STUDIES ON THE TOUGHENING OF EPOXY RESINS

Thesis submitted to the

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

in partial fulfilment of the requirements
for the award of the degree of

DOCTOR OF PHILOSOPHY

under the

FACULTY OF TECHNOLOGY

by

K.P.UNNIKRISHNAN

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022, INDIA.

January 2006

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi - 682 022, India.

Dr. Eby Thomas Thachil
B. Sc. Eng., M. Tech., Ph. D
Reader

Phone: 0484-2575723 (Off)
0484-2331426 (Res)
E mail : ethachil@cusat.ac.in

Date: 23rd January2006

Certificate

*This is to certify that the thesis entitled **"Studies on the toughening of epoxy resins"** which is being submitted by Mr. K.P.Unnikrishnan 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)

PREFACE

Cured epoxy resins are highly cross-linked polymers with a three dimensional molecular structure. The network structure gives rise to high stiffness, high strength, heat resistance and solvent resistance. Due to these excellent properties they are widely used as engineering polymers of choice for structural applications ranging from aerospace structures to high quality flooring. 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 toughening epoxy resins. Consisting of six chapters, the thesis gives an introduction and literature survey in the first chapter. The synthesis of epoxy resin, cardanol based epoxides and various modifier resins and their characterisation by different methods form the body of the second chapter. Modification of the resin by reactive blending with various thermosets such as phenolic resins, epoxy novolac resins, unsaturated polyester resin and cardanol based epoxides forms the basis of the third chapter. In the fourth chapter, modification using various elastomers is dealt with in detail. Physical modification of the resin by incorporating elastomers, maleated elastomers and functional elastomers is also presented. Solution blending technique is employed for solid rubber modifiers compared to the conventional method of mechanical blending. The effect of matrix toughening on the properties of glass reinforced composites and the effect of fillers 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.

The successful completion of the present research endeavour was made possible by the generous, enthusiastic and inspiring guidance of my dear supervising teacher Dr. Eby Thomas Thachil. With great pleasure, I express my heart-felt gratitude for his professional guidance and competent advice. I am extremely grateful to Dr. Rani Joseph, Head of the Department and Dr. A.P. Kuriakose and Dr. K.E. George former Heads of the Department for providing all facilities during my research work. With pleasure, I thank all faculty members especially Dr. Philip Kurian and Dr. Sunil K. Narayanankutty and non-teaching staff of the Department for their wholehearted co-operation throughout the course of this work. Words are insufficient to express my gratitude to my colleagues Ms. Lity Alen Varghese, Dr. Benny Cherian, Mr. Thomas N Abraham, Mr. Rajesh, Mr. Vipin, Mr. Anoop, Prof. Lovely, Dr. Ushamani and Dr. Honey John for their support at various stages of this work. My sincere thanks are due to Mr. Sinto Jacob, Ms. Saritha and Ms. Dhanya for their selfless co-operation. I am grateful to Mr. P.S. Parameswaran, Mrs. Bhuvaneswary, Mrs. Mary Alexander and Mrs. Prema for the encouragement given to me during the course of this project.

It gives me immense pleasure to express my sincere thanks to Dr. C.P. Raghunadhan Nair, Head, F&FFR, PSCD, VSSC, Trivandrum, and Dr. Sam Philip, and Mr. Gurulinga of IISc, Bangalore for their continuous support in analytical studies. I express my wholehearted gratitude to Dr. P.A Unnikrishnan, Department of Applied Chemistry, CUSAT, Kochi for fruitful discussions on spectral studies. I am thankful to Mr. K.V. Jose and Mr. A. Casimir, Department of Instrumentation, CUSAT, Kochi.

I take this opportunity to acknowledge with thanks the help received from the Management, Principal, and colleagues of Union Christian College, Aluva-2. I wish to put on record my deep sense of gratitude to Dr. A.M. Chacko, former Principal who has inspired me greatly through out my career.

At this moment I remember with love and thanks, the inspiration, love and the blessings of my parents and relatives. I owe a lot to my wife Rema and son Rahul for the understanding and patience they have shown at all times.

Above all, I thank God Almighty for showering upon me His choicest blessing for the completion of the research work.

K.P. Unnikrishnan

ABSTRACT

The aim of this investigation is to develop new toughened systems for epoxy resin via physical and chemical modifications. Initially the synthesis of DGEBA was carried out and the properties compared with that of the commercial sample. Subsequently the modifier resins to be employed were synthesised. The synthesised resins were characterised by spectroscopic methods (FTIR and ^{1}H NMR), epoxide equivalent and gel permeation chromatography. Chemical modification involves the incorporation of thermoset resins such as phenolics, epoxy novolacs, cardanol epoxides and unsaturated polyester into the epoxy resin by reactive blending. The mechanical and thermal properties of the blends were studied. In the physical modification route, elastomers, maleated elastomers and functional elastomers were dispersed as micro-sized rubber phase into the continuous epoxy phase by a solution blending technique as against the conventional mechanical blending technique. The effect of matrix toughening on the properties of glass reinforced composites and the effect of fillers on the properties of commercial epoxy resin were also investigated. The blends were characterised by thermo gravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, scanning electron microscopy and mechanical property measurements.

Among the thermoset blends, substantial toughening was observed in the case of epoxy phenolic novolacs especially epoxy para cresol novolac (ECN). In the case of elastomer blending, the toughest blends were obtained in the case of maleic anhydride grafted NBR. Among functional elastomers the best results were obtained with CTBN. Studies on filled and glass reinforced composites employing modified epoxy as matrix revealed an overall improvement in mechanical properties.

CONTENTS

Preface

Abstract

List of abbreviations

List of publications

---

* *Detailed contents are given at the beginning of each chapter*

Chapter 1

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

Plastics play an important role in our daily lives. They are one of the most useful materials ever created. Plastics can be rubbery or rigid and can be shaped into an endless variety of objects, ranging from car bumpers to squeezable bottles and soft fabrics. Plastic products, especially those used by industries, often have a useful life of many years. According to their structure and behaviour, plastics can be classified as thermoplastics and thermosetting plastics or thermosets.

Thermoplastics soften or melt on heating and can be converted into any shape before they cool down to a solid. Melting and solidification of these polymers are 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 re melted, 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 a variety of engineering applications because of a high strength-to-weight ratio, 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 [1]. They are used extensively as reinforced composites, adhesives, high performance coatings and potting and encapsulating materials. They also serve as matrix resins for fibre reinforced composite materials where advantage is taken of favourable properties such as high modulus, low creep and reasonable high temperature performance. Epoxy thermosets have excellent electrical and mechanical properties, low cure shrinkage, good adhesion to many metals and resistance to moisture, thermal and mechanical shock. The wide spread use of epoxies is due to ease of processing, excellent wetting properties with reinforcements, good weathering resistance, excellent dimensional stability and the wide variety of grades available. High chemical and corrosion resistance, good thermal and mechanical properties, outstanding adhesion to various substrates, flexibility, low cure shrinkage, good electrical properties and ability to be processed under a variety of conditions are the characteristic features of epoxy resins. The polar groups in the structure ensure greater adhesion to other substrates.

1.2 THERMOSET RESINS

Thermosetting resins change irreversibly under the influence of heat into a 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, which cause a reaction to occur between the chains, thus producing a complex cross-linked polymer. Sometimes irradiation is employed to achieve cross-linking [2]. Important thermosetting resins are epoxy resins, unsaturated polyesters, alkyds, vinyl esters and allyl resins, phenolics, amino plastics, urethanes, silicones, furfural etc.[3].

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.

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 (See Chapter 2). 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.

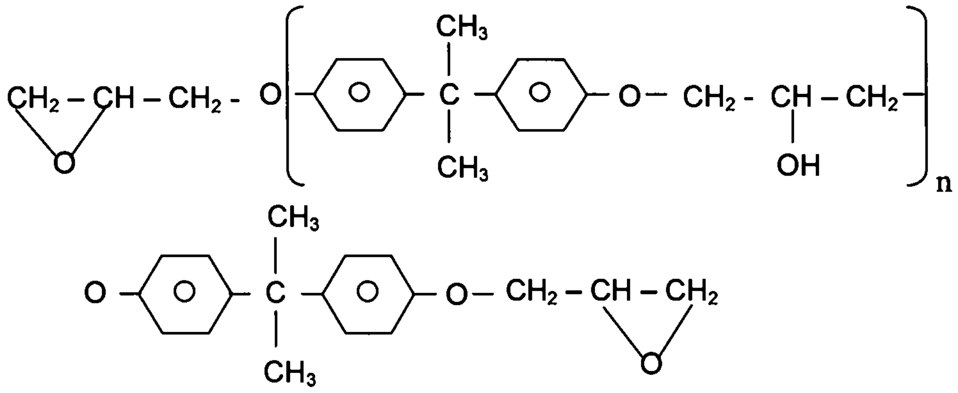


Fig 1.1 Structure of DGEBA

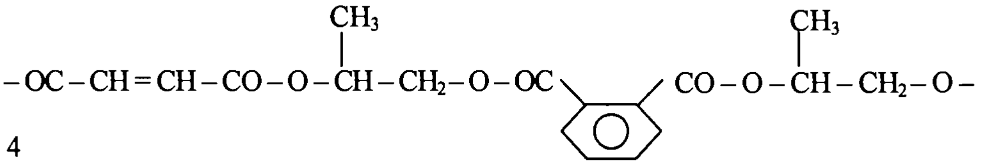
To facilitate processing and modify resin properties other constituents may be included in the compositions; e.g., solvents, diluents, plasticizers flexibilizers and accelerators. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Hardeners 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

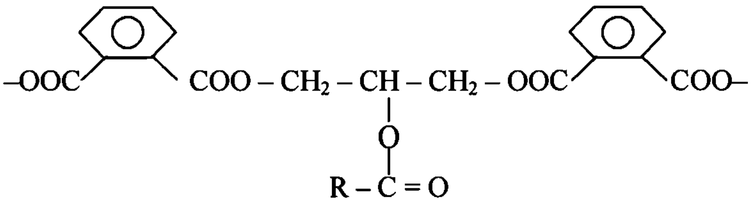
Unsaturated polyesters are prepared by reacting a mixture of unsaturated and saturated dicarboxylic acids with diols. The condensate is then dissolved in an unsaturated co-reactant diluent like styrene, methyl methacrylate or diallyl phthalate to get a resin formulation. Styrene is the commonly used diluent. The degree of flexibility, toughness, tensile strength and hardness depend on the chemical structure of the resin. 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 facilitates cross-linking at the sites of unsaturation in the polyester chains. The saturated acid reduces the number of cross



linking sites and consequently the cross-link density and brittleness of the cured resin. Since cross-linking occurs via free radical addition mechanism across the double bonds in the polyester chain and the reactive diluent no volatiles are given off during cure.

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. Alkyd resins are modified by rosin, phenolic resins, epoxy resins and monomers like styrene. When the resin is applied to a substrate oxidative cross-linking via unsaturated groups in the fatty acid occurs and the resin hardens. These resins have low cost, durability, flexibility, gloss retention and heat resistance. A typical structure of the resin is shown below.

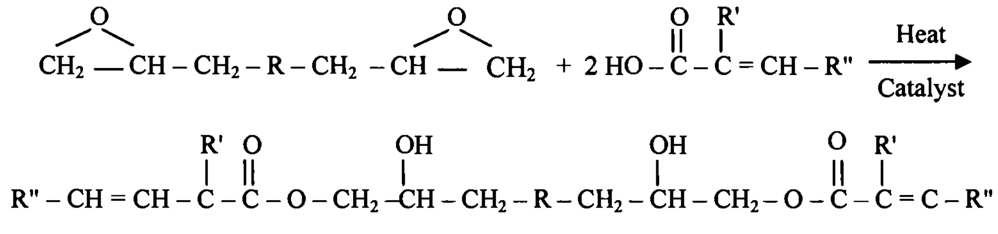


R represents the long chain alkyl radical characteristic of the oil.

c) Vinyl esters

Vinyl esters [4] are chemically the reaction products of epoxy resin and ethylenically unsaturated monocarboxylic acids like methacrylic acid with styrene added as a coreactant. They are similar to unsaturated polyesters in the sense that they are reasonably priced, cure rapidly and have processability. But their mechanical properties are akin to epoxy resins.

The vinyl groups present at the ends of the molecule impart high reactivity, low residual unsaturation and high tensile elongation. The terminal ester groups are protected by pendant methyl groups which give chemical resistance to the resin. The unreacted hydroxyl groups derived from the epoxide moeity are partly responsible for their excellent adhesion to glass. Vinyl ester resins are widely used for reinforced plastic chemical plant equipment such as scrubbers, pipes and tanks and chemically resistant coatings such as tank and flue stack linings. A wide variety of resins can be prepared by simply altering the choice of epoxy resin and / or monocarboxylic acid. The most widely used cross-linking monomer is styrene. Typical reactions are as follows:

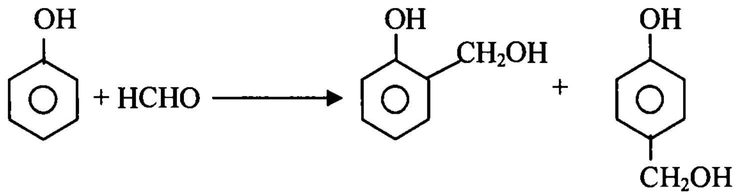


d) Allyl resins

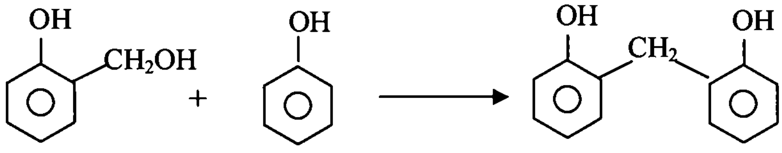
Allyl resins retain their desirable physical and electrical properties on prolonged exposure to severe environmental conditions. Their monomers are employed widely as cross-linking agents in other polyester systems. The principal allylics are the reaction products of allyl alcohol and phthalic acid or 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

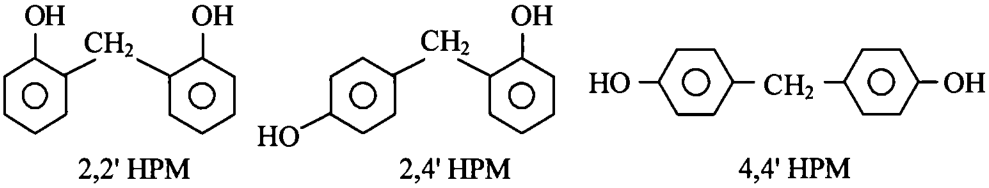
Phenolic resins were the first polymeric resins produced commercially from simple low molecular weight compounds. Phenol formaldehyde (PF) resins are prepared by the polycondensation between phenol and formaldehyde in the presence of either an acid or a base catalyst. The nature of the product is dependent on the type of catalyst and the mole ratio of reactants. 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. Initially these reactants slowly react to form o- and p-hydroxy methyl phenols.



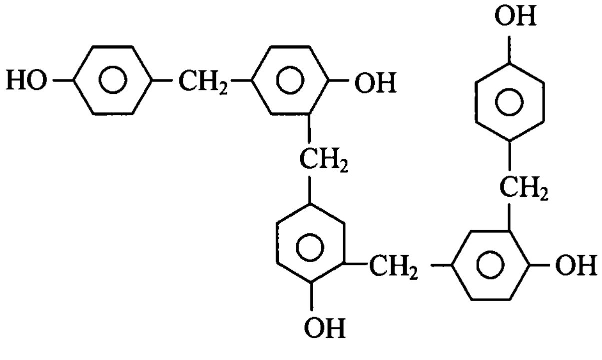
These rapidly condense to form bis (hydroxyphenyl)-methane (HPM).



There are three possible isomers and their proportions depend on the pH of the reaction. 2,4'- and 4,4'- isomers are the main products under acid conditions.

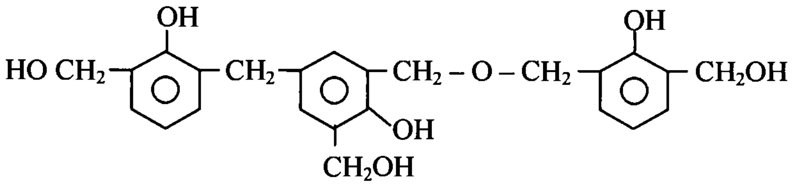


These isomers subsequently react with formaldehyde to form methylol derivatives which rapidly react with more phenol to form novolac resins. These resins are linear molecules containing 5-6 benzene rings. A typical example of the many possible structures is shown below.



The resin can be stored for any length of time without cross-linking. Further cross-linking is effected by heating with compounds like hexa which can form methylene bridges. The novolacs are also referred to as two-stage resins.

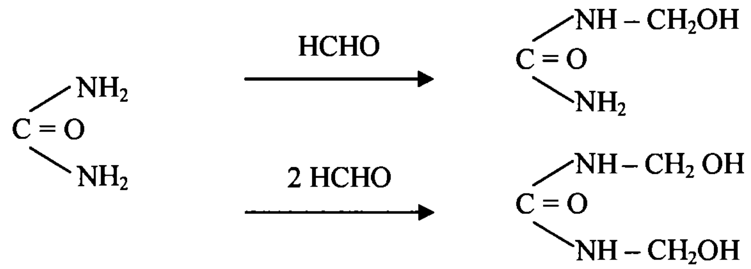
A resol is prepared by reacting phenol with an excess of formaldehyde under basic conditions. Although methylol formation is rapid subsequent condensation is slow. Hence low molecular weight liquid resols containing 2-3 benzene rings are formed. When the resol is heated cross-linking via the uncondenced methylol groups occurs and the resultant products are known as one-stage resins. 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 [5].

1.2.4 Aminoplasts

Aminoplastics 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.



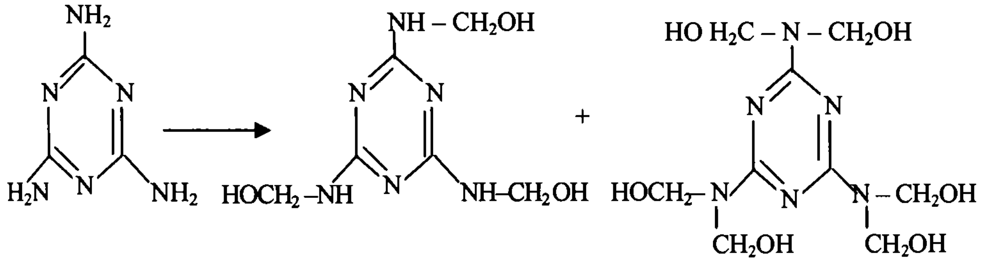
In the second stage these are subjected to acid conditions at elevated temperatures and the following sequence of reactions occur.

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.

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

If excess formaldehyde is used the hydrogen atom of the –NH– group in the linear polymer can be replaced by pendent methylol groups. These methylol groups and the methylol groups on the chain ends undergo crosslinking to form insoluble and infusible products.

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 depend 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.



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

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

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

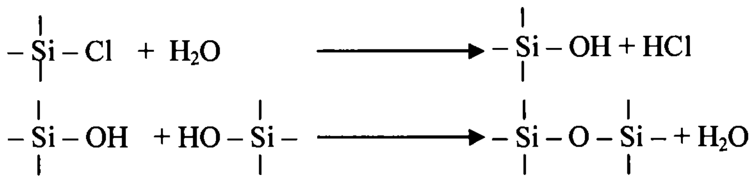
Polyurethanes are extremely versatile polymers. They occur in the liquid, gum or thermoplastic resin state. The method of processing also varies accordingly. It is the ability to form polymers containing not only the urethane linkage but also to include other groups as integral units in or on the polymer chains that leads to their versatility. Specific chemical structures displaying chain stiffness or flexibility can be synthesised. 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 equivalent 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.



$$-\overset{|}{\underset{|}{Si}}-Cl + H_2O \longrightarrow -\overset{|}{\underset{|}{Si}}-OH + HCl$$

$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

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 are characterised by the presence of more than one 1, 2-epoxy group per molecule. 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.

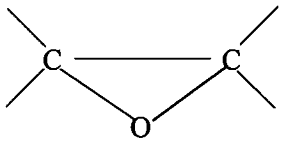


Fig.1.2 Epoxy ring

In 1936, De Trey Freres produced a low melting bisphenol A based epoxy resin which gave a thermoset composition with phthalic anhydride. 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 [6] in 1939 which described liquid poly epoxides. In the early stage 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 [7]. Epoxy resins were first offered commercially in 1946 and are now used in a wide variety of industries. By the beginning of 1980s world capacity for epoxy resins reached about 600000 tonnes per annum. With a global consumption of about 10 million tonnes per annum for thermosetting plastics, epoxies had a share of 3 %.

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.

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 a solid. 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). Commercial EPN 1138 (Ciba-Geigy) has a viscosity of 35000 mPa.s and a weight per epoxy value (wpe) of 178. EPN 1139 has low viscosity (1400 mPa.s) with wpe 175. The high functionality of novolacs (compared to bisphenol A resins) increases the cross-link densities and improves thermal and chemical resistance. 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 [8]. 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 [9].

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.

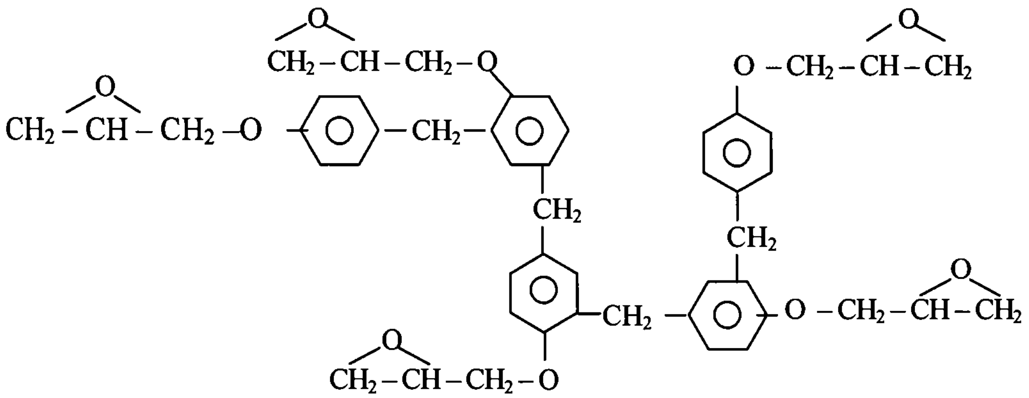


Fig 1.3 Typical structure of EPN

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^{0}C and weight per epoxy value (wpe) 105-115. The trifunctional resin can be cured at 70^{0}C 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^{0}C 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.

*c. **Non-glycidyl ether epoxides*** : 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 recently [10]. 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 Characterisation

Physical and chemical characterisation of epoxies can have three approaches - the analytical chemistry of the epoxy resin intermediates and the curing agents as starting materials, the following of the cross-linking process and the determination of network structure and properties of cured products. 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) [11]. 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 [12]. 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 [13] 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 [14]. HPLC analysis of liquid and solid epoxy resins has been studied in detail using normal phase and reversed phase columns respectively [15].

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 [16]. The usefulness of high resolution NMR for the study of thermosetting polymers has been reported in the literature [17]. High resolution liquid state ^{13}C NMR and solid state ^{13}C-CP-MAS NMR have also been employed for epoxy characterisation [18].

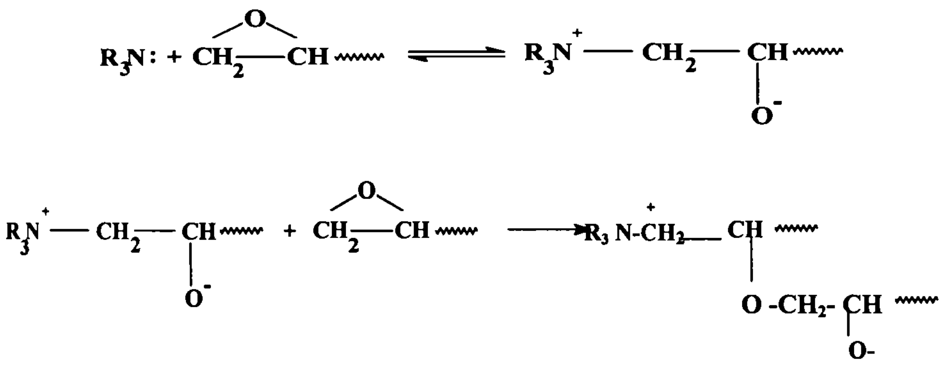
Thermal properties: Melting point of solid resin is measured by the Durrans mercury method. The ASTM heat distortion temperature (deflection temperature under load) test may also be used to characterise the resin. Resins must be compared using identical curing agents and curing conditions. DGEBA resin cured with meta phenylene diamine is found to have a higher heat deflection temperature than that cured by phthalic anhydride. Thermal stability of epoxy resins can be determined by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). DSC and DMTA analysis can study the curing behaviour and glass transition

1.3.4 Cross-linking

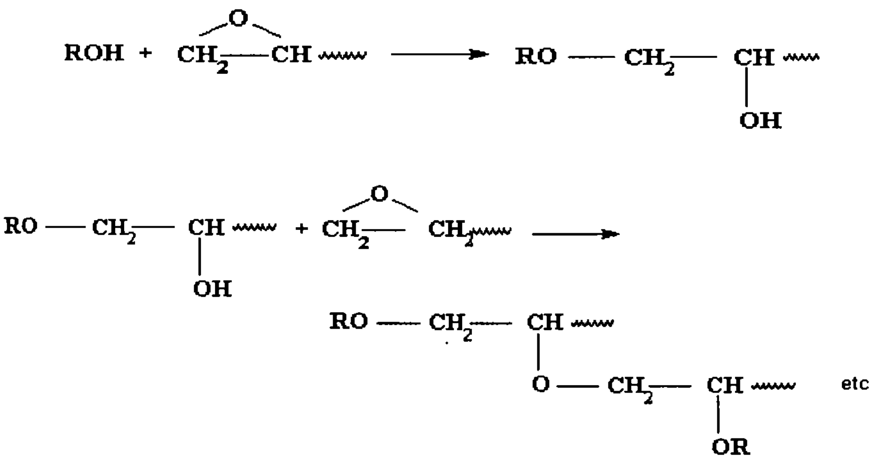
The resin is mixed with a curing agent or hardener; its choice depending upon the processing methods, conditions and the properties required. The reactivity of the epoxy ring is enhanced by the presence of the ether linkage separated from it by a methylene unit.

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) [19]. 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 amines are used for homopolymerisation of epoxies and the reaction involves a zwitter ion. This ion opens up a new epoxy group generating another ion which in turn reacts with a further epoxy group. In the case of glycidyl ether resins this reaction occurs at both



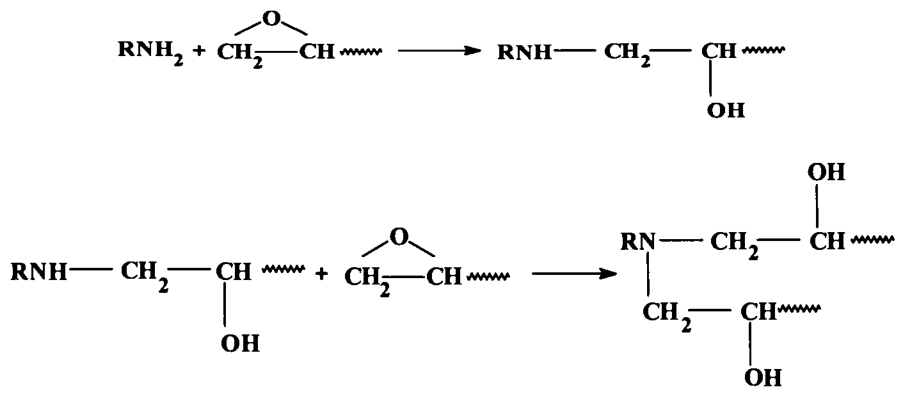
ends of the molecule resulting in a cross-linked structure. The epoxy group can also react with hydroxyl groups particularly when catalysed. Hydroxyl groupswill be present in high molecular weight DGEBA resins or they will be formed during the opening of epoxy ring during cure.



The catalyst system employed influences the predominance of one reaction over the other. 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 few minutes. Complexing boron trihalides with amines is found to enhance the reaction [20].

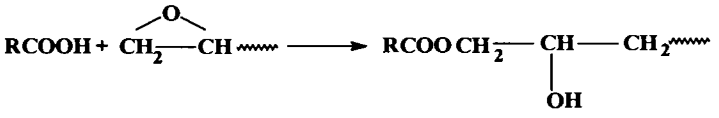
Photo initiated cationic curing of epoxies is a fast developing technique. Photo initiators include aryl diazonium salts ($ArN_2^+X^-$), diaryl iodonium salts and salts of positively charged sulphur ($Ar3S^+X^-$). Electron beam curing of epoxy resins and its exothermic effect have been reported recently [2]. 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 [21]. 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 [22].

ii) Co-reactive cure: Primary and secondary amines are widely used as curing agents for epoxy resins.

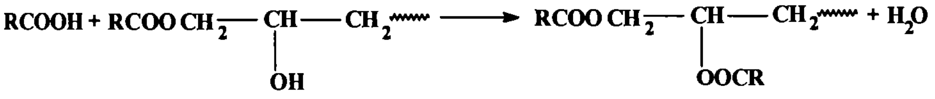


The reaction of an epoxy group with a primary amine initially produces a secondary alcohol and secondary amine. The secondary amine in turn reacts with epoxy group to give a tertiary amine and two secondary hydroxyl groups. Curing with secondary amine affords a tertiary amine and a secondary hydroxyl group. Primary amines react twice as fast as secondary amines [23]. The hydroxyl compounds accelerate the rate of amine curing. During this process, the hydrogen atom of hydroxyl group partially protonates the oxygen atom of epoxy group, making the methylene group susceptible to nucleophilic attack by the amine. Poly functional alcohols give the best results whereas mono functional un-substituted alcohols are poor accelerators.

Carboxylic acids and anhydrides are also employed as curing agents for epoxy resins.The reaction between a carboxylic acid and epoxy resin proceeds as follows.



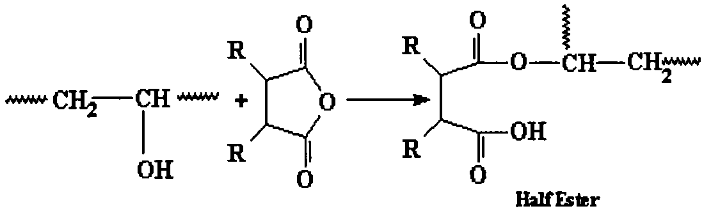
(A)

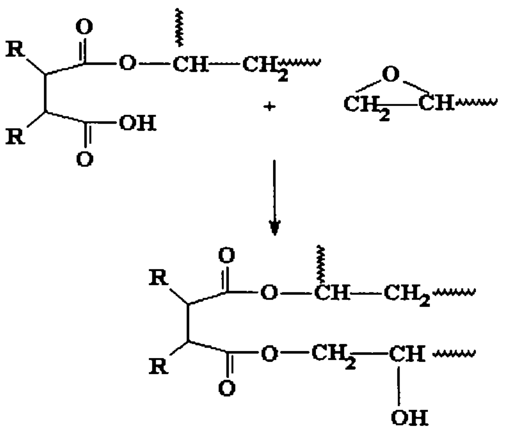


$$\mathrm{RCOOH + RCOOCH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2\sim\sim \longrightarrow RCOOCH_2{-}\underset{\displaystyle OOCR}{\underset{|}{CH}}{-}CH_2\sim\sim + H_2O}$$

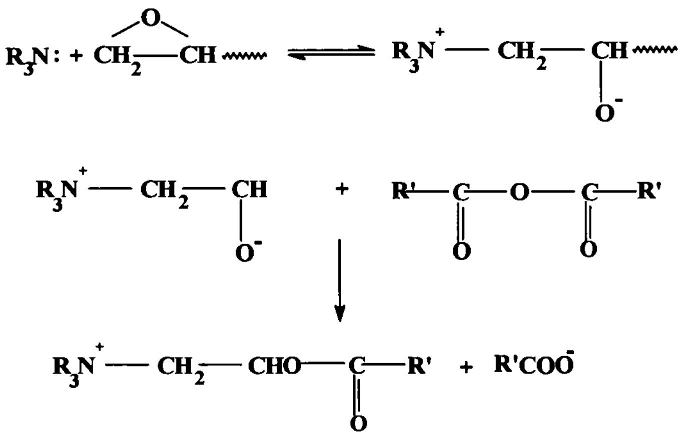
The hydroxyl group in (A) can further react with epoxy groups to form ether linkages. The epoxy –carboxyl reaction can occur in the presence of basic catalysts. Two possible mechanisms have been proposed for the reaction of epoxies with acids in the presence of a tertiary amine of which one involves a cyclic intermediate and the other a tetragonal complex.

Acid anhydrides are generally employed for elevated temperature cure of epoxy resins. The un-catalysed reaction between epoxy resin and acid anhydride proceeds slowly even at 200°C to give both esterification and etherification. The secondary hydroxyl groups from epoxy backbone react with anhydride to form a half ester, which further reacts with an epoxy group to form a diester.

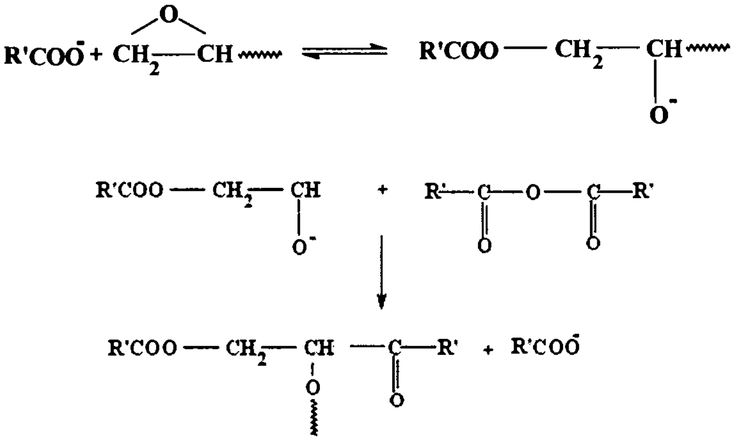




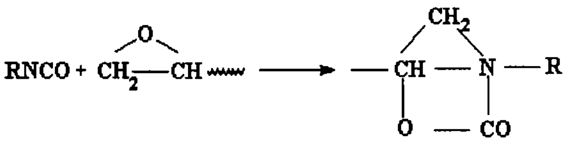
Epoxy-anhydride reaction is catalysed by tertiary amines. In this reaction, the tertiary amine first reacts with the epoxy group to furnish a zwitter ion which contains a quaternary nitrogen atom and an alkoxide anion. The anion interacts with the anhydride to give a quaternary salt and carboxylate anion.

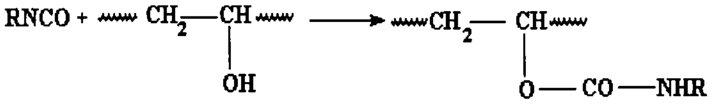


This anion first reacts with the epoxy group and then with the anhydride. This process regenerates the carboxylate anion to reinitiate the cycle of reactions.

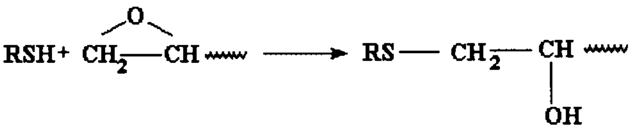


Isocyanates react with epoxy group to form an oxazolidone derivative. They also form urethane linkages through reaction with hydroxyl groups. A cross-linked network is obtained from a polyepoxide and a polyfunctional isocyanate.

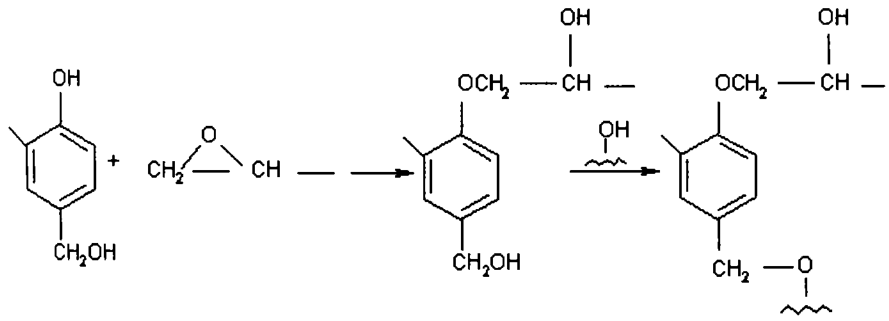




Mercaptans also can be employed for cross-linking epoxies. The epoxy-mercaptan reaction is faster than epoxy-amine reaction especially at low temperatures. The reaction is accelerated by primary and secondary amines.



The hydroxyl groups of high molecular weight epoxy resins can react with a variety of formaldehyde based resins such as phenol-formaldehyde (PF), melamine-formaldehyde (MF) and urea-formaldehyde resins (UF) leading to cross-linked networks. Cross-linking occurs due to the condensation reaction between methylol or alkylated methylol groups of the formaldehyde resin and the secondary hydroxyl groups on the epoxy backbone. The epoxy-PF reaction can be given as follows.



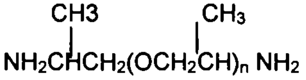
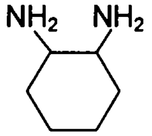
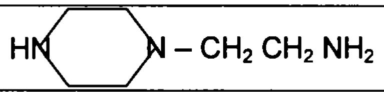
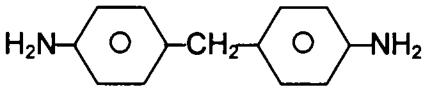
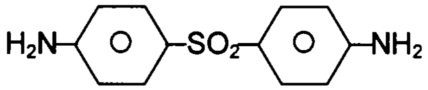
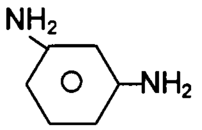
Phenolic novolac resins react with epoxy resins at elevated temperatures to form cross-linked polymers.

1.3.5 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 [3]. 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 [3]

Formula	Name
$NH_2CH_2CH_2NHCH_2CH_2NH_2$ DETA,	Diethylenetriamine
$NH_2CH_2CH_2NHCH_2CH_2NH_2NHCH_2CH_2NH_2$ TETA,	Triethylenetetramine
 $NH_2\underset{\mid}{\overset{CH3}{C}}HCH_2(OCH_2\overset{CH_3}{C}H)_n\ NH_2$	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

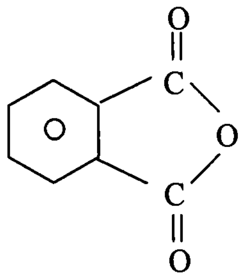
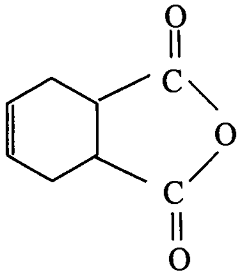
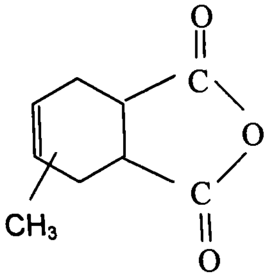
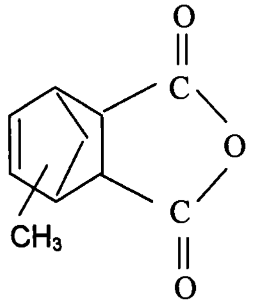
They contain respectively five and six active hydrogen atoms available for cross-linking. DETA is found to give a room temperature pot life of less than an hour at 10 phr concentration. With TETA, 12 to 13 phr concentration is required. However, they are highly volatile, pungent and skin sensitisers. 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 [24]. Relaxation kinetics of DGEBA/MXDA system has been studied using differential scanning calorimetry [25].

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 [26].

Polyamides are the most widely used epoxy hardeners and they amount to 25% of the total US market. They are formed by reacting dimerized / trimerised vegetable oil fatty acids with polyamines. Primary and secondary aliphatic polyamides give good room temperature cure with DGEBA type resins. Aliphatic amines do not react with cycloaliphatic resins at ambient temperature and they require high temperatures. Polyamides can be used in any ratio and they provide good mechanical properties, workable pot lives and cure under mild conditions. The more common commercial amine hardeners are listed in Table 1.1.

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

Table 1.2 Some commercial anhydride curing agents [3]

Phthalic anhydride	
Tetrahydrophthalic anhydride	
Methyl tetrahydrophthalic anhydride	
Nadic methyl anhydride	

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.

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°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 [27]. The mechanical and dynamic characteristics of microwave cured epoxy/anhydride system have been investigated in detail [28]. Modification of epoxy resin with optically active carboxylic acids has been reported [29].

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 [11]. 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.

1.3.6 Cured resin structure

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

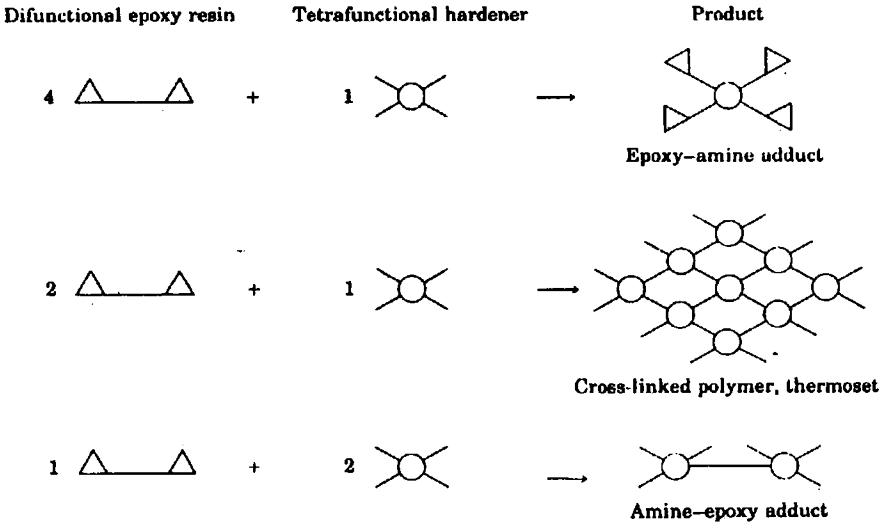


Fig.1.4 Formation of resin-hardener networks

same epoxy resin is less reactive (125^{0}C) 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 [30].

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 [31]. Dielectric measurements are increasingly applied to monitor curing of epoxies [32]. Microdielectrometry is a new method which employs integrated circuit technology to develop a miniaturized dielectric probe [33].

1.3.7 Cured resin properties [34]

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				
1.Compression molding temp.°K	----	----	----	420-440
2. Compression molding pr. MPa	----	----	----	2.07-35
3. Linear mold shrinkage ratio	----	0.0005-0.01	0.001-0.01	0.001-0.005
4.Specific gravity	D-792	1.11-1.4	1.05--1.35	1.6-2
Mechanical				
5.Tensile strength MPa	D-638	28-90	14 -70	69-140
6.Tensile modulus MPa	D-638	2400	----	21000
7. Elongation at break %	D-638	3-6	20-85	4
8.Flexural strength MPa	D.790	55-170	----	90-320
8.Flexural modulus MPa	D.790	3400-5000	----	7000-21000
9.Compressive strength MPa	D-695	100-170	7 -97	140-210
10.Hardness Rockwell	D-785	M80-110	---	M100-110
11.Impact strength Izod .Jm^{-1}	D-256	10 -50	120-270	1600-2100
Thermal				
12. Thermal conductivity Wm^{-1}K^{1}	C-177	0.19/293K	---	1.77
13. Specific heat cal / ^{0}C/g	----	0.25	0.20-0.27	0.19
14. Thermal expansion 10^{-5}in/^{0} C	D-696	4.5-6.5	2-10	1.1-3.5
15. Resistance to heat ^{0} K	----	400-750	400-420	420-770
16. Deflection temperature °K	D-648	115-150	298-350	350-750
Electrical				
18.Volume resistivity ohm-cm	D-257	10^{12}-10^{17}	1.3-15x10^{14}	>10^{14}
19.Dielectric constant at 1 MHz	D-150	3.5 -5.0	3-6	3.5-5.0
20.Dissipation factor at 1 MHz	D-150	0.003-0.028	0.010-0.040	0.01
21.Arc resistance sec	D-495	45-120	50-180	120-180
Optical				
22.Refractive index	D-542	1.55-1.61	---	----
23.Clarity	----	Transparent	Transparent	Opaque
Resistance characteristics				
24.Water absorption %	D-570	0.08-0.15	0.27-0.50	0.05-0.20
25.Effect of weak acid	D543	None		
25 Effect of strong acid	D543	Attacked by some		
26. Effect of weak alkali	D543	None		
27 Effect of strong alkali	D543	Slight		
28 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 264 psi 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 (wpe 180-200) to tetrabromo bisphenol A (wpe value of 450-500). Flame retardance can be improved by incorporating dialkyl(or aryl) phosphate in epoxy/DDS system [35]. Eventhough free of halogens, blends of epoxy resin and unsaturated polyester resin are found to have improved flame retardance [36].

Weathering: Epoxy resins are extensively used for outdoor applications such as boats, tanks, automobile bodies, signs and structural panels. Weathering occurs by chemical exposure or other environmental conditions. The deteriorations occurring are discolouration, erosion and fibre exposure.

1.3.8. 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 [11]. 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. Some amine flexibilizers are made by cyanoethylation of amine hardeners such as DETA to an extent that only two hydrogen atoms remain and the material is only bifunctional.

1.3.9. 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 [3].

In the field of water borne coatings, epoxy resins have provided versatility and inherent properties needed to solve difficult industrial problems. 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. 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. 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 [37]. Metal-metal bonding is very successful with epoxy systems, which are now used extensively in the aircraft and automotive industry [38]. 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 material because they show good adhesion to reinforcement, cure with low shrinkage and provide mechanical, electrical, chemical, thermal and moisture resistance properties. 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.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 [3] are widely used with epoxy resins in the field of 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 in adhesives and grouting systems. 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 TOUGHENING 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.

Reinforcement of the resin matrix with fibres will improve toughness considerably. Although failure in FRP is often limited to the resin-reinforcement interface [39], areas with relatively low amount of fibres are prone to damage when the product is in use or during de-moulding. The damage starts as a micro-fracture of the matrix which on propagation can result in disintegration of the system. Both high T_g and damage tolerance are desirable for high performance composite applications and hence ways of increasing toughness while retaining high temperature performance have been sought for over three decades. Moreover, many applications do not permit the use of reinforcement fibres and yet require improved toughness and impact resistance. Toughening generally refers to improvement in mechanical and thermal stress resistance and does not affect other properties like thermal stability, strength and hardness.

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 [40]. Within the context of failure mechanics [41] 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 [42].

1.4.1 Toughening using modifiers

On the basis of the modifying agent, toughness modification of epoxy resins can be classified into (a) elastomer modification (b) particulate modification (c) thermoplastic modification and (d) 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 [43].

a). Elastomer modification

The various types of elastomeric materials which have been studied with a view to modify epoxy resins are the following. (i) poly siloxanes [44] ii) fluro elastomers [45] (iii) acrylated elastomers [46] and reactive butadiene-acrylonitrile solid [47] and liquid rubbers [48]. Sultan and McGarry in their studies used carboxyl terminated acrylonitrile (CTBN) liquid rubber for modifying Epon 828 diglycidyl ether of bisphenol A epoxy resin with excellent results.

Toughening can be achieved by dispersing a small amount of elastomer as a discreet phase or by incorporation of reactive liquid polymers [49]. Epoxy resin, curing agent and curing accelerator are mixed at room temperature at a definite ratio. To this liquid rubber is added, mixed carefully until the mixture is homogeneous and then moulded [50]. Toughness enhancement of epoxy matrix with elastomers demands a reaction (e.g., esterification) between the elastomer and the resin which leads to an adequate bond between the elastomeric and epoxy phases. In the case of carboxy terminated liquid rubbers like CTBN, chemical modification is done by refluxing a mixture of the rubber and the epoxy resin in presence of triphenyl phosphine as catalyst [51]. The epoxy- rubber adduct formed this way behaves as epoxy terminated rubber which is more compatible with the epoxy matrix. Solid rubber can be used as a solution (e.g., in methyl ethyl ketone) which can be mixed with the resin and the hardener [47].

In rubber modification the rubber is initially miscible with the resin and the hardener. When the reaction starts, the rubber first forms a copolymer with the resin, then phase-separates. Thus the cured thermoset possesses a dispersed rubbery phase. The type of rubber modifier used will depend on the chemical characteristics of the matrix polymer at least in terms of terminal functionality. Several functionalities have been studied including epoxy, phenol, vinyl, hydroxyl, mercaptan, amine and carboxyl with reasonable success [52] (Table 1.4). However the greatest benefit has been reported for elastomers with carboxyl functionality (CTBNs).The rubbery domains precipitate during cure to form a toughened epoxy material. Numerous reports have been devoted to this area in the last two decades [53, 54].

Table 1.4 Effect of functionality on the toughening ability of butadiene-acrylonitrile rubbers [52]

Elastomer	Functionality	Fracture Energy (kJ m^{-2})
CTBN	Carboxyl	2.8
PTBN	Phenol	2.6 -3.0
ETBN	Epoxy	1.8 -2.5
HTBN	Hydroxyl	0.9 -2.6
MTBN	Mercaptan	0.2 -0.4

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 di isocyanate (TDI) capable of reacting with both epoxide and hydroxyl functionalities resulting in the formation of both urethanes [55] and oxazolidone groups between the elastomeric and epoxide components. Toughening of epoxies by chemical modification using hydroxyl terminated polybutadiene (HTPB) and TDI improves the impact strength considerably [56]. Silane coupling agents can also be used to improve epoxy-rubber interface [57].

A number of acrylate based elastomers have been used in epoxy toughening. The usefulness of acrylate based liquid rubbers as toughening agents for epoxy resin has been demonstrated [58, 59, 60]. The impact properties and morphology of MDA (methylenedianiline) cured epoxy resin modified by acrylate based liquid rubber have been studied in detail [61]. Modification of epoxy resin using acrylic co-polymer with side chain mesogenic units has also been carried out [62]. Acrylic rubbers containing a pendant epoxy group have been employed for the toughening of DGEBA resin [63]. Epoxy resin modified by acrylic core shell system (polybutyl acrylate as core and PMMA as shell) is found to have better properties compared to simple epoxy/acrylate system [64].

In an attempt to improve the compatibility between the resin and rubber, recycled rubber has been used [65]. The adhesive properties of blends of epoxy resin and end functionalised polybutadiene have been studied in detail [66]. The toughening process in CTBN modified epoxy resins has been monitored by electron beam radiation [67]. Rubbery epoxy particles can be formed as droplets by curing aliphatic or aromatic epoxy resin in water and these particles are shown to be novel toughening agents for epoxy resins [68].

A variety of polysiloxanes and silicone rubbers act as effective modifiers of epoxy resins. Flexibility of epoxies can be improved by modifying the resin with polysiloxane containing isocyanate groups [69]. Interpenetrating networks of epoxy resin and polydimethyl siloxane are found to have excellent strength and flexibility [70]. Epoxies modified by polysiloxane thermoplastic polyurethane are used in electronic encapsulation [71, 72]. Polydimethyl siloxane is used to toughen tetrafunctional epoxy resin [73]. Silicone rubber particles of varying degree of cross-linking are used as epoxy modifiers and the properties of the modified resin depend on the silicone content and the degree of cross-linking [74]. To improve the toughness of epoxy-silicone system, aramid silicone block co-polymers are employed [75]. The phase structure and toughness of silicone modified epoxy system with added silicon graft polymer have been studied [76].

i). Phase morphology development: To provide toughness enhancement, phase separation followed by the slow development of a two-phase morphology is critically important. To achieve this, the rubber must initially dissolve and become dispersed at a molecular level in the epoxy and get precipitated when epoxy cross-linking takes place. This gives the required two phase morphology with the formation of rubbery particles dispersed and bonded to the cross-linked epoxy matrix. The factors likely to influence morphology include elastomer concentration [52], molecular weight and acrylonitrile content, the type and extent of hardener used and cure conditions [77]. The morphological factors considered important for optimum toughening in rubber modified epoxies are the rubber volume fraction, particle size and particle size distribution [78, 79, 49]. Studies with butadiene-acrylonitrile rubbers show that the size of rubber particles decreases with increasing acrylonitrile content in the rubber and practically no phase separation occurs in epoxies modified with CTBN containing a high amount (about 26%) of acrylonitrile [80,81]. Toughening is found only when the rubber forms a separate phase in the epoxy matrix with a particle size of the order of micrometers.

ii). Bimodal particle systems: The role of particle size and in particular particle size distribution has to be emphasised particularly with respect to some rubber toughened commercial epoxy formulations where a deliberate attempt is made to promote bimodal particle size morphology. The toughening influence of bisphenol A in rubber modified epoxy systems was illustrated by Levita et.al. [82]. Riew et. al. demonstrated a bimodal distribution of rubber particles based on CTBN-bis-phenol A-DGEBA liquid epoxy resin-piperidine [52]. The substantial improvement in toughness achieved by the inclusion of bisphenol A to rubber modified epoxy resin was related to a bimodal particle size morphology.

iii).Volume fraction of dispersed phase: An increase in rubber volume fraction (v_f) of dispersed rubbery phase generally promotes toughness of a multiphase thermoset. With a rubbery volume fraction of 0.1 to 0.2 the fracture energy (G_{IC}) may be increased by ten to twenty times. The main toughening mechanisms initiated by the presence of rubber particles are localized shear deformation in the form of shear bands running between rubber particles [83] and internal cavitation or debonding of rubber particles [84] with subsequent plastic growth of voids in the epoxy matrix. Kinloch and Hunston [85] were able to show that in the case of unimodal distribution of rubbery particles at a low test temperature, G_{IC} increases only slowly with increase in volume fraction and then reaches a plateau value. At high temperature the relationship is almost linear and the rate of increase of G_{IC} with v_f is far greater than that found at low temperature.

iv). Size of rubber particles and toughness: The effect of the rubber particle size on deformation mechanism in epoxy system was studied by Sultan and McGarry [48]. Shear mechanism is enhanced by the presence of small rubber particles while crazing appears as the main reason for toughness improvement with large rubber particles (1.5 to 5μm), and the fracture energy of such a material is five times more than that with smaller rubber particles.. However, Kinloch and Hunston [85] reported that a bimodal distribution of particle sizes (0.1 and 1.3 μm) resulted in higher G_{IC} values than resulting from unimodal distribution (1.2 μm).

v). Mechanism of phase separation: Two mechanisms have been proposed to explain the process of phase separation -the nucleation-growth mechanism and spinodal decomposition. The former [49, 86] derives from the fact that the morphologies consist of spherical domains dispersed in a continuous matrix and this is widely accepted. Yamanaka [87] gave experimental evidence for the presence of spinodal decomposition in fast reacting systems with high rubber concentration. According to Yamanaka the nucleation-growth mechanism is unlikely because it is a very slow process.

The development of morphology and phase separation can be of two different types; a polymerisation –induced phase separation (PIPS) [88,89] and a thermally induced phase separation (TIPS) [90,91]. As per PIPS the driving force of the system is the progressive increase of molecular weight of the polymerisation monomers. Nucleation –growth mechanism may take place in PIPS along with spinodal decompositions. The results furnished by Yamanaka et. al [92] show that curing induced phase separation proceeds mainly by spinodal decomposition . During curing, the system passes through the meta stable region before it is forced into the unstable region. Thus phase decomposition by a nucleation growth mechanism is likely. Some recent studies have revealed the possibility of nucleation growth in such a polymerisation induced phase separation [93,94]. The morphology of DGEBA-HTBN system cured with tetrahydro phthalic anhydride has been studied [95].

b). Particulate modification

Incorporation of particulate fillers such as silica and alumina trihydrate can enhance toughness of cross-linked epoxies. Kaolin, glass beads, $CaCO_3$ fillers etc are used with epoxies with a view to lower the cost while increasing rigidity of the final product. Particulates contribute to a greatly enhanced modulus which is a significant advantage over elastomeric modification where a reduction in modulus is observed [96]. The degree of toughness improvement was found to depend upon the volume fraction as well as the particle size and the shape of the filler [97]. It has been reported that in the case of filled polymers, fracture energy can attain a maximum at a specific volume fraction of the added particles which may also decrease the elongation at break and impact resistance [98,99]. The mechanism of particulate toughening is somewhat different from that of elastomeric modification. Although some modest improvements in toughness have been achieved with particulate reinforcement, these have not been of the same magnitude as elastomeric modification. A substantial modulus increase accompanying toughness enhancement is a major advantage of particulate modification.

Several studies have been conducted exploring the possibilities of combining both particulate and rubber modification of epoxies [100]. The benefits of hybrid structures (filler and rubber simultaneously) in toughening epoxies have been illustrated by Dusek et. al. [101]. Epoxy hybrid composites with glass beads andα,ε, oligo butyl methacrylate diol were found to have improved mechanical properties [102]. Particulate modification of epoxy resin using nickel (II) complex has been done and the reaction kinetics followed by DSC measurements [103]. Reactive microspheres have been used as active fillers in epoxy resins [104]. Toughening of DGEBA resin using rigid glass particles has been demonstrated by Norman et.al.[105]. Hyper branched poly (ester silane), used as coupling agent in glass bead filled epoxy resin is found to enhance the mechanical properties of the composite considerably [106].

c). Thermoplastic modification

Thermoplastic toughening of epoxy resins, studied since the early 1980s, shows considerable progress in property enhancement. The main advantage in using thermoplastics to toughen epoxies is that their inclusion needs not result in any significant decrease in desirable properties such as modulus and yield strength as is the case with rubber toughening. A brief overview of thermoplastic toughening studies performed up to 1990 is available in the literature [107]. A review by Pearson focuses on thermoplastic toughening methods and the common synthetic methods for preparing these materials [108]. A brief account of thermoplastic toughening of epoxies is given by Frigione et, al. [109].

Generally three main epoxy resins are used for thermoplastic modification; DGEBA, tetraglycidyl diamino diphenyl methane (TGDDM) and triglycidyl para amino phenol (TGAP). The most commonly used hardener is diamino diphenyl sulphone (DDS) which is slow reacting but imparts high Tg and thermal stability to the cured resin. Dicy, meta phenylene diamine (MPDA) and methylene di aniline (MDA or DDM) are also used in some systems. Polysulphones (PS), polyether sulphones (PES), poly etherketones (PEK), poly etherether ketones (PEEK) and polyetherimides (PEI) are the major thermoplastics employed in epoxy toughening.

The first two toughening studies with thermoplastic additives were carried out by Bucknall and Partridge in 1983[110]. 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 a 100% increase in fracture energy. McGrath et.al [111] used hydroxyl and amine terminated polysulphones as modifiers for DGEBA type resins. Thermal stability and toughness of polysulphone epoxy system have been evaluated [112]. Epoxy-PES system with continuous phase morphology of the thermoplastic decomposes rapidly and is used in recovering metals from waste [113]. Interpenetrating networks have been prepared from DGEBS/TGDDM/ DDS system by incorporating polyethersulphone and poly ether ether sulphone in 40:60 ratio[114]. 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. Venderbrosch et. al. [115] used polyphenylene ether (PPE) and Pearson and Yee [116] used polyphenylene oxide (PPO) as modifiers of epoxy resin. Polyether esters were also used to toughen epoxy resin [117]. High performance epoxy modified by poly etherimide (PEI) was found to have increased fracture toughness [118,119]. Poly etherimide grafted with amino groups can be used as an effective modifier for epoxy resin [120]. PEI was shown to promote good toughness enhancement without added end groups [121-123]. The cure kinetics of PEI/epoxy/aromatic diamine system has been investigated recently [124]. Modification of epoxy resin using polyethylene oxide cured by bisphenols has been reported in the literature [125]. The effect of reactive thermoplastic end groups in the toughening process has been critically evaluated by Hodgkin et.al.[126].

d). Miscellaneous methods

Semi interpenetrating polymer networks have been made from epoxy/ polycarbonate systems cured by a mixture of three hardeners of different activities

[127]. Toughening of epoxy resin is carried out using polyethylene randomly functionalised using a mono functional epoxy resin. This method increases the miscibility of PE with DGEBA type resins [128]. Cross-linked epoxy network modified by cyanate ester and bismaleimide has improved toughness and flexural strength [129]. N-phenyl maleimide-styrene co-polymers have been used as modifier in anhydride cured epoxy resin [130] and poly (oxy methylene) in aromatic diamine cured resin [131].

Polyesters prepared by direct poly condensation from bisphenol A and alphatic dicarboxylic acids (adipic acid, sebacic acid and dodecanoic acid) are used to improve toughness of DGEBA and diamino diphenyl methane epoxies [132]. Aromatic polyesters and hydroxyl terminated polyesters [133] have been used as modifiers of epoxy resins. Incorporation of epoxy hyper branched polymers based on aliphatic polyester into epoxy resin is shown to double the fracture toughness of the cured resin [134,135]. Epoxy terminated hyper branched aliphatic polyesters used as low viscosity additives in epoxy resin has little effect on Tg; but the fracture properties increase at 15phr additive concentration [136]. Impact strength of epoxy resin is found to increase by 135% by the addition of 16 phr of a polyester with molecular weight 1.9×10^4 [137]. Cycloaliphatic epoxies are toughened by poly (ethylene phthalate) [138]. DGEBA/ cellulose acetate blends are used for making ultrafiltration membranes by phase inversion technique [139].Blends of methylene dianiline (MDA)-cured DGEBA epoxy oligomer and ethylene-vinyl acetate co-polymer rubber (EVA) [140] have been shown to have tensile, flexural, thermal, and hardness properties Blending of two thermosets through interpenetrating network (IPN) has been extensively studied [141]. Toughened interpenetrating network (IPN) materials based on unsaturated polyester resin (UPR) and DGEBA type resin have been prepared using meta xylene diamine (MXDA) and benzoyl peroxide curing agents [142].

Toughness modification of epoxies by polyurethane (PU) pre-polymer based on hydroxyl terminated polyesters by IPN grafting [143] resulted in superior mechanical properties. It was found that hydroxyl aliphatic polyester improved fracture toughness more than amine or acid terminated polyester due to effective molecular weight build-up by a chain extension reaction. In fact hydroxyl terminated polyesters are considered as a special case of polyols which are shown to be effective in enhancing the impact strength as well as fracture toughness of epoxy resin [144]. The use of polycarbonate polyurethane [145] as epoxy modifier has also been reported. A great deal of literature has been devoted to the toughening of epoxies using polyurethane as second phase to form IPNs [146,147]. The effect of amine terminated polyurethane as epoxy modifier has been studied [148]. Toughening of epoxy resin by hydroxyl terminated silicon modified PU oligomers has yielded promising results [149]. Glycidyl terminated polyurethane prepolymer has been used to modify impact strength and fracture energy of epoxy resin [150]. Isocyanate terminated polybutadiene has also been employed as toughness modifier in epoxy resins [151]. Modification of epoxy resin using blocked diisocyantes has also been reported [152].

Studies on chain extended ureas as curing agents and toughness modifiers for epoxies have been conducted with reasonable success [153]. Epoxy resin can be cross-linked by anionically polymerised caprolactam through reaction of the oxirane ring with the amide nitrogen atom and the resulting blends show enhanced electrical and mechanical properties [154]. Plastisols based on PVC and diethyl hexyl phthalate have been used as modifiers for epoxy resins [155]. Schroder et .al. [156] have used telichelic methacrylates as toughening agents for epoxy resins. Epoxy resins can be modified by blending with thermotropic hydroxy ethyl cellulose [157], cresol novolacs catalysed by triphenyl phosphine [158] and by epoxidised soyabean oil [159]. Reinforcement of DGEBF by liquid crystalline diglycidyl ether of 4,4-dihydroxybiphenol (DGE-DHBP) has also been studied [160].Other liquid crystalline polymers are also used for modifying epoxy resin [161]. Toughening studies on ABS/PC modified epoxy system have also been carried out [162]. Ionic polymer toughening is rather a new technique in the field of modification of epoxy thermosets [163].

1.4.2 Mechanisms of Toughening

Several mechanisms have been proposed to account for the toughness improvement in rubber modified 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 rubber particles. It will be relevant to consider each of these mechanisms and to assess their application to rubber modified epoxies.

a). Rubber tear (Particle deformation)

This mechanism was put forward initially by Mertz, Claver and Baer in 1956 to explain the deformation and tearing of the rubber particles present in a two-phase system [164]. 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.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. According to them it is the principal deformation mechanism in the matrix, enhanced by the presence of the second phase which improves toughness. Stretching and tearing of rubber particles embedded in the epoxy matrix result in high energy absorption during failure [165]. Rubber tearing was shown to be the main contributor to the failure energy of high molecular weight NBR-modified epoxies [47]. However, the rubber tear theory does not explain the existence of stress whitening frequently observed in rubber modified epoxies. It does not account for yielding and plastic flow contribution to toughness. Though this mechanism is considered as a weak, secondary mechanism in rubber modified epoxies, it is important for highly cross-linked epoxies modified by larger particles.

b). Multiple crazing

A craze appears to be similar to a crack owing to its lower refractive index than its surroundings. It actually contains fibrils of polymer drawn across, normal to the craze surface in an interconnecting void network. This mechanism was proposed based on several observations like stress whitening ahead of crack tip and the strong dependence of fracture toughness on particle size. 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. This process has been demonstrated with thermoplastics such as high impact poly styrene through optical microscopic studies. Subsequent studies [166] on various rubber modified polymers confirmed that crazes frequently initiate from the rubber particles at regions of high stress concentration at 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. According to Sultan and McGarry [48] crazing is the dominant toughening mechanism in rubber modified epoxies. The detailed mechanism of craze initiation, growth and break down around rubberparticles has been studied by Donald and Kramer [167]. 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 than1μm. With thermosets where crosslink density is high and hence chain length between cross links short, crazing would be suppressed [168]. The frequently observed stress whitening phenomenon was attributed to the generation of crazes. Correlation between stress whitening and fracture toughness of rubber modified epoxies has been reported in the literature [169].

c). Shear yielding

This theory was proposed by Newman and Strella [170] following work on acrylonitrile-butadiene-styrene thermoplastics. The main proposal of this theory is that shear deformation taking place either as shear bands or as a 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. Plastic shear yielding in the resin matrix is enhanced by stress concentrations associated with the embedded soft rubber particles [171]. 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 Kramer the dispersed rubber phase initiates micro shear bands at an angle of 55 to 64 degrees to the direction of the applied stress [172]. In materials having smaller rubber particles crazing was not initiated but shear deformation, promoted by rubber particle cavitation was the major toughening mechanism. Shear bands formed at 45^0 to the stress axis appeared to intersect crazes and to run between rubber particles. Thus shear bands act as craze terminators. The presence of rigid particulate fillers like glass beads, silica etc. may also cause enhanced shear yielding of the matrix. However, they are not as effective as rubber particles in increasing toughness.

A major drawback of shear yielding theory 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 [48]. 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 [173].

d). Cavitation-shear yielding

This toughening mechanism, developed independently by Kinloch, Shaw and Hunston [173] and by Pearson and Yee [174] is regarded as the most consistent in terms of experimental data generated in recent years. The correlation between toughness and the extent of plastic deformation found on fracture surfaces has led to a mechanism based on yielding and plastic shear flow of the matrix as the primary source of energy absorption in rubber modified epoxies. Enhanced plastic deformation in the matrix has been found to accompany the inclusion of rubber particles and the stress distribution existing around rubber particles located in the vicinity of a stressed crack tip becomes important. Initially the development of a triaxial stress dilates the matrix and along with this, the triaxial stresses inherent in the rubber particles (due to differential thermal contraction effects during initial curing) provide the necessary conditions for cavitation of the rubber particles. Rather than crazing of the epoxy matrix, it is the cavitation process which is considered responsible for the stress whitening effects usually observed in rubber modified epoxies. The increasing stress concentrations around rubber particles during loading would promote shear yield deformation zones in the matrix. Since the particles would also act as sites of yield terminations, yielding would remain localized in the vicinity of the crack tip. It is reasonable to assume that both cavitation and shear yielding would occur during the early stages of load application. Once initiated, the rubber particle cavitation would enhance further shear yielding in the matrix. Crack tip blunting would increase extensively resulting in increased development of the plastic zone at the crack tip. Thus toughness would be enhanced as has been observed in practice. At the same time Yee and Pearson attributed an order of magnitude increase in toughness to the cavitation of rubber particles followed by shear yielding of the epoxy matrix [174]. When dispersed acrylic rubber (DAR) is used to modify epoxy matrix, the DAR particles are found to be cavitated around the crack tip and the crack wake.

The absence of cavitation in solid rubber modified epoxies should result from the high molecular weight of solid rubber (e.g., NBR) and a high tensile strength of rubber can eliminate premature cavitation [47]. It is postulated that the low molecular weight CTBN rubber with low tensile strength is readily cavitated at early stages of loading and it is interesting to note that the fracture toughness of the rubber modified epoxy is loading rate dependant [175].The process of cavitation during fracture diminishes the importance of the rubber tearing mechanism because the failed rubber particles require little or no tearing energy [176,177].

e) Crack bifurcation and/or deflection by rubber particles

Rubber particles cause the main crack to fork into many secondary cracks. The local stress intensity of the main crack is distributed to multiple cracks and/or deviating the crack off the principal plane of propagation. This increases the area of the crack surface [178]. This mechanism is ineffective unless it interacts with other mechanisms. It is considered as a secondary mechanism in rubber toughened epoxies. However, this mechanism is important for highly cross-linked epoxies modified by large rubber particles.

f). Crack pinning

This mechanism was developed by Lange and Radford [179] to explain modification by particulate fillers. Lange showed that by inclusion of alumina trihydrate as particulate filler fracture energy of epoxy matrix could be increased. Although particulate reinforcement could impose stress concentrating effects on the epoxy matrix, this is not considered significant. The crack pinning mechanism based on the impeding characteristics of the particles proposes that a propagating crack front, when encountering an inhomogeneity, becomes temporarily pinned at that point [180]. As the load increases the degree of bowing between pinning points increases which results in both a new fracture surface and an increase in the length of the crack front. It is seen that the fracture energy of the particulate composite will increase as the particle spacing decreases. The degree of toughening depends on both the volume fraction and particle size of the filler.

1. 4. 3 Effect on ultimate properties

Toughening refers to mechanical and thermal stress resistance and it does not affect the other properties such as thermal stability, strength and hardness. With the incorporation of rubber into the epoxy matrix, impact strength, fracture toughness and fracture energy are increased while Young's modulus and yield strength are decreased slightly. Incorporation of low levels of liquid rubbers to a normally brittle epoxy matrix significantly improves the crack resistance and impact strength without much reduction in other thermal and mechanical properties. The mechanical properties of blends of DGEBA based epoxy resin and internally epoxidised hydroxyl terminated polybutadiene rubber have been studied by Bussi et.al. [181]. For medium epoxidised rubber (at low rubber content) both modulus and yield stress were independent of rubber content. The DMA analysis showed that most of the medium epoxidised rubber dissolved into the epoxy phase [182]. The tensile test results indicated that dissolved rubber does not affect the properties of the epoxy phase.

The influence of rubber content on the stress – strain curve for rubber modified epoxy system has been studied in detail [183]. The slight decrease in modulus is due to an increase in the dissolved rubber in the epoxy matrix. However, the rate of increase of fracture energy with rubber content varies with test conditions [85]. The poor toughening effect of physical blending was explained by the relative ease with which de-bonding can occur between the two phases during fracture. TG-DTA analysis of the rubber toughened and neat epoxies showed that the percentage weight loss is slightly more for the rubber toughened system. This was due to the high susceptibility of the aliphatic chain of the rubber network in the molecular backbone for thermal and oxidative degradation.

T_g of the matrix generally falls by the incorporation of liquid rubbers due to the gain in ductility. Thus, increased ductility and toughness are frequently observed only at the expense of high temperature properties. A DGEBA based epoxy resin containing 15% epoxy terminated butadiene acrylonitrile (ETBN) when cured with a cycloaliphatic diamine showed a decrease of 25^0C in T_g

compared to that of the neat matrix [184].Rubber that did not phase separate remains dissolved and could plasticize the epoxy matrix resulting in a lowering of T_g [185]. Glass transition temperature generally decreases with increasing rubber content and increases as the compatibility of rubber and epoxy decreases.

The toughness of rubber modified epoxy is strongly influenced by molecular weight [186], thus showing that toughenability of an epoxy resin by elastomers will be dependent largely on the cross link density of the epoxy matrix. The lower the cross link density, the greater will be the toughenability. Incorporation of bisphenol A into rubber modified epoxy system [187] has been shown to provide substantial toughening benefits with solid and liquid rubbers.

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 [188]. 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.

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 [189]. 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 an increasing application 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 FRPindustry.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 [190,191].

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 of 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.

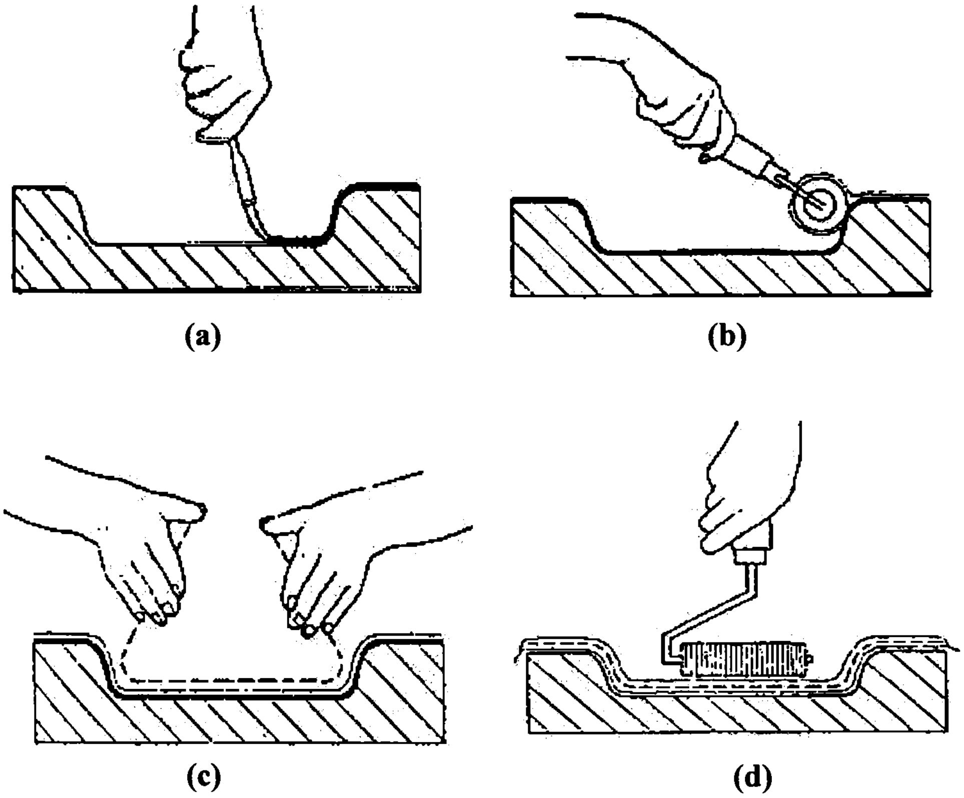
f) Plant Fibres: With the exception of synthetic polymers, most economically important products, such as paper, cordage (cords and rope) and textiles, are derived from plant fibres. Many varieties of plant fibre exist, such as hairs (cotton, kapok), fibre sheaf of dicotylic plants or vessel sheaf of 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).

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.1.5) 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

b) Spray-up technique: Spray-up technique is the principal fabrication process used by the FRP industry. 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



Fg. 1.5 Hand lay up (a) apply gel-coat with brush (b) apply laminating resin with roller (c) cut and fit reinforcement layer (d) consolidate with ribbed roller

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. 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 [189].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 [192] 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 resin injection moulding (RRIM) mixes the resin on the way into the mould.

1.5.3 Toughening of fibre reinforced plastics

Toughness and fracture resistance are important requirements in advanced composites used for most load bearing applications. Several attempts have been made to improve the composite toughness by improving the toughness of the polymer system. But large increase in polymer toughness has not been found to give proportionate increase in composite toughness. Toughness can be enhanced by a variety of techniques, such as modification of the matrix, fibre coating and interleaves between plies. These methods combine the stiffness and processability of thermosetting matrices with the impact resistance of elastomers or thermoplastics.

The essential requirement for toughness enhancement of thermoset matrices is that the additive should be soluble in the uncured resin and phase separation must occur during the curing cycle. If any additive remains after the cure cycle, the T_g of the resin is lowered with deleterious effect on the ultimate performance of the composite. Epoxy resins blended with carboxy terminated butadiene acrylonitrile (CTBN) are the most widely studied system.

An alternative technique to produce tougher composites is to utilise a coating of thermoplastic or thermoset resin on the fibres. This is achieved by electro coating carbon fibres, or more readily for all fibres, from a solution treatment. Good adhesion between the coating and fibres are essential for effective toughening. Electrocoating creates chemical bonds between the carbon and the rubber (eg. CTBN). The application of elastomeric coatings to fibres enhances the inter laminar fracture energy and the impact resistance of the composite. However, the inter laminar shear strength (ILSS) is found to be reduced.

A further approach for toughness enhancement of composite system is to introduce thin layers of a more ductile matrix between the plies of highly cross-linked prepreg. These can be continuous or discrete. The addition of discrete ductile matrix results in the establishment of direct chemical bonds between the plies.

Toughening mechanisms in the laminate are characterised by two different processes. At the crack tip, processes in operation are crazing, matrix micro cracking, plastic deformation, fibre or particle de-bonding and phase transformations. As the crack propagates another set of toughening mechanisms such as fibre or particle bridging, matrix bridging, fibre-pull out and precipitate elongation become operational. Two or more processes may combine to form a synergistic toughening effect. The increase in toughness achieved by a specific mechanism is produced by the energy change in a volume element as a crack propagates through the composite.

Microwave curing is used in glass fibre or graphite fibre reinforced epoxy composites [193]. Newer methods in microwave processing of epoxy composites have been devised by Outifa et.al.[194]. Graphite fibre reinforced epoxies lack impact strength and damage tolerance. Incorporation of PU based IPNs into the epoxy matrix improved these properties [195]. The influence of matrix chemical structure on inter laminar fracture toughness of glass fibre reinforced epoxies [196] and the effect of epoxy /anhydride matrix on processing and fatigue properties of unidirectional glass fibre composites have been studied [197]. Attempts have been made to understand the surface controlled reactions of Kevlar fibres on epoxy composite interface [198,199]. The fatigue properties of glass cloth reinforced epoxy composites can be modified using perfluorinated alkyl ether elastomer [200]. The effect of reinforcing fibres on the morphology of toughened epoxy/amine system has been reported [201]. Isothermal DSC can be used to follow the cure kinetics of carbon nanofibre reinforced epoxies [202]. Flexibility of short glass fibre reinforced epoxy is shown to be improved using liquid elastomer (HTPB) in presence of silane coupling agent [203]. Surface modified multi-walled carbon nano tubes (CNT) are used [204] to enhance the interaction between nanotubes and epoxy resin in epoxy/CNT composites.

1.6 Scope and objectives of the present work

Mechanical performance in high loading conditions is a general requirement for the successful application of thermoset resins. This often calls for high levels of energy absorption. A vast amount of literature exists concerning rubber, thermoplastic and particulate toughening of epoxy resin. The aim of this investigation is to develop toughened polymer systems for DGEBA epoxy resin via physical and reactive blending methods. The strategy for toughening will be three fold;

I.Incorporation of other thermoset resins: Other thermoset resins can be blended with epoxy resin in suitable proportions to obtain improved toughness properties. These resins include epoxidised novolac resins, phenolics, unsaturated polyester resin (UPR) etc.

ii. Elastomer modification: Elastomers in the solid form can be incorporated by dissolution in a suitable solvent and subsequent blending with the epoxy resin. In this study, elastomers, maleated elastomers and functional elastomers are dispersed as micro-sized rubber phase into the continuous epoxy phase by solution blending technique. These blends will then be cured and tested for properties .In the case of liquid rubbers with terminal functionality (e.g., CTBN, HTPB and HTNR) chain extension through common curing agents as well as incorporation of bisphenol A can be a promising approach.

iii. Particulate modification: Inorganic fillers can be incorporated into the epoxy matrix to improve its impact resistant characteristics. Silica, alumina, zinc oxide, calcium carbonate, graphite powder and asbestos powder can be used for this purpose.

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

1. To synthesise DGEBA resin and compare the properties with those of the commercial sample. Also prepare various resins for subsequent modification.
2. To modify the properties of DGEBA by the reactive blending technique employing different thermoset resins.
3. To incorporate different elastomers into DGEBA and study the toughening effect
4. To prepare fibre reinforced and mineral filled composites from modified epoxies and observe the effect of toughening of the resin matrix.

References

1. A. A. Collyer, Ed. *Rubber Toughened Engineering Plastics*, Chapter 6, Chapman & Hall, London (1994).
2. Zuo-Guang Zhang, Yu-Bin Li, Yan Wu and Feng -Mei Li., *J. Appl. Polym. Sci.,* **94**(5), 2217-2222 (2004).
3. 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).
4. A.K. Sharma, *FRP Today*, Feb-Mar (2003).
5. Jiyanying Huang, Meaquing Xu, Quang Ge, Minghuua Lin, Yihong Chen, Jiayan Chu, Lizong Dai, Yousi Zou.,*J.Appl. Polym. Sci*, 97 (2), 652 (2005).
6. German Patent 676,117
7. U.S Patent 2,456,408 and U. S Patent 2,521,911
8. Jiang Ding and Wanfang Shi, *Eu. Polym. J.*, 40 (6),1137-1143 (2004)
9. Metha Rutnakornpituk, *Eu. Polym. J.*, 41(5), 1043-1052 (2005)
10. Soo-Jin Park, Fan-Long Jin, Jae-Rock Lu and Jay-Sup Shin., *Eu. Polym. J.*, 41 (2),231-237 (2005)
11. J. A. Brydson, *Plastic materials,* Ch 26. Butterworths Heinemann, Oxford (1999).
12. H. Jahn and P. Goetzky in *Epoxy Resin Chemistry & Technology*, 2nd Ed. C.A. May ed. Marcel Dekker, NY, p-1049 (1988).
13. D. K. Hadad in *Epoxy Resin Chemistry &Technology*, 2nd Ed. C.A.May ed. Marcel Dekker, NY, p-1049 (1988).
14. A. Kastaneck, M. Bohdanecky and S. Podzimek, *Eu. Polym. J., 41*(2), 319-28(2005).
15. 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).
16. A. Gupta, M. Cizmecisglu, D. Coulter, R.H. Liang, A. Yavrouian, F.D. Tsay and J.C. Moacanin, *J. Appl. Polym. Sci.,***28** ,1011(1983)
17. W.B. Moniz, *Org. Coat. Plast.* **39**, 99 (1981)

18. D. Wolff, K, Schlothauer, M. Fedtke and J. Spracek., *Polymer* ,**32,** (1990)
19. C.A. May, *Epoxy Resins; Chemistry and Technology*, 2nd Edn. Marcel Decker Inc. New York, Page ,551-718 (1988)
20. R.J. Arnold., *Mod.Plast*, **41**(4) 149(1964).
21. A. Kondyurin and B. Lauke, *Eu. Polym. J.,* **40**(8) , 1915- 1923 (2005).
22. E. Frulloni, M. M. Salinas, L. Torre, A. Hariani and J.M. Kenny, *J. Appl. Polym. Sci.,* **96** (5), 1756-1766 (2005).
23. J. Charlesworth, *J. Polym. Sci.,* **18,** 621 (1980)
24. P. I. Engelberg and G. C. Tesoro., *Polym. Eng. Sci.,* **30** (5), 303-307 (2004).
25. F. Fraga, C. Castro Diaz, E. Rodriguez Nures and Martinez Ageitos, J. Appl. Polym. Sci., **96** (5), 1591-1598 (2005).
26. J. King , R. Sellers and R. Castonguay., U S patent 4,330,659, (1982)
27. W.A. Romanchick and J. F. Giebel., *Org. Coat. Appl. Polym. Sci. Proc.* **46,** 410 (1982)
28. V. Tanratanakul and K. Sae Traw., *J. Appl. Polym. Sci.,* **97** (4), 1442-1461(2005)
29. A.B. Samui, D. Ratna, J.G. Chavan and P.C. Deb., *J. Appl. Polym. Sci.,* **86** (10), 2523-2529 (2002)
30. J. Sickfield, and W. Mielke., *Prog. Org. Coat.,***12,** 27 (1984)
31. S.A. Mestan and C. E. M. Morris, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* **24**(1), 117 (1984)
32. A. Wereta Jr. and C.A. May, *J. Adhes.* **12,** 317 (1981)
33. S.D. Senturia, N.F. Sheppard, Jr. H.L. Lee and D.R. Day , *J. Adhes.,* **15,** 69 (1982)
34. James E. Mark, *Polymer Data Handbook*, Oxford University Press, New York (1999).
35. D. Derouet, F. Morvan, and J.C. Bross., *J. Appl. Polym. Sci.,* **62** (11), 1855-1868 (1996).
36. A.D. La Rossa, A. Recca, J.T. Carter and P.T. McGrail., *Polymer,* **40** (14), 4093-4098 (1999).
37. A. Maazouz, H. Sautereau and J.F. Gerard., J, *Appl. Polym* Sci., **50,** 615 (1993).

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

39. F.J. Mc Garry, *Rubber in Cross-linked Polymers*, Applied Science, London (1983).

40. M.F. Ashby, *Materials Selection in Mechanical Design*, Pergamon Press, New York (1992).

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

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

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

44. E.M. Yorkgits, C. Trau, N.S. Eiss, T.Y. Hut, I. Yilgor, G.L. Wilkes, and J.E. McGrath, *Adv. Chem. Ser*, 208 ,137 (1984).

45. J. Mijovic, E.M. Pearce and C.C. Foun, *Adv .Chem .Ser.*, 208, 293 (1984)

46. S.L. Krishenbaum, S. Gazit and J.P. Bell, *Adv .Chem. Ser.*, 208,163 (1984).

47. M. Frounchi, M. Mehrabzadeh and M. Parvary, *Polym. Int,*. **49**,163 (2000).

48. J.N. Sultan and F. Mc Garry., *Polym. Eng. Sci.*,**13** , 29 (1973).

49. B.U. Kang, J.Y. Jho, J. Kim, S.S. Lee, M. Park, S.Lim and C.R.Choe., *J.Appl.Polym.Sci.*,**79**, 38 (2001)

50. E. Yilgor, and I. Yilgor, Polymer, **39**, 8-9 (1998).

51. P. Bartlet, J.P. Pascault and H. Sautereau, *J. Appl. Polym. Sci.,* **30**,2955 (1985).

52. C.K. Riew, E.H Rowe and A.R., Siebert , *Adv.Chem.Ser.*154 , 326(1976)

53. C.K Riew and A.J. Kinloch, Eds. *Toughened plastics* 1; Science and Engineering; Advances in Chemistry 233; ACS; Washington, DC (1993).

54. S.Kar and A.K. Banthia., J. *Appl. Polym.* Sci., **96** (6), 2446-2453 (2005).

55. S. Sankaran and M., Chanda, *J. Appl. Polym. Sci.,* **39**, 1459 (1990).

56. Vera I Pereira Soares, Valeria D Ramos, George W.M. Rangel and Regina Sandra Nascimento., *Adv. Polym. Tech.*, **21** (1), 25-32 (2002).

57. C. Kayanak, C. Celikbilek and G. Akovali, *European Polymer Journal*, **39** (6), 1125 (2003).

58. S. Kar and A.K. Banthia., *J. Appl. Polym. Sci.,* **92** (6), 3814-3821 (2004).
59. C. Dispenza, G. Spadaro, J.T. Carter and P.T. McGrail., *Polym. Eng. Sci.,* **41** (9), 1486-1496 (2001).
60. D. Ratna., A.K. Banthia and P.C. Deb., *J. Appl. Polym. Sci.,* **78** (4), 716 -727 (2000).
61. S. Kar., D. Gupta, A.K. Banthia and D. Ratna. *Polym. Int.,* **52** (8), 1332 - 1338 (2003).
62. Baolong Zhang, Shaowen Liao, Keyu Shi, Zonglie Du, Manquan Du, Lu Zheng and Jifu huang., *J. Appl. Polym. Sci.,***73** (9), 1787-1792 (1999).
63. M. Tomoi., H. Yamazaki., H. Akada and H. Kakuichi., *Angewandte Macromoleculare Chemie,* **163** (1), 63-76 (2003).
64. Ashida Tadashi, Katoh Atsushi, Handa Kohichi and Ochi Mitsukazu., *J. Appl. Polym. Sci.,* **74** (12), 2955-2962 (1999).
65. E. Sipahi-Sadiam, G. Akovali, C. Kayanak, N. Akkas and M. Yetmez., *Polym. Eng. Sci.,* **41** (3), 514-523 (2001).
66. F.L. Barcia, B.G. Soares and E. Sampaio., *J. Appl. Polym. Sci.,* **93** (5), 2370-2378 (2004)
67. J.S. Park, P.H. Kang, Y.C. Nho and D.H. Suh., *J. Macromolecular Science,* pure& Applied Chemistry, A-**40**(6), 641-653 (2003).
68. B.J.P. Jansen., K.Y. Tamminga, H.E.H. Meijer and P.J. Lemstra., *Polymer,* **40** (20), 5601-5607 (1999).
69. W.C. Shih, C.C.M. Ma, J.C. Yang and H.D. Chen., *J. Polym. Sci.,* **73**(13), 2739-2747 (1999)
70. Sung-Po Hou and Wu-Shin Yu., *Polymer,* **39** (26), 7033-7039 (1998).
71. Tsung-Han Ho, Jena-Hwa Wang and Chun- Shan Wang, *J. Appl. Polym. Sci.* ,**60** (8),1097-1107 (1996).
72. T.H. Ho and C.S. Wang., *Polymer,* **37**(13), 2733-2742 (1996).
73. M.C. Lee, T.H. Ho and C.S. Wang., *J. Appl. Polym. Sci.,* **62**(1), 217-225 (1996).
74. Hu -Wei Dang, Zou Yung Fang, Pan Cai Yuan., *J. Appl. Polym. Sci.,*69(3), 619-625 (1998)

75. M. Ochi., K. Takamiya., O. Kiyohara and T. Nakanishi., *Polymer,* **39** (3), 725-731 (1998)

76. M. Ochi and S, Shimaoka., *Polymer,* **40** (5), 1305-1312 (1999)

77. S.J. Shaw and D.A. Tod, *J. Adhes.,* **28,** 331(1989).

78. H.N. Nae, *J. Appl. Polym. Sci.,* **31,** 15 (1986).

79. J. Kinloch, and D.L Hunston, *J. Mater Sci. Lett.,* **6,** 131(1987).

80. Y. Huang, A.J. Kinloch, R.J. Bertsch, and A.R. Siebert, In *Rubber Toughened Plastics*: C.K. Riew, Ed; Advances in Chemistry, 233 , ACS, Washington DC, 195 (1993)

81. A. Lowe, O.H. Kwon and Y.W. Mai., *Polymer.,* **37** (4), 565-572 (1996)

82. G. Levita, A. Marchetti, A. Lazzeri, and V. Frosini, *Polym .Compos,* **8.** 141(1987).

83. H. J. Sue, *Polym. Eng. Sci .,* **31,** 275 (1991).

84. A. Lazzeri and C.B. Bucknall, *J. Mater. Sci.,* **28.,** 6799(1993).

85. A.J. Kinloch, and D. L. Hunston, *J.Mater.Sci. Lett.,* **6,** 137. (1987).

86. A.Vazquez, A.J. Rojas, H.E. Adabbo, J. Borrajo and R.J.J. Williams, *Polymer,* **28,** 1156(1987).

87. K. Yamanaka, Y. Takagi, and T. Inoue, *Polymer,* **60,** 1839 (1989).

88. T. Inoue, *Prog. Polym. Sci.,* **20,** 119 (1995).

89. P.A Oyanguren, P.M. Frontini, R.J.J. Williams, and J.P. Pascault, *Polymer,* **37,** 3087(1996).

90. T. Kyu, and J.H. Lee, *Phys. Rev. Lett,* **76** , 3746 (1996)

91. J. Zhang., H. Zhang, D. Yan, H. Zhou, and Y.Yang, *Sci. China, Ser.* B **40,**15. (1997).

92. K Yamanaka, Y. Takagi and T. Inoue, *Polymer,* **30,** 1840 (1989).

93. D Chen. J.P. Pascault. and H., Sautereau, *Polym. Int.* **32,** 369(1993).

94. M. Okada, K. Fujimoto and T. Nose, *Macromolecules,* **28,** 1795 (1995).

95. J. Zhang, H. Zhang and Y.Yang, *J. Appl. polym. Sci.* Vol. **72,** 59-67(1999).

96. A.C. Moloney, H.H. Kausch and H.R. Stieger, *J. Mater. Sci.* **19,** 5 (1984).

97. C. Moloney, H.H. Kausch, T. Kaiser and H.R. Beer, *J. Mater. Sci.,* **22,** 381(1987).

98. Y.Nakamura, M. Yamaguchi, A. Kitayama, M. Okubo and T. Matsumoto *Polymer*, **32,** 2221(1991).

99. E. Urbaczewski-Espuche, J.F. Gerard., J.P. Pascault., G. Reiffo and J.Sautereau, *J. Appl. Polym. Sci.,* **47,** 991(1993).

100. A.J Kinloch, D. Maxwell. R.J. Young, *J. Mater. Sci.,* **20,** 4169 (1985).

101. K. Dusek., L. Matejka., J. Plesti, and J. Somvarsky, Extended Abstracts 5th *European Symposium on Polymer Blends Preprints*, Vol.322, Maastricht. The Netherlands, May 12-15(1996).

102. N. Schroder, L. Konczol, W. Doll and R.Mulhaupt, *J. Appl. Polym. Sci.,* **88** (4), 1040(2003).

103. M. Ghaemy, A. Omrani and A.A. Rostami, *J. Appl. Polym.Sci.,***97** (1), 265-271 (2005).

104. C. Carfagna, V. Ambrogi, G. Cicala, A. Recca, A. Pollino and G. Costa.,*J. Appl. Polym. Sci.,* **93** (5), 2031-2044 (2004).

105. D.A. Norman and R.E. Robertson., *Polymer,* **44**(8), 2351-2362 (2003).

106. Gang Xu, Ming Gong and Wenfan Shi., *Polymer for Advanced Technology, 16* (6), 473-479 (2005).

107. J. C. Hedrick, N.M. Patel and J.E. McGrath *In Toughened Plastics I: Science and Engineering.,* Eds. C.K. Riew and G.K. Gillham, Advances in Chemistry Series 233, ACS, Washington DC., Ch 11,293 (1993).

108. R.A. Pearson *In Toughened Plastics I: Science and Engineering,* Eds. C.K. Riew and G.K. Gillham, Advances in Chemistry Series 233,ACS Washington DC., Ch.17, 405 (1993).

109. M.E. Frigione, L. Mascia and D. Acierno., *Eu. Polym. J.,***31,** 1021 (1995).

110. C.B. Bucknall and I.V. Partridge, *Polymer,* **24,** 639(1983).

111. J.L Hedrick, I Yilgor. G.L. Wilkes and J.E. McGrath, *Polym, Bull.* **13,** 201(1985).

112. Soo Jin Park and Hyun Chel Kim., *J. Appl. Polym. Sci.,***39** (1), 121-128 (2001).

113. K. Mimura and H. Ita, *J. Appl. Polym. Sci.,* **89** (2), 527(2003).

114. Blanco, G. Cicala, C. Lo Faro and A. Recca., *J. Appl. Polym. Sci.,***89**(1) 268-273 (2003)

115. R.W. Venderbrosch., G.L. Nelisson and P.J Lemstra, *Macromol. Chem.*, Macromol Symp.,**75,** 73 (1993).
116. R. A. Pearson and A.F Yee, *Polymer*, **34**, 3658(1993).
117. F. Hofflin., W. Bohne and R. Mulhaupt, European *Symposium on Impact and Dynamic Fracture and Composites* Preprints, Porto Cervo, Italy, Sept.20-22(1993).
118. S. Seungham, andJ. Jyongsik, *J. Appl. Polym. Sci.*, **65** (11), 2237(1997).
119. D.J. Hourston, J.M. Lane and H.X. Zhang., *Polym. Int.*, **42**,(4),349(1997)
120. L. Bennaud, J.P. Pascault, H. Sauterau, J.Q. Zhao and D.M. Jia., *Eu.Polym. J.*, **40**(11)2637(2004)
121. S.J. Lin, B.L. Hsu, F.W. Haris and S.Z.D. Cheng., *Polym. Mater. Sci .Eng.*, **70.**,51 (1994)
122. D.J. Hourston and J.M. Lane, *Polymer.*, **33** ,1379 (1992)
123. R.S. Baeuer., *Polym. Mater. Sci. Eng.*, **70**, 45 (1994)
124. M. Naffakh, M. Dumon, J. Dupy and J.F. Gerard., *J.Appl.Polym. Sci.*,**96** (3) 660-672 (2005)
125. H.. Lu and S. Zheng., *J.Polym.Sci.Part B, Polym.Phys*, **43**,359(2005)
126. J.H. Hodgkin, G.P. Simon and R.J. Varley., *Polym. Adv. Technol.* **9**,3(1998)
127. Rong Minzhi. and Zeng Hanmin., *Polymer.*, **38** (2)269-277 (1997)
128. Frigione Mariaenrica, Acierno Domenico and Mascia Lena., *J. Appl. Polym.Sci.* **73** (8), 1457 (1999).
129. K. Dinakaran, R.S. Kumar and M. Alagar, *J. Appl. Polym.* Sci., **90** (6),1596 – 1603 (2003)
130. T. Iijima, W. Fukuda, M. Tomoi and M. Aba., Polym. Int.,42 (1), 57 (1997)
131. T. Iijima, A. Sugizaki, W. Fukuda and M. Tomoi., *Polym. Int.*,**44**(2), 125 (1997)
132. S.M Shin., D.K Shin., D.C. Lee, J. *Appl. Polym. Sci.*,**78** (14) ,2464-2473(2000).
133. H . Harani, S. Fellahi and M. Bakar, *J. Appl. Polym. Sci.*, **71** (1), 29 (1999).
134. R.J. Varley and W. Tean., *Polym. Int.*, 53 (1), 69-77 (2004).
135. X.U. Gang, Wenfang Shi., Ming Gong, Fei Yu and Jianping Feng., *Polym. for Adv. Techno*l.., **15**(11) ,639 (2004).

136. R.J. Varley., *Polym. Int.,* **53** (1), 78-84 (2004)
137. Youming Cao, Yuefeng Shao, Jun Sun and Shang An Lin, *J.Appl.Polym. Sci.,* 90 (12), 3384-3389 (2003).
138. T. Iijima, K.I Fujimoto and M. Tomoi., *J. Appl. Polym. Sci.,***84**(2),388(2002).
139. R.Mahendran, R. Malaisamy, D. Mohan, *Eu. Polym. J.,***40** (3),623-633 (2004)
140. S. K. Siddhamali *J. Vinyl. Addi. Technol.,* **6** (4) ,211-220(2000).
141. S.C. Kim, and L.H. Sperling, *IPNs Around the World,* John Wiley & Sons; New York, (1997).
142. M.S Lin, C.C. Liu, and C.T. Lee, J. *Appl. Polym. Sci.,* **72**, 585-592 (1999).
143. H. Harani,., S.Fellahi, M.Bakar, *J. Appl. Polym.Sci.,***70**, n-13, 2603, (1998).
144. H. Harani, *M. S. Thesis,* IAP, Boumerdes, Algeria (1997).
145. Chen Tonghui, Li Hanshing , Gao-Yue , Zhang Minlian, *J. Appl. Polym.Sci.,* **69**, (5) , 887 (1998)
146. Feng Juan Hua, and Chun Pu Hu., *J. Appl. Polym. Sci.,* **37** (18), 3568 (2000)
147. K.F. Hsieh, Y.C. Chern, C.C.M. Ma , and Y.G Gong, SPE ANTEC *Tech. Papers* , **38**, 1488 (1992).
148. H.H. Wang, J.C. Chen, *Polym. Eng. Sci.,* **35**,1468(1995).
149. S. Bhuniya and B. Adhukari, *J. Appl. Polym. Sci.,* **90** (6), 1497 (2003)
150. Ye-Shiu Li, Ming-Shiu Li, Chen-Chi M Ma., Hung-Chung Hsia and Der-Shyang Chen., *Polym. Int.,* **35** (4),371-378 (2003)
151. F.L. Barcia, M.A. Abrahao, and B.G Soares *J. Appl. Polym. Sci.,* **83** (4), 838-849(2002*).*
152. C. C. M. Ma., M. S. Li., Y.D. Wu and Y.F. Su., J. Appl. Polym. Sci., 62 (3), 523-531 (1996).
153. Bao-Long Zhang, , Hui -Qi Zhang., Ying -Cai You., Zon-Jie Du , Pei-Yuan Ding, Tao Wang, Ji- Fu Huang ., *J. Appl. Polym. Sci.,* **69** (2), 339 (1998).
154. Alka Gupta, Reena Singhai and A.K. Nagpal., J. Appl. Polym. Sci., **96** (2)537-549 (2005).
155. J. Lopez, S. Gisbert, S. Ferrandiz, J. Vilaplana, and A. Jemenez, *J. Appl. Polym. Sci,* 67, 10 (1998).

156. N. Schroder, L. Koenczoel, W. Doell and R. Muelhaupt., *J. Appl. Polym. Sci.,* **70,** (4), 785 (1998).
157. Q. Dai, J. Chen, and Y. Huang, *J. Appl. Polym. Sci.,* **70**, 1159 (1998).
158. Lin-Gibson Sheng, *Cresol Novolac-Epoxy Networks; Synthesis, Propertie and Process*. Dissertation. ETD-etd-04262001-142525. (2001).
159. D. Ratna, *Polym. Int.*, **50,** (2), 179 -184(2001).
160. P. Prakaipetch, B. Witold and N.A. D'Souza., *Soc. Plast. Eng.*, **58**(2) 2147 - 2151 (2000).
161. C. Carfagna, L. Nicolais, E. Amendola, C. Carfagna Jr. and A.G. Filippov. *J.Appl. Polym. Sci.*, **44** (8), 1465 (1992)
162. P.K. Natrajan, and R.M.V.G.K. Rao., *High Performance Polymers,* **6** (3), 241-248 (1994).
163. S.C. Chen, H.T. Chin, C.P. Ye., *J. Appl. Polym. Sci.,* **86** (14),3740 (2002)
164. E.H. Mertz, G.C. Claver and C. Baer., *J. Appl. Polym. Sci.*,**22**, 325 (1956)
165. S. Bandyopadhyay, *Mater. Sci. Eng.*, A**: 125,** 157 (1990).
166. C.B. Bucknall, Ed. *Toughened Plastics,* Applied Science Publishers, London (1977)
167. A.M. Donald and E.J. Kramer, *J. Appl. Polym. Sci.*, **71**, 1123 (1982).
168. A.M. Donald and E.J Kramer, *J. Mater. Sci.*, **17**, 1871 (1982).
169. H.S. Kim., P. Ma., *J. Appl. Polym. Sci.*, **61** (4), 659 (1996).
170. Newman and S. Strella, *J. Appl. Polym. Sci.* , **9** , 2297(1965).
171. Y. Huang and A.J. Kinloch, Polym. *Mater. Sci. Eng.*, **63**, 564 (1990).
172. A.M. Donald and E.J Kramer, *J. Mater. Sci.*, **17**, 1765 (1982).
173. A.J. Kinloch, S.J. Shaw, and D.L. Hunston, *Polymer,* **24,** 1355 (1983).
174. R.A. Pearson and A.F. Yee, *Polym. Mater. Sci. Eng.*, **49**, 316 (1983*).*
175. B.J. Cardwell and A.F Yee, *Polymer,* **34, 1695** (1993).
176. Huang, and A.J Kinloch, *J. Mater. Sci. Lett.*, **11**, 484 (1992).
177. R.A. Pearson and A.F. Yee, *J. Mater. Sci.*, 26, 3828(1991).
178. D.R. Paul, C.B. Bucknall.,Eds. *Polymer Blends*, Vol 2, *Performance,* John Wiley & Sons, NY (1999)
179. F.F. Lange and K.C. Radford, J. *Mater. Sci.*, **6,** 1197 (1971).

180. D.J. Green, P.S. Nicholson and J.D Emberg, *J. Mater. Sci.*, **14,** 1657 (1979).
181. P. Bussi and H. Ishida, *J. Appl. Polym. Sci.*, **3,** 441-454(1994).
182. P. Bussi and H. Ishida, *Polymer*, **35,** 956 (1994).
183. D. Verchere, J.P. Pascault, H. Sautereau, S.M. Moschiar, C.C.Riccardi and R.J.J. Williams, *J. Appl. Polym. Sci,* **43,** 293-304(1991).
184. S.M. Moschiar, C.C. Riccardi, R.J.J. Williams, D. Verchere, H. Sauterau and J.P. Pascault, *J. Appl. Polym. Sci.*, **42,** 717-735 (1991).
185. J.K. Gillham, C.A Glandt and C.A. McPherson, Am. *Chem. Sci. Div. Org. Coat. Plast. Chem,* **37** (1), 195 (1997).
186. R.A Pearson and A.F. Yee, J. *Mater. Sci.*, **24,** 2571(1989).
187. G. Levita, *Matrix Ductility and Toughening Of Epoxy resins*; In *Rubber Toughened Plastics*, Ed. C.K. Riew, Ch.4,p-93-117,Advances in Chemistry series 222, ACS, Washington (1989).
188. G. Lubin, Ed., *Handbook of Composites*, Van Nostrand Rheinhold Company, NewYork (1982).
189. Z.G. Shaker, R.M. browne, H.A. Stretz, P.E. Cassidy and M.T. Blanda, *J. Appl. Polym. Sci* ., **84,** 2283-2286 (2002) .
190. A.B.Pereira, A.B. de Morais, A.T Marques, P.T. de Castro., *Compos. Sci. Technol.*,**64,** 1653 (2004).
191. J.A. Hough, S.K. Karad and F.R. Jones., *Compos. Sci. Technol.*,**65,** 1229 (2005)
192. K. Potter, *Resin Transfer Moulding*. Chapman and Hall, London,(1997).
193. A.C. Loos and G.S. Springer, *J. Compos. Mater.***17,** 135 (1983).
194. L.Outifa, H. Julien and M. delmolte, *Polym. Mater. Sci. Eng.*, **66,** 424 (1992).
195. N.A. Prakash, V.M. Liu, B.Z. Jang and J.B. Wang., *Polymer Composites*, **15** (6), 479-487 (1994).
196. Vera Alaverez, Celina R Bernal, Patricia M Frontini and Analia azquez., *Polymer Composites*, **24** (1), 140-148 (2003).
197. E.U. Espuche, J.F. Gerard, J.P. Pascault,G. Rieffo and H. Sautereau., *J. Appl. Polym. Sci.*, **47** (6), 991-1002 (1993)

198. L.S. Penn, G.C. Tesoro and H.X. Zhou., *Polymer Composites*, **9** (3), 184-191 (2004).

199. R.W. Rosser, T.S. Chen and M. Taylor., *Polymer Composites,* **5** (3), 198-201 (1984).

200. S.R. Wu, G.S. Sheu and S.S. Shyu., *J. Appl. Polym. Sci.*,**62** (9), 1347 -1360 (1996).

201. R.J. Varley and J.H. Hodgkin., *Polymer*, **38** (5), 1005-1009 (1997).

202. Hongfeng Xu, Binghua Liu, qing Sun, Zuanru Yuan, Jinayi Shen and Rongshi Cheng., *J. Appl. Polym. Sci, 96* (2), 329-335 (2005).

203. C. Kayanak, A. Arikan and T. Tincer., *Polymer,* **44** (8), 2433 (2003).

204. F.H. Gojny, J. Nastalczyk, Z. Roslaniec and K. Schulte., *Chem. Phys. Lett.,* 370 (5-6), 820 (2003).

Chapter 2

SYNTHESIS AND CHARACTERISATION

2.1 Introduction

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. In general, epoxy resins are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin followed by dehydro halogenation [1].

2.1.1 Raw materials.

The raw material for the commercial synthesis of diglycidyl ether of bisphenol A (DGEBA) are epichlorohydrin and bisphenol A

a) Bisphenol A

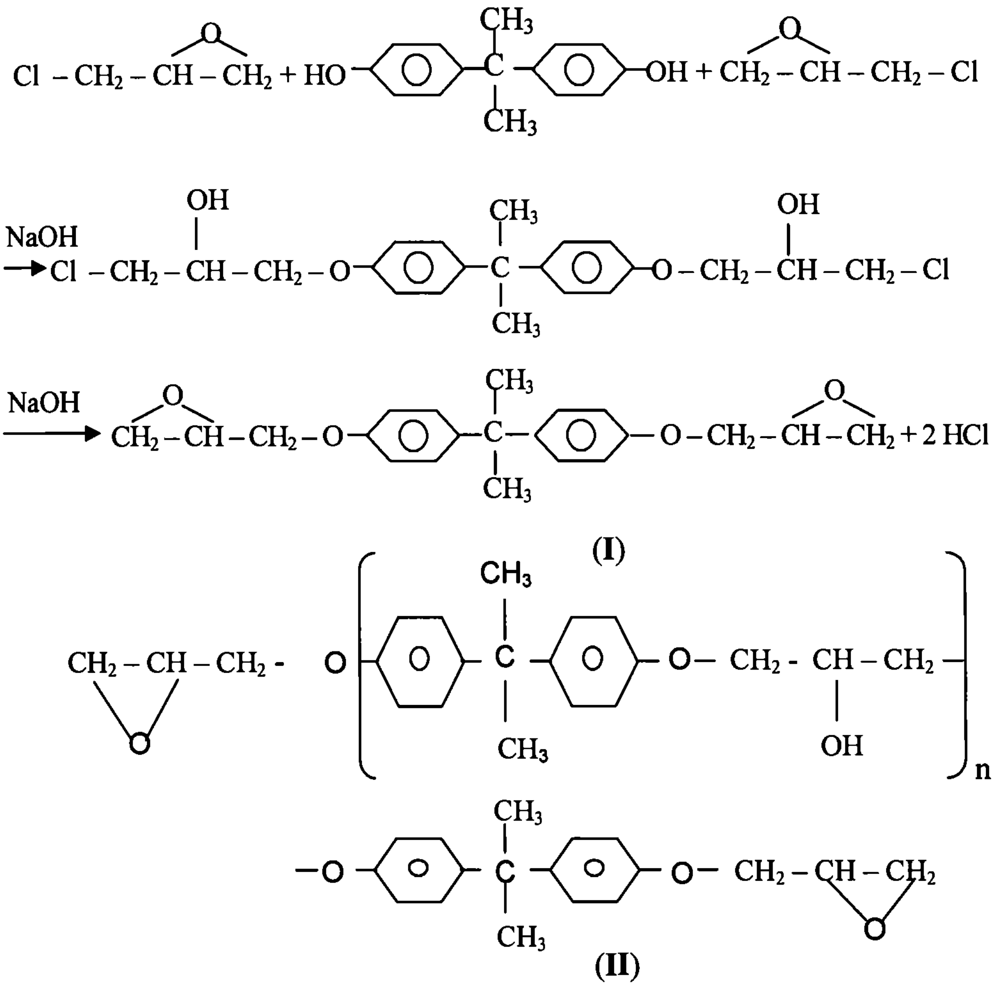
Bisphenol A or bis (4-hydroxy phenyl) dimethylmethane (BPA) is a colourless solid (mol.wt 228) prepared by reacting phenol and acetone. Since phenol and acetone are readily available, synthesis of this intermediate is comparatively inexpensive. This is the reason why it has been the preferred dihydric phenol employed in epoxy resin manufacture. Since most epoxy resins are of low molecular weight and colour is not particularly critical, the degree of purity of bisphenol A need not be always very high. Bisphenol A with a melting point of 153^0C is considered adequate for most applications.

b) Epichlorohydrin

Epichlorohydrin (ECH) is a colourless liquid with the characteristic odour of many chlorinated hydrocarbon solvents. It has been known since 1854 when Berthelot reported its synthesis by saponification of dichlorohydrins. It is now synthesised by chlorination of propylene and is therefore, a petroleum product. The resultant product (allyl chloride) is then reacted with hypochlorous acid to form the dichlorohydrin. This undergoes a 'stripping' reaction in presence of cautic soda at high temperature to yield epichlorohydrin. It is available commercially at 98% purity.

2.1.2 Synthesis of epoxy resin

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 (Scheme 2.1). Many commercial liquid resins consist essentially of the low molecular weight diglycidyl ether of bisphenol A (I) together with small quantities of high molecular weight (II) polymers. The HCl released during the reaction reacts with caustic soda to form NaCl.



Scheme.2.1

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 [3]. The effect of mole ratio of epichlorohydrin to bisphenol A on the average molecular weight of liquid resin [4] is given in Table 2.1. 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^{0}C and weight per epoxide 188.

Table 2.1 Effect of ECH-BPA ratio on resin molecular weight [4]

ECH :BPA	Molecular weight
10: 1	370
2 :1	450
1 : 4.1	791
1.57 :1	900
1.22 : 1	1400

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

i. The Taffy Process

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^{0}C and epichlorohydrin (145 parts by weight) is added rapidly with agitation, giving off heat. The temperature rises to 95^{0}C 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^{0}C 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 detected 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 [5]. 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 [6].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 epoxy group to secondary alcohol group generated in the chain extending process [7]. The extent of branching can be determined by spectroscopic methods [8]. 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-hdroxy 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 [9]. More recently epoxy resin has been synthesised by microwave irradiation technique [10]. Novel nitrogen containing epoxies [11] have been prepared by the condensation of xylene-formaldehyde-phenol (XPF) resin with triglycidyl isocyanurate (TGIC).

2.2 EXPERIMENTAL

2.2.1 Materials

Bisphenol A.(LR, M.W= 228.29,97%assay, M.P. 154-157^{0}C) and epichlorohydrin (L.R., M.W=92.53,98% assay B.P. 114-118^{0}C) were supplied by Research Laboratory, Mumbai, India. Benzene (M.W= 78. 98% assay), triphenyl phosphine (MP=78-82^{0}C, MW=262.3, 98% assay) and caustic soda (MW=40, 97.5% assay) were obtained from E. Merck India, Mumbai. Commercial grade Epoxy Resin 103, and the room temperature amine hardener 301(polyamine) were supplied by M/s Sharon Engineering Enterprises, Cochin.

2.2.2 Synthesis of DGEBA

Bisphenol A (1mole) was dissolved in a mixture of an excess of epichlorohydrin (6 moles) and 50 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 (2 moles) was added in two pellets at a time down the condenser. The reaction was allowed to subside before more alkali was added. When all the caustic soda pellets had been added, the reaction mixture was heated strongly for 45 minutes. 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 distilled in vacuum to remove benzene and dried in vacuum for about 3h. The resin formed was a pale yellow viscous and glassy liquid. The properties of the synthesised resin were compared with those of the commercial epoxy resin.

2.2.3 Synthesis of DGEBA/BPA resin:

Commercial epoxy resin was mixed with 5weight % bisphenol Aand triphenyl phosphine(1%) in a RB flask fitted with a condenser and mechanical stirrer. The mixture was heated over a water bath for half an hour till all the BPA granules disappeared. The reaction mixture was cooled and then dried in vacuum to obtain a thick viscous resin. The resin was cured in presence of 10 weight % room temperature hardener. Resins containing different concentrations of bisphenol A as chain extending agent were synthesised by the same procedure and mechanical properties evaluated.

2.2.4 Characterisation methods

a) Spectroscopic studies

Fourier transform infra red (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, gel time 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. Gel time

The gel time of the epoxy resin was determined as per ASTM D 2471-99. 45 ml of resin was taken in an aluminium foil dish, approximately 70 mm in diameter and 14 mm depth and placed in a temperature-controlled bath maintained at 23 ± 1.0°C. A thermocouple was inserted at the geometric centre of the resin mass and stirred with a glass rod. 10 wt % of the amine hardener was added and a stopwatch was started. When the reactant mass no longer adheres to the glass rod, the gel time was recorded as the elapsed time from the start of mixing. The time temperature recording was continued until the temperature started to drop. The highest temperature reached was recorded as the peak exothermic temperature. The commercial epoxy resin showed a gel time of 67 minutes while the synthesised sample gels somewhat earlier, in 60'.

iv. 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 on gram equivalent of epoxide. The epoxy content is also expressed as equivalent/Kg of the resin.

A common method of analysis of epoxide content of liquid resins involves the opening of the epoxy ring by hydrogen halides (hydrohalogenation)[12]. 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 x 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.

v. Gel permeation chromatography (GPC)

This method, also called size exclusion chromatography, makes use of a chromatographic column filled with the gel or porous solid beads having a pore size similar to that of the polymer molecules [13]. A dilute solution of the polymer is introduced into a solvent stream flowing through the column. Smaller molecules of the polymer will enter the beads while the larger ones will pass on. Thus the larger molecules will have a shorter retention time than the smaller molecules. The chromatogram is a plot of retention time (or volume) against the amount of eluted molecules. The epoxy resin sample was subjected to GPC analysis with a view to identify the different components present in it and to estimate the relative proportion of these components. A Hewlett Packard instrument employing a RI detector and tetrahydrofuran as solvent (flow rate 1ml /min) was used for this purpose.

c) Casting

i) Moulds

a. Tensile properties (ASTM D 638-99)

Dumbbell shaped multicavity moulds were fabricated for casting tensile specimens. Six sets of moulds were machined out of mild steel plates each set containing three dumb bell shaped mould cavities. Each mould consists of a base plate 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.

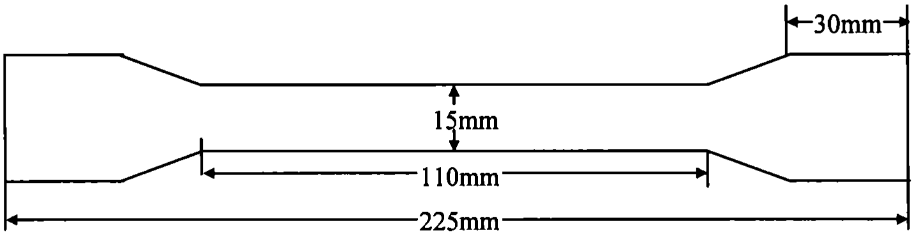


Fig. 2.1 The dimensions of the tensile test specimens

b. Compressive properties (ASTM D 695-99)

The mould for compressive strength specimens having eighteen cylindrical cavities was fabricated out of mild steel. It consisted of a base plate and cavity plate. The cylindrical cavities have 12.7 mm diameter and 25 mm depth.

c. Flexural properties (ASTM D 790-99)

The mould for flexural strength specimens having 6 cavities was fabricated out of mild steel. It consisted of a base plate and cavity plate. The dimensions of each cavity are 127 mm length, 12.7 mm width and 3.2 mm thickness.

d. Impact strength (ASTM D 256-97)

The mould for impact specimens having sixteen cavities was fabricated out of mild steel according to dimensions specified in ASTM D 4812. It consisted of a base plate 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.

e. 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.

f. 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 mild steel plate

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, compressive strength, flexural strength, toughness, impact strength, surface hardness, abrasion loss 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 a measure of the toughness.

ii. Compressive properties

The compressive properties were tested on a Shimadzu Autograph (AG-1 50 kN) Universal Testing Machine (ASTM D 695) at a constant rate of cross head movement of 8 mm/min. The cast specimens in the form of a cylinder were polished using emery paper prior to testing. The diameter of the test specimen was measured to the nearest 0.01 mm and the minimum cross sectional area was calculated. The height of the test specimen was measured to the nearest 0.01 mm. The specimen was placed between the surfaces of the compression plates and aligned. The centre line of the specimen was aligned through the centreline of the compression plates. The machine was adjusted so that the surface of the ends of the test specimen just touched the surface of the compression plate. The machine was started and compressive strength and modulus were recorded. The load-deflection curve was obtained.

iii. Flexural properties

The flexural properties were tested on a Shimadzu Autograph (AG-1 50 kN) Universal Testing Machine (ASTM D 790) at a constant rate of traverse of the moving grip of 1.3 mm/min. The cast specimens in the form of rectangular bars were polished using emery paper prior to testing. The depth and width of the specimen was measured nearest to 0.01 mm. The support span should be 16 times the depth of the specimen. The specimen was centred on the supports with the long axis of the specimen perpendicular to the loading nose and supports. The load was applied to the specimen and flexural strength and modulus were recorded. The load-deflection curve was also obtained. It is calculated at any point on the stress strain curve by the following equation

$$S = \frac{3PL}{2bd^2}$$

where S = stress in the outer fibres at midpoint (MPa), P = Load at any point on the load –elongation curve (N), L = support span (mm), b = width of specimen tested (mm), d = depth of specimen (mm).

Flexural modulus is the ratio of stress to corresponding strain and is expressed in MPa. It is calculated by drawing a tangent to the steepest initial straight line portion of the load- deflection curve and using the equation

$$E_B = \frac{L^3 m}{4db^3}$$

Where E_B = modulus of elasticity in bending (MPa), L = support span (mm), b = width of specimen tested (mm), d = depth of specimen (mm), m = slope of the tangent to the initial straight line portion of the load – deflection curve (N/mm of deflection)

iv. 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 4Joules 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.

$$\text{Impact strength} = \frac{4X \times 100}{d}$$

where X= Impact value and d= depth of specimen *v. 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.

vi. 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.

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

2.2.5 Study of cure parameters of DGEBA

a) Influence of post curing temperature

The effect of variation of post curing temperature for the commercial epoxy resin containing10weight % R.T. hardener was studied. The post curing temperature was varied as 60, 80, 100,120 and 140^{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.

b) 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 120^{0}C.

2.2.6 Synthesis of modifier resins

i. Materials

Phenol (M.W=94.11,M.P.39.5-41^{0}C), p-cresol (MW=108.14, BP=202^{0}C, 98% assay), t-butyl phenol, 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 Loba Chemie, Mumbai, 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. The main constituents of CNSL are phenolic compounds with long side chain substitution at the meta position. CNSL being cheap can be a substitute for phenol in many applications. The use of CNSL in place of phenol is an excellent example gainful of utilization of a cheap agro by-product of renewable nature [14].

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. The structure of cardanol can be represented as in Fig.2.2.

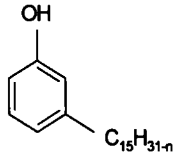


Fig.2.2 Structure of cardanol

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

The components of cardanol are identified as 3-pentadecyl anisole, 3- (8′-pentadecenyl) anisole, 1-methoxy-3-(8′, 11′- pentadecadienyl) benzene and 1-methoxy-3-(8′, 11′, 14′- pentadecatrienyl) benzene [15, 16].

ii. Synthesis of phenol/formaldehyde co-polymers/polymers

a) Resol type resins (PF)

Phenol (1mol) and formaldehyde solution (1.25mol) were taken in a three necked round bottomed flask equipped with a stirrer and a water condenser. To this mixture 33% sodium hydroxide solution was added and refluxed for about one hour over a water bath. The reaction was stopped as the reaction mixture became viscous and hydrophobic. The resin was transferred into a beaker and neutralised with a solution of oxalic acid. The aqueous layer was carefully drained off and the resin was dried in vacuum. The same procedure was used to synthesise resol type resins from cardanol and cardanol/phenol mixtures of varying molar compositions. The resin was subjected to spectroscopic analysis.

b) 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 [1] (Section 1.2.3). The same procedure was used to synthesise novolac resins from t-butyl phenol, cardanol, p-cresol and phenol/cardanol 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.

c) 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 2.2.4).

iii. Epoxidised cardanol (EC) [17]

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 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 EC 1, EC 3, EC 6 and EC 9 respectively. The epoxide equivalents of the resins were determined as given in Section 2.2.4. The resin was characterised by spectroscopic and GPC methods.

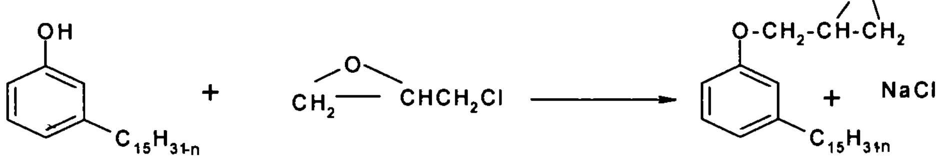


Fig. 2.3 Epoxidation of cardanol

The reaction product of cardanol and phenol when reacted with epichlorohydrin produced epoxy resin which are superior to conventional epoxy resin [18].

iv. Co-epoxidation of bisphenol A/cardanol (BPA/EC)

A mixture of bisphenol A (0.8 mole) and cardanol (0.2 mole) was epoxidised using the procedure cited in Section 2.2.6 (iii).The reaction mixture was heated for six hours after the addition of alkali. The dark brown resin so obtained (designated as BPA/EC-1) was dried in a vacuum oven for 3 h. The synthesis was repeated with bisphenol A and cardanol in varying molar compositions such as 50/50 and 20/80 (designated as BPA/EC-2 and BPA/EC-3). The epoxy equivalents of the resins were determined using the method described in Section 2.2.4.The synthesised resins were characterised by spectroscopic analysis and gel permeation chromatography.

2.3. RESULTS AND DISCUSSION

2.3.1 Spectroscopic data [19]

i. FTIR: The FTIR spectrum of epoxy resin is given in Fig.2.4. The C-H stretching in epoxies is at 2960 -2990 cm^{-1}. Symmetrical stretching or ring breathing frequency is observed at 1245 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), 840 cm^{-1} and 750cm^{-1} are typical of the epoxy group [19]. The disappearance of the strong band at 915cm^{-1} in the FTIR spectrum of the cured sample is indicative of complete curing. The FTIR spectrum of commercial epoxy resin is given in Figure 2.5. The bands at 2966 cm^{-1},914.57cm^{-1} and 1231cm^{-1} denote epoxy group.

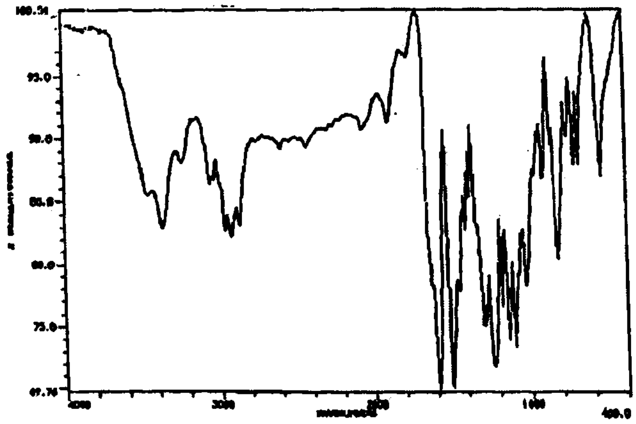


Fig.2.4 FTIR spectrum of epoxy resin

Figures 2.6(a) and (b) give the FTIR spectrum for phenol-formaldehyde (1:1.25) resol and novolac (1:0.8) resins. Characteristic absorptions were found around 3300 cm.$^{-1}$(hydroxyl group, broad band), 3000cm^{-1}(aromatic C-H str. weak), 1500 cm^{-1} (phenyl ring) and 1475 cm^{-1}(CH_2 bending). The two strong bands around 1230 cm^{-1}and 1010 cm^{-1} are characteristic of C-O stretching in phenol and alcohol groups respectively.

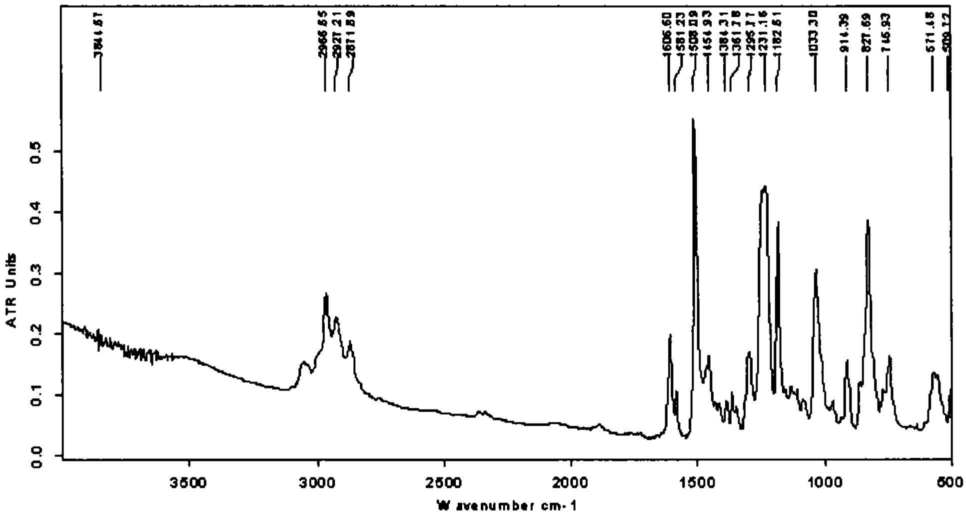


Fig.2.5 FTIR spectrum of commercial epoxy resin

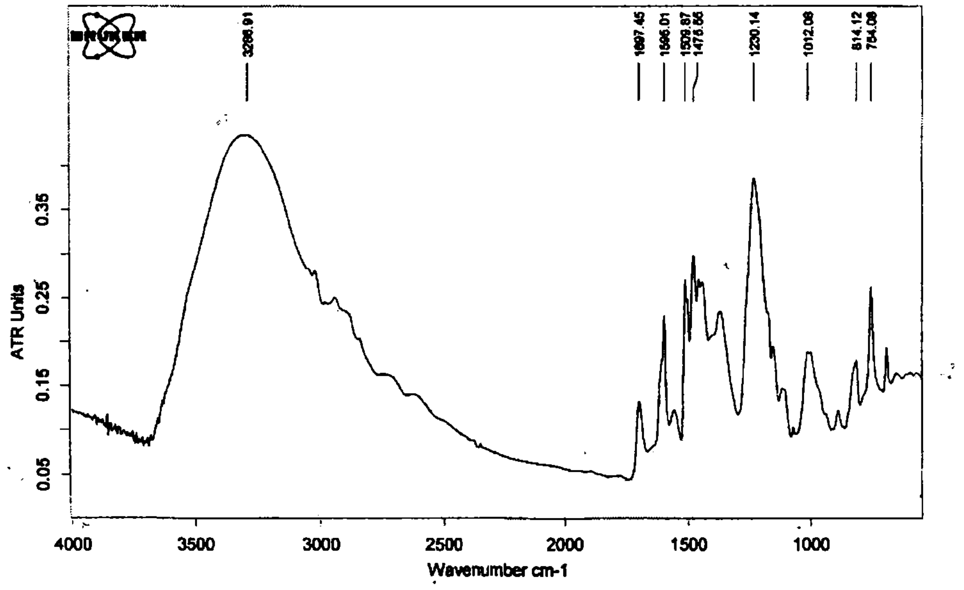


Fig. 2.6a. FTIR spectrum of PF (resol)

The FTIR spectrum of synthesised epoxidised novolac resin (EPN-3) is given in Figure 2.7. 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.

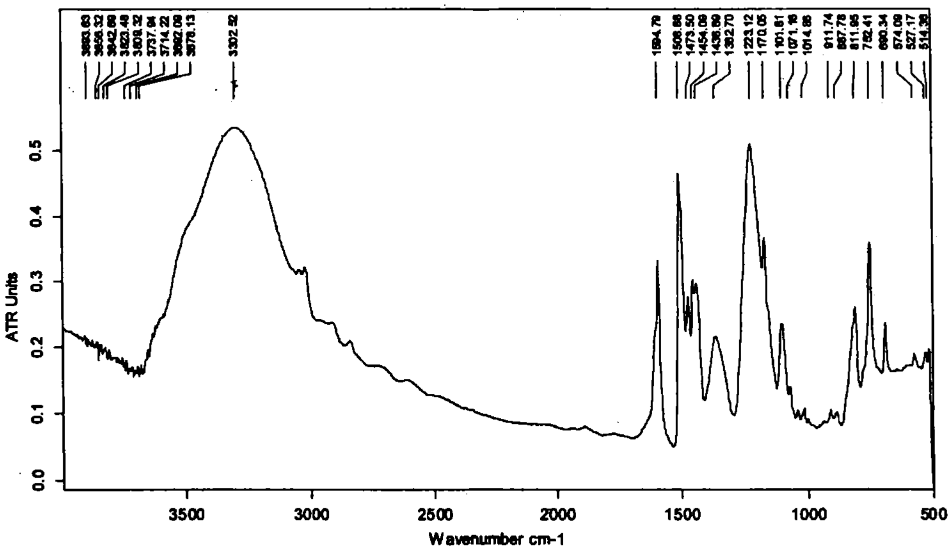


Fig.2.6b. FTIR spectrum of PF (novolac)

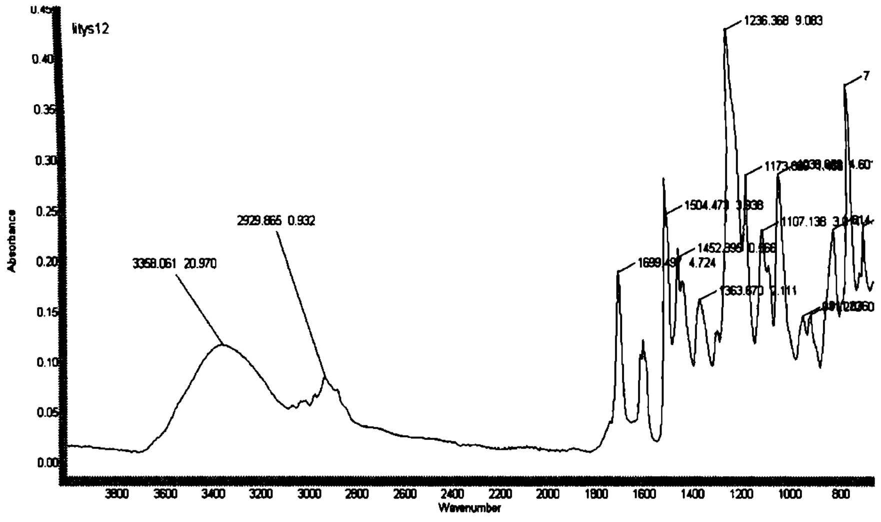


Fig.2.7 FTIR spectrum of EPN

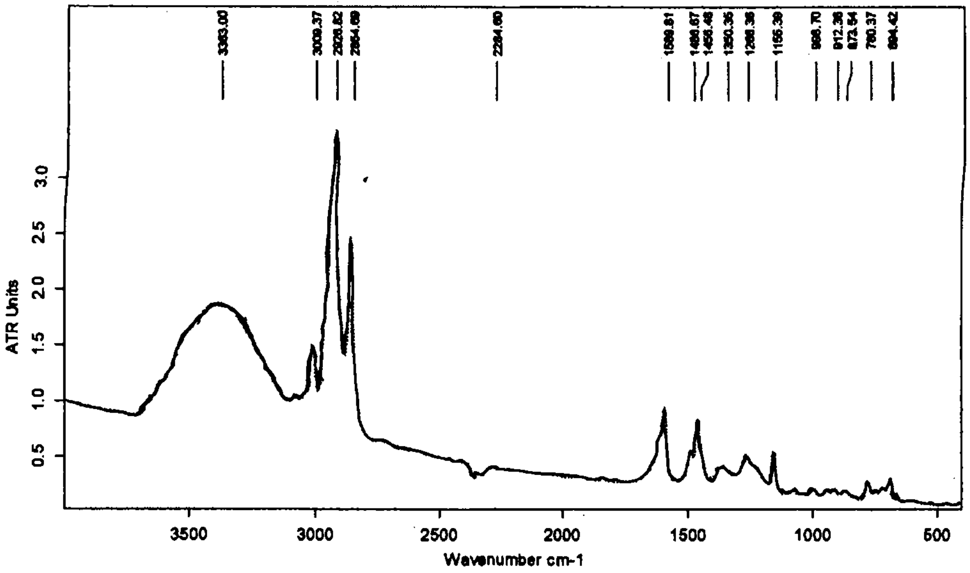


Fig.2.8a. FTIR spectrum of cardanol

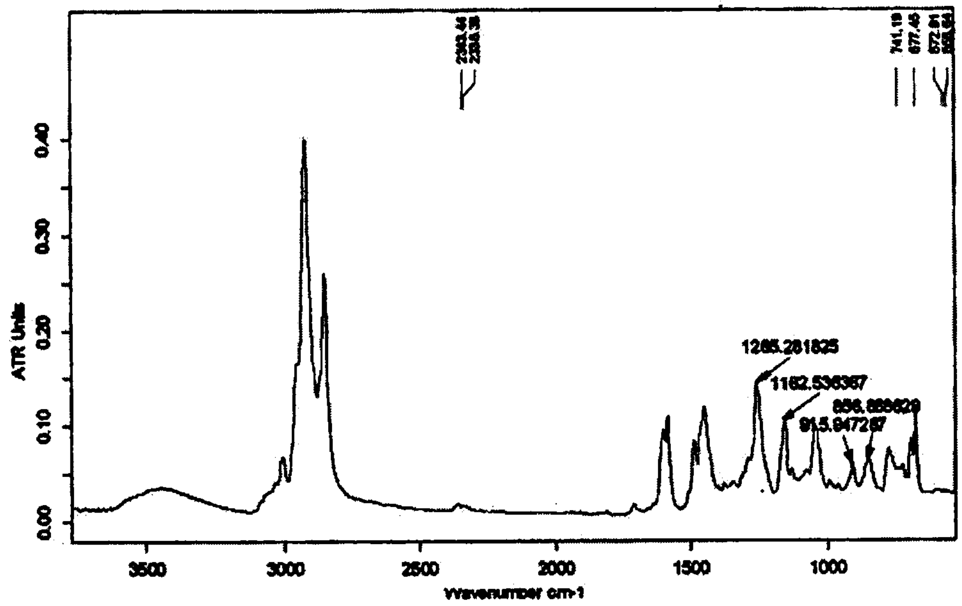


Fig.2.8b. FTIR spectrum of epoxy cardanol (EC)

Figure 2.8 shows the FTIR spectrum of cardanol (a) and the synthesised epoxy cardanol resin(EC-9) (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 (2.8b) indicating the involvement of that group in epoxidation. Figure 2.9 shows the FTIR spectrum of the synthesized BPA/EC-2 resin containing bisphenol A and cardanol in the ratio1:1.The bands at 2925.3cm^{-1} 1246.18$cm^{-1}$and 915.30 cm^{-1} denote the epoxide functionality as detailed above.

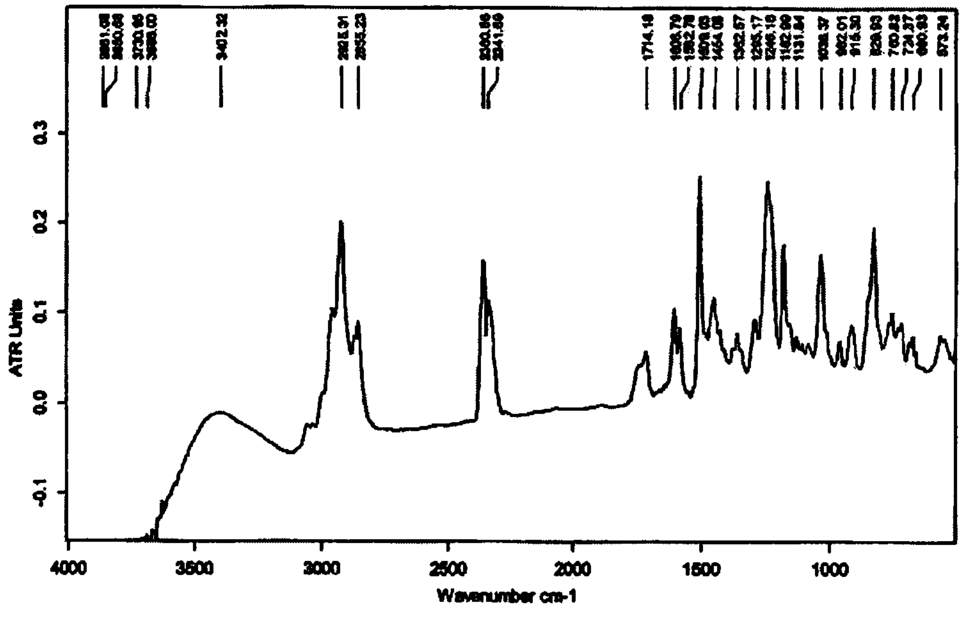
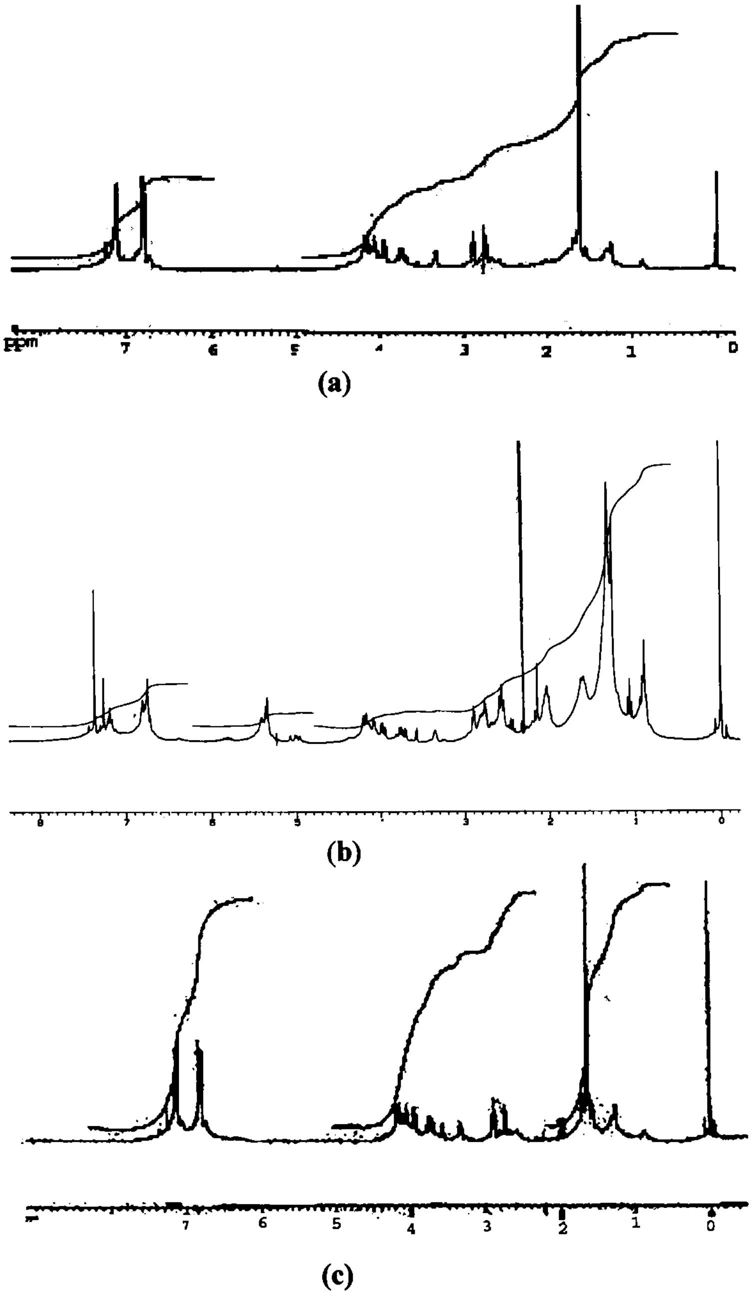


Fig. 2.9 FTIR spectrum of bisphenol A/cardanol (1:1) epoxy resin

ii. NMR: The H^1-NMR spectra of DGEBA, epoxy cardanol (EC) and BPA-cardanol co-epoxide (80/20) (BPA/EC-1) are given in Fig.2.10 (a),(b) and (c) respectively. Fig.(a) and (c) show absorptions at about 7δ as AB quartet which is characteristic of para disubstituted benzene ring. This signal is obtained as a singlet in (b) at 7.4 δ. The absorption at δ=3.4 corresponding to the CH_2 protons adjacent to oxygen linked to the aromatic ring is present in all the three samples. The other signals are δ=2.8 (multiplet, due to CH proton of the epoxy ring), δ=3(doublet, due to CH_2 protons of the epoxy ring) and δ=1.7 (6H, gem-dimethyl group in (a) and (c)). The intense signal at 1.4 δ in (b) corresponds to methylene protons in the long aliphatic side chain of cardanol. A series of overlapping signals between 4.5-6 δ in spectra(b) correspond to HC=C-H (cis) protons present in the side chain of cardanol. These signals are absent in the spectrum of DGEBA (a) BPA/EC-1 (c).



(a)

(b)

(c)

Fig.2.10 FT-NMR spectra of (a) DGEBA (b) Epoxy cardanol(EC) and (c) bisphenol A-cardanol(80/20) co-epoxide (BPA/EC-1)

2.3.2 Epoxide equivalents

The weight per epoxide (wpe) values of the commercial and the synthesised epoxy resin samples were determined using the procedure cited in Section 2.2.4. The commercial and the synthesised samples gave wpe values 187.7 and 180.36 respectively. These values correspond to epoxide equivalents 5.33 eq /Kg and 5.52 eq / Kg respectively. The commercial resin usually contains diluents and flexibilizers and hence it has lesser epoxide content than the synthesised resin.

The epoxide equivalents of the epoxy novolac (EPNs) resins prepared from novolacs of different phenol-formaldehyde ratios were determined. The wpe (epoxy equivalents) for EPN-1,EPN-2,EPN-3and EPN-4 were found to be 181.8 (5.51eq/Kg),175(5.714eq/Kg), 169.5 (5.91eq/Kg) and 202(4.95eq/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.

The wpe value of epoxy cardanol (EC) obtained by epoxidation of cardanol for one hour (EC-1) was found to be 530.65 (1.88eq/Kg). As the epoxidation time was increased to 3h, 6h and 9h (EC-3, EC-6 and EC-9) the wpe values were found to be 511.25, 476.2 and 473.15 respectively. These values correspond to 1.95eq/Kg, 2.099 eq/Kg and 2.12eq/Kg of epoxide respectively (Fig.2.11a.).The epoxide equivalent increased sharply with time of epoxidation and reached almost a limiting value at 9h.

Cardanol being less reactive undergoes epoxidation to a smaller extent than phenol. The wpe values for EC-6 and EC-9 did not vary much and hence maximum epoxidation might have taken place by about nine hours. Theoretically, complete

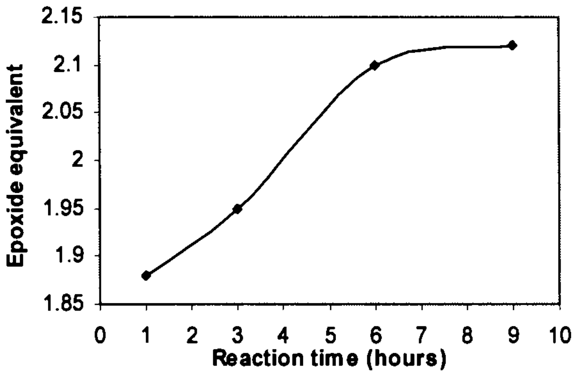


Fig.2.11a. Variation of epoxide equivalent with time of epoxidation of cardanol

epoxidation of cardanol would have given a wpe value of about 360. However, nine hours of reaction resulted in a wpe value of 473.15 which indicated incomplete epoxidation. The wpe values are in good agreement with the GPC data which shows only 61% of epoxidation in 9 hours. Moreover, these resins do not form cross-linked networks as they contain only mono functional epoxide groups.

Epoxide equivalents of bisphenol A/cardanol epoxy resins containing bisphenol A and cardanol in different ratios were also determined by the same procedure. The epoxy values of BPA/EC-1, BPA/EC-2 and BPA/EC-3 were found to be 4.37eq/Kg, 3.31eq/Kg and 2.56eq/Kg corresponding to wpe values 228.38, 302.5 and 391 respectively. The epoxide equivalent of the resin decreased (wpe was increased) as the concentration of cardanol increased (Fig. 2.11b.). This is due to the fact that cardanol molecule with a long aliphatic side chain is much less amenable than bisphenol A to glycidylation.

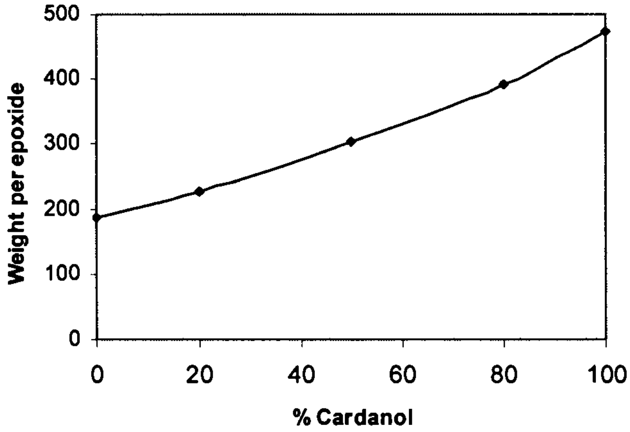


Fig.2.11b. Variation of wpe values with cardanol content in BPA/EC resins

2.3.3 GPC analysis data

The synthesised epoxy resin sample was subjected to GPC analysis with a view to identify the different components present in it and to estimate the relative proportion of these components on the basis of molecular size. The chromatogram (Fig.2.12) of the resin shows two distinct peaks (components A and B) corresponding to the retention times 15.8' and 17.7' respectively. The relative intensities of the peaks were found to be in the ratio1:6.73(A:B) as measured from the area under the peaks. This corresponds to 13% of component A and 87 % of component B. Evidently, the component B corresponds to the diepoxide with a lower molecular weight (higher retention time) and component A, probably a dimer of relatively higher molecular weight. Thus the resin contains only 87% of the diepoxide functionality which is in agreement with its epoxide equivalent.(Section 2.3.2)

The synthesised epoxy cardanol resin (EC9) sample was subjected to GPC analysis with a view to estimate the relative amounts of the different components present in it. The chromatogram (Fig.2.13) of the resin shows three distinct peaks (components A, B and C) corresponding to the retention times 15.3', 16.4'and 17' respectively. The relative intensities of the peaks were found to be in the ratio (A:B:C) 1: 2.11: 4.65 as measured from the area under the peaks. This corresponds to 12% of component A, 27% of component B and 61% of component C.

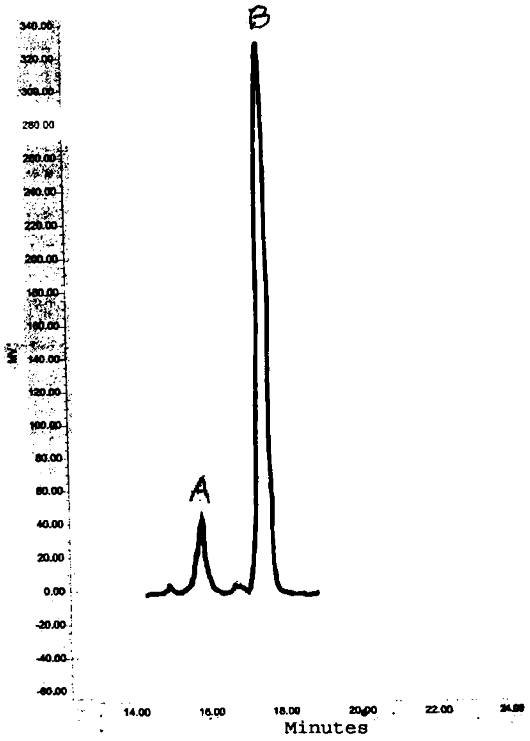


Fig. 2.12 G.P. chromatogram of epoxy resin

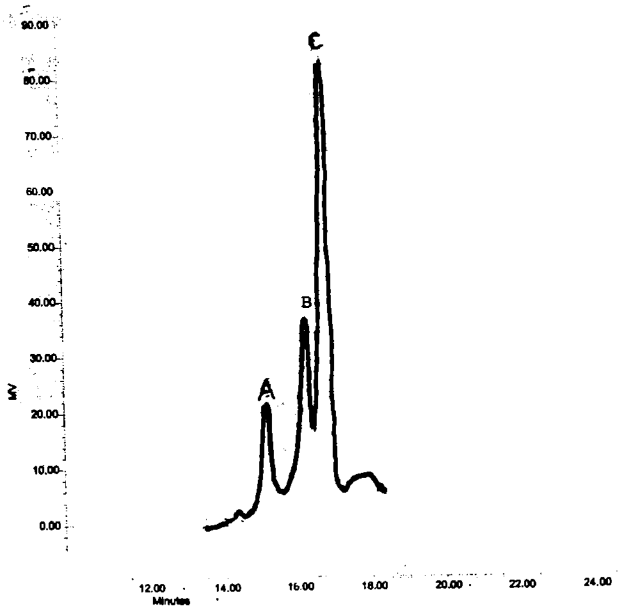


Fig 2.13 G.P.chromatogram of epoxy cardanol (EC)

Evidently, the component C corresponds to the epoxide with a lower molecular weight (higher retention time) and component B, probably a dimer of relatively higher molecular weight. The component A is probably a tetramer since there is a gap between the peaks due to A and B where a trimer can be observed.. Thus the EC resin contains only 61% of the mono epoxide functionality which is in agreement with its epoxide equivalent. Cardanol being less reactive than phenol nine hours of epoxidation resulted in only 61% of the epoxide.

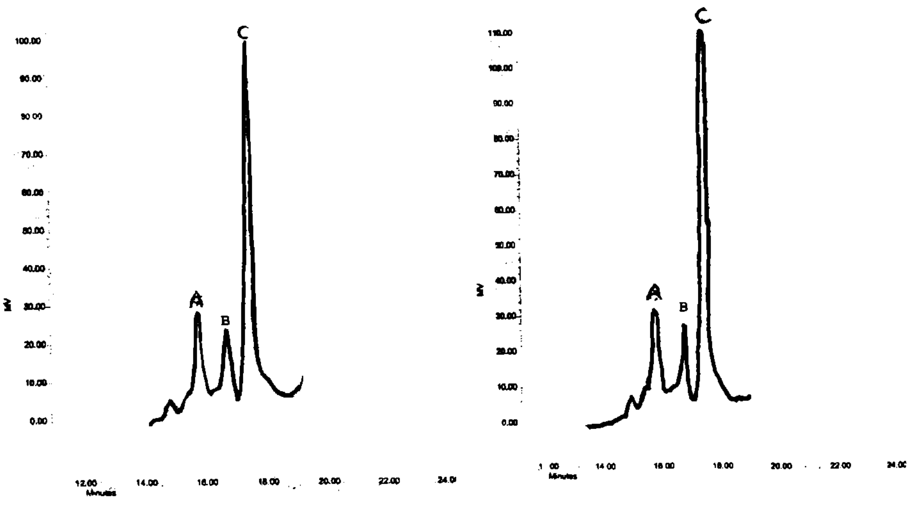
The GP chromatograms of BPA/EC-1 and BPA/EC-2 resins are given in Figure 2.14a. There are three peaks corresponding to retention times15.8, 16.9' and 17.7' in the chromatogram of BPA/EC-1 in the ratio 1.43: 1: 6.41.These values correspond to 16.12 %, 11.3% and 72.48 % of the three components A,B and C. The component C is the diepoxide of relatively lower molecular weight and A and B may be of relatively higher molecular weight trimer and dimer respectively. The GP chromatogram of BPA/EC-2 (Fig.2.14b) is almost similar to that of the above sample. Three peaks at retention times 15.7', 16.9' and 17.9' follow the intensity ratio1.3: 1: 4.4(A:B:C) corresponding to 19.4%component A, 14.68% component B and 66% component C. The component C is the diepoxide and A and B are probably a trimer and dimer respectively. As the amount of cardanol increased from 20% to 50%, the rate of formation of diepoxide decreased from 72.48% to 66% confirming the lower reactivity of cardanol compared to bisphenol A.

2.3.4. Properties of the synthesised resin

i. Physical properties:

Referring to Table 2.2, the synthesised DGEBA resin has greater viscosity and specific gravity compared to the commercial epoxy resin. The commercial resin usually contains added diluents, plasticizers etc which make the resin slightly flexible. The synthesised resin gels in 60minutes while the commercial sample gels in 67 minutes. The BPA/EC-1 resin is still slower to gel due to the presence of un-reacted cardanol. The synthesised resin has greater epoxy content (5.52eq/Kg) than the commercial sample (5.33 eq/Kg) and BPA/EC-1 (4.37 eq/Kg).

The properties of the epoxy resin prepared by the glycidylation of bisphenol A/ cardanol mixture are also given in Table 2.3. Cardanol being mono functional, gives a mono glycidyl ether upon epoxidation which will terminate a growing polymer chain during cure. Thus relatively smaller chains are present in the resin containing cardanol. More over, cardanol is much less reactive than bisphenol A and epoxidation would be incomplete. The GP chromatogram shows that bisphenol A-cardanol (80/20) epoxide contains only 78.48% of the diepoxide. As the amount of cardanol was increased to 50% (BPA/EC-2), the resultant resin was found to contain only 66% of the diepoxide.



(a) (b)

Fig.2.14. G.P.chromatograms of (a) BPA-EC-1 (80:20) (b) BPA-EC-2 (50:50) epoxy resins

The epoxide equivalents of these resins showed a steep decrease as the amount of cardanol was increased. While BPA/EC-1 and BPA/EC-2 resins could be cured extremely slowly, the sample containing 80%cardanol (BPA/EC-3) did not cure at all. Evidently, this is due to the presence of excess cardanol monoepoxides which fail to give cross-linked networks.

ii. Mechanical properties:

The mechanical properties of commercial and synthesised DGEBA epoxy resins are shown in Table 2.2. The commercial epoxy resin was found to have improved tensile strength and compressive strength compared to the synthesised resin. There is not much variation in their elongation values at break. However, the synthesised resin was found to have greater modulus and flexural strength. This reflects enhanced stiffness in the synthesised epoxy resin. Introduction of 20 mol % cardanol into bisphenol A (BPA/EC-1) resulted in a resin having reduced tensile, impact and compressive strengths. However the resin showed considerable improvement in elongation at break without much decrease in energy absorption. An increase in the amount of cardanol resulted in deterioration of tensile and compressive strengths and a sharp increase in elongation without appreciable lowering in the energy absorbed to break.

Table-2.2. Properties of commercial and the synthesised epoxy resins

Properties	Commercial DGEBA	Synthesised DGEBA	Bisphenol A/ cardanol epoxy 80/20	Bisphenol A/ cardanol epoxy 50/50
Tensile strength.(MPa)	48	44.5	31.7	23.5
Elongation at break (%)	3.10	3.02	5.68	8.42
Modulus. (MPa)	2420	2405	2045	1926
Energy to break. (J/mm^2)	2.95	2.913	2.788	2.77
Impact strength. Izod. (J/m)	28.5	27.35	22.25	20.4
Compressive strength.(MPa)	108	102.5	92.55	78
Flexural strength. (MPa)	91.45	94	80.8	71.45
Max. displacement.(mm)	2.54	2.42	4.42	5.85
Surface hardness. (Shore D)	86	87.5	85.5	85
Water absorption. (%)	0.27	0.257	0.35	0.405
Gelation time .(min)	67	60	78	104
Weight per epoxide (wpe)	187.7	180.36	228.38	302.5
Epoxy equivalent. Eq/Kg	5.33	5.52	4.37	3.31
Specific gravity	1.214	1.222	1.194	1.187
Viscosity (cp)	11895	12010	10485	9868

Referring to Table 2.2, the flexural strength of synthesised DGEBA resin is more than that of the commercial resin and the synthesised BPA/EC resins. This is due to the fact that the commercial sample is slightly more flexible than the synthesised DGEBA resin. It is probably because the commercial samples contain added flexibilizers and diluents. The epoxy resins made from bisphenol A – cardanol mixtures are still more flexible. Incomplete conversion of cardanol and the shorter chain lengths after epoxidation account for the reduced stiffness of bisphenol-cardanol epoxy systems. The cardanol monoepoxide reduces the molecular weight of the resin by producing shorter polymer chains through chain termination and the bulky side chain in cardanol permits room for molecular rearrangement. Cured BPA/EC-2 sample containing 50% cardanol behaved almost like a rubber sample during three point bending experiment.

The mechanical properties of DGEBA/BPA advancement resins containing varying amounts of BPA as chain extender are furnished in Table 2.3. It was observed that incorporation of BPA into low molecular weight commercial epoxy resin leads to enhanced mechanical properties. The added BPA extends the DGEBA polymer chains resulting in an immediate increase in the molecular weight of the resin. Hence the added BPA could also be regarded as a toughening agent for DGEBA matrix. It was pointed out that because the molecular weight of the resin increases when it reacts with BPA, the free energy of mixing decreases rapidly and the separation of a large amount of soft phase is favoured [20].

Table2.3. Mechanical properties of BPA modified DGEBA resin

Property	DGEBA	DGEBA-BPA 5%	DGEBA-BPA 10%	DGEBA-BPA 15%	DGEBA -BPA 20%
Tensile strength. MPa	48	54.5	58.8	61	60.35
Modulus. MPa	2420	2459	2417	2376	2320
Elongation at break %	3.10	3.80	4.82	4.74	4.39
Energy absorbed. J/mm^2	2.95	4.07	5.8	6.15	6.04
Compressive strength. MPa	108	122	147.7	152	150.8
Impact strength. J/m	28.5	34.6	44	51.5	50.7
Flexural strength. MPa	91.45	100.2	92	86.95	84.6

BPA acts as a toughener partly because the volume fraction of the separated phase tends to be higher than in binary blends. The unmodified DGEBA is brittle due to lack of post yield deformability but in BPA-DGEBA systems yielding is followed by consistent softening. The mechanical properties showed a steady increase with increase in concentration of added bisphenol A up to about 15%. Properties such as tensile strength, compressive strength and impact strength did not vary much above 15% BPA loading. The modulus does not change drastically.

2.3.5 Influence of post curing temperature

Properties of cured commercial resin at different post curing temperature are shown in Table 2.4. 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 120°C. Post curing was done for four hours.

2.3.6 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 2.5. Properties like tensile strength, modulus and elongation at break, toughness and impact strength show maximum values at a post curing time of 4 h.

Table 2.4 Properties of epoxy resin cured at different post curing temperatures *

Property	Post curing temperature (°C)				
	60	80	100	120	140
Tensile strength (MPa)	44.6	47.05	47.45	48	46.9
Tensile modulus (MPa)	2389	2408	2412	2420	2393
Elongation at break (%)	2.875	2.90	2.97	3.10	2.90
Energy absorbed to break. J.mm^{-2}	2.76	2.822	2.932	2.95	2.915
Impact strength (J.m^{-1})	26.80	27.25	27.90	28.50	28.15
Compressive strength (MPa)	99	104.5	107	108	106.45
Surface hardness. Shore D	85	85.5	86	86	87.5
Water absorption (%)	0.235	0.25	0.262	0.27	0.28

* post curing for 4 h, 10 wt% hardener

Table 2.5 Properties of epoxy resin cured at different post curing time *

Property	Post curing time (hrs)				
	1	2	3	4	5
Tensile strength (MPa)	44.8	46.25	47.8	48	47.35
Tensile modulus (MPa)	2307	2327.8	2358	2420	2414.7
Elongation at break (%)	2.74	2.822	2.975	3.10	3.04
Energy absorbed to break. J.mm^{-2}	2..76	2.88	2.914	2.95	2.937
Impact strength (J.m^{-1})	27.36	27.7	28.20	28.5	27.55
Compressive strength MPa	98.65	100.5	103	108	106.5
Surface hardness. Shore D	85.5	85.5	86	86	87.5
Water absorption (%)	0.219	0.24	0.264	0.27	0.276

* Post curing at 120°C, 10 wt% hardener

2.4 CONCLUSIONS

The synthesised DGEBA epoxy resin possesses slightly greater viscosity and specific gravity than the commercial resin. Optimum mechanical properties were obtained for the commercial resin by curing with 10wt % amine hardener and post curing at 120^{0}C for four hours. Even though the synthesised resin exhibited lower strength and modulus, both showed almost similar values of elongation and energy absorbed at break.

Analysis of the mono functional epoxy resin synthesised from cardanol showed maximum epoxidation of 61% in nine hours of reaction time. Epoxies prepared from bisphenol A-cardanol mixtures were less viscous and remarkably more flexible than commercial DGEBA resin. 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. The use of cardanol as substitute for phenol or diphenol in epoxy resin synthesis is significant. Incorporation of bisphenol A into commercial epoxy resin resulted in a tougher resin possessing better strength as well as elongation. This opens up a novel pathway for achieving extra toughness in epoxy resin by blending the resin with modifiers in presence of a small amount of bisphenol A.

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. 2,444,333 (1948)
3. Applegath. et.al., Epoxy Novolacs., SPEJ, January, 1959
4. H.F. Mark, N.M. Bikales, C.G. Overberger and G. Menges., Eds. *Encyclopedia of Polymer Science and Engineering,* Vol.6, Third Edn., John Wiley, New York (1964).
5. N. Hata, J. Kumanotani., *J. Appl. Polym. Sci.*, **17**, 3545 (1973)
6. P.N. Son and C.D. Weber., *J. Appl. Polym. Sci* **17**, 2415 (1973)
7. S.A. Zahir and S. Bantle., ACS *Symp. Ser.*, **221**, 245 (1983)
8. J.F. Giebel, *Org. Coat. Plast. Chem.*, **43,** 545 (1980).
9. W.A.Romanchick and J.F. Giebel., *Org. Coat. Appl. Polym. Sci. Proc.*, **46**, 410 (1982).
10. Dariusz Bodgal and Jaroslaw Gorezyk., *J. Appl. Polym. Sci.*, **94**(5),1969 (2004).
11. Xing Hong Zhang, Hing Mei Wan, Yu Qin Min and Guo Rong Qi., *J. Appl. Polym. Sci.*, **96** (3), 723-731(2005).
12. Hans R Kricheldorf., Ed. *Handbook of Polymer Synthesis*, 1496-1498
13. Gowariker ., *Polymer Science*, New Age International (P) Ltd. New Delhi.
14. S. Manjula, J.D. Sudha, S.C. Bera and C.K.S.Pillai., *J. Appl. Polym. Sci.*,**30**, 1767 (1985).
15. W.F. Symes and C.R. Dawson., *Nature.*, **171**, 841(1953).
16. J.A. Cornelius., *Trop. Sci.* **8** (2), 79,(1966).
17. D. Narayana Murthy., *Res. Ind.*, **13** (3), 134-136 (1968).
18. Y.K. Kamath, S.V. Puntumbekkar and D.B. Vidwans., *Paintindia*,**14**, (4) 21 (1964)
19. 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).
20. C.B. Bucknall and T. Yoshii., *Br. Polym. J.* **10**,53 (1978)

Chapter 3

MODIFICATION BY REACTIVE BLENDING

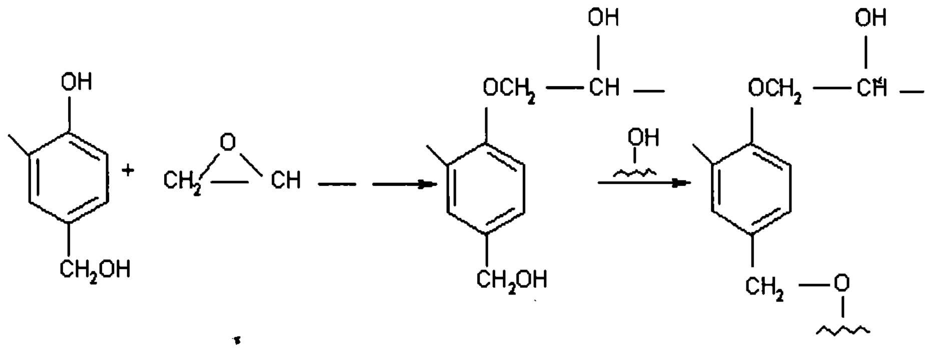
3.1 INTRODUCTION

This chapter presents details of reactive blending studies involving various phenolic and epoxy resins. Such reactive blending often results in hybrid polymer networks (HPN). A HPN is composed of a backbone polymer containing two types of reactive groups that can take part in cross-linking reactions via different mechanisms. A comparative account of the modification of epoxy resin by reactive blending with phenolic resins [1] such as resols, novolacs (PN), epoxy phenol novolacs (EPN) forms the first part of this chapter. Phenolic resins based on cardanol, a renewable natural resource, were also used as epoxy modifiers. These resins were blended with commercial epoxy resin and the physical properties of the cured blends were compared with those of the control resin. The effect of ageing on DGEBA epoxy resin modified by epoxy phenol novolac was also studied. In the second part, modification of commercial epoxy resin using cardanol based epoxides is carried out. The influence of cardanol, on the properties of epoxy resin was investigated by blending the resin with different types of cardanol-formaldehyde copolymers and epoxidised cardanol. Bisphenol A-cardanol epoxy systems were also employed as modifiers of epoxy resin. Recently interpenetrating polymer networks of epoxy resin and UP resin have been reported [2]. A study of the thermal and mechanical properties of DGEBA-unsaturated polyester resin (UPR) blends was also carried out using commercial GP resin.

The addition of a reactive thermoset resin into epoxy resin increases the overall ductility of the polymer. Reinforcement of the resin matrix with fibres can also improve toughness properties. However, areas with relatively low amount of fibres are still prone to damage when the product is in use; hence the need of toughening the resin matrix. Incorporation of phenolic thermosets has been found to cause significant reduction in mould shrinkage.

3.1.1 Reactive blending

DGEBA contains two epoxide functionalities per molecule which are chemically sensitive to a variety of substrates. The cure of epoxy resin involves little molecular reorientation and no evolution of volatile by-products. Hence shrinkage is low and the cured products are relatively strain free; they are usually somewhat tough. Due to the presence of reactive groups embrittlement of the fibre reinforced epoxy composites occurs when exposed to moisture. Reactive blending

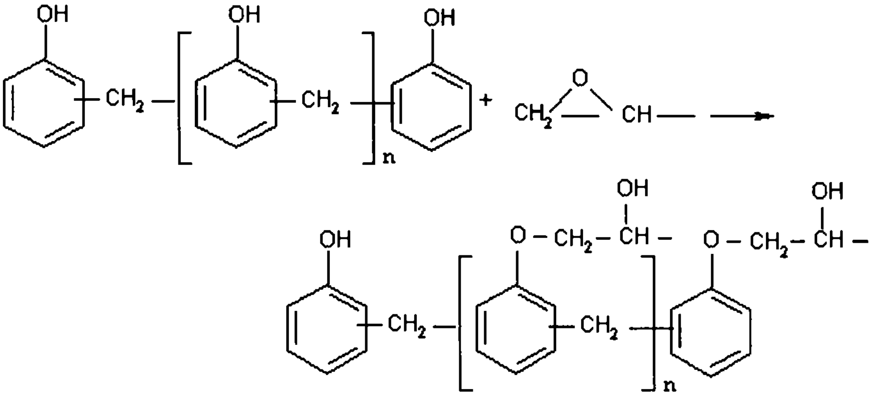


Scheme. 3.1

with thermoset resins can lead to deactivating the end groups [3]. The mechanical properties of resins and laminates are improved by this technique.

Hybrid polymer networks based on DGEBA epoxy resin and different types of phenolic resins can be prepared by reactive blending. The phenolic resins most widely used are low molecular weight butylated resols, which contain phenolic hydroxyl groups and etherified and un-etherified methylol groups. 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 3.1). The net result is a cross-linked polymer network which shows the best chemical and heat resistance of all epoxy coating systems [3].

Novolac resins are low molecular weight polymers consisting of phenolic nuclei linked in the ortho and para positions by methylene groups. The acidic hydroxyl groups in phenolic novolacs (Scheme3.2) react readily with the epoxide group leading to cross-linking [3]. Epoxy resins when cured with phenolic hardeners give good adhesion, strength and chemical and flame resistance. Phenolic novolac-cured epoxy resins are used for encapsulation due to their low water absorption and resistance to heat and electricity. Phenolic novolacs when used as curing agents in epoxies require an accelerator for completion of curing. Modification of epoxies by cresol novolac catalysed by latent triphenyl phosphine has been reported [4]. Compared to standard bisphenol A resins, the high functionality of novolacs increases crosslink densities and improves thermal and chemical resistance.



Scheme.3.2

Novolac resins are epoxidised through the phenolic hydroxyl groups by treatment with epichlorohydrin. 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 [5]. Branching takes place due to the reaction of the hydroxyl groups in the epoxy back bone and epoxy functional group in EPN [6]. 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 (EC) and bisphenol A/cardanol epoxies (BPA/EC) into DGEBA will lead to chain extension of the epoxy back bone.

The basic reaction possible between epoxy resin and unsaturated polyester (UPR) is esterification which involves the opening up of the epoxy ring by the carboxyl group of the poly ester [7].This reaction is catalysed by trace amounts of triphenyl phosphine or tertiary amine. Esterification can be due to the reaction of carboxyl group of the ester either with the epoxy group or with the secondary hydroxyl groups present in the epoxy resin. The latter is more probable in the case of high molecular weight epoxies which contain secondary hydroxyl groups. However, in the presence of the curing agent, low molecular weight DGEBA can also form secondary hydroxyl groups which can enter into reaction with the carboxyl functionality of the polyester. Simultaneous polymerisation of epoxy resin and UPR in a mixture leading to interpenetrating polymer networks (IPN) is another technique used in the modification of epoxies. The reaction takes place in the presence of both an epoxy hardener and a free radical cross-linking agent for the unsaturated polyester [8].

3.2 EXPERIMENTAL

3.2.1 Materials

Toluene (MW=92.14, 99% assay), benzene (MW=78.11, 99%assay), chloroform (BP=61^{0}C,d^{20}=1.489,99%assay,MW=119.38), carbontetrachloride (MW=153.82, 99% assay, BP=76-77^{0}C), triphenylphosphine (MW=262.3, MP=78-82^{0}C,98% assay), benzoyl peroxide and methylene dianiline(MDA) were supplied by E. Merck India Ltd., Mumbai. Unsaturated polyester resin (GP grade, HSR 8113M) was supplied by Ms. Sharon Engineering Enterprises, Cochin.

3.2.2 Morphological studies- Scanning electron microscopy [9]

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology [10]. 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.

3.2.3 Thermal studies [11]

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) Differential Scanning Calorimetry (DSC)

DSC is used to investigate thermal transitions, including phase changes, crystallization, melting, or glass-rubber transitions, of a material as a function of temperature. Heat flow, i.e. heat absorption (endothermic) or heat emission (exothermic), per unit time for the sample is measured and the result is compared with that of a thermally inert reference. TA Instruments DSC Q 100 equipped with a RCS cooling system was used to study thermal transitions in the samples at a rate of heating of 10°C/min. The sample weight was between 7 and 10 mg

c) Dynamic mechanical analysis (DMA) [12]

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.

3.2.4 Soxhlet extraction and swelling studies of cured samples [13]

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 [13].

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

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.

3.2.5 Modification of epoxy resin with resol resins

Phenol –formaldehyde resole type resins (PF) prepared (Section 2.2.6) from phenol, cardanol and phenol-cardanol mixtures were used as the modifier resins. Initially, unmodified resin was cured at room temperature using 10 wt% of the room temperature hardener. It was then degassed in vacuum and poured in to a tensile mould with dumb bell shaped cavities coated with a release 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 at120°C for four hours. Subsequently, varying amounts of the PF resin (2.5to20 weight %) were added to the resin. The mixture was homogenized by gentle agitation using a stirrer and degassed in vacuum at 50° C. The blends were cured by the procedure employed for the neat resin.

The post-cured samples of modified and un-modified resins were subjected to all the tests outlined in Section 2.2.4(c), taking six trials in each case. Thermal properties of the blends were determined by TGA, DSC and DMA (Section3.2.3) Soxhlet extraction and swelling studies were carried out according to the methods cited in Section 3.2.4. The fractured surfaces (tensile samples) of the blends were subjected to morphological studies using SEM (Section 3.2.2).

Resol type resins derived from cardanol (CF) and cardanol- phenol mixtures prepared at different proportions viz.20/80, 40/60,60/40 (designated as CPF-1 CPF-2, CPF-3 respectively) between cardanol and phenol were employed as epoxy modifiers. The blends were prepared in each case and the cured samples tested for mechanical, thermal and morphological properties. The properties were compared with those of the un-modified sample.

3.2.6 Modification with novolac resins

The commercial epoxy resin was mixed with phenolic novolac resins derived from different types of phenolic compounds (Section 2.2.6) and the blends were prepared, cured and tested by the procedures described in Section 3.2.5. The properties were compared with those of the un-modified sample.

3.2.7 Modification with cardanol based novolacs

Novolac resins derived from cardanol (CDN) and cardanol- phenol mixtures containing cardanol and phenol in varying ratios viz. 20/80, 40/60 and 60/40 (designated as CPN-1, CPN-2, CPN- 3 respectively) were used for blending with commercial epoxy resin. In each case the blends were prepared, cured and tested by the methods outlined in Section 3.2.5. The properties were compared with those of the un-modified sample.

3.2.8 Modification with epoxidised phenolic novolacs

Epoxidised novolac resins prepared (Section 2.2.6) from phenol (EPN) and p-cresol (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 3.2.5. 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 169.5, 180 and 188 respectively.

3.2.9 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. The epoxy equivalents (wpe) for these EPNs were estimated as 181.8, 175, 169.5 and 202 respectively. The blends were prepared, cured and tested using the methods outlined in Section 3.2.5. The properties were compared with those of the un-modified sample.

3.2.10 Ageing studies on epoxy resin modified by epoxy novolacs

Cured samples of neat epoxy resin and epoxy resins modified by EPN (15%) and ECN (15%) were prepared as described in Section 3.2.5. 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 3.2.5. The properties of the cured samples were compared.

3.2.11 Modification with cardanol based epoxy compounds

a) Epoxidised cardanol: Epoxidised cardanol (EC) samples synthesised (Section 2.2.6) for different reaction intervals such as 1h, 3h, 6h and 9h (designated as EC1, EC-3, EC-6 and EC-9) 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 3.2.5. The mechanical and thermal properties of the cured blends were determined and compared with those of the control resin.

b) Bisphenol A –cardanol epoxy resins: Epoxy resins synthesised *in situ* (Section 2.2.6) using bisphenol A and cardanol in different stoichiometric ratios viz. 80/20, 50/50 and 20/80 (designated as BPA/EC-1, BPA/EC-2 and BPA/EC-3) were used as modifying agents for commercial epoxy resin. Blends were prepared by adding different amounts of the above modifier resins into commercial epoxy resin and cured by the method described in Section 3.2.5. The properties of the blends were compared with those of the control resin. The variation in mechanical properties of the blends with the cardanol content in the modifier resin was also examined.

3.2.12 Modification with unsaturated poly ester resin.

Unsaturated polyester resin (UPR) was used to modify epoxy resin in three different ways.

a) Direct blending: In this approach, varying amounts of UPR were added to commercial epoxy resin and the blends were cured using the room temperature epoxy hardener. The post-cured samples were tested for mechanical and thermal properties (Section3.2.5).

b) Modification through chemical reaction: Varying amounts of UPR were added to commercial epoxy resin and the mixtures were heated over a water bath for 40minutes in presence of 0.5% triphenyl phosphine catalyst. The reaction mixtures were cooled and cured in presence of 10 weight % room temperature epoxy hardener. The post cured samples were tested for their mechanical properties.

c) Interpenetrating polymer networks: Interpenetrating polymer networks were prepared by mixing UPR with commercial epoxy resin in various ratios and simultaneously curing both the thermosets in presence of their respective curing agents. Samples of different weight ratios of DGEBA /UPR viz. 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0 containing methylene dianiline (MDA,20phr based on DGEBA) and benzoyl peroxide(BPO,1phr based on UPR) were mixed well, degassed to eliminate air bubbles and poured into teflon moulds. It was heated to

100^0C for 4 hrs followed by post-curing at 140^0C for 6 hrs in an air oven. The samples after post-curing were tested for thermal and mechanical properties as described in Section 3.2.5.

3.3 RESULTS AND DISCUSSION

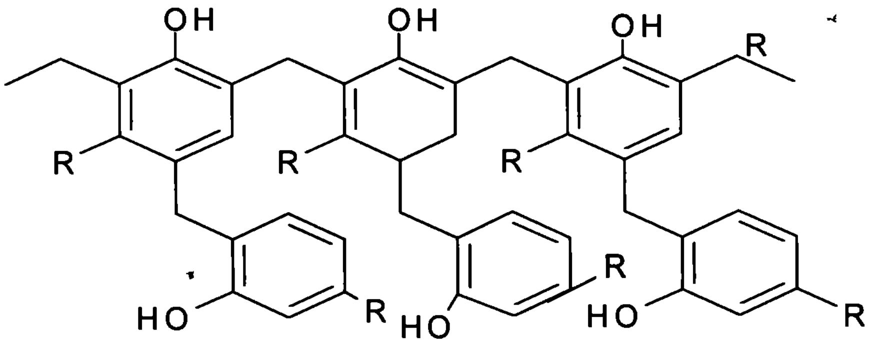
Reactive blending of epoxy resin with different types of phenolic resins, cardanol based epoxy compounds and unsaturated polyester resin were carried out and the mechanical, thermal and morphological properties of the blends were determined and compared with those of the un-modified epoxy resin. It appears more reasonable to look for resins of epoxy functionality to improve the toughness characteristics of a given epoxy system. With this perspective, we have investigated the behaviour of blends of DGEBA with novolac epoxies and epoxides based on cardanol, a renewable natural resource. Due to better miscibility these modifiers can be incorporated in relatively larger percentages (of the order of 20%) in the epoxy resin. The solubility parameters of epoxy resin (21-22 $(J/m^3)^{1/2} \times 10^{-3}$) and UPR (19.4-26.4 $(J/m^3)^{1/2} \times 10^{-3}$) are almost in the same range rendering them highly compatible. All the above modifying resins gave stable homogeneous blends with epoxy resin. The high volume fractions of gel content (V_p) in the modified resins during swelling studies indicate extensive cross-linking.

Cross-link density is found to have great influence on toughening. Practically, toughness exhibits a maximum for intermediate cross-linking densities [14]. The toughness achieved by the blends is evaluated in terms of the magnitude of energy absorbed for failure.

3.3.1 Modification of epoxy resin with resol resins

During blending of epoxy resin with PF resin the following reactions can take place. (i) The methylol group in the resol resin can condense with the secondary hydroxyl group of the epoxy system to form cross linked structures. (ii) At high temperatures, the phenolic hydroxyl groups react with the epoxy groups leading to chain extension. (iii) The resol resin can also react with the amino group of the hardener through the methylol groups giving $-CH_2NH-$ groups, which in turn can open up epoxy rings. Moreover, hydroxyl groups can catalyse the curing action of DGEBA. This catalytic effect of -OH on the curing of epoxide by amine has been reported in the literature [15]. The net result is a cross-linked polymer that exhibits chemical and heat resistance.

The structure of cardanol –formaldehyde (CF) polymer can be given as follows [16].



R=$C_{15}H_{31\text{-}n}$

i. Tensile properties

Referring to Fig.3.1 tensile strength values obtained by blending epoxy resin with phenol-formaldehyde resin are higher compared to that of the unmodified resin. Tensile strength reaches a maximum on adding progressively larger amounts of PF beyond which the strength is found to be lower. The improvement in tensile strength over that of the base resin at all percentages of the PF resol resins considered is due to the high degree of compatibility and enhanced cross-linking. At a certain blend composition the degree of cross-linking becomes optimum beyond which further addition of resol does not show any strengthening effect.

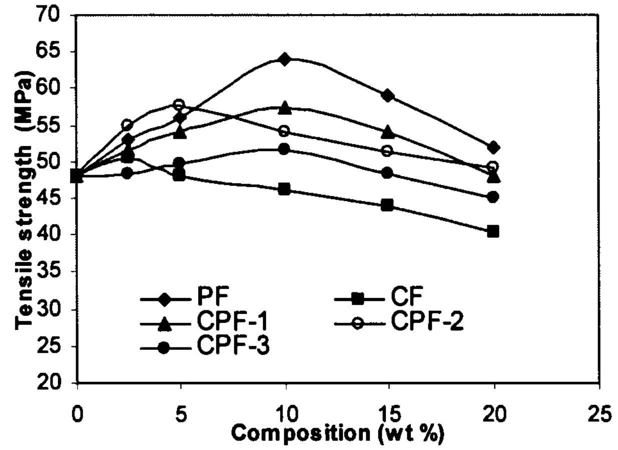


Fig. 3.1 Tensile strength of modified epoxy resin versus resol concentration

However, incorporation of cardanol generally lowers the tensile strength. This can be attributed to the bulky nature of the cardanol molecule with a long aliphatic side chain which can hinder cross-linking to some extent. Figure 3.2 shows the effect of phenolic resol type resins on the tensile modulus. After the initial loss of modulus at about 2.5%, the blends do not show lowering of modulus on adding more of the modifier resin.

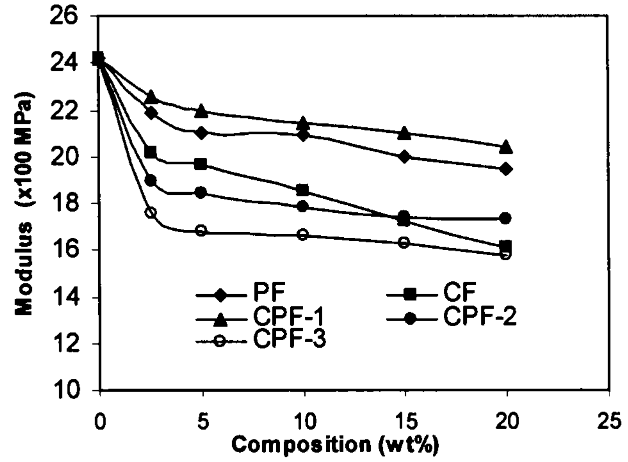


Fig. 3.2 Modulus of modified epoxy resin versus resol concentration

The modulus of epoxy-phenolic blends is lower than that for the neat resin indicating improved flexibility. This effect is pronounced in the case of epoxy/CF blends suggesting the ability of CF to reduce the inherent brittleness of the epoxy matrix.

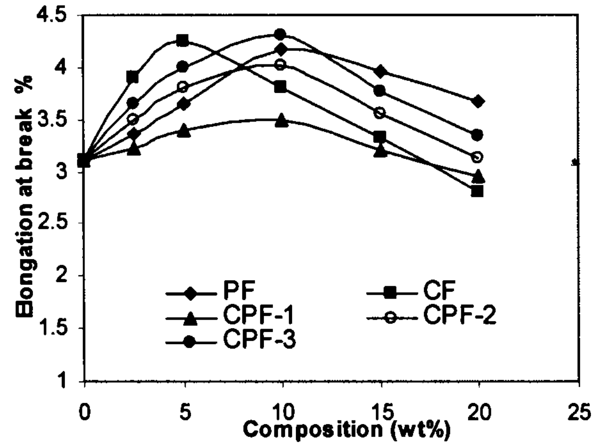


Fig. 3.3 Elongation at break of modified epoxy resin versus resol concentration

The effect of addition of phenolic resols on elongation at break is given in Fig.3.3. Compared to unmodified resin the blends show substantial improvement in elongation especially at lower modifier concentrations. In particular, incorporation of CF imparts enhanced flexibility to the epoxy matrix. This may be due to loose packing of the polymer chains by virtue of the branched structure of cardanol. The extent of toughening attributed to the epoxy resin due to phenolic blending is measured in terms of the energy absorbed to break.

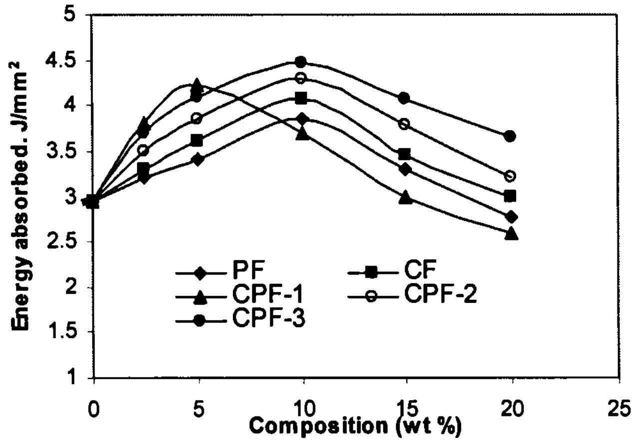


Fig 3.4a. Variation of energy absorbed (to break) of modified epoxy resin versus resol concentration

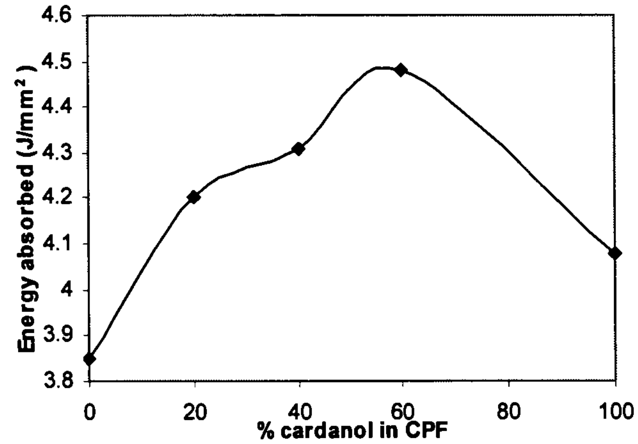


Fig.3.4b. Variation of energy absorbed to break of modified resin versus cardanol concentration in CPF resin

Figure 3.4(a) gives the variation of energy absorbed by blends of epoxy resin with phenolic resol resins. The blends absorb more energy than that by the neat resin. The energy absorption is more when the cardanol content is higher. This may be due to the bulky structure of cardanol molecule with a long side chain which gives molecular flexibility. The epoxy/CPF mixtures show increased energy absorption compared to those with PF or CF alone.

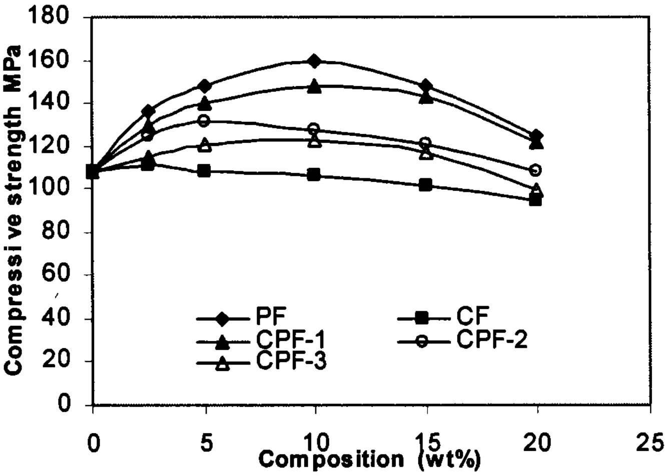


Fig.3.5 Compressive strength of modified resin versus resol concentration

Energy absorbed (to break) increases with increase in cardanol content in the resin mixture up to about 60% as given in Fig 3.4(b).The variation in compressive strength for the blends of epoxy resin with various resols follows a trend similar to that of tensile strength.(Figure 3.5). There is a general increase in compressive strength for PF blends compared to the base resin. However, the epoxy/CF blends show no improvement in compressive strength. This can be attributed to a less compact structure resulting from the presence of cardanol.

Figure 3.6 illustrates the variation of impact strength. Maximum improvement in impact resistance was observed with 15%PF (71.4%). However, epoxy/CPF systems show better impact resistance (CPF-3, 87%improvement) at a lower resol loading. Cardanol can improve the impact strength by virtue of the side chain which can cause entanglement with polymeric chains. But too many cardanol molecules can possibly cause steric hindrance and lower the properties. Here also an increase in cardanol content in CPF resins above 60% was found to lower the impact strength.

ii. Surface hardness and water absorption

Figure 3.7 indicates the variation in surface hardness. The epoxy/resol blends generally show only a slight decrease in surface hardness compared to the unmodified resin in terms of Shore D units. Water absorptions of various PF resol -

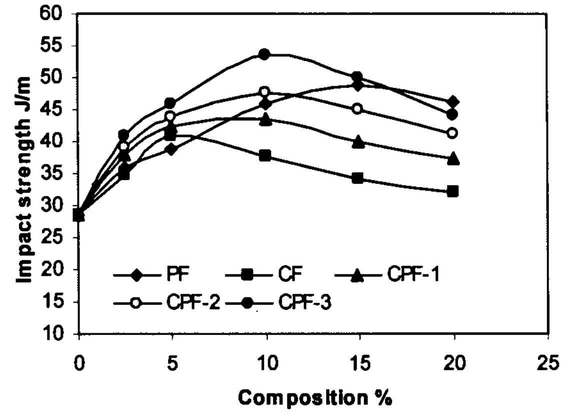


Fig. 3.6 Variation of impact strength of modified resin versus resol concentration

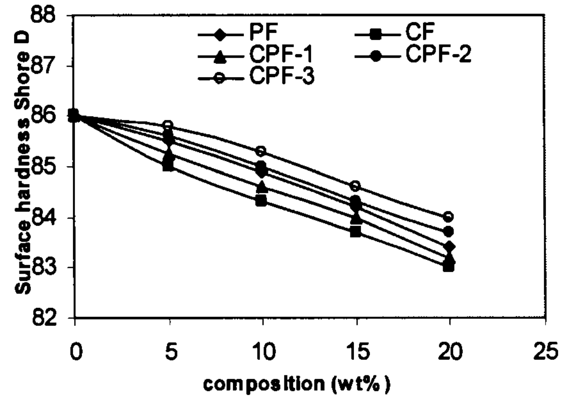


Fig. 3.7 Variation of surface hardness of modified resin versus resol concentration

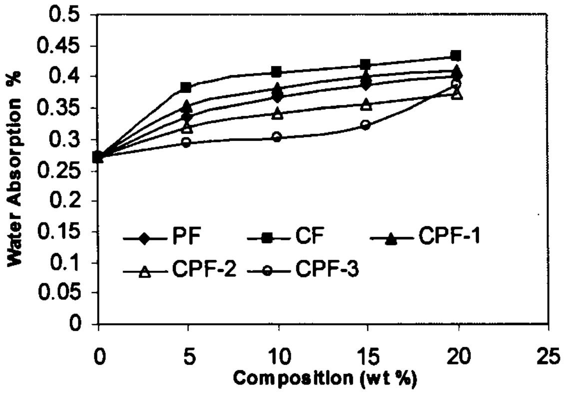


Fig 3.8 Water absorption of modified resin versus resol concentration

modified epoxy resins are given in Figure 3.8. Epoxy–PF blends are found to be inferior in water resistance to the unmodified epoxy resin. This can be due to the presence of methylol functionalities capable of hydrogen bonding with water.

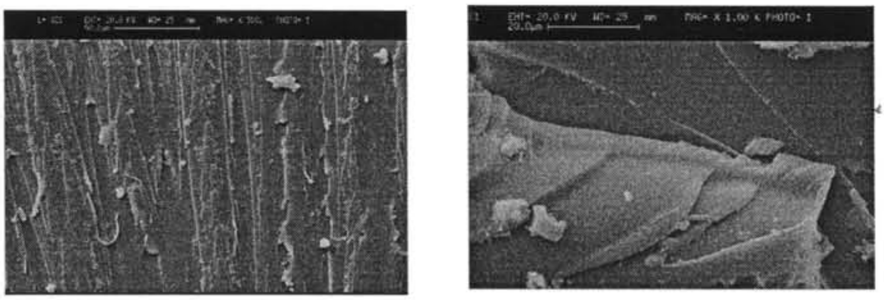
Table 3.1 summarizes the effect of adding varying amounts of phenolic resol resins in the base resin. The maximum improvement acquired in each property and the corresponding concentrations are tabulated.

Table 3.1 Summary of properties of epoxy resin modified with 0-20% PF resol resin

Properties	Neat	% Improvement / composition (wt %)				
		PF	CF	CPF-1	CPF-2	CPF-3
Tensile strength (MPa)	48	40.2/10	5/2.5	19/10	20/5	7 /10
Modulus (x10^2 MPa)	24.2	-19.4/20	-34/20	-16/20	-27.7/20	-34/20
Elongation at break (%)	3.1	34.5/10	38.8/5	20/10	29/10	38.5/10
Energy absorbed to break (J /mm^2)	2.95	46/10	53.7/10	62.3/5	71.4/10	82.7/10
Compressive strength (MPa)	108	47.2/10	3.2/2.5	37/10	21.3/5	14/10
Impact strength J/m	28.5	71/15	48/5	47/10	67/10	87.5/10
Hardness Shore D	86	-3./20	-3.5/20	-3.3/20	-2.6/20	-2.3/20
Water absorption (%)	0.27	48/20	57/20	52/20	43/20	32/20

iii. Morphology [10]

Fig. 3.9(a) is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Fracture paths are mostly straight and constitute failure bands from bottom to top. The fracture surface is characterized by pinpoint crazes within the material. Though crazing is the major mechanism for toughness in epoxies, a combination of crazing and shear yielding would explain the energy absorption in epoxy -PF blend. Figure 3.9 (b) shows the fractured surface of an epoxy-PF blend. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure and increased toughness.



(a) (b)

Fig.3.9.Scanning electron micrographs of the fracture surface of a) un-modified epoxy resin b) Epoxy/PF

iv. Soxhlet extraction and swelling studies

The Soxhlet extraction and swelling data are given in Table 3.2. The cured modified samples yielded slightly smaller amounts of soluble matter compared to the unmodified sample. This is further confirmed by the slightly higher V_p values of the modified samples obtained from the swelling studies. This indicates cross-linking between epoxy resin and the modifier resin. There is an obvious fall in degree of cross-linking at 15% CF concentration.

Table 3.2 Soxhlet extraction and swelling data

Sample	DGEBA	5%PF	15%PF	5%CF	15%CF
Soluble matter %	5.34	5.21	5.312	5.282	5.36
V_p	0.904	0.910	0.917	0.907	0.893

v. Thermal properties

i. TGA : The TGA curves of the neat resin and DGEBA- 10% CF blend are shown in Fig.3.10. The CF modified resin shows slightly higher onset and half loss temperatures than the unmodified sample as shown in Table 3.3. However the CF modified sample yielded less residue (6.448 %) indicating its decreased ablative property. This may be due to the presence of the long aliphatic side chain in the cardanol molecule.

ii. DSC : The DSC thermograms of the neat resin and its blends with PF (10wt %) and CF (10 wt %) are given in Fig.3.11. For the neat resin T_g is observed at 70.64^0C. For the PF (10 wt %) and CF (10 wt %) blends a single Tg each (76.44^0C and 78.82^0C respectively) is recorded indicating their homogeneous nature.

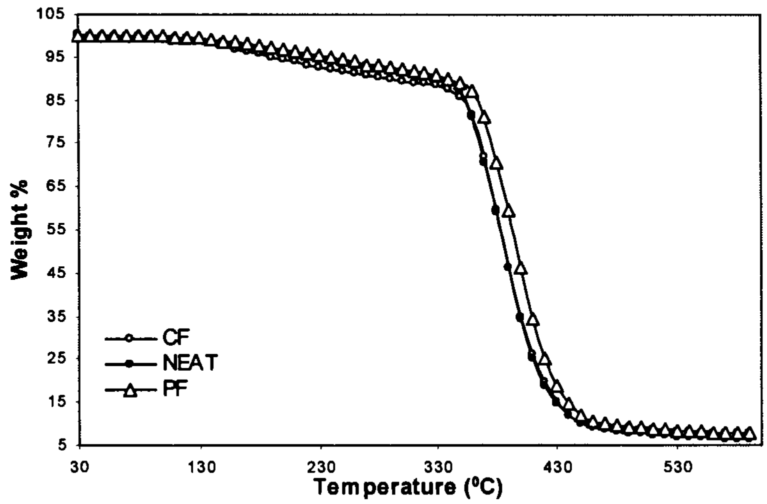


Fig.3.10 TGA curves for unmodified and resol modified epoxy resins

Table 3.3 Thermal properties

Sample	Onset temperature (°C)	Temperature maximum rate.(° C)	Temperature half loss .(° C)	Residue %
Neat resin	310.56	386.12	367.24	7.664
CF blend	315.98	379.86	386.63	6.483
PF blend	317.43	381.22	377.67	7.721

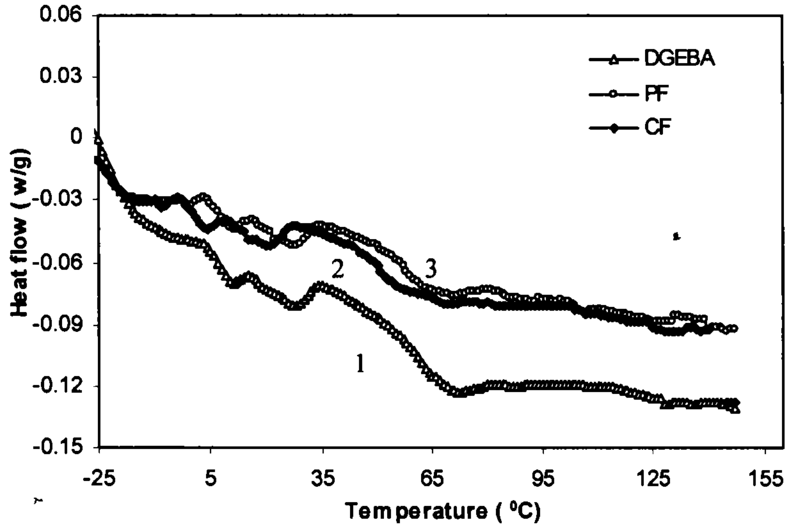


Fig. 3.11 DSC curves for 1.DGEBA 2.CF Blend 3.PF Blend

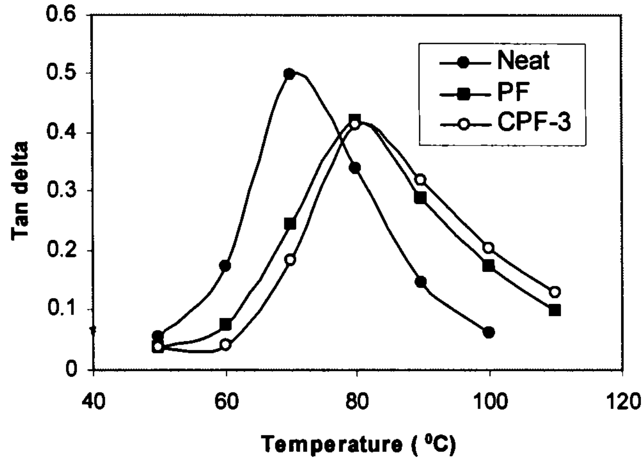


Fig.3.12a. DMA -Tan delta curves for unmodified and resol modified epoxy resins

iii. DMA: Figs.3.12 (a), (b) and (c) illustrate the DMA-tanδ, loss modulus and storage modulus curves respectively. The glass transition of neat epoxy obtained from DMA-tanδ curves (71.3^{0}C corresponding to tan δ= 0.497) is in agreement with the DSC measurement. Incorporation of 10wt% PF and10 wt % CPF-3 shifts the T_g to higher values 79.53^0 C and 81.6^{0}C respectively. The damping peaks occur at lower tan δ values in the case of the blends due to sufficiently higher storage moduli. This is indicative of a greater extent of cross-linking in the blends. In general, a more cross-linked material would show higher storage modulus. The DGEBA/PF and DGEBA/ CPF blends show higher storage moduli.

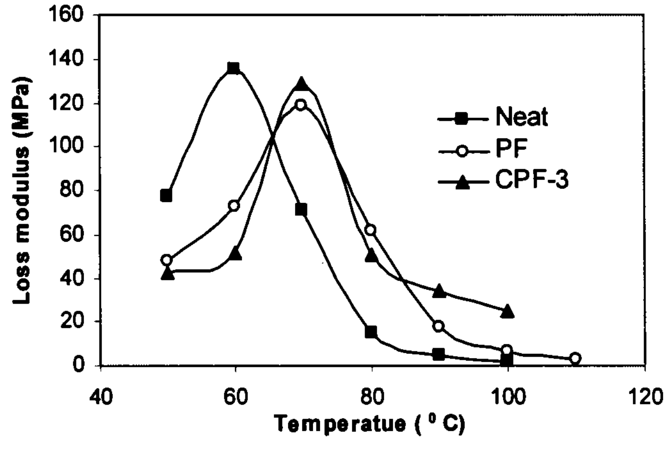


Fig.3.12b. Loss modulus curves for unmodified and resol modified epoxy resins

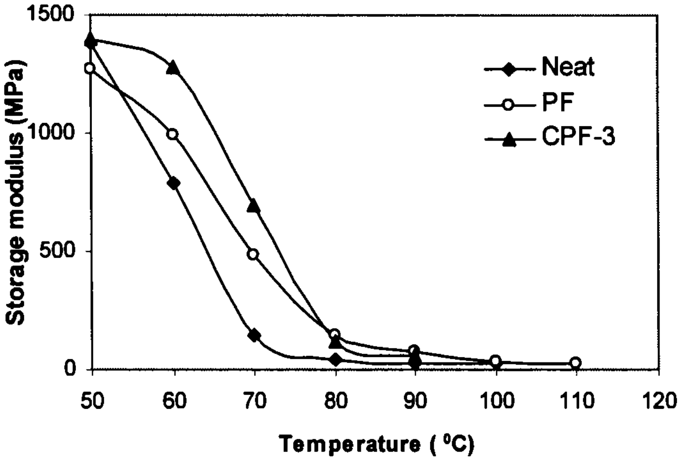


Fig.3.12c. Storage modulus curves for unmodified and resol modified epoxies

3.3.2. Modification with novolac resins

Novolac resins prepared from phenol, p-cresol, t-butyl phenol and cardanol (designated as PN, PCN, BPN and CDN respectively) were used as modifiers of commercial epoxy resin. The stoichiometric ratio between phenolic material and formaldehyde in the novolacs was optimized (1:0.8) for maximum property enhancement

At high temperatures, the phenolic hydroxyl groups react with the epoxy groups leading to chain extension. In the presence of amine catalyst, the reaction of acidic phenolic hydroxyl groups with the epoxide ring is facilitated even at room temperature. Moreover, hydroxyl groups can catalyse the curing reaction of DGEBA. This catalytic effect of -OH on the curing of epoxide by amine has been reported in the literature [13]. The net result is a cross-linked polymer that can be expected to show the thermal resistance of phenolics and an overall improvement in mechanical properties because of the hybrid network. Though novolacs are brittle, hybrid polymer networks consisting of epoxy and novolac resin blends are seen to have improved properties. Phenolic novolac-cured epoxy resins are used for encapsulation due to their low water absorption and resistance to heat and electricity. Compared to standard bisphenol A resins, the high functionality of novolacs increases cross-link densities and improves thermal and chemical resistance.

i. Tensile properties

Referring to Fig.3.13, tensile strength values obtained by blending epoxy resin with 2.5 to 20% phenolic novolacs are significantly higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 10-15 wt % of novolac beyond which it decreases. 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 entangling among the polymer chains due to hybrid network structure. This results in increased tensile strength, lower extent of soluble matter and increased volume fraction of polymer in the swollen samples.

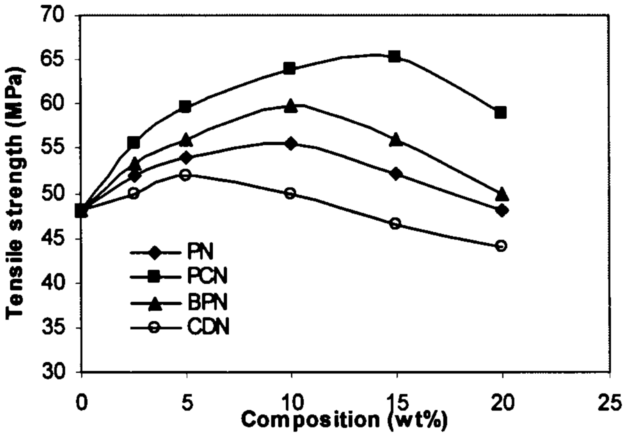


Fig.3.13 Tensile strength of modified epoxy resin Vs novolac concentration

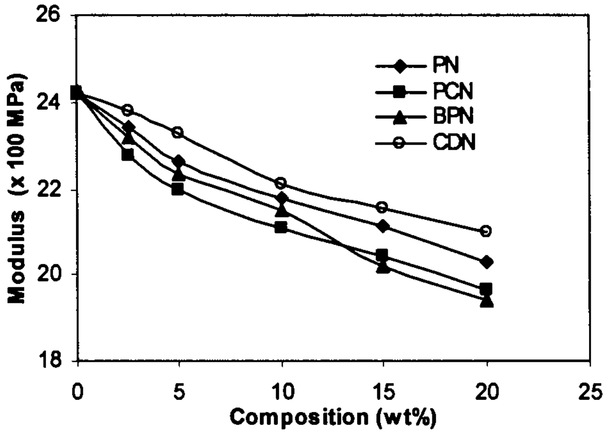


Fig. 3.14 Modulus of modified epoxy resin versus novolac concentration

The modifying effect of PCN and BPN are found to be superior to that of the other novolacs. This can be due to a more linear structure resulting from the structures of p-cresol and p-t-butyl phenol which have only two possible sites per molecule for condensation with formaldehyde.

Fig.3.14 shows the effect of novolacs on the tensile modulus. The slight reduction in modulus on addition of novolacs shows improved molecular flexibility.

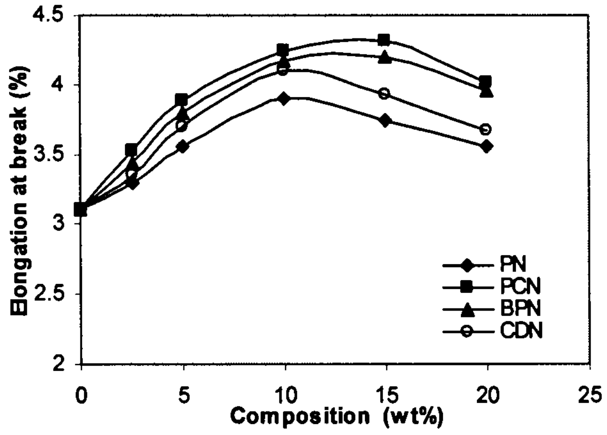


Fig. 3.15 Elongation at break of modified epoxy resin versus novolac concentration

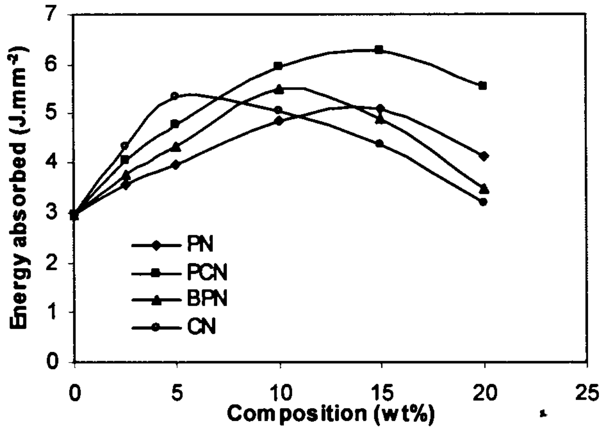


Fig. 3.16 Energy absorbed (to break) of modified epoxy resin Vs novolac concentration

The effect on elongation at break is shown in Fig. 3.15. Compared to unmodified resin the blends show an increase in elongation. Epoxy / PCN and epoxy / BPN blends show maximum elongation at 15wt % of novolac while the epoxy/CDN and epoxy/PN blends show maximum improvement in elongation at a lower novolac loading. A higher elongation may be the result of straightening of the entangled chains. Fig. 3.16 gives the variation of energy absorbed (to break) by the blends of epoxy resin with novolacs. This can be taken as a measure of the toughness. At 15wt % PCN shows 112% improvement in energy absorption. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement. The greater energy absorption shown by blends of para substituted phenol novolacs (novolacs of p-cresol (PCN) and t-butyl phenol (BPN)) confirms this observation. The variation in compressive strength for the blends is given in Fig 3.17. There is considerable increase in compressive strength for these blends compared to the unmodified resin. This can also be explained in terms of increased levels of cross-linking.

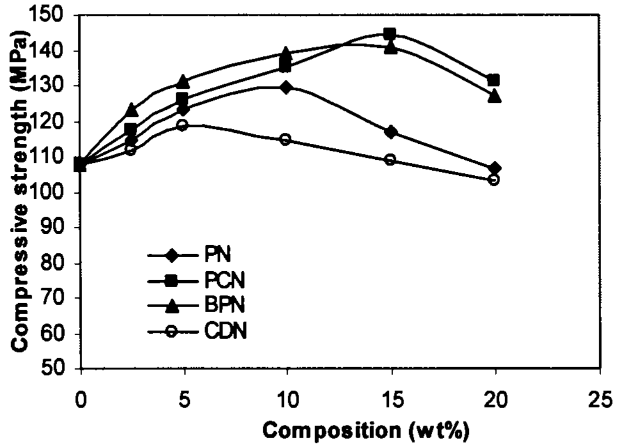


Fig. 3.17 Compressive strength of modified epoxy resin Vs novolac concentration

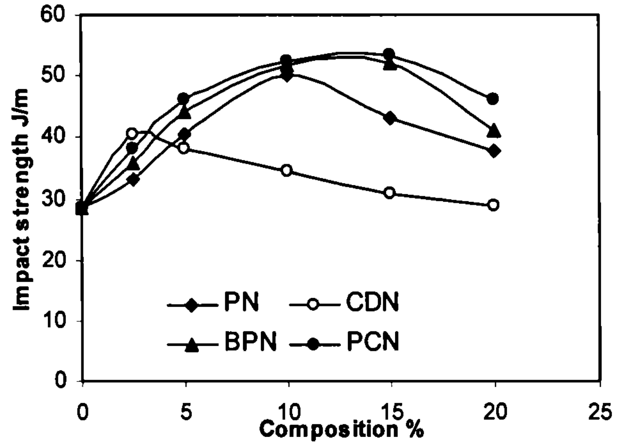


Fig.3.18 Impact strength of modified epoxy resin Vs novolac concentration

Fig.3.18 shows the variation of impact strength with the addition of novolac resins. Compared to PN and CDN, PCN and BPN exhibit improved impact resistance. This is possibly due to increased cross-linking and the presence of more linear polymer chains arising from para substituted phenols.

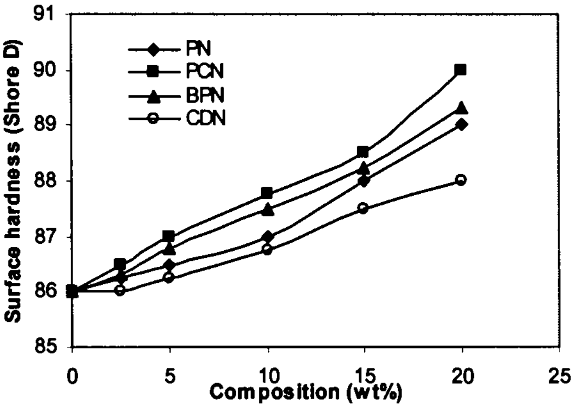


Fig. 3.19 Surface hardness of modified epoxy resin Vs novolac concentration

ii. Surface hardness and water absorption

Fig.3.19 indicates a general improvement in surface hardness upon blending epoxy resin with novolacs. However, the increase is only marginal. Water absorption of novolac-modified epoxy resins is given in Fig.3.20. The blends show increased water resistance. This is possibly due to a greater extent of aromatic rings and methylene groups, which are hydrophobic in nature. Table 3.4 summarizes the mechanical properties of epoxy–EPN blends. The maximum improvement acquired in each property and the corresponding concentrations are tabulated.

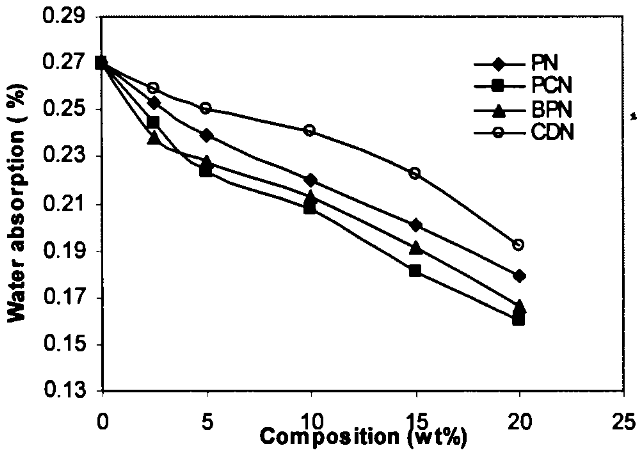


Fig. 3.20 Water absorption of modified epoxy resin Vs novolac concentration

iii. Morphological studies

Figure 3.21(a) is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Fracture paths are mostly straight and constitute failure bands. The fractured surfaces of DGEBA/novolac blends (Fig 3.21(b) and(c)) show distinct signs of increased energy absorption. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure. The massive stress whitening is indicative of crazing. Formation of voids, drawn out fibril like structure and peaks can be distinguished as a characteristic feature of extreme ductile failure. This points to high toughness and load bearing characteristics.

Table 3.4 Summary of properties of DGEBA/novolac blends

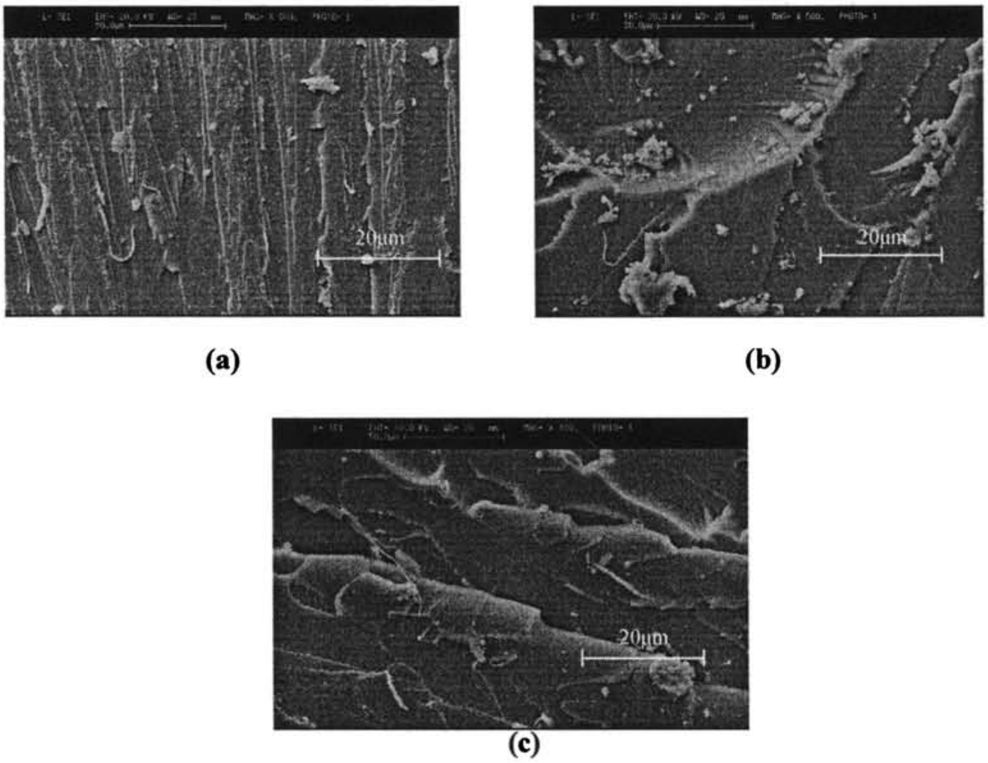
Property	Neat resin	%Maximum improvement / Composition (wt %)			
		PN	PCN	BPN	CDN
Tensile strength (MPa)	48	18/10	38/15	26/10	9.5/10
Modulus (x 100 MPa)	24.2	-16/20	-19.5/20	-20/20	-13/20
Elongation at break (%)	3.1	26/10	40/15	35.5/15	32/10
Energy absorbed (Jmm^{-2})	2.95	72/15	112/15	89.7/10	81/5
Compressive strength (MPa)	108	20/10	35/15	31.5/10	11.25/5
Impact strength (J/m)	28.5	75/10	88/15	83.5/15	43/2.5
Surface hardness (Shore D)	86	3.5/20	4.7/20	4.05/20	2.5/20
Water absorption (%)	0.27	-34/20	-42/20	-39/20	-29/20

iv. Soxhlet extraction and swelling studies

The Soxhlet extraction and swelling data are given in Table 3.5. The cured modified samples yielded slightly smaller amounts of soluble matter compared to the unmodified sample. This is further confirmed by the slightly higher V_p values of the modified samples obtained from the swelling studies. This indicates cross-linking between epoxy resin and the modifier novolac resin and a higher content of cross-linked matter.

Table 3.5 Soxhlet extraction and swelling data

Sample	DGEBA	PN 10%	PCN 10%	BPN 10%	CDN 10%
Soluble matter %	5.34	4.88	4.581	4.692	5.083
V_p	0.904	0.914	0.928	0.921	0.901



(a) (b)

(c)

Figure.3.21. SEM micrographs of the fracture surfaces a) DGEBA b)DGEBA/PCN and c) DGEBA/BPN

v. Thermal properties

i. TGA: The TGA curves of the neat resin and DGEBA / PCN (15wt) show marginally better thermal stability for the modified samples %)(Fig 3.22). An increased level of cross-linking as well as the presence of phenolic groups gives better thermal resistance to the blends (Table 3.6). The PCN modified sample gave 8.193% residue at 600^0C compared to 7.66 %by the un-modified resin.

ii. DSC: The DSC thermograms of the neat resin and its blend with 15 wt %PCN are given in Fig.3.23. For the neat resin glass transition is obtained at 70.64^0C (T_g). Addition of 15wt % PCN to the epoxy matrix shifts the T_g to a higher temperature of about 77.47^{0}C. This effect is in conformity with the higher level of cross-linking facilitated by the novolac. This is also in agreement with the data obtained from Soxhlet extraction and swelling studies. The higher functionality and phenolic content of novolac resins increase cross-link densities and improve thermal and chemical resistance.

Table 3.6 .Thermal properties

Sample	Onset temperature (^{0}C)	Temperature maximum rate.(^{0} C)	Temperature half loss .(^{0} C)	Residue %
Neat resin	310.56	386.12	387.24	7.664
PCN	308.5	376.72	383.03	8.193

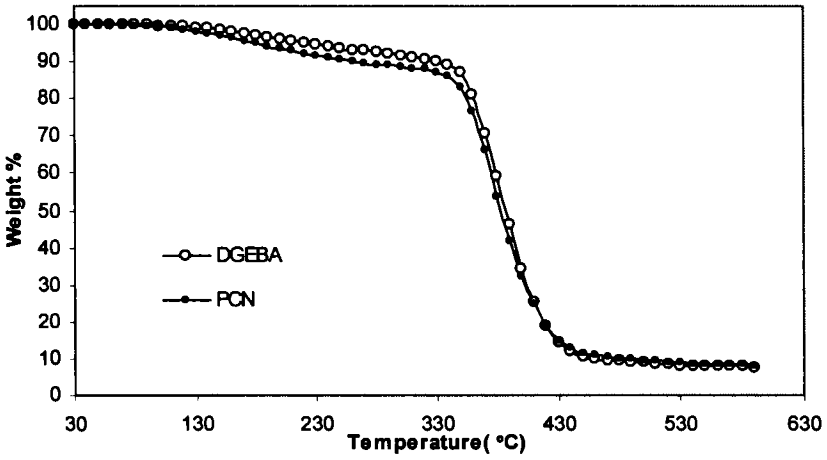


Fig. 3.22 TGA curves for novolac modified and un modified epoxy resin

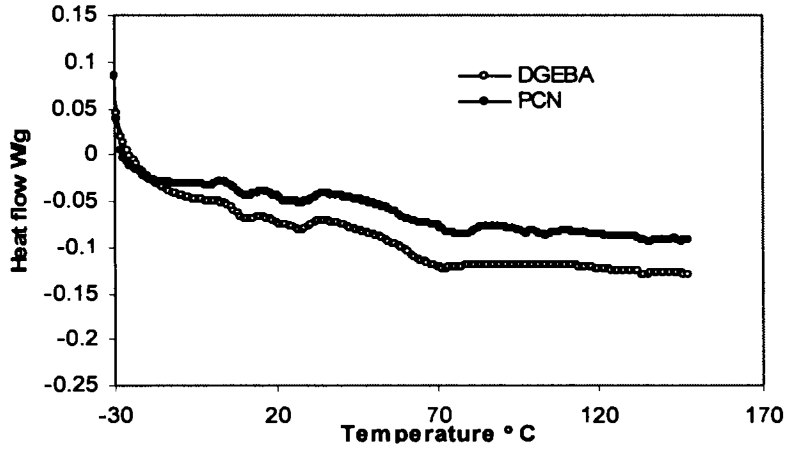


Fig.3.23 DSC curves for novolac modified and unmodified epoxy resins

iii. DMA: The glass transition of neat epoxy obtained from tanδ curves (Fig.3.24a) (71.3^{0}C corresponding to tan δ=0.497) is in agreement with the DSC data. The reduction in height of the tanδ curve compared to that of the neat resin is indicative of a plasticizing effect due to the novolac resin. Incorporation of 15 wt % PCN (tan δ=0.4392) and 10 wt %BPN (tan δ=0.4194) shifts the T_g to higher values, 79.96^{0}C and 79.53^0 C respectively. The damping peaks occur at lower tan δ values in the case of these blends due to higher storage moduli (Fig 3.24b). This is indicative of a greater extent of cross-linking in the blends. The blends show higher loss modulus (Fig 3.24c) compared to the unmodified sample. A higher loss modulus causes more mechanical energy to turn into heat via molecular relaxation.

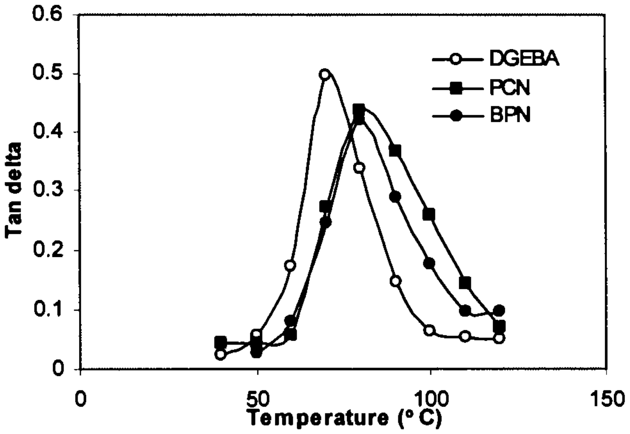


Fig.3.24a. Tan delta curves for novolac modified and unmodified epoxy resins

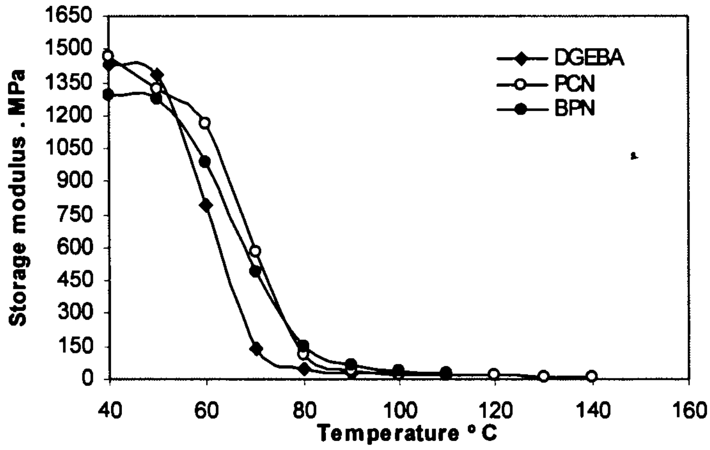


Fig.3.24b.DMA-Storage modulus curves for novolac modified and unmodified epoxy resins

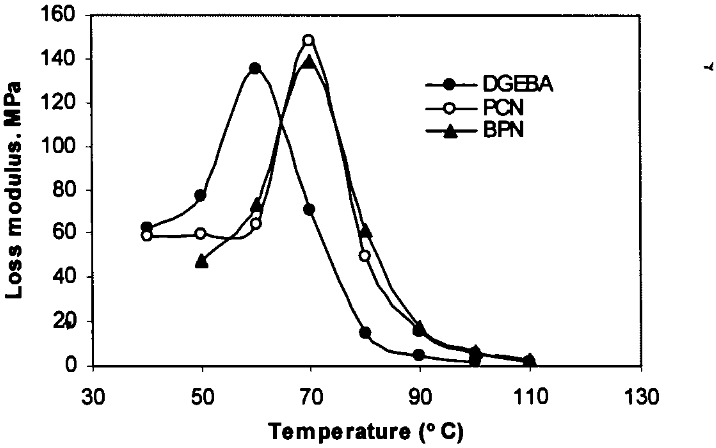


Fig.3.24c. DMA-loss modulus curves for modified and unmodified epoxy resins

3.3.3 Modification with cardanol based novolacs

Novolac resins derived from cardanol (CDN) [16] and cardanol- phenol mixtures with ratios of 20/80, 40/60 and 60/40 (designated as CPN-1, CPN-2, CPN- 3 respectively) between cardanol and phenol were used as modifiers for commercial epoxy resin. The stoichiometric ratio between phenolic material and formaldehyde in the novolacs was optimized (1:0.8) for maximum property enhancement. The property profiles of the blends imply a toughening action by novolacs especially phenol-cardanol-formaldehyde novolac resins (Fig.3.25). At elevated temperatures, the phenolic hydroxyl groups react with the epoxy groups leading to hybrid polymer networks through chain extension and cross-linking. In the presence of

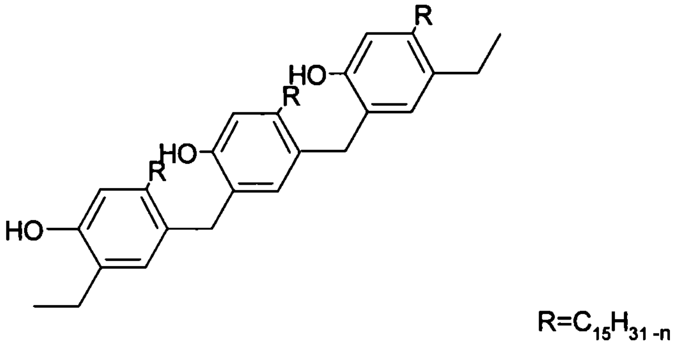


Fig.3.25 Typical structure of cardanol -formaldehyde novolac

amine hardener, the reaction of phenolic hydroxyl groups with the epoxide ring is facilitated even at room temperature.

i. Tensile properties

Referring to Fig.3.26, tensile strength values obtained by blending epoxy resin with 2.5 to 20% novolacs are significantly higher compared to that of the control resin. Tensile strength reaches a maximum at 5 -10 wt % of novolac 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.

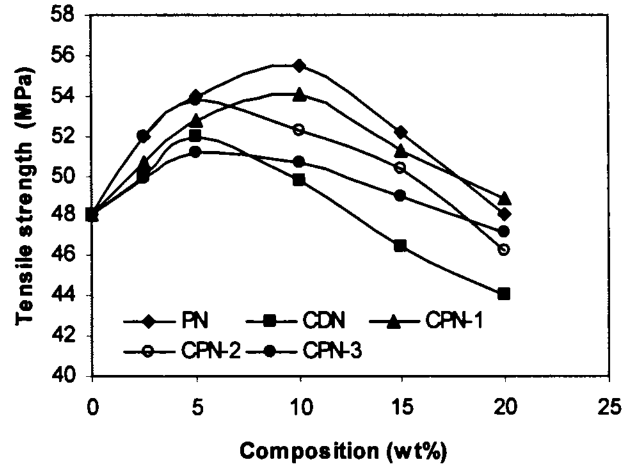


Fig.3.26. Tensile strength of DGEBA-C/PNs Vs novolac concentration

This can also be attributed to some amount of entangling among the polymer chains. This results in increased tensile strength, lower extent of soluble matter and increased volume fraction of polymer in the swollen samples, V_p. The slight reduction in modulus (Fig.3.27) on addition of novolacs shows improved molecular flexibility.

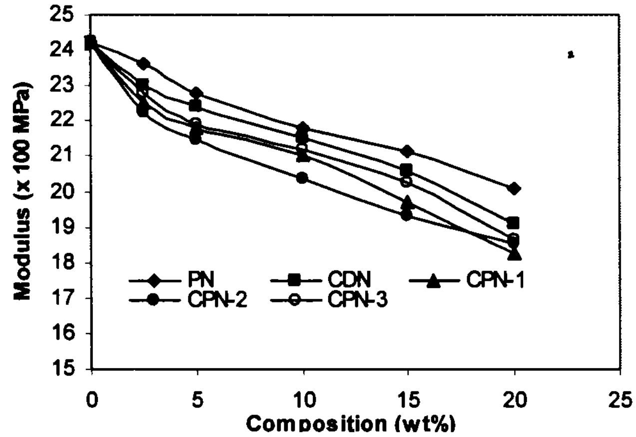


Fig. 3.27 Modulus of DGEBA-C/PNs Vs novolac concentration

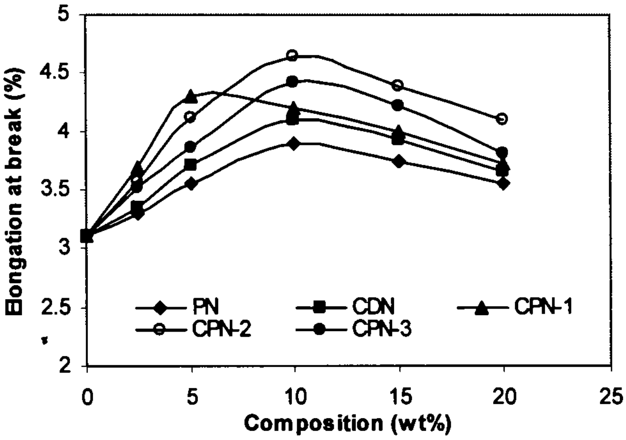


Fig. 3.28 Elongation at break of DGEBA-C/P Ns versus novolac concentration

The effect on elongation at break is shown in Fig.3.28. Compared to unmodified resin the blends show an increase in elongation. Epoxy / CPN -2 blend shows maximum elongation at 10wt % of novolac. A higher elongation may be the result of straightening of the entangled chains.

Fig.3.29 (a) gives the variation of energy absorbed by the blends at break. The enhanced energy absorption indicates inherent toughness of these blends. The epoxy/CDN blend exhibits better energy absorption than epoxy/PN blend. This may be due to the structure of cardanol molecule with a long side chain, which leads to a higher extent of realignment. The epoxy/CPN blends show increased energy absorption compared to those with PN or CDN alone. Energy absorbed (to break) increases with increase in cardanol content in the resin mixture up to about

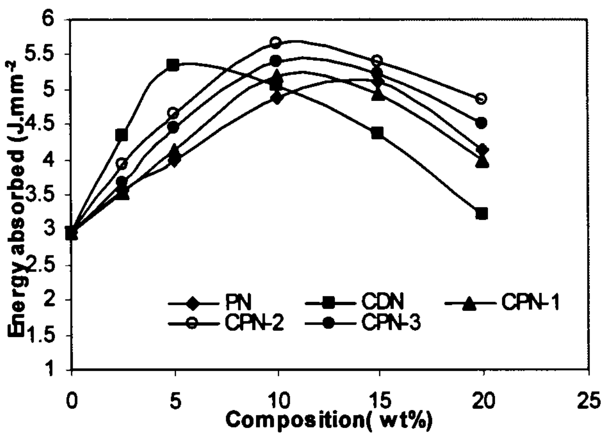


Fig.3.29a.Energy absorbed (to break) of DGEBA-C/PNs Vs novolac concentration

40 wt% CDN concentration as shown in Fig 3.29(b). At 10wt %CPN-2 shows 92% improvement in energy absorbed at break. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement.

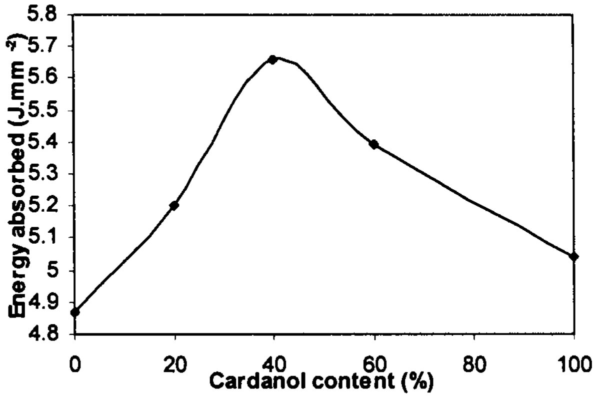


Fig.3.29b. Energy absorbed by modified resin Vs % cardanol in the modifier resin.

The variation in compressive strength for the blends is given in Fig 3.30. There is considerable increase in compressive strength for the blends compared to the unmodified resin. This can also be explained in terms of increased levels of cross-linking. Epoxy/CPN -1 blend shows maximum compressive strength at 10 wt %.

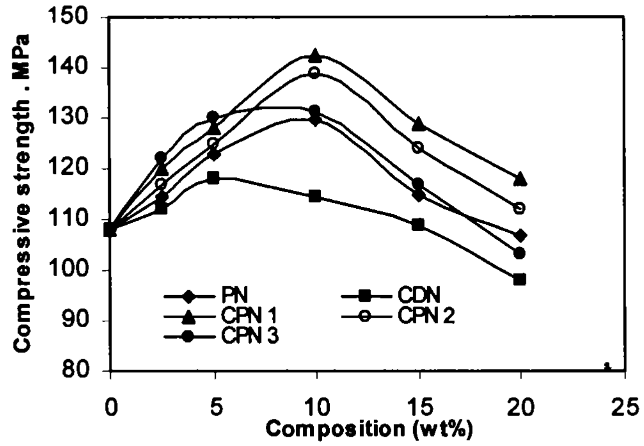


Fig.3.30. Compressive strength of DGEBA-C/PNs Vs novolac concentration

The variation in impact strength of DGEBA/novolac blends at different concentrations of cardanol in the modifier resin is given in Fig.3.31. Among the novolacs studied those prepared from cardanol- phenol mixtures (CPNs) yielded comparatively higher impact resistance and this property increases with increase in

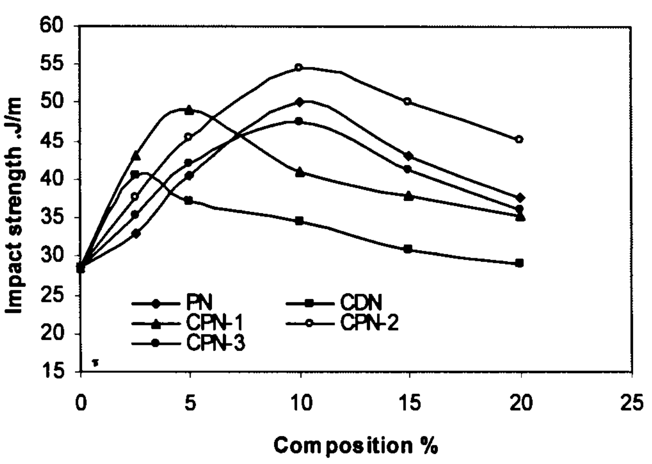


Fig. 3.31 Impact strength of DGEBA-C/PNs versus novolac concentration

cardanol content in the modifier resin up to 40%. CPN-2 containing 40% cardanol showed 96% improvement in impact strength. This is due to the enhanced flexibility offered to the matrix by cardanol by virtue of its characteristic molecular structure.

ii. Surface hardness and water absorption

Fig.3.32 indicates a general improvement in surface hardness upon blending epoxy resin with novolacs. However, the increase is only marginal. Water absorption of novolac-modified epoxy resins is given in Fig.3.33.

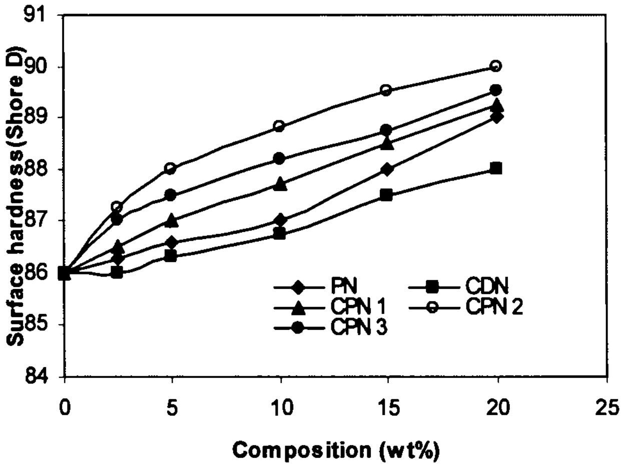


Fig.3.32 Surface hardness of DGEBA-C/PNs Vs novolac concentration

The blends show increased water resistance. This is possibly due to a greater extent of aromatic rings and methylene groups, which are hydrophobic in nature.

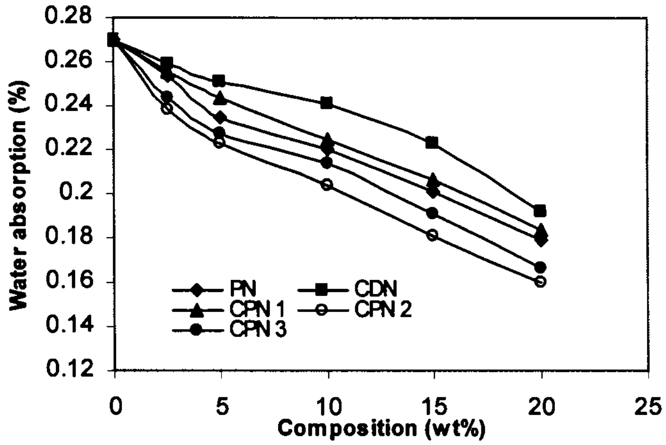


Fig.3.33 Water absorption of DGEBA-C/PNsVs novolac concentration

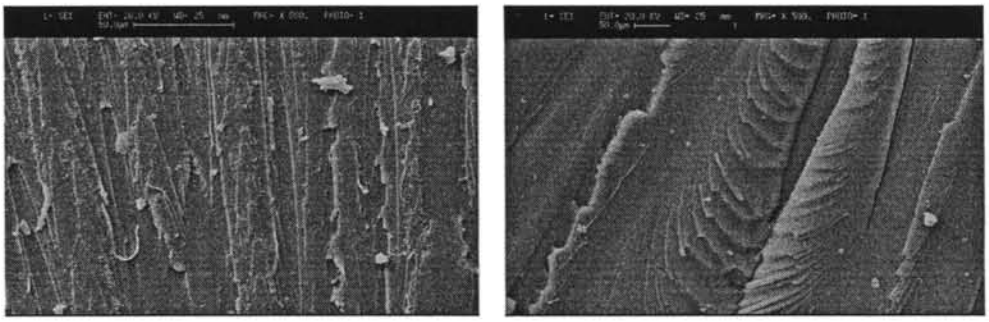
Table 3.7 summarizes the mechanical properties of the epoxy–CPN blends. Maximum improvement acquired in each property and the corresponding concentrations are tabulated.

Table 3.7 Properties of DGEBA modified by cardanol-phenol novolacs (CPNs)

Property	Neat	% improvement / composition %				
		PN	CPN-1	CPN-2	CPN-3	CDN
Tensile strength MPa	48	18/10	12.5/10	13/10	7/10	9.5/10
Modulus x 10^2 MPa	24.2	-2/2.5	-7/2.5	-8/2.5	-6/2.5	-5/2.5
Elongation at break (%)	3.10	26/10	38.7/10	52/10	43./10	32/10
Energy absorbed . $J.mm^{-2}$	2.95	73/15	76.5/10	92/10*	83/10	81/5
Compressive strength. MPa	108	20/10	32/10	28.7/10	21/10	9.2/10
Impact strength. J/m	28.5	75/10	82/5	96/10	69/10	43/2.5
Surface hardness Shore D	86	3./20	3.85/20	4.7/20	4.1/20	2.4/20
Water absorption (%)	0.27	-6/2.5	-8/2.5	-10/2.5	-11/2.5	-4/2.5

iii. Morphological studies

Figure 3.34 (a) is a SEM micrograph of the unmodified epoxy resin. It is a typical case of brittle fracture. Fracture paths are mostly straight and constitute failure bands. The fractured surface of epoxy-CPN blend (Fig.3.34b) shows distinct signs of increased energy absorption such as crazes and shear bands. Multilevel fracture paths with ridges and fibrils indicate energy absorption on a large scale during failure. The extent of stress whitening (characteristic of crazing) is less compared to PCN or BPN (Fig.3.21b,c). This confirms that the toughness in epoxy/CPN system is not merely due to crazing; it is a case of crazing combined with shear yielding.



(a) **(b)**

Fig.3.34 SEM micrographs of the fracture surface a) DGEBA b) DGEBA/CPN-2

iv. Soxhlet extraction and swelling studies

The Soxhlet extraction and swelling data are given in Table 3.8. The cured modified samples yielded somewhat smaller amounts of soluble matter compared to the unmodified sample. This is further confirmed by the slightly higher V_p values of the modified samples obtained from the swelling studies. This indicates cross-linking between epoxy resin and the modifier resin. The CDN modified sample gave the lowest V_p.

Table. 3.8 Soxhlet extraction and swelling data

Property	DGEBA	CDN 10%	PN 10%	CPN-2 10%
Soluble matter %	5.34	5.083	4.88	4.677
V_p	0.904	0.901	0.914	0.923

v. Thermal properties

i .TGA: The TGA curves of the neat resin and DGEBA/CDN (5 wt%) and DGEBA/PN (10 wt%) blends (Fig 3.35) show marginally better thermal stability for the modified samples. An increased level of cross-linking as well as the presence of phenolic groups give better thermal resistance to the blends (Table 3.9). The PN modified sample gave 8.043% residue at 600^{0}C compared to7.66 % given by the un-modified resin. However the CDN modified sample yielded less residue (6.88%) indicating its decreased ablative property. This may be due to the presence of the long aliphatic side chain in the cardanol molecule.

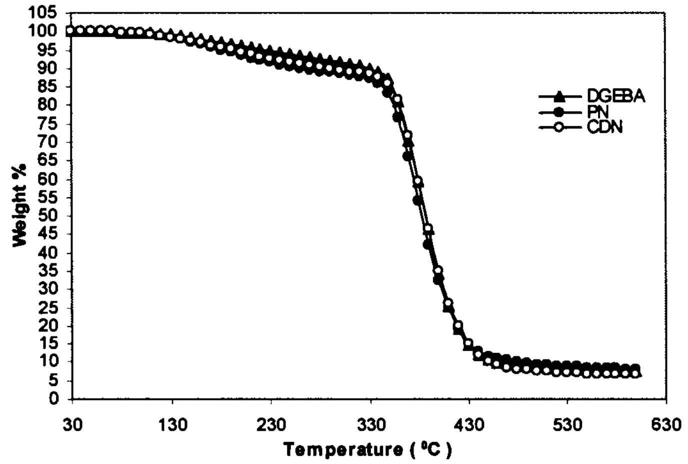


Fig.3.35 TGA curves for DGEBA, DGEBA/CDN and DGEBA/PN

ii. DSC: The DSC thermograms of the neat resin and its blend with 5 wt % CDN are given in Fig.4. For the neat resin an endothermic transition is obtained at 70.64^{0}C (T_g). Addition of 5wt % CDN to the epoxy matrix shifts the T_g to a higher temperature of about 74.27^{0}C (Fig 3.36). This effect is in conformity with the higher level of cross-linking facilitated by the novolac resin. This is in agreement with the data obtained from Soxhlet extraction and swelling studies. The higher functionality and phenolic content of novolac resins increase cross-link densities and improves thermal and chemical resistance.

Table 3.9 TGA data for DGEBA, DGEBA/CDN and DGRBA/PN

Sample	Onset temperature (^{0}C)	Temperature maximum rate.(° C)	Temperature half loss .(° C)	Residue %
DGEBA	310.56	386.12	367.24	7.664
CDN	315.98	379.86	386.63	6.883
PN	308.5	376.72	383.03	8.043

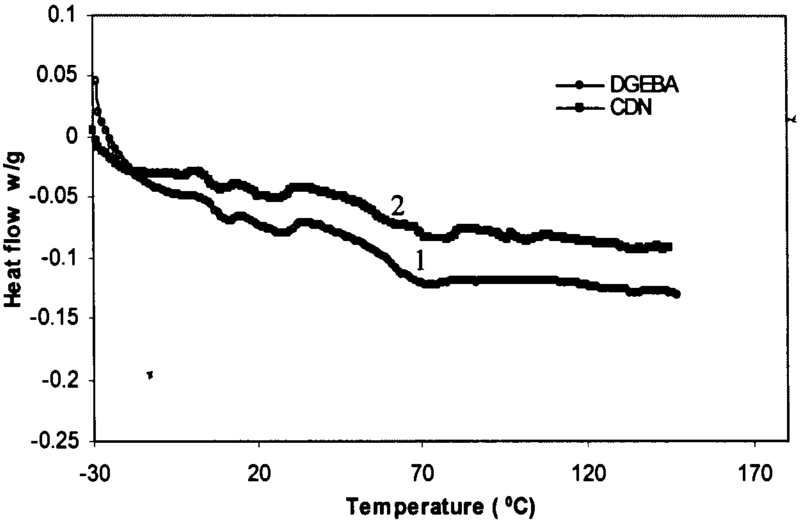


Fig.3.36 DSC thermogram of 1.DGEBA and 2.DGEBA/CDN

iii. DMA: The glass transition of neat epoxy obtained from DMA tanδ curves (Fig. 3.37a) (71.3^{0}C corresponding to tan δ=0.497) is in agreement with the DSC measurement. Incorporation of 10wt% PN (tan δ=0.4196) and 10 wt % CPN- 2 (tan δ=0.4058) shifts the T_g to higher values, 81.06^{0}C and 79.5^0 C respectively. The damping peaks occur at lower tan δ values in the case of these blends due to higher storage moduli (Fig 3.37b). This is indicative of a greater extent of cross- linking in the blends. Further, the decrease in height of the tanδ curves relative to that of the neat resin indicates some plasticizing action by the modifier resins. The CPN-2

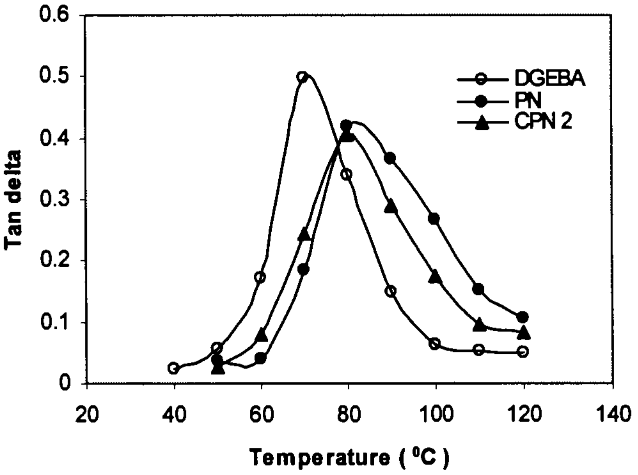


Fig.3.37a. Tan δ curves for DGEBA, DGEBA/PN and DGEBA/CPN-2

blend shows higher loss modulus (Fig 3.37c) compared to the unmodified sample. A higher loss modulus causes more mechanical energy to turn into heat via molecular relaxation.

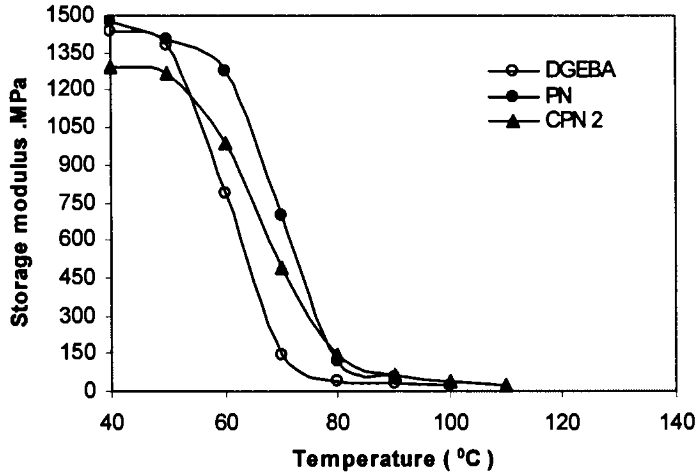


Fig.3.37b. Storage modulus curves for DGEBA, DGEBA/PN and DGEBA/CPN-2

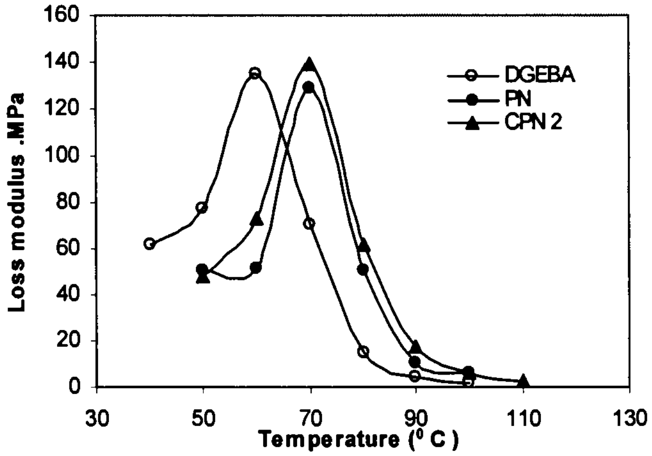


Fig.3.37c.Loss modulus curves for DGEBA, DGEBA/PN and DGEBA/CPN-2

3.3.4 Modification with epoxidised phenolic novolacs

In contrast to modification by non-epoxy resins it appears more reasonable to look for resins of epoxy functionality to improve the toughness characteristics of a given epoxy system. With this perspective, we have investigated the behaviour ofblends of DGEBA with two novolac epoxies namely epoxy phenol novolac (EPN) and epoxy p- cresol novolac (ECN). The phenol-formaldehyde ratio in the novolacs was maintained at 1:0.8 for maximum property enhancement.

Epoxy novolacs are highly compatible with DGEBA resin because both are almost similarly polar. 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/ECN 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/ECN. 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/ECN.

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

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

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. The epoxy equivalents (wpe) for EPN , ECN and neat epoxy resin were found to be 169.5, 181.8 and 188 respectively. The epoxy functionality of epoxy novolac is between 2.2 and 3.8.

i. Tensile properties

Referring to Fig.3.38, tensile strength values obtained by blending epoxy resin with 2.5 to 20% epoxy novolacs are significantly higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 15 wt % for ECN 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 entangling among the polymer chains. It is likely that about 15% ECN the cross-linking process reaches an optimum level. This results in increased tensile strength, lower extent of soluble matter and increased volume fraction of polymer in the swollen samples, V_p.

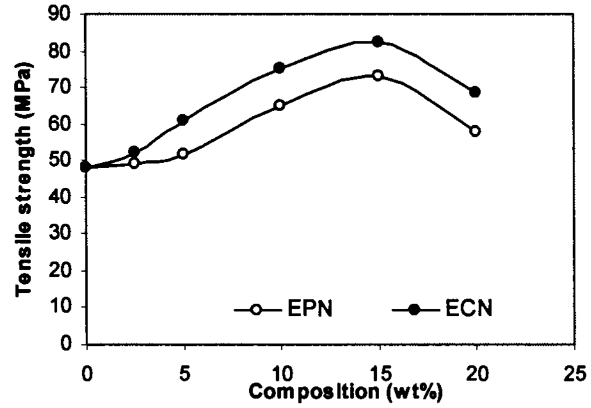


Fig. 3.38 Tensile strength of modified resin Vs EPN concentration

The modifying effect of ECN is superior to that of EPN. This can be due to a more linear structure resulting from the structure of p-cresol which has only two possible sites for condensation with formaldehyde

Fig.3.39 shows the effect of epoxy novolacs on the tensile modulus. The slight reduction in modulus on addition of EPN/ECN shows improved molecular flexibility. The effect of addition of epoxy novolacs on elongation at break is shown in Fig.3.40. Compared to unmodified resin the blends show an increase in elongation. Epoxy-EPN/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 EPN/ECN content goes up, it becomes increasingly difficult for the chains to disentangle and elongation falls.

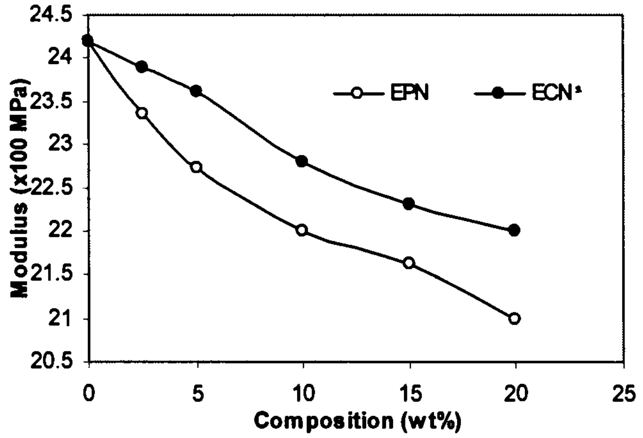


Fig. 3.39 Modulus of modified resin Vs EPN concentration

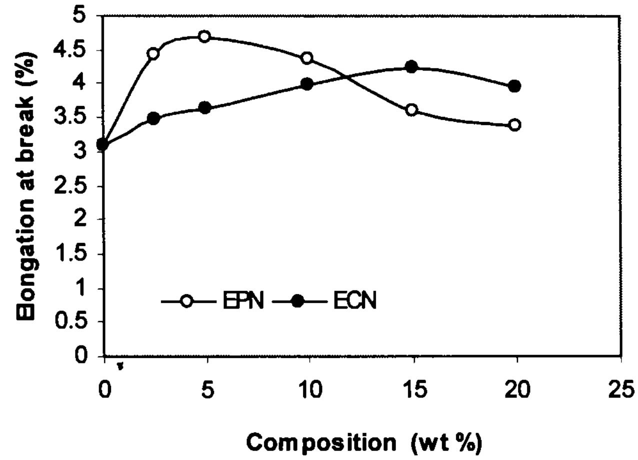


Fig. 3.40 Elongation at break of modified resin Vs EPN concentration

Fig. 3.41 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 ECN, the improvement in energy absorption (to break) is about 135%.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. The variation in compressive strength for the blends is given in Fig 3.42. There is considerable increase in compressive strength for these blends compared to the base resin. This can also be explained in terms of increased levels of entanglement and cross-linking. In this case, the optimum occurs at a lower novolac epoxy loading. Fig.3.42 (a) shows the variation of impact strength of modified resin with the concentration of epoxy novolac. DGEBA/ECN blend shows about 104% improvement in impact resistance. The improvement in impact strength of epoxy

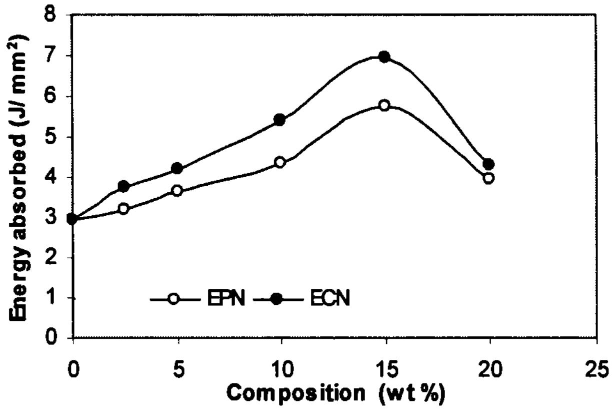


Fig. 3.41 Energy absorbed (to break) of modified resin Vs EPN concentration

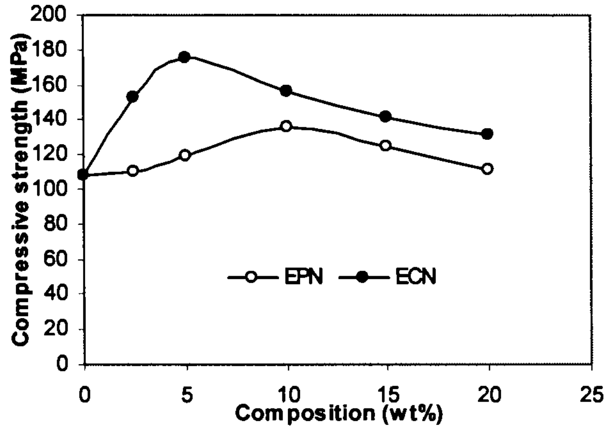


Fig. 3.42 Compressive strength of modified resin Vs EPN concentration

novolac modified resins is a direct consequence of compatibility, chain entanglement and enhanced cross-linking. ECN, with a more linear structure can produce blends with increased network flexibility and this result in the absorption of a larger amount of energy.

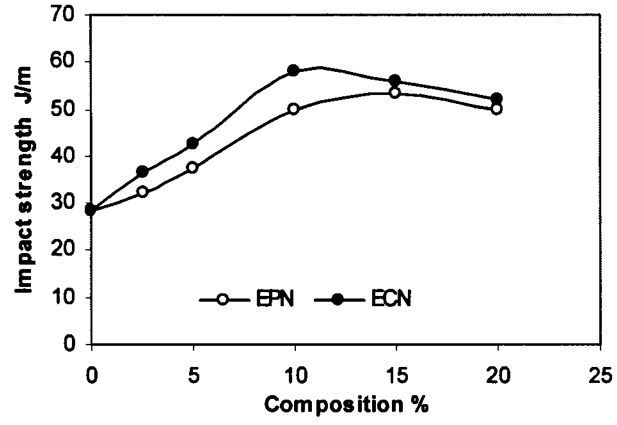


Fig. 3.42(a). Impact strength of modified resin Vs EPN concentration

ii. Surface hardness and water absorption

Fig.3.43 indicates a general improvement in surface hardness upon blending epoxy resin with epoxy novolacs. However, the increase is only marginal. Water absorption of various epoxy novolac - modified epoxy resins are given in Fig. 3.44. The blends show increased water resistance up to about 5% EPN/ECN. This is possibly due to a greater extent of methylene groups which are not amenable to hydrogen bonding.

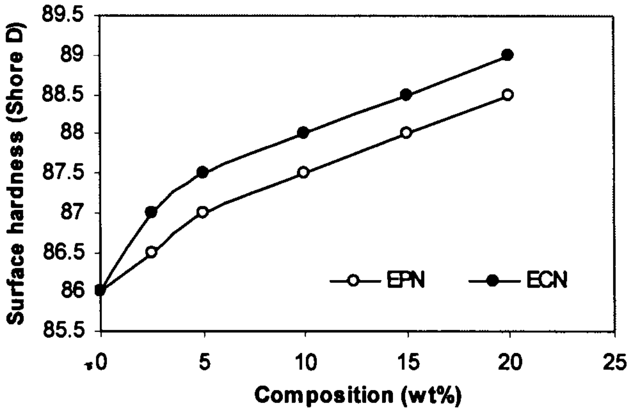


Fig. 3.43 Surface hardness of modified resin Vs EPN concentration

Table3.10b. summarizes the effect of adding varying amounts of epoxy novolac resins to the base resin. The maximum improvement acquired in each property and the corresponding concentrations are tabulated.

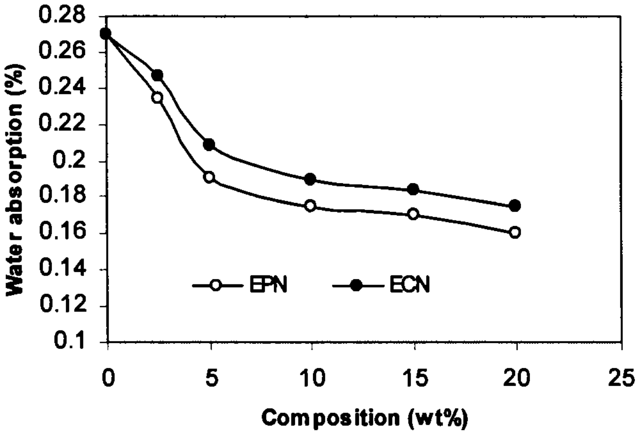


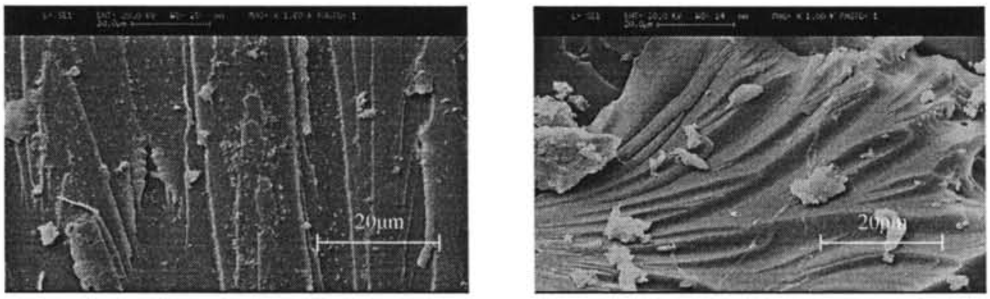
Fig.3.44 Water absorption of modified resin versus EPN concentration.

Table 3.10b. Properties of epoxy-EPN/ECN blends

Properties	% Improvement/ composition (wt %)		
	DGEBA	DGEBA/EPN	DGEBA/ECN
Tensile Strength (MPa)	48	53/15	70/15
Modulus (MPa)	24.2	-13.2/ 20	-9/20
Elongation at break (%)	3.1	51.6/10	37.2/10
Energy absorbed (J/mm^2)	2.95	96.3/15	136/15
Compressive Strength (MPa)	108	26/10	62.2/5
Impact strength (J/m)	28.5	87/15	104/10
Hardness (Shore D)	86	3/20	3.45/20
Water absorption (%)	0.27	-37/20	-32/20

iii. Morphological studies

Fig.3.45 (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. 3.45 SEM micrographs of a) DGEBA b) DGEBA/ECN

The fracture surface is characterized by pin point crazes within the material. Fig.3.45 (b) shows the fractured surface of an epoxy-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 and swelling data are given in Table 3.10(a). 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. This is further confirmed by the high V_p values of the modified samples obtained from swelling studies.

Table 3.10(a) Soxhlet extraction and swelling data

Samples	Neat Resin	EPN Blend		ECN Blend	
		5%	15%	5%	15%
Soluble matter %	5.34	4.89	4.63	4.03	3.82
V_p	0.904	0.911	0.918	0.922	0.944

v. Thermal properties

i. TGA: The TGA curves of the neat resin and DGEBA-ECN blend are shown in Fig.3.46. The modified resin has marginally better thermal stability as shown in

Table 3.11. This may be due to an increased level of cross-linking as well as the presence of phenolic groups. The ECN modified sample gave 11.39 % residue at 600^{0}C compared to 7.66 % 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.

ii.DSC: The DSC thermograms of the neat epoxy and ECN blend are shown in Fig.3.47. The glass transition temperature of neat epoxy is seen to be 70.64 ^{0}C. The addition of 15 wt % ECN to the epoxy matrix shifts the glass transition to a higher temperature of about 76.24^{0}C. This effect is in conformity with the higher level of cross-linking facilitated by ECN. The shift of T_g to a higher value is indicative of increased cross-linking in the modified samples. The soxhlet extraction data indicate a lower extent of soluble matter in cured EPN/ECN modified samples compared to the un-modified resin indicating effective cross-linking between the epoxy resin and the epoxy-novolacs. This is further confirmed by the higher V_p values of the modified samples obtained from the swelling studies.

Table 3.11 Thermal Properties of DGEBA and DGEBA-EPN/ECN blends

Sample	Onset temp. (°C)	Temp.of max. rate.(°C)	Temp-half loss .(°C)	Residue %
DGEBA	310.56	386.12	367.24	7.664
DGEBA/ECN	312.34	374.22	375.11	11.39

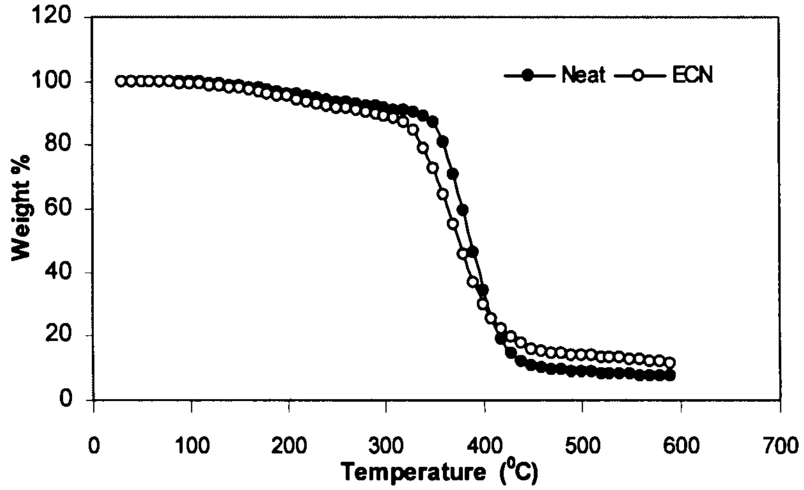


Fig.3.46 TGA curves for DGEBA and DGEBA/ECN

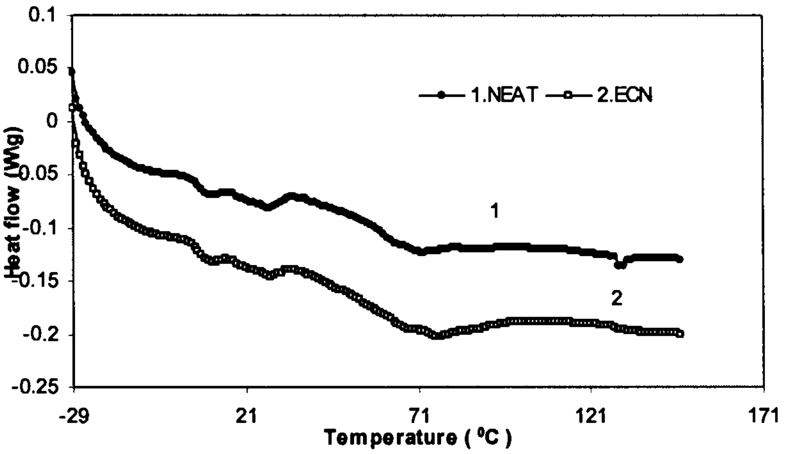


Fig.3.47 DSC Thermograms for 1.DGEBA and 2. DGEBA/ECN

iii. DMA: Figures 3.48(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 (71.3^{0}C corresponding to tan δ 0.497) is in agreement with the DSC measurement. Incorporation of ECN (15 wt %) and EPN (10 wt %) increases the glass transition temperature to 82.6 ^{0}C and 83.69^{0}C corresponding to tan δ values 0.3852 and 0.3872 respectively. The shift of T_g to a higher value is indicative of increased cross-linking in the modified samples. The soxhlet extraction data show very little soluble matter in cured EPN/ECN modified samples compared to the un-modified resin. This is further confirmed by the high V_p values of the modified samples obtained from the swelling studies.

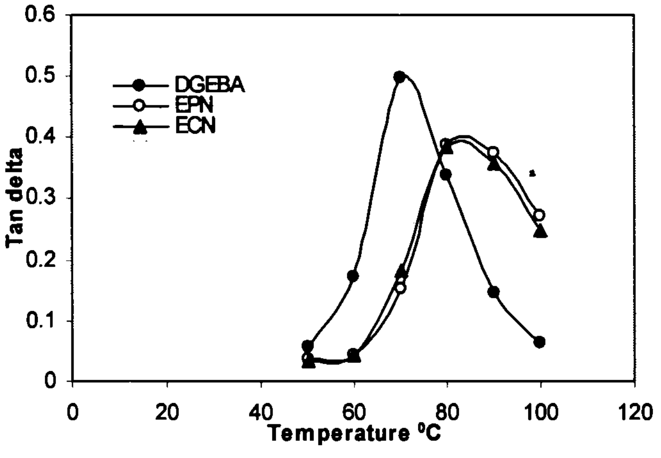


Fig.3.48 a. Tan delta curves for DGEBA, DGEBA/EPN and DGEBA/ECN

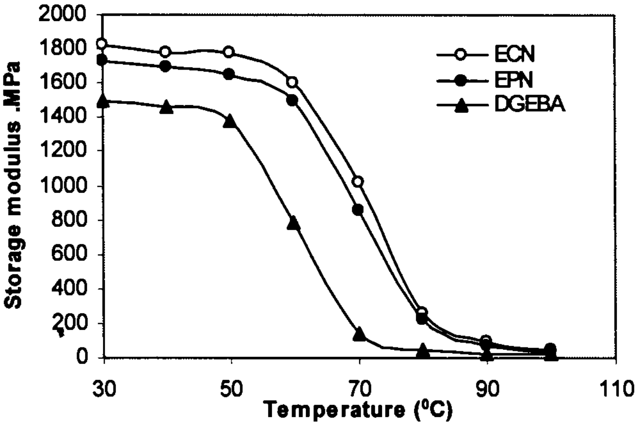


Fig. 3.48b Storage modulus curves for DGEBA, DGEBA/EPN and DGEBA/ECN

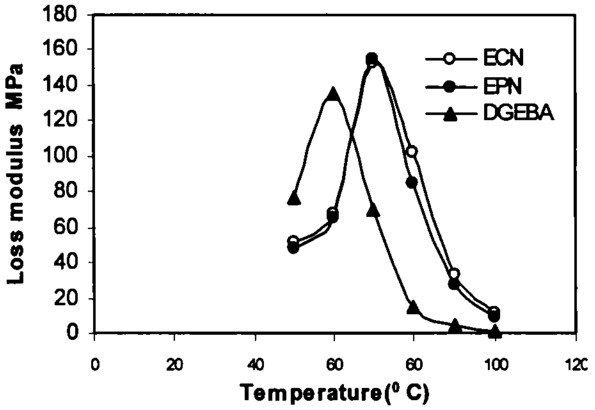


Fig. 3.48c. Loss modulus curves for DGEBA, DGEBA/EPN and DGEBA/ECN

The blends have higher storage modulus than the neat resin which again points to a higher level of cross-linking in the blends. DMA- storage modulus curve for the neat resin indicates a lowering of modulus from 1400 MPa to 790 MPa at the glass transition region while the modulus of EPN and ECN modified samples show a decrease from relatively higher modulus values; 1780 Mpa to 1010 Mpa and 1655 MPa to 850 MPa respectively at the glass transition region

3.3.5 Influence of P-F stoichiometry of epoxidised novolacs

Hybrid polymer networks of DGEBA with epoxidised phenolic novolac resins (EPN) containing phenol and formaldehyde in different stoichiometric ratios were prepared. The modified epoxy resins were found to exhibit improved mechanical and thermal properties compared to the neat resin. DGEBA resins containing 2.5 to

20 weight % of epoxidised novolac resins (EPN) prepared in various stoichiometric ratios viz.1:0.6, 1:0.7, 1:0.8 and 1:0.9 (designated as EPN-1,EPN-2,EPN-3 and EPN-4) between phenol and formaldehyde were cured using a room temperature amine hardener. The epoxy equivalents (wpe) for these EPNs were found to be 181.8, 175, 169.5 and 202 respectively.

The property profiles of epoxy – EPN blends imply a toughening action by epoxidised novolac resins and the extent of modification is found to depend on the molar ratio between phenol and formaldehyde in the novolac. The simultaneous cross-linking of DGEBA and EPN can take place in different ways as described in section 3.3.4

i. Tensile properties.

Referring to Fig.3.49, tensile strength values obtained by blending epoxy resin with 2.5 to 20% epoxy novolacs are significantly higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 10wt % for EPN-3 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 entangling among the polymer chains. This results in increased tensile strength, lower extent of soluble matter and increased volume fraction of polymer in the swollen samples, V_p. 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.3.50 shows the effect of epoxy novolacs on the tensile modulus. The slight reduction in modulus on addition of EPN shows improved molecular flexibility.

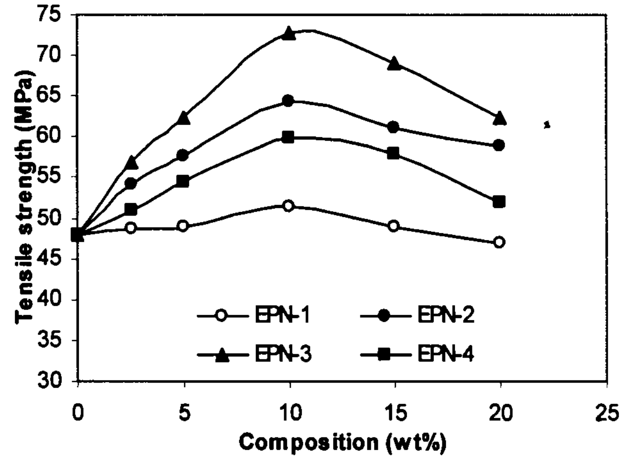


Fig. 3.49. Tensile strength of modified resin Vs EPN concentration

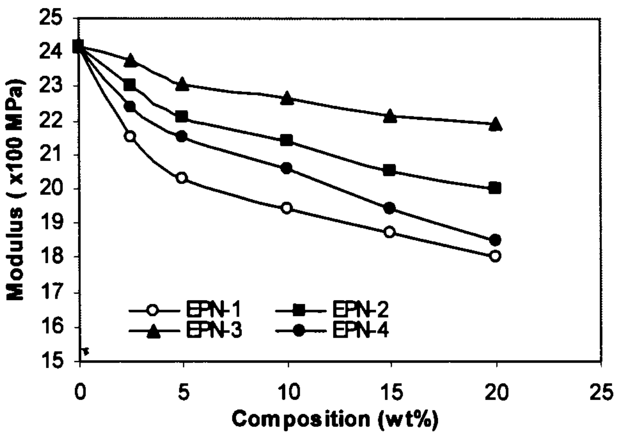


Fig. 3.50. Modulus of modified resin Vs EPN concentration

The effect on elongation at break is shown in Fig.3.51. Compared to unmodified resin the blends show an increase in elongation. Epoxy-EPN blends show maximum elongation at 10 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. 3.52 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 10wt % of EPN-3, the energy absorbed (at break) is improved by about 97 % of that of the neat resin. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement.

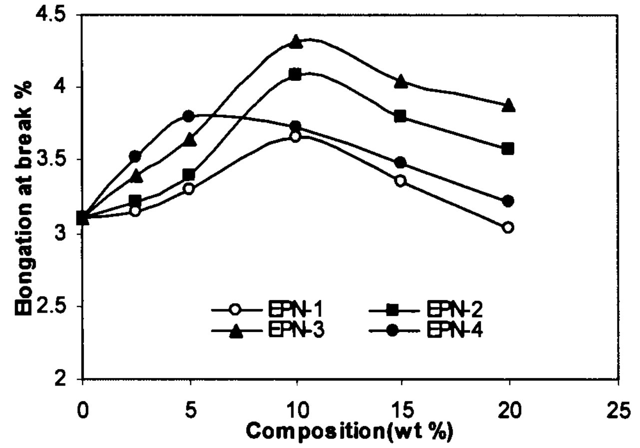


Fig. 3.51. Elongation (at break) of modified resin Vs EPN concentration.

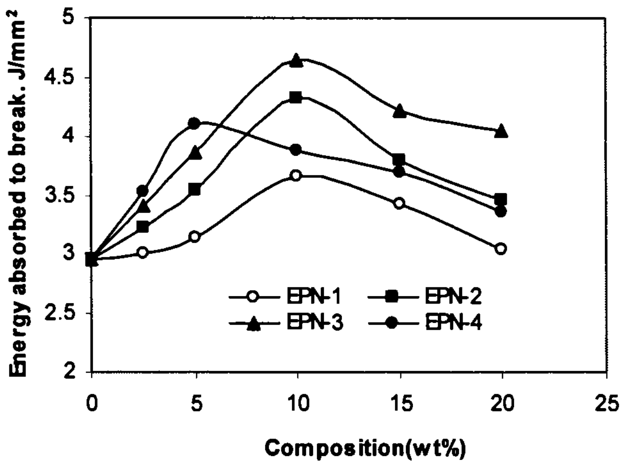


Fig. 3.52. Energy absorbed (to break) of modified resin Vs EPN concentration

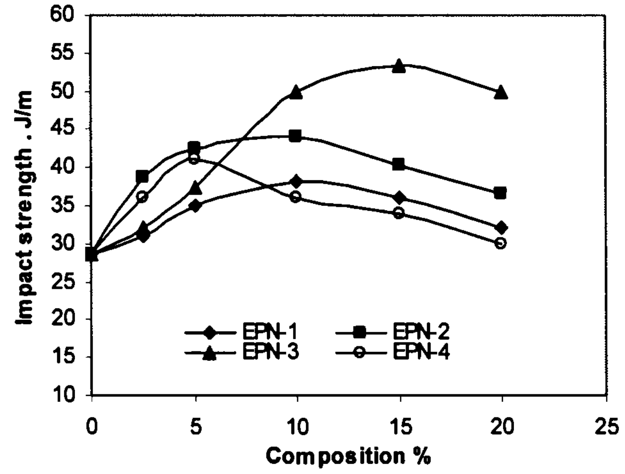


Fig. 3.53. Impact strength of modified resin Vs EPN concentration

The superiority of EPN-3 is observed in the impact strength values also (Fig.3.53). At 15 weight% EPN-3 shows about 87% improvement in impact strength compared to the un-modified resin. 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-3.

ii. Surface hardness and water absorption

Fig.3.54 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. 3.55. 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).

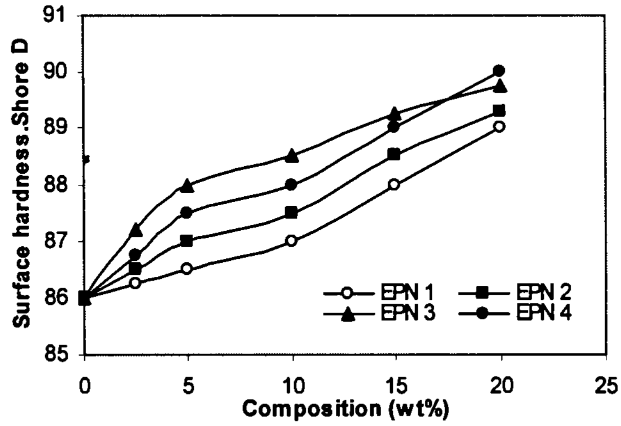


Fig. 3.54 Surface hardness of modified resin Vs EPN concentration

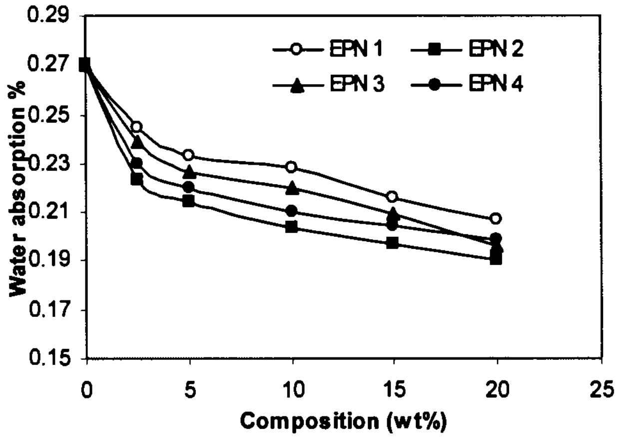


Fig. 3.55 Water absorption of modified resin Vs EPN concentration

Table 3.12 summarizes the mechanical properties of epoxy–EPN blends. The maximum improvement acquired in each property and the corresponding concentrations are tabulated

iii. Thermal properties

i. TGA: The TGA curves of the neat resin and DGEBA / EPN-3(10wt%) blend (Fig3.56) 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 EPN-3 modified sample gave 10.43 % residue at 600^{0}C compared to 7.66 % by the un-modified resin. The higher functionality and phenolic content of novolac resins increase cross-link densities and improve thermal and chemical resistance.

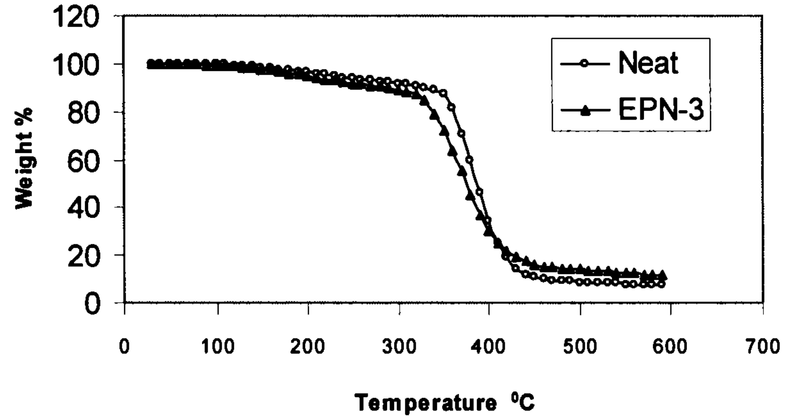


Fig. 3.56 TGA curves for DGEBA and DGEBA/EPN-3

Table .3.12 Properties of DGEBA/epoxy phenol novolac blends

Property	DGEBA	% improvement / weight % EPN			
		EPN-1	EPN-2	EPN-3	EPN-4
Tensile strength (MPa)	48	7.32/10	53/10.	70/10	24/10
Modulus (x 100 MPa)	24.2	-25.6/20	-13/20.	-10/20	-23/10
Elongation at break (%)	3.1	18.2/10	46/10.	52/10	22.5/5
Energy absorbed (J/mm^2)	2.95	24/10	91/10	97/10	39/5
Impact strength .(J/m)	28.5	35/10	54/10	87/15	43/10
Surface hardness (Shore D)	86	3/20	4.2/20.	4/20	4.7/20
Water absorption %	0.27	-31/20	-23/20	-27/20	-25/20

ii. DSC: For the neat resin an endothermic transition is obtained at 70.64^{0}C (T_g). The DSC thermograms reveal that addition of 10wt % EPN-3 to the epoxy matrix shifts the T_g to a higher temperature of about 78^{0}C. This effect is in conformity with the higher level of cross-linking facilitated by EPN. This is in agreement with the data obtained from Soxhlet extraction and swelling studies.

Table 3.13 Thermal properties of DGEBA/EPN blends

Sample	Onset temp. (°C)	Temp.of max. rate.(°C)	Temp-half loss .(°C)	Residue %
DGEBA (Neat)	310.56	386.12	367.24	7.664
DGEBA/EPN-3	312.34	377.42	377.18	10.43

iv. DMA: The glass transition of neat epoxy obtained from DMA-tanδ curves (Fig.3.57a) (71.3°C corresponding to tan δ 0.497) is in agreement with the DSC measurement. Incorporation of EPN-3 and EPN-2 (10 wt %) results in a broader transition which indicates better energy dissipation. Also the decrease in height of tanδ peak with the addition of EPN points to a moderate plasticizing effect by epoxy novolacs. The damping peaks occur at lower tan δ values in the case of the blends due to sufficiently higher storage moduli. This is indicative of a greater extent of cross-linking in the blends. The modified samples show a higher storage modulus (Fig 3.57b) than that of the neat resin thereby confirming this observation. The epoxy-EPN blends show higher loss modulus (Fig 3.57c) compared to the unmodified sample.

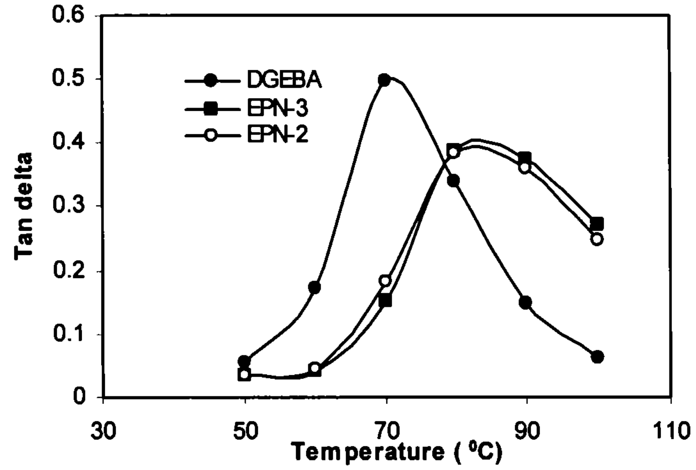


Fig.3.57a.Tan delta curves for DGEBA and DGEBA/EPN blends

iv. Soxhlet extraction and swelling studies

Among the different EPNs used, EPN-3 was found to give the least soluble matter during Soxhlet extraction and the highest V_p (Table 3.13a). 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.

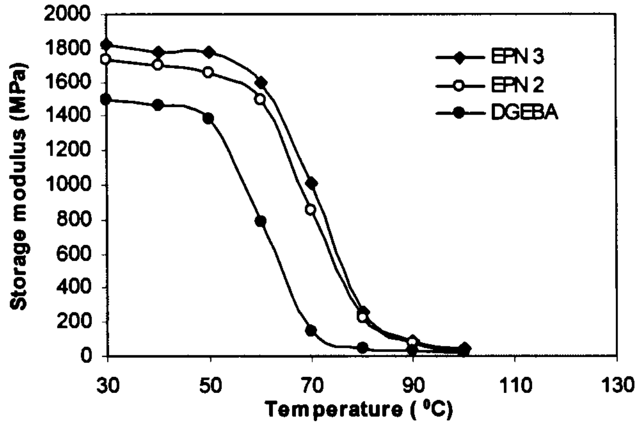


Fig.3.57b.DMA-storage modulus curves for DGEBA and DGEBA/EPN blends

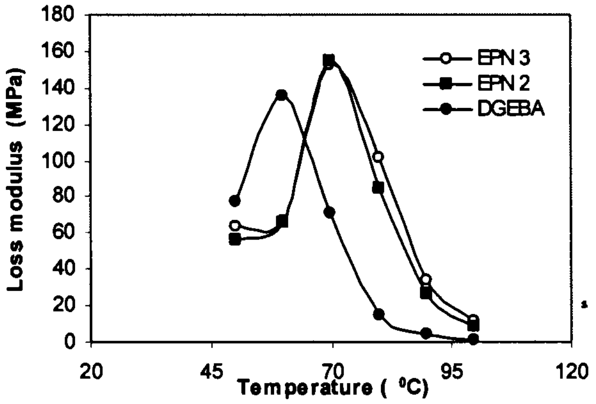


Fig.3.57c. DMA- loss modulus curves for DGEBA and DGEBA/EPN blends

Table 3.13(a) Soxhlet extraction and swelling data

Samples	DGEBA	EPN-1	EPN- 2	EPN-3	EPN-4
Soluble matter %	5.34	4.69	4.13	3.82	4.29
V_p	0.904	0.911	0.928	0.942	0.917

3.3.6 Ageing studies on epoxy resin modified by epoxy 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/EPN blend (15 wt %) and DGEBA/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.3.58 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 41% in tensile strength while the reduction is 30% in the case of DGEBA/EPN and 32% in DGEBA/ECN blends.

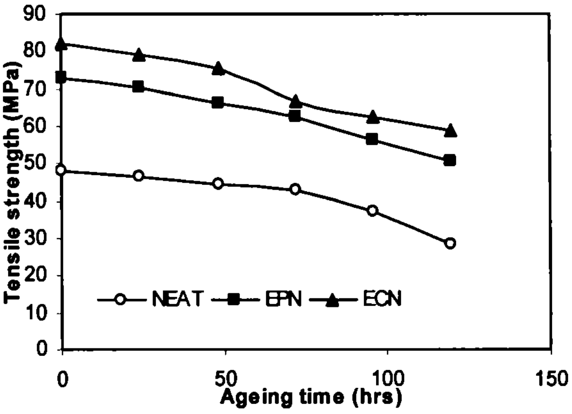


Fig. 3.58. Tensile strength of modified resin Vs ageing time

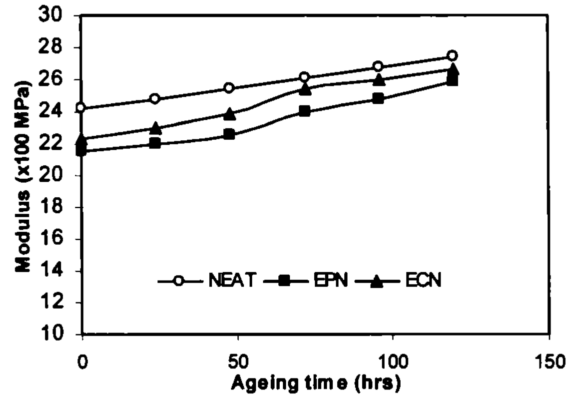


Fig. 3.59. Tensile modulus of modified resin Vs ageing time

Fig 3.59 shows the effect of ageing time on tensile modulus. Modulus values increase with ageing time due to stiffening of the chains caused by additional cross-linking. The increase in modulus is more for the blends (20-22 %) than for the neat resin (14 %).

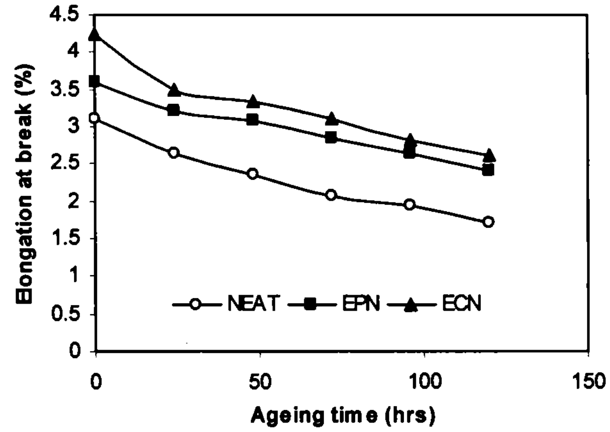


Fig. 3.60. Elongation at break of modified resin Vs ageing time

Fig.3.60 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. 3.61.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 45% in energy absorption at break, the EPN and ECN blends show a reduction of only 30-32%. This suggests the superiority of these phenolic resins in improving the ageing characteristics.

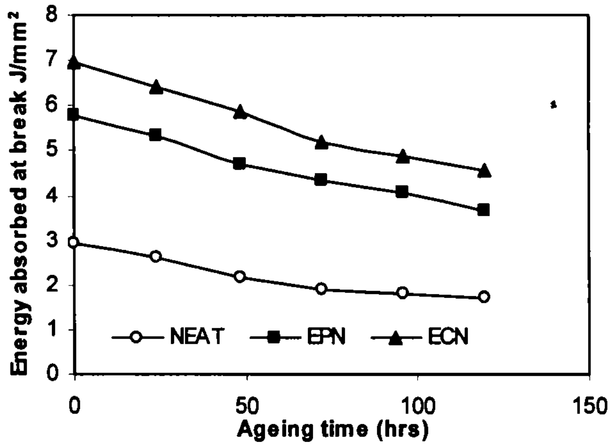


Fig. 3.61. Energy absorbed (to break) of modified resin Vs ageing time

The variation in impact strength of the modified resin during ageing is given in Fig.3.62. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blends (EPN 28% and ECN32%) compared to the unmodified sample (44%). This confirms the ability of epoxy novolacs to improve the ageing properties.

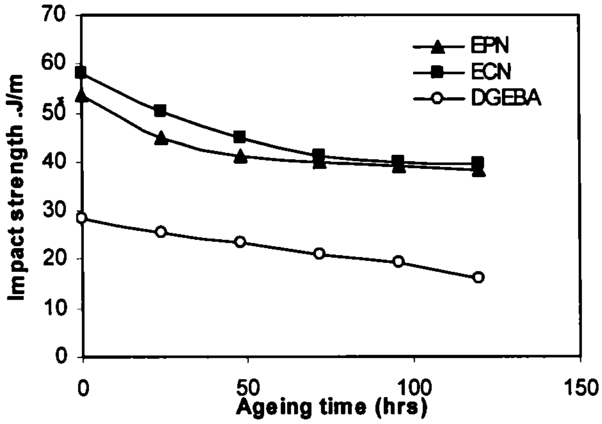


Fig. 3.62. Impact strength of modified resin Vs ageing time

ii. Surface hardness and water absorption

Ageing improves the surface hardness of the blends. Additional cross-linking is responsible for the improved hardness (Fig.3.63). Water absorption decreases steadily with ageing time (Fig 3.64). DGEBA/EPN and DGEBA/ECN blends show better water resistance than DGEBA resin. This is also due to additional cross-linking accompanying the ageing process.

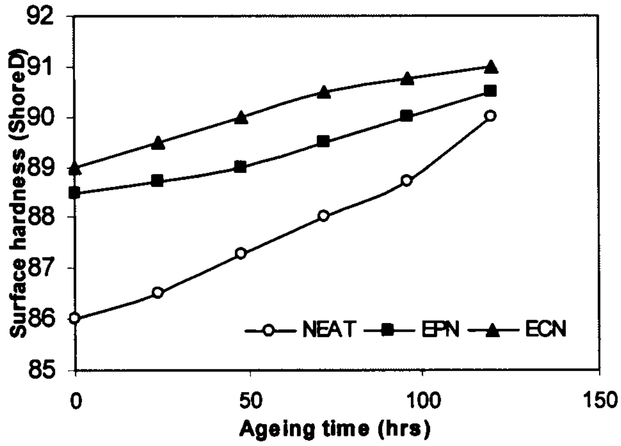


Fig. 3.63. Surface hardness of modified resin Vs ageing time

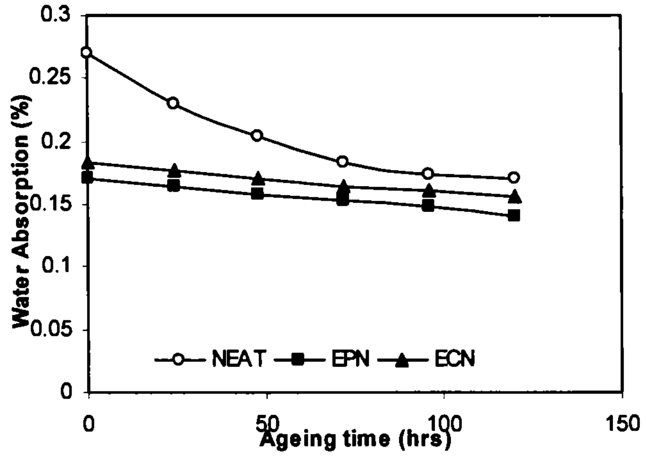


Fig. 3.64. Water absorption of modified resin Vs ageing time

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.

3.3.7 Modification with cardanol based epoxy coumpounds

a) Modification using epoxidised cardanol (EC)

Cardanol, the major constituent of cashew nut shell liquid, was epoxidised (Section 2.2.6) for different periods and used as an epoxy modifier. The extent of epoxidation was monitored by determining the epoxide equivalents (Section 2.3.2). These resins are designated as EC-1, EC-3, EC-6 and EC-9 corresponding to reaction times 1h, 3h, 6h and 9h respectively.

Table.3.14. Epoxy equivalents of epoxidised cardanol at different reaction times

Epoxidised cardanol	EC-1	EC-3	EC-6	EC-9
Reaction time	1h	3h	6h	9h
Epoxy equi valent (eq/Kg)	1.78	1.95	2.099	2.12
Weight per epoxide	531.9	512.8	476.2	471.7

The property profiles of the DGEBA/EC blends show some toughening effect by EC. 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. GPC data shows that EC-9 contains only 61% of the monoepoxide. As cardanol is less reactive towards epichlorohydrin some amount of un-reacted cardanol will be present in EC. The un-reacted cardanol can behave like a filler material at the same time assisting in the cross-linking process by virtue of its acidic hydroxyl groups. Since EC is mono functional, relatively shorter chains are formed during cross-linking and thus an improvement in the molecular weight of the blends cannot be expected. However, the bulky structure of cardanol molecule containing a long aliphatic side chain can provide sufficient flexibility to the blends which is evident from the enhanced elongation, reduced tensile modulus and flexural strength exhibited by the blends.

i. Tensile properties

Fig.3.65 shows the variation in tensile strength obtained by adding varying amounts of EC into epoxy resin. Only a slight increase in tensile strength was observed at lower concentrations of EC. At higher EC loading the polymer chains might become so small that an optimal crosslink density is difficult to be achieved.

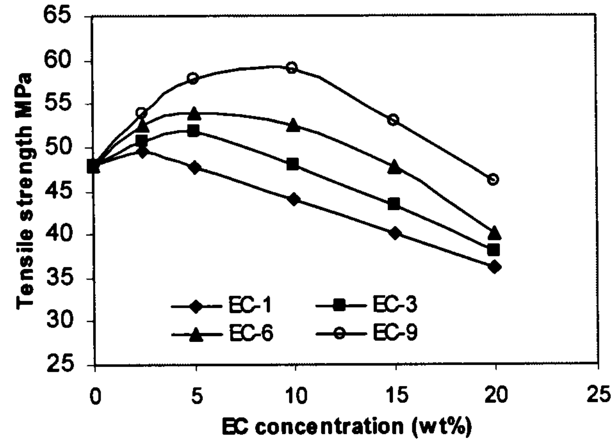


Fig. 3.65 Tensile strength of EC modified resin Vs EC concentration

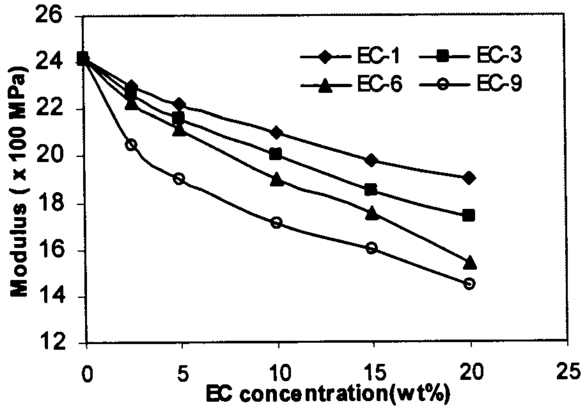


Fig. 3.66 Tensile modulus of EC modified resin Vs EC concentration

EC samples prepared at higher reaction times (EC-6, EC-9) are found to give improved tensile strength at still higher EC concentrations. However, the improvement is only marginal. 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.

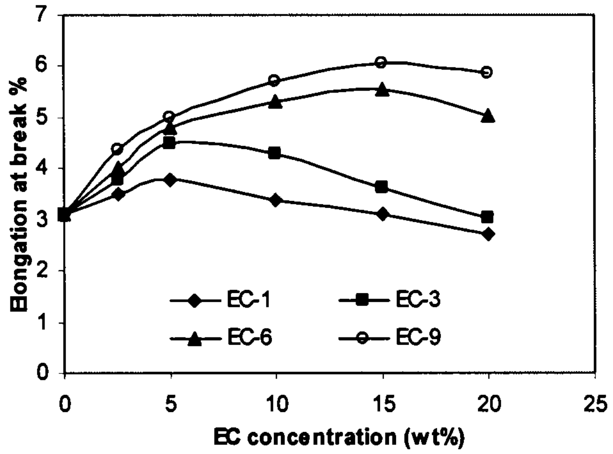


Fig. 3.67 Elongation (at break) of EC modified resin Vs EC concentration

The variation in modulus on adding increasing amounts of EC into epoxy resin is shown in Fig.3.66. Modulus decreases steadily with increase in EC concentration in the case of all the DGEBA/EC samples. This reflects the ability of the blends to absorb energy and provide a higher level of flexibility. The reduced molecular weight due to the mono functional matrix of epoxidised cardanol can also be responsible for this. Entangling of polymer chains is favoured by the structure of cardanol with a bulky side chain.

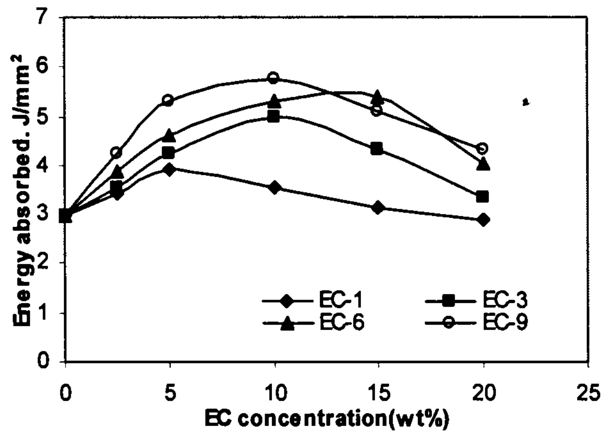


Fig. 3.68 Energy absorbed (to break) of EC modified resin Vs EC concentration

Figure 3.67 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-6 and EC-9 show substantial increase in elongation at higher EC concentrations (about 15%) due to better compatibility arising from increased epoxy content. A higher extent of mono functional EC molecules (EC-6 and EC-9) causes more entanglement of the side chain and potential for elongation.

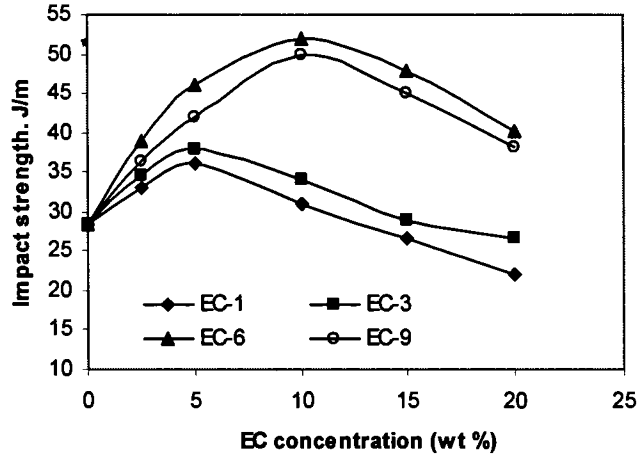


Fig. 3.69 Impact strength of EC modified resin Vs EC concentration

Figure 3.68 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-9 sample exhibited almost 100% 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. The variation in impact strength of EC-modified resin is given in Fig.3.69. Impact strength shows maximum values at about 5-10 weight % for the different EC samples. EC-6 and EC-9 samples gave substantial improvement in impact strength due to better compatibility with the matrix resin.

ii. Flexural properties

Fig. 3.70 gives the change in flexural strength of EC modified epoxies. The flexural strength is found to decrease steadily with the addition of EC. Since the blends contain relatively shorter chains, flexing becomes increasingly easier with higher EC concentrations. More over, the bulky structure of cardanol can induce free spaces within the polymer. The same trend was observed in flexural modulus values also.

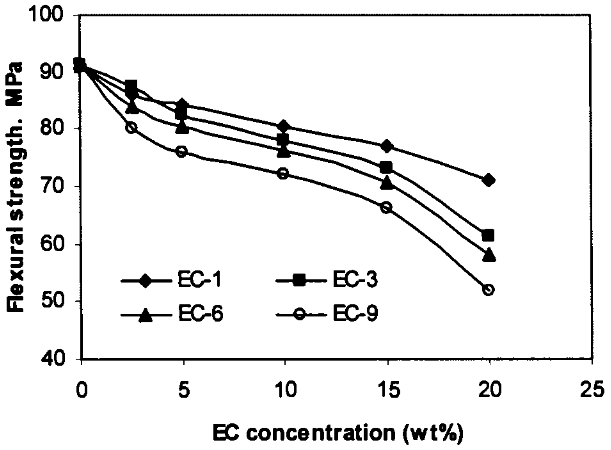


Fig. 3.70 Flexural strength of EC modified resin Vs EC concentration

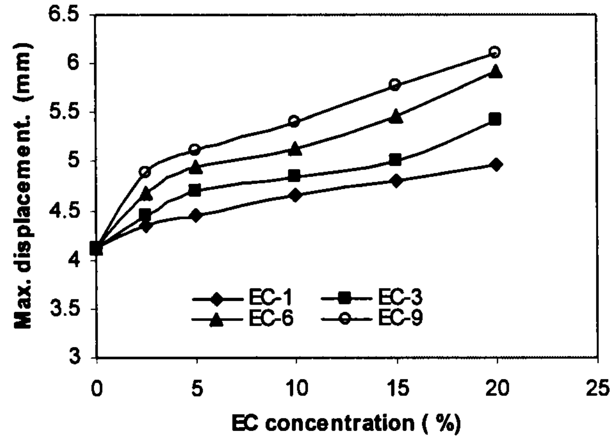


Fig. 3.71 Maximum displacement of EC modified resin Vs EC concentration

The flexural energy is found to increase with EC concentration. During three point bending experiment, DGEBA/EC blends exhibited higher displacements compared to the un-modified resin (Fig.3.71). These properties confirm the presence of a flexible structure in EC modified epoxy resins.

iii. Surface hardness and water absorption.

Fig. 3.72 indicates a general lowering of surface hardness on addition of EC to epoxy resin. This is in tune with the lowering of tensile modulus. 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. 3.73. In general the blends show reduced water resistance. The relatively better water resistance of DGEBA/EC-9 can be explained on the basis of a greater epoxy content. The hydroxyl groups in unreacted cardanol can form hydrogen bonds with water.

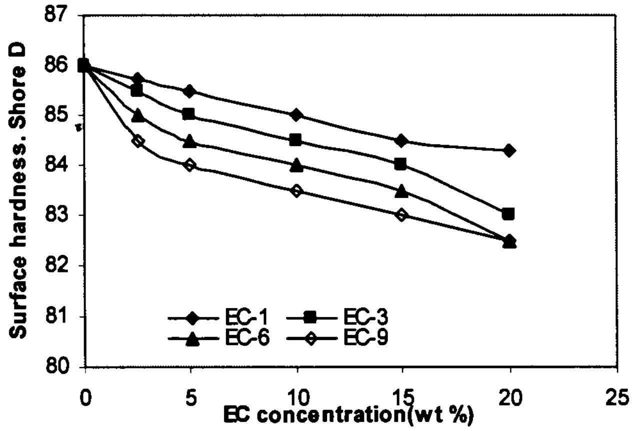


Fig. 3.72 Surface hardness of EC modified resin Vs EC concentration

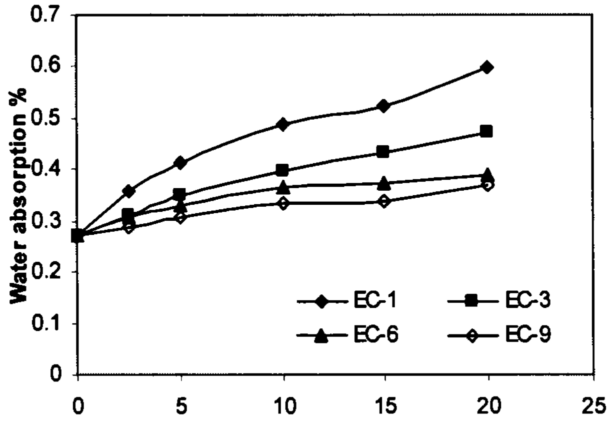
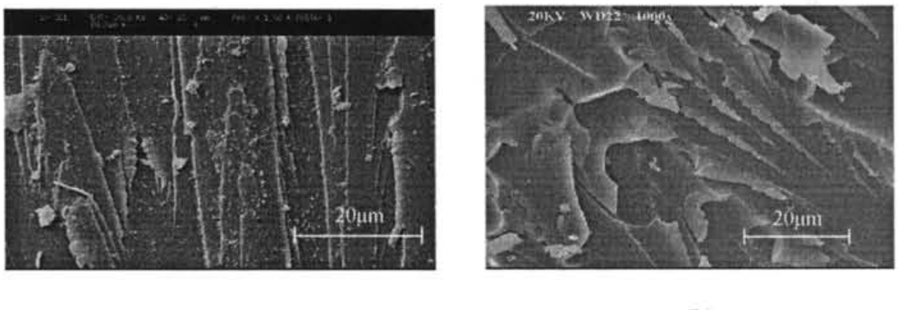


Fig. 3.73 Water absorption of EC modified resin Vs EC concentration

Table 3.15 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. 3.74. 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. Referring to the EC-9 modified sample (b), the fracture paths have a feathery texture with large breadth. They are also discontinuous and convoluted. 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.



(a) **(b)**

Fig. 3.74 Scanning electron micrographs of the fracture surfaces of a) DGEBA b) DGEBA/EC

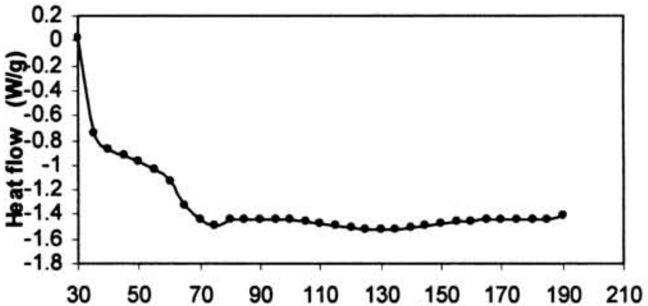


Fig. 3.75 DSC thermogram for DGEBA/EC -9

v. Thermal properties

I .DSC: For the neat resin glass transition is obtained at 70.64^{0}C (T_g).The DSC thermogram for DGEBA/EC-9 blend is given inFig.3.75. Addition of 10 weight % EC shifts the T_g to a lower temperature (67.29^{0}C). This shows the flexibility attained by the blend in presence of EC.

Table 3.15 Properties of EC modified epoxy resins

Property	% maximum improvement / % composition				
	DGEBA	EC-1	EC-3	EC-6	EC-9
Tensile strength (MPa)	48	3/2.5	8/5	13/5	24/10
Modulus (x 100 MPa)	24.2	-20/20	-29/20	-37/20	-41/20
Elongation at break, (%)	3.10	22/5	47/5	79/15	95./15
Energy absorbed (.J/mm^2)	2.95	32/5	68/10	83/15	97/10
Impact strength (J/m)	28.5	29/5	32/5	82/10	76/10
Flexural strength (MPa)	91.35	-22/20	-33/20	-37/20	-43/20
Max. displacement (bend) (mm)	4.12	20/20	32/20	43/20	51/20
Flexural energy J/mm^2	0.2655	9/20	14/20	24/20	32/20
Surface hardness. Shore D	86	-1.8/20	-3.5/20	-4.1/20	-4.1/20
Water absorption (%)	0.27	120/20	74/20	41/20	38/20

ii. DMA: Fig 3.76 indicates the DMA curves for the EC-modified and unmodified resin. Referring to tan δ curves (a) the peak occurs at 77.9^{0}C at tan δ 0.3988 for the modified sample compared to 71.3^{0}C corresponding to tan δ 0.497 for the neat resin. The decrease height of tan δ peak of the blend indicates effective plasticizing

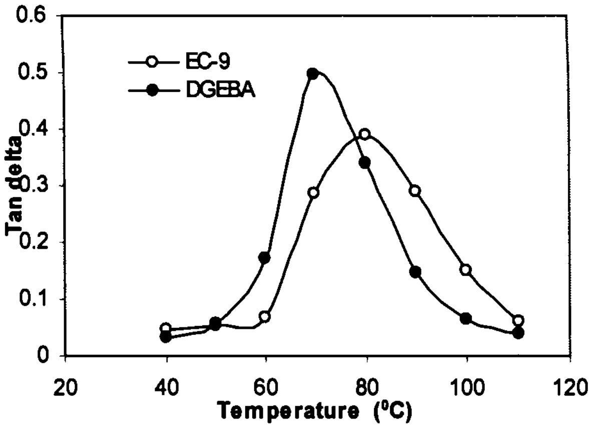


Fig.3.76a. Tan δ curves for EC-modified and unmodified epoxy resins

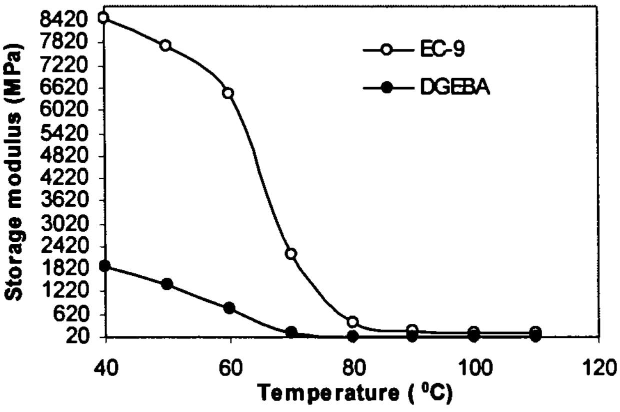


Fig.3.76b.Storage modulus curves for EC-modified and unmodified epoxy resins

action offered by EC. The DGEBA/EC blend has higher storage modulus (Fig.3.76b) showing a greater extent of cross-linking in the blend than in the unmodified sample. This is in tune with the Soxhlet extraction and swelling data obtained for the blend. The temperature corresponding to the inflection point on the storage modulus curve (66.99^{0}C) agrees well with the T_g obtained from DSC scan. Effective cross-linking between the shorter polymer chains gives flexibility to the cured matrix which in turn lowers the glass transition temperature.

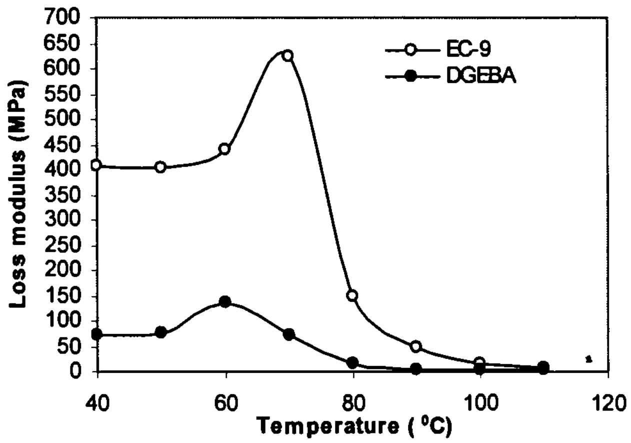


Fig.3.76c. Loss modulus curves for the EC-modified and unmodified epoxy resins

vi. Soxhlet extraction and swelling studies

The Soxhlet extraction and swelling data are given in Table 3.16. The cured modified samples yielded somewhat smaller amounts of soluble matter compared to the unmodified sample. This is further confirmed by the slightly higher V_p

values of the modified samples (except for EC-3) obtained from the swelling studies. This indicates cross-linking between epoxy resin and the modifier resin

Table 3.16 Soxhlet extraction and swelling data

Samples	DGEBA	EC-3	EC-6	EC-9
Soluble matter %	5.34	4.309	3.57	3.312
V_p	0.904	0.887	0.919	0.933

b) Modification using bisphenol A/cardanol co-epoxides (BPA/EC)

Epoxy resins prepared by co-epoxidising bisphenol A and cardanol in different compositions viz. 80/20, 50/50 and 20/80 (Section 2.2.6) were employed for blending with commercial epoxy resin. They were designated as BPA/EC-1, BPA/EC-2 and BPA/EC-3 respectively. The epoxide equivalents of these co-epoxides were determined (Section 2.3.2) as 4.37, 3.31and 2.56 Eq/Kg respectively.

BPA/EC resins were highly compatible with the epoxy resin and homogeneous blends were obtained at room temperature. The property profiles of the blends show significant toughening effect by these co-epoxides without much deterioration in strength. The mechanism of DGEBA-BPA/EC reaction is expected to be similar to that of DGEBA/EPN reaction. In the presence of the epoxy hardener, the epoxy groups in both the matrix resin and the modifier resin are opened up resulting in chain extension and cross-linking. GPC analysis shows that BPA/EC-1 and BPA/EC-2 contain 73% and 66% epoxide respectively. Since EC is mono functional, relatively shorter chains are formed during epoxidation. As the concentration of EC in the modifier resin increases, the blends will contain more of shorter chains. Thus a lowering of tensile strength is possible with modifiers containing greater amounts of cardanol. When the modifier resins were themselves cured and tested (Table 2.2, Chapter 2) the tensile strength was low and elongation increased with increase in EC content.

i. Tensile properties

Referring to Fig.3.77, tensile strength values obtained by blending epoxy resin with 2.5 to 20% BPA/EC are higher compared to that of the unmodified resin. Tensile strength reaches a maximum at 15 wt % for BPA/EC-1 beyond which the strength is found to decrease. The improvement in tensile strength over that of the base resin is due to chain extension. This can also be attributed to some amount of entangling among the polymer chains.

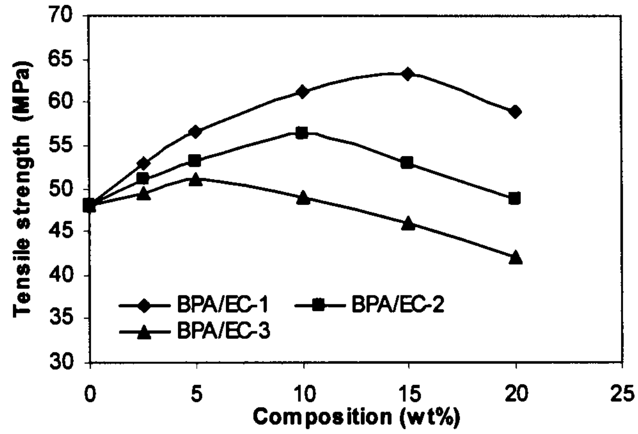


Fig. 3.77 Tensile strength of modified resin Vs BPA/EC concentration

The modifying effect of BPA/EC-1 is superior to the other modifier resins in tensile strength. Presence of increasing amounts of epoxy cardanol in BPA/EC-2 and 3 result in deterioration of strength by way of forming shorter chain segments.

Fig.3.78 shows the effect of bisphenol A-cardanol co-epoxides on the tensile modulus. Modulus decreases steadily on adding increasing amounts of the co-epoxides. This shows improved molecular flexibility. The extent of decrease in modulus increases with the concentration of the epoxy cardanol component in the modifier resin. This again confirms the ability of cardanol epoxides to decrease the stiffness of the matrix resin.

The effect of addition of BPA/EC on elongation at break is shown in Fig.3.79. Compared to unmodified resin the blends show an increase in elongation. Epoxy-BPA/EC blends show maximum elongation at 10 and 15 wt % of the modifier resin. A higher elongation may be the result of straightening of the entangled chains. There is a steady increase in elongation with the EC content in BPA/EC. Cardanol molecule, by virtue of its bulky structure can provide sufficient room for the relatively shorter matrix chains to stretch when stress is applied. The sample with 80% cardanol (BPA/EC-3), however, showed a slight decrease in elongation compared to BPA/EC-2. This is probably due to the presence of a large extent of shorter chains arising from a higher amount of cardanol in the modifier which reduces the tensile strength.

Fig.3.80 gives the variation of energy absorbed by the blends of epoxy resin with BPA-cardanol co-epoxides. This can be taken as a measure of the toughness. At 5% BPA/EC-2, energy absorption was maximum (104% of that of unmodified resin) while the other modifier samples showed maximum values at a higher loading. The enhanced energy absorption can be attributed to a greater level of flexibility and capacity for spatial rearrangement.

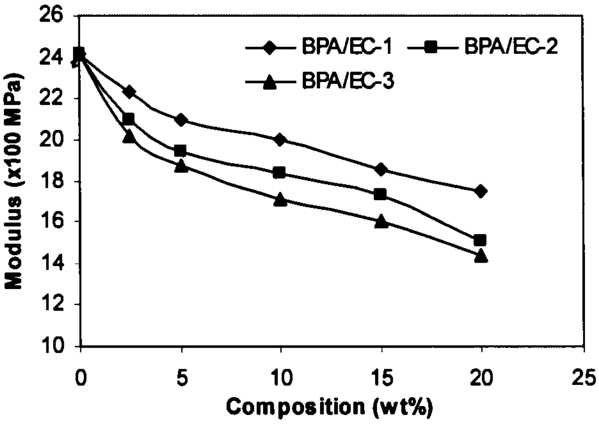


Fig. 3.78 Modulus of modified resin Vs BPA/EC concentration

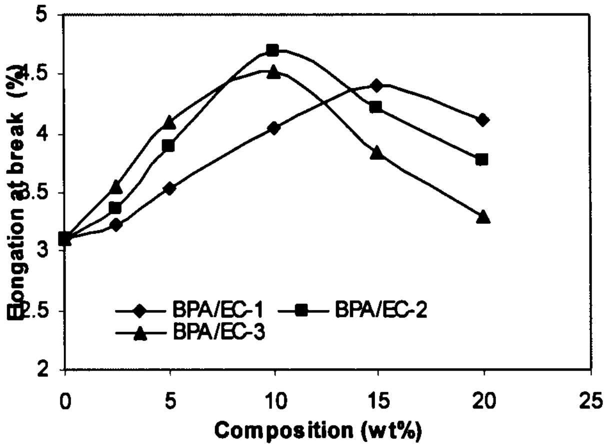


Fig. 3.79 Elongation at break of modified resin Vs BPA/EC concentration

BPA/EC-2 containing BPA and cardanol in the ratio 1:1exhibits greater elongation coupled with toughness in its blends whereas BPA/EC-1 with BPA-cardanol ratio 4:1 has greater strength. In general, a profusion of cardanol epoxides beyond 50 mol % in the modifier resin is found to lower the strength and energy absorption capacity of the blends while improving elongation. Fig.3.81 indicates the variation of impact strength by the addition of 0 to 20 % bisphenol A-cardanol co-epoxides into epoxy resin. At 10 wt % BPA/EC-2 showed about 90% improvement in impact strength. This is attributed to a higher degree of molecular flexibility and capacity for spatial molecular reorganization when relatively smaller chains are present.

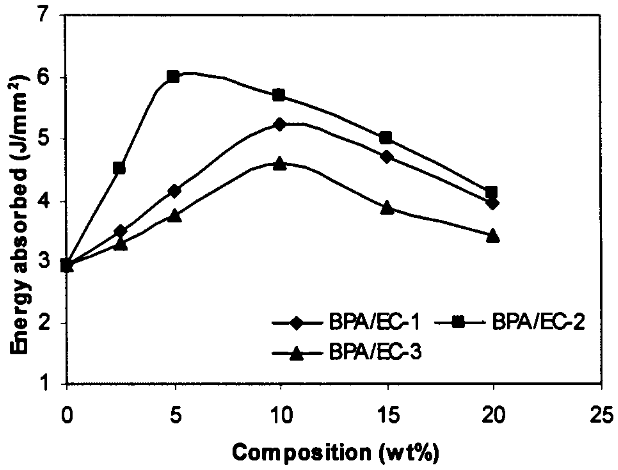


Fig.3.80.Energy absorbed (to break) of modified resin Vs BPA/EC concentration

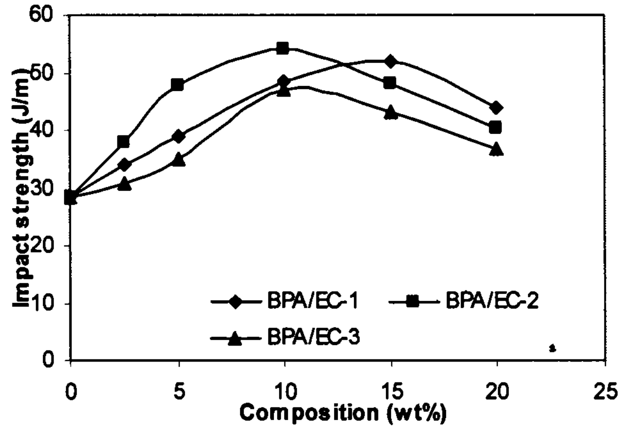


Fig.3.81.Impact strength of modified resin Vs BPA/EC concentration

ii. Flexural properties

Fig.3.82 illustrates the variation of flexural strength upon addition of 0 to 20% bisphenol A-cardanol co-epoxide resin into commercial epoxy resin. Flexural strength decreases steadily with increase in modifier concentration. Moreover, the decrease in flexural strength is more as the amount of cardanol epoxide in the modifier resin increases. This reflects the ability of cardanol epoxides to make the matrix more flexible. The shorter the chains in the cured matrix, the greater will be the ease with which it can be flexed. In three point bending experiment, maximum displacement was observed for the modifier resin (BPA/EC-3) containing greatest amounts of cardanol epoxide. Flexural energy also was found to be greater for BPA/EC-3 blends than those for others (Fig 3.83).

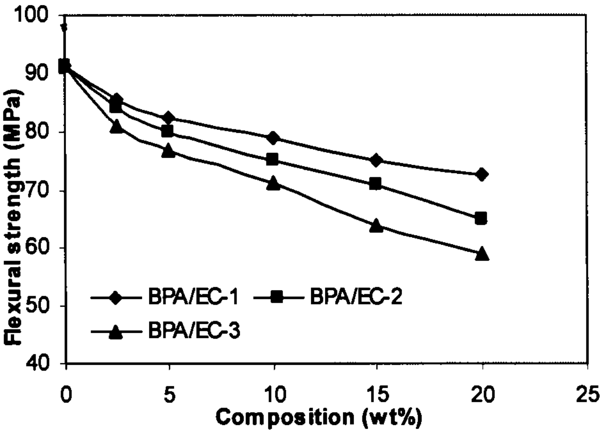


Fig. 3.82 Flexural strength of modified resin Vs BPA/EC concentration

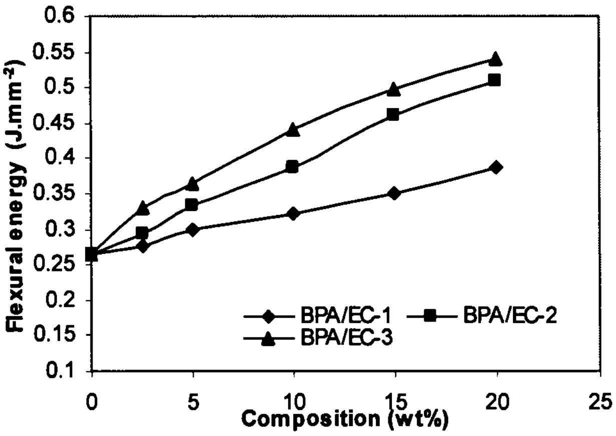


Fig. 3.83 Flexural energy of modified resin Vs BPA/EC concentration

iii. Surface hardness and water absorption

Incorporation of bisphenol A/cardanol co-epoxides into epoxy resin was found to reduce the surface hardness of epoxy resin. Fig. 3.84 shows the variation of surface hardness in presence of varying amounts of BPA/EC resins. Lowering of surface hardness is in agreement with the reduction in modulus.

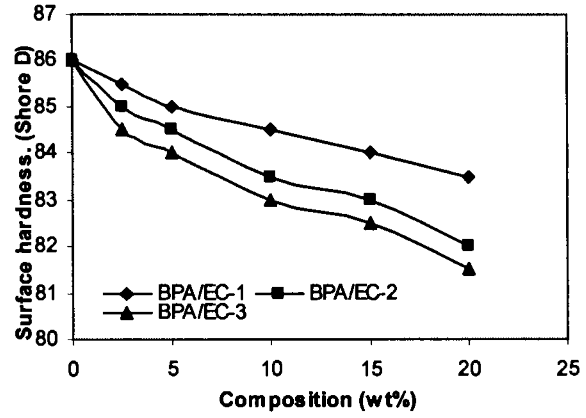


Fig.3.84 Surface hardness of modified resin Vs BPA/EC concentration

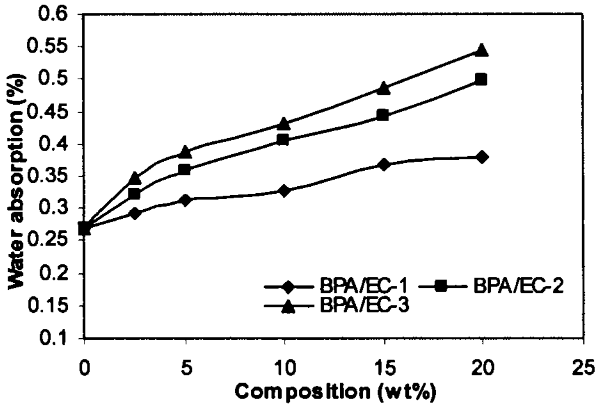


Fig.3.85 Water absorption of modified resin Vs BPA/EC concentration

Blends with BPA/EC-3 having greater concentration of cardanol epoxide exhibit greater lowering of surface hardness. This can be due to the extra flexibility offered by the EC component of the modifier resin. Fig. 3.85 indicates the variation of water absorption of the blends. The blends are found to be less water resistant than the unmodified resin. Greater the concentration of cardanol epoxide in the modifier resin the greater is the water absorption. Table 3.17 summarises the properties of the BPA/EC modified and unmodified epoxy resins.

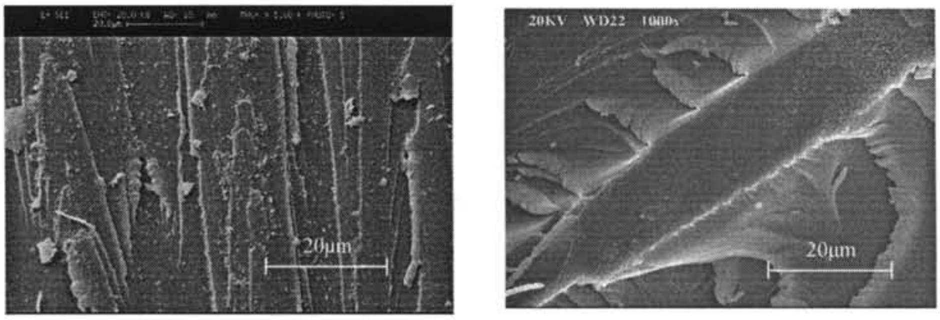
iv. Morphological studies

Scanning electron micrographs of unmodified and BPA/EC modified epoxy resin fractured at low deformation are shown in Fig. 3.86A. The fracture surface of the blend is characterised by a morphology indicating extensive crazing. Figure (a)

Table 3.17 Properties of DGEBA and DGEBA-BPA/EC modified resins

Property	% Improvement / % composition			
	DGEBA	BPA/EC-1	BPA/EC-2	BPA/EC-3
Tensile strength (MPa)	48	33/15	18/10	10/10
Modulus (x 100 MPa)	24.2	-28/20	-39/20	-42/20
Elongation at break (%)	3.1	42/15	53/10	47/10
Energy absorbed (Jmm^{-2})	2.95	78/10	103/5	56/10
Impact strength (J/m)	28.5	82/15	90/10	65/10
Flexural strength (MPa)	91.35	-21/20	-29/20	-34/20
Max. displacement (mm)	4.12	39/20	48/20	51/20
Flexural energy (J. mm^{-2})	0.2655	46/20	91/20	102/20
Surface hardness (Shore D)	86	-3/20	-4.7/20	-5.2/20
Water absorption (%)	0.27	41/20	84/20	100/20

is the micrograph of the unmodified resin and it shows typical brittle fracture. Referring to theBPA/EC-2 modified sample (b), the multi level fracture paths have a feathery texture with large breadth. Peaks and parallel fibril structures in pulled up wavy crests indicate the stretching prior to fracture. Stress whitening indicative



(a) **(b)**

Fig. 3.86A Scanning electron micrographs of the fracture surfaces of a) DGEBA and b) BPA/EC-2 modified epoxy resin

of crazing is also observed. The fracture surface (b) clearly points to a combined mechanism of crazing and shear yielding leading to higher energy absorption.

v. Soxhlet extraction and swelling studies

The Soxhlet extraction and swelling data are given in Table 3.18. The cured modified samples yielded somewhat smaller amounts of soluble matter compared to the unmodified sample. Except BPA/EC-3, all the blends gave higher values of V_p during swelling studies. This indicates cross-linking between epoxy resin and the modifier resin. The extent of cross-linking is the most in BPA/EC-1blend because it contains relatively greater amount of epoxide functionality as is evident from GPC and epoxy equivalent data.

Table 3.18 Soxhlet extraction and swelling data

Samples	DGEBA	BPA/EC-1	BPA/EC-2	BPA/EC-3
Soluble matter %	5.34	3.91	4.417	4.932
V_p	0.904	0.946	0.919	0.881

vi. Thermal properties

i.TGA: The TGA thermograms of unmodified and BPA/EC-2 modified epoxy resins are given in Figure 3.86B. BPA/EC-2 modified sample gave 15.04% residue against 7.664% by the DGEBA at 600°C. The modified resin has better ablation

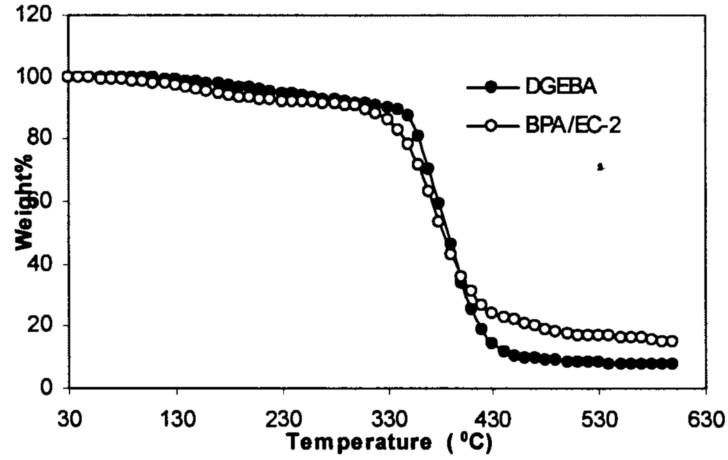


Fig.3.86B. TGA curves of unmodified and BPA/EC2 modified epoxy resins

resistance than DGEBA. The temperature of maximum rate and half loss are 387.48^{0}C and 393.3^{0}C respectively for the modified resin. Though the onset of degradation is at a lower temperature than that of DGEBA, the blend. has marginally improved thermal resistance

ii.DSC : For the neat resin glass transition is obtained at 70.64^{0}C (T_g). The DSC thermogram for DGEBA- BPA/EC-2 blend is given in Fig.3.86C. Addition of 10 weight % BPA/EC-2 shifts the T_g to lower temperature (63.75^{0}C). This shows the flexibility attained by the resin in presence of BPA/EC.

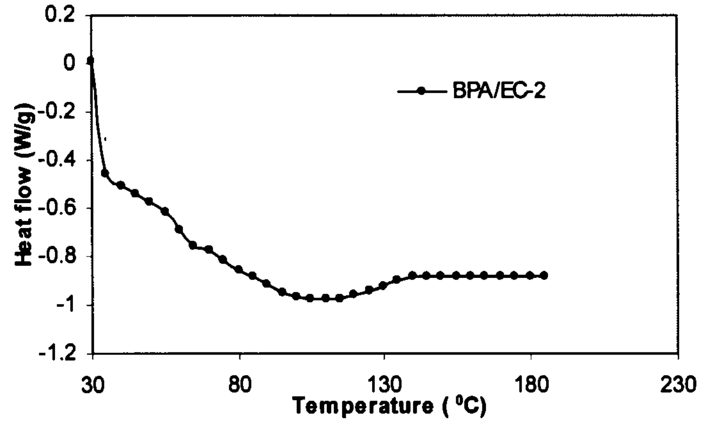


Fig.3.86C. DSC thermogram of DGEBA-BPA/EC-2 blend

ii. DMA: Fig 3.87 indicates the DMA curves for the BPA/EC-2 modified and unmodified resin. Referring to tan δ curve (Fig.3.87a) the peak occurs at 82.79^{0}C at

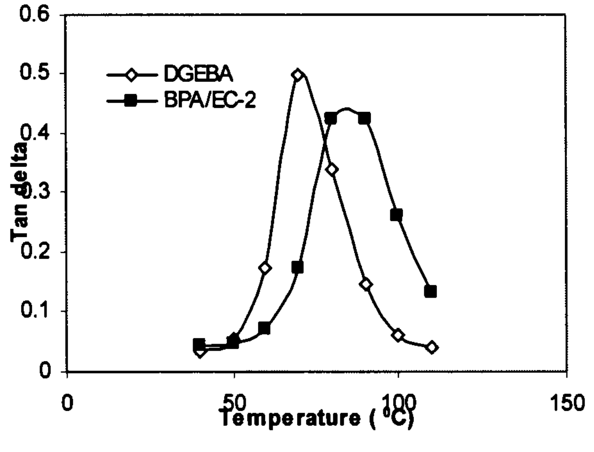


Fig.3.87a. Tan δ curves for BPA/EC-2 modified and unmodified resin

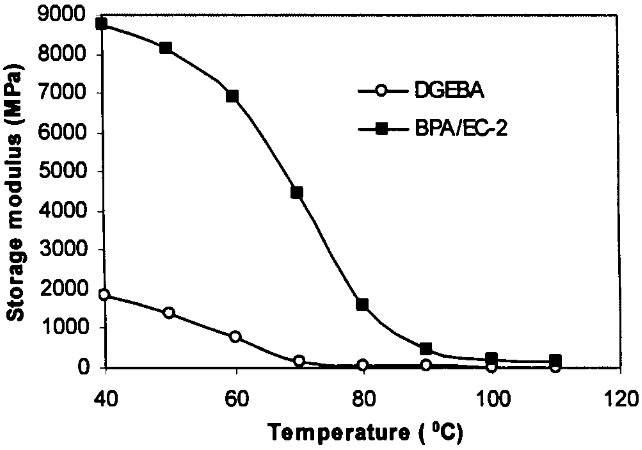


Fig.3.87b.Storage modulus curves for BPA/EC-2 modified and unmodified resin

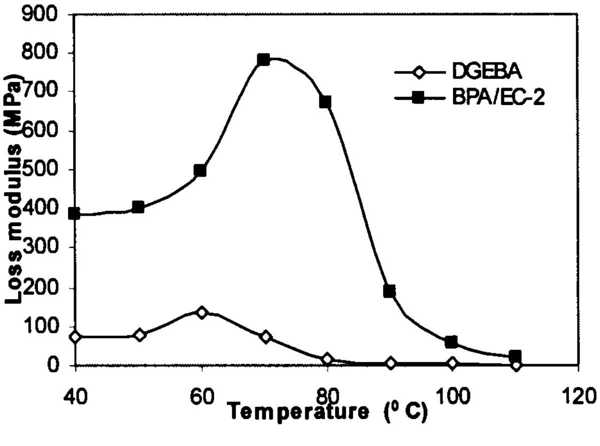
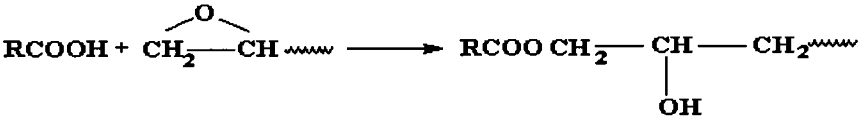


Fig.3.87c. Loss modulus curves for BPA/EC-2 modified and unmodified resin

tan δ =0.4238 for the modified sample compared to 71.3^{0}C corresponding to tan δ=0.497 for the neat resin. The decrease in height of the tan δ peak is indicative of effective plasticizing action by the modifier resin. The blend has higher storage modulus (Fig.3.87b) showing greater extent of cross-linking than in the unmodified sample. Also the blend shows higher loss modulus than the neat resin (Fig.3.87c). This is in tune with the Soxhlet extraction and swelling data obtained for the blend. The temperature corresponding to the inflection point on the storage modulus curve (65.89^{0}C) agrees well with the T_g obtained from DSC measurement. Effective cross-linking between the shorter polymer chains gives flexibility to the cured matrix which in turn lowers the glass transition temperature.

3.3.8 Modification with unsaturated polyester resin (UPR)

a) By reactive blending: Solubility parameter of UPR (containing 35-40% styrene) is 19.4 – 26.4 and that of epoxy is 22.3 $(MPa)^{1/2}$. Hybrid polymer networks between epoxy resin and unsaturated polyester resins can be prepared by reactive blending and by chemical reaction (3.2.12b). In this study, ortho phthalic resin (UPR-1) and iso phthalic resin (IUPR) have been used as modifier resins. IUPR is the condensation product of isophthalic acid and maleic anhydride with 1,2 propylene glycol. It has better chemical and thermal resistance and is used as a matrix for high quality FRPs for outdoor applications. In addition, UPR has been incorporated to epoxy resin by chemical reaction in presence of a Lewis base (designated as UPR-2). The acidic and alcoholic end groups in UPR are chemically sensitive and they readily react with epoxide functionality. During blending, the carboxyl /hydroxyl group in UPR can react with the epoxide ring leading to chain extension and/or cross-linking.



$$\mathrm{RCOOH} + \overset{O}{\mathrm{CH_2{-}CH}}\sim\sim \longrightarrow \mathrm{RCOO\,CH_2{-}\underset{OH}{CH}{-}CH_2}\sim\sim$$

i. Tensile properties

Fig. 3.88 shows the variation of tensile strength of epoxy resin modified by 0 to 20% unsaturated polyester resins. Tensile strength values show slight increase at low UPR concentrations. At higher concentrations tensile strength decreases

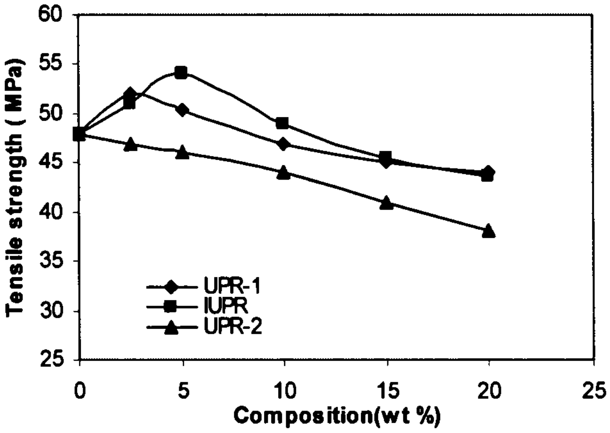


Fig.3.88. Tensile strength of UPR modified resin Vs UPR concentration

steeply. In the case of chemically reacted sample (UPR-2), tensile strength decreased sharply with increase in UPR concentration. Epoxy- carboxy reaction in presence of Lewis base is esterification of epoxy group which results in chain extension. The reduced tensile strength of these blends may be the result of un - polymerised styrene diluent or alternatively due to inferior properties of UPR.

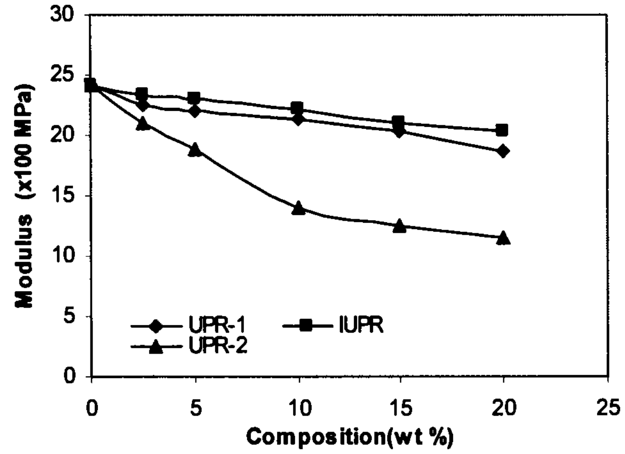


Fig.3.89. Modulus of UPR modified resin Vs UPR concentration

Fig. 3.89 indicates a steady decrease in modulus of the blends. This is indicative of the flexibility due to UPR chains. The steep fall in modulus of UPR-2 blend indicates a higher extent of chain lengthening and decreased cross-linking. Fig. 3.90 illustrates the change in elongation at break of the epoxy-UPR blends. A higher elongation is obtained for UPR-2 and marginal increase in the case of UPR1

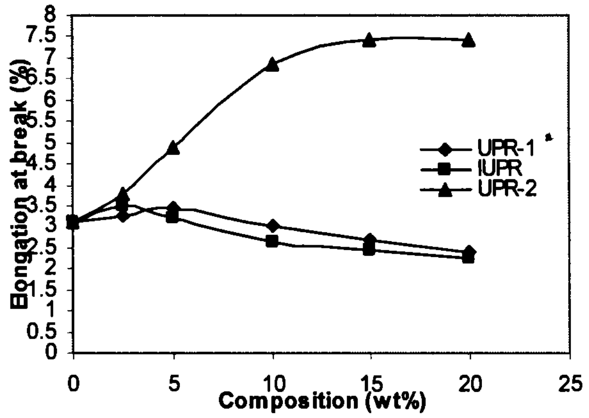


Fig.3.90. Elongation at break of UPR modified resin Vs UPR concentration

and IUPR at lower concentrations.. Elongation becomes a maximum for 15%UPR-2(138% in excess of that of neat resin). Due to chain extension, the polymer chains are more linear resulting in a greater entangling of chains. Fig.3.91 shows the variation of energy absorbed to break by the blends. UPR-2 is found to be superior in energy absorption compared to the other blends. This is again attributed to the grater extent of entangling and capacity for spatial rearrangement.

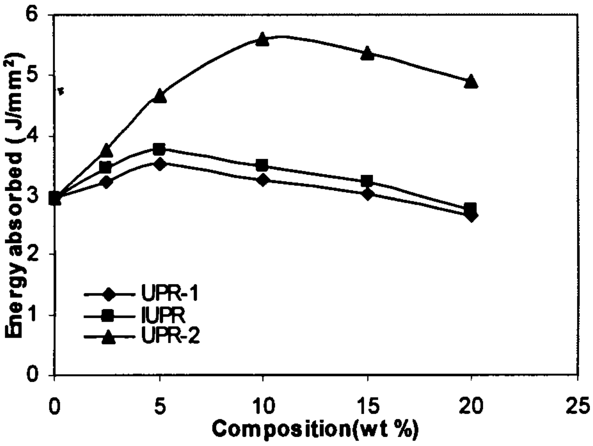


Fig.3.91. Energy absorbed (to break) of UPR modified resin Vs UPR concentration

Fig. 3.92 indicates the improvement in impact strength of epoxy-UPR blends. Compared to UPR-1 and IUPR, UPR-2 sample has greater impact strength. The increase in impact strength may be due to a plasticizing action by styrene as well as chain extension by polyester chain. The improvement in impact strength is not as pronounced as in elongation or energy absorption.

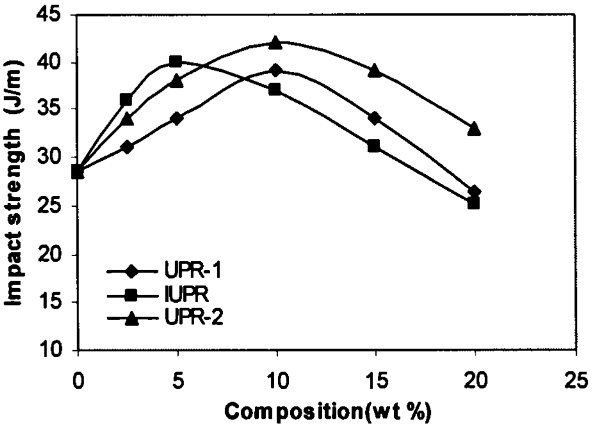


Fig.3.92. Impact strength of UPR modified resin Vs UPR concentration

ii. Flexural properties

Variation in flexural strength and flexural energy of DGEBA/UPR blends are given in Fig 3.93(a) and (b) respectively. There is a gradual decrease in flexural strength with increase in concentration of modifier resin. This reflects the flexibility achieved by the blends by the presence of UPR. The flexural energy increases with UPR concentration and UPR-2 shows the best result in this case.

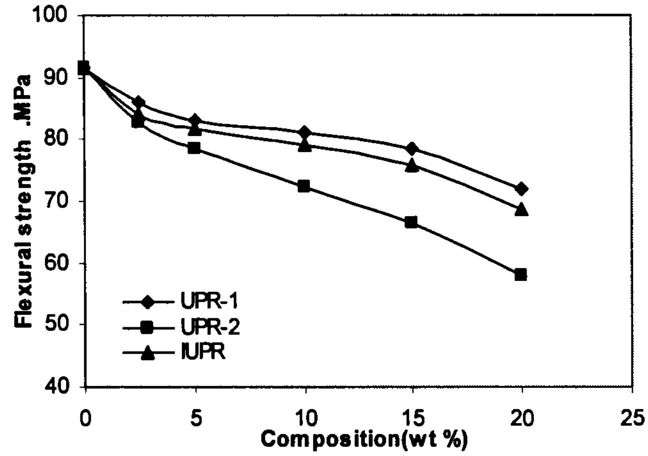


Fig. 3.93a. Flexural strength of UPR modified resin Vs UPR concentration

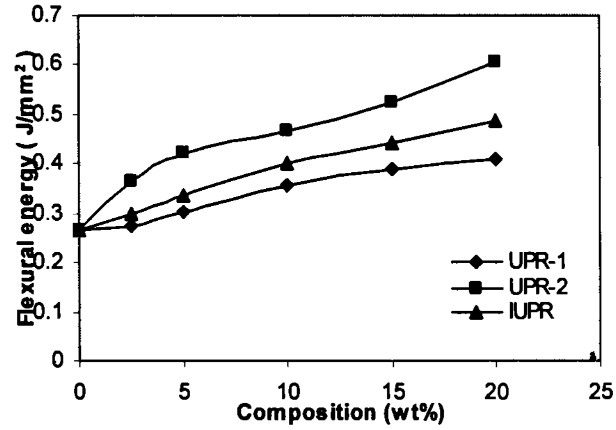


Fig. 3.93b. Flexural energy of UPR modified resin Vs UPR concentration

iii. Surface hardness and water absorption

Fig 3.94 indicates the variation in surface hardness of UPR modified resin with UPR concentration. In general the blends show decreased hardness compared to neat resin. Referring to Fig 3.95 the water resistance of UPR modified resins are found to be slightly less than that of the unmodified resin. The presence of more

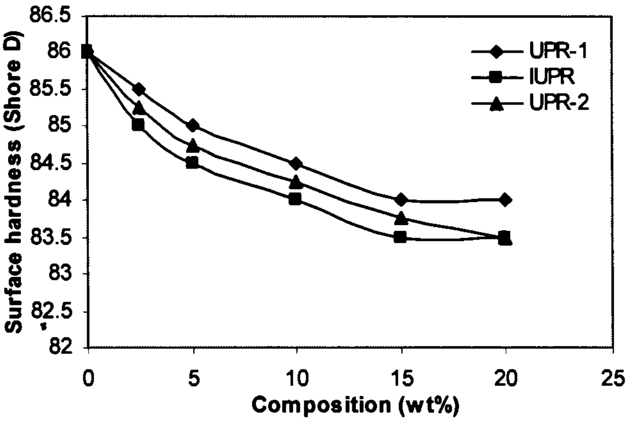


Fig. 3.94 Surface hardness of UPR modified resin Vs UPR concentration

polar groups and possibility for hydrogen bonding may be responsible for this. The presence of more polar groups and possibility for hydrogen bonding may be responsible for this. The lower water absorption value of UPR-2 is due to more effective grafting of UPR chains to the epoxy matrix.

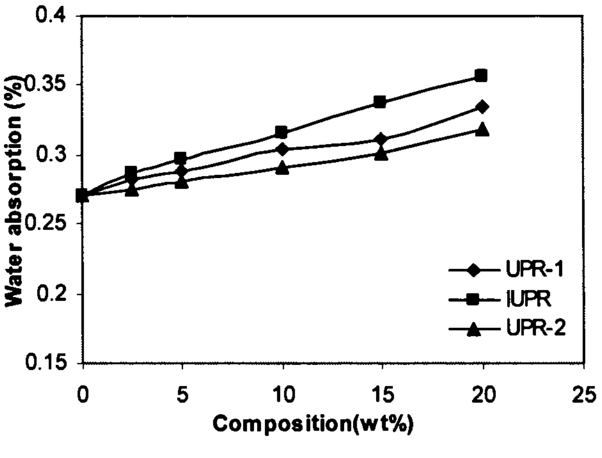


Fig. 3.95. Water absorption of UPR modified resin Vs UPR concentration

The physical properties of DGEBA/UPR blends are summarised in Table3.19. The extent of improvement in every property and the corresponding compositions are shown.

Table 3.19 Summary of properties of DGEBA/UPR blends

Property	% Improvement / % composition			
	DGEBA	UPR-1	UPR-2	IUPR
Tensile strength (MPa)	48	9/2.5	-21/20	13/5
Modulus (x 100 MPa)	24.2	-23/20	-53/20	-16/20
Elongation at break (%)	3.1	12/5	128/15	15/2.5
Energy absorbed (Jmm^{-2})	2.95	19/5	89/10	27/5
Impact strength (J/m)	28.5	39/10	49/10	43/5
Flexural strength (MPa)	91.35	-19/20	-37/20	-37/20
Max. displacement (mm)	4.12	22/20	64/20	27/20
Flexural energy (J. mm^{-2})	0.2655	53/20	116/20	83/20
Hardness (Shore D)	86	-2.5/20	-4/20	-4/20
Water absorption (%)	0.27	23/20	19/20	33/20

iv. Thermal properties

i.TGA: Fig. 3.96(a) indicates the TGA curves for the UPR modified and unmodified epoxy resin. The modified sample gives more residue at 600^{0}C (9.246%) than the unmodified sample (7.664%) showing improved resistance to thermal degradation (Table3.20).

Table.3.20. TGA data for UPR modified and unmodified DGEBA

Sample	Onset temperature (^{0} C)	Temperature Max.rate (^{0}C)	Temperature half loss(^{0}C)	Residue %
DGEBA	310.56	386.12	367.24	7.664
DGEBA/UPR	310.43	383.99	384.9	9.246

ii.DSC: For the neat resin T_g is obtained at 70.64^{0}C The DSC thermogram for DGEBA/UPR blend is given in Fig. 3.96(b). Addition of 10 weight % UPR-1shifts the T_g to a lower temperature (65.76^{0}C). This shows the flexibility attained by the blend in presence of UPR. The incorporation of UPR produces considerable plasticizing effect in the matrix and it is evident from DMA data..

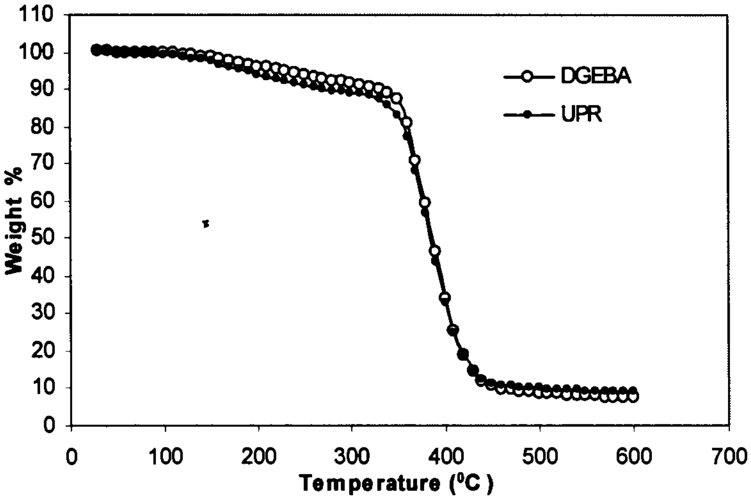


Fig.3.96a. TGA curves for DGEBA and DGEBA/UPR

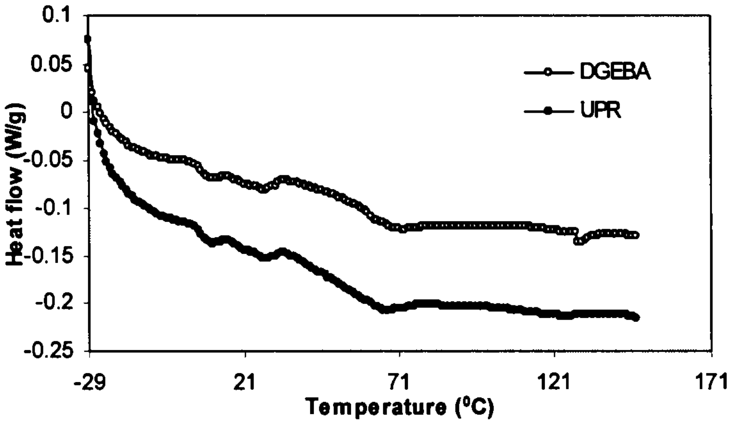


Fig. 3.96b. DSC curves for DGEBA and DGEBA/UPR

iii. DMA: Fig 3.96(c) indicates the DMA-tan delta curves for the UPR-modified and unmodified resin. The damping peak occurs at 75.62^{0}C at tan δ = 0.3523 for the modified sample compared to 71.3^{0}C corresponding to tan δ= 0.497 for the neat resin. The decreased height of tan δ peak of the blend indicates effective plasticizing action by UPR. The DGEBA/UPR blend has higher storage modulus (Fig.3.96d) showing greater extent of cross-linking in the blend than in the unmodified resin. The inflection point on the storage modulus curve corresponds to 67.16^{0}C which agrees with the glass transition temperature obtained by DSC.

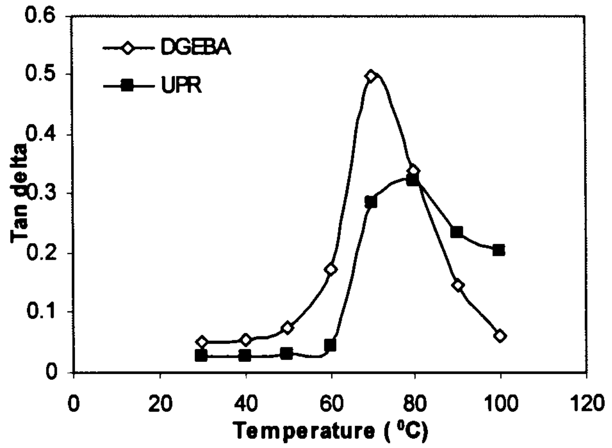


Fig.3.96c. Tan delta curves for DGEBA and DGEBA/UPR

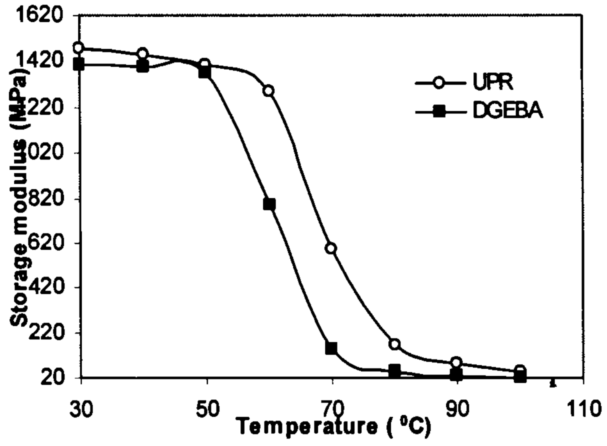
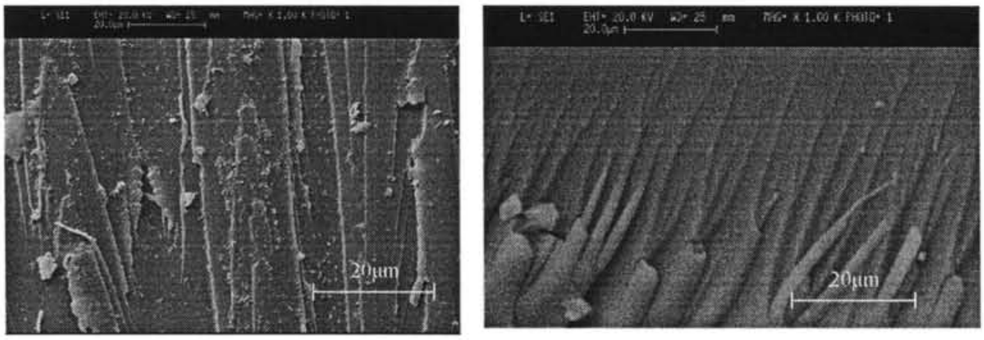


Fig.3.96d. DMA-Storage modulus curves for DGEBA and DGEBA/UPR

v. Morphological studies

Fig. 3.97(a) and (b) are the scanning electron micrographs of the unmodified and UPR modified epoxy resin respectively. The micrograph (a) due to the unmodified resin shows typical brittle fracture with crazes. River markings and pulled out splinters indicate brittle failure. Figure (b) corresponds to that of UPR modified resin. Multilevel fracture paths with pulled up crests indicate energy absorption on a large scale during failure. There is distinct sign of stress whitening which is indicative of crazing.



(a) (b)

Fig.3.97 Scanning electron micrograph of a) DGEBA and b) DGEBA/UPR

b) Epoxy-UPR interpenetrating polymer networks

In recent years, blending of two thermosets via interpenetrating polymer networks (IPNs) has been widely reported [17, 18]. Interpenetrating networks are formed when a mixture of two different monomers are allowed to polymerise simultaneously in the same vessel. IPNs are a mixture of two or more cross-linked polymers with a physically interlocked network structure between the component polymers [19]. The mechanical properties of resins and laminates are improved by this technique. In this investigation, unsaturated polyester and epoxy resins are blended in different ratios and cured (Section 3.2.12c) simultaneously by using benzoyl peroxide (BPO) and methylene dianiline (MDA) as curing agents, which results in IPNs.

i.Tensile properties

Referring to Table 3.21, tensile strength values obtained by blending UPR with epoxy resins are significantly higher compared to that of both unmodified resins. The improvement in tensile strength over that of the base resin is due to mutual interpenetration between the UP and epoxy networks. Tensile strength reaches a maximum at DGEBA/UP=20/80, w/w. The equivalent ratio of epoxy/UP is much closer to 1 than other compositions and results in a larger extent of chain entanglements. The presence of hydroxyl groups will accelerate the amine curing of epoxy resin. Compared to unmodified resins the blends show substantial increase in elongation indicating compatibility. Blends show maximum elongation at 20wt %of epoxy resin. The higher elongation may also be the result of entanglement of chains and some uncured DGEBA and /or UP molecules acting as plasticizers. The 20/80 sample would have more chain entanglement and this is associated with enhanced tensile strength as reported by Han et.al. [20].The moduli of the blends are lower than that for the neat resin. This reflects the capacity of the IPNs to absorb energy and provide a higher degree of molecular flexibility.

Since the networks are closely interlocked, the cracking energy would be dissipated simultaneously by both the networks via molecular interactions and relaxations and synergistic cracking energy absorption is observed [21]. The entanglement of the interlocked networks shows significant toughness improvement. The toughness of the blend is maximum at 40-wt % epoxy concentration (Table 3.21). Impact strength values obtained by blending UPR with epoxy resins are significantly higher compared to that of the unmodified resin. This can be attributed to higher degree of molecular flexibility.

Table 3.21 Mechanical and thermal properties of DGEBA/UPR interpenetrating networks

Property	DGEBA/UPR composition w/w					
	0/100	20/80	40/60	60/40	80/20	100/0
Tensile strength (MPa)	37	70.25	64.45	58.4	53.25	48.00
Modulus (x10^2MPa)	18.5	17.40	18.25	19.50	20.10	24.20
Elongation at break (%)	2.2	4.65	4.10	3.77	3.41	3.10
Energy absorbed (J/mm^2)	2.32	3.98	4.48	3.41	3.17	2.95
Impact strength (J/m)	18.70	51.20	48.47	41.35	36.76	28.50
Temperature of Half loss (^{0}C)	408.9	411.3	408.50	396.24	394.35	390.5
Residue (%)	1.3	9.616	9.17	8.504	8.22	7.664
T_g(^{0}C)	92	64.45	66.57	68.15	68.88	70.64

ii.Thermal studies

The TGA data of DGEBA and the DGEBA/UPR IPNs are shown in Table 3.21. The DGEBA/UP- 20/80 has marginally better thermal stability compared to the other samples. The DSC data of the blends show a single lowered T_g due to the

IPN formation (Fig.3.98a). Each network enjoys some amount of mobility relative to the other. The tan δ values are slightly higher for the IPNs (Fig 3.98b) resulting from higher tensile properties. The higher tan δ value of the blend means a higher loss modulus, which would turn more mechanical energy into heat via molecular relaxation.

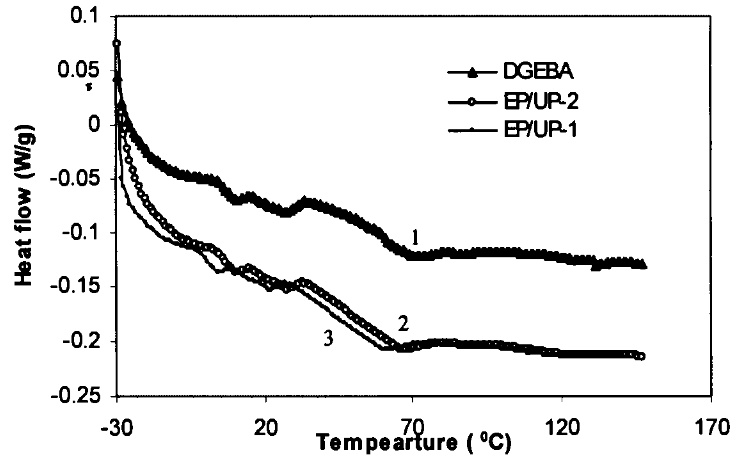


Fig. 3.98a.DSC thermogram of 1.DGEBA, and 2.DGEBA/UPR 40/60 (EP/UP-2) 3. DGEBA/UPR20/80 (EP-UP-1)

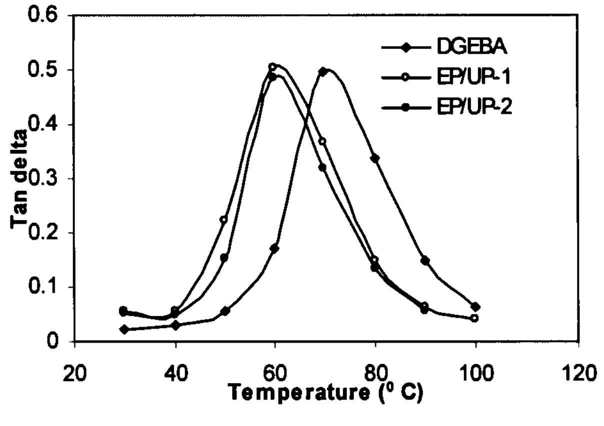


Fig. 3.98b.DMA-tan delta curves of DGEBA, DGEBA/UPR20/80 (EP-UP-1) and DGEBA/UPR 40/60 (EP/UP-2)

The IPN compositions especially DGEBA/UPR 20/80 and 40/60 showed lower storage moduli due to network interlock during cure reactions. This is evident from their higher % of soluble matter (lower gel fraction) obtained during Soxhlet extraction. Larger the amount of uncured material, lower will be the T_g and damping temperature. The damping peaks occur at lower temperatures for the IPN compositions because they have less cross-linking and some uncured material.

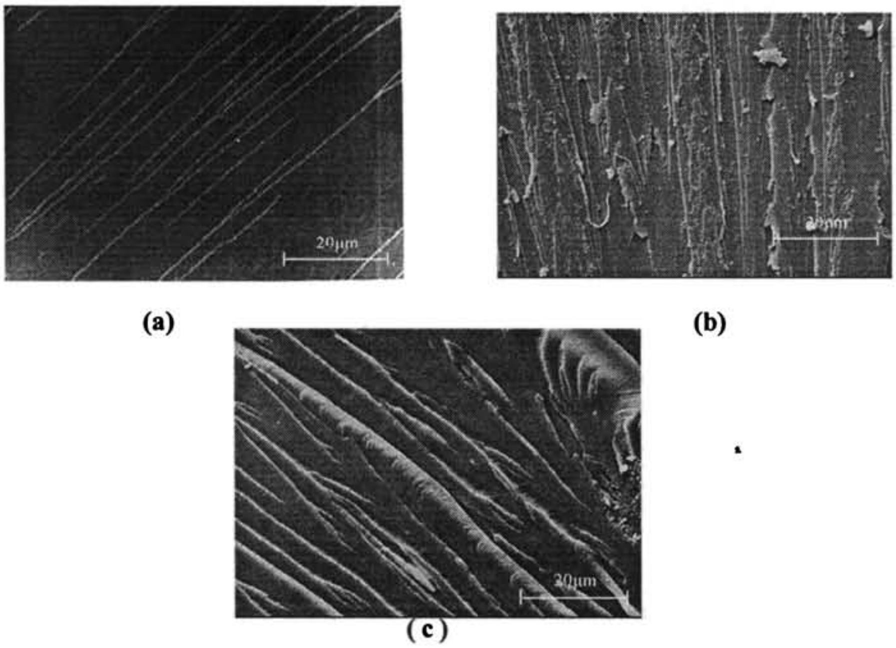
iii. Soxhlet extraction studies

The different IPN compositions gave higher amounts of soluble matter compared to unmodified epoxy resin. DGEBA/UPR 20/80 sample gave 8.334% soluble matter as against 5.34% for the neat epoxy (Table 3.22). This clearly indicates the existence of uncured or low molecular weight material present in the samples. This also indicates reduced cross-linking in these IPN compositions.

Table 3.22 soxhlet extraction data for Epoxy/UPR IPNs

Samples	DGEBA	DGEBA/UPR 20/80	DGEBA/UPR 40/60	DGEBA/UPR 60/40
Soluble matter %	5.34	8.334	7.502	7.03

iii. Morphological studies



(a) (b) (c)

Fig.3.99 Scanning electron micrographs of fracture surfaces (a) UPR (b) DGEBA and (c) DGEBA/UPR- 20/80 IPN

Scanning electron micrographs of UPR, DGEBA/UPR-20/80 and DGEBA fractured at low deformation rate are shown in Fig.3.99. Referring to the micrograph (a) the fracture path for UPR is narrow and continuous indicating rapid crack propagation along the axis of crack growth. The fracture surface is smooth with low ridges and shallow grooves.

The micrograph of DGEBA (b) is typical of brittle fracture with river markings and pulled out splinters. The fracture pattern of the 20/80 sample is shown in micrograph (c). Multi level fracture paths with peak structures and fibrils characteristic of ductile fracture are indicative of energy absorption on a large scale during failure. Newly sheared internal surfaces with uniform distribution are also seen. The energy dissipation is proportional to the number of internal surfaces newly produced (i.e., shear banding yield mechanism). This reflects high toughness, impact resistance and load bearing characteristics.

3.4 Conclusions

In this investigation, hybrid polymer networks of commercial epoxy resin with phenolic resins and other epoxy compounds were prepared and their properties studied. Unlike elastomers, phenolic resins such as PF resols, novolacs and epoxy novolacs are highly compatible with epoxy resin. Among phenol-formadehyde copolymers, resols of phenol-cardanol mixtures gave the best property improvements in commercial epoxy resin. Properties such as energy absorption and impact strength exhibit maximum improvement (83% and 88% respectively)at 60% cardanol content in a cardanol/phenol modifier resin. The use of cardanol, a renewable natural resource, as a phenol substitute is of significance. DGEBA–novolac blends also showed significant improvement in toughness properties and water resistance. Novolacs derived from phenol-cardanol mixtures of different compositions were also effective epoxy modifiers. A 40%cardanol-phenol-formaldehyde novolac copolymer gave appreciable improvement in energy absorption (92%) of the cured epoxy matrix.

Compared to epoxy phenol novolac (EPN), the one derived from p-cresol (ECN) gave significant improvement in mechanical and thermal properties. A 15 wt% DGEBA/ECN system exhibited 135 % improvement in toughness compared to the neat resin. 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. Further, the epoxy novolacs were found to considerably improve the ageing behaviour of the epoxy matrix

Epoxidised cardanol (EC) was found to be effective in improving the elongation and energy absorption (95% and 97% respectively) of the modified epoxy matrix. However, the improvement in tensile strength was only marginal. This problem was solved, to some extent, by using co-epoxidised resins of bisphenol A–cardanol mixtures (BPA/EC) as modifiers which imparted enhanced tensile strength, toughness as well as elongation to the epoxy matrix. BPA/EC-1 containing BPA and cardanol in the ratio 80:20 exhibited the best results in tensile strength. BPA/EC-2 containing BPA and cardanol in 50:50 ratio showed maximum improvements in toughness (103%) and impact strength (90%). Both the EC based modifiers lowered the T_g of the matrix.

Blends of epoxy resin with UPR showed marginal improvements in mechanical properties of epoxy matrix. Incorporation of UPR into the epoxy matrix by chemical reaction (esterification) produced blends with significant elongation but with lowered strength. Interpenetrating polymer networks of epoxy resin with UPR with a single lowered T_g exhibited enhanced toughness properties. This effect was best with an IPN composition of 20/80 between epoxy and UPR.

Of the various modifiers used for reactive blending, epoxy cresol novolac (ECN) gave the best results in improving the toughness and impact resistance of commercial DGEBA.

References

1. Herman F. mark, Norbert M.Bikales, Charles G Overberger and George Menges., Eds. *Encyclopedia of Polymer Science and Engineering*, 2nd Edn. Vol-11, 45-56, John Wiley, New York (1964)
2. Z.G. Shakes, R.M. Brown, H.A. Streetz, P.E. Cassidy and M.T. Blanda., *J. Appl. Polym. Sci.*, **84**, 2283-2286 (2002).
3. K.J. Saunders.,'*Organic Polymer Chemistry*, Chapter 16, p-380-390 Chapman and Hall, London (1976).
4. Lin-Gibson Sheng, *Cresol-Novolac-Epoxy Networks.*, Dissertation, ETD-D 4262001-142525 (2001).
5. J.F. Gabriel, *Org.Coat.Plast.Chem.*,**43**, 545(1980)
6. W. Burchard, S.Bantle and S. A. Zahir., *Makromol.Chem.*,**182**, 145 (1981)
7. R.S. Drake, D.R. Egen and W.T. Murphy, *ACS Symp. Ser*, **221**,1(1983)
8. M.S. Lin, C.C. Liu and C.T. Lee., *J. Appl. Polym.Sci.*,**72**,588 (1999)
9. Arthur E Woodward, *Atlas of Polymer Morphology*, Hanser Publishers, New York, (1988)
10. Lothar Engel, Hermann Klinglee, Gottfried W Ehrenstein and Helmut Schaper, *An Atlas of Polymer Damage*, Wollfe Science Books,Munich (1981)
11. E.A. Turi, *Thermal Characterisation of Polymeric Materials*, Academic Press, New York (1981)
12. T. Murayama, *Dynamic Mechanical analysis of Polymer Materials.*, Elsevier Scientific Publishing Company, Amsterdam (1982)
13. R. Brown., Ed. *Handbook of Polymer Testing*, Marcel Decker Inc., New York (1999).
14. L. Valette and Chin Pin Hsu, *Polymer*, **40**, 2059 (1999).
15. M.S. Lin, R.J. Chang, T. Yang and Y.F. Shih, *J. Appl. Polym. Sci.*, **55**, 1607(1995)
16. J.H.P. Tyman., Chem. Soc. Rev., 8, 499-537 (1973)

17. S.C. Kim and L.H. Sperling, Eds. *IPNs Around the World*, p-139-153, John Wiley & Sons, New York (1997)

18. L.H. Sperling., *Interpenetrating Polymers and related Materials.*, Plenum Press, New York (1981)

19. S.C Kim, *Trans. Mater. Res. Soc.*, Jpn, **15**A,215 (1994)

20. X. Han, B. Chen and F. Guo, In *IPNs Around the World*, Eds. S.C. Kim and L.H. Sperling., p-241-257 , John Wiley & Sons, New York (1997)

21. H. Xia, Z.H. Ping, J. Xie and T.Y. Yu, *J. Appl. Polym. Sci, Polym. Chem. Ed.*, **28**, 585 (1990)

Chapter 4

MODIFICATION BY ELASTOMERS

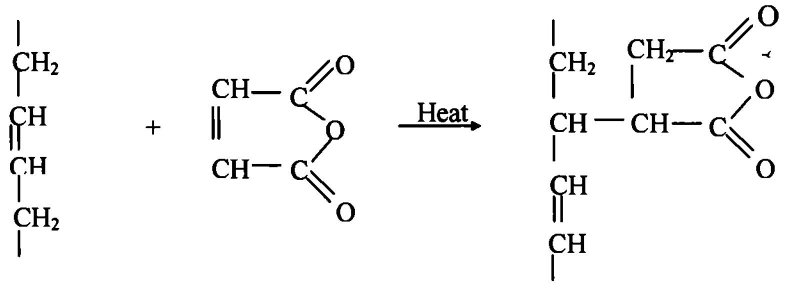
4.1 INTRODUCTION

The most successful method for epoxy toughening is the incorporation of a second elastomeric phase into the glassy epoxy matrix resulting in phase separation [1].Toughening can be done by dispersing a small amount of elastomer as discreet phase or by incorporation of reactive liquid polymers [2]. This chapter deals with the modification of commercial epoxy resin by blending with each of different elastomers, maleated elastomers and functional elastomers. Masticated rubber was dissolved in methyl ethyl ketone and blended with commercial epoxy resin. Acrylonitrile butadiene rubber (NBR), maleated NBR (MA-g-NBR), cross-linked NBR (NBR-C) and polyurethane rubber (PU) were incorporated into epoxy resin by such solution blending. Blends of epoxy resin were also prepared with liquid functional rubbers such as hydroxyl terminated polybutadiene (HTPB), hydroxyl terminated natural rubber (HTNR) and carboxyl terminated butadiene-acrylonitrile rubber (CTBN). The fracture behavior and the particle size distribution were studied by scanning electron microscopy (SEM). The thermal properties of the toughened resin were studied by thermo gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and DSC. The physical properties of the cured blends were compared with those of the control resin.

The addition of elastomeric phases increases the overall ductility of the polymer over a wide range of temperature and also improves toughness and impact resistance. Reinforcement of the resin matrix with fibres can also improve toughness properties. But reinforcement is not always feasible. Even when reinforced, areas with relatively low amount of fibres are still prone to damage and can suffer breakage when the product is in use. Hence the need for toughening the matrix. Incorporation of elastomers has also been found to cause significant reduction in mould shrinkage.

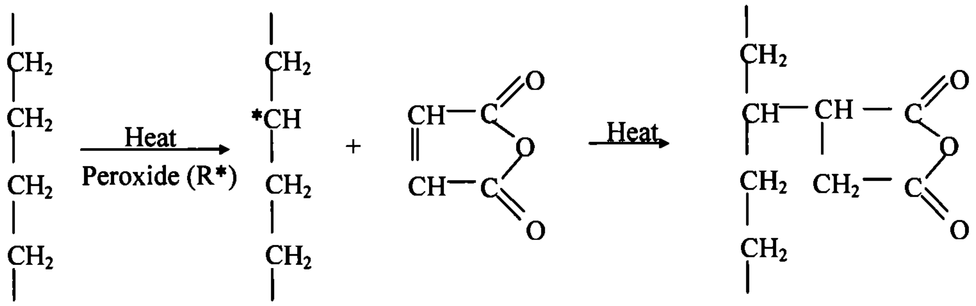
4.1.1 Maleated rubbers

Maleic anhydride (MA) is often used to functionalise elastomers. Farmer and Wheeler [3] patented the method of modifying rubbers with MA. When a solution of natural rubber is heated in the presence of MA and benzoyl peroxide for several hours at 70-100°C, new elastomers with altered physical and chemical behaviour are obtained. MA readily reacts with polymeric double bonds and free radicals by an 'ENE' reaction [4, 5]. The allylic hydrogen reacts with the double bond of MA as shown in scheme 1.



Scheme I: MA reaction with elastomer containing main chain or side chain unsaturation

MA can also functionalise saturated elastomers at high temperatures or in presence of organic peroxides, to form polymeric free radicals which add to MA as shown in the scheme II.



Scheme II: MA reaction with saturated elastomers

MA modified elastomers get dispersed within the resin matrix to an optimum morphology (or size) and adequately coupled to the matrix [6]. In the study reported below, NBR was modified by MA grafting in presence of benzoyl peroxide in a torque rheometer.

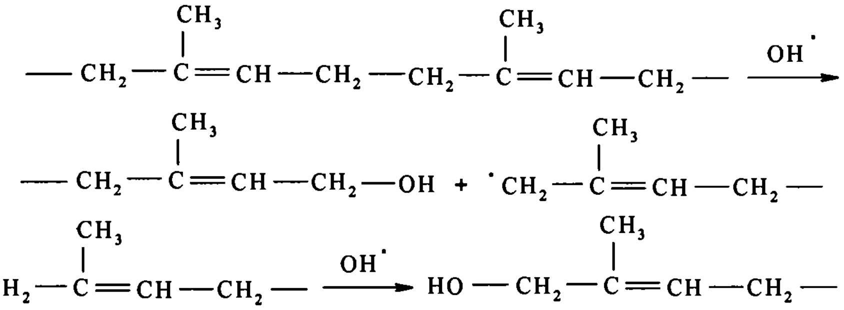
4.1.2 Functional rubbers

Elastomers bearing reactive functional groups show better compatibility with the resin on blending and the rubber phase is dispersed as particles of optimum size in the continuous epoxy phase. In this study, the functional elastomers used for toughening are, hydroxy terminated natural rubber (HTNR), hydroxy terminated polybutadiene (HTPB), maleated nitrile rubber (MA-g-NBR) and carboxy terminated nitrile rubber (CTBN). Of these, maleated NBR and HTNR were prepared in the laboratory.

HTNR is prepared by the photochemical degradation of natural rubber as reported by Ravindran et.al. [7]. Degradation of natural rubber (NR) into shorter chain segments with reactive end groups is carried out in the presence of hydrogen peroxide. It is also reported that HTNR with any range of molecular weight can be prepared by suitably varying the composition of the reaction mixture and exposure time. The following mechanism has been suggested for the de-polymerisation and hydroxylation of NR in the presence of strong sunlight.

$$H_2O_2 \overset{h\nu}{\rightleftharpoons} H_2O_2^{\bullet}$$

$$H_2O_2^{\bullet} \longrightarrow 2OH$$



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \xrightarrow{OH^{\bullet}}$$

$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-OH + {}^{\bullet}CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

$${}^{\bullet}CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \xrightarrow{OH^{\bullet}} HO-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

4.2 EXPERIMENTAL

4.2.1 Materials

a) Chemicals

Hydrogen peroxide (30% w/v, $d^{20}=1.1$), benzene (MW=78.04, 98% assay, methanol (MW=32.04, 99% assay), chloroform (BP=61°C, $d^{20}=1.489$), maleic anhydride, benzoyl peroxide, epichlorohydrin (MW=92.53, 98% assay, BP 114-118^{0}C), bisphenol A(MW=228.29, 97% assay, MP=154-157^{0}C) and caustic soda were LR grade supplied by E. Merck India Ltd, Bombay.

b) Elastomers

Aparene-N553 grade NBR was obtained from Apar Polymers Ltd., Gujarat, India (Mooney viscosity, ML (1+4) at 100°C = 50, acrylonitrile content=33%]), HTPB ($\overline{Mn}$= 2620) and CTBN ($\overline{Mn}$ =3500, ACN content=18%) were obtained from Vikram Sarabhai Space Centre, Thiruvananthapuram, India.

The NBR cross-linking agent, PR 307 (X-Pro India Ltd., Melting range 75-85^{0}C, Norton flow of 50-75 @125^{0}C, 8-9% hexa content) was procured from Ms.Grain Rolls, Thrissur, Kerala., India.

Maleated elastomers were prepared by grafting elastomers with MA by the following procedure. The elastomer was mixed with 2.5% MA and 0.25% benzoyl peroxide in a Brabender torque rheometer at 100°C and 50 rpm speed for 10 minutes. The grafting reaction was confirmed by FTIR spectroscopy and titration methods.

HTNR ($\overline{Mn}$=3000 and hydroxyl value=36.35 mg of KOH/g) was prepared from ISNR-5 grade natural rubber dissolved in toluene by photo-depolymerisation in the presence of H_2O_2 [8]. Natural rubber was first masticated for 30 minutes. A 5 wt % solution of this NR in toluene was mixed with a 30 wt % H_2O_2 solution and methanol in the volume ratio 20:1:3 respectively. Irradiation using sunlight was carried out in a closed glass vessel for 50 hrs with constant stirring. The depolymerised and hydroxy terminated NR was recovered by precipitation with methanol and purified by repeated precipitation. Molecular weight was determined by end group analysis and the hydroxyl value was estimated by established procedures.

4.2.2 Modification of epoxy resin by elastomers/ functional elastomers

a) Unmodified solid elastomers

The blends were prepared by the following procedure. The elastomers were initially masticated in a two-roll mill for about 7 minutes, at tight nip. The milled sample was dissolved in methyl ethyl ketone (MEK) over a period of 24 hrs at a concentration of 25 g/100 ml. The solution was further homogenised by gentle agitation using a stirrer. Varying amounts of the elastomer solution were added to the epoxy resin which was pre-heated to 70^{0}C to reduce viscosity. The mixture was stirred well with the hardener (and the rubber cross-linking agent in some formulations) to give a homogeneous liquid and poured into Teflon moulds. The filled moulds were kept at room temperature in a vacuum oven. Evaporation of the solvent and curing of the epoxy took place simultaneously in controlled vacuum for 48h. The blends were post-cured at 120^{0}C for 4 h. The formulations containing rubber cross-linking agent were heated at 140^{0}C for 4h to cross-link the acrylonitrile –butadiene rubber. The samples of both modified and unmodified cured resin were subjected to all the tests outlined in Section 2.2.4(d).

b) *MA- grafted elastomers*

Both saturated and unsaturated elastomers were modified by the maleic anhydride reaction by the following procedure. The elastomer was mixed with 5% MA and 0.5% benzoyl peroxide in a Brabender torque rheometer at 100°C and 50 rpm speed for 10 minutes. The amount of maleic anhydride reacted is determined by refluxing a solution of maleated NBR in xylene saturated with water for 1 hr and then titrating with a solution of 0.05N ethanolic KOH using 1 % thymol blue as an indicator [9].Varying amounts of MA modified elastomer solution in MEK were blended with epoxy resin and cured by the procedure given in Section 4.2.2(a). The cured samples were tested.

4.2.3 Modification of epoxy resin by reactive liquid elastomers

a. Un-modified liquid elastomers: Varying amounts of the liquid elastomer were added to commercial epoxy resin and the mixtures were stirred with the hardener to get a homogeneous solution. The mixtures were degassed in a vacuum oven before pouring into the moulds. The samples were cured at room temperature for 24h and post-cured at 120^{0}C for 4h. The cured samples were subjected to the tests outlined in Section 2.2.4(d). HTNR, HTPB and CTBN were the liquid elastomers employed for modification.

b) *Modified liquid elastomers*:

i) *Epoxidation*: Hydroxy terminated polybutadiene rubber (HTPB) was epoxidised using epichlorohydrin in presence of alkali. 1mole of epichlorohydrin was used for 65.5g of HTPB which corresponds to one equivalent of hydroxyl group. The product was vacuum distilled to remove excess epichlorohydrin and then extracted with benzene to remove NaCl. The epoxidised HTPB so formed (designated as ETPB) was dried in vacuum. The epoxide equivalent of ETPB was determined by the method cited in Section 2.2.4(b) and the presence of epoxide group was confirmed by FTIR. Epoxy resin was blended with varying amounts of ETPB and the hardener and cured by the same procedure given above.

ii) *Carboxylation:* HTPB was reacted with 10% maleic anhydride by refluxing over a water bath for 5h. The amount of maleic anhydride reacted is determined by refluxing the product with water for 1 hr and then titrating with a solution of 0.05N ethanolic KOH using 1 % thymol blue as an indicator. The product is carboxyl terminated poly butadiene (CTPB) and this was confirmed by FTIR. Epoxy resin was blended with varying amounts of CTPB and the hardener and cured by the same procedure given above.

HTPB has been incorporated into DGEBA in the presence of a silane coupling agent (SCA) also. Varying amounts of HTPB were added to commercial DGEBA resin in presence of 1% silane coupling agent (SI 69). The mixture was stirred well, degassed and then cured using the procedure cited in Section 4.2.2(a).The corresponding formulation was designated as HTPB-S.

4.2.4 Effect of bisphenol A on blends of epoxies and elastomers

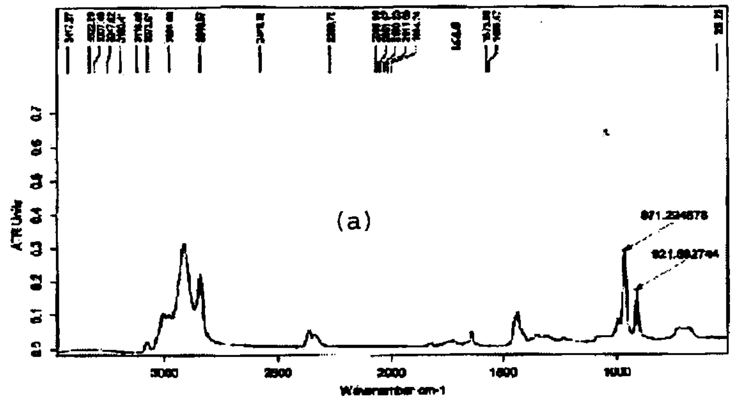
Epoxy resin-elastomer systems show significant improvement in properties when used along with bisphenol A (BPA) as chain extender [10,11]. This technique has been employed in preparing DGEBA-liquid elastomer blends. Elastomer compositions which gave maximum improvement in properties (Section 4.2.3a) were employed for this purpose. DGEBA resin was mixed with varying amounts of bisphenol A (2.5-10%) and the mixtures were heated till the bisphenol particles dissolved completely. The mixtures were cooled to room temperature and a fixed amount of liquid elastomer and the epoxy hardener added to each formulation. The resulting mixtures were stirred well and then degassed in vacuum for ten minutes. Curing of the blends was done as described in Section 4.2.2a. The cured blends were tested for mechanical and thermal properties. The liquid elastomers used were 10 wt % CTBN, 5 wt % HTPB and 5 wt % HTNR and the corresponding epoxy blends were designated as CTBN-1, HTPB-1 and HTNR-1 respectively.

4.3 RESULTS AND DISCUSSION

Adequate interaction between the elastomer and matrix resin is necessary for successfully modifying epoxies with elastomers. While liquid CTBN rubbers with low molecular weights and terminal functionalities are the most frequently used modifiers for epoxies, only limited attempts have been done to use solid acrylonitrile butadiene rubber(NBR) with high molecular weight and no terminal functional groups to modify epoxies. This study highlights the modifying influence of solid NBR (33% acrylonitrile content) and its modified versions such as MA-g-NBR and cross-linked NBR (NBR-C) on the toughness of epoxy resin. The toughening effect of polyurethane rubber has also been investigated. The addition of NBR to epoxy resin produced significant improvements in resin toughness. The high volume fraction of epoxy resin (V_p) in the modified resins noticed during swelling studies indicates efficient cross-linking.

Liquid functional elastomers such as CTBN, HTPB and HTNR have also been used for modification of epoxy resin. The epoxy-CTBN reaction is esterification of the epoxy which takes place at higher temperature or in presence of a catalyst (triphenylphosphine) at a lower temperature. The reaction between hydroxyl and epoxy groups is very slow at ordinary conditions. To improve compatibility and to felicitate interaction with epoxy resin HTPB has been modified by epoxidation (ETPB) and esterification (CTPB). The ETPB resin prepared has been characterised by determining the epoxide equivalent and by FTIR spectroscopy. The epoxide equivalent of ETPB was found to be 0.702 Eq/Kg corresponding to wpe of 1424. The synthesised CTPB has been characterised by FTIR spectroscopy and acid value. The acid value was found to be 39.72mg KOH/g. The effect of addition of bisphenol A and silane coupling agents during the rubber modification of epoxies has also been investigated.

Spectral data: The FTIR spectra of HTPB and ETPB are given in Fig.4.1.



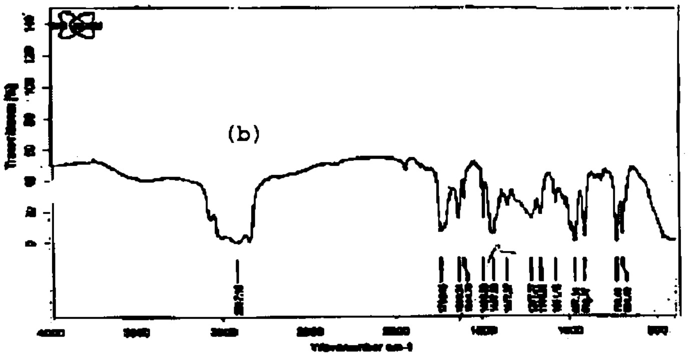


Fig.4.1 FTIR spectra of (a) HTPB and (b) ETPB

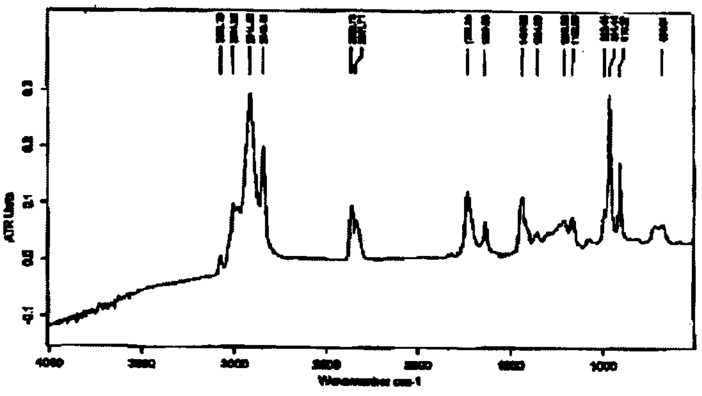


Fig.4.2 FTIR spectrum of CTPB

The characteristic peaks of HTPB are; 3070cm^{-1} (C-H str. of $CH_2=CH_2$), 1640cm^{-1}(C-C str. in -C=CH), 2917.6 cm^{-1}(C-H str of CH_2), 3417.27cm^{-1}(broad, -OH str) and 971.22 & 921.58cm^{-1}(C=C bending). The epoxidised sample (Fig.4.1b ETPB) shows typical absorptions at 911.77cm^{-1} and 1217.77cm^{-1} characteristic of epoxide group. The FTIR spectrum of CTPB (Fig.4.2) shows the following characteristic absorptions of ester at 1732.25 cm^{-1}(C=O str.) and 1206.96 cm^{-1} (C-O str). The broad band around 3400cm^{-1}(-OH str) which slopes into aliphatic C-H str. band around 3073.76cm^{-1} is characteristic of the carboxyl group.

4.3.1 Modification by solid elastomers/functional elastomers

The solubility parameter of NBR (20.11-20.26 (MPa)$^{1/2}$) is close to that of epoxy resin (22.3(MPa)$^{1/2}$) suggesting good compatibility with the resin. There is also sufficient compatibility between PU rubber and epoxy resin.

i. Tensile properties

Referring to Fig.4.3, tensile strength values obtained by adding NBR are higher than that obtained by adding PU elastomer. Tensile strength values reached a maximum on adding progressively larger amounts of rubber, but addition of rubber beyond this point resulted in a reduction of tensile strength. The improvement in tensile strength, in comparison to that of the base resin at all levels of NBR considered, is due to the high degree of compatibility and interaction of NBR with the epoxy matrix. More over, the high molecular weight of NBR imparts greater entanglement and subsequently, tensile strength to the rubber. It can be expected that interactions (like hydrogen bonds) between the nitrile group (-CN) in the rubber and hydroxyl groups on the epoxy chain take place [12]. The fall in tensile strength with increasing rubber content is more for PU rubber.

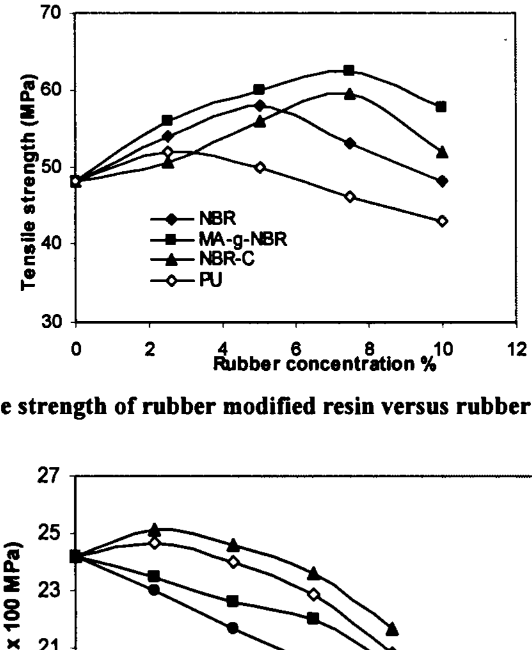


Fig.4.3 Tensile strength of rubber modified resin versus rubber concentration.

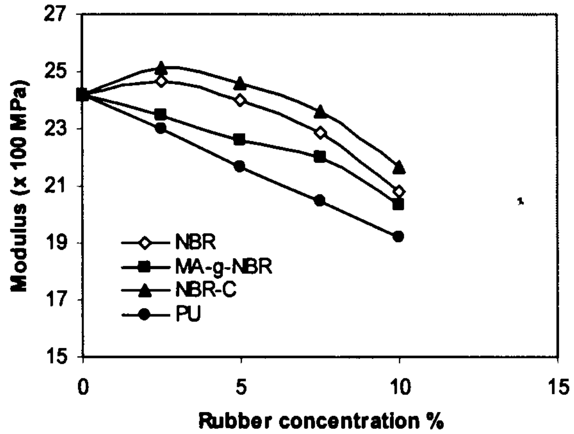


Fig.4.4 Modulus of rubber modified resin versus rubber concentration.

MA-g-NBR and cross-linked NBR were found to be superior to NBR in improving tensile strength. Fig.4.4 shows the effect of elastomers on tensile modulus. For cross-linked NBR (NBR-C) and to some extent NBR, the modulus increases slightly at a lower rubber loading and then decreases with increase in rubber concentration. But for other elastomer samples, modulus decreases with increase in rubber content. At higher rubber content, the rubber may be dissolved to some extent in the epoxy resin and can impart a plasticizing effect. It has been shown that higher acrylonitrile content enhances the compatibility between epoxy and the rubber [13].

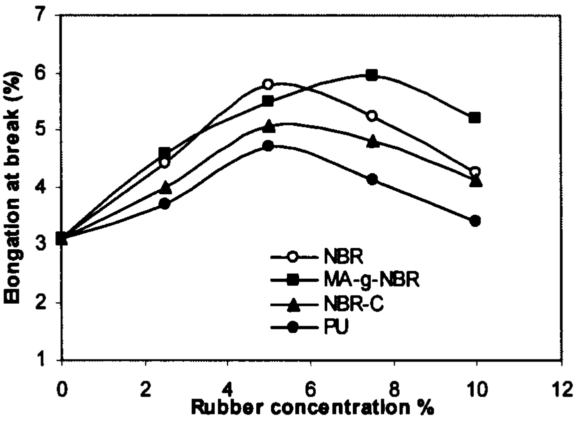


Fig.4.5 Elongation at break of rubber modified resin versus rubber concentration

The effect of elastomer addition on the elongation at break is shown in Fig.4.5. The addition of maleated NBR produced the greatest increase in elongation at break, at 7.5% rubber concentration, indicating maximum compatibility. For PU and the other NBR systems maximum elongation occurred at lower rubber concentrations. Improvement in elongation may be the result of spatial molecular rearrangements possible in the flexible matrix under stress and compatibility. The elastomers presumably behave as inert fillers at higher concentrations.

The variation in toughness of the cured resin with increase in rubber content is shown in Fig. 4.6 as a function of energy absorbed to break. At 7.5% NBR concentration, the energy absorption of the blend is at a maximum (about 174% in excess of that of epoxy resin). This is due to higher compatibility between epoxy and rubber resulting from high acrylonitrile content. The performance of

MA-g-NBR is superior to NBR, NBR-C and PU, due to better dispersion of the rubber phase as particles in the continuous epoxy phase and enhanced interaction between rubber and epoxy backbone. Fig.4.7 shows the variation of impact strength with rubber content. The NBR modified samples showed a steady increase in impact strength with rubber content. With increasing rubber concentration over 7.5wt %, the impact strength increases only marginally or for some cases decreases. At 10 wt % NBR the improvement in impact strength is almost 195% of that of the neat resin. However, cross-linking the same rubber improved impact strength more significantly (about 220% in excess of that of the neat resin.

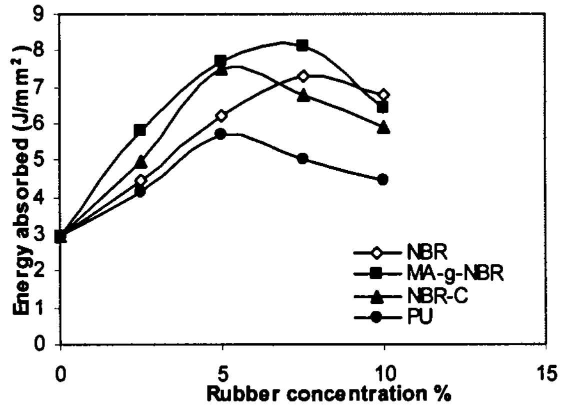


Fig.4.6 Energy absorbed (to break) of rubber modified resin versus rubber concentration

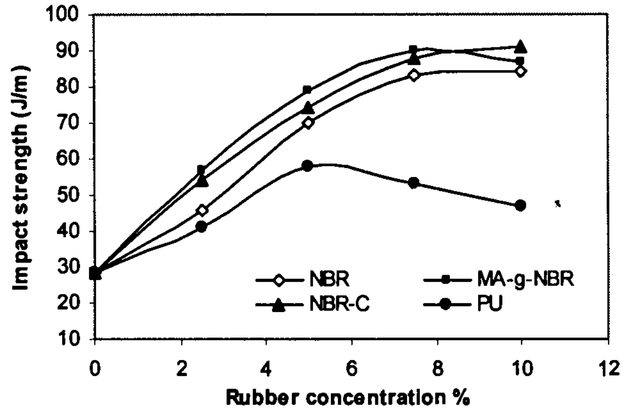


Fig.4.7 Impact strength of rubber modified resin versus rubber concentration

Maleated NBR exhibited maximum impact strength at a lower (7.5%) rubber concentration. The impact strength reaches a maximum at 5% and falls steeply at higher levels of PU rubber. In this case also the blend of MA-g- NBR is superior to other samples. The increase in impact strength results from improved compatibility and better dispersion of the rubber phase in the epoxy phase. The rubber particles absorb the energy of impact and crack propagation is prevented. The results for NBR modified epoxies are comparable with those for the CTBN toughened epoxies as reported in the literature [14].

ii) Flexural properties

Referring to Fig.4.8, the flexural strength of the modified resins is lower compared to the un-modified resin. This is due to the flexibility attained by the blends. Flexural energy increases (Fig.4.9) with rubber content to reach a limiting value around 7.5 % rubber and then decreases very gradually for NBR and MA-g-NBR. This decrease is slightly more in the case of PU and NBR-C. This may be due to the fact that at higher rubber concentrations, the rubber particles behave as ordinary fillers.

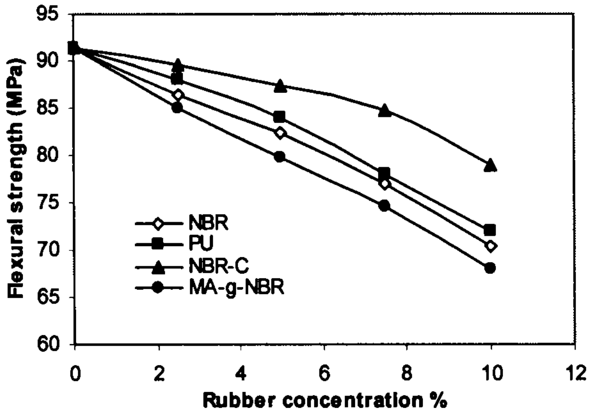


Fig. 4.8 Flexural strength of modified resin Vs rubber concentration

iii. Surface hardness and water absorption

Fig.4.10 indicates a general lowering of surface hardness on addition of all types of elastomers. This is due to the lower surface hardness values of the rubbers [15]. This effect is maximum for PU rubber and minimum for NBR-C. Water absorption of various rubber modified resins is shown in Fig.4.11. PU is far inferior to other elastomers, especially compared to NBR and NBR-C. PU presumably offers more possibilities for hydrogen bonding with water. Table 4.1 summarises the overall effect of adding varying amounts of different elastomers.

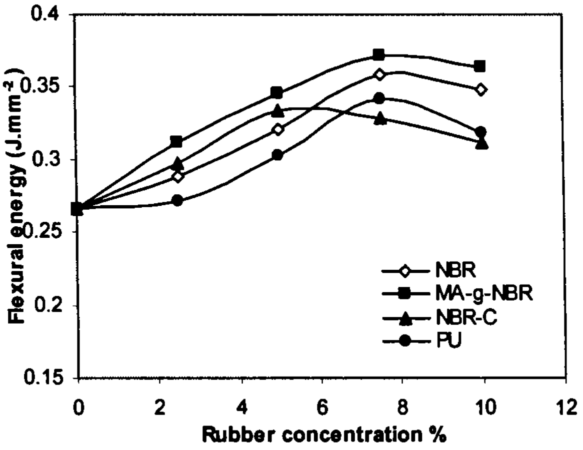


Fig. 4.9 Flexural energy of modified resin Vs rubber concentration

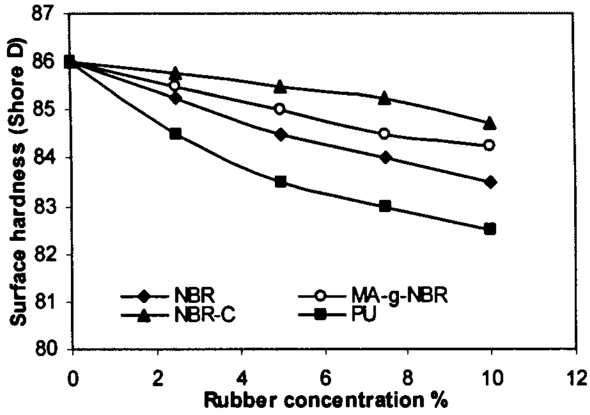


Fig.4.10 Surface hardness of rubber modified resin versus rubber concentration

It is evident that MA-g-NBR enjoys a clear superiority over other elastomers. The toughness properties reach a maximum at about 7.5% rubber concentration beyond which the properties deteriorate. It is possibly due to the fact that when rubber particles come closer to each other than a critical distance a crack path is provided and this hastens the failure rather than delaying it.

iv. Soxhlet extraction and swelling studies

Soxhlet extraction and swelling **data** are given in Table.4.2. Cured rubber modified resin samples yielded very little soluble matter compared to unmodified resin. This suggests that the rubber particles are attached to the resin matrix by strong interaction. The least amount of soluble matter results in the case of MA-g-NBR-modified resin. This may be due to interaction between carboxyl group from the anhydride and epoxy ring/-OH groups.

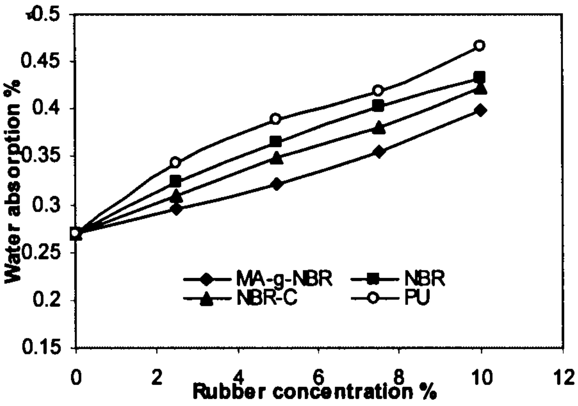


Fig.4.11 Water absorption of rubber modified resin versus rubber concentration

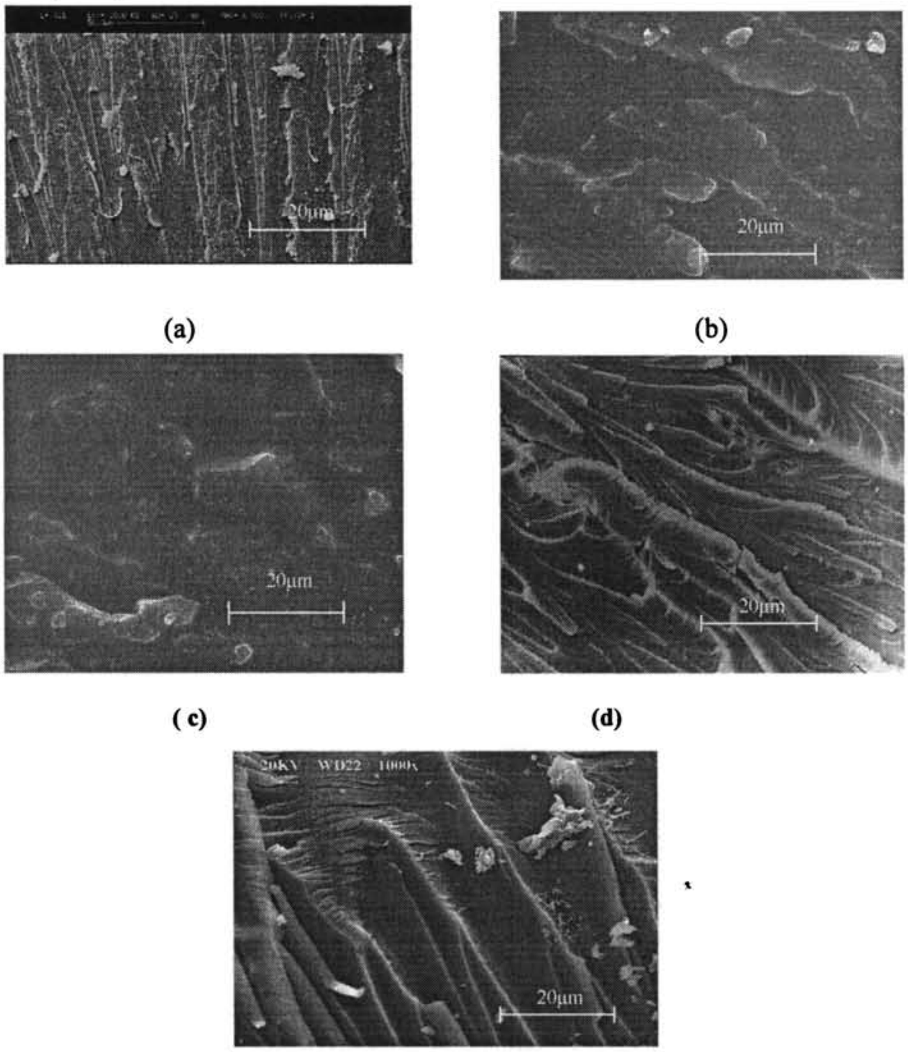
Table 4.1 Summary of properties of DGEBA modified with 0 to 10% elastomers

Property	DGEBA	% Improvement /%composition			
		NBR	MA-g-NBR	NBR-C	PU
Tensile strength (MPa)	48	21/5	30/7.5	24/7.5	10/5
Modulus ($\times 10^2$ MPa)	24.2	-14/10	-18/10	4/2.5	-21/10
Elongation at break (%)	3.10	87/5	94/7.5	65/5	52/5
Energy absorbed to break. J/mm^2	2.95	147/7.5	174/7.5	154/5	93/5
Impact strength (J/m)	28.5	195/10	216/7.5	220/10	102/5
Flexural strength (MPa)	91.45	-23/10	-26/10	-14/10	-21/10
Flexural energy (J/mm^2)	0.2655	35/7.5	41/7.5	26/5	29/7.5
Water absorption (%)	0.270	60/10	48/10	57/10	74/10
Hardness (Shore D)	86	-3/10	-2.1/10	-1.5/10	-4/10

Table.4.2 Soxhlet extraction and swelling data –elastomer (5%) / DGEBA

Samples	DGEBA	NBR	MA-g-NBR	NBR-C	PU
Soluble matter %	5.34	3.704	3.47	3.508	4.15
V_p	0.904	0.931	0.963	0.957	0.922

v. Morphological studies



(a) (b)

(c) (d)

(e)

Fig.4.12. SEM of fracture surfaces of a)DGEBA b) DGEBA/NBR c) DGEBA/NBR-C d) DGEBA/Ma-g-NBR and e) DGEBA/PU

Scanning electron micrographs of unmodified and modified epoxy resin fractured at low deformation rate are shown in Fig. 4.12. The micrograph (a) for the fracture path for unmodified DGEBA resin indicates typical brittle fracture with failure bands and pulled out splinters. NBR modified resin fracture pattern is shown in micrograph (b).Unlike in CTBN toughened epoxy resin (See Fig.4.25e) the micrograph does not indicate any cavitation of rubber particles. The absence of cavitation might be the result of the high molecular weight of solid NBR which imparts greater tensile strength to the rubber. This high tensile strength not only eliminates premature cavitation but gives higher tear energy. Consequently rubber tearing should be a significant contributor to the failure energy of NBR modified epoxy resins. Micrographs (c) and (d) corresponding to respectively cross-linked NBR and MA-g-NBR modified epoxy resins also do not show any signs of cavitaion of rubber. In (d) the fracture paths have a feathery texture with large breadth. A peak like fibril pattern is formed along the rims of the grooves characteristic of ductile fracture. However, PU modified epoxy resin (e) shows long grooves which look like extended cavitation bands. A correlation between toughness and plastic deformation on fracture surfaces suggests a mechanism based on yielding and plastic shear flow of the matrix for rubber modified epoxies [16]. Thus, while multilevel fracture paths and rubber particle deformation (rubber tear) contribute to the toughening mechanism in NBR modified epoxies, cavitation followed by shear yielding explains the toughness of PU modified epoxies.

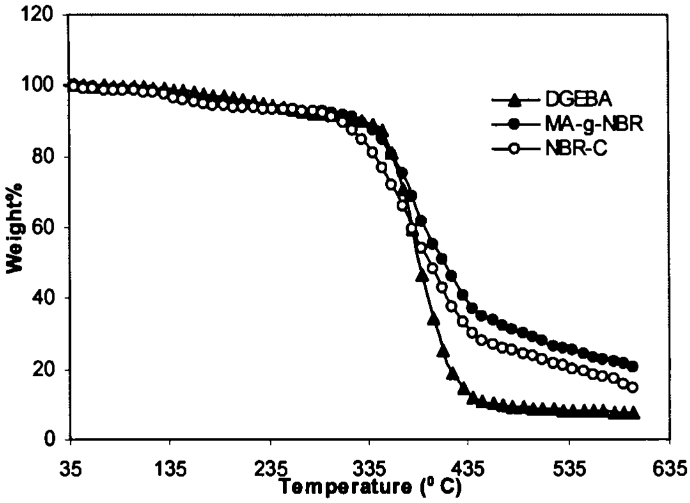


Fig. 4.13 TGA curves of DGEBA and DGEBA/NBR blends

vi) Thermal studies

i. TGA: The TGA curves for the unmodified and NBR modified epoxy resins are shown in Fig, 4.13. MA-g-NBR and NBR-C modified resins yielded 20.36% and 14.64 % residue at 600^{0}C respectively. This reflects their better thermal resistance. Table 4.3 shows relatively better thermal stability for the blends, especially that of MA-g-NBR. This can be due to an increased level of cross-linking / grafting.

Table 4.3 Thermal properties

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue % (600°C)
DGEBA	310.56	386.12	387.24	7.664
DGEBA/ MA-g-NBR	308.43	380.87	398.57	20.36
DGEBA/NBR-C	300.87	376.94	391.22	14.64

ii. DSC: Referring to the DSC thermogram Fig. 4.14, the glass transition temperatures of the DGEBA/NBR blends are slightly lower than that for the un-modified DGEBA resin (70.64 ^{0}C). Incorporation of 5% NBR-C and 5% MA-g-NBR shifts the glass transition temperature to lower values 62.740Cand 64.72^{0}C. This reflects better segmental mobility of the blends due to the presence of rubber. The glass transition of NBR occurs around -43^{0}C.

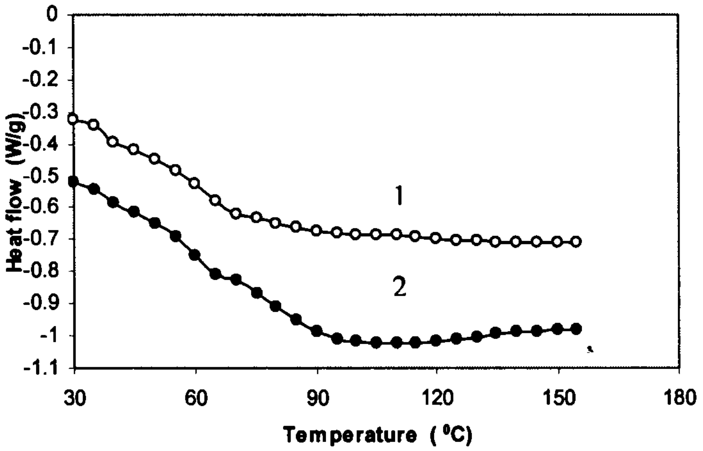


Fig. 4.14 DSC thermograms for 1. DGEBA/MA-g-NBR 2.DGEBA/NBR-C

iii. DMA: Fig. 4.15(a) shows the DMA-tan δ curves for the unmodified and NBR modified epoxy resins. MA-g-NBR (5%) gives a tan δ maximum of 0.3214 at

74.82^{0}C against 0.497 at 71.3^{0}C for the unmodified resin. The DSC and DMA results clearly indicate a two phase morphology in rubber modified epoxy resins because a single phase structure would possess a single T_g for the pure epoxy and the pure rubber. The decrease in height as well as broadening of tan δ peak compared to that of DGEBA indicate significant plasticizing effect of the elastomer

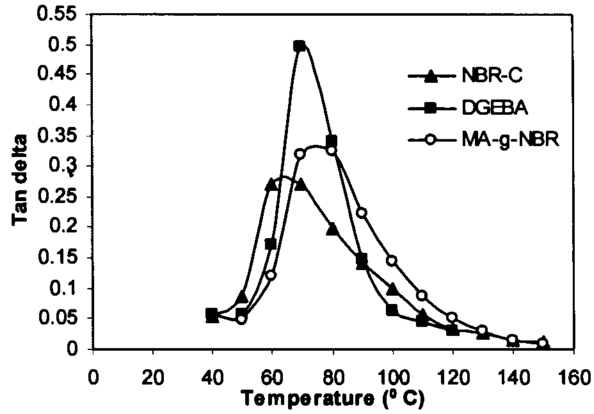


Fig. 4.15a. Tan delta curves for NBR modified epoxy resins

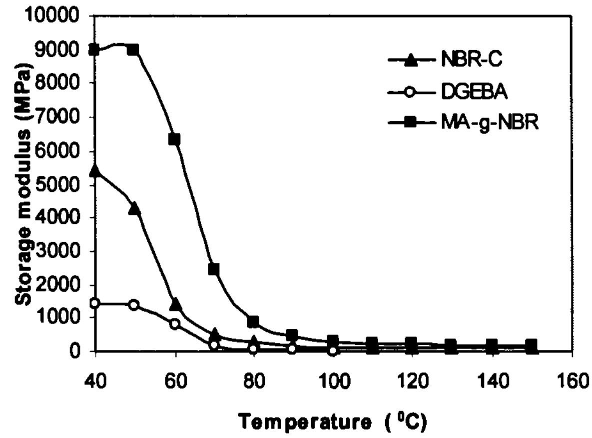


Fig. 4.15b. Storage modulus curves for NBR modified epoxy resins

used in the blend. The presence of the acrylonitrile group enables the rubber to dissolve to some extent in the epoxy resin matrix. Cross-linked NBR is found to shift the damping peak to still lower temperatures. The damping peaks occur at lower tan δ values in the case of these blends due to higher storage moduli (Fig 4.15b). A higher storage modulus corresponds to greater extent of cross-linking. The NBR-C and MA-g-NBR blends show higher loss moduli than the unmodified resin. The maximum in loss modulus (Fig 4.15c) for maleated NBR modified sample corresponds to 65.03 ^{0}C which agrees with the T_g as determined. by DSC. A higher loss modulus causes more mechanical energy to turn into heat via molecular relaxation.

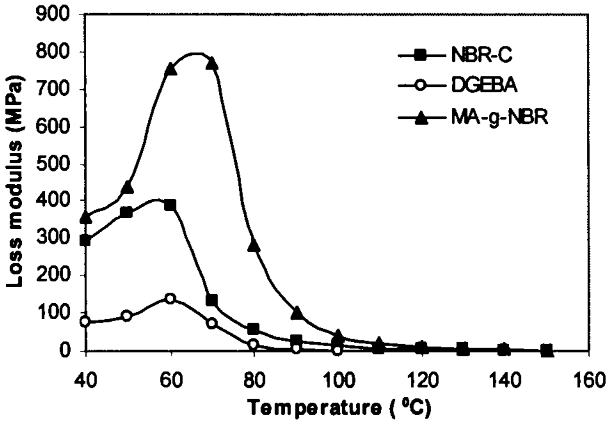


Fig. 4.15c. Loss modulus curves for NBR modified epoxy resins

4.3.2 Modification by reactive liquid elastomers.

In this study, liquid elastomers such as CTBN, HTNR and HTPB were used to modify commercial DGEBA resin. CTBN is highly compatible with the epoxy resin. But it was difficult to incorporate more than 10% of HTPB and HTNR due to their lower compatibility. It is known that the conditions required to promote a hydroxyl-epoxy reaction often lead to self polymerisation of the epoxy resin [16]. However, this problem has been solved to some extent by epoxidising HTPB (ETPB) which is highly compatible with epoxy resin[17]. Similarly HTPB has been esterified in presence of maleic acid to form CTPB.

i) Tensile properties

In Fig.4.16 tensile strength values obtained by adding CTBN and CTPB are significantly higher than those obtained by adding other functional elastomers. Tensile strength reaches a maximum at 7.5 -10% rubber concentration on adding progressively larger amounts of rubber [18]. Beyond this point, addition of more rubber results in lowering of tensile strength. The improvement in tensile strength over that of the base resin at all percentages of CTBN and CTPB considered is due to the high degree of compatibility and strong interaction of carboxyl group with the epoxy at the higher post cure temperature(120^{0}C). The presence of the amine hardener may also catalyse epoxy-carboxy interaction to some extent.

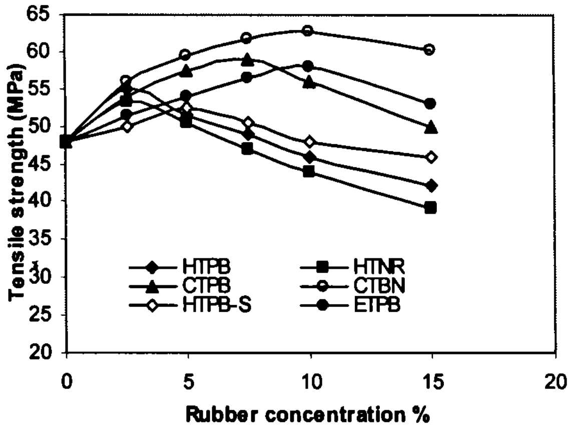


Fig.4.16 Tensile strength of rubber modified resin versus rubber concentration

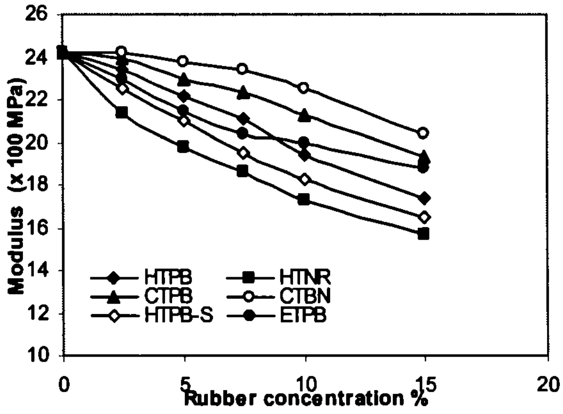


Fig.4.17 Modulus of rubber modified resin versus rubber concentration

The maximum strengthening takes place at a higher rubber concentration (10%) in the case of CTBN and ETPB. HTNR, HTPB and silane coupled HTPB (HTPB-S) show maximum strength at lower concentrations. Tensile strength values of HTNR and HTPB are lower, presumably due to low molecular weight of the elastomers. Fig.4.17 shows the effect of elastomers on tensile modulus. The change in modulus on addition of elastomers is maximum for HTPB-S and HTNR. HTNR causes a dramatic fall in modulus of the resin. This is attributed to several factors like the presence of pendent methyl groups, comparatively lower molecular weight and a lower extent of interaction with the matrix.

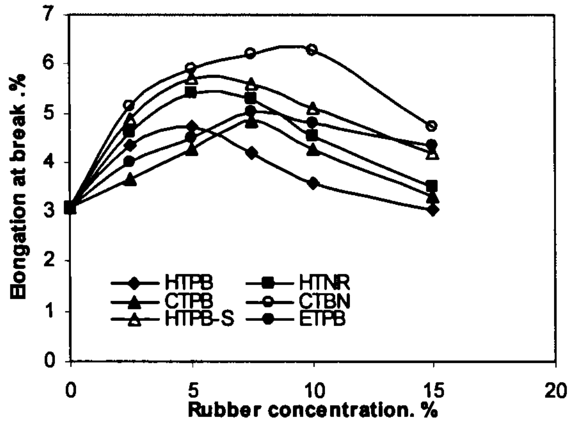


Fig.4.18 Elongation (at break) of rubber modified resin versus rubber concentration

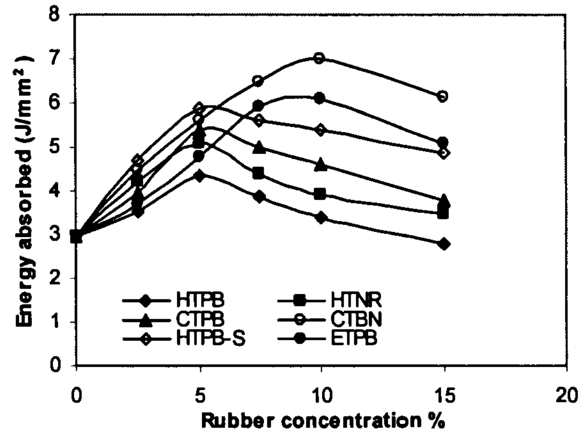


Fig.4.19 Energy absorbed (to break) of modified resin versus rubber concentration

The effect of elastomer addition on the elongation at break is shown in Fig.4.18. The greatest improvement in elongation was for 10% CTBN. The variation in energy absorbed (to break) by the cured resin with rubber content is shown in Fig.4.19. The effect of adding CTBN is far superior to all other elastomers. A 10% CTBN blend shows 137% improvement in energy absorption. Higher tensile strength and elongation increase the toughness of CTBN modified resin. This can be attributed to better dispersion of the rubber phase as particles in the continuous epoxy phase and to possible chemical interaction [19].

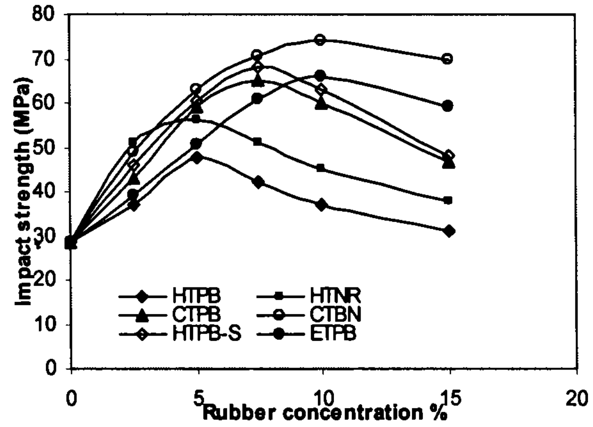


Fig.4.20 Impact strength of rubber modified resin versus rubber concentration

Fig.4.20 shows the variation in impact strength with rubber concentration. In this respect also CTBN shows maximum improvement (160% of that of the control resin) at a concentration of 10%. Both CTPB and HTPB-S show almost identical behaviour. In this case also the superiority of HTNR over HTPB can be explained by the enhanced strength and flexibility of HTNR. The increase in impact strength results from better dispersion of the rubber phase in the form of particles. The rubber particles absorb the energy of impact and prevent crack propagation.

ii. Flexural properties

Referring to Fig.4.21 the flexural strength values of rubber modified resins are lower than that of the neat resin. In the case of HTPB, flexural strength increased slightly at a very low concentration (2.5%) and then decreased gradually with rubber content. All the other elastomers showed a regular decrease in flexural strength with increase in rubber concentration. The flexural energy (Fig.4.22) was found to increase with rubber content to reach almost a limiting value around 10 wt % of CTBN and HTNR beyond which no further noticeable increase was observed. While ETPB and HTPB-S showed a steady increase in flexural energy with rubber content, HTPB and CTPB registered slight drop after reaching a maximum around 10% concentration. These results point to significant reduction in the stiffness of the blends which results from the introduction of softer segments in the cured resin matrix

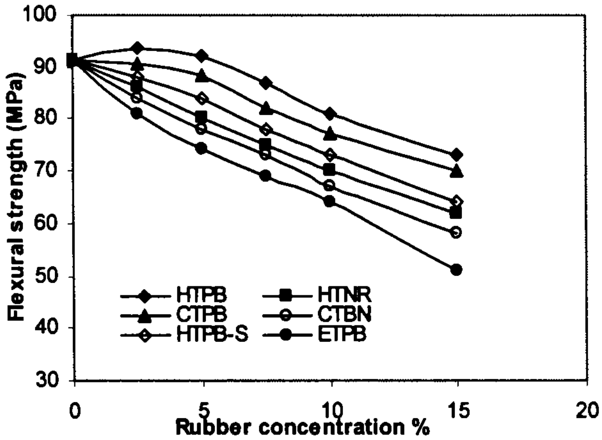


Fig.4.21 Flexural strength of rubber modified resin versus rubber concentration

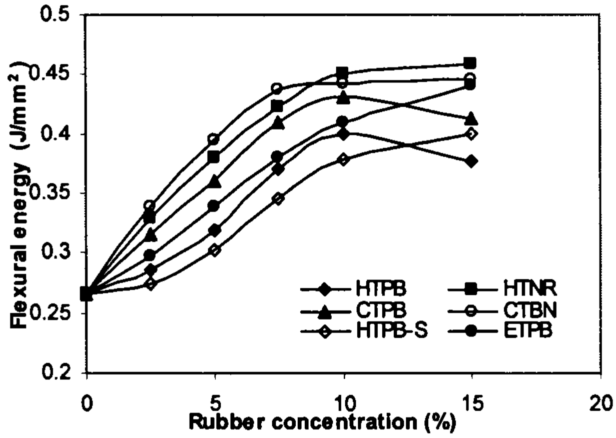


Fig.4.22 Flexural energy of rubber modified resin versus rubber concentration

iii. Surface hardness and water absorption

Fig.4.23 indicates a general lowering of surface hardness on addition of all types of elastomers. This could be due to the lower surface hardness values of the elastomers. This effect is maximum for HTPB and minimum for CTBN and ETPB.

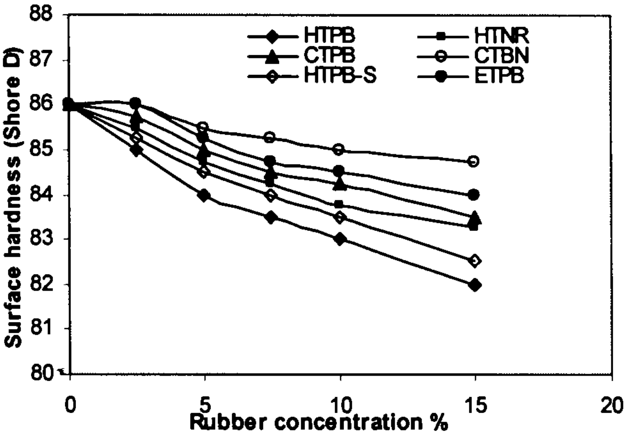


Fig.4.23 Surface hardness of rubber modified resin versus rubber concentration

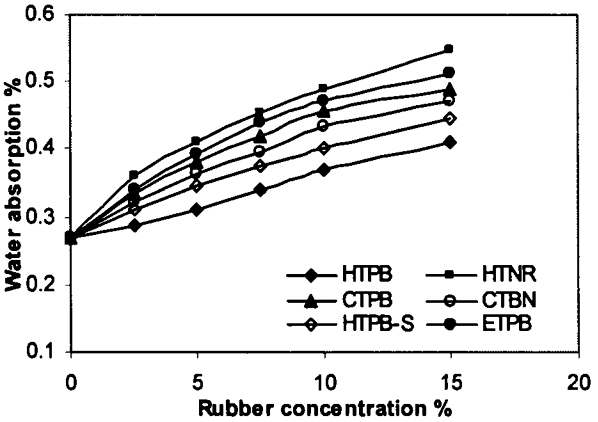


Fig.4.24 Water absorption of rubber modified resin versus rubber concentration

Water absorption of various modified resins is shown in Fig.4.24. HTNR showed maximum water absorption. The non-rubber constituents of natural rubber can be responsible for this. CTPB and EPPB also show substantial water absorption possibly due to the presence of polar groups. Table 4.4 summarises the properties of epoxy/liquid functional elastomer systems. The improvement in each property and the corresponding composition are also tabulated.

iv. Soxhlet extraction and swelling studies

Soxhlet extraction studies show that very little soluble matter could be extracted from functional rubber-modified DGEBA compared to unmodified

DGEBA. This suggests that functional elastomers are tightly held to the epoxy matrix by grafting and cross-linking between elastomer chains and epoxy chains. Functional elastomers can also influence properties of epoxy resin either by causing chain extension or by increasing inter-chain attraction by dipole-dipole interactions. The grafting is indicated by higher values of V_p during swelling studies.

Table 4.4 Summary of properties of DGEBA/ liquid functional elastomer blends

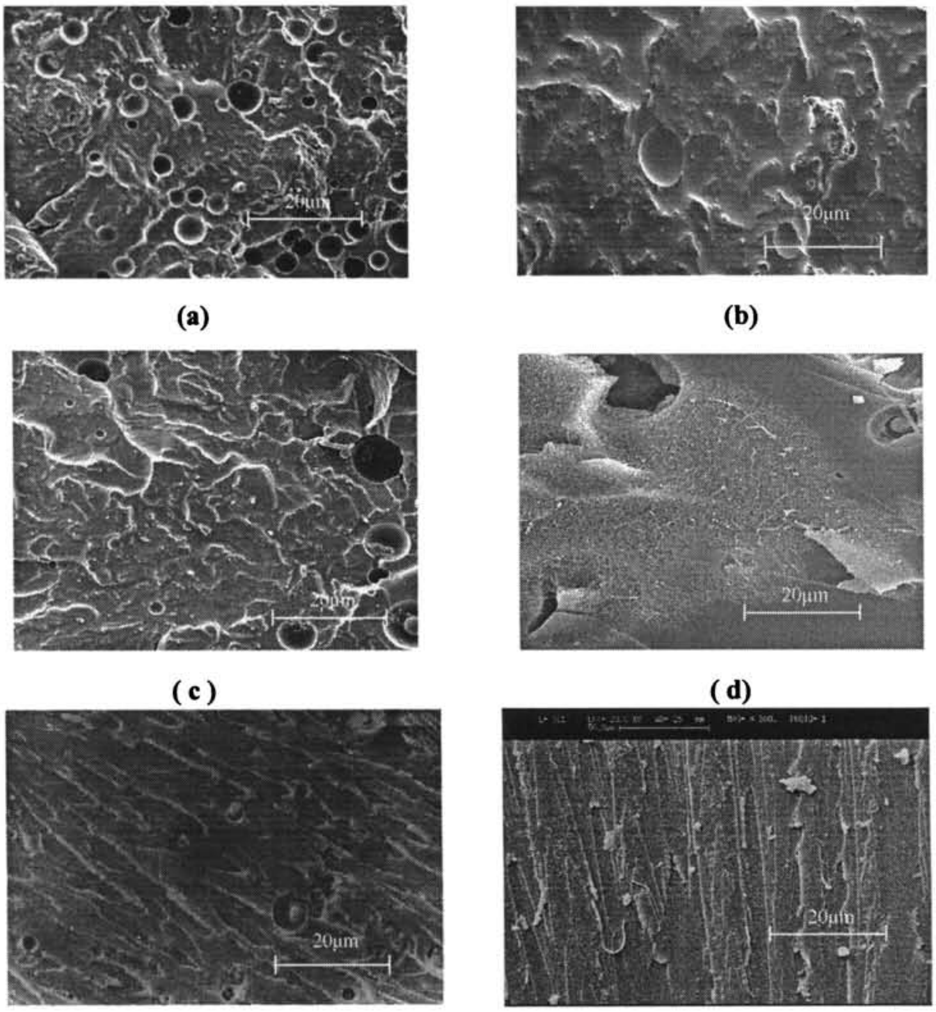
Property	DGEBA	% improvement / elastomer concentration (wt %)					
		HTPB	HTNR	CTPB	CTBN	HTPB-S	ETPB
Tensile strength (MPa)	48	15/2.5	11/2.5	23/7.5	31/10	10/5	21/10
Modulus ($\times 10^2$ MPa)	24.2	-24/15	-35/15	-21/15	-16/15	-30/15	-22/15
Elongation at break. %	3.1	52/5	75/5	56/7.5	102/10	84/5	63/7.5
Energy absorbed to break .(J/mm^2)	2.95	48/5	73/5	84/5	137/10	99/5	109/10
Impact strength.(J/m)	28.5	67/5	98/5	128/7.5	161/10	139/7.5	132/10
Flexural strength. MPa	91.45	3/2.5	-33/15	-23/15	-38/15	-30/15	-44/15
Flexural energy. J/mm^2	0.2655	53/5	72/15	62/10	67/15	54/15	70/15
Water absorption (%)	0.270	51/15	103/15	81/15	74/15	65/15	89/15
Hardness (Shore D)	88	-5/15	-3.5/15	-3/15	-1.5/15	-4/15	-2.5/15

Table.4.5 Soxhlet extraction & swelling data- DGEBA /elastomer (5%)

Samples	DGEBA	HTPB	HTNR	CTPB	CTBN	HTPB-S	ETPB
Soluble matter %	5.34	3.62	3.04	4.32	4.05	3.43	3.86
V_p	0.904	0.915	0.958	0.95	0.941	0.97	0.93

c) Morphological studies

Scanning electron micrographs of different elastomer modified epoxy resins fractured at low deformation rate are shown in Fig.4.25. All the fracture surfaces of the blends are characterised by a morphology in which the rubber is segregated into spherical shaped domains dispersed in the epoxy matrix. A bimodal distribution of particle size and massive stress whitening are seen in most cases. Unlike in NBR modified samples, these blends show extensive cavitations associated with stress whitening. Micrograph (b) representing epoxy/ETPB 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 elastomer particles [20]. Most of the large holes however contain round inclusions which are hard. The initiation and growth of voids in the rubbery particles give rise to stress whitening often observed before crack tip and on the fractured surface. Referring to CTBN modified resin (e), the fracture surface shows furrows and cavitation. The circular depressions represent the sites of rubber domains. Excessive stress whitening is also observed. The fracture surface of CTPB modified resin (d) shows



(a) (b)

(c) (d)

(e) (f)

Fig.4.25 Scanning electron micrographs of fracture surfaces of a) DGEBA/HTPB b) DGEBA/ETPB c)DGEBA/HTNR d)DGEBA/CTPB e) DGEBA/CTBN and f) DGEBA

broader and less continuous fracture paths. Compared to the fracture surface of the neat resin *(f)*, *the elastomer blends show distinct signs of energy absorption by cavitation, stress whitening and broadening of fracture paths.*

vi. Thermal properties

i.TGA: The TGA curves for various DGEBA/rubber systems are given in Fig.4.26. Evidently the blends possess better thermal properties than the neat resin. Of the rubbers, CTBN gives the largest amount of residue (12.02%) at 600^{0}C and the epoxy HTPB (ETPB) the least (8.077%) as against 7.664% for DGEBA. DGEBA and DGEBA/CTBN show 367.24^{0}C and 396.42^{0}C as half maximum temperature respectively.

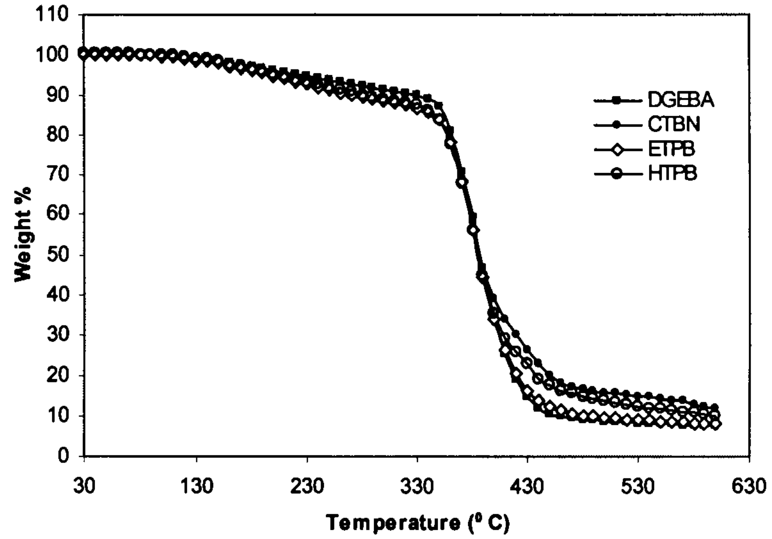


Fig. 4.26. TGA curves for DGEBA modified by liquid functional elastomers

ii. DSC: DGEBA/ liquid functional elastomer blends gave endothermic transitions during DSC analysis. While DGEBA showed a T_g of 70.64^{0}C, its HTPB, ETPB and CTBN blends showed slightly higher T_g values namely 70.83^{0}C,72.09^{0}C and 71.24^{0}C respectively. Cross-linking may be the reason for the enhanced T_g values.

iii. DMA: Fig.4.27a shows the Tan δ curves for the rubber modified epoxy resins. The damping peaks occur at 81.04^{0}C, 79.34^{0}C and 71.44^{0}C corresponding to tan δ values 0.4502, 0.4321 and 0.2588 for HTPB.ETPB and CTBN modified resins respectively. For CTBN modified resin the temperature of maximum tan δ agrees with the T_g as per DSC. The modified samples exhibit lower tan δ values than that for the unmodified resin (0.497 at 71.3^{0}C). The considerable decrease in height of tan δ peak for CTBN modified resin indicates appreciable plasticizing action offered by CTBN rubber. The loss modulus peaks (Fig 4.27b) occur at 72.76°C and 72.31°C for HTPB and ETPB respectively which agree well with the Tg values recorded as per DSC measurements. In general the blends (but for CTBN) show increased loss moduli values compared to the control resin. A higher loss modulus causes more mechanical energy to turn into heat via molecular relaxation. The blends show higher storage moduli (Fig 4.27c) than the neat resin which indicates increased elastic behaviour.

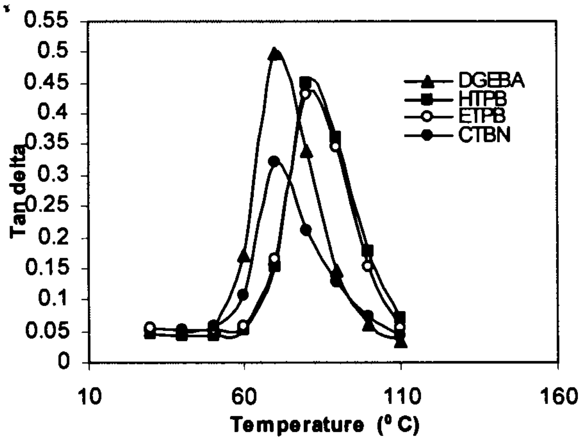


Fig.4.27a. Tan δ curves for unmodified and rubber modified epoxy resin

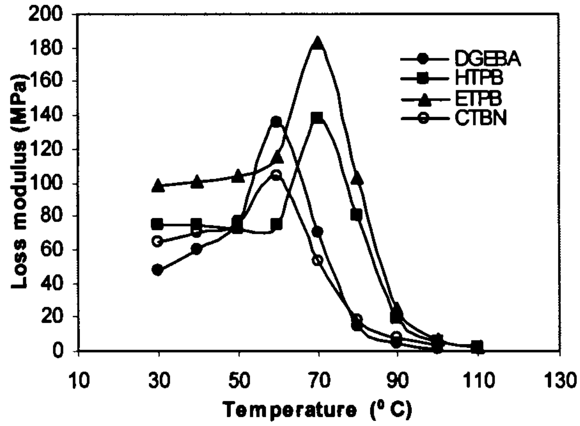


Fig.4.27b. Loss modulus curves for unmodified and rubber modified epoxy resin

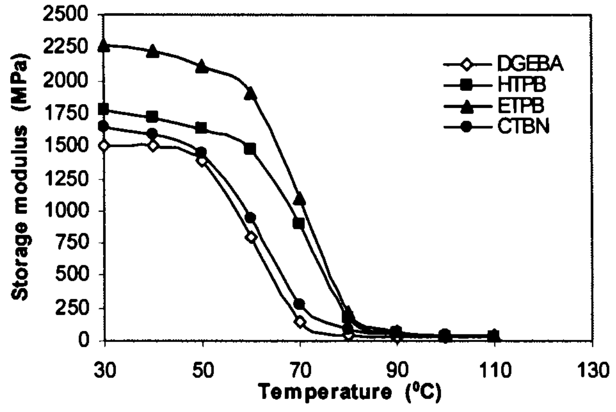


Fig.4.27c. Storage modulus curves for unmodified and rubber modified epoxy resin

4.3.3. Effect of bisphenol A on the modification of epoxy resin by liquid elastomers

An immediate molecular weight increase can be obtained for low molecular weight epoxy resin on reacting with bisphenol A (BPA) and curing with amine hardeners [19]. The resultant resin is superior to DGEBA in mechanical and thermal properties. Two competitive processes have been shown to take place; chain extension and cross-linking. The fracture energy of CTBN modified epoxy resin was found to be significantly increased in presence of added BPA [21]. The influence of BPA in rubber modified epoxies has been investigated specifically by Levita et.al [10]. The un-modified DGEBA is brittle because of a of post yield rigidity. But, in presence of BPA yielding is followed by the formation and propagation of a neck in the specimen. Rubber modified formulations greatly benefit from the greater ductility produced by BPA. The greater toughness of ternary DGEBA-BPA-rubber blends over that of binary DGEBA-rubber systems was supposed to arise from modifications of soft-phase geometric parameters. According to Riew [22], the effect of BPA is in the production of a bimodal particle size distribution. As the molecular weight of the resin increases on reaction with BPA, the free energy of mixing decreases rapidly and the separation of a larger amount of soft phase is favoured.

BPA acts as a toughener partly because the volume fraction of the separated phase tends to be higher than in binary blends. BPA is a good catalyst for epoxy-rubber reaction and the high reaction rate causes some rubber to remain undissolved before gelation. This may give rise to complex morphologies. However, the most important effect of BPA consists in modifying the properties of the matrix. Since tough systems are more sensitive to deformation rate [23] than brittle ones, as a crack propagates, most of the energy is absorbed to deform the matrix. In this study, DGEBA has been modified by different liquid functional elastomers in the presence of varying amounts of BPA and the properties of the blends were studied. Rubber compositions which gave maximum improvement in properties in earlier studies (Section 4.3.2; 10wt%CTBN, 5wt%HTPB and 5wt%HTNR) were selected for this purpose.

i. Tensile properties.

Fig.4.28 indicates the effect of varying amounts of BPA on the tensile strength of DGEBA/ 10%CTBN, DGEBA/5%HTPB and DGEBA/5%HTNR. Tensile strength increased sharply with increase in BPA content up to 10-15% BPA beyond which only a marginal change was observed. DGEBA/BPA/CTBN ternary system was found to be far superior to the others in this aspect. Tensile strength increased by 58% at 15% BPA compared to DGEBA/CTBN binary blend (31%). An increase in molecular weight of the matrix resin is responsible for the enhanced tensile strength of these ternary blends. The presence of additional BPA units may also alter the spacing of the cross-links and take it to optimal values. HTNR and HTPB exhibited maximum strength at a lower BPA loading.

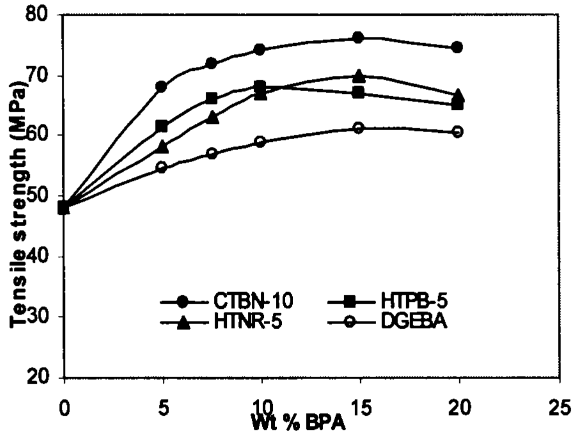


Fig.4.28.Tensile strength of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

Figure 4.29 gives the variation in modulus of DGEBA/rubber by the addition of increasing amounts of BPA. All the samples show lower modulus than that of the control resin. Though the modulus values did not vary much on adding BPA, the extent of decrease in modulus was less than that in the case of corresponding binary blends. This may be due to an immediate increase in molecular weight of the matrix.

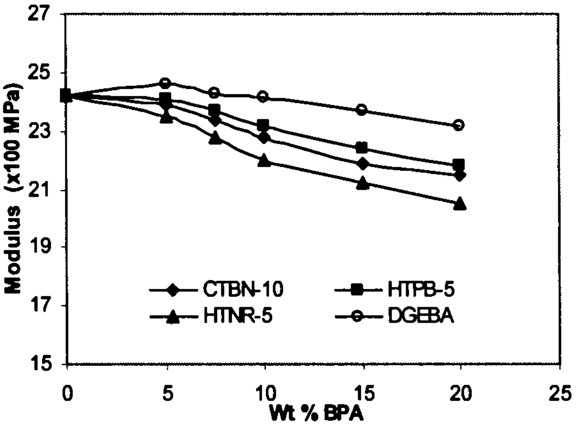


Fig.4.29. Modulus of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

Fig. 4.30 indicates the variation of elongation at break of epoxy/rubber blends in presence of added BPA. All the ternary blends except that of HTPB showed increase in elongation at 10% added BPA. DGEBA/BPA/CTBN blend showed

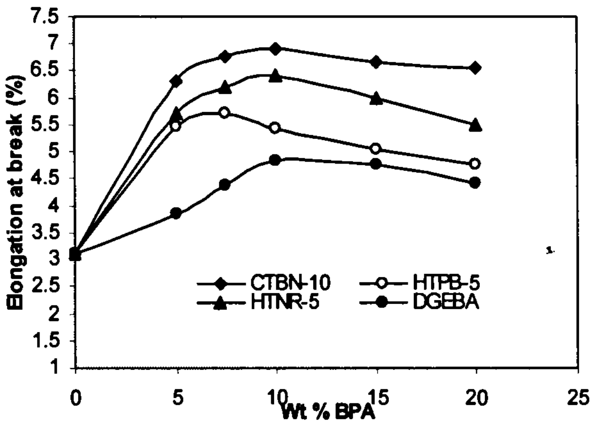


Fig.4.30. Elongation at break of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

122% increase in elongation compared to 102% in the absence of BPA. This can be due to straightening of the entangled chains. An increased entanglement of the polymer chains is possible due to chain extension by BPA. The extended matrix chains can induce greater spatial molecular rearrangements under the influence of an applied stress. The ternary blend of HTNR was found to have better elongation than HTPB blend. This is probably due to the presence of the pendant methyl groups in HTNR

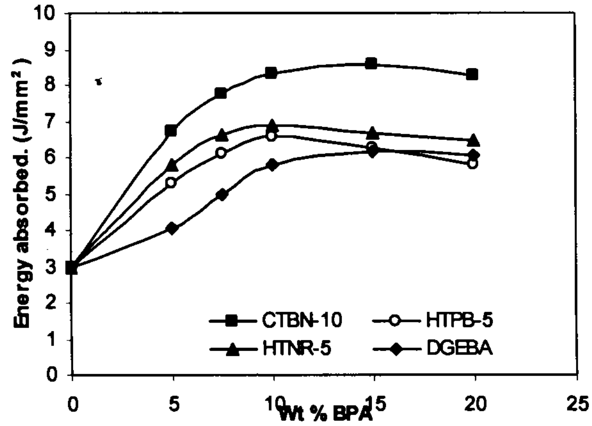


Fig.4.31. Energy absorbed (to break) of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

Referring to Fig.4.31the energy absorption (to break) by the ternary blends are higher than those by the binary epoxy/rubber blends as well as the neat resin. Hence, the addition of BPA as a chain extender into epoxy-rubber system increases the toughness considerably. DGEBA/BPA/CTBN showed a maximum improvement of 191% at 15% BPA compared to 137% by DGEBA/CTBN blend in energy absorption. Beyond 15% BPA, energy absorption does not vary much. It may be surmised that at 15% BPA content, the spacing between cross-links reaches an optimum value as mentioned earlier. In this case also, the HTNR blend was found to be superior to HTPB blend. The presence of BPA makes the volume fraction of the separated phase higher than in binary blends. Also, BPA is a good catalyst for epoxy- rubber reaction and hence the high reaction rate causes some rubber to remain un-dissolved before gelation resulting in increased phase separation.

Fig. 4.32 indicates the variation of impact strength with the addition of increasing amounts of BPA into epoxy/rubber blends. While the impact strength of

DGEBA increases by 82% for DGEBA/CTBN blend, it increases by about 160% in presence of 10% BPA. The chain extended matrix will have a greater extent of cross-linking and thus the grafted rubber particles absorb the energy of impact and prevent crack propagation.

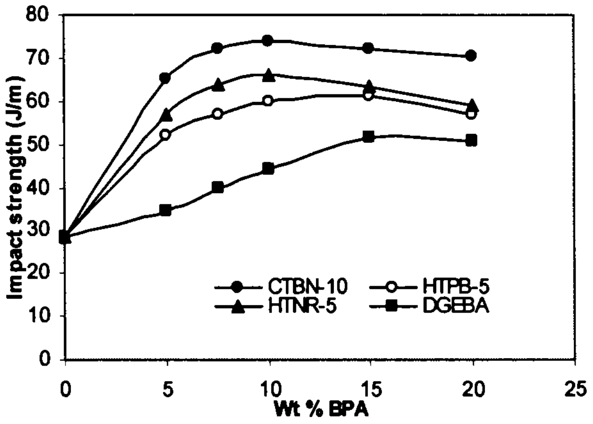


Fig.4.32. Impact strength of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

ii. Flexural properties

Referring to Fig. 4.33, the flexural strength values of DGEBA/BPA/ rubber ternary blends are lower than those of the unmodified resin. In addition to the presence of rubber, separation of soft phases [21] induced by BPA makes the cured matrix flexible. The DGEBA/BPA/CTBN blend showed maximum lowering in flexural strength indicating its improved flexibility Fig.4.34 shows the steady increase in flexural energy with BPA content. The DGEBA/BPA/ CTBN system showed maximum improvement (95% of the neat resin) in flexural energy compared to DGEBA/CTBN system (67%of the neat resin). The HTNR blend was superior to HTPB. The maximum displacement values also showed a similar trend. These results indicate the enhanced flexibility and ductility attained by the DGEBA/rubber blends in presence of BPA as a chain extending agent.

Table 4.6 shows the summary of the mechanical and flexural properties of BPA modified epoxy-rubber systems. The %improvement in each property is shown with the concentration of BPA.

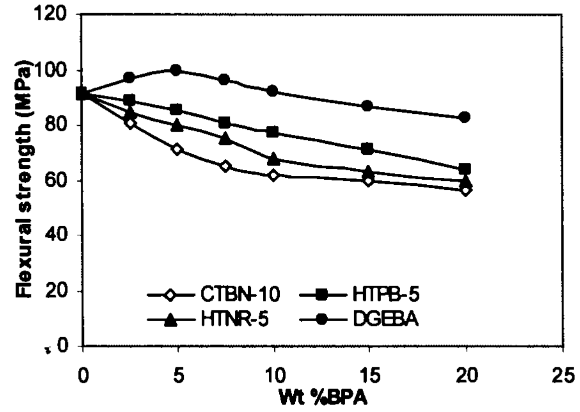


Fig.4.33. Flexural strength of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

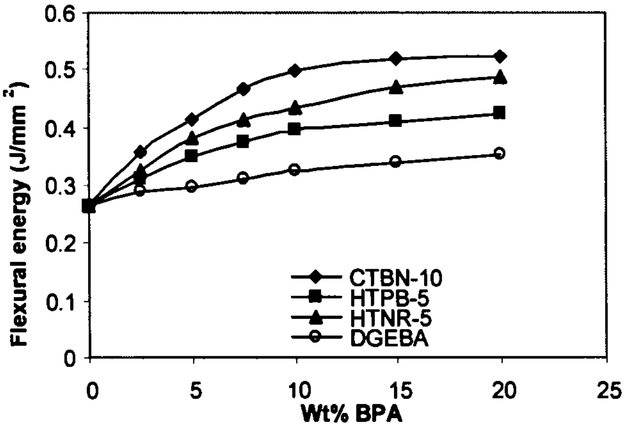
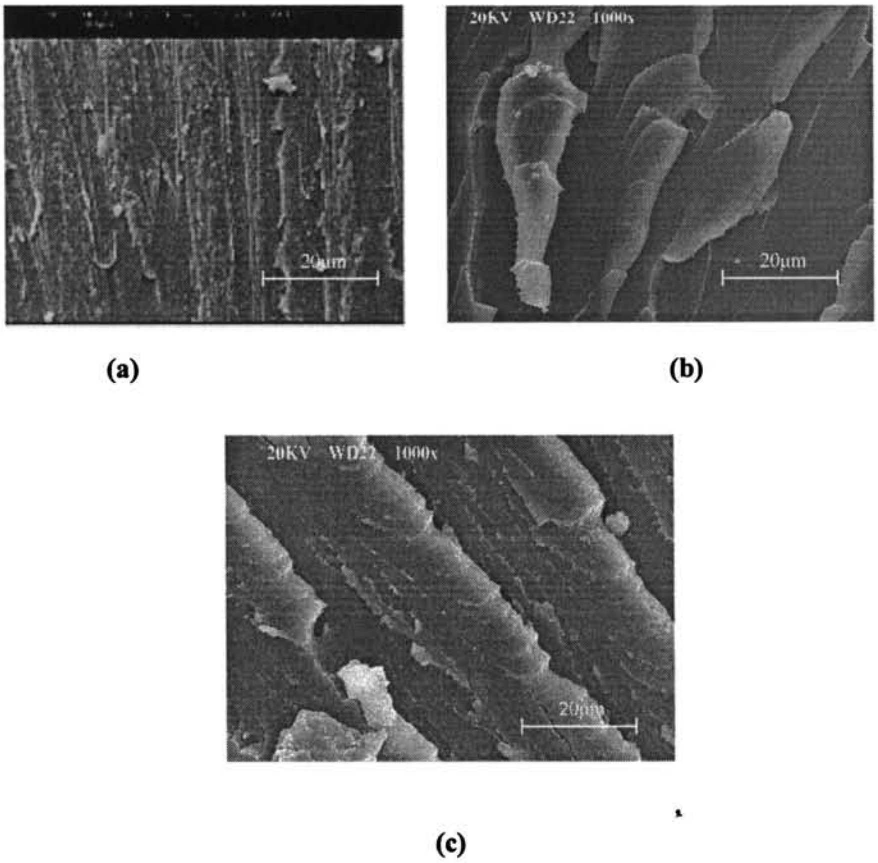


Fig.4.34. Flexural energy of DGEBA/BPA /rubber blends containing 10% CTBN, 5%HTPB and 5%HTNR Vs BPA concentration

iii. Morphological studies

Fig. 4.35(a) shows the SEM of the fractured surface of commercial DGEBA resin. Addition of 10% BPA has induced sufficient ductility to the matrix as evidenced by the micrograph (b). Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure. Figure(c) shows the fractured surface of the ternary blend DGEBA/BPA/CTBN. Cavities formed by the rubber particles are seen particularly along the parallel ridges formed as a result of enhanced energy absorption. Such cavitation in presence of shear yielding has been observed in many rubber modified epoxies. 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. Thus, rubber modified epoxy formulations greatly benefit from the greater ductility produced by BPA.



(a) **(b)**

(c)

Fig.4.35. Scanning electron micrographs of a) DGEBA b) DGEBA/ 10%BPA and c) DGEBA/ 10% BPA/ 10%CTBN

Table 4.6 Properties of DGEBA/BPA/rubber blends

Property	Neat	*% Improvement /%composition*			
		Neat / BPA	CTBN/BPA	HTNR/BPA	*HTPB/BPA*
Tensile strength (MPa)	48	28/15	57-8/15	46/15	*42/10*
Modulus (x 100 MPa)	24.2	-4/20	-12/20	-15/20	*-10/20*
Elongation at break (%)	3.10	56/10	122/10	106/10	*84/7.5*
Energy absorbed ($J.mm^{-2}$)	2.95	107/15	191/15	134/10	*122/10*
Impact strength ($J.m^{-1}$)	28.5	82/15	160/10	132/10	*114/15*
Flexural energy ($J.mm^{-2}$)	0.265	33/20	95/20	83/20	*59/20*
Flexural strength (MPa)	*91.45*	*11/5*	*-39/20*	*-34/20*	*-30/20*

iv. Thermal properties

i. DSC: Fig.4.36 shows the DSC thermograms of DGEBA/10%BPA and DGEBA/10%BPA/10%CTBN. For the BPA-modified epoxy resin an endothermic transition was observed at 71.96 ^{0}C which is quite close to the T_g of the neat resin (70.64^{0}C). This shows that addition of BPA does not alter the T_g much. However, the glass transition temperature of DGEBA/BPA/CTBN system (78.59^{0}C) was found to be slightly higher which indicates additional cross-linking in the ternary blend.

ii. DMA: Fig. 4.37a shows the DMA –tan δ curves for BPA modified DGEBA and DGEBA/BPA/CTBN systems. The damping peak for DGEBA/10%BPA occurs at 89.25^{0}C corresponding to tan δ =0.5212. Incorporation of 10% CTBN to the above shifts the tan δ maximum (0.3573) to a higher temperature of 96.1^{0}C. These values agree with the DSC data.

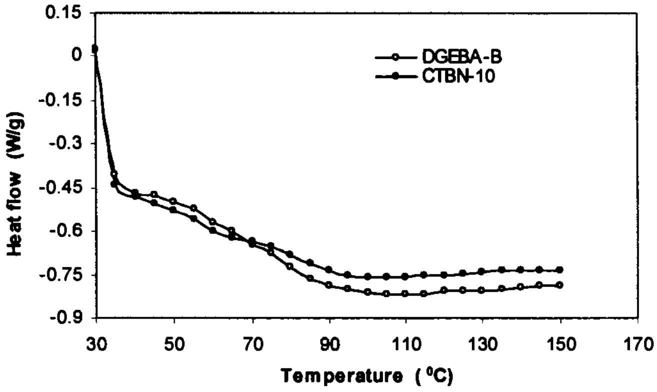


Fig. 4.36 DSC thermogram of DGEBA/10%BPA and DGEBA/10%BPA/10%CTBN

A decrease in the height of tan δ for the ternary system indicates significant plasticizing effect of CTBN. That is, the CTBN gets dissolved to some extent in the epoxy resin and exerts some sort of a dilution effect. This is in fact a direct consequence of a simultaneous fall in both loss modulus (E") and storage modulus (E') in presence of rubber. The loss modulus maxima (Fig 4.37b) for DGEBA/BPA and its ternary CTBN blend occur at 81.14°C and 88.69°C respectively. The CTBN blend also shows lower storage modulus (Fig.4.37c) than that of the BPA modified DGEBA.

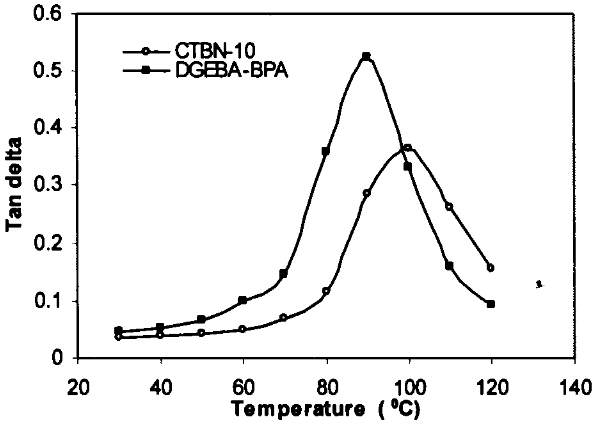


Fig.4.37a.Tan δ curves for DGEBA /BPA and DGEBA/ BPA/ 10%CTBN

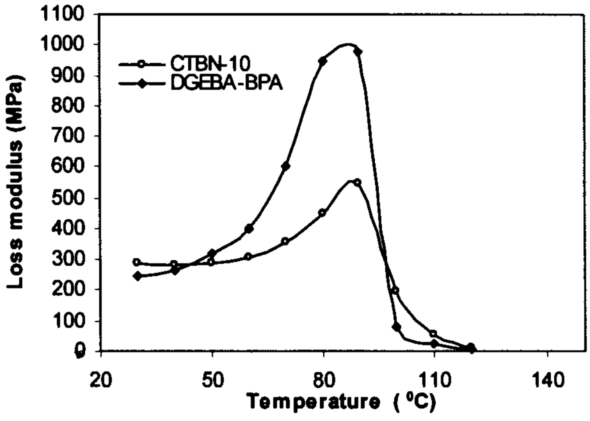


Fig.4.37b. Loss modulus curves for DGEBA/BPA and DGEBA/ BPA/10%CTBN

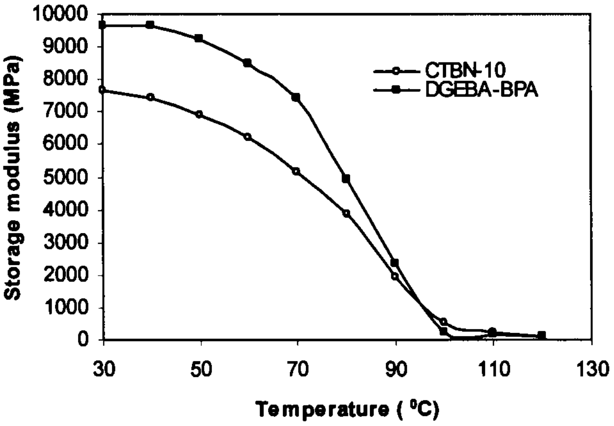


Fig.4.37c. Storage modulus curves for DGEBA/BPA and DGEBA/ BPA /10% CTBN

4.4 Conclusions

High molecular weight MA-g-NBR with 33% acrylonitrile content is an effective toughening agent for commercial epoxy resin. Thermal studies clearly indicate two phase morphology in NBR modified epoxy system. NBR and MA-g-NBR enhance the energy absorption (to break) considerably (147% and 174% in excess of the control resin respectively). The impact toughness of DGEBA is improved by 216% in presence of 7.5% maleated NBR. Cross-linking of NBR (Section4.2.1 (b)) further increases the impact toughness by 220% at a higher concentration. The fracture surfaces show multilevel fracture paths in contrast with cavitated and smooth fracture surfaces of CTBN modified epoxies. Rubber tearing and bridging predominate the toughening mechanism of NBR modified epoxies. PU rubber modifies the epoxy matrix to a lower extent compared to NBR and its different derivatives.

Of the different reactive liquid rubbers CTBN is, by all means, most effective for toughening epoxy system. CTBN is highly compatible with epoxy resin and at10% loading it shows maximum improvement in tensile and flexural properties. HTNR gives better results than HTPB and both are less compatible with epoxy resin beyond 10% concentration. Compatibility as well as inter-component grafting of HTPB with epoxy resin is improved by re-functionalization of the hydroxyl groups by way of epoxidation (ETPB) and esterification (CTPB). These derivatives produce better results in mechanical and thermal properties than HTPB when blended with DGEBA resin. Further, the inclusion of small amount of silane coupling agent (SCA) improves the mechanical properties of the HTPB blend.

Incorporation of bisphenol A is found to magnify the effect of rubber. A 10% CTBN/DGEBA system increases the energy absorption (to break) by 190 % when 15% BPA is added. In the absence of added BPA, the same system shows lesser improvement in toughness (only 137%). The ternary blends such as DGEBA/5%HTNR/BPA and DGEBA/5%HTPB/BPA also exhibit enhanced tensile and toughness properties. This is because rubber modified epoxy formulations greatly benefit from the greater ductility offered by BPA.

References.

1. A.J. Kinloch, In *Rubber Toughened Plastics*: C.K. Riew, Ed. Advances in Chemistry, 222, American Chemical Society: Washington DC., p 67 (1989).
2. S. Montarnal et.al. In *Rubber Toughened Plastics*., Ed. C.K Riew, *Adv. Chem. Ser* ; 222 , 193-208 (1989).
3. E.H. Farmer and J. Wheeler., *U.S. Patent* 2,227,777 (to British Rubber Products Research Association), January 6 (1940)
4. D.F. Lawson, W.L. Hergenrother and M.G. Matlock, *J. Appl. Polym. Sci.,* **39**, 2331 (1990).
5. B.C. Trivedi and B.M. Culbertson, *Maleic Anhydride Plenum*., pp-172-173, New York (1982)
6. A. A. Collyer, Ed. *Rubber Toughened Engineering Plastics*, Ch.5.,pp-160(1994)
7. T.Ravindran, M.R.G. Nair and Joseph Francis *J. Appl. Polym.Sci.,***35**,1227-1239(1988)
8. T.Ravindran, M.R.G. Nair and Joseph Francis, *Makromol. Chem, Rapid Commun*, 7: 159-163(1986)
9. N. Gaylord, M. Mehta and R. Mehta., *Am. Chem. Soc. Symp. Ser.,* **364**,438(1988)
10. G. Levita, A. Marchetta and E. Butta., *Polymer*, **26**, 1110(1985)
11. A.F. Yee and R.A. Pearson, *J. Mater. Sci*., **21**, 2462(1986)
12. M. Frounchi, M. Mehrabzadeh and M. Parvary., *Polym. Int*., **49**, 163-169(2000)
13. Y. Huang, A.J. Kinloch, R.J. Bertsch and A.R. Siebert In *Toughened Plastics I,* Eds. C.K. Riew and A.J. Kinloch, Adv. In Chem. Ser. **233,** American Chemical society, Washington DC,p-193 (1993)
14. S. Bandopadhyay., *Mater. Sci. Eng*., A **125**, 157 (1990)
15. D.C. Blackley., *Synthetic Rubbers, their Chemistry and Technology*, Applied science Publishers, London & New York, **264** (1978)

16. A. A. Collyer, Ed. *Rubber Toughened Engineering Plastics.*,Ch.6, p-170-177 (1994)

17. P.B. Latha, K. Adhinarayanan and R. Ramaswamy, *Int. J. Adhes. Adhe.* **14**,57(1994)

18. S. Montarnal, J.P. Pascault and H. Sautereau., *In Rubber Toughened Plastics.,* Ed. C.K. Riew, Advances in Chemistry Series **222**. American Chemical Society., Washington DC, pp-211-213 (1989)

19. V. Nigam, D.K. Seuta and G.N. Mathur, *Rub. Chem. Technol,* **73**,830(2001)

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

21. N. Hata and J. Kumanotani., J. Appl. Polym. Sci., **17**, 354 5 (1973)

22. C.K. Riew, E.H. Rowe and A.R. Siebert In T*oughness and Brittleness of Plastics,* R.D. Deanin and A.M. Crungola Eds. Advances in Chemistry Series.,**154**, American Chemical Society., Washington DC, pp-326 (1976)

23. W.D. Bascom, R.Y. Ting, R.J. Moulton, C.K. Riew and A.R. Siebert., *J. Mater. Sci.,* **16**, 2697(1981).

Chapter 5

REINFORCED AND FILLED EPOXY RESIN

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, woven roving mat and unidirectional fibres and mechanical properties such as tensile strength, flexural strength, water absorption and impact strength were compared. The fracture behaviour was studied by SEM. A comparative account of the effect of reinforcing fillers on the properties of epoxy resin is also given. Non-black fillers like silica, calcium carbonate, magnesium oxide, zinc oxide and asbestos powder are also studied. Also, the effect of silane coupling agents on the modification of epoxies by particulates was investigated.

i. Particulate modification:

Investigations have shown that the incorporation of particulate fillers such as silica and alumina can enhance toughness of cross-linked epoxies whilst contributing to a greatly enhanced modulus. This is a significant advantage over rubber modification where a reduction in modulus is observed [1]. Variables such as particle size, size distribution, particulate volume fraction etc. have been studied. The fact that particulates impose stress concentrating effects on the epoxy matrix is not generally considered significant. A mechanism based on the impeding characteristics of the particles, called the 'crack pinning' mechanism [2] has been proposed to explain particulate modification. As per this mechanism, when a propagating crack front encounters an inhomogeneity, it becomes temporarily pinned to that point. An increase in load increases the degree of bowing between the pinning points resulting in both a new fracture surface and an increase in length of the crack front. This process absorbs energy and thus fracture toughness increases. However the extent of toughness enhancement obtained through particulate modification is generally much lower than that achieved by rubber modification. Several studies have been conducted exploring the possibilities of combining both particulate reinforcement and rubber modification [3]. Recently, nanoparticles are used to enhance the properties of epoxy resins [4,5].

ii. 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. Rubber toughened epoxies are found to reduce micro cracking in composites [6,7]. It is also reported that the flexibility of short glass reinforced epoxy resin is increased with HTPB modification [8].

iii. Oxide spinels

Spinels form a large class of compounds whose crystal structure is similar to that of the mineral spinel itself, $MgAl_2O_4$. The general formula of spinels is AB_2O_4 in which A and B are respectively divalent and trivalent metals in such a way that the total oxidation number of the metal ions in the spinel is eight [9]. The structure can be described in terms of cubic close packing (ccp) of the anions, bound together by suitably placed interstitial cations. $MgAl_2O_4$ has a 2-3 charge distribution of cations and is called a 2-3 oxide spinel. A spinel is said to be 'normal' if A cations occupy tetrahedral sites and B cations the octahedral sites. When half of B cations occupy T -sites and all the A cations together with the other half of B cations ocuupy O- sites, it said to be an 'inverse' spinel [10]. Spinel oxides containing iron are called ferrospinels. The interesting electrical and magnetic properties of them are governed by their chemical compositions. Spinel phase in oxides can be characterized by X-ray diffraction (XRD) methods.

Spinels show interesting catalytic properties. The catalytic activity of spinels containing transition metal ions is influenced by the redox properties and the acid-base properties of these ions [11]. Catalytic ability of spinels arises from their Lewis acid character and has been established in reactions like oxidative dehydrogenation of hydrocarbons, hydrodesulphurization of petroleum crudes, treatment of automobile exhaust gases etc. Unlike single oxides, spinel type binary and ternary oxides show extra structural stability and greater reactivity.

In this investigation spinel oxides of the general formula AB_2O_4 have been prepared and blended with commercial epoxy resin with a view to study their influence on the mechanical properties of commercial epoxy resin.

5.2. EXPERIMENTAL

5.2.1. Materials

Chopped strand mat (CSM-Binani-IS:11551/BS:3496, 450g/m^2), woven roving mat (WRM- Binani-IS:11273/BS:3749, 610g/m^2) and direct roving (Binani-BS:3690) were supplied by M/s Sharon Engineering Enterprises, Cochin. Commercial grade precipitated silica (sp. gravity=2.03, SiO_2 hydrate=90 %, surface area=234m^2/g, mean particle diameter=20 nm) was supplied by M/s Sameera Chemicals, Kottayam. Calcium carbonate (sp. gravity=3.6) and magnesium oxide (sp.gravity=3.6) were laboratory grade supplied by M/s Fine Chemicals Ltd., Mumbai. Zinc oxide (sp. gravity=5.7, 98.5 % assay) was supplied by M/s Meta Zinc Ltd., Mumbai. 3-Amino propyl triethoxy silane was laboratory grade supplied by M/s E. Merck India Ltd, Bombay. Magnesium nitrate, zinc nitrate, aluminium nitrate and ferric nitrate were extra pure grade supplied by M/s. E. Merck, India Ltd., Mumbai.

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 and the catalysed and accelerated 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 120°C for 4 h.

Specimens used for testing were cut from the glass-reinforced laminates using a diamond tipped jigsaw. The tensile properties (ASTM D 638) and flexural strength (ASTM D 790) 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. The samples for flexural strength were cut into rectangular bars with dimensions of 63.5 mm x 12.7 mm x 3 mm. The crosshead speed of the machine was fixed at 1.27 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 are 76.2 mm length, 25.4 mm wide and 3 mm thick. The samples were immersed in distilled water for 24 hrs at 23°C. Water absorption during accelerated weathering was also determined by immersing the samples in boiling distilled water for 2 hrs. This accounts for aging due to humidity and thermal effects.

a) Modification using elastomers

Glass reinforced laminates were prepared using both unmodified and elastomer modified commercial DGEBA epoxy resins. The elastomers used for blending were NBR (5%), CTBN (10%) and ETPB (10%). (Sections 4.2.2 & 4.2.3) The samples were cut and tested.

b) Modification by reactive blending with phenolic resins

Glass reinforced laminates were prepared using reactive blends of DGEBA and phenolic resins such as EPN, PF and epoxy cardanol (EC). These reactive blends were prepared by taking optimum concentrations (10 wt %) each of EPN-3 (Section 3.2.8), PF resole (Section 3.2.5) and EC-9 (Section 3.2.11). The test samples were cut and tested.

5.2.3 Particulate filled epoxies

a) Non-black fillers

The non-black fillers such as precipitated silica, magnesium oxide, zinc oxide, calcium carbonate and asbestos powder were each initially dried at 120°C for 24 hours and ground in a mortar. Varying amounts of the fillers (0-10 wt %) were added to the epoxy resin and stirred well by gentle agitation using a stirrer The mixture was degassed for 15 min. Curing was done in presence of 10 wt% amine hardener at room temperature for 24h followed by post curing at 120^0C for 4h. Samples were cast and tested as described in Section 2.2.4.

b) Effect of silane coupling agent

Zinc oxide, magnesium oxide and calcium carbonate were dried at 120°C for 24 hours and ground in a mortar. Varying amounts of the fillers (0-10 wt %) were added to each of epoxy resin and epoxy containing 1 % 3-aminopropyl triethoxy silane, stirred by gentle agitation using a stirrer and degassed for 15 min. The samples were cured and tested as outlined in Section 2.2.4.

c) Preparation of oxide spinels and incorporation into commercial epoxy resin

i. Preparation of oxide spinels [12]

Aqueous solutions of zinc nitrate (0.06M) and aluminium nitrate (0.12M) were mixed together and stirred well. To this mixture, 1:1 ammonia was added slowly while stirring to precipitate the metal hydroxides. The precipitate was kept overnight and then washed several times with water until free from nitrate ions and alkali. It was filtered under suction and dried in an air oven at 120 °C. It was then calcined at 300 °C for three hours in a muffle furnace to transform into spinel phase ($Zn\ Al_2O_4$). The same procedure was used for the preparation of other oxide spinels such as $Mg\ Al_2O_4$, $Zn\ Fe_2O_4$ and $Mg\ Fe_2O_4$.

ii. Characterization of oxide spinels

X-ray diffraction (XRD) by crystals is the most widely employed method for determining the three dimensional structure of solids [13]. Powder diffractometer can produce accurate data in less than half an hour. The sample is initially activated by heating to 300^0C for 3h before analysis. The cooled sample is packed in the widow of an aluminium holder backed by a glass slide. The plate containing the specimen is rotated and the diffracted X-rays are detected. The usual scan speed is 2^0 2θ per minute. The x-rays reaching the detector are registered and displayed on a paper chart recorder as a series of peaks.

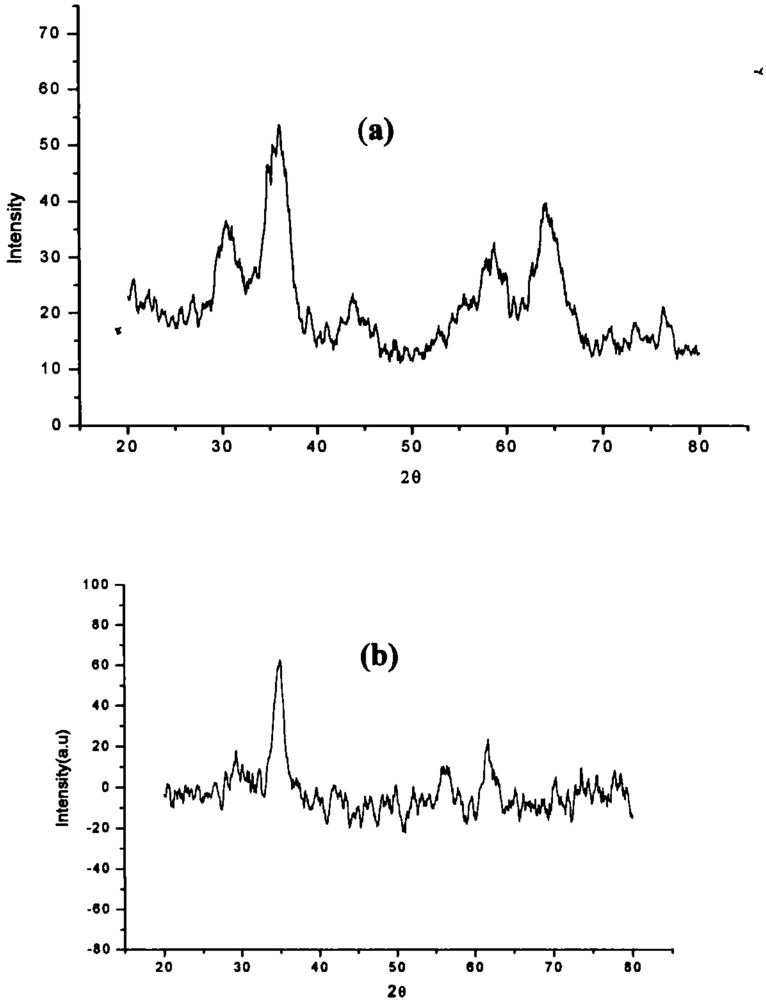


Fig. 5.1. XRD of a) $MgAl_2O_4$ and b) $ZnFe_2O_4$

Every crystalline substance has a unique X-ray powder pattern because line positions depend on unit cell size, and line intensity depends on the type of atoms present and on their arrangement in the crystal. Materials are identified from these values in conjunction with the 'Joint Committee on Powder Diffraction Standards' (JCPDS) Powder Diffraction File [14]. The file consists of sets of cards containing X-ray data for most known crystalline phases. The appropriate data card is retrieved and the experimental data, especially those of the three strongest peaks are matched with the standard values. Rough estimate of particle size can be obtained using the relation,

$$t = 0.9\lambda / B \cos \theta.$$

Where B= FWH (Full Width at Half Maximum) of the strongest peak (in radians), θ= Bragg angle, λ= wavelength and t = the crystal diameter. The line broadening gives the size of the crystals and not the size of the particles since a particle may contain a number of crystals [15]. The particle sizes of $MgAl_2O_4$ and $ZnFe_2O_4$ are found to be 3.17 nm and 6.956nm respectively.

The X-ray diffraction analysis has been done using RIGAKU D/ MAX-C powder diffractometer and a few diffractometer traces are given in Table.5.1. The2θ angles and the corresponding crystal planes (hkl values) for the samples agree closely with the standard values given in the JCPDS data cards for these systems. This identifies and confirms the spinel phase in the samples. The strongest peaks occur at 2θ values 36.3^0 and 34.96^0 in the case of $MgAl_2O_4$ and $ZnFe_2O_4$ respectively (Fig 5.1).

Table 5.1 XRD data of oxide spinels

$MgAl_2O_4$			$ZnFe_2O_4$		
Exptl	JCPDS data		Exptl	JCPDS data	
$2\theta^0$	$2\theta^0$	hkl	$2\theta^0$	$2\theta^0$	hkl
36.30	36.277	311	34.96	35.2	311
44.01	44.105	400	61.61	62.16	440
64.31	64.143	440	29.24	29.91	220
58.75	58.384	511	56.54	56.61	333
30.66	30.792	220	42.24	42.82	400

5.3 RESULTS AND DISCUSSION

5.3.1 Reinforced laminates from elastomer-modified epoxy resin

This section deals with laminates made from commercial epoxy resin containing 5wt % NBR, 10 wt % CTBN and 10 wt %ETPB.

a) ***Properties of laminates***

Table 5.2 summarises the tensile properties, flexural properties, toughness properties, surface hardness and water absorption of glass-reinforced resins. Laminates were prepared using WRM and CSM in each case.

i. Mechanical properties

Tensile strength of glass-reinforced modified resin is better than that of reinforced un-modified epoxy resin. This can be attributed to the strengthening of the interface by the elastomer modified matrix. The extent of strengthening by elastomers in glass-reinforced samples is less compared to un-reinforced modified samples. NBR and CTBN were found to impart greater tensile strength compared to ETPB. Interaction between the rubber and epoxy chains is responsible for strengthening of the matrix. The toughening of the matrix-fibre interface leads to a more efficient load transfer between fibre and matrix .The decrease in tensile moduli is marginal for rubber modified reinforced compositions.

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 [16]. Reactive liquid rubbers enhance the bonding at the interface and crack growth is delayed [17].

Modified resins are found to impart greater impact strength to the glass reinforced laminates. The rubber particles absorb the energy of impact. NBR and CTBN show enhanced impact strength compared to ETPB. The acrylonitrile group imparts better dispersion of rubber particles leading to toughening of the epoxy matrix.

ii. Flexural properties

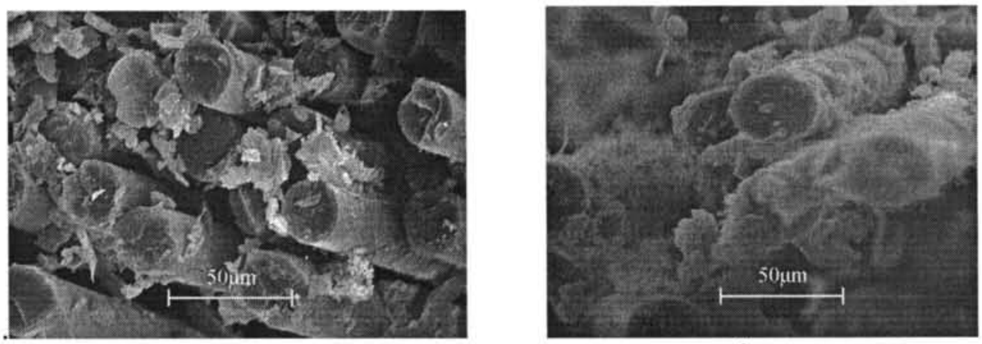
Flexural strength of reinforced modified resin is slightly higher for NBR modified sample than for unmodified epoxy resin laminate. This may be due to the higher tensile strength and high molecular weight of NBR [18]. However, CTBN and ETPB modified laminates show lower flexural strength due to their enhanced flexibility. Flexural moduli decrease steadily for rubber modified reinforced compositions compared to the unmodified version.

iii. Surface hardness and water absorption

Surface hardness values are lower than that for unmodified samples. This is due to the poor hardness values of rubbers. Water absorption by rubber modified reinforced samples during 24 hrs immersion is greater than those by unmodified reinforced samples.

Table-5.2 Summary of properties of glass fibre-reinforced DGEBA modified by elastomers

Property	Type of mat	DGEBA	NBR	CTBN	ETPB
Tensile strength (MPa)	CSM	193.8	210.5	205.2	199.5
	WRM	229.7	256.2	261.7	243.6
Tensile modulus (MPa)	CSM	6127	6078	6107	6008
	WRM	6891	6798	6811	6717
Flexural strength (MPa)	CSM	212.2	216.6	208.3	210.4
	WRM	246.7	251.5	240.8	231.3
Flexural modulus (MPa)	CSM	5586	5478	5525	5410
	WRM	8867	8655	8701	8802
Energy absorbed (J)	CSM	30.52	39.17	42.43	34.78
	WRM	35.93	44.68	48.31	40.04
Impact strength (J/m)	CSM	118.5	124.57	134.7	121.05
	WRM	131.8	140.15	146.32	135.25
Hardness (Shore D)	CSM	87.5	87	87.5	86
	WRM	88	87.5	88	87
Water absorption (%) (24 h. immersion)	CSM	0.571	0.755	0.632	0.795
	WRM	0.482	0.576	0.602	0.683



(a) (b)

Fig. 5.2. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA and (b) DGEBA/ CTBN

b) Morphological studies [19]

Scanning electron micrographs of unmodified and modified epoxy glass reinforced laminates fractured at low deformation rate are shown in Fig.5.2 Referring to the micrograph (a) the neat resin has poor adhesion to the fibres. The micrograph of CTBN modified laminate (b) shows good adhesion of the rubber modified matrix and the fibre ends are still covered with the polymer.

5.3.2 Reinforced laminates from phenolic modified epoxy resin

This section deals with laminates made from commercial DGEBA resin containing 10weight % each of epoxy phenol novolac (EPN), phenol-formaldehyde resin (PF resol) and epoxidized cardanol (EC).

a) Properties of laminates

Table 5.3 summaries the tensile, flexural and toughness properties, surface hardness and water absorption of glass-reinforced resins.

i. Mechanical properties

Tensile strength of glass-reinforced resin modified by10%EPN is superior to those from PF 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 10weight %EPN (Section 3.3.4) Enhanced compatibility and greater cross-linking are responsible for greater strengthening of the matrix. This leads 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. While the decrease in tensile modulus is only marginal for the EPN and PF modified laminates, the EC modified laminate shows greater lowering of modulus indicating its reduced stiffness.

ii. Flexural properties

The flexural strength of EC modified laminate is much lower compared to the unmodified resin laminate. This reflects the enhanced flexibility of the EC modified matrix. EPN and PF modified laminates show only a marginal increase in flexural strength. Flexural moduli decrease steadily for phenolic-modified epoxy resin laminates with the greatest lowering in the case of EC modified laminate.

iii. Surface hardness and water absorption

The surface hardness of EPN modified laminate is more than that of the un-modified DGEBA laminate and that of the PF modified sample does not show much change. Hardness decreases for both CSM and WRM in the case of EC-modified laminate. Water absorption is high for PF and EC modified laminates due to the presence of relatively more hydrophilic groups in the form of methylols and phenolic hydroxyl groups. However, the EPN modified laminate is considerably water resistant.

Table-5.3 Summary of properties of glass fibre-reinforced DGEBA modified with 10% phenolic resins

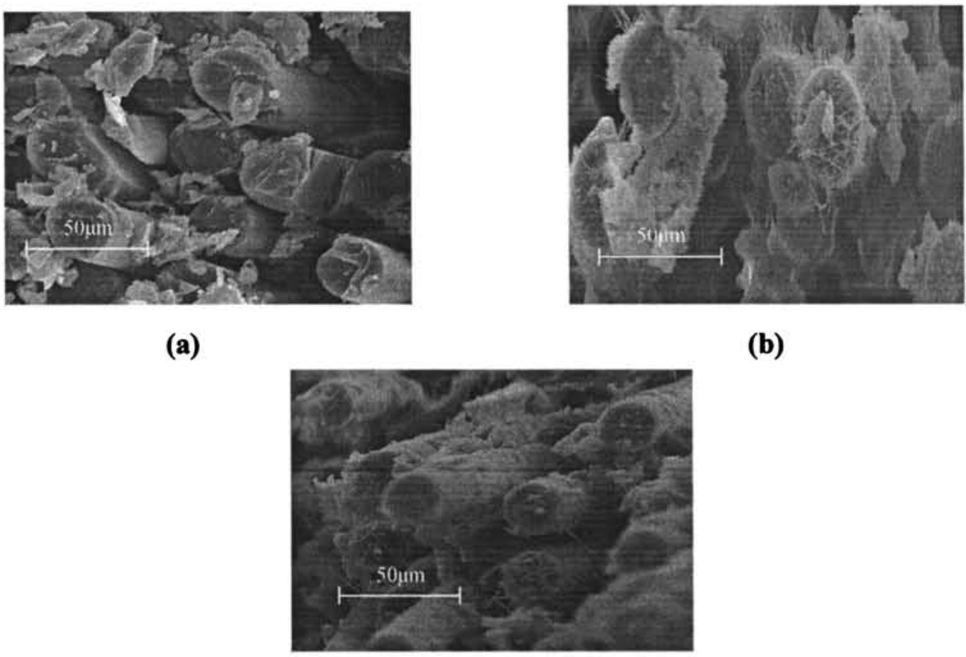
Property	Type of mat	DGEBA	EPN	PF	EC
Tensile strength (MPa)	CSM	193.8	219.8	208.4	196.7
	WRM	229.7	251.8	240.2	233.6
Tensile modulus (MPa)	CSM	6127	5632	5703	5380
	WRM	6891	6312	6479	5911
Flexural strength (MPa)	CSM	212.2	220.3	217.6	199.4
	WRM	246.7	277.8	254.5	222.6
Flexural modulus (MPa)	CSM	5586	5212	5345	4927
	WRM	8867	8225	8403	7826
Energy absorbed (J/mm^2)	CSM	30.52	43.65	38.85	36.72
	WRM	35.93	47.11	43.38	40.34
Impact strength (J/m)	CSM	118.5	137	128.8	122.4
	WRM	131.8	145.8	140.9	137.6
Hardness (Shore D)	CSM	87.5	88	87.5	86.5
	WRM	88	90	88.5	87
Water absorption (%) (24 hr immersion)	CSM	0.571	0.545	0.652	0.783
	WRM	0.482	0.468	0.636	0.722

b) Morphological studies

Scanning electron micrographs of unmodified and EPN modified epoxy- glass reinforced laminates fractured at low deformation rate are shown in Fig. 5.3. Referring to the micrograph (a) the neat resin has poor adhesion with the fibres. The micrograph of EPN modified laminate (b) shows moderate adhesion of the modified matrix and the fibre ends are only lightly covered with the polymer. The micrograph of EC-modified epoxy glass reinforced laminate (c) indicates good adhesion of the matrix resin to the glass fibres. The residual phenolic hydroxyl groups that may be present in EC resin can interact with the glass surface giving rise to greater grafting of the matrix resin with the reinforcing glass.

5.3.3 Effect of non-black fillers on the properties of epoxy resin

The properties commercial DGEBA resin containing different types of non-black particulate materials (0 -10 wt %) such as precipitated silica, calcium carbonate, zinc oxide, asbestos powder and magnesium oxide have been studied in this section.



(a) **(b)**

(c)

Fig. 5.3. Scanning electron micrographs of the fracture surfaces for glass reinforced laminates of (a) DGEBA (b) DGEBA/ 10% EPN and c) DGEBA/10%EC

i. Mechanical properties

Fig. 5.4 shows the variation of tensile strength of DGEBA resin with different concentrations of non-black fillers. In the case of $CaCO_3$ and ZnO, the tensile strength increased with filler concentration up to 2.5% and 5% respectively and a further increase in filler concentration lowered the tensile strength. Fillers with very fine particle size have high packing fraction and hence have a very high order of adhesion with the matrix. At higher concentrations, the dispersion becomes poor and the binding forces decrease leading to reduction in tensile strength. Silica also shows a similar behaviour at a lower loading. But the tensile strength decreases at all concentrations for the other filler materials used.

Fig. 5.5 shows the variation in tensile modulus with filler concentration. The tensile modulus generally increases with filler concentration. At higher filler concentrations the rate of modulus increase is considerably less. While there is a steady increase of modulus for magnesium oxide, the modulus for asbestos powder increases up to about 5% and then decreases. Fig.5.6 shows the variation of elongation at break with filler concentration. Elongation decreases with increase in filler concentration.

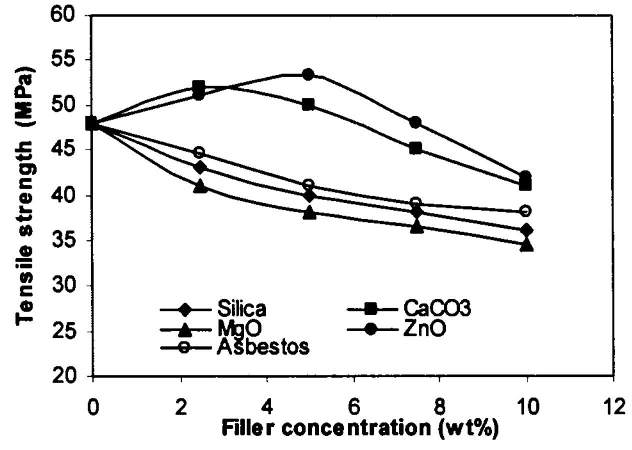


Fig. 5.4 Tensile strength of epoxy composites versus non-black concentration

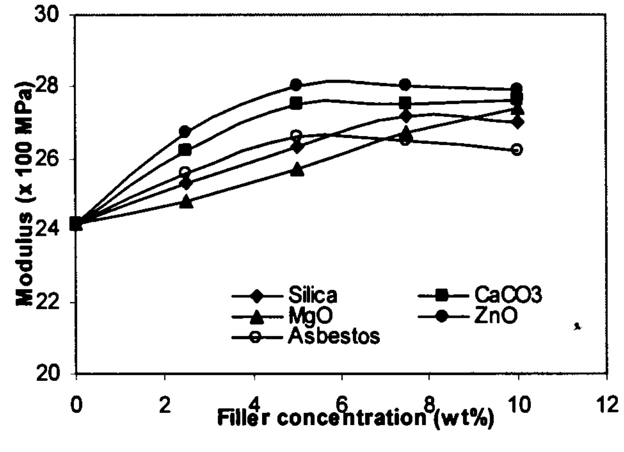


Fig. 5.5 Tensile modulus of epoxy composites versus non-black concentration

Epoxy composites containing ZnO and $CaCO_3$ show a marginal increase of elongation up to 2.5 % beyond which there is a steady decrease. This is because, smaller particles at low concentrations are freer to move with the matrix and correspondingly, the matrix is freer to stretch around them. The viscous drag of small particles with good adhesion to the matrix can produce an apparent strength improvement and greater tenacity, resulting in higher ultimate elongations [20]. It is possible that ZnO, due to its amphoteric nature, can have greater affinity to the epoxy – amine system than the other fillers.

Fig.5.7 shows the variation of toughness of the epoxy resin with filler concentration as a function of the energy absorbed (to break) by the composite. In the case of zinc oxide and $CaCO_3$ the energy value increases gradually up to 5% and thereafter decreases. The fine filler particles pin propagating cracks there by preventing crack growth. Silica shows only a marginal increase in energy absorption at 2.5% concentration. The other filler materials show a regular decrease in energy absorption with increase in filler concentration.

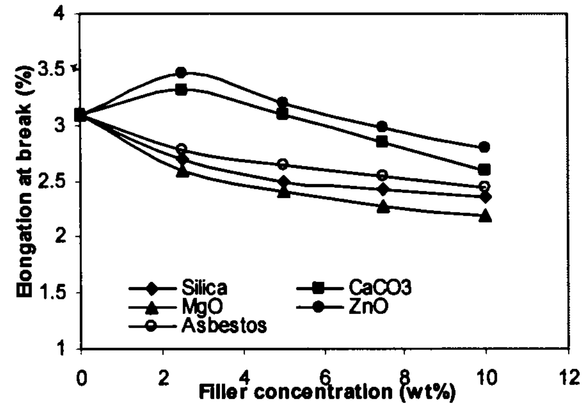


Fig. 5.6 Elongation (at break) of epoxy composites versus non-black concentration

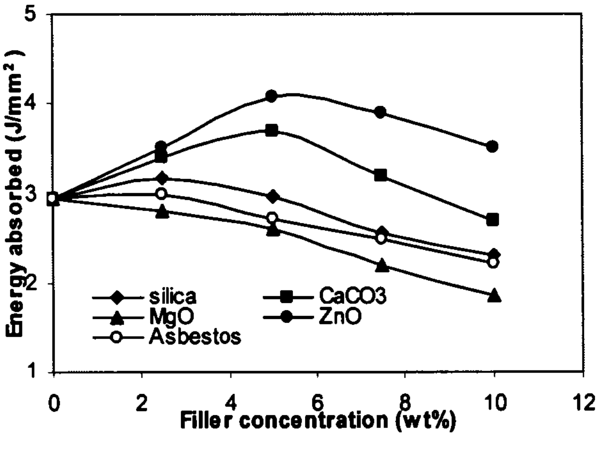


Fig. 5.7 Energy absorbed (to break) Vs non-black concentration

Fig.5.8 shows the variation of compressive strength with filler concentration. Compressive strength also shows the same behaviour as tensile strength. The compressive strength of ZnO and $CaCO_3$ modified samples show a gradual increase up to 5% and 2.5% respectively and then decreases at higher filler concentrations.

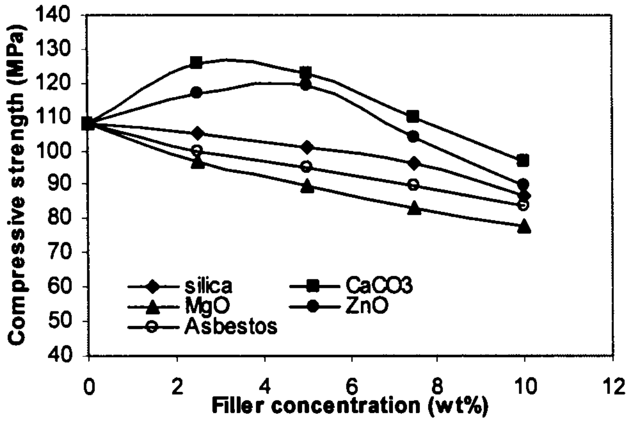


Fig. 5.8 Compressive strength Vs non-black concentration

The fine particle size of the particulates promotes their adhesion to the matrix to a greater extent. The impact strength shows a marginal increase at very low filler loading (Fig.5.9) for $CaCO_3$ and ZnO and then decreases. For the other fillers there is a steady decrease in impact strength with increase in filler concentration. This is in tune with their tensile strength values. The impact energy is absorbed by the filler particles that bridge propagating cracks together.

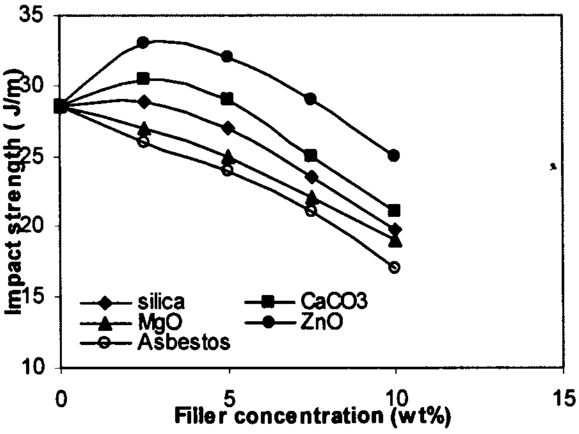


Fig. 5.9 Impact strength Vs non-black concentration

ii. Surface hardness

Fig.5.10 shows the variation of surface hardness with filler concentration. The hardness values increase steadily with filler concentration up to 5 to 7.5% beyond which they decrease slowly at higher filler concentrations. At higher filler loading, the dispersion is poor and there is a negative effect on the hardness.

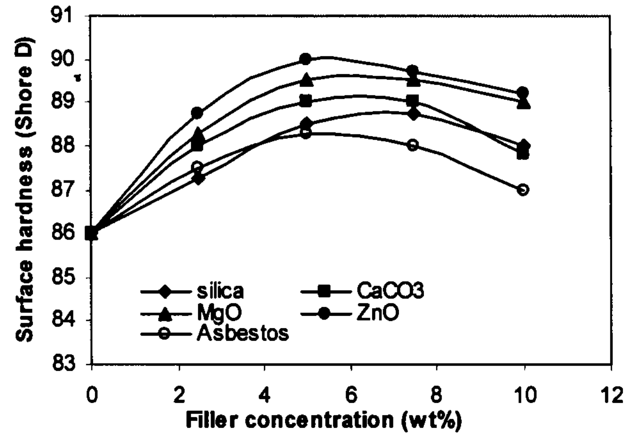


Fig. 5.10 Surface hardness versus non-black concentration

Table-5.4 Summary of properties of DGEBA blended with 0--10% non- black fillers

Property	Neat	%improvement/ %composition					
		Silica	$CaCO_3$	MgO	ZnO	Asbestos powder
Tensile strength (MPa)	48	-25/10	9/2.5	-28/10	11/5	-21/10
Modulus ($\times 10^2$ MPa)	24.2	11/7.5	14/10	13/10	16/7.5	8/10
Elongation at break%	3.10	-24/10	7/2.5	-29/10	12/2.5	-23/10
Energy absorbed to break (Jmm^{-2})	2.95	8/2.5	26/5	-6/5	39/5	2/2.5
Impact strength J/m	28.5	2/2.5	7/2.5	-6/2.5	16/2.5	-9/2.5
Compressive strength (MPa)	108	-19/10	17/2.5	-28/10	10/5	-22/10
Hardness (Shore D)	86	3.2/7.5	3.5/7.5	4/7.5	5/5	2.6/5

Table 5.4 summarises the effect of adding varying amounts of different non-black fillers. The maximum improvement acquired in each property and the filler concentration corresponding to it is tabulated. Zinc oxide and calcium carbonate were found to be superior to the other fillers.

5.3.4 Effect of silane coupling agent on the properties of filled epoxies

Commercial DGEBA resin was mixed with varying proportions of $CaCO_3$, ZnO and MgO separately in the presence of 1% 3-aminopropyl triethoxy silane as coupling agent. The formulations containing the above fillers with silane coupling agent are designated as CaCO3-S, ZnO-S and MgO-S respectively. The mechanical properties of the blends with and without silane were compared.

a) Mechanical properties

Fig. 5.11 shows the variation of tensile strength of filled DGEBA epoxy resin with and with out silane coupling agent. Substantial improvement in tensile strength was observed in the case of ZnO (at 2.5%) and $CaCO_3$ (at 5%) in the presence of silane. The tensile strength of the MgO reinforced resin, though moderate, still shows improvement on incorporation of silane. Silane coupling enhances the interfacial adhesion between filler and matrix.

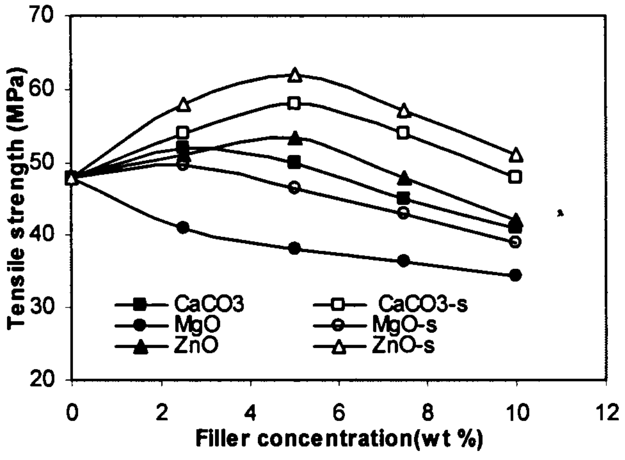


Fig.5.11 Tensile strength of filled DGEBA with and without silane(1%) Vs filler concentration

The decrease in property at higher filler loading may be due to the fact that silane becomes insufficient at higher filler concentrations. Fig.5.12 illustrates the variation in modulus by the addition of particulate fillers to DGEBA resin containing 1% silane coupling agent. In general, modulus increases with filler concentration up to about 7.5% and then either decreases slightly or remains almost

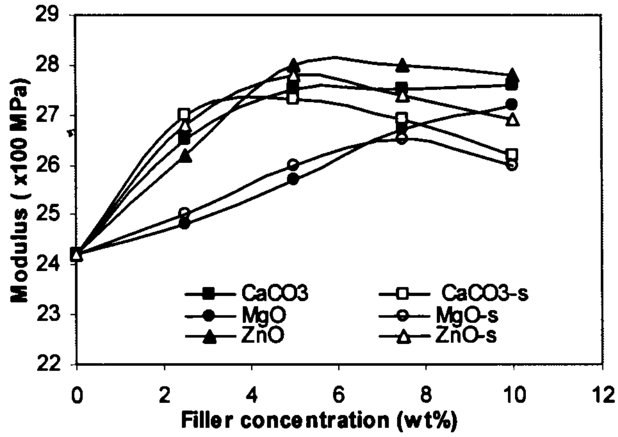


Fig.5.12Modulus of filled DGEBA with and without silane(1%) Vs filler concentration

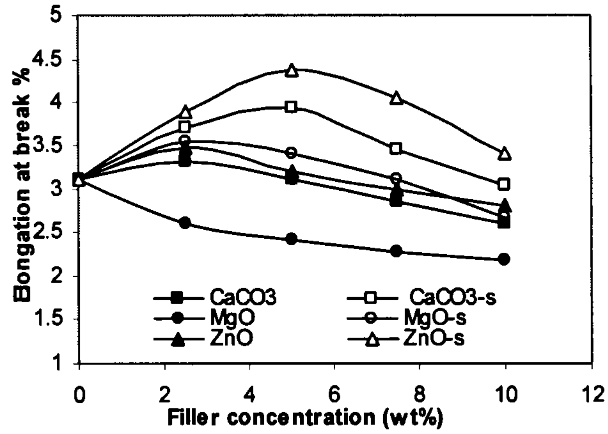


Fig.5.13 Elongation of filled DGEBA with and without silane(1%) Vs filler concentration

a constant with the notable exception of MgO. Particulate matter stiffens the epoxy matrix and the presence of silane reduces the stiffness only slightly at higher filler concentrations. At lower concentrations the filled resins with and without silane show almost a similar trend in modulus. The variation in elongation at break of filled epoxy resin containing 1% silane coupling agent is given in Fig.5.13. $CaCO_3$ and ZnO filled samples show improvement in elongation at lower (5%) filler concentration. The silane coupled ZnO sample gave 26% increase in elongation (at break) against 12% without silane at 2.5% filler concentration. This can be the result of interface strengthening by silane. At lower concentrations, finer particles

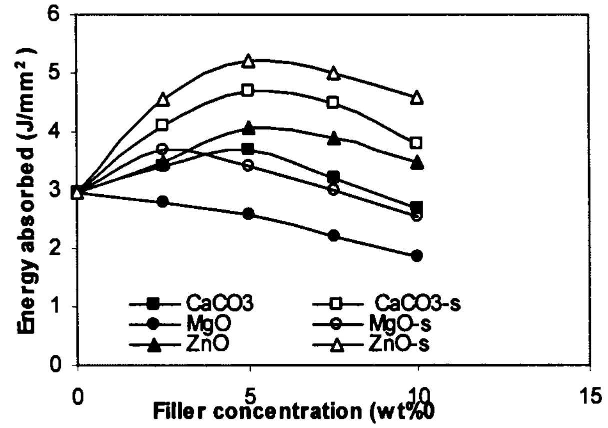


Fig.5.14 Energyy absorbed (to break) of filled DGEBA with and without silane(1%) Vs filler concentration

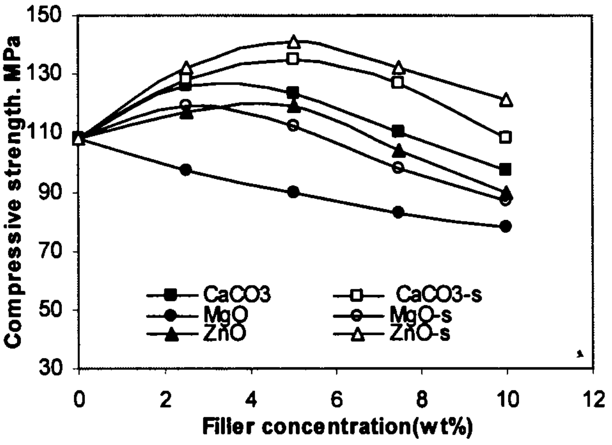


Fig.5.15 Compressive strength of filled DGEBA with and without silane(1%) Vs filler concentration

move freely in the matrix and correspondingly the matrix can freely stretch around them. The variation in the toughness of filled DGEBA resin containing silane coupling agent is given in Fig.5.14 in terms of the energy absorbed by the samples to break. Obviously, the incorporation of silane has improved considerably the energy absorption of filled DGEBA resin. The 5% ZnO-silane system shows the maximum improvement in toughness (76% of that of the neat resin) compared to

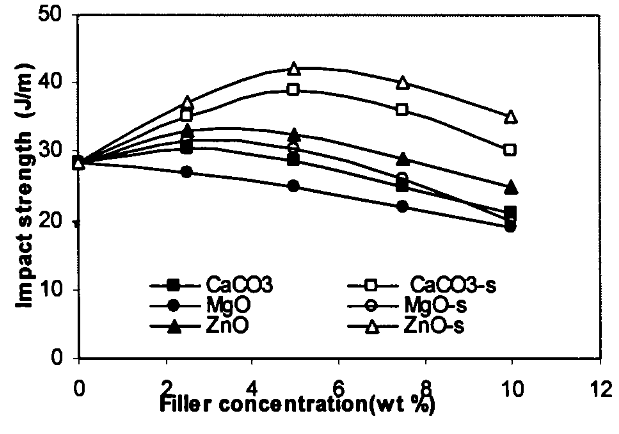


Fig.5.16 Impact strength of filled DGEBA with and without silane(1%) Vs filler concentration

40% improvement at 5% in the absence of silane. Similarly, $CaCO_3$ filled resin shows better energy absorption in the presence of silane than in its absence. Silane enhances the interfacial adhesion between filler and matrix and the well grafted particles can bridge cracks more effectively.

Compressive strength shows almost the same behaviour as tensile strength (Fig. 5.15). The compressive strength increases up to 5% in the cases of $CaCO_3$ and ZnO and then decreases. Due to finer particle size and the presence of silane, adhesion of filler with the matrix is maximum. This increases the compressive strength.

Fig. 5.16 gives the variation of impact strength with filler concentration. Again, ZnO is superior to the other filler materials in improving the impact strength. The silane coupled 5% ZnO sample gave 48% (compared to the control resin) increase in impact strength against 16% increase in the absence of silane at a lower filler concentration. $CaCO_3$ filled sample shows more improvement in impact resistance than MgO filled resin in the presence of silane. The presence of silane imparts enhanced interaction between the epoxy matrix and the filler. This gives rise to increase in impact resistance of the filled resin. Fig. 5.17 shows the variation of surface hardness with filler concentration. The hardness values increase steadily with filler concentration up to 5-7.5% and thereafter decreases slowly at higher filler concentrations. There is not much variation in the pattern of variation in hardness between filled epoxy resin with and without silane for different fillers.

Table 5.5 gives a comparison of the properties of filled epoxy resin with and without silane coupling agent. The improvement in each property and the corresponding compositions are tabulated.

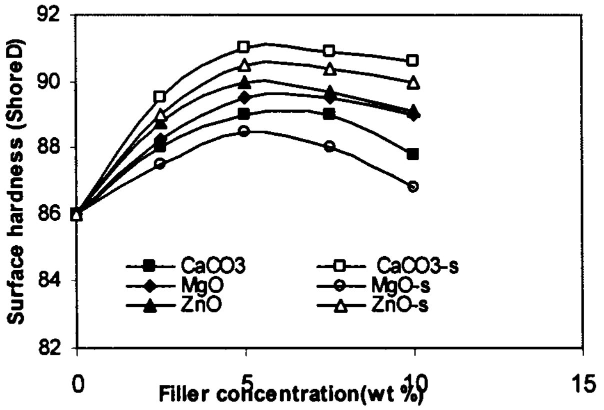


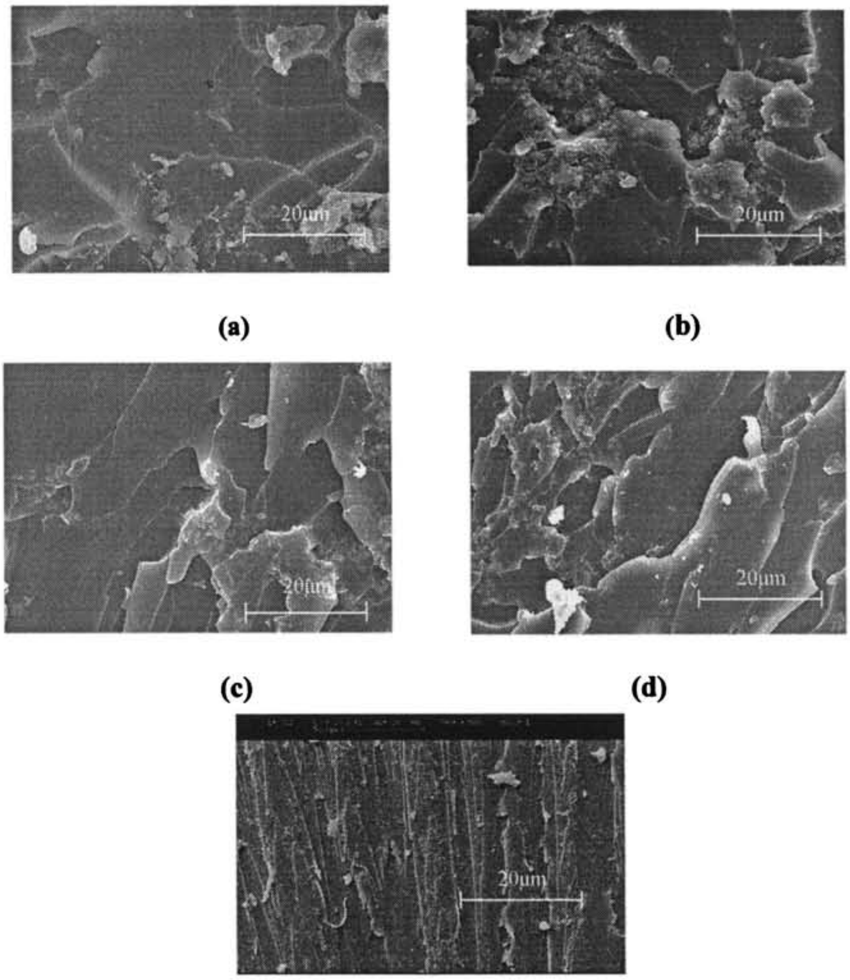
Fig.5.17 Hardness of filled epoxy resin with and without silane Vs filler concentration

Table 5.5 Summary of properties of filled (0-10%) epoxy resin with and without silane coupling agent (1%)

Property	Neat	% Improvement / filler concentration %					
		$CaCO_3$	$CaCO_3$ s	MgO	MgO-s	ZnO	ZnO-s
Tensile strength (MPa)	48	9/2.5	21/5	-28/10	6/2.5	11/5	29/5
Modulus (x100MPa)	24.2	14/5	13/5	13/10	9/7.5	16/7.5	15/5
Elongation at break (%)	3.10	7/2.5	27/5	-29/10	15/2.5	12/2.5	41/5
Energy absorbed (J/mm^2)	2.95	26/5	59/5	-6/2.5	24/2.5	40/7.5	76/5
Compressivestrength MPa	108	17/2.5	25/5	-28/10	10/2.5	10/5	31/5
Impact strength (J/m)	28.5	7/2.5	37/5	-6/2.5	11/2.5	16/2.5	47/5
Surface hardness. Shore D	86	3/7.5	6/5	4/7.5	3/5	4.5/5	5/5

b) Morphological studies

Scanning electron micrographs of filled DGEBA fractured at low deformation rate are shown in Fig.5.18. Referring to the micrograph (a) the fracture path for calcium carbonate filled resin shows moderate adhesion of the epoxy matrix and the filler. The effect of silane on the fracture pattern is shown in micrograph (b). Fairly good adhesion of filler to matrix is seen. In the case of ZnO filled epoxy (c) the fracture path is relatively smooth and show good adhesion between filler and matrix. Silane coupling agent (d) enhances the adhesion further. Due to the extreme ductility of the matrix ductile fracture occurs in the matrix. The micrograph for the unmodified epoxy resin (e) shows typical brittle fracture. Compared to this, the fracture paths of the filled samples give indications of energy absorption on a large scale during failure.



(a) **(b)**

(c) **(d)**

(e)

Fig. 5.18 Scanning electron micrographs of fractured surface of a) DGEBA/$CaCO_3$ b) DGEBA/$CaCO_3$/silane c) DGEBA/ZnO d)DGEBA/ZnO/silane and e) DGEBA

5.3.5 Effect of oxide spinels on the properties of commercial epoxy resin

Oxide spinels such as Zn Al_2O_4, Mg Al_2O_4, Zn Fe_2O_4 and Mg Fe_2O_4 were employed for reinforcement of epoxy resin. Particulates are known to modify toughness properties of cross-linked epoxy matrix [21] while contributing to enhanced modulus. This has been regarded as the advantage of particulate modification over rubber modification of epoxy resin.

a) Mechanical properties

Fig. 5.19 shows the effect of varying amounts of oxide spinels on the tensile strength of filled epoxy material. All the spinels gave moderate increase (less than 10%) in tensile strength at very low concentrations. The tensile strength was found to decrease thereafter with increase in filler concentration. Fillers with fine particle size have high packing fraction and show good adhesion with the matrix. At higher concentrations dispersion becomes relatively poor and the filler-matrix binding becomes less effective. XRD calculations show very fine particle sizes for magnesium aluminate and zinc ferrite (3.17nm and 6.956nm respectively) compared to the other fillers and they exhibit relatively better tensile strength.

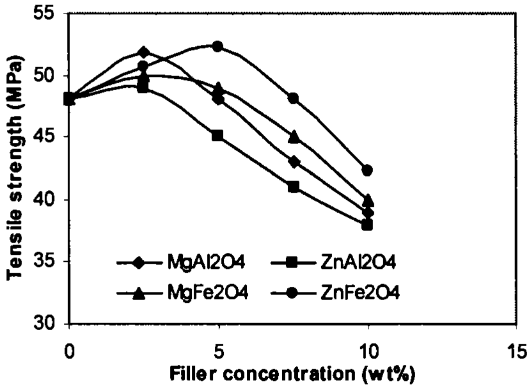


Fig.5.19 Tensile strength of filled DGEBA Vs concentration of oxide spinel

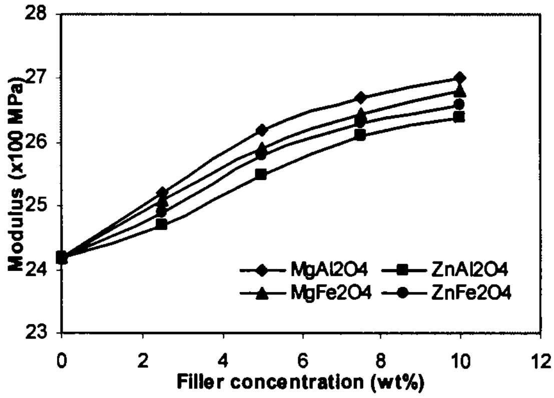


Fig.5.20 Modulus of filled DGEBA Vs concentration of oxide spinel

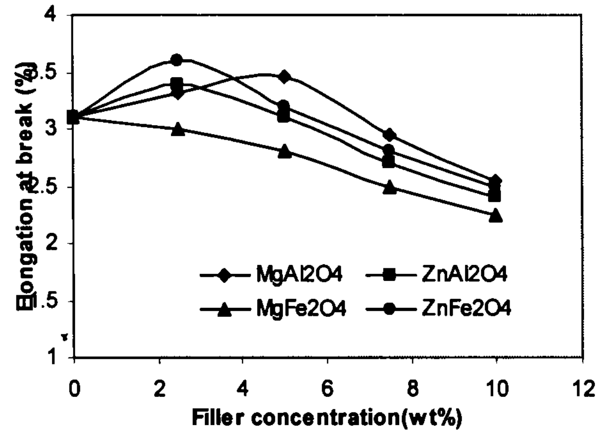


Fig.5.21 Elongation (at break) of filled DGEBA Vs concentration of oxide spinel

There is a steady increase in modulus with increase in spinel concentration (Fig.5.20). However, the rate of increase is less at higher filler concentrations. Particulates in general increase the stiffness of the cured matrix. Except $MgFe_2O_4$, the other fillers show a slight increase in elongation at very low concentrations (Fig.5.21). Here also, $ZnFe_2O_4$ and $MgAl_2O_4$ exhibit better elongation. Relatively smaller particles move freely with the matrix and this allows the matrix to stretch freely around such particles. Fig.5.22 shows the variation of toughness of filled epoxy resin as a function of the energy absorbed to break. In general, the aluminates are found to be superior in energy absorption (to break) to the ferrites.

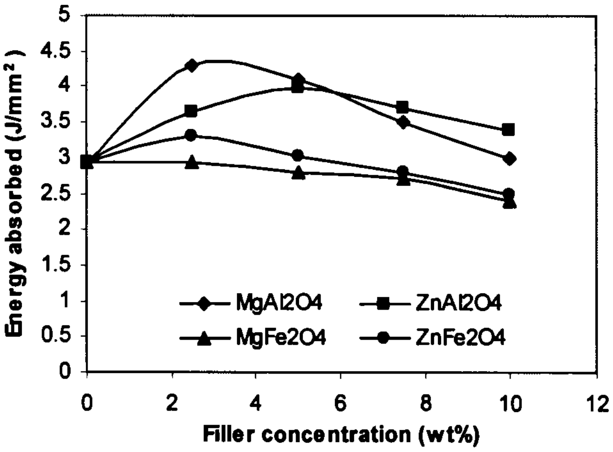


Fig.5.22 Energy absorbed (to break) of filled DGEBA Vs concentration of oxide spinel

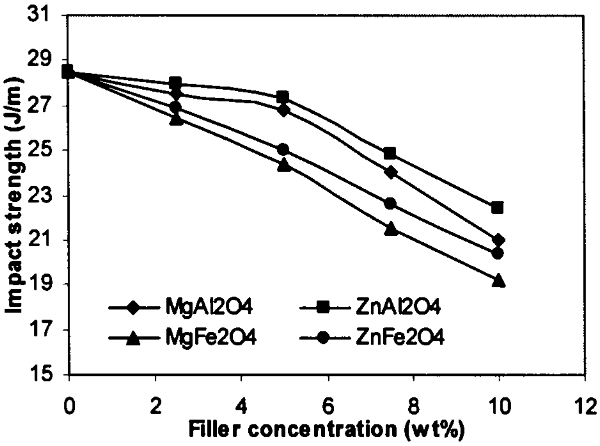


Fig.5.23 Impact strength of filled DGEBA Vs concentration of oxide spinel

$MgAl_2O_4$ shows the maximum increase in energy absorption (46% of the neat resin) at 2.5% concentration. Smaller particles induce grater interfacial adhesion with the matrix and effectively bridge cracks in the cured matrix. The effect of spinel oxides on the impact resistance of filled epoxy resin is given in Figure.5.23. Unlike in the case of ordinary non-black fillers (Section 5.3.3) the impact strength of spinel-filled epoxy resin shows a steady decrease with increase in filler concentration. The extent of decrease is more at higher filler concentrations. This may be due to enhanced stiffness which acts against the ductility of the matrix.

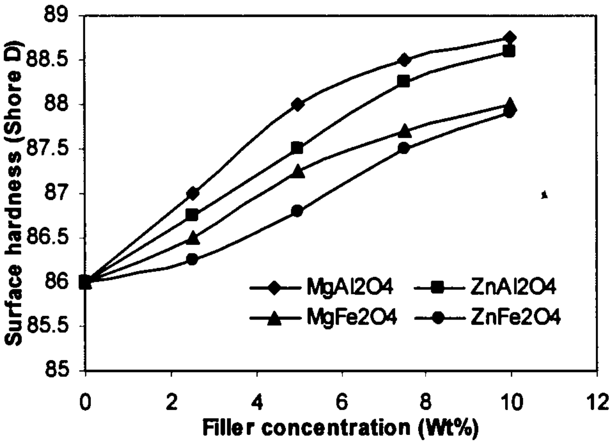


Fig.5.24 Surface hardness of filled DGEBA Vs concentration of oxide spinel

ii. Surface hardness

Fig.5.24 gives the variation of surface hardness of filled epoxy resin with filler concentration. Surface hardness increases steadily with increase in filler concentration up to 7.5% beyond which the rate of increase is less.

Table 5.6 Summary of properties of spinel oxide filled epoxy resins (0-10%)

Property	Neat resin	% Improvement / % composition			
		$MgAl_2O_4$	$ZnAl_2O_4$	$MgFe_2O_4$	$ZnFe_2O_4$
Tensile strength (MPa)	48	8/2.5	2/2.5	5/2.5	9/5
Modulus (x100 MPa)	24.2	12/10	8/10	11/10	9/10
Elongation at break (%)	3.10	12/2.5	9/2.5	-26/10	16/5
Energy absorbed . J/mm^2	2.95	46/2.5	35/5	-5/5	12/2.5
Impact strength (J/m)	28.5	-4/2.5	-2/2.5	-8/2.5	-6/2.5
Surface hardness. Shore D	86	3.2/10	3/10	2.4/10	2.2/10

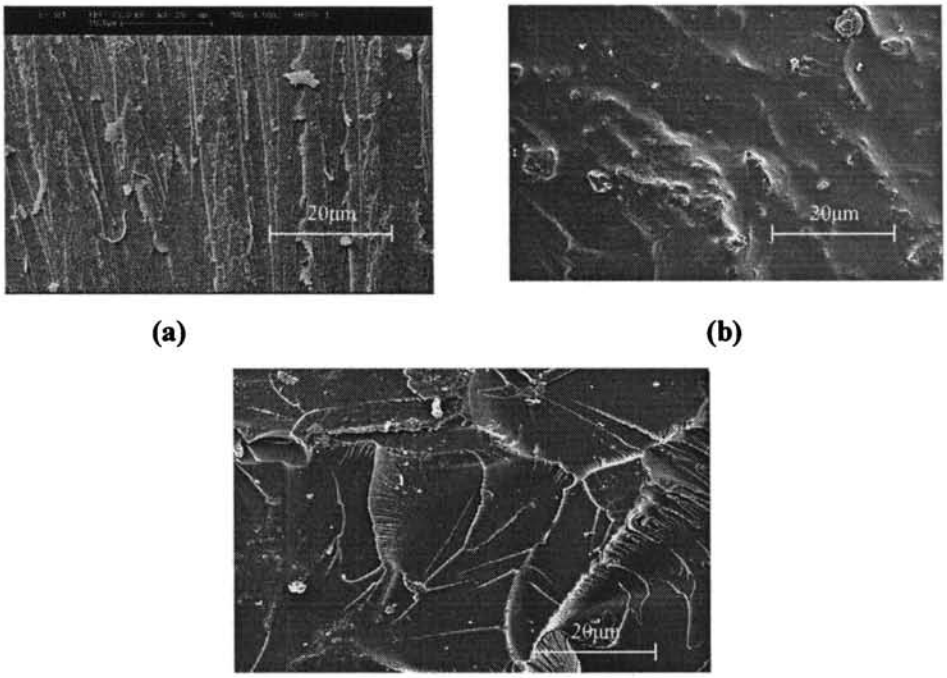
b) Morphological studies

Scanning electron micrographs of filled DGEBA fractured at low deformation rate are shown in Fig.5.25. The micrograph for the unmodified epoxy resin (a) shows typical brittle fracture. Referring to the micrograph (b) the fracture path for $MgAl_2O_4$ filled resin shows good adhesion of the epoxy matrix and the filler. The surface is non-uniform with ridges and crests. Fairly good adhesion of filler to matrix is seen in the case of Zn Fe $_2O_4$ filled epoxy (c) also. The fracture path is relatively smooth and multi layered. This indicates energy absorption during failure. In general the filled samples show considerable ductile behaviour.

Thermal properties

i.TGA: Thermogravimetric analysis indicates better thermal stability for the filled resins than the unmodified epoxy resin.$MgAl_2O_4$ filled sample gave 10.3%residue at 600^{0}C showing its improved thermal stability (Figure 5.26). The $ZnFe_2O_4$ filled resin yielded 7.739% residue compared to the un-modified sample (7.664%). The

TGA data furnished in Table 5.7 reflects improved thermal resistance for the epoxy systems filled with oxide spinels.



(a) **(b)**

(c)

Fig.5.25. Scanning electron micrographs of the fractured surfaces of a) Unmodified DGEBA b) DGEBA/MgAl $_2$O$_4$ and c) DGEBA/ZnFe$_2$O$_4$

ii. DMA: The tan δ curves for the epoxy resin and the MgAl$_2$O$_4$ filled sample are given in Fig.5.27. The damping peak occurs at 71.23^{0}C for the control resin and that of filled resin occurs at a higher temperature 79.24 ^{0}C, (Fig 5.7a). This shows better adhesion between the filler and the epoxy resin. Moreover, the reduced tan δ value of the filled sample is indicative of enhanced coupling. The filled sample also shows greater storage modulus compared to the control resin (Fig.5.27b).

Table 5.7 Thermogravimetric data for epoxy and spinel oxide filled epoxy resins

Sample	Onset temperature (^{0}C)	Temperature(^{0}C) maximum rate	Temperature of half loss (^{0}C)	Residue %
DGEBA	310.56	386.12	367.24	7.664
MgAl $_2$O$_4$	308.68	390.46	379.42	10.37
ZnFe$_2$O$_4$	305.85	387.07	372.37	7.739

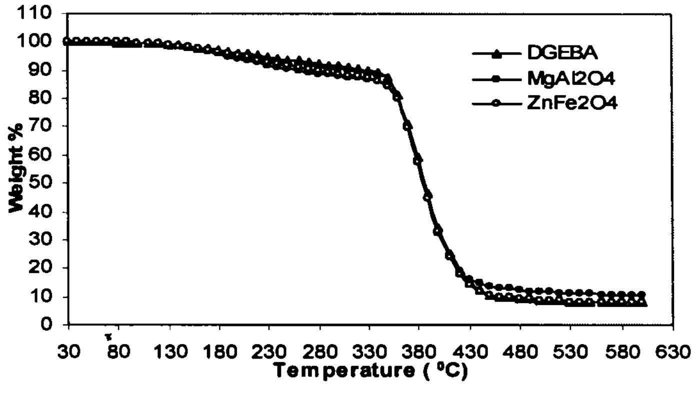


Fig. 5.26 TGA curves for the unmodified and the spinel oxide filled epoxy resins

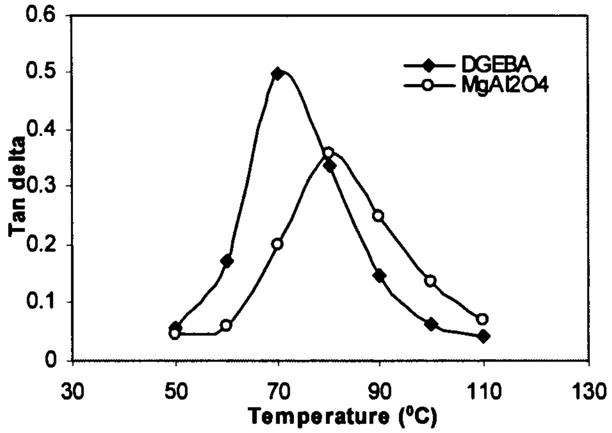


Fig. 5. 27a. Tan δ curves for the unmodified and the MgAl $_2$O$_4$ filled epoxy resins

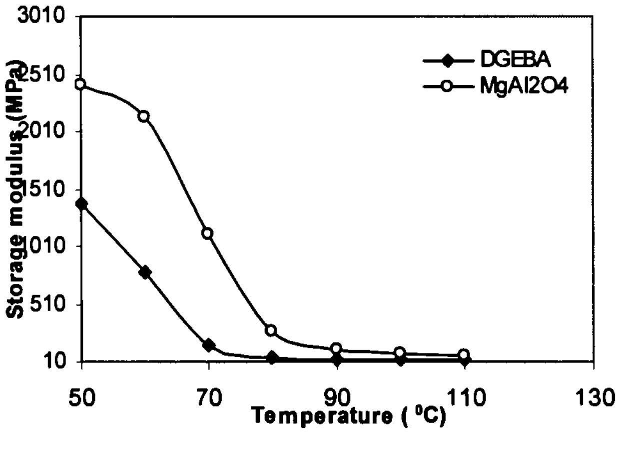


Fig. 5.27b. Storage modulus curves for the unmodified and the MgAl $_2$ O$_4$ filled epoxy resins

5.4 Conclusion

Matrix toughening is found to increase tensile strength, flexural strength and energy absorption (during failure) of epoxy-glass composites. The epoxy-CTBN-glass composite shows the best energy absorption at break while the NBR modified composite gives enhanced tensile strength. Among the phenolic modifiers used EPN is found to give the best performance. However the percentage improvement in properties achieved by matrix modification is less in reinforced samples than un-reinforced samples.

Among the non-black fillers zinc oxide and calcium carbonate are found to give improved properties. However, ZnO provided by far the best results compared to all the reinforcing fillers considered in this investigation. The addition of silane coupling agent is found to improve the interfacial bond between the filler and the matrix resin. Superior mechanical properties are obtained in the case of epoxy-ZnO-silane system. The incorporation of 1% silane is found to raise the increase in energy absorption (to break) of epoxy-ZnO composite from 40% to76% at 5% concentration. Epoxy composites containing spinel oxides as fillers show better properties at relatively lower concentrations. $MgAl_2O_4$ gives the best properties among the aluminates and $Zn\ Fe_2\ O_4$ among the ferrites. In general the aluminates give better performance than ferrites. The oxide spinels, especially the aluminates are found to improve the thermal behaviour of commercial epoxy resin.

References

1. A.C.Moloney, H.H.Kausch and H.R.Stieger, *J. Mater. Sci.*,**19**,1125 (1984)
2. F.F. Lange and K.C. Radford, *J. Mater. Sci.*,**6**, 1197 (1971).
3. A.J. Kinloch, D. Maxwell and R.J. Young, *J. Mater. Sci*, **20**, 4169 (1985).
4. D. Kong and C.E Park., *Chem. Matter.*,**15**, 419(2003)
5. K. Wang, L. Chen, J. Wu, M.L. Toh, C. He and A.F. Yee, *Macromolecules* **38**,788 (2005)
6. M. Nobelen, B.S. Hayes, J.C. Seferis.,*J. Appl. Polym. Sci.*, **90**,2268 (2003)
7. J.R. Pelch, J.E. Ritter, A.J. Lesser, T.P. Russel, T.J. Lardener. *J. Mater.Sci,* **37**, 3269 (2002)
8. C. Kayanak, A. Arikan and T. Tineer., *Polymer,* **44**, 2433 (2004)
9. A.R.West *'Solid state Chemistry and its Applications'*, John Wiley, New York, 569(1989)
10. A.F. Wells, *'Structural Inorganic chemistry'* 4thEdn. ELBS, London, 491 (1991)
11. J.P. Beaufils and Y.Barbaux, *J.Appl.Crystallogr.* **15**, 301(1982).
12. P.S Anilkumar, J.J. Shrotri, S.D. Kulkarni, C.E. Deshpande and S.K. Date., *Materials Letters,* **27**, 293 (1996)
13. L.S. Dent Glasser 'Crystallography and its Applications' Van Nostrand Reinhold Company Ltd, New York, 114 (1977).
14. Clive Whiston *'X-ray Methods-Analytical Chemistry by Open Learning'* Ed. P.E. Prichard, John Wiley, New York, Ch.3, (1987)
15. H. Lipson and H. Steeple *'Interpretation of X-ray Powder Diffraction Patterns'* Macmillan, London, 261(1970)
16. W.L. Bradely In *Thermoplastic Composite Materials*, L.A. Carlsson, Ed. Composite Materials Series, Elsevier, New York Ch-9 (1991).
17. C.K. Riew and A.J. Kinloch, Eds. *Rubber Toughened Plastics*, Ch.1, American Chemical Society, Advances in Chemistry Series 233, Washington DC (1993).

18. M. Frounchi, M. Mehrabzadeh and M. Parvary, *Polym. Int,.* **49**,163 (2000).

19. L. Engel, H. Klingele and G.W. Ehrenstein and H. Schaper, *An Atlas of Polymer Damage,* Wolfe Science Books, Munich (1981).

20. A.Benny Cherian and Eby Thomas Thachil., *Studies on toughening of unsaturated polyester resins,* PhD thesis; Ch. 6., p-253 (2004).

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

Chapter 6

SUMMARY AND CONCLUSIONS

6.1 INTRODUCTION

This concluding chapter provides a glimpse of the summary and conclusions of the work carried out on toughening of epoxy resins. A small amount of modifier can greatly improve the crack and impact resistance of brittle epoxies. The improvement is accomplished without significant deterioration of the thermo mechanical properties of the resin. These toughened resins can be used as matrix materials for various epoxy based composites.

6.2 SUMMARY

The focus of this study is to develop new toughened systems for amorphous epoxy resin via physical and chemical modifications. The contents of the various chapters in this thesis are summarized below.

A literature survey on toughening of epoxy resin, a brief discussion on various thermoset resins, curing of epoxy resins, an account of the included mechanical properties and toughening methods of epoxy resin and toughening of fibre reinforced plastics are included in Chapter 1.

Synthesis of DGEBA, the methods of characterisation and a comparative account of the properties of synthesised DGEBA and commercial epoxy resin are presented in Chapter 2. Results of characterisation studies on various modifier resins such as phenolic resins, epoxy phenol novolacs (EPNs) and cardanol based epoxy compounds are also furnished. Synthesised resins are characterised by spectroscopic methods (^{1}H NMR and FTIR) and gel permeation chromatography. The epoxy systems are characterised by epoxide equivalent determination also.

Experimental details of the toughening of commercial epoxy resin by reactive blending with other thermosets are given in Chapter 3. These resins include (i) phenolic resins of the resol and novolac types ii) epoxy phenolic novolacs iii) unsaturated polyester resin and iv) cardanol based epoxy compounds. The effect of ageing on epoxy resin modified by epoxy novolacs and unmodified resin is also investigated. The use of epoxy derivatives prepared from cardanol and cardanol-bisphenol A mixtures as epoxy modifiers is reported in this chapter. Interpenetrating polymer networks (IPNs) of epoxy resin with unsaturated poly ester resin have been prepared and their properties studied. Thermal properties of the modified resin are monitored using TGA and DSC, 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 control resin.

Modification of commercial epoxy resin by various elastomers by physical blending is dealt with in Chapter 4. A detailed account of the toughening of epoxy resin by blending with solid elastomers, maleated elastomers and functional elastomers is presented. Nitrile rubber (NBR), cross-linked nitrile rubber (NBR-C) and polyurethane rubber are employed for physical blending with epoxy resin. The mechanical properties of cured blends are compared with those of the unmodified resin. Blends of epoxy resin are also prepared with functional elastomers such as hydroxyl terminated polybutadiene(HTPB), epoxidised HTPB (ETPB), carboxyl terminated polybutadiene (CTPB), hydroxyl terminated natural rubber(HTNR) and carboxyl terminated butadiene-acrylonitrile rubber(CTBN). The influence of added bisphenol A in the modification of epoxy resin by some functional rubbers is also investigated. Thermal properties of the modified resin are monitored using TGA and DSC, dynamic mechanical properties by DMA and the fracture behaviour by SEM.

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 elastomers such as NBR, CTBN and ETPB and thermosets such as EPN, PF and epoxy cardanol(EC) are used for making the glass reinforced laminates. The fracture behaviour is studied by SEM. A comparative account of the effect of reinforcing fillers on the properties of epoxy resin is also provided in this chapter. Non-black fillers such as silica, calcium carbonate, zinc oxide, magnesium oxide and asbestos powder are studied. In addition, the preparation of oxide spinels and their effect as reinforcing fillers on the mechanical and thermal properties of epoxy resin are also presented.

6.3 CONCLUSIONS

The following conclusions can be drawn from this investigation.

- The synthesised epoxy resin has in general properties comparable to commercial epoxy resin.
- The co-epoxidation of BPA and cardanol gives more flexible resins The use of cardanol as substitute for phenol or diphenol in epoxy resin synthesis is of importance because it is a cheap renewable natural resource.
- Incorporation of additional bisphenol A into commercial epoxy resin results in a tougher resin possessing better strength as well as elongation.
- Among phenol-formadehyde copolymers used as modifiers, resols of phenol-cardanol mixtures are found to be the most effective choice for toughness enhancement in commercial epoxy resin.
- Hybrid polymer networks of DGEBA and novolacs show significant improvement in toughness properties and water resistance.
- Among epoxy phenolic novolacs (EPNs), the one derived from p-cresol (ECN) leads to maximum improvement in mechanical and thermal properties of epoxy resin. Incorporation of ECN leads to about 135% improvement in toughness at 15% concentration.
- Epoxy resin blended with epoxidised novolac resin shows better aging resistance compared to the unmodified resin.
- Epoxisided cardanol (EC) resin is found to be effective in improving the elongation and energy absorption of the epoxy matrix.
- Co-epoxidised resins of bisphenol A–cardanol mixtures (BPA/EC) are effective modifiers imparting enhanced tensile strength as well as

toughness to the cured epoxy matrix. The resin containing BPA and cardanol in the ratio 80:20 exhibits the best results.

- Incorporation of UPR into the epoxy matrix by chemical reaction (esterification) produces blends with significant elongation but with lowered strength.
- Interpenetrating polymer networks (IPN) of epoxy resin with UPR with a single lowered T_g exhibit enhanced toughness properties. This effect was best with an IPN composition of 20/80 between epoxy and UPR.
- From studies conducted using solid elastomers as modifier, the best toughening effect is exhibited by MA-g-NBR. It gives about 174% improvement in energy absorption of epoxy resin.
- Rubber tearing and bridging predominate in the toughening mechanism of NBR modified epoxies.
- Among different reactive liquid rubbers CTBN is the most effective agent for toughening epoxy resins. Moreover the presence of 15% added bisphenol A magnifies this effect.
- Compatibility as well as interaction of HTPB with epoxy resin can be dramatically improved by re-functionalization of the hydroxyl groups by epoxidation (ETPB) and esterification (CTPB). These derivatives exhibit better mechanical and thermal properties than HTPB when blended with DGEBA
- Matrix toughening is found to marginally increase tensile strength and flexural strength of epoxy glass composites over those of composites based on the unmodified resin. The best result in energy absorption is obtained for EPN among thermoset modifiers and CTBN among rubber modifiers.
- Zinc oxide provides by far the best results compared to all other reinforcing fillers considered in this investigation. Oxide spinels as non-black fillers impart improved thermal properties to the composites.

6.4 FUTURE OUTLOOK

The toughening of unsaturated epoxy resins is an area which calls for extensive research in the coming years. Some specific areas are outlined below:

- Large scale manufacture of toughened resins has to be investigated and problems relating to regular production have to be solved.
- The improvement in properties of glass-reinforced composites employing toughened resins has to be comprehensively investigated. Fundamental phenomena leading to increase in composite tensile strength on matrix toughening have to be identified.
- Commercial significance of using toughened resins has to be further studied. Field trials and performance reports can be procured from actual users.
- A better insight to epoxy-EPN and epoxy-EC blends can be achieved only through investigations into the chemical reactions involved.
- The superiority of certain particulate fillers such as ZnO and $CaCO_3$ in improving the properties of epoxy resin invites thorough investigation.

……………….o………………..

ABBREVIATIONS AND SYMBOLS

ASTM	American standards and testing methods manual
ACN	Acrylonitrile
b	Width of specimen tested
BMC	Bulk molding compounds
BP	Boiling point
BPA	Bisphenol A
BPN	Butyl phenol novolac
BPO	Benzoyl peroxide
BPA/EC	Bisphenol A /cardanol epoxides
CDN	Cardanol novolac
CF	Cardanol-formaldehyde resol
CPF	Cardanol-phenol-formaldehyde resol
CPN	Cardanol-phenol novolac
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
EPN	Epoxidised phenolic novolac
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
HTNR	Hydroxyl terminated natural rubber
HTPB	Hydroxyl terminated polybutadiene
Hz	Hertz
IA	Isophthalic acid
IPN	Interpenetrating polymer networks
IUPR	Isophthalic resin
L	Support span
L.R.	Laboratory reagent
MA	Maleic anhydride
MA-g-NBR	Maleated nitrile rubber
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
PEEK	Poly(ether ether ketone)
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
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)
TGA	Thermogravimetric analysis
T_g	Glass transition temperature
TIPS	Thermally induced phase separation
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

Publications in international journals

1. 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.
2. Studies on the modification of commercial epoxy resin using cardanol - formaldehyde copolymers, K. P. Unnikrishnan and Eby Thomas Thachil, *International Journal of Polymeric Materials* (In press).
3. Ageing and thermal studies on epoxy resin modified by epoxy novolacs, K.P.Unnikrishnan and Eby Thomas Thachil, *Polymer-Plastics, Technology and Engineering* (In press. PPTE # 206902065)
4. Hybrid polymer networks of epoxy resin and substituted phenolic novolacs, K.P.Unnikrishnan and Eby Thomas Thachil, *International Journal of Polymeric Materials* (Accepted.)
5. Toughening of epoxy resins-a review., K.P. Unnikrishnan and Eby Thomas Thachil, *Polymer-Plastics, Technology and Engineering* (Accepted. PPTE # 221010275)
6. Effect of phenol / formaldehyde stoichiometry on the modification of epoxy resin using epoxidised novolacs, K.P.Unnikrishnan and Eby Thomas Thachil, *International Journal of Polymeric Materials* (Accepted. GPOM-66138)
7. Studies on the modification of commercial epoxy resin using cardanol based phenolic resins, K.P. Unnikrishnan and Eby Thomas Thachil, *Journal of Elastomers and Plastics* (Communicated id.,# JEP 4344)
8. Ageing and thermal studies on unsaturated polyester resin modified by epoxy resins, Benny Cherian. A, Unnikrishnan K.P. and Eby Thomas Thachil, *Journal of Applied Polymer Science* (I.D. #16394 Communicated).

Papers presented in international seminars/conferences

1. Studies on blends of epoxy resin with epoxidised novolac resins. *International Seminar on Advances in Polymer Technology*, Jan 16 to17, 2004, Eindhoven University of Technology, The Netherlands and PSRT, CUSAT, Kochi.

2. Influence of phenol - formaldehyde ratio on the modification of epoxy resin using epoxidised novolacs, *Proceedings of the ICBC 2005, International Conference on "Advances in Polymer Blends, Composites, IPNs and Gels: Macro to Nano Scales,* March 21-23, 2005, School of Chemical Sciences, MG University, Kottayam

3. Interpenetrating Polymer Networks of Unsaturated polyester and Epoxy Resins, (A.Benny Cherian and K.P.Unnikrishnan), *ICBC 2005, International Conference on "Advances in Polymer Blends, Composites, IPNs andGels: Macro to Nano Scales,* March 21-23, 2005, School of Chemical Science. M.G. University, Kottayam.

Paper presented in national seminars/ symposia

1. Effect of silane coupling agent on the mechanical properties of filled epoxy composites *Proceeding of the UGC sponsored National Seminar, Read MS-2005, Recent Advances Membrane Science and Technology*, March 09-10, 2005, NSS College, Nenmara, University of Calicut.