resin Vs TPN concentration

ii Impact Strenth

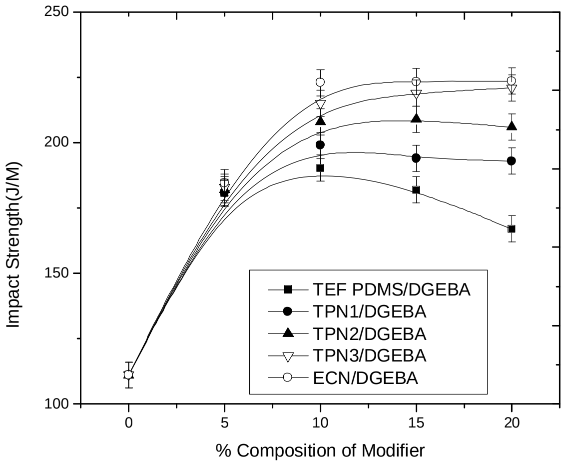


Fig. 4.15. Impact strength of modified resin Vs modifier concentration

Impact strength values obtained by blending epoxy resin with 5 to 20% modifiers are shown in (Fig.4.15). p-ECN modified epoxy resin shows a maximum improvement of 98% .The improvement in impact strength of epoxy novolac modified resins is a direct consequence of compatibility, chain entanglement and enhanced cross-linking. TEF PDMS modified resin shows a maximum improvement of 66%. In the case of three component system increase in concentration of ECN improves the impact strength and TPN3/DGEBA shows superior properties over other three component systems.

iii. Thermal properties

The TGA values from thermogram (Fig. 4.16) of the neat resin, TEF PDMS/DGEBA, TEN-3/DGEBA and p-ECN/DGEBA are given in Table 4.2. There is slight improvement in thermal properties of DGEBA by the addition of modifier resin. Residue values indicate slight improvement in charring properties. TEF PDMS and TPN modified samples shows better properties due to presence of TEF PDMS. The siloxane segments improve thermal stability probably due to better heat dissipation by the siloxane chains, thus reducing the temperature at the epoxy networks.

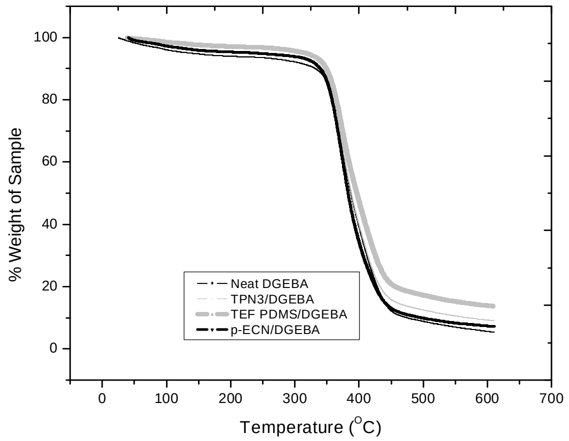


Fig. 4.16.Thermogram of neat and modified DGEBA

Table 4.2 TGA characteristics of DGEBA, TEF PDMS/DGEBA, p ECN/ DGEBA and TPN/DGEBA

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
p-ECN	340	366	380	8.4
TEF PDMS/DGEBA	350	369	382	10.43
TPN3 /DGEBA	349	367	381	10.4

b) Dynamic mechanical analysis

The storage modulus values of blends containing the modified as well as neat epoxy are shown in Fig.4.17. The storage modulus decreases with increase in temperature. At room temperature p-ECN/DGEBA showed a higher value compared to other blends and neat DGEBA due to the cross linking of the epoxide groups of ECN. The decrease in the storage modulus for TEF PDMS/DGEBA and TPN3/DGEBA is due to the reduced crosslink density and plasticization effect of siloxane in the epoxy matrix.

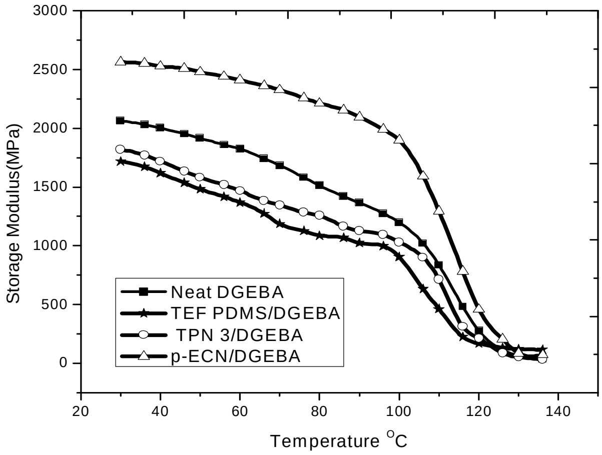


Fig.4.17 Storage modulus of (a) DGEBA (b) TEF PDMS/DGEBA (c) pECN/DGEBA (d) TPN/DGEBA

The tan δ (loss factor) values are shown in Fig.4.18. 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_{max}) becomes lower as the distance between the crosslinks decreases. The tan δ_{max} for neat DGEBA decreases on blending with ECN indicating increased crosslink density. The Tg of the epoxy rich phase increased with the addition of ECN. This is due to the increase in crosslink density of the blends on addition of ECN. The tan δ_{max} for neat DGEBA increases on blending with siloxane indicating reduced crosslink density. The glass transition temperature T_g corresponding to tan δ peak of neat DGEBA decreases when TEF PDMS and TPN3 are incorporated. The lowering of T_g is due to the flexible siloxane segments in the co- polymer.

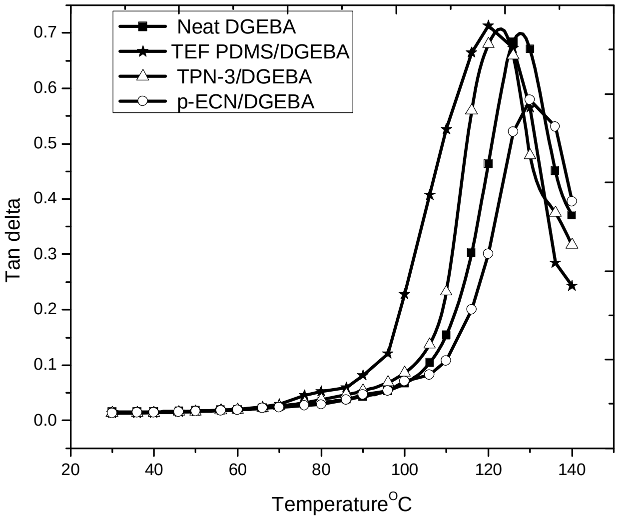


Fig.4.18 Tan δ relaxations of (a) DEBA (b) pECN/DGEBA and (c) TEF PDMS/ DGEBA (d)TPN3/DGEBA

iv Water absorption

The variation in water absorption is given in Fig. 4.19. The water absorption can be reduced by adding TEF PDMS and p-ECN. The same trend can be seen in TPN modified samples also. This is possibly due to a greater extent of methylene groups, phenolic groups and hydrophobic siloxane molecues .

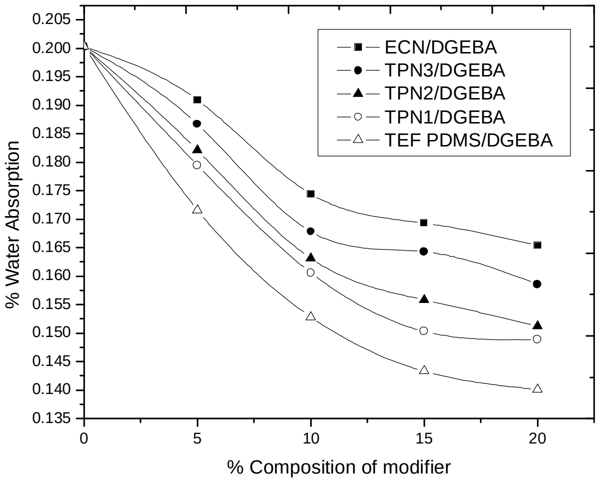
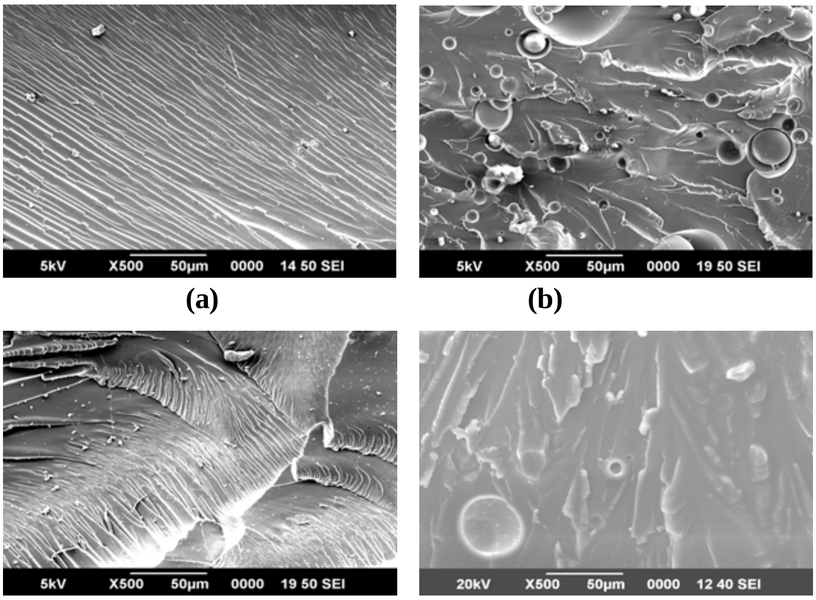


Fig. 4.19. Water absorption of modified resin Vs TPN concentration

iv. Morphological studies

Scanning electron micrographs of neat DGEBA, p-ECN modified, TEF PDMS modified and TPN modified epoxy resins fractured at low deformation are shown in Fig. 4.20. 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.

The fracture surface shows furrows and cavitation in the case of terminal epoxy functional PDMS (TEF PDMS/DGEBA) modified epoxy resin, (b). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. Referring to pECN modified sample (c), 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. Micrograph (d) representing epoxy/TPN blend is characterised by shallow cavities as well as non-uniform ridges. The holes in the stress-whitened regions presumably result from dilation and rupture of siloxane (TEF PDMS) particles [14]. These features point to improved toughness and load bearing characteristics of modified resin.



(a) **(b)**

(c) **(d)**

Fig. 4.20 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/TEF PDMS c)DGEBA/pECN d) DGEBA/TEN

The addition of TEF PDMS can improve the thermal properties and impact properties with slight reduction in tensile properties. p-ECN can improve the mechanical properties without much deterioration in thermal properties. So addition of mixture of p-ECN and TEF PDMS to DGEBA can lead to improvement in mechanical properties, thermal properties and water resistance.

4.3.4 Ageing studies on epoxy resin modified by a mixture of p-ECN and TEF PDMS

In this study, three 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 %), DGEBA/TEF PDMS blend (5 wt %) and DGEBA/TPN blend (15 wt%) were aged in a temperature controlled air oven kept at 100 ^{0}C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties, water absorption

i. Tensile properties

The effect of variation of tensile strength with ageing time is shown in Fig.4.21 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 28% in the case of DGEBA/p-ECN, 25% in DGEBA/TEF PDMS but only 23% in DGEBA/TPN blend.

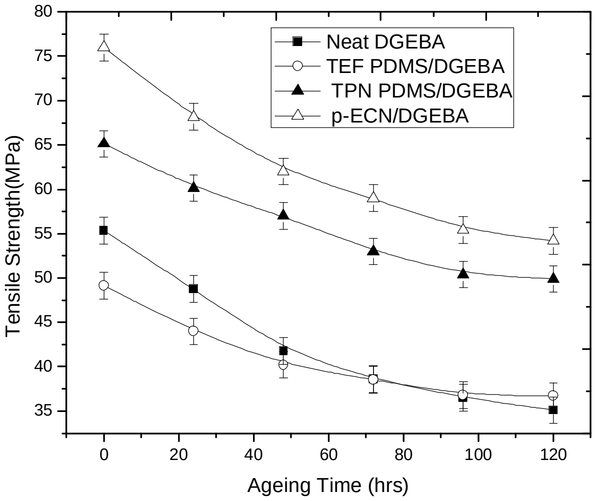


Fig. 4.21. Tensile strength of modified resin Vs ageing time

Fig.4.22 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. After ageing for 120 hrs the neat resin shows a reduction of 45.5 % in elongation while it is 21% in the case of DGEBA/TEF PDMS, 23% in DGEBA/p-ECN and only 17% in DGEBA/ TPN blends.

The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 4.23.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 and DGEBA/TEF PDMS shows a reduction of 20%, the p-ECN blend shows a reduction of 31%. The reduction is 21% in the case of TPN modified resins. This suggests the superiority of TEF PDMS resins in improving the ageing characteristics.

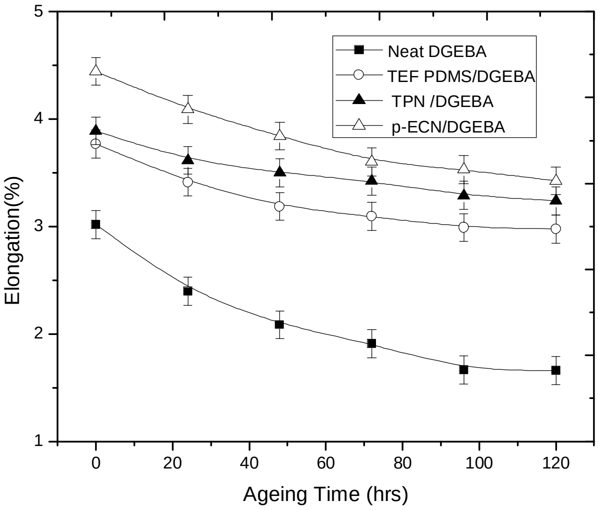


Fig. 4.22 Elongation at break of modified resin Vs ageing time

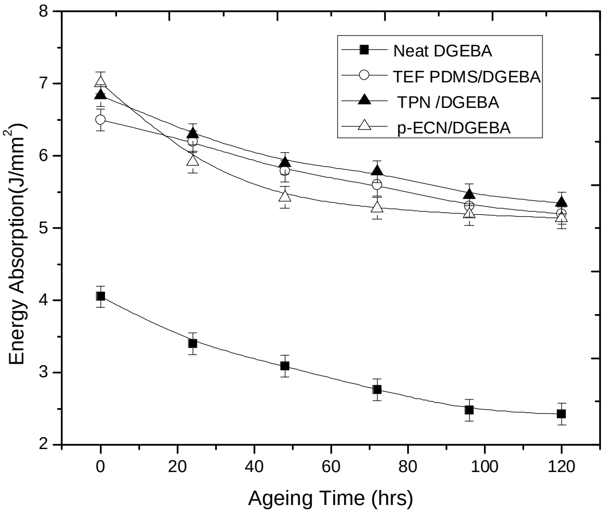


Fig. 4.23 Energy absorbed (to break) of modified resin Vs ageing time

ii) Impact strength

The variation in impact strength of the modified resin after ageing is shown in Fig.4.24. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blends (TEF PDMS/DGEBA (21%), p-ECN/DGEBA (26.4%) and TPN/DGEBA (25%)) compared to the unmodified sample (33%) This confirms the ability of TEF PDMS to improve the ageing properties.

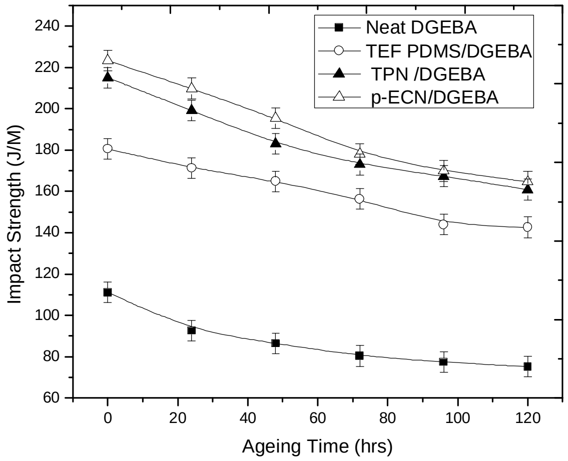


Fig. 4.24. Impact strength of modified resin Vs ageing time

ii. Water absorption

DGEBA/p-ECN TEF PDMS/DGEBA and DGEBA/TPN blends show better water resistance (Fig.4.25) than neat DGEBA resin after ageing. This is also due to additional cross-linking accompanying the ageing process. TEF PDMS and TPN modified samples shows the greatest water resistance after ageing.

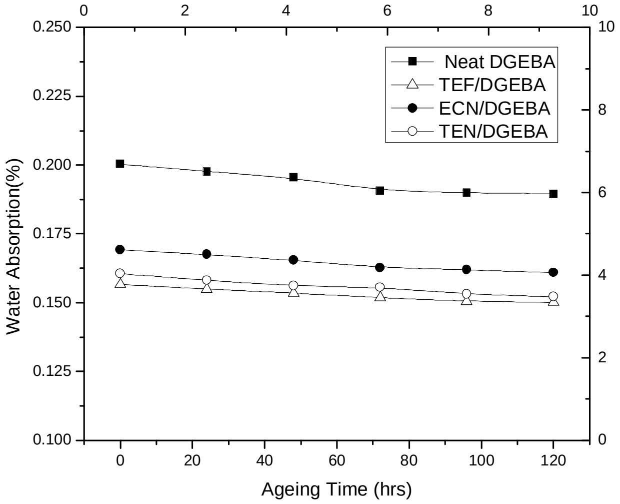


Fig. 4.25. Water absorption of modified resin Vs ageing time

The study reveals that a mixture of p-ECN and TEF PDMS as modifiers improves the ageing properties of the neat resin with improvement in mechanical and thermal properties. This modification gives better water resistance than the neat resin.

4.3.5 Modification of DGEBA using a mixture of p-ECN and PEF PDMS 50

i) Tensile properties

Referring to Fig.4.26 tensile strength values obtained by blending epoxy resin with 5 to 20% modifiers show that addition of p-ECN shows a maximum improvement of 36%. But addition of PEF PDMS50 shows reduction in tensile properties. This is due to the presence of flexible PEF PDMS50 segments in the cross linked networks of the epoxy resin blend. By using a mixture of pECN and PEF PDMS50 (PEN) tensile properties can be improved. PEN-3 shows clear superiority over other three component systems.

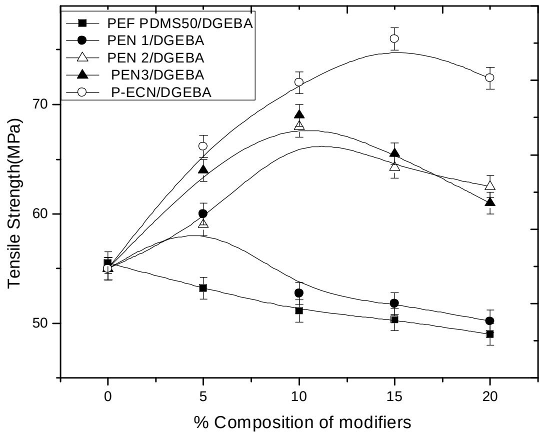


Fig. 4.26. Tensile strength of modified resin Vs TPN concentration

The effect on elongation at break is shown in Fig.4.27. Compared to unmodified resin all the blends show an increase in elongation. ECN modification shows a maximum improvement of 41%, the improvement of PEF PDMS modification is 23%, the improvement of PEN-1 modification is 25%, and improvement of PEN-2 modification is 27% and the improvement of PEN-3 modification is 37%. From this we can see that PEN-3 enjoys clear superiority over the other three component systems.

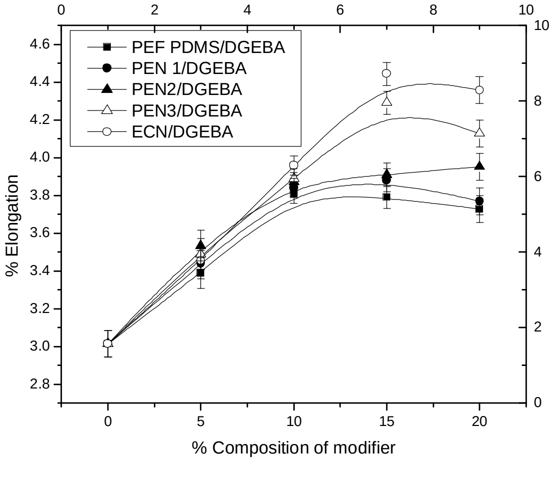


Fig. 4.27 Elongation (at break) of modified resin Vs modifier concentration

The variation of energy absorbed (to break) by the blends of epoxy resin with modifiers is shown in Fig.4.28. At 10% loading of the modifier PEF PDMS50/DGEBA shows a maximum improvement of 63% and ECN/DGEBA shows only 57 %. The increase is due to greater energy dissipation by the soft siloxane segments. At higher concentrations of PEF PDMS energy absorption decreases due to lack of compatibilisation. The maximum improvement of energy absorption by the p-ECN modified DGEBA is 75.5% at 15% p-ECN concentration. The improvement in energy absorption over that of neat DGEBA is due to the formation of a hyper branched network structure. This can also be attributed to some amount of entanglement among the polymer chains. Among the mixtures, PEN-3 modified DGEBA shows improved properties. PEN-3/DGEBA shows an improvement of 67 % in energy absorption.

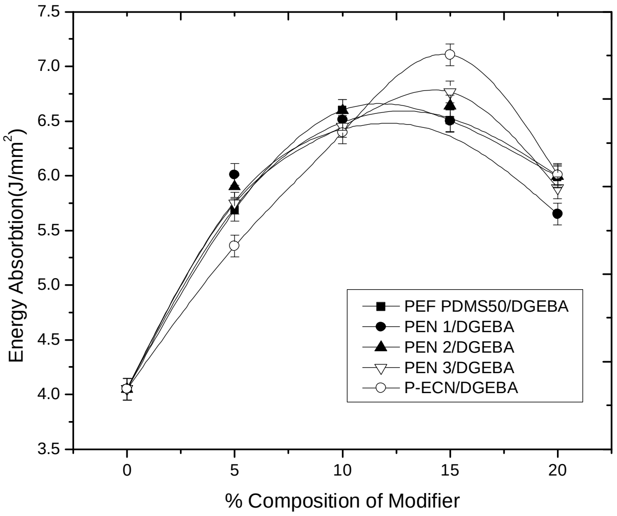


Fig.4.28. Energy absorbed (to break) of modified resin Vs PEN concentration

ii Impact strenth

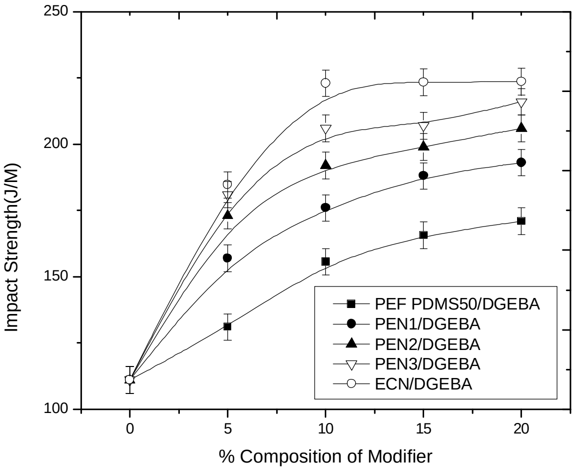


Fig. 4.29 Impact strength of modified resin Vs modifier concentration

Impact strength values obtained on blending epoxy resin with 5 to 20% modifiers are shown in Fig.4.29. p-ECN modified epoxy resin shows a maximum improvement of 98% .The improvement in impact strength of epoxy novolac modified resins is a direct consequence of compatibility, chain entanglement and enhanced cross-linking. PEF PDMS modified resin shows a maximum improvement of 44 %. In the case of three component systems, PEN-3/DGEBA shows superior properties over other three component systems.PEN-3 modified DGEBA shows an improvement of 89% over the neat DGEBA.

iii. Thermal properties

The TGA values of the neat resin, PEF PDMS/DGEBA, PEN-3/DGEBA and p-ECN/DGEBA are given in the table (Table4.3.)

Table 4.3 TGA characteristics of DGEBA, PEF PDMS/DGEBA, pECN/ DGEBA and PEN3 /DGEBA

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
p-ECN/DGEBA	340	366	380	8.4
PEF PDMS 50/DGEBA	357.28	376.79	394.36	15.71
PEN /DGEBA	354	371	388	14.6

Compared to neat DGEBA and ECN/DGEBA, PEF PDMS and PEN modified samples show improvement in thermal properties due to the presence of siloxane(PEF PDMS). The siloxane segments improve thermal stability probably due to better heat resistance of silanes. The thermal stability and the residual weight are improved when a greater amount of PEF PDMS segments are incorporated into the cured epoxy networks.

b) Dynamic mechanical analysis

The storage modulus values of blends containing the modified as well as neat epoxy are shown in Fig.4.30. The storage modulus decreases with increase in temperature. At room temperature p-ECN/DGEBA showed a higher value compared to other blends and neat DGEBA due to the cross linking of the epoxide groups of ECN. The decrease in the storage modulus for PEF PDMS/DGEBA and PEN3/DGEBA is due to the reduced crosslink density and plasticization effect of siloxane in the epoxy matrix.

The tan δ (loss factor) values are shown in Fig.4.31 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_{max}) becomes lower as the distance between the crosslink decreases. The tan δ_{max} for neat DGEBA decreases on blending with ECN indicating increased crosslink density. The Tg of the epoxy rich phase increased with the addition of ECN. This is due to the increase in crosslink density of the blends on ECN. The tan δ_{max} for neat DGEBA increases on blending with siloxane indicating reduced crosslink density. The glass transition temperature T_g corresponding to tan δ peak of neat DGEBA decreases when PEF PDMS50 and PEN3 are incorporated. The lowering of T_g is due to the flexible siloxane segments in the co- polymer.

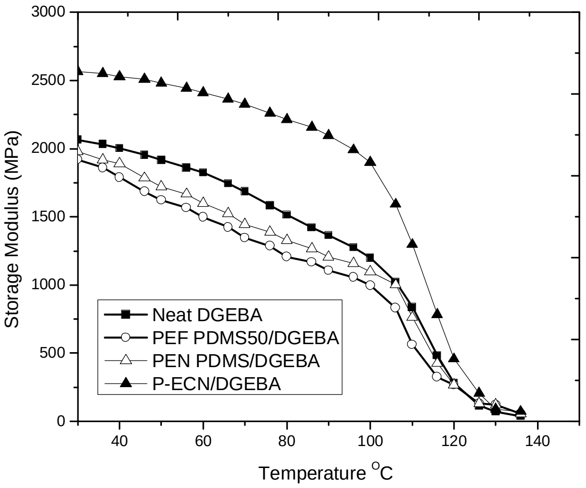


Fig.4.30 Storage modulus of (a) DGEBA (b) PEF PDMS/DGEBA c)pECN/ DGEBA (d) PEN/DGEBA

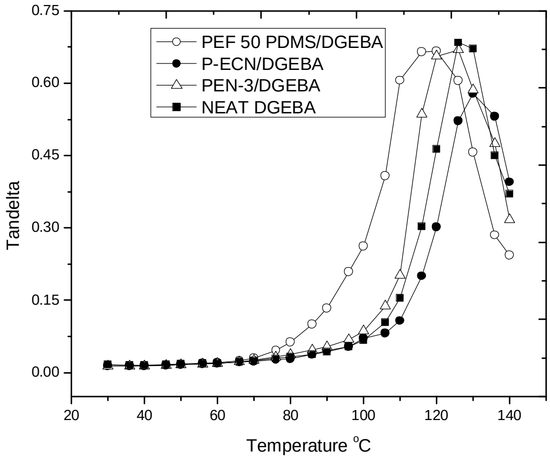


Fig.4.31 Tan δ relaxations of (a) DEBA (b) p-ECN/DGEBA and (c) PEF PDMS/ DGEBA (d) PEN /DGEBA

iv Water absorption

The variation in water absorption is given in Fig. 4.32. The water absorption can be decreased by adding PEF PDMS and p-ECN. The same trend can be seen in PEN modified samples also. This is possibly due to a greater extent of methylene groups, phenolic groups and hydrophobic siloxane molecues .

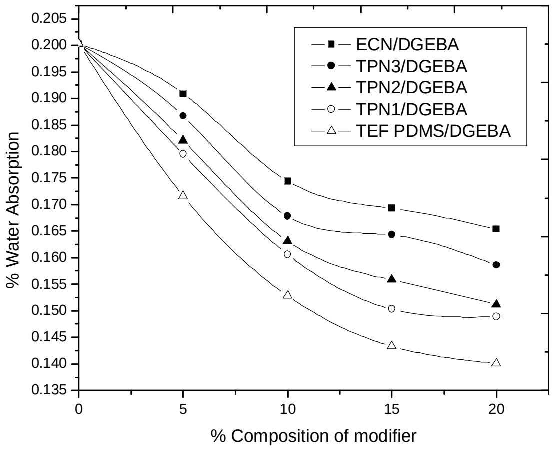
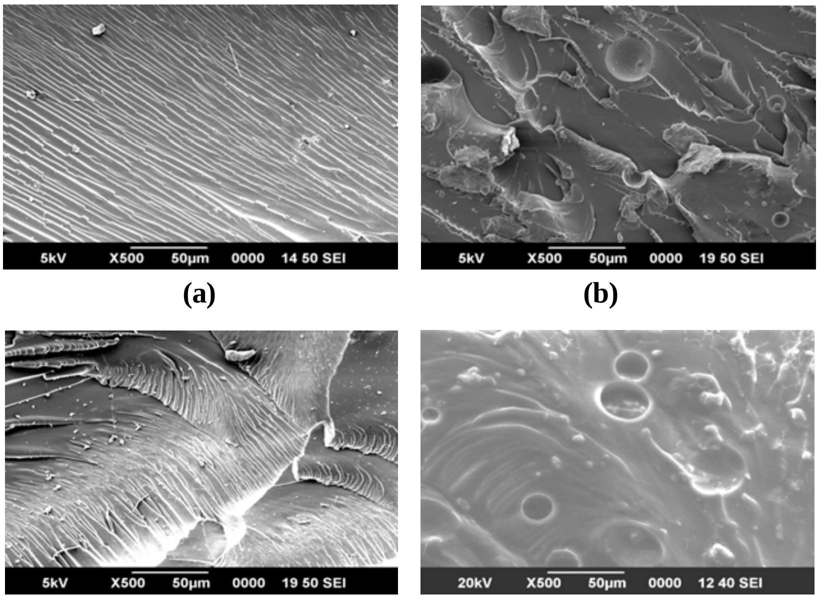


Fig. 4.32. Water absorption of modified resin Vs TPN concentration

iv. Morphological studies

Scanning electron micrographs of NEAT DGEBA, p-ECN modified, PEF PDMS modified and PEN modified epoxy resin fractured at low deformation are shown in Fig. 4.33. 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.



(a) **(b)**

(c) **(d)**

Fig. 4.33 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/PEF PDMS50 c)DGEBA/pECN d) DGEBA/PEN

The fracture surface shows furrows and cavitation in the case of PEF PDMS/DGEBA. (b). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. Referring to pECN modified epoxy (c), 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. Micrograph (d) representing epoxy/PEN blend is characterised by shallow cavities as well as non-uniform ridges. The holes in the stress-whitened regions presumably result from dilation and rupture of siloxane particles .These features point to the improved toughness and load bearing characteristics of modified resin.

The addition of PEF PDMS to neat DGEBA slightly reduces tensile strength but improves the thermal and impact properties. p-ECN can improve the mechanical properties without much deterioration in thermal properties. So addition of PEN (mixture of p-ECN and PEF PDMS) to DGEBA can lead to improvement in mechanical properties, thermal properties and water resistance.

4.3.6 Ageing studies on epoxy resin modified by a mixture of p-ECN and PEF PDMS50

Three 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 %), DGEBA/PEF PDMS blend (10wt %) and DGEBA/PEN blend (15 wt%) were aged in a temperature controlled air oven kept at 100 ^{0}C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties and water absorption

i. Tensile properties

The effect of variation of tensile strength with ageing time is shown in Fig.4.34 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 28% in the case of DGEBA/p-ECN, 24.7% in DGEBA/PEF PDMS but only 24.6% in DGEBA/PEN blend.

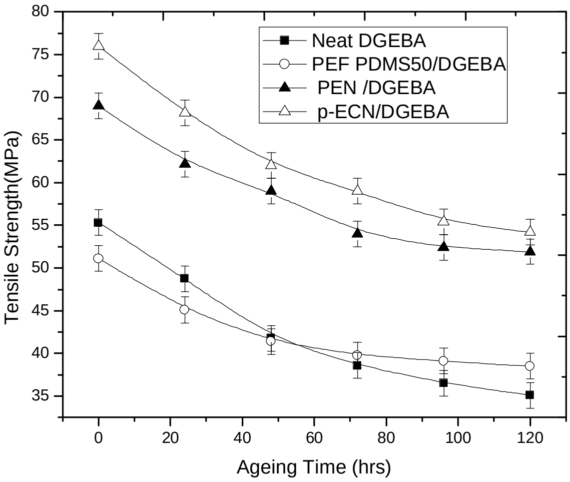


Fig. 4.34. Tensile strength of modified resin Vs ageing time

Fig.4.35 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. After ageing for 120 hrs the neat resin shows a reduction of 45.5 % in elongation while the reduction is 18% in the case of DGEBA/PEF PDMS, 23% in DGEBA/p-ECN and 20% in DGEBA/PEN blends.

The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 4.36. 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 and DGEBA/PEF PDMS shows a reduction of 18%, the p-ECN blend shows a reduction of 31% and PEN modified resins shows a reduction of 21%. This suggests the superiority of siloxane resins in improving the ageing characteristics.

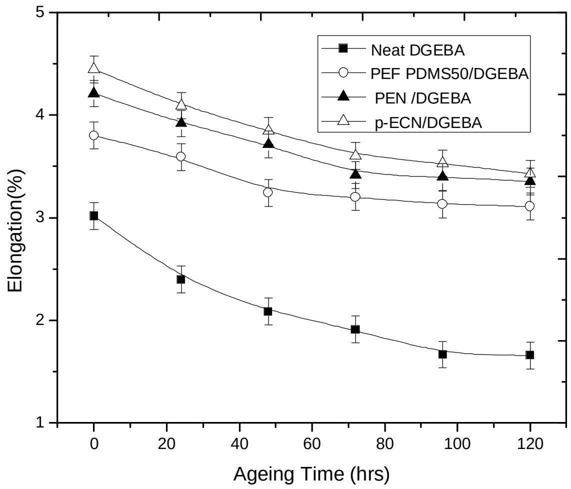


Fig. 4.35 Elongation at break of modified resin Vs ageing time

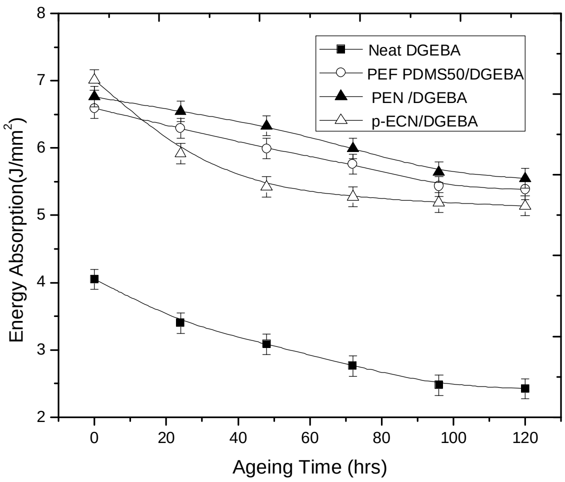


Fig. 4.36 Energy absorbed (to break) of modified resin Vs ageing time

The variation in impact strength of the modified resin during ageing is given in Fig.4.37. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However, the extent of decrease is less in the blends (PEF PDMS50/DGEBA (21%), p-ECN/DGEBA (26.4%) and PEN/DGEBA (20.2%)) compared to the unmodified sample (33%) This confirms the ability of PEF PDMS to improve the ageing properties.

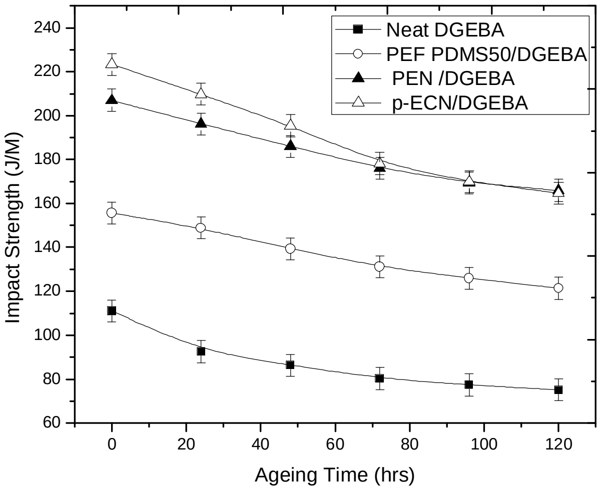


Fig. 4.37. Impact strength of modified resin Vs ageing time

ii. Water absorption

DGEBA/p-ECN, PEF PDMS/DGEBA and DGEBA/PEN blends show better water resistance (Fig.4.38) than neat DGEBA resin after ageing. This is also attributable to additional cross-linking accompanying the ageing process.

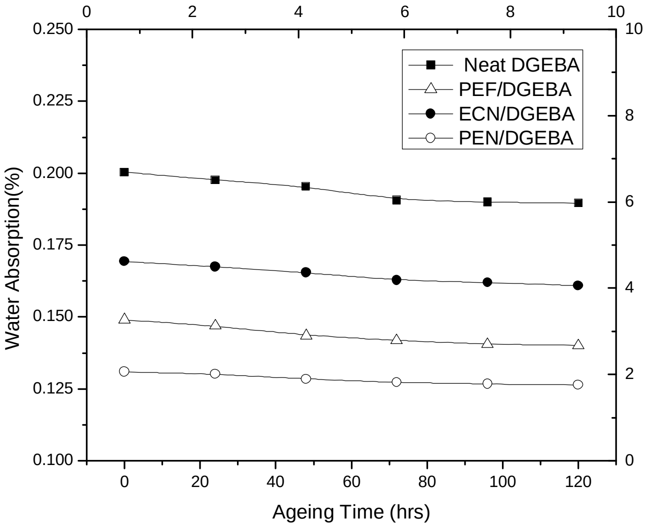


Fig. 4.38. Water absorption of modified resin Vs ageing time

The study reveals that modification with PEN (a mixture of p-ECN and PEF PDMS) can improve the ageing properties of neat DGEBA. This modifier has better water resistance than the neat resin.

4.4 Conclusions

Cardanol as an agro-byproduct has the advantages of low cost and renewable supply. Epoxidized cardanol can be used as a good cost effective modifier but it somewhat reduces water resistance and thermal properties somewhat. Addition of a mixture of pECN and EC to DGEBA can considerably improve water resistance and thermal properties along with mechanical properties. So a mixture of EC and p-ECN can be used as a cost effective modifier. It also improves the ageing properties of DGEBA.

Modification of DGEBA with siloxanes (TEF PDMS and PEF PDMS) improves the water resistance, impact strength and marginally, the thermal properties with slight reduction in tensile strength. Addition of a mixture of p-ECN and siloxane shows improvement in tensile properties, impact strength, thermal properties and water resistance.

Ageing studies show that addition of both siloxanes(TEF PDMS and PEF PDMS) improve thermal ageing. Siloxane modified samples show only slight reduction in tensile properties and impact strength when compared to neat DGEBA and p-ECN modified DGEBA samples.

P-ECN improves the mechanical properties. Siloxanes, in general, improve the thermal properties, water resistance with slight reduction in tensile strength. Also, siloxanes can considerably improve the ageing characteristics. So a mixture of p-ECN with siloxanes(TEF PDMS and PEF PDMS) improve mechanical properties, thermal properties, water resistance with improvement in ageing characteristics

References

[1] K.J. Saunders., *Organic Polymer Chemistry,* Chapter 16, p-380-390 Chapman and Hall, London (1976).

[2] J.F. Gabriel, *Org.Coat.Plast.Chem*.,43, 545(1980).

[3] Blends of epoxy and epoxidised novolac resins, K. P. Unnikrishnan and Eby Thomas Thachil,. *Journal of Elastomers and Plastics*, Vol.37, No. 4, 347-359, 2005.

[4] Wassermann, and Dawson, C.R. Ind. Eng.Chem., 37: 396, (1945).

[5] Carraher, C.E and Sperling, l.H. Polymer applications of Renewable Resource Materials, Plenum press, NewYork. (1981).

[6] Roy, S.S Kundu, A.K. MaMaili, S.. J.Applied Polymer Sci., 36: 1283. (1988).

[7] Manjula, S. Sudha, J.D Bera, S.C. Pillai, C.K.S ; J. Applied polymer Sci., 30: 1767(1985).

[8] Crespy A, Caze C, Loucheux C. Synthesis of macromolecular coupling agents and binders J Appl Polym Sci 1992;44:2061.

[9] Le Huy HM, Bellenger V, Verdu J. Polym Degrad Stab 1993;41:149.

[10] Crivello JV, Bi DS. J Polym Sci: Polym Chem 1993;31:3109.

[11] Crivello JV, Bi DS. J Polym Sci: Polym Chem 1993;31:3121.

[12] Epoxy resins modified with reactive low molecular weight siloxanes *European Polymer Journal, Volume 48, Issue 4, April 2012, Pages 769-773*Piotr Murias, Hieronim Maciejewski, Henryk Galina.

[13] Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. J. Org. Chem.1999, 64, 2494-2499.

[14] M.L. Arias, P.M. Frontini and R.J.J. Williams, *Polymer,* 44, 1537 (2003).

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Chapter 5

GLASS REINFORCED EPOXY

Contents

5.1 Introduction

The effect of matrix toughening on the mechanical properties of glass-reinforced composites is discussed in this chapter. Glass reinforced laminates made of modified as well as unmodified epoxy resin were prepared using chopped strand mat and woven roving mat and mechanical properties such as tensile strength, surface hardness, water absorption and impact strength were compared. The fracture behaviour was studied by SEM.

Fibre reinforced plastics:

Fibre reinforced plastics have polymer as matrix and fibre as reinforcement. Thermosets have historically been the principal matrix material for FRPs. Epoxy resins; in particular, have been used extensively in this field due to their excellent adhesion, strength, low shrinkage, corrosion resistance, processing versatility and many other attractive properties. Glass fiber reinforced composites perform well only when stress can transfer efficiently across the interphase between the fibers and matrix. In order to improve fiber wettability or to enhance affinity between fiber and matrix, modification of the fiber surface can be done by coating the fiber with: (a) a silane with reactive end groups, (b) a rubber emulsion or (c) a solution of different polymers such as polyurethane, polystyrene, etc. [1,2]. Today, glass fibers are commonly treated with silane coupling agents (SCA).

In 1992 Kaushal [3] studied the flexural behavior of glass/epoxy composites toughened by a liquid rubber. In this investigation, E-glass fabric reinforced epoxy matrix resin was modified by amine terminated copolymer of butadiene and acrylonitrile (ARBN). It was reported that rubber toughening by ARBN also resulted in flexibility improvement. Bussi et al. [4] in 1994 studied the flexural properties of blends of DGEBA based epoxy resin and hydroxyl terminated, internally epoxidized polybutadiene rubber. In order to improve flexibility and also toughness, the epoxidized polybutadiene rubber was prereacted with excess diepoxide to achieve better bonding between the rubber particles and epoxy matrix. Then, Tong and coworkers [5] used polysiloxanes as flexibilizer for epoxy resin. They reported that flexibility was increased by increasing molecular weight and concentration, and decreasing particle size of the polisiloxane particles.

In 1995 Matheswaran and Padmanabhan [6] worked on specimens of DGEBA type epoxy resin matrix reinforced with glass fiber fabric. They indicated that addition of plastisol and polycarbonate independently to the glass fiber-epoxy system increases flexibility and also toughness. Amine terminated polysulfone (ATPS) was used by Ratna et al. [7] in 1997 as a modifier for DGEBA type epoxy resin. They observed that ATPS forms a compatible blend with epoxy, and due to the presence of the flexible ether and sulfone linkages, ATPS increased flexibility of the epoxy matrix. Shih et al. [8] in 1999 used a synthesized polydimethylsiloxane containing isocyanate group to improve the flexibility of o-cresol formaldehyde novalac epoxy resin. They showed that modified epoxy resin showed flexibility improvement with increasing modifier content. Nigam et al. [9] also reported that if epoxy cresol novalac resin was modified with carboxyl terminated copolymer of butadiene and acrylonitrile (CTBN), then flexibility of the system could be improved due to the possible chemical interaction between the oxirane ring of epoxy and carboxyl function of the CTBN.

Barcia et al [10] used hydroxyl terminated polybutadiene (HTPB) to modify the surface of carbon fibers. They observed that HTPB formed a flexible interface between carbon fibers and epoxy matrix increasing the toughness and flexibility of the system. In 2001, Ozturk, Kaynak and Tincer [11,12] used HTPB and a special SCA to improve flexural properties of a DGEBA type epoxy resin. It was shown that by using certain orders of mixing of constituents flexibility could be improved.

5.2. Experimental

5.2.1. Materials

Chopped strand mat (CSM-Binani-IS:11551/BS:3496, 450g/m^2) and woven roving mat (WRM- Binani-IS:11273/BS:3749, 610g/m^2) were supplied by M/s Sharon Engineering Enterprises, Cochin. Epoxy resin GY 250(WPE 188) and amine hardener HY951 were procured from Petro Araldite Pvt. Ltd. Chennai. TEF PDMS [Terminal epoxy functional PDMS](Section 3.2.2), PEF PDMS [Pendant epoxy functional PDMS]

(Section 3.2.3), epoxidized cardanol (EC) (Section 2.2.4) and epoxidized p-cresol novolac(p-ECN)(Section 2.2.4) were synthesized in the laboratory.

5.2.2 Preparation and testing of glass reinforced laminates employing different resin systems

Initially, glass reinforced laminates (3 mm thickness) were prepared using unmodified as well as toughened resins by the hand lay-up method. The inside surface of two iron plates (30 cm x 30 cm) were coated with a releasing agent (wax) and the catalysed resin was applied on one plate. Sufficient glass mats, CSM or WRM were placed and impregnated with the resin using a brush one after another. The laminate was consolidated to give volume fractions of 35-40%. The second plate was kept over this and clamped with a set of C-clamps. Curing was done at room temperature for 24 hrs, followed by post curing at 100°C for 4 hrs.

Specimens used for testing were cut from the glass-reinforced laminates using a diamond tipped jig saw. The tensile properties (ASTM D 638) were tested on a Shimadzu Autograph Universal Testing Machine. The tensile specimens were 150 mm long, 25.4 mm wide and 3 mm thick. The specimens were stretched until failure occurred. The crosshead speed of the machine was 5 mm/min. Impact tests were conducted on an Izod Impact tester according to ASTM D 256. The samples were 63.5mm long, 12.7 mm wide and 3 mm thick. Water absorption of glass-reinforced laminates was determined as per ASTM D 570-98. The specimen dimensions were 76.2 mm length, 25.4 mm wide and 3 mm thick. The samples were immersed in distilled water for 24 hrs at 25°C.

5.2.3 Modification by reactive blending using epoxy novolac and epoxidised cardanol

Glass reinforced laminates were prepared using reactive blends of DGEBA and phenolic resins such as EPN, ECN and epoxy cardanol (EC). These reactive blends were prepared by taking optimum concentrations (15 wt %) each of EPN-3 (Section 2.2.5), ECN (Section 2.2.7) and EC (Section 2.2.9). The test samples were cut and tested.

5.2.4 Modification by reactive blending with epoxy functional siloxanes

Glass reinforced laminates were prepared using both unmodified and siloxane modified commercial DGEBA epoxy resins. The elastomers used for blending were TEF PDMS (5%) and PEF PDMS50 (10%) (Sections 3.2.7 & 3.2.9) The samples were cut and tested.

5.2.5 Modification by reactive blending with a mixture of P-ECN and EC

Glass reinforced laminates were prepared using both unmodified and modified commercial DGEBA epoxy resins. The mixture used for blending were EEN (a mixture of ECN and EC)(15%) (Sections 4.2.2) The samples were cut and tested and properties were compared with p-ECN modified and EC modified DGEBA laminates.

5.2.6 Modification by reactive blending with a mixture of P-ECN and TEF PDMS

Glass reinforced laminates were prepared using both unmodified and two component modified commercial DGEBA epoxy resins. The mixture used for blending was TPN(a mixture of TEF PDMS and ECN) (15%).(Sections 4.2.4) The samples were cut and tested and properties were compared with p-ECN modified and TEF PDMS modified DGEBA laminates.

5.2.7 Modification by reactive blending with a mixture of P-ECN and PEF PDMS50

Glass reinforced laminates were prepared using both unmodified and two component modified commercial DGEBA epoxy resins. The mixture used for blending was PEN (a mixture of PEF PDMS50 and ECN) (15%) (Sections 4.2.6) The samples were cut and tested and properties were compared with p-ECN modified and PEF PDMS modified DGEBA laminates.

5.3 Results and discussion

5.3.1 Modification by reactive blending with epoxy novolacs and epoxidised cardanol

i. Mechanical properties

Tensile strength of glass-reinforced resin modified by15%EPN and 15% p-ECN is superior to those from neat and EC modified laminates. This can be attributed to a greater strengthening / toughening of matrix at this composition. In the case of un-reinforced samples also the optimal concentration is 15 weight %EPN and ECN (Section 2.3.4) Enhanced compatibility and greater cross-linking are responsible for greater strengthening of the matrix. This may lead to an efficient load transfer between fibre and matrix by preventing cracking of the interface. The EC modified laminate gives only a marginal increase in tensile strength. This is because the matrix resin contains relatively shorter chains due to the presence of mono functional EC.

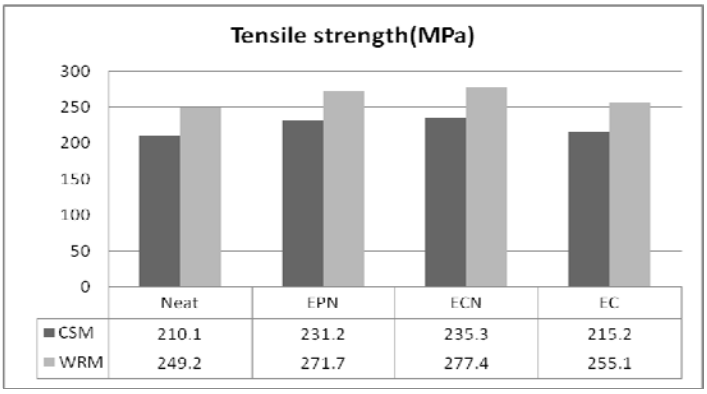


Fig. 5.1. Tensile strength of epoxy novolac modified DGEBA composites

EPN improves the energy absorption by 15-16% and ECN improves the energy absorption by 18-20%. The enhanced energy absorption of reinforced modified resin can be attributed to capacity for special rearrangement and more effective load transfer across the interface .In the case of EPN and ECN, enhanced compatibility and greater cross-linking are responsible for greater strengthening of the matrix. In the case of EC modified laminates, the matrix resin contains relatively shorter chains due to the monofunctionality of EC. Thus, for EC modified laminate, improvement in energy absorption is only 6-12%.

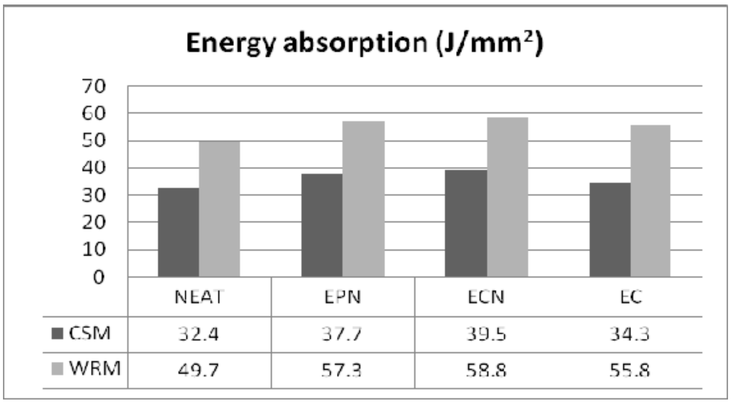


Fig. 5.2. Energy absorption of epoxy novolac modified DGEBA Composites

Modified resins are found to impart greater impact strength to the glass reinforced laminates (Fig 5.3). EPN modification improves the impact strength of epoxy laminate by 7-7.5% , ECN modification by 9-10% and EC modification by 2%.This is the result of effective cross-linking and chain extension taking place in the blend by virtue of the relatively higher epoxy content in EPN and ECN.

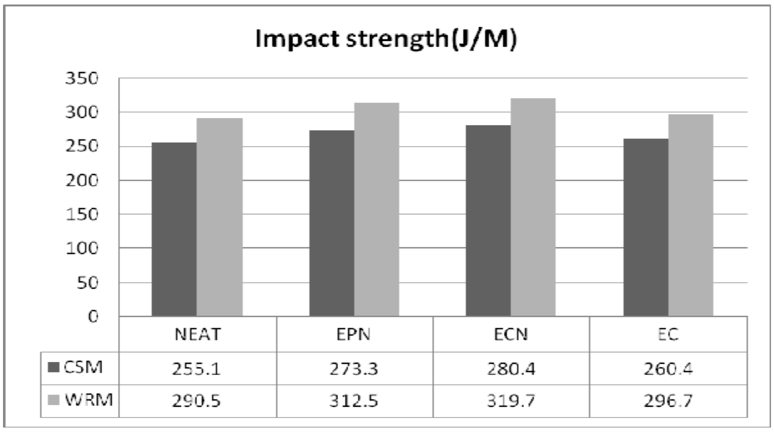


Fig. 5.3. Impact strenth of epoxy novolac modified DGEBA Composites

ii. Surface hardness and water absorption

The surface hardness of EPN and ECN modified laminate is more than that of the un-modified DGEBA laminate. Hardness decreases for both CSM and WRM in the case of EC-modified laminate. This can be due to a higher degree of flexibility and the creation of free volumes within the polymer. Water absorption is high for EC modified laminates due to the presence of relatively more hydrophilic groups in the form of methylols and phenolic hydroxyl groups. However, the EPN and ECN modified laminate is considerably more water resistant due to the presence of more aromatic rings.

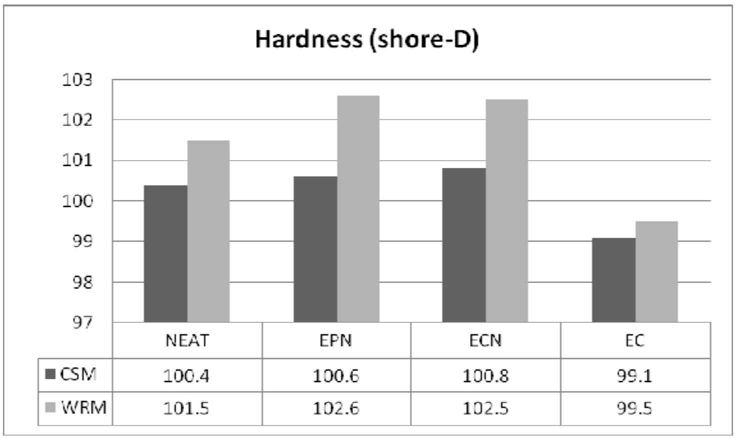


Fig 5.4 Surface hardness of epoxy novolac modified DGEBA composites

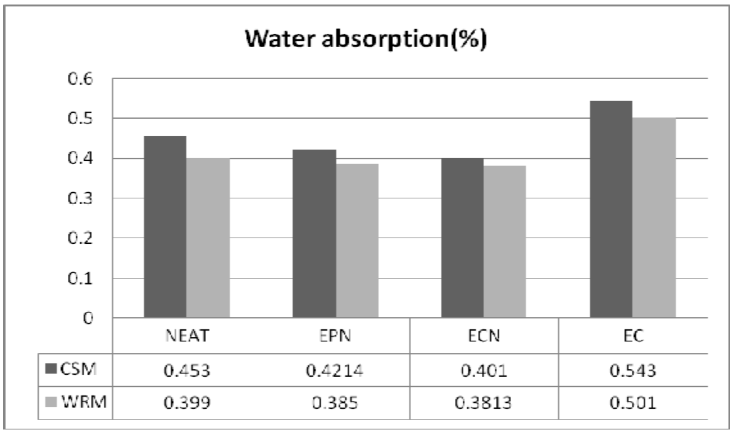
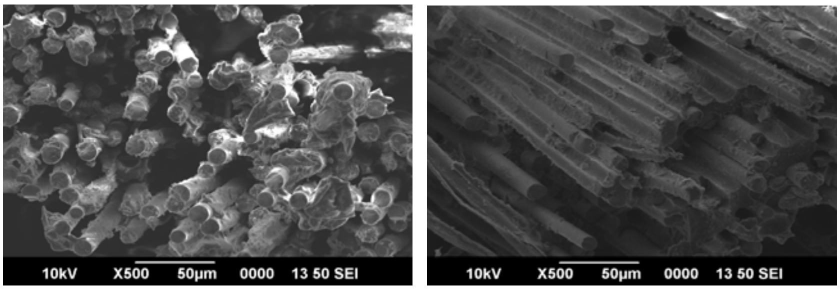


Fig5.5 Water absorption of epoxy novolac modified DGEBA Composites

iii. Morphological studies

Scanning electron micrographs of unmodified and ECN modified epoxy-glass reinforced laminates fractured at low deformation rate are shown in Fig. 5.6. Referring to the micrograph (a) the neat resin has poor adhesion with the fibres. The micrograph of ECN modified laminate (b) shows moderate adhesion of the modified matrix and the fibre ends are only lightly covered with the polymer.



(a) (b)

Fig. 5.6. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA and (b) DGEBA/ ECN

5.3.2 Reinforced laminates from siloxane modified epoxy resin

This section deals with laminates made from commercial DGEBA resin containing 5weight % of terminal epoxy functional PDMS (TEF PDMS), and 10% pendant epoxy functional PDMS (PEF PDMS50).

i. Mechanical properties

Tensile strength of glass-reinforced modified epoxy (12-13% improvement for TEF PDMS modified and 16-18% for PEF PDMS modified DGEBA laminates) is better than that of reinforced un-modified epoxy resin. This can be attributed to the strengthening of the interface by the siloxane modified matrix. The toughening of the matrix-fibre interface leads to a more efficient load transfer between fibre and matrix. Addition of both siloxanes to DGEBA resin reduces the tensile properties in nonreinforced samples, but in fibre reinforced laminates siloxanes modified samples shows greater tensile strength than neat resin. This may be due to enhanced interfacial adhesion between siloxanes and the glass fibre.

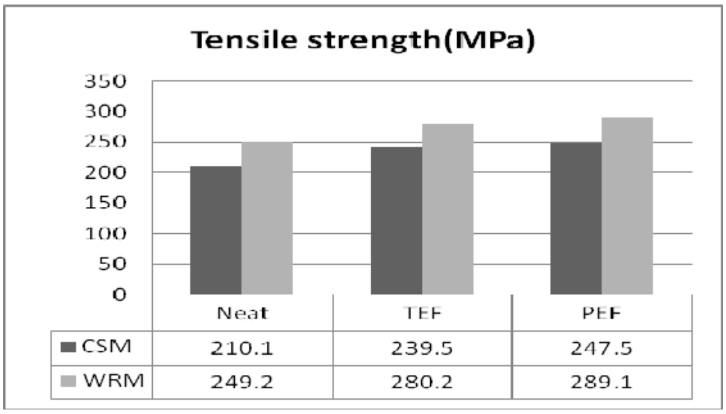


Fig. 5.7. Tensile strength of siloxane modified DGEBA Composites

TEF PDMS improves the energy absorption by 25-37% and PEF PDMS50 improves the energy absorption by 28-49%. The enhanced energy absorption of reinforced siloxane modified resin(Fig 5.8) can be attributed to a greater level of flexibility and more effective load transfer across the interface [13]. Greater energy dissipation by the soft siloxane segments also improves the energy absorption. It is known that reactive liquid rubbers enhance the bonding at the interface and crack growth is delayed [14].

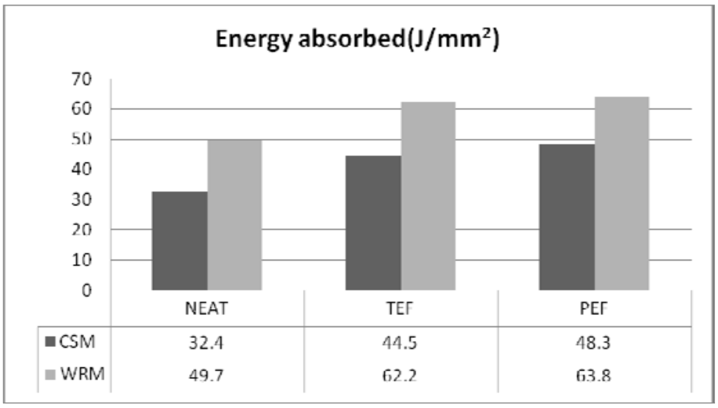


Fig 5.8 Energy Absorption of siloxane modified DGEBA composite

Siloxane modified laminates are found to impart greater impact strength to the glass reinforced laminates (Fig 5.9). TEF PDMS modification improves the impact strength of epoxy laminate by 11-12.6 % and PEF PDMS improves by11-13%. The increase in impact strength is due to the energy dissipation by the soft siloxane segments occurring during the propagation of the fracture.

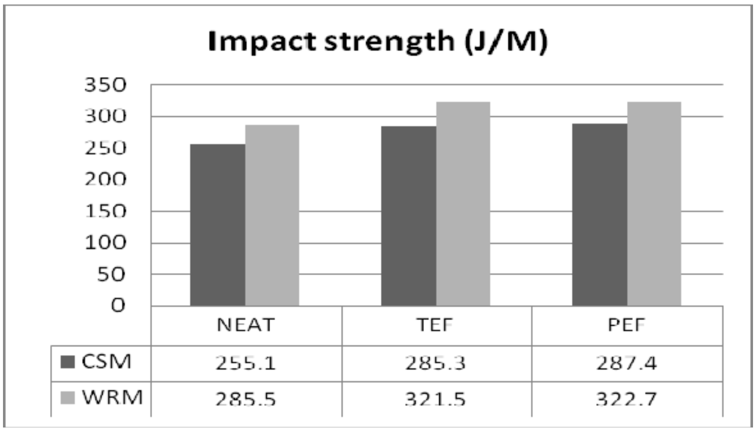


Fig 5.9 Impact strength of siloxane modified DGEBA composite

iii. Surface hardness and water absorption

Surface hardness values of both siloxane(TEF PDMS and PEF PDMS50) modified laminates are lower than that for unmodified samples (Fig. 5.10). This can be due to a higher degree of flexibility and the creation of free volumes within the polymer. Water absorption by siloxane modified samples during 24 hrs immersion is less than (Fig.5.11) those by unmodified reinforced samples. This is due to the presence of hydrophobic siloxane particles

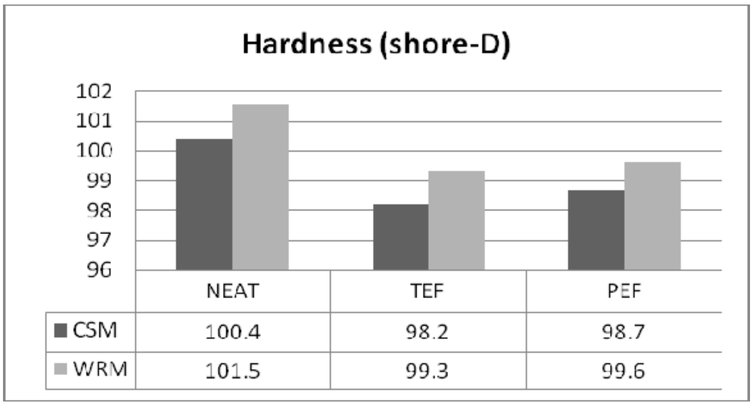


Fig. 5.10 Surface hardness of siloxane modified DGEBA composite

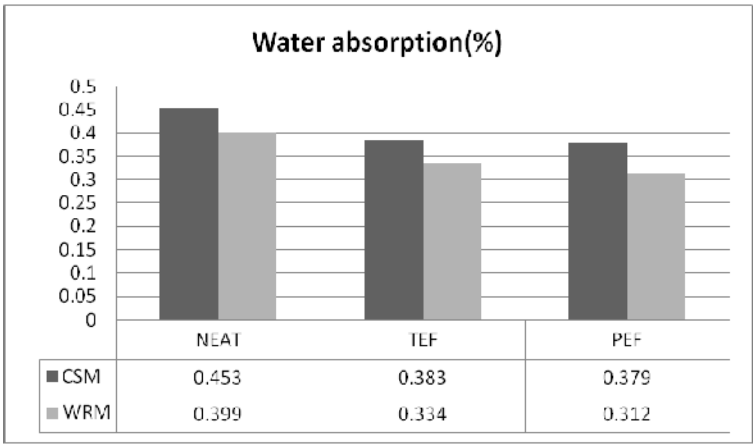
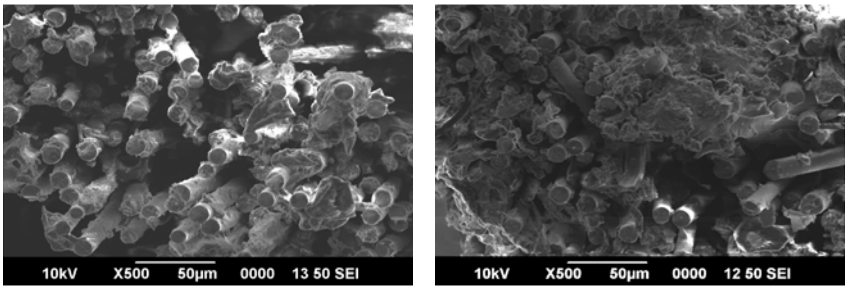


Fig 5.11 Water absorption by siloxane modified DGEBA composite

iii) Morphological studies

Scanning electron micrographs of unmodified and siloxane modified epoxy glass reinforced laminates fractured at low deformation rate are shown in Fig.5.12 Referring to the micrograph (a) the neat resin has poor adhesion to the fibres. The Micrograph of PEF PDMS modified laminate (b) shows good adhesion of the siloxane modified matrix and the fibre ends are still covered with the polymer. Fig. 5.12 (b) shows that some siloxane domains acted as coupling agent and the resin adhered to the glass fiber surfaces. Therefore, the siloxane also increased the interaction at the fiber/epoxy matrix interface.



(a) **(b)**

Fig. 5.12. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA (b) DGEBA/ PEF PDMS

5.3.3 Modification by reactive blending with mixture of p-ECN and epoxidised cardanol (EEN)

i. Mechanical properties

Tensile strength of glass-reinforced DGEBA modified by 15% EEN, 10%EC, 15% ECN are shown in Fig. 5.13. Epoxidised cardanol can be used as a good low cost modifier for laminates, but the improvements in properties are very little. The EC modified laminate gives only a marginal increase in tensile strength of only 1-2%. This is because the matrix resin contains relatively shorter chains due to the monofunctional EC. But if we use a mixture of p-ECN and EC the tensile strength can be improved.

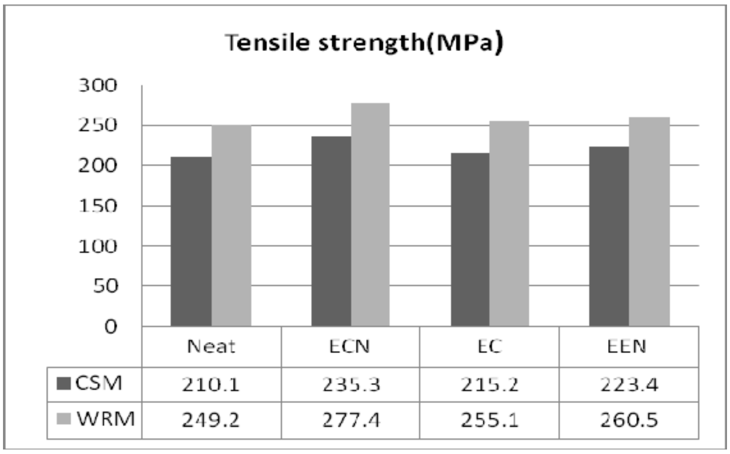


Fig. 5.13. Tensile strength of EC, EEN, ECN modified DGEBA composite

In the case of energy absorption the reinforced EC modified resin shows slight improvement (6%) Fig (5.14). By ECN modification we can improve the energy absorption of DGEBA reinforced laminates by 21%. Epoxidised cardanol can be used as a good low cost modifier for laminates, but the improvements in properties are not much. By using EEN (a mixture of ECN and EC) we can improve the energy absorption up to 20%.

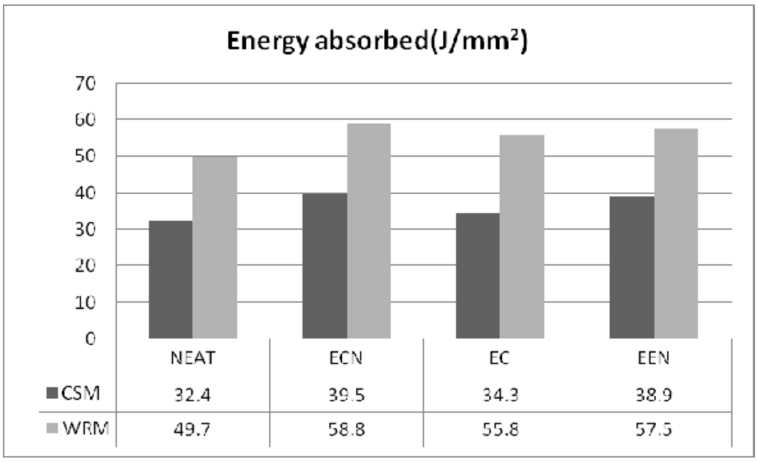
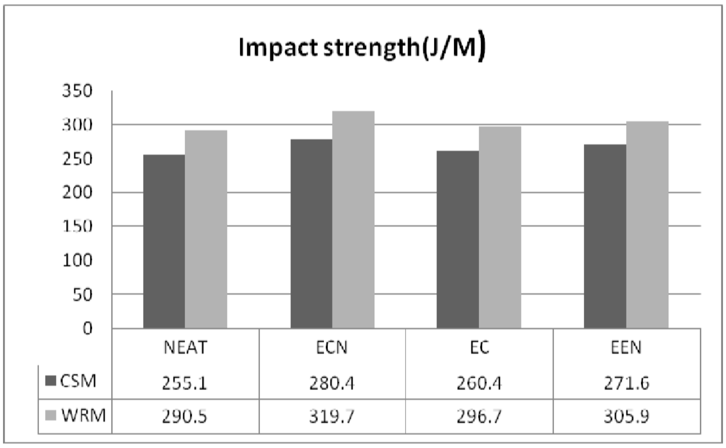


Fig. 5.14. Energy absorption by EEN, EC, ECN modified DGEBA composites

ECN modified resins are found to impart greater impact strength to the glass reinforced laminates (Fig 5.15.) This is the result of effective cross-linking and chain extension taking place in the blend by virtue of the relatively higher epoxy content in ECN. But by EC modification improvement in impact strength is only upto 2%. By using EEN (a mixture of ECN and EC) we can further improve the impact strength value.



	NEAT	ECN	EC	EEN
■ CSM	255.1	280.4	260.4	271.6
■ WRM	290.5	319.7	296.7	305.9

Fig. 5.15. Impact strength of EEN, EC, ECN modified DGEBA composites

iii. Surface hardness and water absorption

Hardness decreases for both CSM and WRM in the case of EC-modified laminate. But the surface hardness of EEN modified laminate is more than that of the un-modified DGEBA laminate. Water absorption is high for EC modified laminates due to the presence of relatively more hydrophilic groups in the form of methylols and phenolic hydroxyl groups. However, the EEN modified laminate is considerably water resistant.

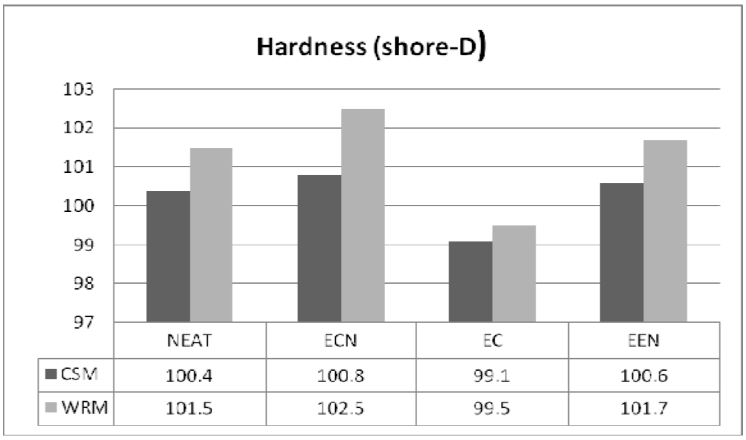


Fig. 5.16.Surface hardness of EEN, EC, ECN modified DGEBA composites

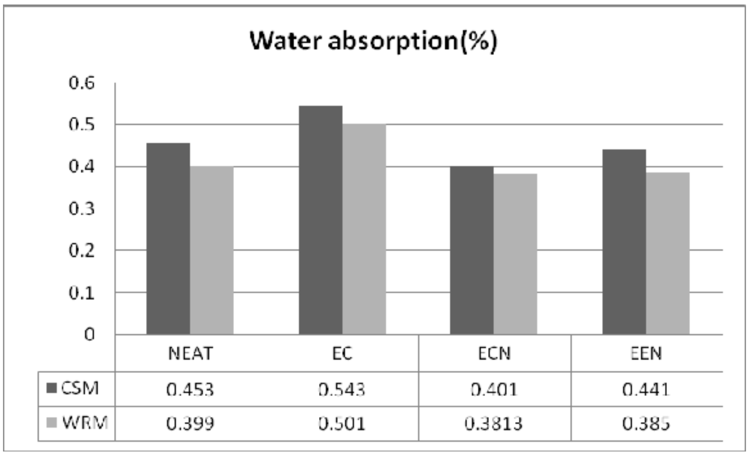
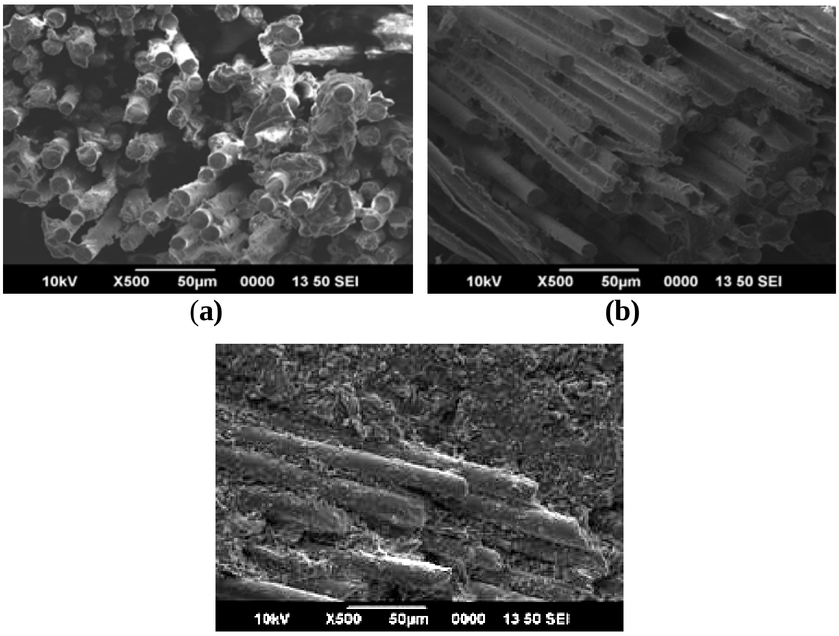


Fig. 5.17. Water Absorption of EEN, EC, ECN modified DGEBA composites

iii Morphological studies

Scanning electron micrographs of unmodified EEN, ECN modified epoxy-glass reinforced laminates fractured at low deformation rate are shown in Fig. 5.18. Referring to the Micrograph (a) the neat resin has poor adhesion with the fibres. The micrograph of ECN and EEN modified laminates (b and c) shows moderate adhesion of the modified matrix and the fibre ends are only lightly covered with the polymer.



(a) (b)

(c)

Fig. 5.18. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA and (b) DGEBA/ ECN (c) DGEBA/EEN

5.3.4 Modification by blending with mixture of p-ECN and TEF PDMS (TPN)

i. Mechanical properties

Tensile strength of glass-reinforced TEF PDMS and TPN modified resins are better than that of reinforced un-modified epoxy resin.TEF PDMS improves the tensile strength by 12-14% in reinforced DGEBA laminates. This can be attributed to the strengthening of the interface by the siloxane modified matrix. The toughening of the matrix-fibre interface leads to a more efficient load transfer between fibre and matrix. Addition of TEF PDMS to unreinforced DGEBA resin reduces the tensile properties, but in fibre reinforced laminates siloxane modified samples show greater tensile strength than neat resin.

Improvement in tensile strength of ECN modified reinforced samples (11-12%) is less than that of TEF PDMS modified samples. Addition of TEF PDMS generally reduces the tensile strength of DGEBA resin, but when it comes to FRP, siloxanes slightly improve the tensile strength value. Siloxane domains act as coupling agent and adhere to the glass fibre surfaces. This increases the interaction at the fiber/epoxy matrix interface. TPN (mixture of TEF PDMS and ECN) modified reinforced laminates showed an improvement of 14-17% in tensile strength which is greater than the TEF PDMS and ECN modified samples. This is because TEF PDMS improves the adhesion between fibre and matrix and ECN improves the touhness of neat DGEBA.

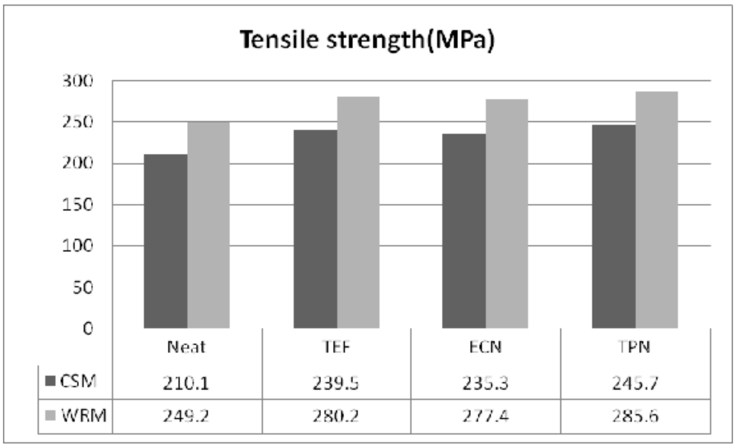


Fig. 5.19. Tensile strength of TPN, ECN and TEF PDMS modified DGEBA composite

Fig 5.20 shows the energy absorption of TPN, ECN and TEF PDMS modified DGEBA composites. The improvement in energy absorption of TPN modified reinforced sample is 28-42%, of TEF PDMS modified sample is 25-37% and of ECN modified sample is 18-20%. The enhanced energy absorption of reinforced modified resin can be attributed to a greater level of flexibility and more effective load transfer across the interface. TEF PDMS modified and TPN (mixture of TEF PDMS and ECN) modified samples show greater energy absorption than neat and ECN modified composite due to the presence of siloxanes. Siloxanes enhance the bonding at the interface and crack growth is delayed.

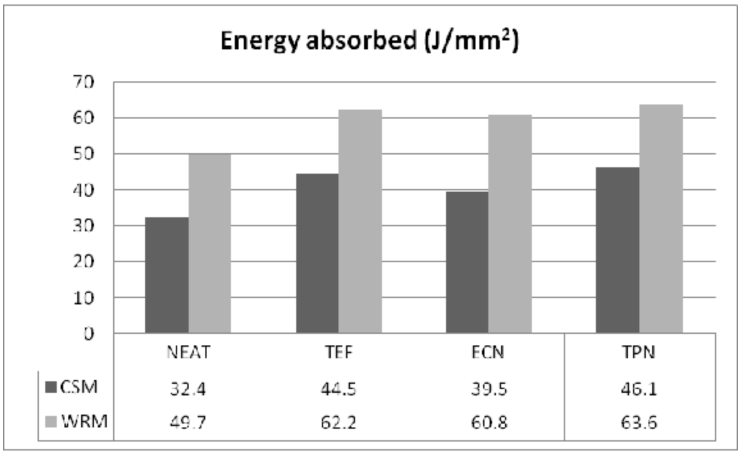


Fig. 5.20. Energy absorption of TPN, ECN and TEF PDMS modified DGEBA composite

TEF PDMS and TPN modified laminates are found to impart greater impact strength to the glass reinforced laminates than unmodified samples (Fig 5.21). The increase in impact strength is due to the energy dissipation by the soft siloxane segments during the propagation of the fracture. For TEF PDMS and TPN modified samples, improvement in impact strength (11-13%) is higher compared to ECN modified laminates (10-11%). This is due to improved adhesion between fibre and matrix due to the presence of TEF PDMS.

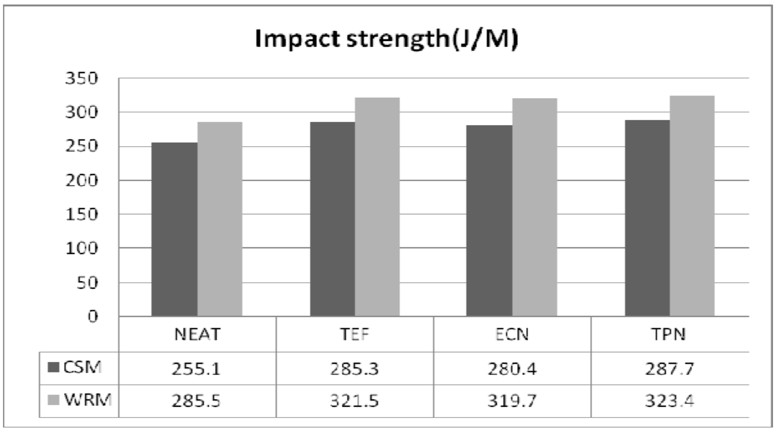


Fig. 5.21. Impact strength of TPN, ECN and TEF PDMS modified DGEBA composite

iii. Surface hardness and water absorption

Surface hardness values are lower than that for unmodified samples and ECN modified samples for TEF PDMS and TPN modified samples. This is due to the poor hardness values of rubbery siloxanes. In the case of water absorption, TEF PDMS and TPN modified reinforced samples show lower values during 24 hrs immersion compared to unmodified reinforced samples and ECN modified samples. This is due to the presence of hydrophobic siloxane particles.

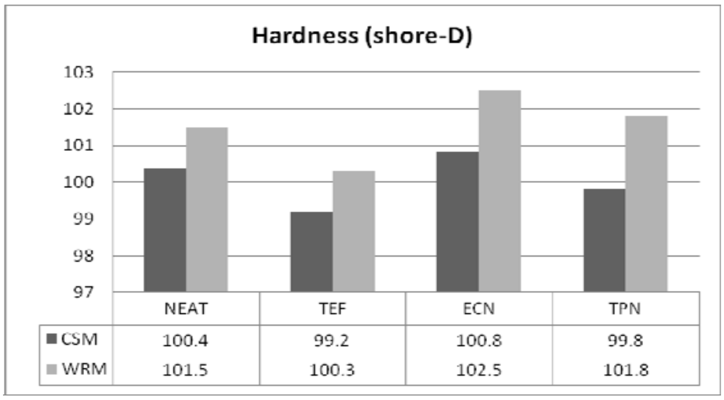


Fig. 5.22. Hardness of TPN, ECN and TEF PDMS modified DGEBA composite

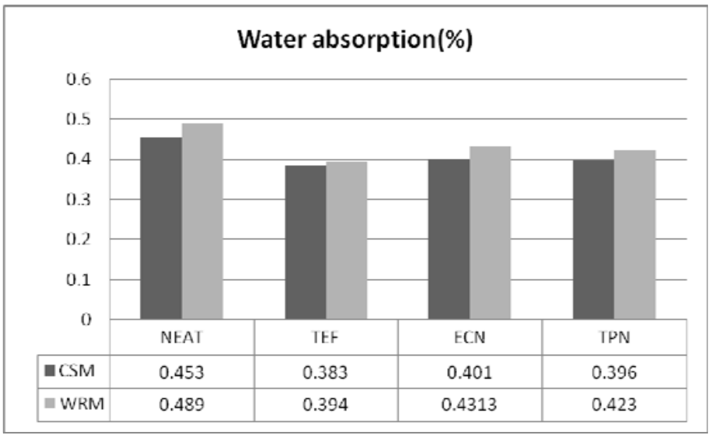
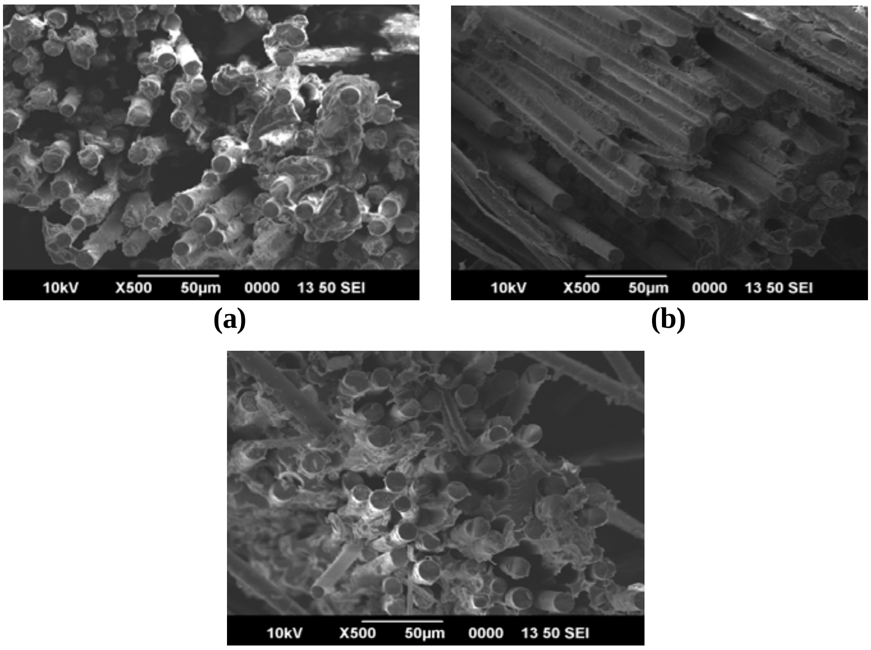


Fig. 5.23. Water absorption of TPN,ECN and TEF PDMS modified DGEBA composite

iii) Morphological studies



(a) **(b)**

(c)

Fig. 5.24. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA (b) DGEBA/ ECN (c) DGEBA/ TPN

Scanning electron micrographs of unmodified and modified epoxy glass reinforced laminates fractured at low deformation rate are shown in Fig.5.24 Referring to the Micrograph (a and b) the neat resin and ECN have poor adhesion to the fibres. But from the Fig 5.24 (c) we can see that the addition of siloxanes improves the adhesion to the fibre. Siloxanes can interact with the glass surface giving rise to greater grafting of the matrix resin with the reinforcing glass.

5.3.5 Modification by blending with mixture of p-ECN and PEF PDMS50 (PEN)

i. Mechanical properties

Tensile strength of glass-reinforced PEF PDMS50 and PEN modified resins are better than that of reinforced un-modified epoxy resin. PEF PDMS improves the tensile strength to 16-18% in reinforced DGEBA laminates. This can be attributed to the strengthening of the interface by the siloxane modified matrix. The toughening of the matrix-fibre interface leads to a more efficient load transfer between fibre and matrix. Addition of PEF PDMS to DGEBA resin reduces the tensile properties somewhat, but in fibre reinforced laminates siloxanes modified samples show greater tensile strength than neat resin. Improvement in tensile strength of ECN modified reinforced samples (11-12%) is less than PEF PDMS modified samples.

Addition of siloxanes generally reduces the tensile strength of DGEBA resin, but when it comes to FRP siloxanes slightly improve the tensile strength values. Siloxane domains act as coupling agent and adhere to the glass fiber surfaces. This increases the interaction at the fiber/epoxy matrix interface. PEN (mixture of PEF PDMS50 and ECN) modified reinforced laminates showed an improvement of 15-19% in tensile strength which is greater than the PEF PDMS and p-ECN modified samples. This may be because PEF PDMS improves the adhesion between fibre and matrix and ECN improves the tensile properties of neat DGEBA.

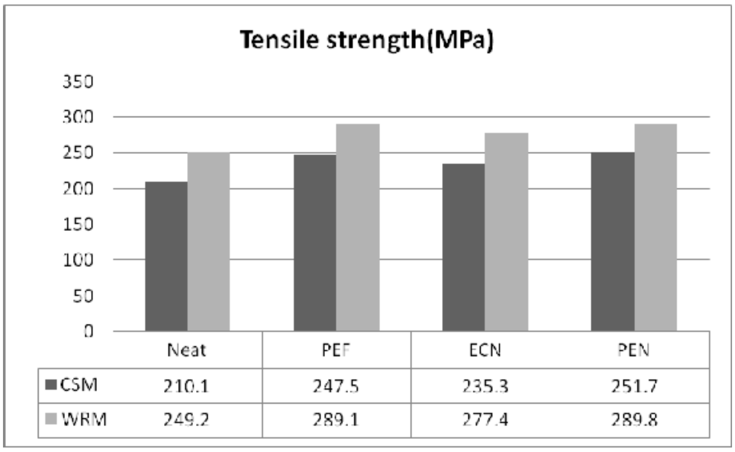


Fig. 5.25. Tensile strength of PEN, ECN and PEF PDMS modified DGEBA composite

The energy absorption of PEN, ECN and PEF PDMS50 modified DGEBA is shown in Fig 5.26. The improvement in energy absorption of PEN modified reinforced sample is 34-56%, that of PEF PDMS modified sample is 28-49% and that of ECN modified sample is 18-20%. The enhanced energy absorption of reinforced modified resin can be attributed to a greater level of flexibility and more effective load transfer across the interface. PEF PDMS modified samples and PEN (mixture of PEF PDMS and ECN) show greater energy absorption than neat and ECN modified composites due to the presence of PEF PDMS. Siloxanes enhance the bonding at the interface and crack growth is delayed.

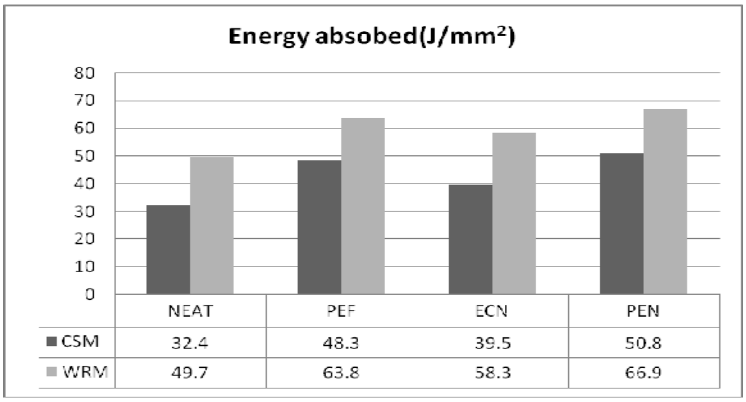


Fig. 5.26. Energy absorption of PEN, ECN and PEF PDMS modified DGEBA composite

PEF PDMS and PEN modified laminates are found to impart greater impact strength to the glass reinforced laminates than unmodified samples (Fig 5.27). The increase in impact strength is due to the energy dissipation by the soft siloxane segments during the propagation of the fracture. For PEF PDMS50 and PEN modified samples, improvement in impact strength (12-14%) is higher compared to ECN modified laminates (10-11%). This may be due to improved adhesion between fibre and matrix due to the presence of siloxane(PEF PDMS50).

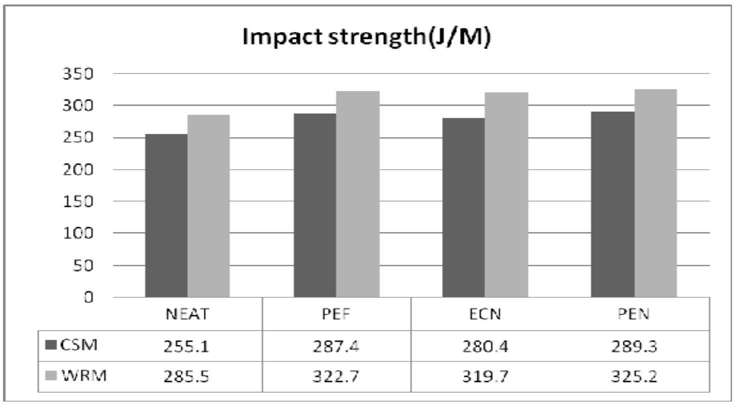
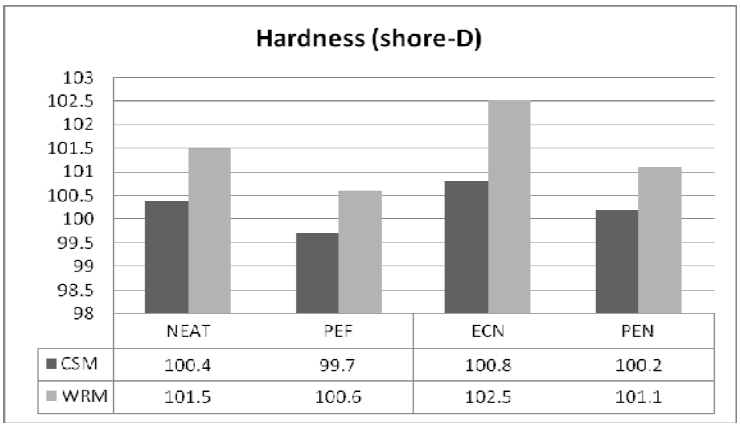


Fig. 5.27. Impact strength of PEN, ECN and PEF PDMS modified DGEBA composite

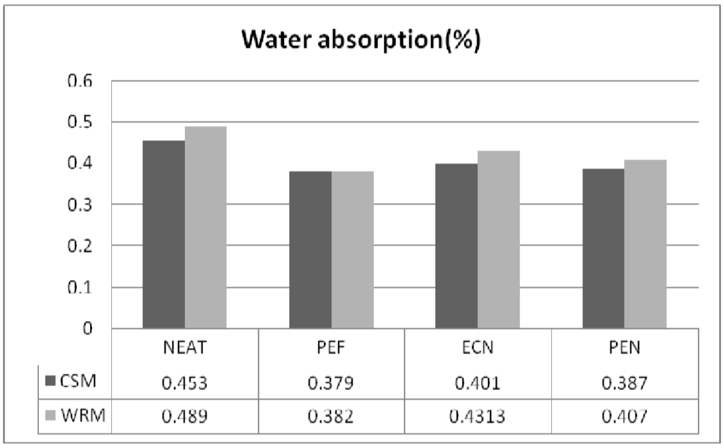
iii. Surface hardness and water absorption

Surface hardness values of PEN, ECN and PEF PDMS modified DGEBA resinforced laminates are shown in Fig 5.28. Surface hardness values of PEF PDMS and PEN modified samples are lower than that for unmodified samples and ECN modified samples. This is due to the poor hardness values of rubbery siloxanes.



	NEAT	PEF	ECN	PEN
■ CSM	100.4	99.7	100.8	100.2
■ WRM	101.5	100.6	102.5	101.1

Fig. 5.28. Hardness of PEN, ECN and PEF PDMS modified DGEBA composite



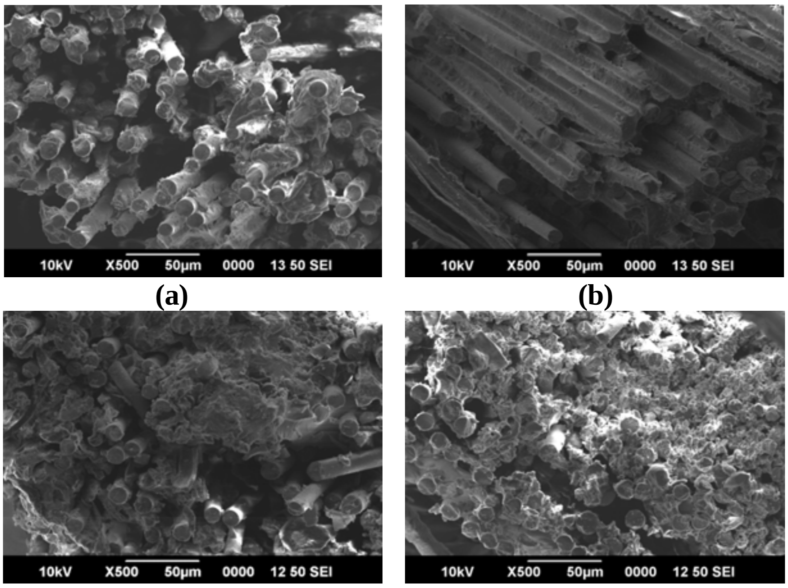
	NEAT	PEF	ECN	PEN
■ CSM	0.453	0.379	0.401	0.387
■ WRM	0.489	0.382	0.4313	0.407

Fig. 5.29. Water absorption of PEN, ECN and PEF PDMS modified DGEBA composite

Water absorption (Fig.5.29) by PEF PDMS and PEN modified reinforced samples during 24 hrs immersion is less than that by unmodified reinforced samples and ECN modified samples. This is due to the presence of hydrophobic siloxane particles.

iii) Morphological studies

Scanning electron micrographs of unmodified and modified epoxy glass reinforced laminates fractured at low deformation rate are shown in Fig.5.30 Referring to the micrographs (a and b), the neat resin and ECN have poor adhesion to the fibres. But from the Fig. 5.30 (c and d) we can see that the addition of PEF PDMS improves the adhesion to the fibre. Siloxanes can interact with the glass surface giving rise to greater grafting of the matrix resin with the reinforcing glass.



(a) (b)

(c) (d)

Fig. 5.30. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA (b) DGEBA/ ECN (c) DGEBA/ PEF PDMS (d) DGEBA/PEN

5.4 Conclusion

Matrix modification is found to increase tensile strength and energy absorption (during failure) of epoxy-glass composites. Among the phenolic modifiers used (EPN, ECN and EC) ECN is found to give the best performance. Addition of siloxanes generally reduces the tensile strength of DGEBA resin, but in the case of FRP both siloxanes(PEF PDMS50 and TEF PDMS) marginally improve the tensile strength values. Siloxane domains act as coupling agents and adhere to the glass fiber surfaces. This increases the interaction at the fiber/epoxy matrix interface. Among siloxanes, PEF PDMS is found to give the better performance due to the presence of a larger number of epoxide groups.

Epoxidised cardanol can be used as a good low cost modifier for laminates, but the improvement in properties are minimal. By using a mixture of ECN and EC (EEN) we can improve the properties. Siloxanes (TEF PDMS and PEF PDMS50) and mixtures (TPN and PEN) show greater energy absorption than neat DGEBA and ECN modified composites due to the presence of siloxanes. Siloxanes enhance the bonding at the interface and crack growth is delayed. Surface hardness values are decreased in siloxane, TPN and PEN modification due to the presence of rubbery siloxane molecules. But siloxanes improve the water resistance.

Reference

[1] Hirai Y, Hamada H, Kim JK. Compos Sci Technol 1998;58:91–104.

[2] Cevdet K, Aslihan A, Teoman T, Polymer 44 (2003) 2433–2439.

[3] Kaushal S. J Mater Sci Lett 1992;11:86–8.

[4] Bussi P, Ishida H. J Appl Polym Sci 1994;53:441–54.

[5] Tong J, Bai R, Zou Y, Pan C, Ichimura S. J Appl Polym Sci 1994;52:1373–81.

[6] Matheswaran M, Padmanabhan K. J Mater Sci Lett 1995;14:951–4.

[7] Ratna D, Patri M, Chakraborty BC, Deb PC. J Appl Polym Sci 1997; 65:901–7.

[8] Shih WC, Ma CC, Yang JC, Chen HC. J Appl Polym Sci 1999;73: 2739–47.

[9] Nigam V, Setua DK, Mathur GN. Polym Engng Sci 1999;39:1425–32.

[10] Barcia FL, Soares BG, Gorelova M, Cid JA. J Appl Polym Sci 1999;74:1424–31.

[11] Ozturk A, Kaynak C, Tincer T. Eur Polym J 2001;37(12):2353–63.

[12] Kaynak C, Ozturk A, Tincer T. Polym Int 2002;51:749–56.

[13] W.L. Bradely In Thermoplastic Composite Materials, L.A. Carlsson, Ed. Composite Materials Series, Elsevier, New York Ch-9 (1991).

[14] C.K. Riew and A.J. Kinloch, Eds. Rubber Toughened Plastics, Ch.1, American Chemical Society, Advances in Chemistry Series 233, Washington DC (1993).

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Chapter 6

Summary and Conclusions

6.1 Introduction

This concluding chapter provides a quick look of the summary and conclusions of the work carried out on Modification of DGEBA with epoxidised resins. A small amount of modifier can greatly improve the energy absorption and impact resistance of brittle DGEBA. The improvement is accomplished without significant deterioration of the thermo mechanical properties of the resin. These resins can be used as matrix materials for various epoxy based composites.

6.2 Summary

The focus of this study is to develop new modified systems for amorphous DGEBA resin via physical and chemical modifications. The contents of the various chapters in this thesis are summarized below.

A literature survey on modification of epoxy resin, a brief discussion on various thermoset resins, curing of epoxy resins, an account of the included mechanical properties and modification methods of epoxy resin and toughening of fibre reinforced plastics are included in Chapter 1.

Optimization of weight percentage composition of hardener for curing, post curing time and post curing temperature of DGEBA resin are discussed in Chapter 2. Modification of DGEBA with epoxidised novolac resin from phenol, ortho cresol, p-cresol, phenol naphthol mixture and epoxidised cardanol and measurement of various properties are also dealt in this chapter. The effect of ageing on DGEBA resin modified by epoxy novolacs (EPN, ECN and EC) and unmodified resin is also investigated. Thermal properties of the modified resin are monitored using TGA and dynamic mechanical properties by DMA and the fracture behaviour by scanning electron microscopy (SEM).

Synthesis of epoxy functional polydimethyl siloxanes(PDMS) and modification of DGEBA with synthesised siloxanes are given in Chapter 3. Modifiers include (i) Terminal epoxy functional PDMS (TEF PDMS) ii) Pendant epoxy functional PDMS(PEF PDMS) iii) pendant epoxy functional PDMS synthesised from PDMS containing 50% silyl hydride group(PEF PDMS50). Synthesised resins are characterised by spectroscopic methods (^{1}H NMR and FTIR). The epoxy systems are characterised by epoxide equivalent determination also. Thermal properties of the modified resin are monitored using TGA, dynamic mechanical properties by DMA and the fracture behaviour by scanning electron microscopy (SEM). The physical properties of the cured blends are compared with those of the neat resin. The effect of ageing on DGEBA resin modified by siloxanes and unmodified resin is also investigated.

Modification of commercial DGEBA resin by two component systems by physical blending is dealt with in Chapter 4. Two component used are EEN (mixture of EC and pECN), TPN (mixture of TEF PDMS and pECN) and PEN (mixture of PEF PDMS50 and pECN). Thermal properties of the modified resin are monitored using TGA, dynamic mechanical properties by DMA and the fracture behaviour by SEM. The effect of ageing on DGEBA resin modified by two component and unmodified resin is also investigated.

The effect of matrix toughening on the mechanical properties of glass-reinforced composites is presented in Chapter 5. Glass reinforced laminates made of both virgin resin and modified resin are prepared using chopped strand mat (CSM) and woven roving mat (WRM) and mechanical properties compared. Epoxy resin modified by EPN, pECN, EC, TEF PDMS, PEF PDMS, EEN, TPN and PEN are used for making the glass reinforced laminates.

6.3 Conclusions

The following conclusions can be drawn from this investigation.

- Commercial DGEBA showed optimum mechanical properties by curing with 10wt % amine hardener and post curing at 100^0C for four hours.
- 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.

- 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 a sharp increase in elongation without appreciable lowering of the energy absorbed to break.
- The epoxy novolacs were found to considerably improve the ageing behaviour of the DGEBA matrix
- Fuctionalised siloxanes epoxy blends show a general improvement in properties compared to nonfunctionalised siloxane epoxy blends.
- The epoxy functionalised PDMS blends show substantial improvement in thermal stability as evident from TGA and damping data.
- DGEBA/PEF-PDMS and DGEBA /TEF PDMS blends showed improved thermal and impact properties with marginal lowering in tensile strength and modulus.
- The functionalised siloxane/DGEBA blends show appreciable water resistance.
- Siloxane modified resin retains the mechanical properties to a greater extent than the unmodified resin after ageing.

- Addition of a mixture of pECN and EC to DGEBA can considerably improve water resistance and thermal properties along with mechanical properties. So a mixture of EC and p-ECN can be used as a cost effective modifier. It also improves the ageing properties of DGEBA.
- Modifications of DGEBA with siloxanes (TEF PDMS and PEF PDMS) improve the water resistance, impact strength and marginally the thermal properties with slight reduction in tensile strength.
- Addition of a mixture of p-ECN and siloxanes showed improvement in tensile properties, impact strength, thermal properties and water resistance.
- Ageing studies showed that addition of both siloxanes(TEF PDMS and PEF PDMS) improve thermal ageing. Siloxane modified samples show only slight reduction in tensile properties and impact strength when compared to neat DGEBA and p-ECN modified DGEBA samples after ageing
- A mixture of p-ECN with siloxanes(TEF PDMS and PEF PDMS) improves mechanical properties, thermal properties, water resistance with improvement in ageing characteristics
- Matrix modification is found to increase tensile strength and energy absorption (during failure) of DGEBA-glass composites.
- Among the phenolic modifiers (EPN, ECN and EC) used for DGEBA-glass composites. ECN is found to give the best performance.

- Additions of siloxanes generally reduce the tensile strength of DGEBA resin, but when in FRP both siloxanes (PEF PDMS and TEF PDMS) slightly improves the tensile strength value.
- Among siloxanes PEF PDMS is found to give the best performance due to the presence of more number of epoxide groups.
- Epoxidised cardanol can be used as a good low cost modifier for laminates, but the improvement in properties is only marginal. By using EEN (a mixture of ECN and EC) we can get a balance of properties.
- Siloxanes (TEF PDMS and PEF PDMS) and mixtures(TPN and PEN)show greater energy absorption than neat DGEBA and ECN modified composite due to the presence of siloxanes.

6.4 Future Outlook

The modification of DGEBA resins with epoxidised resins is an area which calls for extensive research in coming years. Some specific areas are outlined below:

- A better insight to DGEBA-EPN, DGEBA-ECN and DGEBA-EC blends can be achieved only through investigations into the chemical reactions involved.
- Optimization of epoxy content in siloxanes has to be investigated.
- The improvement in ageing properties of siloxane modified DGEBA has to be comprehensively investigated. Other ageing

processes like photochemical ageing, environmental ageing and salt water ageing has to be investigated.

- The improvement in properties of glass-reinforced composites employing modified DGEBA has to be comprehensively investigated. Fundamental phenomena leading to increase in composite tensile strength on matrix modification with siloxanes and ECN have to be identified.
- Commercial significance of using modified DGEBA has to be further studied. Field trials and performance reports can be procured from actual users.
- Large scale manufacture of toughened resins has to be investigated and problems relating to regular production have to be solved.

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Abbreviations and Symbols

ASTM	American standards and testing methods manual
ATBN	Amine terminated butadiene-acrylonitrile rubber
ACN	Acrylonitrile
b	Width of specimen tested
BMC	Bulk molding compounds
BP	Boiling point
BPA	Bisphenol A
BPO	Benzoyl peroxide
BPA/EC	Bisphenol A /cardanol epoxides
cps	Centipoise
CSM	Chopped strand mat
CTBN	Carboxyl terminated butadiene-acrylonitrile rubber
CTPB	Carboxyl terminated polybutadiene
d^{20}	Density at 20^0C
d	Depth of specimen
DGEBA	Diglycidyl ether of bisphenol A
DICY	Dicyandiamide
DMA	Dynamic mechanical analysis
DMC	Dough moulding compounds
DSC	Differential scanning calorimetry
EB	Elongation-at-break
E_B	Modulus of elasticity in bending
EC	Epoxy cardanol
ECN	Epoxy cresol novolac
o-ECN	Epoxy cresol novolac from ortho cresol
p-ECN	Epoxy cresol novolac from para cresol
EPN	Epoxidised phenolic novolac
ETBN	Amine terminated butadiene-acrylonitrile rubber
ETPB	Epoxidised HTPB
FRP	Fibre reinforced plastics
FTIR	Fourier Transform infrared
GP	General purpose
GPC	Gel permeation chromatography
h	Hours
NMR	Nuclear magnetic resonance

HDT	Heat deflection temperature
HPN	Hybrid polymer networks
HTBN	hyroxyl terminated butadiene-acrylonitrile rubber
HTNR	Hydroxyl terminated natural rubber
HTPB	Hydroxyl terminated polybutadiene
Hz	Hertz
IPN	Interpenetrating polymer networks
IUPR	Isophthalic resin
L	Support span
L.R.	Laboratory reagent
MDA	Methylene dianiline
MF	Melamine- formaldehyde
min	Minutes
$\overline{M}_n$	Number average molecular weight.
mol	Mole
m	Slope of the tangent to the initial straight line portion of the load-deflection curve
MP	Melting point
MPa	Mega Pascal
N	Normality
NBR	Acrylonitrile-butadiene rubber (nitrile rubber)
nm	Nanometre
NR	Natural rubber
P	Load at any point on the load -elongation curve
PA	Phthalic anhydride
P_B	Breaking load
PDMS	Polydimethy siloxane
PEEK	Poly(ether ether ketone)
PEF PDMS	Pendant epoxy functional Polydimethy siloxane
PEI	Poly(ether imide)
PEK	Poly(ether ketone)
PEO	Polyethylene oxide
PES	Poly(ether sulfone)
PF	Phenol formaldehyde
phr	Parts by hundred parts by weight of resin
PN	Phenol novolac
PU	Polyurethane

PIPS	Polymerisation induced phase separation
PSHF PDMS	Pendant Silyl Hydride functional Polydimethy siloxane
rpm	Revolutions per minute
RRIM	Reinforced resin injection moulding
RTM	Resin transfer moulding
S	Stress in the outer fibres at midpoint
SEM	Scanning electron microscopy
SMC	Sheet molding compounds
SRIM	Structural resin injection moulding
TDI	Toluene diisocyanate (TDI)
TEF PDMS	Terminal epoxy functional Polydimethy siloxane
TGA	Thermogravimetric analysis
T_g	Glass transition temperature
TIPS	Thermally induced phase separation
TSHF PDM	Terminal Silyl Hydride functional Polydimethy siloxane
UF	Urea-formaldehyde
UP	Unsaturated polyester
UPR	GP grade Orthophthalic resin
UTM	Universal Testing Machine
UV	Ultra violet
VARI	Vacuum assisted resin injection
V_p	Volume fraction of polymer
wpe	Weight per epoxy
WRM	Woven roving mat

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LIST OF PUBLICATIONS

[1]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil., Synthesis of pendant epoxy functional polydimethyl siloxane for modification of Diglycidyl Ether of Bis-phenol A ; Advances in Polymer Science and Technology: An International Journal, 2011; 1 (2): 22-29

[2]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil; Terminal epoxy functional polydimethyl siloxane for modification of DGEBA. *Polymer-Plastics Technology and Engineering (communicated* - manuscript ID-LPTE-2014-0835)

[3]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil; Ageing Studies of epoxy cresol novolac modified DGEBA, Journal of applied polymer science. *(communicated* -manuscript id -APP-2014-05-2516)

[4]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil modification of epoxy reisn using polydimethyl siloxane , international Conference on Advances in Polymer Technology ,September 25-27 2008, CUSAT Kochi.

[5]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Reactiveblending of epoxy reisn using epoxidised cresol novolac presented at Polymcon 09 international seminar at NIT Calicut in 10th Jan 2009

[6]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil modification of epoxy reisn using epoxidised novolac resin synthesized from phenol and cardanol presented at APM 10 international seminar at Bhubaneswar February 2010

[7]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Reactive blending of epoxy reisn using epoxidised novolac synthesized from phenol naphthol mixture was presented at APT 10 international seminar at Rubber Park in 27th February 2010

[8]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Synthesis of epoxyterminal polydimethyl siloxane for modification of DGEBA was presented at LAP 10 international seminar at Rubber Park in 13th August 2010

[9]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Ageing studies of epoxyterminal polydimethyl siloxane modified DGEBA was presented at PSE 10 international seminar at Punjab university at 25th November 2010

Papers Presented in National Level

[1]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Modification of epoxy resin using epoxidised phenol novolac resin is presented in national seminar at St. Mary's College Thrissur in 6th August 2008

[2]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Modification of DGEBA using epoxidised cresol novolac presented in ACS 08 national seminar at Sacred Heart college Thevara in 27th November 2008

[3]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil; Ageing studies of terminal epoxy functional siloxane modified DGEBA; NCMS 2012 at U.C.College Aluva February 2012

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List of Publications

[1]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil., Synthesis of pendant epoxy functional polydimethyl siloxane for modification of Diglycidyl Ether of Bis-phenol A ; Advances in Polymer Science and Technology: An International Journal, 2011; 1 (2): 22-29

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Papers Presented in National Level

[1]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Modification of epoxy resin using epoxidised phenol novolac resin is presented in national seminar at St. Mary's College Thrissur in 6th August 2008

[2]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil Modification of DGEBA using epoxidised cresol novolac presented in ACS 08 national seminar at Sacred Heart college Thevara in 27th November 2008

[3]. Jenish Paul, A.Benny Cherian, K.P.Unnikrishnan and Eby Thomas Thachil; Ageing studies of terminal epoxy functional siloxane modified DGEBA; NCMS 2012 at U.C.College Aluva February 2012

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