Modification of Phenol Formaldehyde Resin for Improved Mechanical Properties

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by

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DECEMBER 2009

To My Parents and Teachers…

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Certificate

This is to certify that the thesis entitled **"Modification of Phenol Formaldehyde Resin for Improved Mechanical Properties"** which is being submitted by Mr. Parameswaran P. S. in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi-22 is a record of the bonafide research work carried out by him under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Cochin-682 022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

Dr. Eby Thomas Thachil
(Supervising Teacher)

Declaration

I hereby declare that the work presented in this thesis entitled **"Modification of Phenol Formaldehyde Resin for Improved Mechanical Properties"** is based on the original research work carried out by me under the guidance and supervision of Dr. Eby Thomas Thachil, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

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Parameswaran P. S.

Cured phenolic resins are highly cross-linked polymers with a three dimensional molecular structure. The network structure imparts high stiffness and strength, heat resistance and solvent resistance. Due to these excellent properties they are widely used as engineering polymers of choice for structural applications in aerospace structures to household articles. But their use in many fields is restricted by some inherent drawbacks. Resol resins undergo curing by a condensation mechanism either in the presence of a catalyst or by heat. The condensation byproducts, mainly water, lead to the formation of microvoids in the cured resin. This necessitates the application of pressure during curing to get void free articles. The chemical linkages in the cured phenolic resol resin, involving rigid benzene rings connected by short methylene groups, render it brittle. In addition to the above shortcomings, formaldehyde emission and poor shelf life of resols limit the use of these phenolic resins. Consequently, there is a need to modify phenolic resins for wider applicability.

In this study it has been attempted to modify the properties of phenolic resols by the addition of other thermosets. Consisting of seven chapters, the thesis gives a general introduction in the first chapter. The optimisation of the stoichiometry of phenol/formaldehyde reaction is covered in the second chapter. Chapter 3 consists of the comparative evaluation of cardanol based phenolic resol resins prepared by different methods. Modification of resols by unsaturated polyester and epoxies forms the basis of fifth and sixth chapter respectively. The effect of matrix modification on the properties of glass and cotton reinforced composites is discussed in Chapter 6. The major findings of the study along with scope for future research are summarised in the last chapter.

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, Professor and Head, Dept. of

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ABSTRACT

Phenolic resins suffer from the presence of microvoids on curing. This often leads to less than satisfactory properties in the cured resin. This disadvantage has limited the use of phenolic resins to some extent. This study is an attempt to improve the mechanical properties of the phenolic resol resins by chemical modification aimed at reducing the microvoid population. With this end in view various themoset resins synthesised under predetermined conditions have been employed for modifying phenolic resols. Such resins include unsaturated polyester, epoxy and epoxy novolac prepolymers.

The results establish the effectiveness of these resins for improving the mechanical properties of phenolics. Experimental and analytical techniques used include FTIR, DMA, TGA, SEM and mechanical property evaluation. While most of the modifier resins employed give positive results the effect of adding UP is found to be surprising as well as impressive.

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Chapter **1**

INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

The development of new and improved polymers and their application in novel areas have led to innumerable new products. Polymers differ in characteristics because of their unique structural complexities. Eventhough polymers are broadly classified as elastomers, plastics and fibers, the properties of individual members of the same group vary widely. A change in the nature of pendant groups, arrangement of the monomeric units or change in the reaction conditions, catalysts etc. can tremendously change the properties of individual polymers.

For the last five decades researchers have been extensively exploring all possibilities to discover novel polymers. But now, a large amount of work is aimed at modification of existing polymers [1-7]. This has been achieved by the modification of monomers in the initial stage, blending different types of polymers together so that the properties of one polymer offset the drawbacks of the other or by other techniques like addition of filler or reinforcements [8-11].

The general classification of polymers mentioned earlier is according to certain common patterns of behaviour. Elastomers are characterized by large deformability, lack of rigidity, large energy-storage capacity, nonlinear stress-stain curves and compressibility of the same order of magnitude as most liquids [12]. Certain elastomeric materials possess additional useful characteristics to a relative degree, such as corrosion and chemical resistance, oil resistance, ozone resistance, temperature resistance and resistance to other environmental conditions. The rubbery polymers are characterized by low molar cohesion (<2 kcal/g mol per 5Å chain length) [13].

Of the three different types, polymers show greatest strength in the fiber form. Fibers are characterized by high mechanical strength. They exhibit molar cohesion in the range of 4-10kcal/g mol per 5Å chain length.

Plastics usually possess greater strength than rubbers. Some of them are hard, horny, rigid, stiff and dimensionally stable while others may be soft and flexible.

lastics usually exhibit molar cohesion in the range of 2-5 kcal/g mol per 5Åchain
·ngth. Plastics are generally classified as thermoplastics and thermosetting plastics.

Table 1.1 shows some of the important thermoplastics and their properties.

Table 1.1 Important thermoplastics and their properties [12, 14]

Thermoplastics	Properties
Polyethylene	Easy processability, excellent electrical insulation properties and chemical resistance, toughenss and flexibility even at low temperatures, low water vapour permeability and reasonable clarity of thin films.
Polypropylene	Good appearance, low density sterilisability, environmental stress cracking resistance and good heat resistance and excellent flex resistance.
Poly vinyl chloride (PVC)	Plasticised PVC has moderate heat resistance and good chemical, weather and flame resistance, good electrical insulation properties and good resistance to hydrocarbons.
Polystyrene	Good electrical insulation properties, low water absorption, easy processability, good barrier properties, good dimensional properties, reasonable chemical resistance and low thermal conductivity.
Poly methyl methacrylate	Excellent transparency, good weathering resistance, good optical properties and moderate impact resistance.
Polyamides	Good toughness, rigidity, abrasion resistance, good hydrocarbon resistance and reasonable heat resistance.
Polycarbonates	Rigidity, good toughness, excellent transparency, good insulation properties, virtually self-extinguishing and physiological inertness.
Polyacetals	High mechanical strength, predictable dimensional behaviour, chemical and corrosion resistance, light weight, acceptability for food contact applications and ease of processing.
Acrylonitrile-Butadiene-Styrene (ABS)	Good processability, appearance, lower cost along with a good balance of engineering properties including, low creep, good dimensional stability and high strength and rigidity

Thermosetting plastics [12], as the name implies, can be cured, set or hardened into a permanent shape. Curing is an irreversible chemical reaction also known as crosslinking. It usually occurs under the influence of heat and/or catalyst and leads to a three dimensional rigidized chemical structure. For some thermosetting materials, curing is initiated or completed even at room temperature. Although the cured part can be softened by heat, it cannot be remelted or restored to the flowable state that existed before curing. Continued heating for long times leads to degradation or decomposition.

The load-bearing qualities of plastics can be improved by reinforcing with fibers. Such fiber-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.

Phenol formaldehyde (PF) resins are a type of thermosets which are, inter alia, used as a matrix for fibre reinforced plastics (FRP). The widespread use of these resins is due to their low cost, ease of processing, excellent wetting properties with reinforcements, weathering resistance, dimensional stability, thermal resistance, chemical resistance and ablative properties [15]. The most important properties, however, that differentiate phenolics from other plastic composites are excellent creep resistance at high temperatures and ablative properties. This particular study aims at the modification of PF resins for improved mechanical properties.

1.2 Thermoset resins

Thermosetting resins change irreversibly under the influence of heat and/or catalyst into infusible and insoluble materials by the formation of covalently cross-linked, thermally stable networks. Preparation of thermosetting polymers is a two stage process involving the formation of long chain molecules with reactive groups. In the second stage these chains are crosslinked by heat and/or the addition of

curatives. Sometimes irradiation is employed to achieve cross-linking [16]. Important thermosetting resins are phenolics, aminoplasts, epoxy resins, unsaturated polyesters, alkyds, vinyl esters, allyl resins, polyurethanes, silicones, furfurals etc. [17].

1.2.1 Phenolic resins

Phenolic or PF resins were the first polymeric resins produced commercially from simple low molecular weight compounds [15]. These 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. Novolacs do not contain any reactive groups and hence require the addition of a crosslinking agent and heat to achieve cure. 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 initial methylol formation is rapid, subsequent condensation is slow. This results in low molecular weight liquid resols containing 2-3 benzene rings. When the resol is heated cross-linking via the uncondensed methylol groups occurs. Resols are also known as one-stage resins.

1.2.2 Aminoplasts

Aminoplasts 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.

$$H_2N - CO - NH - CH_2OH + H_2N - CO - NH - CH_2OH \rightarrow \sim\sim HN - CO - NH - CH_2 \sim\sim$$
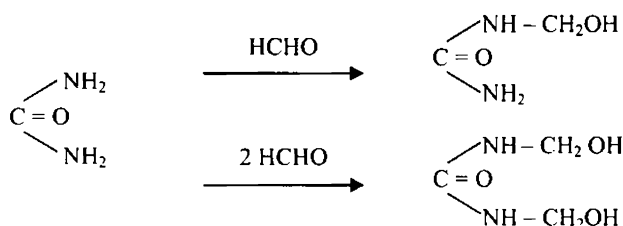
In the second stage these are subjected to acid conditions at elevated temperatures and the following sequence of reactions occurs. Methylol ureas condense with each other by the reaction between the $-CH_2OH$ group of one molecule and the $-NH_2$ group of another to form linear chains.

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

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 at 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 depends on the melamine to formaldehyde ratio and the reaction conditions. The methylols formed enter into reactions similar to UF resins and give a cross- linked polymer. The main resinification reaction involves methylol-methylol condensation.

$$\sim\sim NH - CH_2 - OH + HO - H_2C - HN \sim\sim \rightarrow \sim\sim NH - CH_2O - H_2C - HN \sim\sim + H_2O$$
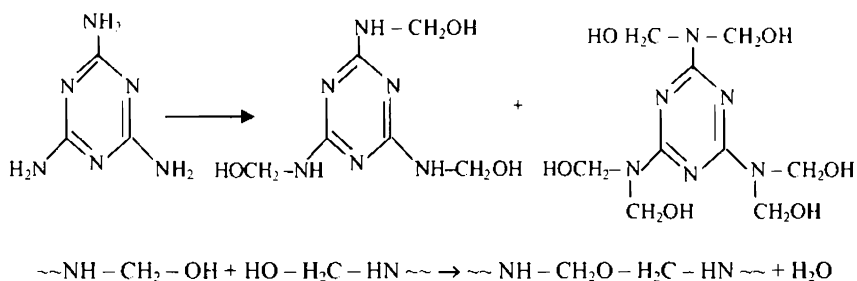
The tensile strength and hardness of UF resins are better than that of phenolics. MF resins have better hardness, heat resistance and moisture resistance than UF

resins. Amino resins are used as moulding and laminating resins apart from adhesive formulations.

1.2.3 Epoxy resins

Epoxy resins mostly consist of the diglycidyl ether of bisphenol A (DGEBA). They are characterised by the presence of more than one 1,2 epoxide groups in the structure. They are prepared by reacting a dihydric phenol like bisphenol A with excess epichlorohydrin in an alkaline medium. The reactions involved are shown below.
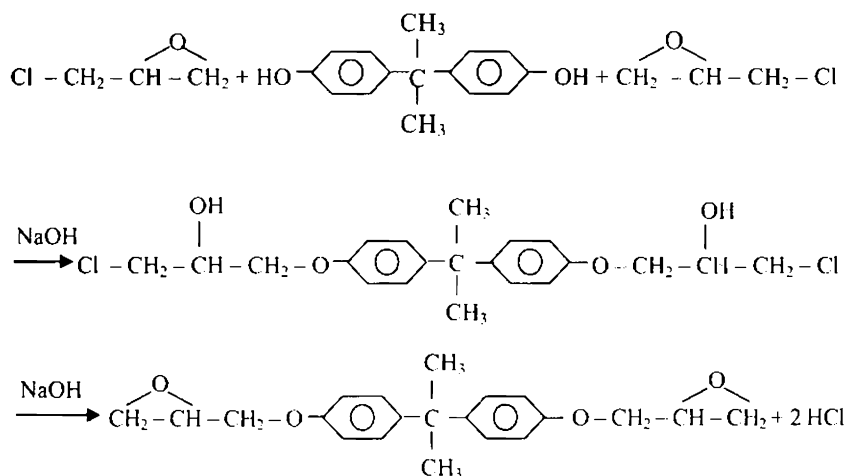
High molecular weight resins are prepared by reducing the amount of excess epichlorohydrin and reacting under strongly alkaline conditions. Cross-linking is achieved by adding curatives that react with epoxy and hydroxyl groups situated on adjacent chains. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Some of the commonly used hardeners are anhydrides (acids), amines, polyamides and dicyandiamide. High chemical and corrosion resistance, good thermal and mechanical properties, outstanding adhesion to various substrates, low cure shrinkage and good electrical properties are the characteristic features of epoxy resins. The polar groups in the structure ensure greater adhesion. These resins are mainly used for lamination, surface coating applications, industrial floorings and electrical and electronic engineering applications.

1.2.4 Polyester resins

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

a)   Unsaturated polyesters

Unsaturated polyesters (UP) are prepared by condensing 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 most 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 reduces 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. The chemical structure of the unsaturated polyester is shown below.

$$-OC-CH=CH-CO-O-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-O-OC \underset{\langle O \rangle}{\diagup} CO-O-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-O-$$
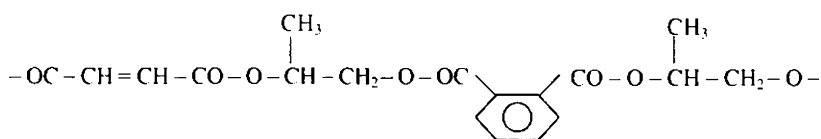
b)   Alkyd resins

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.

$$-OOC \text{—} \underset{}{\bigcirc} \text{—} COO - CH_2 - CH - CH_2 - OOC \text{—} \underset{}{\bigcirc} \text{—} COO-$$

$$\underset{R - C = O}{\overset{O}{|}}$$
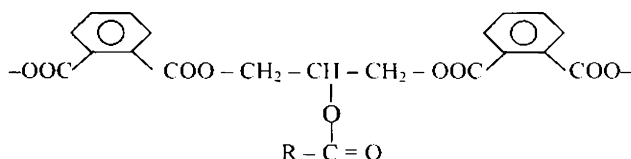
R represents the long chain alkyl group, characteristic of the oil.

c) Vinyl esters

Vinyl esters [18] 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 excellent 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:

$$H_2C\overset{O}{\overset{/\backslash}{—}}CH\text{-}CH_2\text{-}R\text{-}CH_2\text{-}CH\overset{O}{\overset{/\backslash}{—}}CH_2 \;+\; 2\; HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{R'}{\overset{|}{C}}\text{=}CH\text{-}R'' \xrightarrow[\text{Catalyst}]{\text{Heat}}$$

$$R''\text{-}CH\text{=}\overset{R'}{\overset{|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}\overset{OH}{\overset{|}{CH}}\text{-}CH_2\text{-}R\text{-}CH_2\text{-}\overset{OH}{\overset{|}{CH}}\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{R'}{\overset{|}{C}}\text{=}CH\text{-}R''$$

9
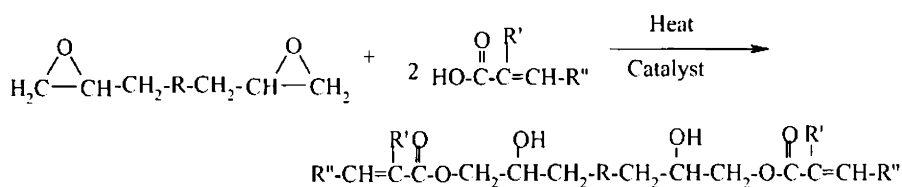
d)   Allyl resins

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. 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. They are cured by heat and/or free radical catalysts.

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-R-OH + n OCN-R'-NCO $\rightarrow$ H -(OR-OOCNH-R`)$_n$-NCO-
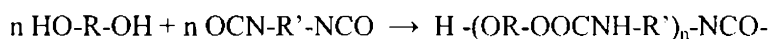
Polyurethanes are extremely versatile polymers. They occur in the liquid, gum or thermoplastic resin state. The method of processing also varies accordingly. It is the ability to form polymers containing not only the urethane linkage but also other groups as integral units in or on the polymer chains 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 with high elongation at break. This combination of properties is not possessed by any other commercial rubber or plastic. Urethane elastomers also have greater energy absorption properties than other similar rubbers and plastics.

1.2.6 Silicones

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

These 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.

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

$$-\underset{|}{\overset{|}{Si}} - OH \ + HO -\underset{|}{\overset{|}{Si}} - \ \longrightarrow \ -\underset{|}{\overset{|}{Si}} - O -\underset{|}{\overset{|}{Si}} - + H_2O$$
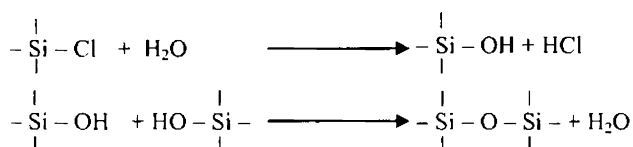
Silicone polymers are thermally stable and are available in liquid, waxy and rubbery forms. These polymers are used in surface coatings and adhesives where chemical resistance and water repellence are important. Silicone polymers are also used for laminates which can withstand high temperatures without 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 chemistry of resinification of either furfuryl alcohol or furfural has not been established satisfactorily. The important applications are lining of tanks and piping, manufacture of alkali resistant cements and preparation of laminates for chemical plants.

1.3 Phenolic resins

Phenolic resins are one of the oldest commercial polymeric resin systems often identified with the advent of the plastic industry. Phenol-aldehyde type reactions were first reported by Von Baeyer in 1872 [19]. He discovered that the reaction between phenol and acetaldehyde in the presence of an acid catalyst gave an unexpected resinous mass. The resins he produced, however, were of little commercial or technical interest. In 1891, Kleeberg

was the first to use formaldehyde in the synthesis of the resins. Blumer later applied this chemistry in 1902 by using less than one mole of aldehyde per mole of o-cresol [20]. He produced novolacs which later served as substitutes for shellac.

It was Dr. Leo H. Baekeland in 1905 who made the most significant contributions in the field of phenol-formaldehyde type reactions [15]. He was convinced of the commercial value of these products and in 1909 he started to work with phenol and formaldehyde to synthesize the first cross-linkable resins. His work was significant as it brought out the differences between acid and alkali catalysis as well as the importance of the phenol to formaldehyde ratio. Dr. Baekeland was granted a patent in 1909 describing his alkaline catalyzed Bakelite resins ("Resols") and also the acid-cured "Novolac" product [21-23].

1.3.1 Resols

Resols are formed by the base catalysed reaction of formaldehyde and phenol (F:P) at a molar ratio between 1:1 to 1:3. Typical F:P molar ratios used in the preparation of resol resin are between 1.5:1 and 2.5:1.0.

The mechanisms of the reactions leading to the formation of resol phenolic resins have been the object of a number of studies [24-27]. The reaction product is a complex mixture of oligomers containing free hydroxymethyl end groups. During the reaction, hydroxymethylation on the ortho and para position of the phenol takes place to form o-&p-hydroxymethyl phenols (2-&4-HMPs), o,o-dihydroxymethylphenol, o,p-dihydroxymethylphenol and 2,4,6-trihydroxymethyl phenol as per reaction Scheme1.

Scheme 1
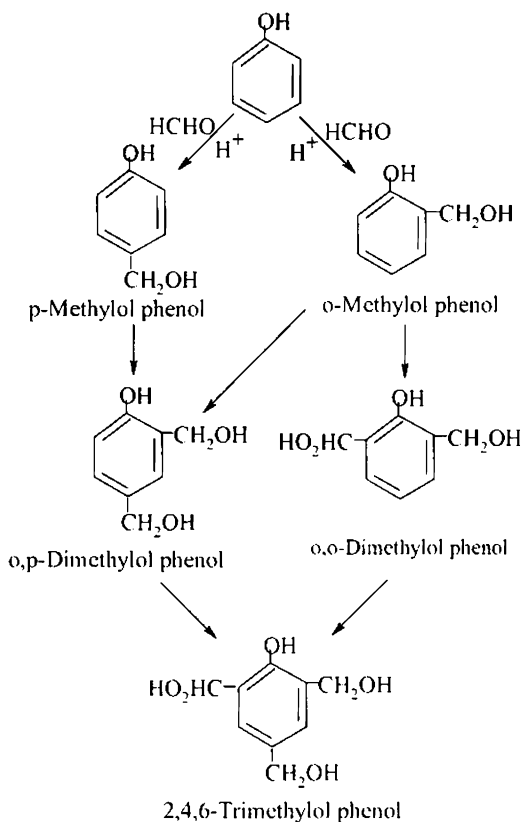
1.3.1.1 Hydroxymethylated phenols

When phenol is added to aqueous formaldehyde in the presence of a base, the phenolic hydroxyl group is readily deprotonated into a reactive phenoxide ion, which is resonance stabilized. (Fig. 1.1).
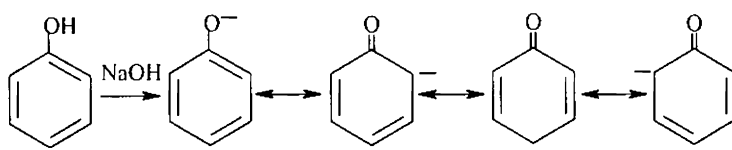
Fig. 1.1 Reactive phenoxide ion under basic conditions

The electron density in the phenoxide ion results in an electrophilic aromatic substitution with methylene glycol, the hydrated form of formaldehyde, both at the para and ortho positions (Fig. 1.2).

13
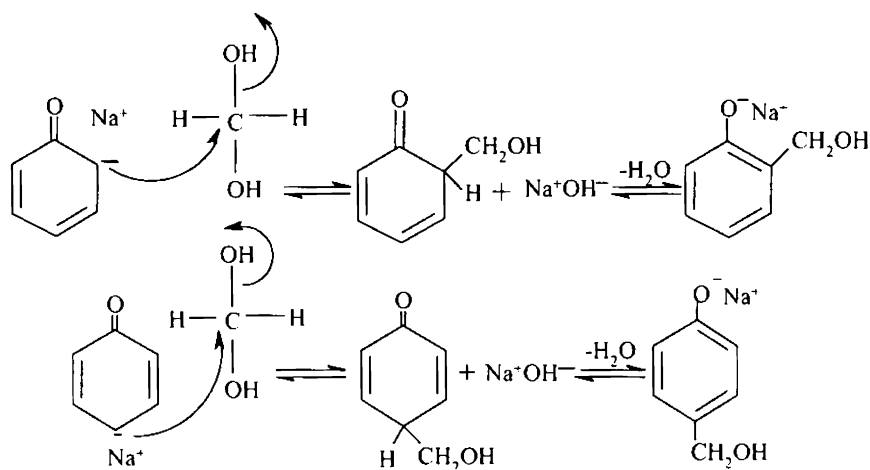
Fig. 1.2 Electrophilic aromatic substitution of methylene glycol on phenol ortho (top) and para (bottom) positions

The para position is believed to be more reactive than the ortho position [28]. Since there are two ortho sites for one para site, ortho substitution predominates and proceeds at a faster rate than para substitution [15]. Generally, different catalytic mechanisms produce specific isomeric compositions of the HMPs mixture [15, 29, 30]. For instance, when metal hydroxides are utilized, a chelate ring mechanism, first proposed by Caesar and Sachanen, favours ortho substitution (Fig. 1.3) [31].
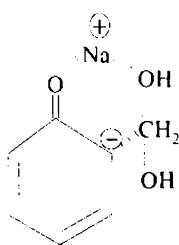
Fig. 1.3 Chelate ring intermediate in sodium hydroxide based catalysis

When ammonia and amine catalysts are utilized on the other hand, nitrogen containing intermediates are likely to form as illustrated in Fig. 1.4 [32].

14
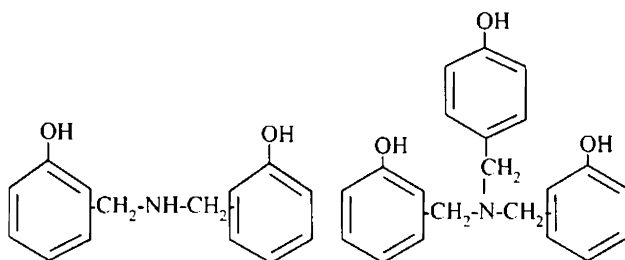
Fig. 1.4 Di(hydroxybenzylamine) (left) and Tri(hydroxybenzylamine)(right) intermediates in ammonia based catalysis of PF polymerization

Regardless of catalytic mechanism, hydroxymethylation proceeds rapidly thereby yielding a high level of hydroxymethyl substitution prior to the slower condensation [25]. Typically the reaction mixture comprises mono, di and tri substituted HMPs. In fact, electrophilic aromatic substitutions of formaldehyde on mono and di substituted HMPs proceed at a faster rate than the initial hydroxymethylation so that high proportions of difunctional and trifunctional derivatives result [33]. At this stage of the polymerization, excess formaldehyde may also react with phenolic hydroxymethyl groups to produce substituted hemiformal moieties. Such molecular structures have been detected by solution nuclear magnetic resonance (NMR) spectroscopy [34]. Fig. 1.5 illustrates some common hydroxymethylated derivatives present at the initial stage of PF polymerization. At this stage, HMPs are amenable for condensation reactions.
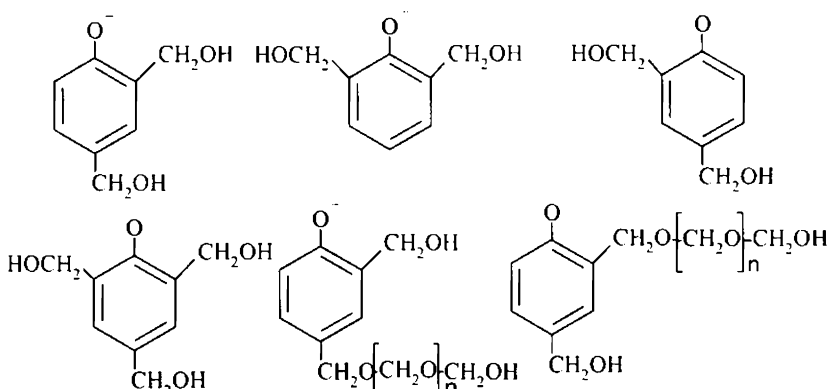
Fig. 1.5 HMP derivatives

15

1.3.1.2 HMP condensation

The condensation of hydroxymethylated species is a step growth polymerization in that a byproduct, water is released. Jones first proposed the existence of quinone methide intermediates (Fig. 1.6) [35].
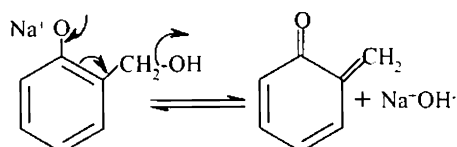
Fig. 1.6 Quinone methide formation from HMP

Quinone methides are very reactive and will react with nucleophilic sites from another phenol or substituted phenol molecule. In this subsequent electrophilic aromatic substitution, methylene bridges are generated (Fig. 1.7). Methylene bridges form predominantly in the ortho-para and para-para positions, while ortho-ortho methylene bridges are rarely formed [34, 36].

It is also thought that hydroxymethyl groups can condense to form ether bridges. Methylene ether bridges can be formed by the reaction of a hydroxymethyl group on a quinone methide intermediate as illustrated in Fig. 1.8.
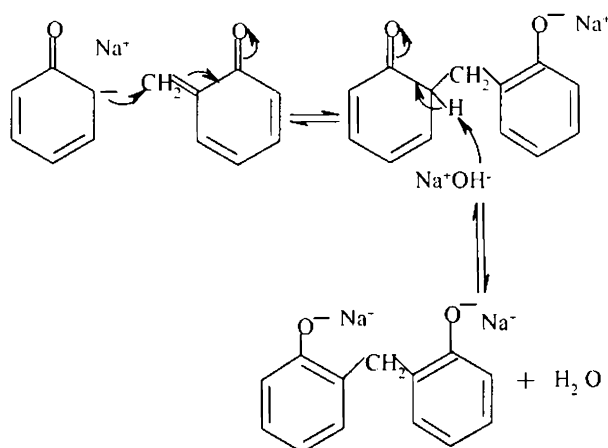
Fig. 1.7 Condensation reactions via quinone methide intermediates
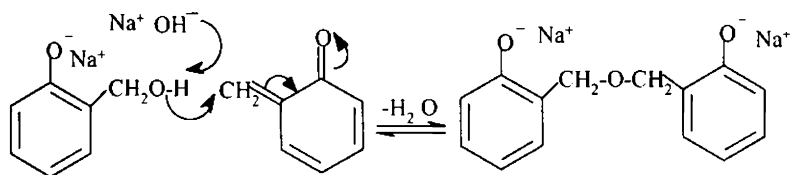
Fig. 1.8 Mechanism for methylene ether bridge formation

A number of studies have been conducted on the self-condensation of 2-HMP and 4-HMP or their reactions with phenol [37, 38, 39]. These studies have shown that the self-condensation of 4-HMP is 6-7 time faster than that of 2-HMP and the major condensation products formed from self condensation at low reaction temperatures are dimers (Scheme 2).

Scheme 2
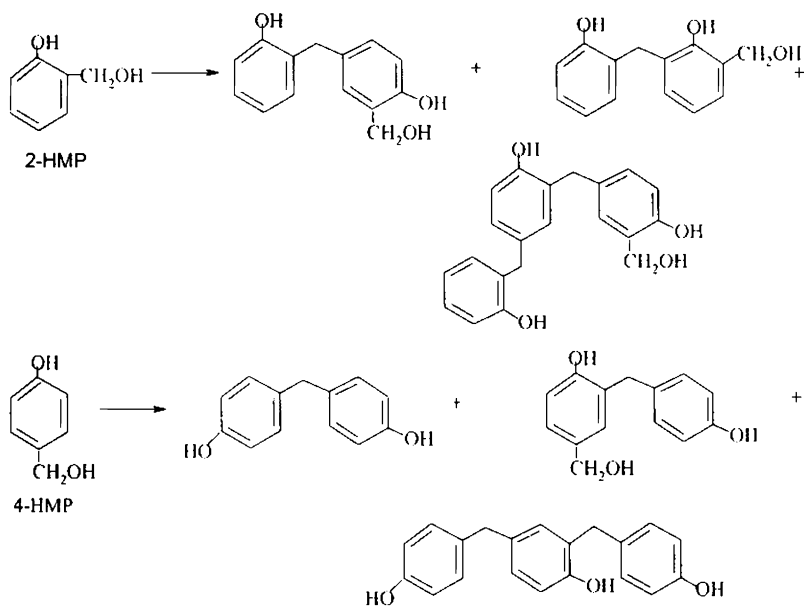
A number of mechanisms have been proposed for the condensation of hydroxy methyl groups [15]. The first mechanism involves the formation of a quinone methide intermediate [28, 40] and the second is an SN2 type mechanism [15, 41].

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1.3.1.3 Curing behaviour of phenolic resol resin

One of the significant properties of the phenolic resins is their ability to transform from the liquid state to the solid state by forming covalently bonded three dimensional network structure. Because of the difficulty of eliminating water most commercial phenol-formaldehyde grades contain water. During the crosslinking, resols can undergo the following morphological stages.

Stage A: Beginning stage, resin is liquid, meltable and soluble

Stage B: Middle stage, crosslinking is commenced and the resin is thermoplastic, unmeltable, unsoluble

Stage C: End stage, resin is completely thermoset, unmeltable, unsoluable (See Scheme 3)

Scheme 3

Resol

Crosslinked resin
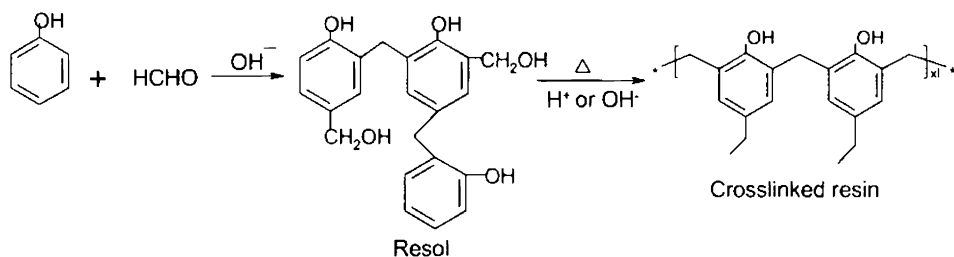
The presence of methylol groups in the prepolymers make them reactive in the absence of crosslinking agents. Hence resols cure on long standing at room temperature. The curing reaction can be accelerated either by heating or in the presence of catalysts like p-toluene sulphonic acid (PTSA), HCl or phosphoric acid.

During the curing reaction either methylene bridges or dimethylene ether linkages are formed between the benzene rings (see Figs. 1.7 & 1.8). This depends on the curing conditions. The formation of dihydroxydibenzyl ether is very unlikely under strong alkaline conditions. This reaction, however, is considered the prevalent one under neutral or weakly acidic conditions and temperatures up to 130°C which

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normally exist during the curing of resols [42]. Above 130-150°C methylene bridge formation becomes predominant [43].

Being a polycondensation reaction, the molecular weight increases rapidly with conversion. However, as the molecular weight increases, the water already present in the resin and that produced during the reaction becomes incompatible with the curing resin and phase separates to produce water domains. These are observed as 'microvoids' of 2-10 μm in diameter in the cured matrix. The size of these domains is governed by the surface tension of the resin and the rate and extent of the curing reaction [44]. A typical scanning electron micrograph (SEM) showing the microvoids on the fractured surface of cured resol resin is shown in Fig. 1.9 [45].
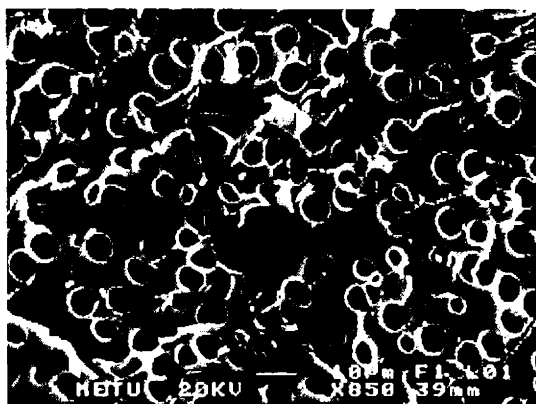
Fig. 1.9 SEM picture of the fractured surface of cured phenolic resol resin

1.3.1.4 Synthesis conditions and prepolymer properties

A large number of studies have assessed PF properties on the basis of reaction conditions [32, 36]. It has long been established that catalyst choice and reagent ratios significantly impact resol characteristics. Likewise, synthesising procedures have been empirically developed to respond to novel end use specifications [36]. The important parameters on PF synthesis/structure/properties relationships are presented below.

a. Catalyst

Catalyst is an important influence on the resol isomeric structure and hence on its properties. For instance, preferential ortho substitution increases in the following sequence of catalysts KOH< NaOH< LiOH< $Ba(OH)_2$< $Sr(OH)_2$< $Ca(OH)_2$< $Mg(OH)_2$ [46]. Ammonia-based catalysts are believed to favour more linear resols [47]. Of significance also, is the catalyst impact on PF solubility. For resins prepared from p-cresol and formaldehyde with HCl, NH_4OH or NaOH as catalysts, the oil solubility decreases in the above order [48]. Sodium hydroxide for instance enhances PF solubility in water thus lowering viscosity. Consequently more advanced resols can be manufactured by increasing the sodium hydroxide content while maintaining adequate flow properties. Likewise, reagent dilution can be adjusted to permit more advanced resols with adequate flow properties. Such practices are used in plywood PF resins, which have higher sodium hydroxide contents and lower resin solids [36].

Tertiary amines are also used as catalyst for resol synthesis [49]. Tertiary amines with C_1-C_4 alkyl substituents are good catalysts for the resol synthesis reactions, although their activities are not as high as that for sodium hydroxide. The advantages of the resols obtained in the presence of trialkylamines are longer gelation time, least ash content after incineration and improved hydrolysis resistance. The main drawback for these catalysts is their emission from resins in the setting process. Tetraalkyl ammonium hydroxides can also be used as potential catalysts for resol synthesis [46]. But the catalytic activity is lower than that of sodium hydroxide. Tetraalkyl ammonium hydroxide catalysed resins have similar properties of trialkyl amine catalysed resins with the added advantage of better binding ability. Ammonia and amine catalysed resols have limited miscibility with water and these are generally soluble in alcohols and oils.

Thermal degradation, flammability and mechanical performance of resol resins are strongly dependent on the nature of the catalyst used in their synthesis [50].

b. Reagent ratio

PF resol properties are largely governed by the initial F:P molar ratios [28, 51-56]. Generally, high F: P ratios produce highly branched resins whereas low F:P ratios

favour more linear structures. So et al. utilized Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and NMR to obtain detailed information on PF characteristics as a function of F:P molar ratios [56]. As expected, higher F:P ratios were found to enhance hydroxymethylation and increase the degree of polymerization [56]. Similarly, hemiformal and ether bridge structures were directly related to excess formaldehyde. As the F:P molar ratio increased, the molecular weight and activation energy increased while the gel time, peak temperature, resin pH, and nonvolatile solids content decreased [57]. More surprisingly, a synergy between F:P ratio and cure temperature on PF chemical structure was reported. Specifically, higher cure temperatures were required to convert methylene ether to methylene bridges when high F:P ratios were utilized [56]. While So et al. reported no F:P ratio influence on the resol isomeric structure, another study suggests direct correlation between ortho substituted proportions and F:P molar ratio [55]. Holopainen and coworkers detected greater proportions of o-substitution, hemiformal species and p-p' methylene bridges with increasing F:P molar ratio [55]. The authors further confirmed greater degrees of polymerization with greater F:P molar ratios, whereas polydispersity exhibited the opposite trend. The study also assessed F:P ratio influence on resol cure properties with differential scanning calorimetry (DSC). It was found that hydroxymethylation and condensation reactions lead to more reaction steps with increasing F:P molar ratios. These studies reveal that the F:P ratio is a key factor to tailor PF morphology, molecular weight and curing properties.

c.   Phenols and aldehydes.

Simple phenol is most commonly used for the synthesis of PF resins. Other phenols are used only for the synthesis of specialty applications. Alkyl phenols (o-cresol, p-cresol and m-cresol) are used for the production of coating resins because of their good compatibility with natural oils and increased flexibility or as cross-linking agents in the rubber industry.

Resorcinol, a dihydric phenol (1,3-dihydroxybenzene), is a very interesting material for the production of PF resin. However, the relatively high price limits its

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application to where high performance is required. The reaction rate with formaldehyde is considerably higher compared to that of phenol [58]. This is of great technical importance for the preparation of cold setting adhesives [59].

Formaldehyde is the almost exclusively used carbonyl component for the synthesis of technically relevant phenolic resins [60]. Special resins can also be produced with other aldehydes, for example acetaldehyde, furfural or glyoxal, but have not achieved technical importance. Ketones are very seldom used instead of aldehydes.

d.   Additives

In the production of industrial PF resins a variety of additives are utilized to modify the storage, application and cure properties of resols. Methanol is commonly added at the onset of the synthesis in order to control the polymerization exotherm. The addition of urea at the end of resol synthesis is also a common practice of PF manufacturers [36]. Urea not only reduces the resin cost but also plays the role of free formaldehyde scavenger. Urea is also useful for lowering the preparation viscosity thereby allowing for more advanced resols which require less cure to achieve their final properties. Other additives include plasticizers, antifoams, starches and tackifiers [36]. Aromatic amines like aniline, ortho-, para- and meta- phenylenediamine, aliphatic diamides and thioamides are also used to synthesize mixed copolymer resins exhibiting superior properties over conventional phenolic resins [61-63].

1.3.2 Novolacs

Novolacs are formed by the acid catalysed reaction of formaldehyde and phenol in the ratio between 0.5:1 to 0.9:1. The reaction between phenol and formaldehyde in the acidic pH range occurs as an electrophilic substitution. The catalysts most frequently used are oxalic acid, hydrochloric acid, sulphuric acid, PTSA or phosphoric acid. Most commonly, oxalic acid is preferred because resins of low colour may be prepared. In addition, oxalic acid decomposes at high temperatures to CO_2, CO and water, which facilitates the removal of the catalyst thermally. Typically, 1-6 weight% catalyst is used.

In the first step, formation of a hydroxymethylene carbonium ion from methylene glycol occurs (Eq.1). This ion is the hydroxyalkylating agent.

$$HO-CH_2-OH + \overset{+}{H} \rightleftharpoons \overset{+}{C}H_2OH + H_2O \longrightarrow (1)$$
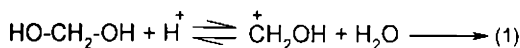
The following addition of the hydroxymethylene carbonium ion to phenol (Eq.2) occurs relatively slowly and is therefore rate determining.

$$\longrightarrow (2)$$
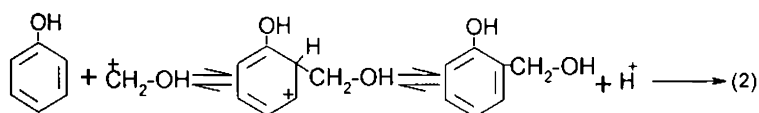
However, the methylol group is very unstable under acidic conditions. Benzylic carbonium ions result (Eq.3) under these conditions which can react very fast with phenol yielding dihydroxydiphenylmethane [42, 64, 65], according to Eq.4.

$$\longrightarrow (3)$$

$$\longrightarrow (4)$$
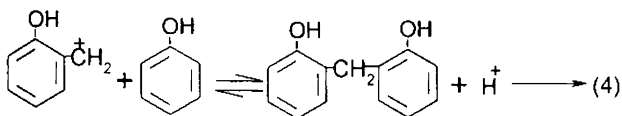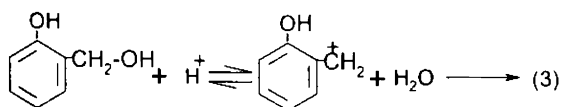
Thus, methylol phenols cannot be isolated as intermediates in contrast to alkaline hydroxymethylation. However, their existence as transient species can be detected by NMR spectroscopy [66]. Under acidic conditions, both methylol substitution and methylene bridge formation occur preferentially at the para position.

High ortho structured novolacs are produced in the weak acidic range at pH 4 to 6 and by use of specific catalysts, mainly salts of bivalent metal acetates including Zn^{2+}, Ca^{2+}, Mg^{2+} and Cd^{2+} [67-70]. Bromomagnesium salts of phenols, through quinone methide intermediates, have also been employed for this purpose [71]. They are designated as 'high ortho' novolacs because of the domination of ortho-ortho linkages. It can be shown by FTIR and NMR spectroscopy that they also contain dibenzylether structures [72].

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1.3.2.1 Curing behaviour of novolacs

Novolac resins which are thermoplastic in nature must generally be cured by addition of a cross-linking agent, a formaldehyde source. The most widely used curing agent is hexamethylenetetramine (HMTA or hexa). Paraformaldehyde or trioxane is of only limited importance. Most commonly 8-15 weight% of HMTA is used. The properties of cured parts are determined to a great extent by the ratio of the two reactants.

The hydrolysis of HMTA leads to aminomethylated products and formaldehyde. These aminomethylated products, formaldehyde and dihydroxydiphenylmethane undergo a Mannich type reaction. Substituted benzoxazines and benzylamines are the major first-formed intermediates produced during the curing process. Further reaction of these intermediates leads to a highly crosslinked network [66, 73-75].
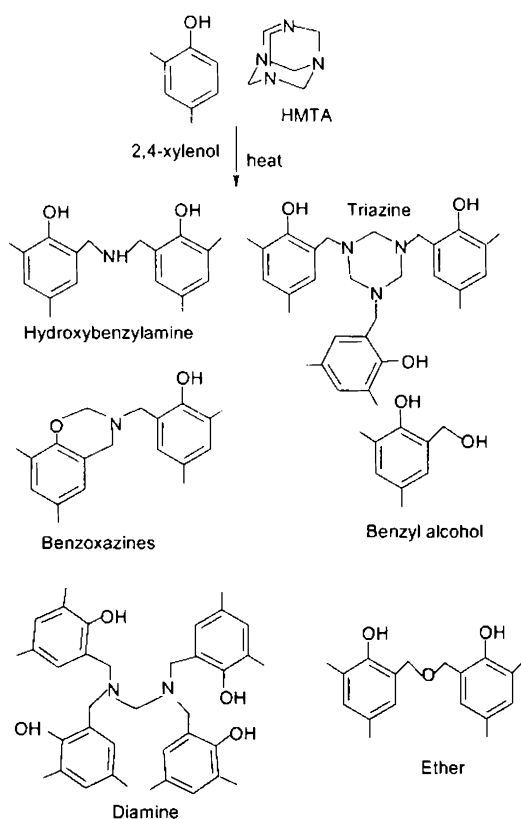
Fig. 1.10 Reaction intermediates proposed from the model study of the reaction of 2,4-xylenol and HMTA

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A model study of the reaction of 2,4-xylenol with HMTA was performed by Zhang et al. [76-80] to investigate the novolac/HMTA reaction mechanism. Several reaction intermediates including hydroxylbenzylamines, benzoxazines, triazines, diamines and in the presence of trace amounts of water, benzylalcohols and ethers were proposed (Fig. 1.10).

The HMTA concentration was determined to be a major factor in the resulting structure of the networks formed from 2,4-xylenol/HMTA reactions. The formation of heterocyclics was observed to enhance mechanical strength and toughness. However, curing reactions employing HMTA produce several volatile side products, including ammonia gas. The evolution of volatiles results in voids in the networks, although novolac/HMTA networks demonstrate this phenomenon to a lesser extent than resol networks.

1.3.3 Properties of phenolics [81, 82]

Phenolic resins are typically opaque and range from pale and dark brown to black in colour. The dark colour of phenolic resins limits their application to some extent. Phenolics are available in flakes, films, liquid and power forms.

Phenolics are brittle in the absence of fillers. It is customary to use fillers and other additives to achieve desired properties and characteristics. These resins exhibit a high degree of property variance due to physical and chemical variation in composition. The various types of phenolic resins available in the market are: general-purpose grade (wood flour filled), non-bleeding grade (resol based, glass filled), heat resistant grade (mineral filled, mica), impact grade (cellulose, rubber, glass, fabric filled), special or electrical grade (mica, glass filled) etc.. Table 1.2 presents the typical properties of different forms of phenolic resins.

The important properties of phenolic molding resins include:

a) Ease of moulding: Phenolic resins can be easily moulded into intricate shapes and to finished dimensions with little or no extra finishing touches.

b) Good dimensional accuracy and stability: They have very good dimensional accuracy and stability at normal atmospheric conditions. Novolac based compounds are more dimensionally stable than resol based moulding compounds.

c) High creep resistance: The high dimensional stability of phenolic resins is complemented by their high creep resistance.

d) They have high resistance to deformation under load. Hence they have comparatively better flexural and compressive strength.

e) Good heat and electrical resistance: Phenolic mouldings have low thermal conductivities and are good heat insulation materials. The dielectric strength of mouldings is in the range 260-400 V/mm and the dissipation factor is from 0.03 to 0.3. This indicates that they are suitable for low voltage electrical insulation.

f) Good chemical resistance: Phenolic mouldings are resistant to common solvents, weak alkalies, weak acids, hydrocarbons and detergents but attacked by strong alkalies and concentrated oxidising acids.

g) Low water absorption: Water absorption of phenolic mouldings is only about 0.03 to 1.75%. The resol based mouldings are more water resistant than novolac based mouldings.

h) Good weather resistance: They can be used outdoors for short periods, but prolonged outdoor exposure to ultra violet light and heat can cause failure.

i) Good machining qualities: Machining qualities are fair to good for moulding compounds but are excellent for casting resins.

Table 1.2 Properties of cured neat and filled phenolic resins [83, 84]

Properties	ASTM test method	Casting resin unfilled	Moulding resin			
			Unfilled	Cellulose filled	Wood flour filled	Glass fiber filled
Tensile strength (10^3 psi)	D638	5-9	7-9	5-9	5-9	7-18
Elonation at break(%)	D638	1.5-2.0	---	0.4-0.8	0.4-0.8	0.1-0.2
Flexural strength (10^3 psi)	D790	11-17	11-14	7-14	7-14	15-60
Izod impact strength (notched)(ft-ib/in)	D256A	0.24-0.4	0.2-0.36	0.2-0.6	0.24-0.6	0.5-1.8
Compressive strength (10^3 psi)	D695	12-15	10-30	22-31	25-31	26-70
Hardness (Rockwell)	D785	M93-120	M124-128	E64-95	M100-115	E54-101
Heat deflection temperature at (at 264 psi) (°F)	D648	165-175	---	300-350	300-370	350-600
Coefft. of linear expansion 10^{-6} (in./in. °C)	D696	1700-1800	640-1520	30-45	30-45	8-21
Thermal conductivity 10^{-4} (cal/sec cm °C)	C177	3-5	---	---	4-8	8-14
Linear mould shrinkage (10^{-2} in./in.)	D955	0-1	0-1	0. 4-0.6	0.4-0.9	0.1-0.4
Dielectric strength (V/mm)	D149	250-400	200-350	300-380	260-400	140-400
Water absorption (24H) (%)	D570	0.2-0.4	0.1-0.2	0.05-0.9	0.3-1.5	0.03-1.2
Specific gravity	D792	1.236-1.320	1.25-1.30	1.37-1.46	1.30-1.35	1.69-2.0

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1.3.4 Applications [15, 82]

Phenolic resins are commercially used in coatings and structural applications. Phenolic resins have excellent adhesion to various substrates, outstanding chemical and corrosion resistance, very good electrical insulation, high tensile, flexural and compressive strengths, thermal stability and low shrinkage upon cure. The largest single use of phenolics is in coatings where high chemical and corrosion resistance and adhesion are important.

a)   Wood composites

Phenolic resin bonded wood materials-particle boards (PB), plywood, fiber boards (FB) and glued wood construction elements are used for outdoor construction and in high humidity areas because of the high water and weathering resistance of the phenolic adhesive bond and the high specific strength. Wood ceramics based on phenolics, a new kind of porous carbon materials, find applications in many industrial applications such as heaters, gas filters, heat insulating materials, damping materials, electromagnetic shielding materials, light structural ceramics and machinable ceramics due to their excellent properties such as heat resistance, friction and wear resistance, and corrosion resistance. It also shows high damping property, good electrical properties, electromagnetic shielding ability and high specific surface area [85,86].

b)   Moulding compounds

Phenolic moulding powders offer properties like high temperature resistance, modulus retention over a wide temperature range, flame and arc resistance, resistance to chemicals and detergents, high surface hardness, good electrical properties and low costs. Because of these benefits, they are ideal for use in a wide range of applications in household and other appliances, electrical engineering and the automotive industry. Typical examples are dishwashers, air conditioners, coffee machines, toasters, refrigerators and flat or steam iron handles. Light sockets, switch and transformer components, blower wheels, relays, connectors, coil forms and wiring devices represent examples in the field of electrical engineering. In the automotive industry, phenolics are

mainly used for under-the-hood components such as distributor caps, coil towers, commutators, fuse blocks, bulkheads, connectors and brake components [87].

c)   Phenolic resin foams

The high fire resistance, low smoke generation, high temperature resistance and good thermal and acoustical insulation properties abundantly qualify phenolic resin foam as insulation material in the construction field. Phenolic foams are commonly produced by acid curing of resol-type resin by the addition of blowing agents, surfactants and colourants [88]. Fillers like talc, asbestos and glass fibers are also used to improve the homogeneity and increase the compressive strength.

d)   Industrial laminates and paper impregnation

Non-cured phenolic resin is hydrophilic and hence it is used for the impregnation of paper and cotton fabrics to be used in the manufacture of electrical and decorative laminates, moulded parts, filter papers and battery separators. Low molecular hydroxyl methylol phenols penetrate into the capillary cavities of the cellulose fibers and due to a cross-linking reaction, fill the cavities. During the hardening reaction, a chemical reaction between the cellulose and phenol alcohols may occur which contributes to increased water and chemical resistance.

Both paper and glass fiber are used for making electrical laminates. Cotton fabrics are mainly used for making high strength laminates and shaped parts. Such shaped parts are used as construction material in mechanical engineering and as insulating materials in electrical engineering.

Decorative laminates, a type of paper and wood based high pressure laminates, find application in the furniture industry. The hard and easy to clean surface is an important prerequisite of decorative laminates. They find applications in the manufacturing of kitchen cabinets, laboratory furniture and wall elements in buildings, ships and boats.

e)   Coatings

High adhesion and low water vapour and oxygen transmission of phenolic resin lead to its use in high efficiency coatings. The other advantages of phenolic resin coatings are excellent resistance to chemicals and temperature. Since neat phenolic resin results in very brittle coatings, it is always formulated in combination with more flexible, hydrophobic resins like epoxy, alkyd or natural resins, maleinized oils and polyvinylbutyral. Because of their individual coloration and tendency towards discoloration, they are used mainly as primers and undercoats. The most important fields of application for phenolic coating resins are automotive primers, coatings for metal containers, anticorrosive marine paints and printing inks.

f)   Abrasive materials:

Coated abrasives and grinding wheels are the most important abrasive materials. In these, the abrasive grain is bound on a flexible support by means of an adhesive. The most commonly used adhesive is phenolic resin. The main advantage of phenolic resin is its high temperature resistance. In normal practice a combination of liquid phenolic resin and pulverized phenolic resin are used as the binding system. The liquid resin serves as wetting agent for the abrasive grain, powder resin and fillers.

g)   Foundry resins

Phenolic resins and blends are used as the binding material for sand based lost core moulds. Lost core moulding is used for the precision moulding of novelty items, such as jewellery, and specialty products, such as titanium-based jet turbine blades. The automotive, steel, construction, and machine parts industries are major users of lost core moulding.

1.4   Modification of phenolic resin

Phenolic resins form highly crosslinked three dimensional network structures on curing. The sturdy methylene bridges lead to very rigid and brittle behaviour in the cured resin. The brittle character of phenolic resin is one of their major

drawbacks. The microvoids formed as a result of the release of water and other byproducts during curing of resin also adversely affect the properties. In current practice, the microvoids are controlled to a great extent by the application of high pressure. But their elimination by suitable modification of phenolic resin is a challenging problem from the academic point of view. Various attempts have been done to improve the mechanical properties of phenolic resin and are still continuing.

a) **Modification by selection of reactants**

One of the easiest ways to tailor the properties of phenolic resin is by using different types of phenols and aldehydes at the synthesis stage or modifying the reactants initially and then synthesising the phenolic resin.

Tsutomu et al. synthesized phenolic resin using butyl, isoamyl and cyclohexyl phenol and the products were found to have better hydrophobic character [89]. Phenolic resin prepared from CNSL is found to be more resistant to alkali, less brittle and suitable for many purposes [90]. Internally plasticized phenolic resin was prepared successfully by Hermann et al. [91]. It was synthesized by allowing phenols and fatty acids to react with each other under the influence of certain catalysts. The polyphenols thus formed further condensed by reacting with formaldehyde and were characterized by being both elastic and highly resistant to chemical reagents. A review covers the production and utilisation of liquids from the thermal processing of biomass and related materials to substitute for synthetic phenol and formaldehyde in phenol formaldehyde resins. These resins are primarily employed in the manufacture of wood panels such as plywood and particle-board. The most important thermal conversion methods for this purpose are fast pyrolysis and vacuum pyrolysis, pressure liquefaction and phenolysis [92].

Compounds such as maleic anhydride and glycerol have been used for hardening phenolic resin [93, 94]. Plasticised phenolic resin blends with increased impact strength, improved tear and ageing resistance and improved mould release properties were obtained by blending three resinous components viz, a phenol-aldehyde resin from a C_6-C_{25} phenol and a C_1-C_7 aldehyde, an acrylic nitrile-diene

copolymer and a copolymer of isoolefin with styrene [95]. Phenolic resins from formaldehyde and a phenol with a long aliphatic side chain blended with a rubbery diolefin-nitrile polymer yielded products with excellent flexibility, extensibility, abrasion resistance, solvent resistance and ageing resistance [96]. The flexibility of phenolic resin was improved by modifying phenol formaldehyde resin by epichlorohydrin [97, 98]. The resol resin was refluxed with epichlorohydrin before separating and dehydrating the resin layer.

Condensation products consisting of an unsaturated carboxylic acid, a polymerisable monomer and phenol which still have a phenolic character were made to react with formaldehyde to give resins having good flexibility and resistance to chemicals [99]. Plasticization of phenolic resin could also be achieved by polyvinyl butyral by Arther et al. [100]. Flexibility of phenolic resins can be improved by using alkyl substituted phenols in the synthesis stage and also by etherifying resol resins by polyhydric alcohols like ethylene glycol, propanediol, pentanediol and glycerol. The properties of cured phenolics modified by etherification not only depend on the type of the polyhydric alcohol but also on the pH at which the etherification was carried out [101-103].

Hardeners like PTSA play an important role in controlling the microvoid formation in the cured resin. The formation of voids, however, is influenced by the resin and the cure cycle also [104-107]. The interdependence between the structure and both mechanical and thermal properties of resol resins are well established [108]. It was shown that the hardener concentration predominately influenced the microstructure and the mechanical properties of the resin system. A significant decrease in the average void diameter as a result of the polycondensation reaction with an increasing hardener concentration was detected. However, the hardener concentration shows almost no influence on the glass transition temperature.

Both organic mono and dicarboxylic acids have been used for modifying phenolic resin [109,110]. Mono carboxylic acids like salicylic acid, 4-hyrdoxybenzoic acid and sodium salicylate are used to tailor the properties of

phenolic resin. These not only accelerate the phenolic polymerization but also exhibit a significant improvement in the mechanical strength of the composite based on phenolic resol resin. Dicarboxylic acids with varying chain lengths, viz, adipic acid, suberic acid, sebacic acid and dodecanedioic acid were used for modifying the phenolics. It was found that the mechanical properties of modified phenolic resin with diacids were significantly dependent on the diacid chain length. Among the above diacids suberic acid showed better properties for the cured resin. Recently it is reported that organic esters with varying chain length are useful in modifying phenolic resol resin [111].

b)   Modification by rubbers

Rubber toughening is one of the most important ways to improve the properties of thermoset resins. The various types of elastomeric materials which have been studied with a view to modify thermoset resins are the following. (i) poly siloxanes [112], (ii) fluro elastomers [113] (iii) acrylated elastomers [114] and reactive butadiene-acrylonitrile solid and liquid rubbers [115-118]. A Large number of works have been reported on rubber toughening of epoxy resins [115,119-121]. But only a few investigations have been reported on modification of phenolic resin by rubbers.

Nitrile-phenolics were developed in the early1950s by blending nitrile rubber (NBR) with phenolic resins [122]. Nitrile rubber-phenolic resin blends find applications in the aerospace industry for structural bonding of metals, in the automobile industries to bond brake shoes and clutch disc assemblies and in the preparation of high abrasion-resistant tough mouldings, O-rings, gaskets, and cables [123-125]. The effect of reactive compatibilisation on adhesive and composite properties of NBR/phenolic resin blends was studied by Sasidharan Achary et al. [126]. The study revealed that the reactive compatibilisation by p-cresol leads to enhanced miscibility and strong interfacial adhesion of the phases.

The adhesive characteristics of maleimide-functional phenolic (PMF) resins on elastomeric modification has been extensively studied by Gouri et al.

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[127]. They found that the properties of PMF resin self-cured as well as cocured with epoxy systems when modified by the addition of elastomers like CTBN, epoxidised hydroxyl terminated polybutadiene and epoxy functional butyl acrylate-acrylonitrile copolymer were found to depend on the nature and concentration of the elastomer as well as on the nature of the thermoset matrix being modified.

A new kind of elastomeric nanoparticles (ENP), nitrile butadiene elastomeric nanoparticle (NBENP) and carboxylic nitrile butadiene elastomeric nanoparticles (CNBENP), are found to be effective in enhancing the properties of novolac type phenolic resin [128]. Phenolic nano-composites with 5 wt% of ENP, show simultaneous improvement of impact strength, flexural strength and heat resistance. CNBENP shows better modifying effect than NBENP. Kaynak et al. have also used powder rubber nitrile particle for toughening of resol type phenolic resin [129]. The use of coupling agent, 3-aminopropyltriethoxysilane, along with the rubber particles lead to a synergistic effect on the properties of the cured resin. 0.5 wt% nitrile rubber and 2 wt% amino silane (with respect to nitrile rubber) is the best modifier combination leading to the highest properties.

Hydroxyl terminated polybutadiene (HTPB) was successfully used to modify phenolic novolac using resol as compatibilizer [130]. Lower concentrations of HTPB improved the fracture toughness by forming two phases. The optimum level was the result of competition between the interfacial adhesion reaction which improved the toughness and an increase in the solubility of HTPB at higher concentrations which led to higher cross-linking. Modification with 10 wt% HTPB and above resulted in finer particle dispersion with a diffused phase morphology. Reactive compatibility is the mechanism responsible for the enhanced miscibility and strong interfacial adhesion between the two phases.

d) Modification by thermoplastics

Modification of highly crosslinked thermoset resins by blending with various thermoplastics has attracted great interest lately [8, 131-135]. Toughening of novolac

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type phenolic resin by polyamides has been successfully done by Wu et al. [136, 137]. The phenolic resin/polyamide blend is a completely miscible system in which the flexible amide chain of the polyamide backbone penetrates the rigid phenolic resin structure and hence imparts flexibility to the matrix. Polystyrene-ran-acrylonitrile copolymers have been established an efficient modifiers for novolac type phenolic resin [138].

Blends of phenolic resin with polydimethylsiloxane adipamide showed good miscibility and better properties as a result of the establishment of intermolecular hydrogen bonding between the two phases [139]. An enhancement in mechanical properties was observed by blending phenolic resin with polymethyl methacrylate (PMMA) [140]. An interpenetrating network was formed between the phenolic resin and PMMA as a result of the polymerization of methyl methacrylate in the resin system. The soft segments thus introduced imparted better toughness to the phenolic resin.

d)   Modification by using particulate fillers

Reinforcement with particulate filler is another method to modify the properties of phenolic resin [141-144]. Particulates contribute to greatly enhanced modulus which is a significant advantage over elastomeric modification where a reduction in modulus is observed [145,146].

Novel organic-inorganic hybrid materials composed of phenolic resin and silica have been prepared by in situ polymerization of silicon alkoxide in a phenolic resin matrix by Haraguchi et al.[141]. The hybrid materials exhibited excellent mechanical properties in which modulus, strength, strain at break and impact strength were improved simultaneously. An ordered SiO_2-phenol formaldehyde resin in situ nanocomposite has been synthesized successfully by generating SiO_2 particles in situ by the hydrolysis of tetraethoxysilane in the presence of modified phenol formaldehyde resin (MPFR) and also by adding SiO_2 sol into a solution of MPFR in ethanol [144, 147].

Chian et al. synthesized novel phenolic resin/silica nanocomposites by sol-gel process for better thermal and flame retardance [148]. Layered silica is found to be efficient in modifying phenolic resin [45]. About 1.5 wt% of layered silica in the phenolic matrix leads to a certain degree of exfoliation and consequently better structural and mechanical properties. A novolac phenolic resin/silica hybrid organic-inorganic nanocomposite have been synthesised from a glycidyl alkylene trialkoxy silane grafted novolac phenolic resin by Yand et al. [149].

Recently, carbon nanotubes have been effectively utilized to modify phenolic resin [150]. Both network multi-walled nanotubes (MWNT) and dispersed MWNTs were used to reinforce the phenolic resin. Activated carbon spheres have also been used to modify phenolic resin [151]. Phenolic resin-trisilanolphenyl polyhedral oligomeric silsesquioxane hybrid nanocomposites for better thermal properties have been developed by Zhang et al. recently [152]. Nano silver dispersed phenolic resin composite for advanced technologies has been synthesized by Linjie Zhi et al. [153]. It was prepared by in situ reduction of silver nitrate in the novolac resin, in which HMTA in the resin system acted as curing agent of the novolac and also as the reducing agent for silver ions.

1.5 Fibre reinforced plastics (FRP)

A composite is a heterogeneous material created by the assembly of two or more components, fillers or reinforcing agents and a compatible matrix binder in order to obtain specific characteristics and properties [154]. 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. [155]. Fibre reinforced composites have low specific gravity, high strength-

weight and modulus-weight ratios, excellent chemical resistance, weatherability, versatility of product design and ease of fabrication and consequently possess a distinct advantage over conventional materials. Today, fibre reinforced composites have emerged as a major class of structural materials with increasing application in weight-critical components for industry, particularly the aerospace, marine, and automotive sectors. Phenolic, epoxy and unsaturated polyester resins are the most widely used matrix materials in the FRP industry. The properties of composites and factors influencing the properties have been studied extensively [156, 157].

Glass-fibre-reinforced polymers (GRP) are finding increasing use in many applications as high strength, lightweight structures and components in transport, building and maritime industries. Phenolic resins and glass/phenolic composites are inherently fire-retardant and have superior flammability properties to polyester, vinyl ester and epoxy resins and composites [158-161]. In addition, phenolics yield very low levels of smoke and combustion products under both flaming and smouldering fire conditions. A lot of work has been done for improving the properties of GR phenolics [162-166]. The main disadvantage of glass-reinforced phenolics is the weak interface between the phenolic resin and the glass fiber. The interlaminar shear strength (ILSS) of these composites can be improved to some extent by applying silane coupling agents [167, 168].

Natural fiber reinforced polymer composites are superior to synthetic fiber reinforced composites in properties such as enhanced biodegradability, combustibility, light weight, non toxicity, decreased environmental pollution, low cost and ease of recyclability. These properties place natural fiber composites among high performance composites offering economical and environmental advantages. Reports show that the versatile high performance applications of natural fiber composites replace glass and carbon fiber composites to a large extent. [169,170]. Reinforcement of polymers with natural fibers offers possibilities for the effective utilization of agricultural by-products. A large number of studies have been done in developing natural fiber/phenolic composites [171-177].

1.5.1 Reinforcement fibres

When a material is loaded to failure, the fracture may occur in three stages: the initiation of a crack, its stable growth under rising or constant load and finally its unstable propagation. All the three stages do not necessarily occur in all materials especially in brittle materials as they contain inherent flaws such as surface scratches, embryonic crack etc..

The high strength of reinforcement fibres like glass can be explained in the light of the Griffith theory. Griffith [178] proposed a thermodynamic argument that a crack could not grow unless stored elastic energy which is released during crack growth, together with any external work done during fracture, is equal to or greater than the thermodynamic surface energy (γ_1) of the material, i.e.

$$\frac{dU}{dA} > \gamma_T \qquad\qquad (1.1)$$

where dU/dA is the elastic energy released by unit area extension of crack. From elasticity theory it is possible to calculate dU/dA for a sharp crack of length 2c under an applied tensile stress 'σ' as

$$\frac{dU}{dA} = \frac{\pi\sigma^2 c}{2E} \qquad\qquad (1.2)$$

where E is young's modulus. Unstable crack growth can not occur until,

$$\frac{\pi\sigma^2 c}{2E} = \gamma_T \qquad\qquad (1.3)$$

$$\sigma = \sqrt{\frac{2E\gamma_T}{\pi c}} \qquad\qquad (1.4)$$

Equation 1.4 is known as Griffith equation.

The sizes of the flaws can be roughly estimated from the Griffith equation. In other words the strength of a brittle material is controlled by a combination of its fracture energy, Young's modulus and the size of the fracture initiating flaw.

The Griffith theory underlines the significance of flaw size in a material. The dependence of strength of the material on the flaw size is nonlinear. Even a small change in flaw size results in a large change in the strength of the material. This is the basic reason for the high strength of materials, when reduced to fibre form. With reduction in crossectional area, the flaw size is sharply reduced.

The reinforcing agents used most widely are glass fibers 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

They are also known as Kevlar fibres. 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. Ceramic fibres combine high strength and elastic modulus with high-temperature capability and, in general, freedom from environmental attack. Alumina fibres and silicon carbide (SiC) 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,

40

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 and resin transfer moulding .

a)   Hand lay-up

The hand lay-up technique (Fig. 1.11) 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 in industrialized countries. 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.
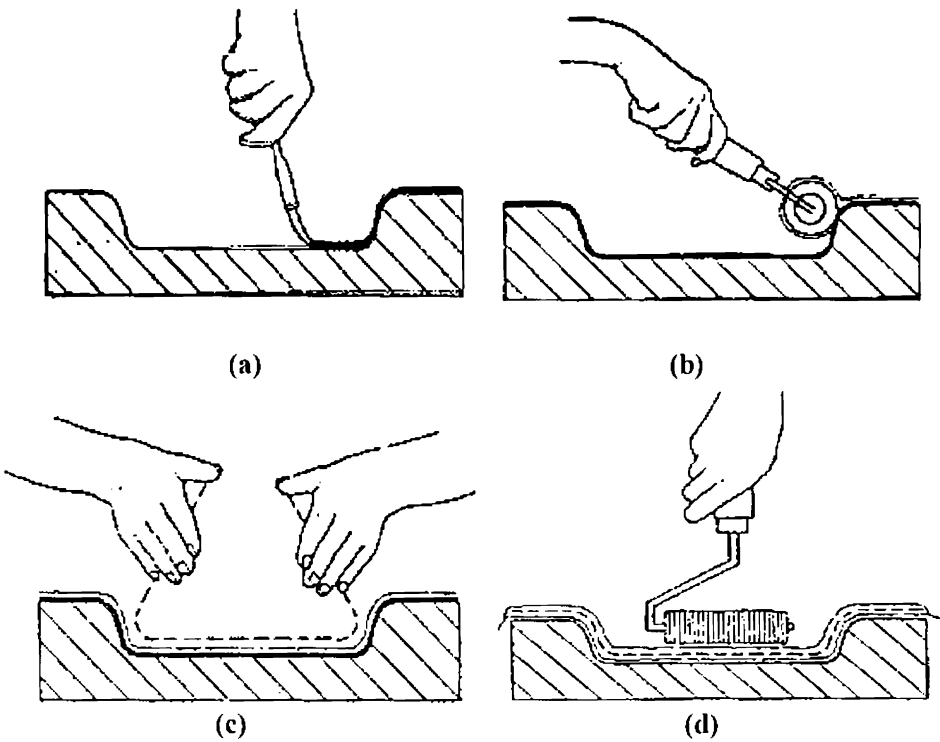
Fig. 1.11 Hand lay up **(a)** apply gel-coat with brush **(b)** apply laminating resin
with roller **(c)** cut and fit reinforcement layer **(d)** consolidate with
ribbed roller

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 which uses either glass roving continuously wetted with resin or preimpregnated roving which is formed and cured as it is drawn through a heated steel die [179] . 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. These compounds contain ingredients which ensure very low shrinkage and appropriate flow properties for the compound inside the mould.

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)

RTM [180] 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 containing the necessary curing agents by injection 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. At its simplest, this involves placing the glass reinforcement 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. RTM uses premixed resin, rather like a development of hand-lay-up with a closed mould. In vacuum assisted resin injection vacuum helps to speed up the fill rate. This resembles vacuum injection, but it is quicker and less sophisticated. Structural resin injection moulding 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 mixes the resin on the way into the mould.

1.6   Scope and objectives of the work.

Despite the emergence of a large number of new high performance polymers, phenol formaldehyde resin retains industrial and commercial interest even a century after its introduction as commercial commodity. However, their acceptance as a

universal engineering material is restricted to some extent by characteristics derived from their special chemical structure.

These resins cure at moderately high temperature by a condensation mechanism with the evolution of volatiles. This necessitates application of pressure during moulding to form void-free components. The limited shelf period and the need for the use of catalyst for curing in some cases are also major shortcomings of phenolic resins. They also suffer from poor impact strength.

Mechanical performance in high loading conditions is a general requirement for the successful application of thermoset resins. The voids present in the cured phenolic resin affect the mechanical properties. The aim of this investigation is to formulate modified phenolic resin with improved mechanical properties. This necessitates the control or, if possible, the elimination of microvoids.

A stochiometric study of the synthesis reaction is essential to optimize the properties especially when a mixture of phenols is used as a starting material.

Cardanol is naturally occurring substituted phenol separated from cashew nut shell liquid (CNSL). The influence of including this phenol in the reaction mixture is a matter of interest. It is worth studying how far this step can improve the properties of the final product.

Polyols such as ethylene glycol, propylene glycol and glycerol are used as diluents for PF resin. They reduce the microvoids in the cured phenolics to some extent appreciably both in size and numbers. It is well established that phenolics can chemically link to double bonds through the intermediate quinone methide structure of phenolics. Also reports suggest that dicarboxylic acids can enhance the properties of phenolics. Unsaturated polyester which is an esterification product of these two is thus a good candidate for modification.

During the crosslinking reaction large amounts of condensation products are released. These condensation products are responsible for the microvoids in the cured

resin. Epoxies can undergo reaction with active methylol groups of PF resin without releasing any condensation products. This can help to both reduce the microvoids and also impart flexibility to the cured structure. Different epoxy resins will be utilized for this purpose.

The objectives of the present work are spelt out below.

The broad objectives of the work is to improve the properties of the phenolic resin by various techniques like blending of monomers, incorporation of other thermoset resins, fiber reinforcement etc.. More specifically the studies proposed under this project are the following:

- To prepare PF resol resin of different stoichiometries and optimize the F:P ratio for optimal mechanical properties.

- To prepare cardanol phenol formaldehyde resin and blends of cardanol formaldehyde and phenol formaldehyde resins and evaluate and compare their properties.

- To study the effect of unsaturated polyester on the properties of the commercial PF resol resin.

- To study the influence of epoxidised novolac resins on the properties of commercial PF resol resin.

- To study the effect of matrix modification by the above methods on the properties of glass and cotton reinforced composites.

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PREPARATION OF PHENOLIC RESOL RESINS AND EVALUATION OF PROPERTIES

Contents

2.1 Introduction

The prime factor which determines the properties of phenolic resol resin is F:P molar ratio [1-3]. Control of the F:P molar ratio is necessary to get a cured system with optimal properties.

The main disadvantage of phenolic resin is the formation of microvoids on curing which adversely affect the mechanical properties of phenolics. This problem can be solved to a large extent by applying pressure during curing. Microvoids can also be partially eliminated by applying a slow cure schedule, progressing from a low temperature to a high temperature.

In this part of the study PF resol resins with varying F:P molar ratios were synthesised in the presence of a constant catalytic amount of sodium hydroxide under identical reaction conditions. The synthesised resol resins were then cured in an open mould by applying heat at a pre-set time-temperature schedule starting from a low temperature. The variations in mechanical and some physical properties were estimated to arrive at the best F:P molar ratio.

2.2 Experimental
2.2.1 Materials

Phenol (MW = 94.11, MP = 39.5-41°C) was supplied by S.D.Fine-Chem Ltd., Mumbai, India. Sodium hydroxide (MW = 40, 97% assay), formaldehyde (37-41% w/v, d^{20} = 1.08) and glacial acetic acid were L. R. grade supplied by E. Merck India Ltd., Mumbai.

2.2.2 Preparation of PF resol resin

Resols of varying F:P molar ratios, viz. 1.5:1, 1.75:1, 2.0:1, 2.25:1 and 2.5:1 were synthesised and designated as R1.5, R1.75, R2.0, R2.25 and R2.5 resins respectively.

Phenol and sodium hydroxide were charged into a two necked RB flask. 0.25 mole% of sodium hydroxide was taken on a phenol basis. The two necked RB

flask was provided with a mechanical stirrer and a reflux condenser. The whole system was then kept in a water bath which was maintained at 90-95°C. Formaldehyde was then added at a constant rate with stirring. The addition of formaldehyde was completed within fifteen minutes in all cases. After the commencement of the reaction a few drops of the reaction mixture were taken at regular intervals of five minutes and added to water. When it caused a permanent turbidity the reaction was deemed to be over. At that stage the mixture was taken out of the water bath and allowed to cool.

The alkaline resin was then poured into a beaker and neutralised with glacial acetic acid until the pH reached ~ 7.0. The condensate was kept overnight. The aqueous layer was decanted off and the resin dehydrated by applying vacuum continuously.

2.2.3 Studies on the synthesised resol resin.
2.2.3.1 Spectroscopic studies

FTIR spectra of the samples (in finely powered form) were taken in Bruker FTIR spectrophotometer model Tensor 27 (spectral range of 7500 to 370 cm^{-1} with standard KBr beam splitter) in attenuated total reflectance (ATR) mode. It uses zinc selenide as the crystal material with high sensitivity DLATGS detector with KBr window.

2.2.3.2 Physical properties

The specific gravity, gel time and total solid content of the synthesised resin were determined by the following standard methods.

i.   Specific gravity

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

ii.   Total solid content (TSC)

TSC was determined by evaporating an accurately weighed sample (about 0.5g) to dryness at 170°C for 30 min [4].

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iii.   Gel time

The gel time of the resin was found out by the method outlined in DIN 16945. A weighed amount of resin was filled into a test tube and dipped into an oil bath at 130°C. The increase in viscosity was identified with a glass rod used like a piston. The gel point of the resin is identified as the instant when the glass rod gets stuck in the resinous mass.

2.2.3.3 Mould preparation and casting of the resin
i)   Preparation of moulds for different test specimens
a.   Tensile properties (ASTM D 638-99)

Dumbbell shaped multicavity moulds were fabricated for casting tensile specimens. Three sets of moulds were machined out of Teflon sheets of 10mm thickness each set containing eight dumb bell shaped mould cavities. The dimensions of the tensile test specimens are shown in Fig. 2.1. The specimens were cast according to ASTM D 638.
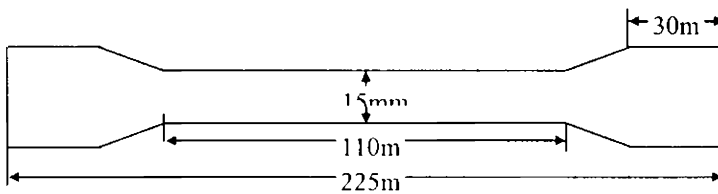

Fig. 2.1 The dimensions of the tensile test specimens
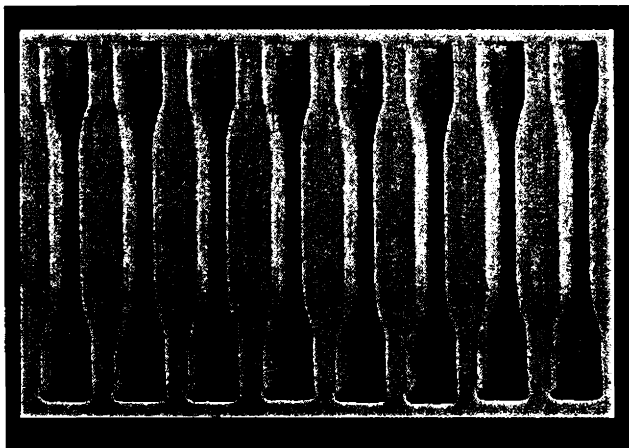
A photograph of the Teflon mould is shown in Fig. 2.2

Fig. 2.2 Photograph of Teflon mould for tensile specimen

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b.   Compressive properties (ASTM D 695-99)

The mould for compressive strength specimens having eighteen cylindrical cavities was fabricated out of mild steel (MS). 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 Teflon. 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 Teflon. The dimensions of each cavity are 60 ± 0.2 mm length, 12.7 ± 0.21 mm width and 4.0 ± 0.1 mm thickness.

e.   Abrasion resistance

These samples were made according to ASTM 1044. The mould was machined from MS plates containing eight cylindrical cavities having 16 ± 0.2 mm diameter and 10 mm depth.

f.   Surface hardness (ASTM D 2240-86)

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

ii)   Curing

Considerable amount of water is generated during the curing of phenolic resin. Also, the resin becomes more and more viscous as the curing process advances. This results in unfavourable conditions for the water of condensation to escape from the bulk. Therefore, the curing was carried out at low temperatures for evaporating the bulk of the water and the temperature was then increased in steps to achieve sufficient levels of cure.

The Teflon mould was cleaned and a thin coating of silicone mould release agent was spread on the inner surfaces of the cavities using cotton cloth. The application of silicone mould release agent was observed to be effective in avoiding entrapment of air at the bottom surface the sample. The mould was then kept in an air oven at a temperature of 70-75°C for 10 minutes to dry off the water present in the mould release agent.

The mould was filled by pouring the resin carefully to avoid air entrapment at the corners and bottom of cavities during filling. For this, the mould was kept in a slightly inclined position. The resin was poured from one end and allowed to flow towards the lower end filling the corners of the cavities. The mould was then kept level on the perforated steel tray inside the oven with the help of a spirit level and cavities were filled carefully to completion.

The mould after filling was subjected to a controlled temperature schedule. This was arrived at by trial and error. The schedule consisted of 60°C - 2hrs, 70°C - 12hrs, 80°C - 3hrs, 90°C - 1hr, 100°C - 1hr, 110°C - 1hr and 120°C - 2hrs inside the air oven. After completing the 90°C stage a steel plate of 2mm was placed on the top of the mouldings and a metallic block was kept over it to prevent bending of samples at higher cure temperatures. After the completion of the curing temperature cycle the mould was taken out and cooled for 10 minutes. The cured samples were removed carefully and tied together to avoid any chance of bending during further cooling.

2.2.3.4 Testing of cast samples [5]

The samples after 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 cast specimens were polished using emery paper prior to testing. The dimensions were measured using a thickness guage. The tensile properties were

then 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. 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 the machine is started. 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, 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, also provided by the microprocessor, 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 crosshead 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 of 0.01 mm and the minimum cross sectional area was calculated. The height of the test specimen was measured to the nearest of 0.01 mm. The specimen was placed between the surfaces of the compression. The centre line of the specimen was aligned through the centreline of the compression plates. The machine was adjusted so that the end surfaces of the test specimen just touched the surface of the compression plate. The machine was started and compressive strength and modulus were progressively recorded until failure. 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. The flexural strength was 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 Resil Impact Analyser (Junior) as per ASTM D 256-88 specifications. Impact strength is the energy absorbed by the specimen during the impact process and is given by the difference between the potential energy of the hammer or striker before and after impact.

The specimens were tested on the impact tester having a 4 Joules capacity hammer and striking velocity of 3.96 m/sec. A sample was clamped vertically

(Izod) in the base of the machine. The pendulum was released. The impact resistance or strength was evaluated from the impact values directly read from the tester.

Impact strength = (4X x 100)/d

where X= Impact value and d = depth of specimen

v.   Abrasion resistance

Abrasion resistance was tested on a Zwick DL 100 machine as per DIN 55516. The apparatus consists of the following: a rotating cylinder, a specimen holder, suitable mechanism for driving the cylinder at 23.5 rpm and suitable abrasive Al_2O_3 paper of grain size 320. The test piece was mounted vertically on the sample holder. The samples were held in contact with the abrasive by a force of 5N weight. The sample was run over the abrasive paper to get an even surface. Initial weight of the sample was then taken. The sample was then replaced and run under the same conditions. The weight loss of the sample was found out.

Specific gravity of the sample was also found out. The volume loss derived from weight losses is obtained by dividing the weight losses by density of the sample determined by Archmedis' principle.

$$\text{Abrasion loss} = \frac{\text{weight loss}}{\text{specific gravity}} \times 27.27 \ cc/hr.$$

vi.   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.

vii)   Thermogravimetric analysis (TGA)[6]

A TA Instruments' TGA Q 50 model was used to investigate thermal degradation. A temperature ramp was run from room temperature to 800°C at 20°C/ minute in nitrogen. Sample weights were between 5 and 10 mg.

viii)   Dynamic mechanical analysis (DMA)[7]

Polymers are viscoelastic materials. Elastic component of a polymeric material under dynamic conditions indicates the capacity to store the mechanical energy. It is represented by storage or dynamic modulus, E'. The viscous property of a polymeric material indicates the capacity to dissipate the mechanical energy. This is known as loss modulus, E''. The ratio between these two quantities, tanδ, is an index of the damping property of the polymeric material.

The dynamic material properties such as dynamic modulus, E', the loss modulus, E'', and the damping, tanδ (E''/E'), are measured by taking the response of material to periodic forces.

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 of 32 mm length, 10 mm breadth and 3mm height were used. The tests were conducted at a constant frequency of 1 Hz. A temperature ramp was run from room temperature to 250°C at a heating rate of 1°C/ min to get an overview of the thermo mechanical behaviour of cured resin samples.

2.2.3.5 Soxhlet extraction

The samples were ground to fine particles and packets containing 2 grams of the ground sample in Whatman No.1 paper were extracted with acetone in a Soxhlet apparatus for 48 h. The loss in weight of the packets after

extraction gave the amount of soluble matter and the percentage soluble matter was calculated.

2.3 Results and Discussion

2.3.1 Spectroscopic data [8]

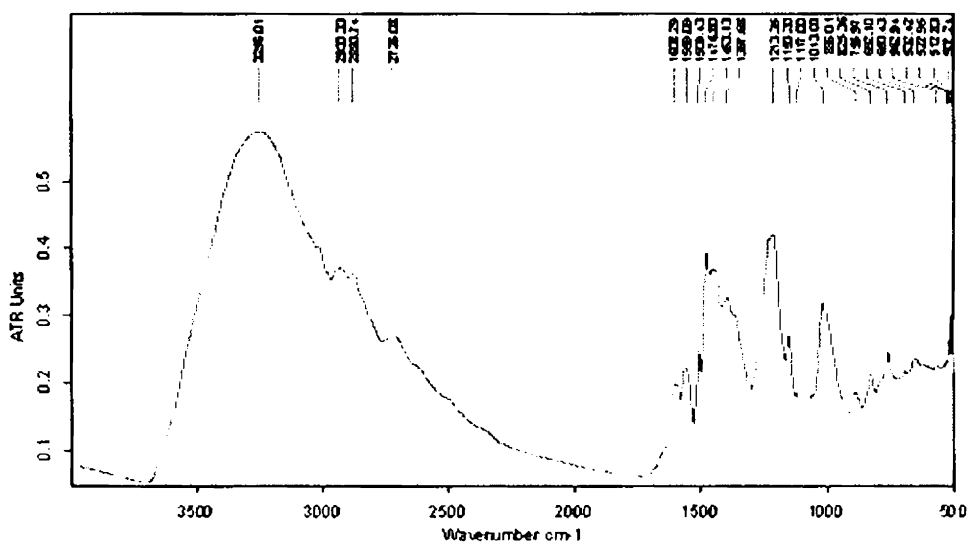The FTIR spectrum of synthesised uncured phenol formaldehyde resin is given in Fig. 2.3.

Fig. 2.3 FTIR spectrum of uncured resol

The band at 3256 cm^{-1} is the characteristic absorption peak for the -OH group in the phenolic resol resin. The peaks between 2950-2800 cm^{-1} represent the absorption due to symmetrical and asymmetrical stretching of -CH$_2$- group in the phenolic resin. The peaks in the range 1620-1480 cm^{-1} are due to the -C=C- stretching in the aromatic ring. The bending mode of vibration of -CH$_2$- group resulted in the absorption at 1450 cm^{-1} and 1350 cm^{-1}. The peak at 1213 cm^{-1} is due to the absorption by C-O stretching. The stretching of ether linkage, C-O-C, is indicated by the absorption at 1013 cm^{-1}. The absorptions at 825, 766 and 690 cm^{-1} are characteristics of ortho disubstituted, meta disubstituted and monosubstituted benzenes respectively.
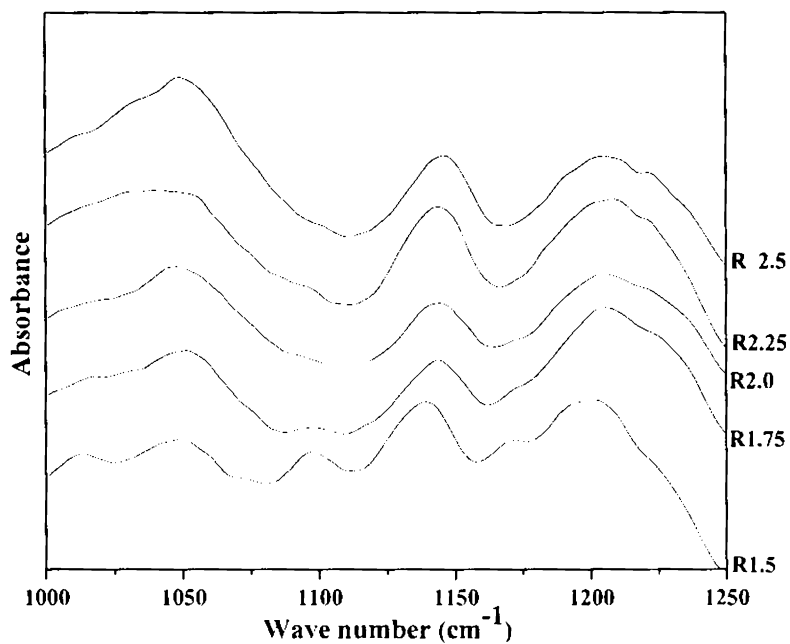
Fig. 2.4 FTIR spectra of cured resol resins in the region 1000-1250cm^{-1}

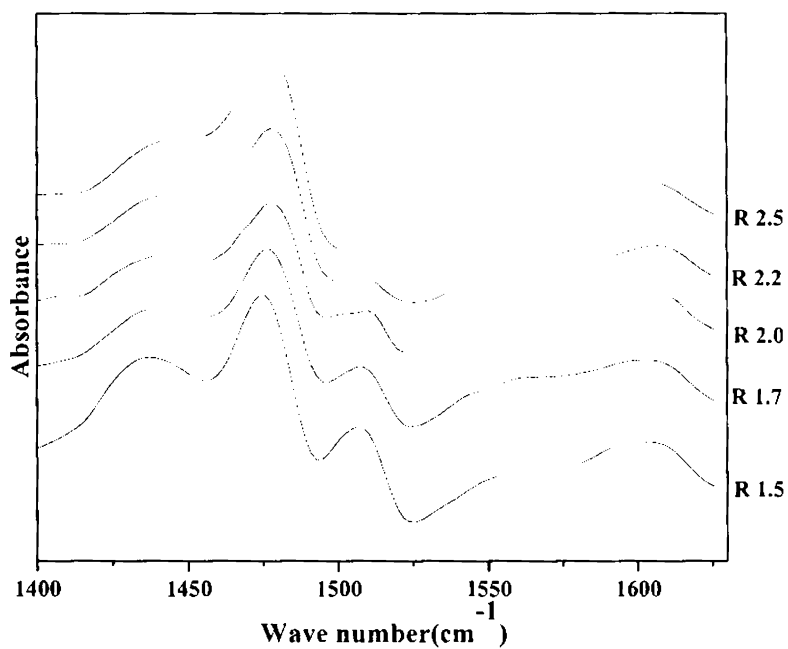**Fig. 2.5** FTIR spectra of cured resol resins in the region 1400-1650cm^{-1}

Figs 2.4-2.6 show the FTIR spectra of cured resins in the regions of interest. The dibenzyl ether linkages in cured phenolic resin show absorption at ~1050 cm^{-1}. The relative intensity at ~1610 cm^{-1} due to -C=C- stretching of benzene ring was almost constant in all cured samples and hence it was taken as a basis for comparison.
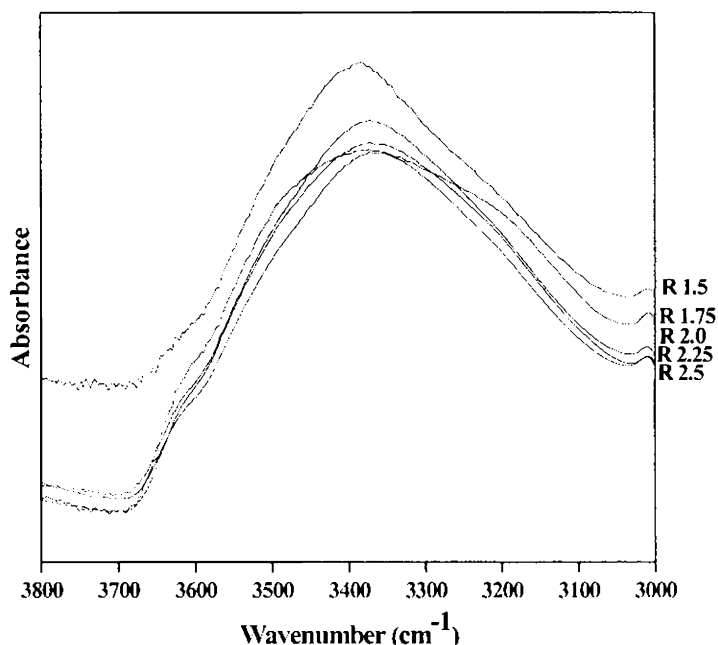

Fig. 2.6 FTIR spectra of cured resol resins in the -OH stretching region

The -OH stretching frequency (3390cm^{-1}) of the cured resin with F:P molar ratio 1.5:1 is slightly higher than for other samples. The shifting towards a lower frequency (~3372cm^{-1}) for all other samples indicates a greater amount of weak hydrogen bondings at higher F:P molar ratios. Hydrogen bonding is possible between the phenolic -OH groups and ether linkages. Because the number of phenolic -OH groups remain the same, any change in the extent of hydrogen bonding is brought about by the change in number of ether groups. But beyond a certain concentration of ether linkages no further shift in the frequency is observed. So at higher F:P molar ratios, no positive effects of hydrogen bonding are noticeable.

The ratio of the relative intensities, I_{1050}/I_{1610}, as a function of the F:P molar ratio is given in Fig. 2.7. The ratio of the relative intensities, I_{1050}/I_{1610}, increases

with increase in the F:P molar ratio. This indicates that ether linkages steadily increase as the F:P molar ratio increases.
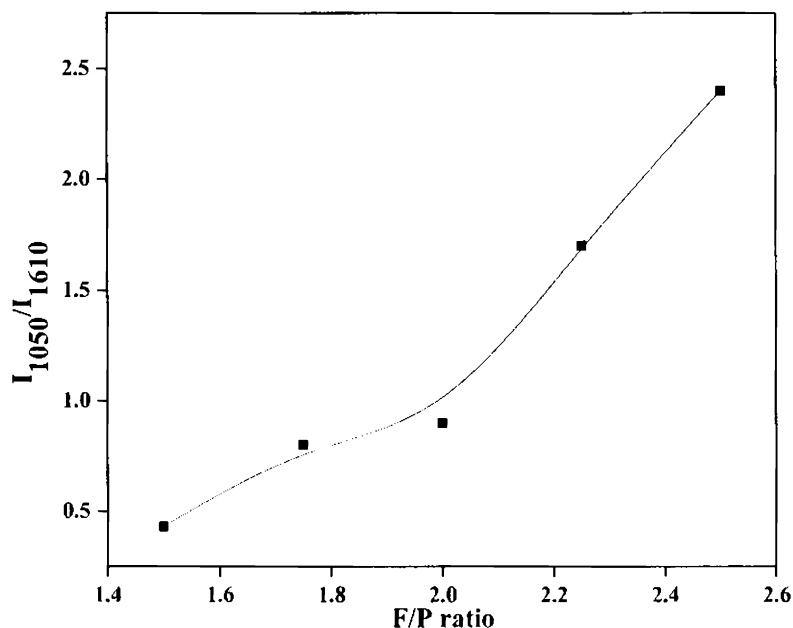

Fig. 2.7 Variation of I_{1050}/I_{1610} with F:P molar ratio

2.3.2 Properties of the liquid resin

The variation of physical properties such as gel time, specific gravity and TSC are shown in Table 2.1.

Table 2.1 Variation of physical properties of the resin with F:P molar ratio

F:P molar ratio	Gel time (sec.)	Specific gravity	TSC
R1.50	495	1.2472	79
R1.75	440	1.2675	78
R2.00	435	1.2790	79
R2.25	330	1.2820	79
R2.50	310	1.2875	77

The gelation time of the phenolic resol resin decreases with increase in the F:P molar ratio. This is due to the progressive increase in the methylol groups as the amount

of formaldehyde increases. The increase in the number of methylol groups speeded up the crosslinking reaction and resulted in an early attainment of the gel point.

The specific gravity of the resin increases as the F:P molar ratio increases. The increase in the methylol groups with increase in the amount of formaldehyde causes the crosslinking reaction to take place at a faster rate. This resulted in an increase in the average molecular mass of the prepolymers with F:P molar ratio and hence an enhancement of the specific gravity.

The TSC remains almost the same for all samples. Large variations in the TSC lead to a decrease or increase in the dimensions of the castings. This leads to greater deviations in mechanical properties and makes the study less reliable. Since TSC is seen to remain almost constant for resins with various F:P molar ratios, a comparative study of the mechanical properties of these resins is useful.

2.3.3 Cured resin properties

2.3.3.1 Soxhlet extraction of the cured resin

Soxhlet extraction of cured phenolics is useful in ascertaining the extent of soluble matter in the cured resin. It also helps to estimate the extent of crosslinking of the phenolic network [9].
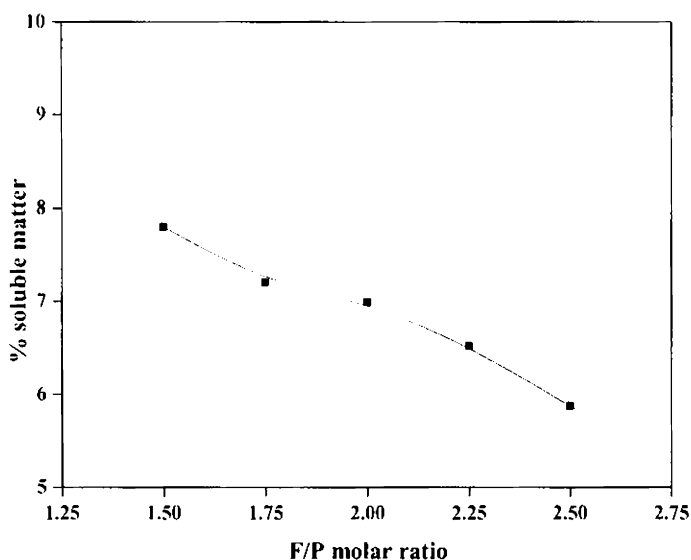

Fig. 2.8 Variation of soluble matter with F:P molar ratio

Fig. 2.8 shows the variation of the soluble matter with F:P molar ratio. As we can see from the graph, the amount of soluble matter decreases with increase in the F:P molar ratio. This may be due to the increase in the methylol groups as the amount of formaldehyde increases. As the number of methylol groups increases the degree of crosslinking also increases. This results in a lower percentage of soluble matter.

2.3.3.2 Mechanical properties of the cured resin

Fig. 2.9 shows the variation of tensile strength and flexural strength with F:P molar ratio. Both properties show similar trends as the F:P molar ratio varies.

The highest strength is shown by the resin with molar ratio 1.75, i.e., R1.75. At higher F:P molar ratios the presence of too many ether groups, as indicated by FTIR studies, leads to a deterioration of properties. The positive effects of hydrogen bonding are offset by this effect above a F:P molar ratio of 1.75 so that there is a net fall in performance.
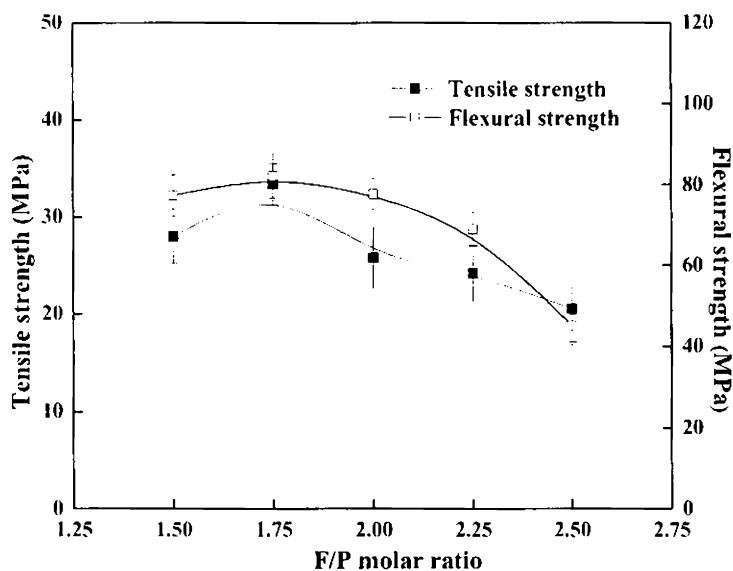

Fig. 2.9 Tensile and flexural strength versus F:P molar ratio

Fig. 2.10 depicts the variation of the elongation at break and maximum displacement in flexure with F:P molar ratio. The elongation at break is maximum for a F:P molar ratio of 1.75:1. Maximum displacement on flexural

deformation is also the highest at the same ratio. Above this ratio both elongation at break and maximum displacement are seen to have a decreasing tendency. Although the ether linkages give more flexibility than methylene bridges the poor bond strength of the former leads to failure of the samples at lower loads. This is also reflected in the fall of elongation and maximum displacement at higher ratios.
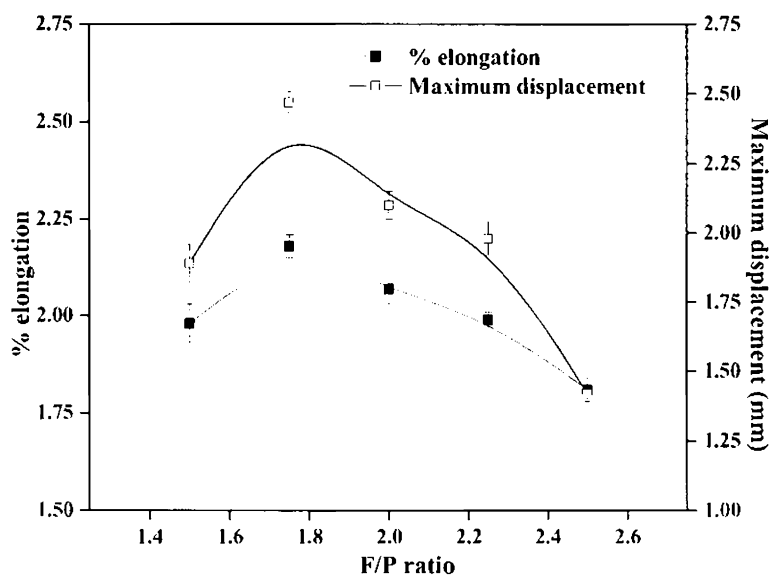

Fig. 2.10 % elongation and maximum displacement in flexure versus F:P molar ratio

Fig. 2.11 shows the variation of tensile and flexural moduli with F:P molar ratio. Modulus values are almost similar for F:P molar ratios 1.5:1 and 1.75:1. The decrease in the modulus values at higher F:P molar ratios may be due to the presence of relatively higher amounts of ether linkages. This gives more flexibility to the cured resin and hence leads to low modulus. However, the higher amounts of hydrogen bonds and lower amounts of ether linkages in R1.5 and R1.75 make them more rigid. At still higher F:P ratios the hydrogen bonding between chains is not found to increase further (as observed in Fig. 2.6)
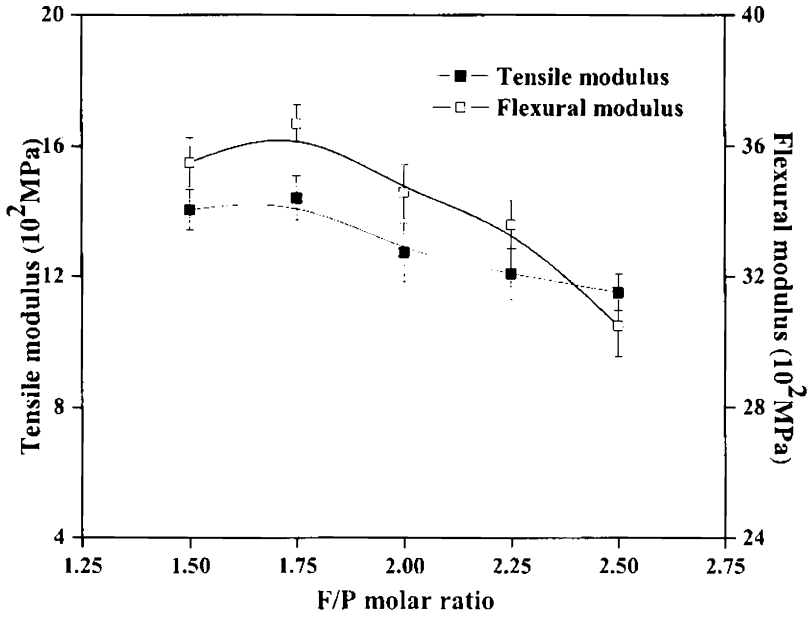
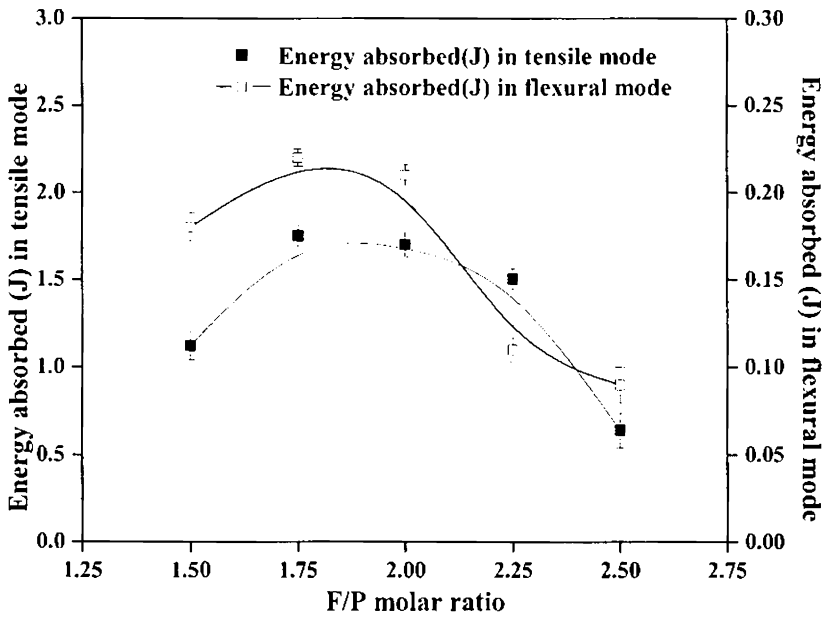**Fig. 2.11** Tensile and flexural moduli versus F:P molar ratio

Fig. 2.12 Variation of energy absorbed during tensile & flexural modes of fracture with F:P molar ratio

Fig. 2.12 shows the variation of the energy absorption (toughness) with F:P molar ratio in both tensile and flexural modes of fracture. The cured resin with F:P molar ratio 1.75:1 exhibits maximum energy absorption. Even though R1.75 shows maximum energy absorption, only a gradual decrease in the energy absorption can be seen for the nearest F:P molar ratios. This indicates that the flexible $-CH_2-O-CH_2-$ groups in the crosslinked structure have a role in reducing the brittle nature of the phenolic resol resin. However, a great increase in the ether linkages in R2.25 and R2.5, as indicated in the Fig. 2.7, does not give rise to any improvement in the toughness of the samples.

Fig. 2.13 refers to the variation of impact and compressive strengths with F:P molar ratio. Impact strength initially shows an increase upto an F:P molar ratio of 1.75:1. Afterwards it decreases gradually. This again indicates that the ether linkages in the phenolics help to reduce the brittleness to some extent. The flexibility imparted by the ether linkages and the moderate number of crosslinks might have contributed to the less brittle nature of the phenolic resol resin with F:P molar ratio = 1.75:1.
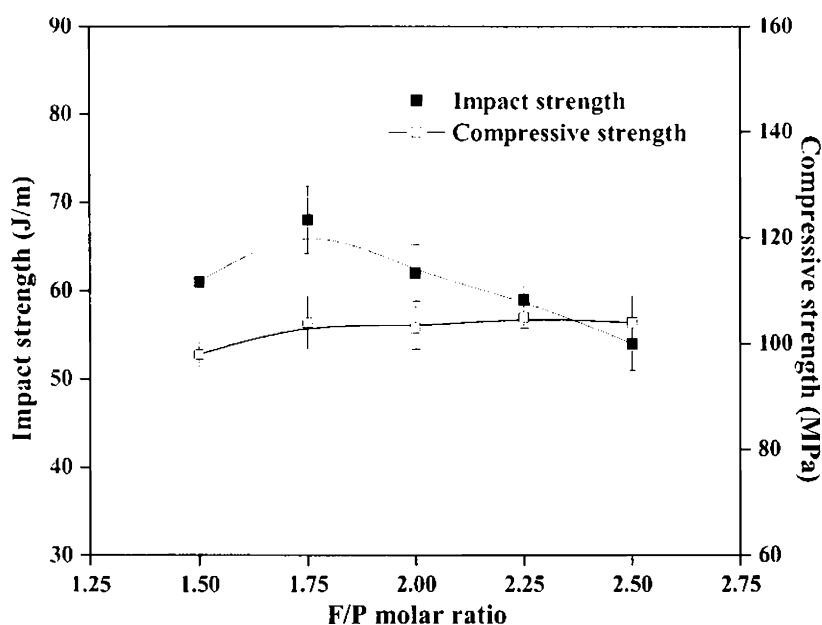

Fig. 2.13 Impact strength and compressive strength versus F:P molar ratio

Unlike other properties the compressive strength increases gradually with increase in the F:P molar ratio. This may be due to the increase in the crosslinks with increase in the F:P molar ratio.

Fig. 2.14 depicts the variation of surface hardness and abrasion loss as the F:P molar ratio increases. Hardness remains almost constant for all resols irrespective of the F:P molar ratio whereas the abrasion loss gradually increases with the F:P molar ratio. As the formaldehyde content increases, the number of methylol groups introduced into the phenol also increases. This leads to an increase in the condensation by-products and trapping of the same inside the cured resin. The trapping of the condensation products produces voids in the resin and hence the density of the material decreases. This might be the reason for the increase in the abrasion loss as the F:P molar ratio increased.
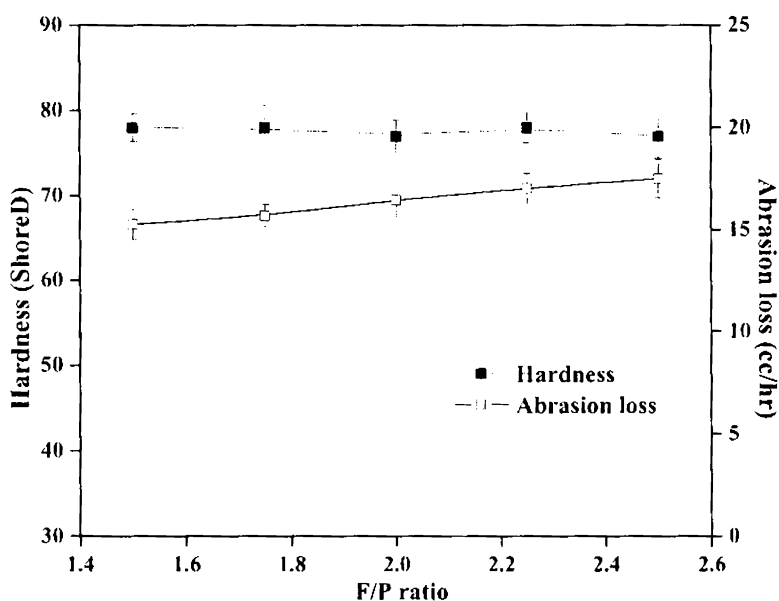

Fig.2.14 Hardness and abrasion loss versus F:P molar ratio

2.3.3.3 Thermal properties

i)   DMA

Fig. 2.15 shows the variation of storage modulus (E') of samples R1.5, R1.75 and R2.0 with temperature. The R2.25 and R2.5 samples were too brittle to withstand

the dynamic mechanical testing. Hence only three cases, viz. R1.5, R1.75 and R2.0 were subjected to dynamic mechanical analysis. The three samples have slightly different initial moduli. But the moduli at higher temperatures become constant for all the three samples. The plot shows that the E' values decreases with temperature and then increases to a constant value. For R1.5 and R1.75 the increase is not so prominent, but for R2.0 the E' values decreases sharply and then increases to a constant value. This sharp decrease in E' value and also a sudden increase indicate that the sample R2.0 has undergone further crosslinking during the dynamic mechanical analysis. As the methylol content increases with F:P molar ratio the resin undergoes curing at a faster rate and becomes more and more viscous with time. This leads to a cured resin with free –CH$_2$OH groups. These –CH$_2$OH groups could be able to undergo condensation reactions as the cured resin becomes more flexibile at higher temperatures during testing. But R1.5 and R1.75 became completely crosslinked under the curing conditions. It is possible that a small amount of residual crosslinking remains in samples with F:P ratios higher than 1.75.
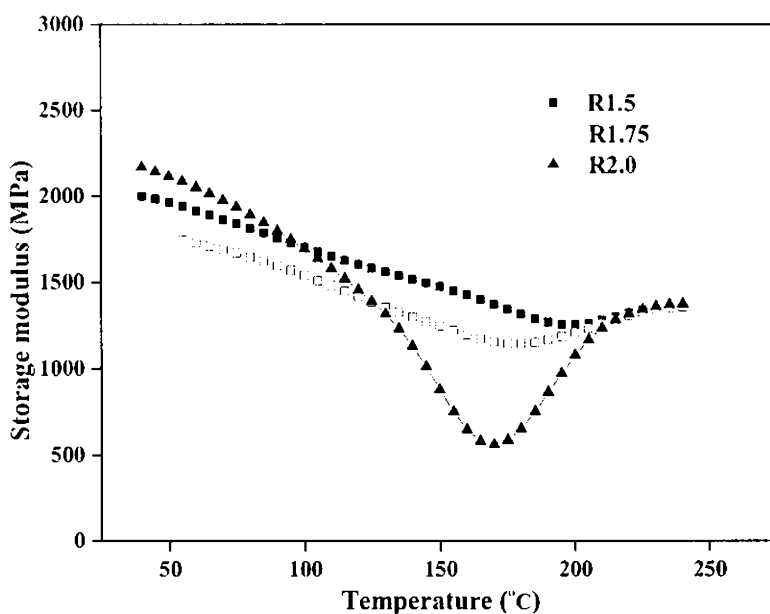

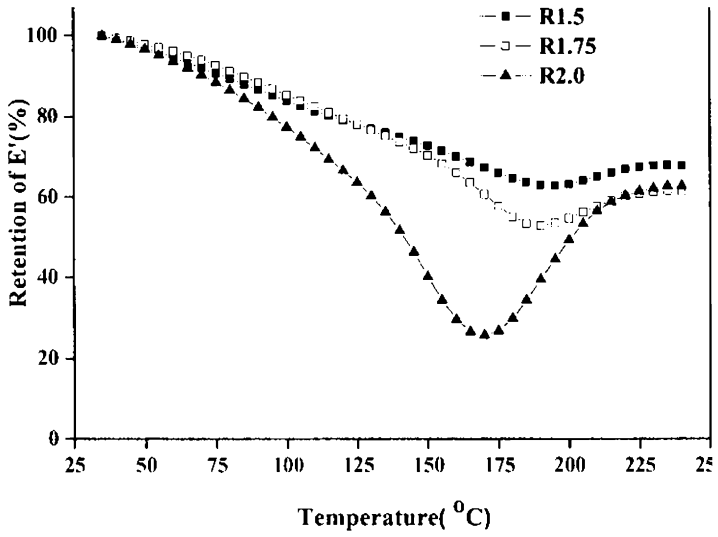**Fig. 2.15** Storage modulus (E') with temperature

Fig. 2.16 % Retention of E' with temperature

Fig. 2.16 represents the % retention of E' with temperature. The
of E' for all the samples is around 60-65%. The high % retention o
high temperature confirms the high thermal stability of phenolic resin [

Fig. 2.17 Tanδ versus temperature

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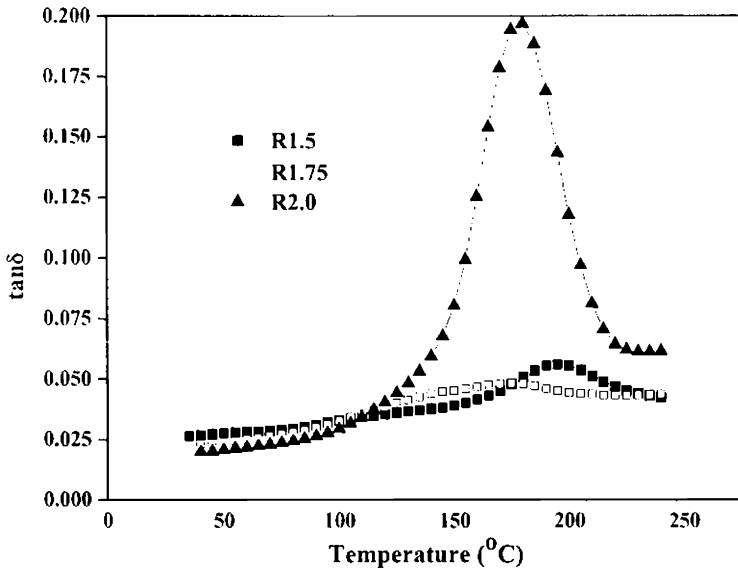
Variations of tanδ with temperature are given in Fig. 2.17. tanδ values are high for R2.0. This can be attributed to further crosslinking in the case of R2.0.

ii)   TGA

The thermograms of cured samples are shown in Fig. 2.18. The details of the analysis are shown in Table 2.2.
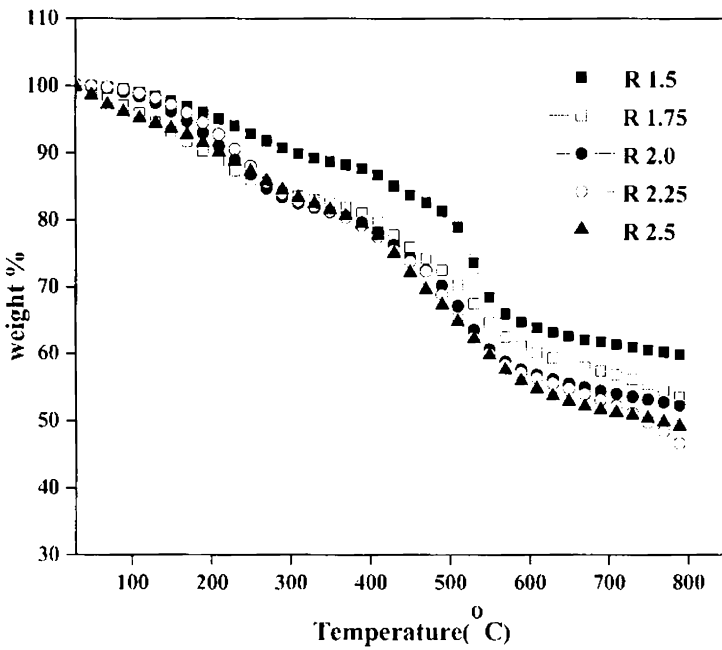
Fig. 2.18 Thermograms of cured resol resins

Table 2.2 Thermal properties of different PF resins

F:P molar ratio	Temperature (°C) at various stage of decomposition				Residue at 800°C	Temp. at max.deg. rate(°C)
	10%	20%	30%	40%		
R1.5	309	504	542	781	59	530
R1.75	194	406	512	614	53	532
R2.0	220	381	491	555	52	518
R2.25	234	377	485	549	46	487
R2.5	212	381	466	547	49	434

Both R1.5 and R1.75 show comparatively better thermal stability. This may be due to the lower amount of ether linkages in these samples. The temperature of maximum degradation falls sharply from ~ 530°C to 434°C as the F:P molar ratio increases from 1.5:1 to 2.5:1. A greater amount of formaldehyde is detrimental to the thermal stability of the resin.

2.4   Conclusions

The gel time of the synthesised resins was found to decrease with the increase in the formaldehyde content whereas the specific gravity of the uncured resin followed an opposite trend. The solid content of all the resins were almost identical.

The absorption bands in FTIR spectrum of the synthesized resin are identical to that in the standard spectra. The ratio of the relative intensity values of $-CH_2-O-CH_2-$ stretching to that of aromatic C-H stretching indicate that the dimethylene ether linkages increase with increase in the F:P molar ratio. For ratios higher than 1.5:1 the extent of hydrogen bonding is maximum and remains constant at higher ratios.

The cured resin with F:P molar ratio of 1.75:1 exhibits the best mechanical properties. Tensile, flexural and impact strengths were maximum for this particular ratio. Dynamic mechanical studies show that at higher F:P ratios the resin undergoes further crosslinking at higher temperatures.

The thermal studies on the cured resins show that the thermal stability is decreased with the increase in the F:P molar ratio. Resols with F:P molar ratio 1:1.5 and 1:1.75 exhibit better thermal stability.

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Chapter **3**

PREPARATION AND PROPERTY EVALUATION OF PHENOL CARDANOL FORMALDEHYDE RESOL RESIN

3.1 Introduction

This chapter contains the details of the study conducted on the preparation and modification of phenol cardanol formaldehyde resol resins. Cardanol is one of the important naturally occurring phenols. It is obtained from cashew nut shell liquid (CNSL). Cashew nut shell liquid, a byproduct of the cashew industry, is obtained from the shell of the cashew nut. About 30-35% CNSL is present in the shell, which amounts to approximately 67% of the weight of the nut. Natural CNSL contains four main components namely, cardanol, cardol, anacardic acid and 6-methyl cardol[1]. Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during the heating process which converts anacardic acid to cardanol. The three main components of cardanol are themselves mixtures of four constituents differing in side chain unsaturation viz. saturated, monoene, diene and triene. The structures of the side chains in the four major components of CNSL are identical. Fig.3.1 represents the chemical structure of the main components.
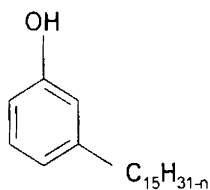
Fig. 3.1 Structure of cardanol

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

n=0, $(CH_2)_7$-$(CH_2)_7CH_3$;   n=2, $(CH_2)_7CH$ =$CH(CH_2)_5CH_3$

n=4, $(CH_2)_7CH$ =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
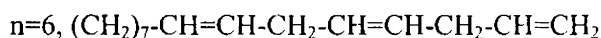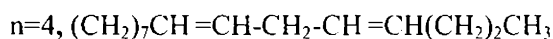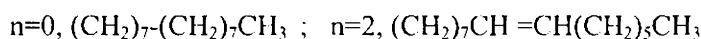
Cardanol gives most of the reactions of phenol even though the reactivity of cardanol is less. Therefore, complete or partial replacement of phenol by cardanol in phenol formaldehyde resin will be a desirable step because of various

advantages like cost effectiveness, support to the agricultural sector and the indirect conservation of petroleum deposits. But it is known that resins entirely based on cardanol do not possess good mechanical properties. It is also a matter of interest to find out how far various properties of phenol formaldehyde resin are affected by replacement of phenol by cardanol.

A number of works have been reported on the synthesis and modification of cardanol formaldehyde resins and its applications[2],[3],[4],[5],[6],[7][2-7]. Some reports have also appeared on the use of CNSL for this purpose. Incorporation of CNSL into phenol, in both resol and novolacs, decreased the tensile strength but led to an improvement in impact strength in the case of wood flour-based laminates of these resins[8][8]. But the thermal properties of phenol-cardanol based resin show deterioration with increase in the cardanol content[9][9].

In this part of the study, first, resols were synthesized by the reaction of a mixture of phenol and cardanol in various molar ratios (ranging from 1:0 to 0.9:0.1) with formaldehyde (PCF resin) keeping the total phenol to formaldehyde ratio as 1:1.75. Further, prepolymers of phenol-formaldehyde (PF) and cardanol-formaldehyde resin (CF) with the same F/P ratio were separately synthesized and blended (PFCF). The physical, mechanical, and thermal properties of these resins were estimated for comparison as well as to find out the optimal ratio between phenol and cardanol.

3.2 Experimental
3.2.1 Materials

Commercial CNSL was supplied by Vijayalakshmi Cashew Exports Pvt. Ltd., Kollam, Kerala, India. Cardanol was separated from it by distillation under reduced pressure (1mmHg). The pale yellow fraction collected at 230-240°C is cardanol[10][10].

3.2.2 Synthesis of PCF resin and resin blend PFCF

Phenol and cardanol in the percentage molar ratios 100:0, 98:02, 96:04, 94:06, 92:08 and 90:10 were mixed in a two necked RB flask provided with a

mechanical stirrer and a reflux condenser. 1 mole of this blend was then reacted with formaldehyde (1.75 moles) in the presence of NaOH (0.25 moles on a total phenolic component basis) as per the procedure in Section 2.2.2. These five resins were designated as PCF2, PCF4, PCF6, PCF8 and PCF10 corresponding to molar percentages of cardanol 2, 4, 6, 8 and 10 respectively.

Both PF and CF resol resins with phenol to formaldehyde ratio 1:1.75 were also synthesized separately as per the procedure given earlier. Blends of these resins (PFCF) were prepared by mixing both PF (R1.75) and CF (1.75) in such a way that each blend maintained the same phenol to cardanol molar ratio as in the PCF resin. PFCF blends were designated as PFCF2, PFCF4, PFCF6, PFCF8 and PFCF10. Due to the high viscosity of CF resin, it was dissolved in a minimum quantity of methyl ethyl ketone (MEK) initially and then mixed with PF resin using a mechanical stirrer. The solvent was subsequently removed by applying vacuum.

3.2.3 Morphological studies- Scanning electron microscopy[11]

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology. Scanning electron microscope (JOEL JSM 840A Scanning Microscope) 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 a JFC-1100E ion-sputtering unit for gold coating of the sample to make it conducting. The gold-coated sample was subjected to SEM.

3.2.4 Thermogravimetric analysis

Thermogravimetric analysis of the cured resins were performed as described in Chapter 2, Section 2.2.3.

3.2.4.1 Evaluation of kinetic parameters

The TGA data can also be used to study the kinetics of decomposition which provide an insight into the thermal stability of polymeric materials. There are many proposed methods to calculate the kinetic parameters of decomposition and the reported values depend not only on the experimental conditions, but also on the mathematical treatment of data.

i) Formulation of the rate equation

For many kinetic processes, the rate of reaction may be expressed as a product of a temperature dependent function; k(T), and a composition- or conversion- dependent term; $f(X)$:

$$r = dX/dt = k(T) f(X) \qquad \qquad (3.1)$$

where T is the absolute temperature in Kelvins; X is the conversion i.e. weight of polymer volatilized/initial weight of polymer and r is the rate of change of conversion or composition per unit time, t. The temperature dependent term in Equation (3.1) is the reaction rate constant, which is assumed to obey the usual Arrehenius relationship:

$$k(T) = A \exp(E_a/RT) \qquad \qquad (3.2)$$

where E_a is the activation energy of the kinetic process, A is the pre-exponential factor and R is the universal gas constant. The conversion-dependent function, $f(X)$, is generally a complicated form. A particular term is usually valid only for a limited range of experimental conditions. If it is assumed that a simple n[th] order kinetic relationship holds for the conversion-dependent term such that:

$$f(X) = (1 - X)^n \qquad \qquad (3.3)$$

and that the quantity (1-X) can be replaced by W, the weight fraction remaining in a TGA run, then:

$$r = dW/dt = AW^n \exp(-E_a/RT) \quad\text{...............................}(3.4)$$

$$\ln r = \ln(-dW/dt) = \ln A + n \ln W - E_a/RT \quad\text{.................}(3.5)$$

Published methods of deriving the kinetic parameters from TGA data center around Equation 3.5. They may be either differential i.e. involving the derivative term, -dW/dt or intergral i.e. based upon an integration of Equation 3.5. The emphasis in these methods is on finding a way of plotting the data to provide a rapid visual assessment of the order of the reaction and its activation energy.

ii)   Integral method

The integral methods involve the integration of Equation (3.1) by separation of variables. By substituting Equation (3.2) into this expression and defining $\beta = (dT/dt)$ as the heating rate, the following is obtained:

$$F(X) = \int_0^X dX/f(x) = \int_{T_0}^T (A/\beta) \exp(-E_a/RT) dT \quad\text{................}(3.6)$$

where T_0 is the initial temperature in the TGA analysis and T is the final tempetature. For constant heating rate β and if $T_0 \approx 0$, Equation (3.6) becomes:

$$F(X) = (A/\beta) \int_0^T \exp(-E_a/RT) dT \quad\text{....................................}(3.7)$$

The different integral methods involve an approximation of the right-hand integral term in Equation (3.7).

Among the integral methods, the Coats and Redfern approach[12][12] seems to be the most suitable from a practical point of view and is preferred over others and is applied here. The activation energy and the order of reaction were evaluated utilizing this equation for reaction order n $\neq$ 1, which when linearised for a correctly chosen n yields the activation energy from the slope.

$$\ln[1 - (1-\alpha)^{1-n}/T^2(1-n)] = \ln[AR/\beta E] - E_a/RT \quad\text{........}(3.8)$$

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For all n values this equation can be written as:

$$\ln\left[g(\alpha)/T^2\right] = \ln\left[(AR/\beta E)(1 - 2RT/E)\right] - E/nRT \quad \ldots\ldots\ldots(3.9)$$

for $n \neq 1$, $g(\alpha) = \{1-(1-\alpha)^{1-n}/(1-n)$; for $n = 1$, $g(\alpha) = -\ln(1-\alpha)$.

where α is the fraction decomposed, T the temperature (K), n is the order of reaction, A is the Arrehenius constant, R the universal gas constant, E_a the activation energy and β the heating rate. The plot of the left hand side of the Equation (3.9) against 1/T should be a straight line with slope = E_a / R for the correct value of n.

In the case of crosslinked polymers (as the present one), a first order kinetics is usually assigned since they undergo degradation by a random process. The activation energy (E_a) was determined from the plot of $\ln[-\ln(1-\alpha)/T^2]$ against the reciprocal of absolute temperature (1/T).

3.3 Results and discussion

3.3.1 Physical properties

Table 3.1 shows the variation of gel time, specific gravity and TSC of PCF and PFCF resins.

Table 3.1 Specific gravity, gel time and total solid content of resol resins

Mole% of Cardanol in the resin	Gel time (sec.)		Specific gravity		TSC	
	PCF	PFCF	PCF	PFCF	PCF	PFCF
0	440	440	1.2675	1.2675	78	78
2	455	455	1.2663	1.2570	80	83
4	485	470	1.2515	1.2408	79	81
6	525	495	1.2448	1.2328	78	80
8	543	530	1.2319	1.2170	76	83
10	575	555	1.2190	1.2042	77	81

PFCF samples show lower gel time and specific gravity than PCF resins. The lower gel time of PFCF resin may be due to a faster rate of curing of PF resin

compared to CF resin. In PCF resin, cardanol units have been incorporated into the backbone and become an integral part of the main chain. This can slow down the curing process. The general lowering of specific gravity in cardanol-containing PF resins may be due to the bulkiness of cardanol units. The total solid content is slightly higher for PFCF resin in most cases.
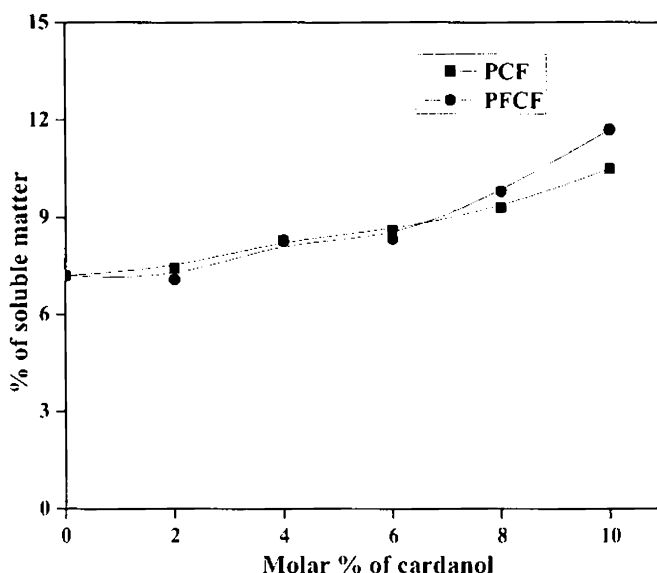

Fig. 3.2 Variation of % soluble matter with cardanol content

Fig.3.2 shows the variation of soluble matter in the cured resin with cardanol content in the resin. For both resins the soluble matter gradually increases. This indicates that the amount of unreacted cardanol or extractable oligomers increases with increase in cardanol content.

3.3.2 Mechanical properties

The effect of cardanol content on the tensile strength of resol resin is shown in Fig. 3.3. Tensile strengths of both PCF and PFCF resins decrease gradually with increase in the cardanol content. But up to 6 molar % of cardanol content in the resin, the tensile strength of the resin is not seriously affected. The fall in the tensile strength with further increase in the cardanol content may be due to a lower extent of crosslinking. This is understandable in view of the lengthy side chain. On comparing

the tensile strengths, the PCF resin shows comparatively higher strength. A more even distribution of cardanol rings can be expected in the case of PCF resin. This may lead to better tensile strength whereas a higher local concentration of cardanol can cause lower levels of polycondensation and crosslinking.
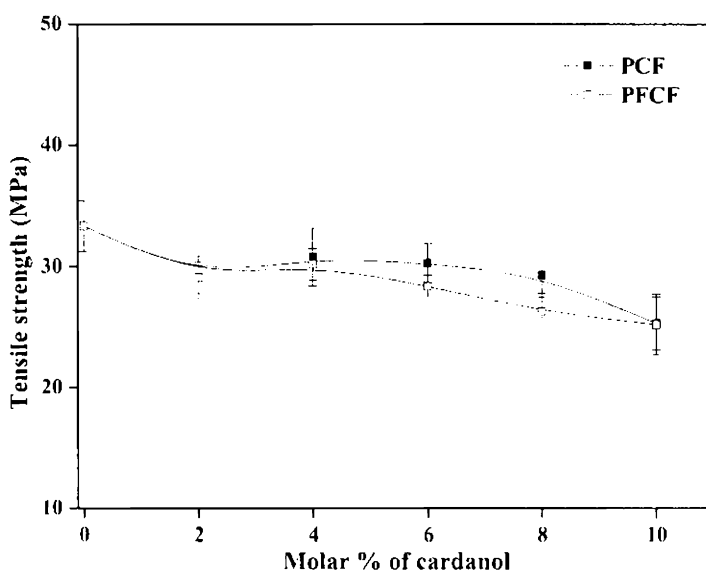

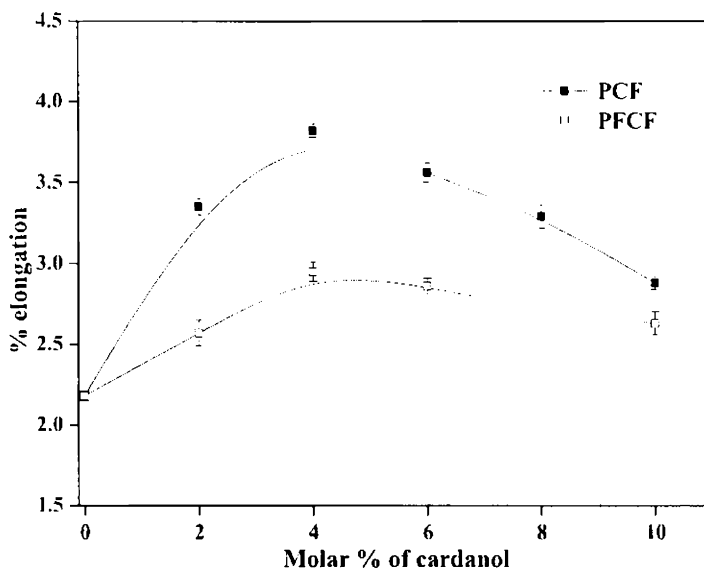**Fig. 3.3** Variation of tensile strength with cardanol content

Fig. 3.4 Variation of % elongation with cardanol content

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The effect of cardanol content on elongation at break is shown in Fig. 3.4. The elongation at break increases in both cases and shows a maximum between 4-6 mole percent of cardanol. The PCF resin exhibits greater increase in elongation at break compared to the PFCF resin. This may presumably be due to the difference in the distribution of cardanol units in the resin. In the case of PCF resin, the cardanol units are directly linked to the phenol units and became an integral part of the prepolymer chain. Hence the cardanol side chain is more likely to impart a plasticizing effect

Variation of the tensile modulus of resol resin with cardanol content is shown in Fig. 3.5. Both PCF and PFCF show similar trends in tensile modulus values. Tensile moduli of both types of resols gradually decrease with increase in the cardanol content. But the decrease is more prominent in PFCF resol resin. The decrease in the modulus may be due to the plasticizing effect of the hydrocarbon chain in the cardanol.
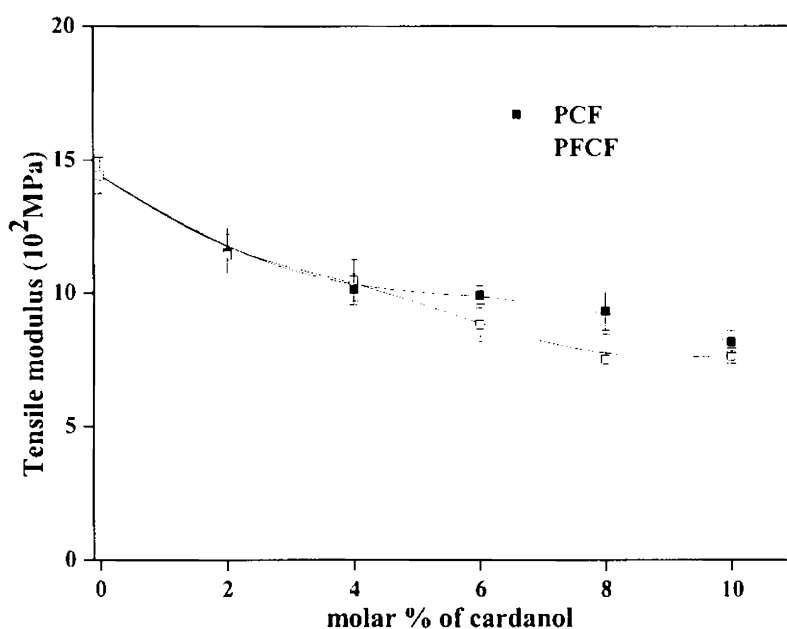
Fig. 3.5 Variation of tensile modulus with cardanol content

The variation of energy absorption during tensile fracture is shown in Fig. 3.6. Both show similar variations in energy absorption. Here also 4-6 mole % of

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cardanol content in the resol resin shows a maximum. The increase in the energy absorption indicates improved toughness of the modified resin.

Fig. 3.6 Variation of energy absorbed (at break) in tensile mode of fracture with cardanol content

Fig. 3.7 Variation of flexural strength with cardanol content

Fig. 3.7 depicts the variation of flexural strength with cardanol content. In both cases the flexural strength decreases gradually with increase in cardanol content.

At lower cardanol contents, flexural strength falls only marginally in PCF resin whereas it is still considerable in the case of PFCF resin. This may possibly be due to the heterogeneous nature of the PFCF resin. The general decrease in the flexural strength of both resol resins is due to the flexibility imparted by the aliphatic side chain in the cardanol unit. Flexural modulus of resol resins containing cardanol shows a regular decrease with increasing cardanol content (Fig. 3.8) in both cases as expected. The plasticizing effect of cardanol units and reduction in crosslink density may be responsible for the reduction of flexural modulus. An appreciable decrease in the modulus values can be observed in PFCF resol resin above 4 mole % of cardanol.

Fig. 3.9 depicts the variation of maximum displacement with molar % of cardanol. The variations in maximum displacement values with cardanol content show almost similar trends by PCF and PFCF resins in the early stages. In PCF resins the value increased slightly up to 6 molar % of cardanol and then sharply decreased. The maximum displacement values of PFCF resols showed almost steady values in the beginning. However at higher molar % of cardanol the maximum displacement values are found to have a gradual decreasing tendency.

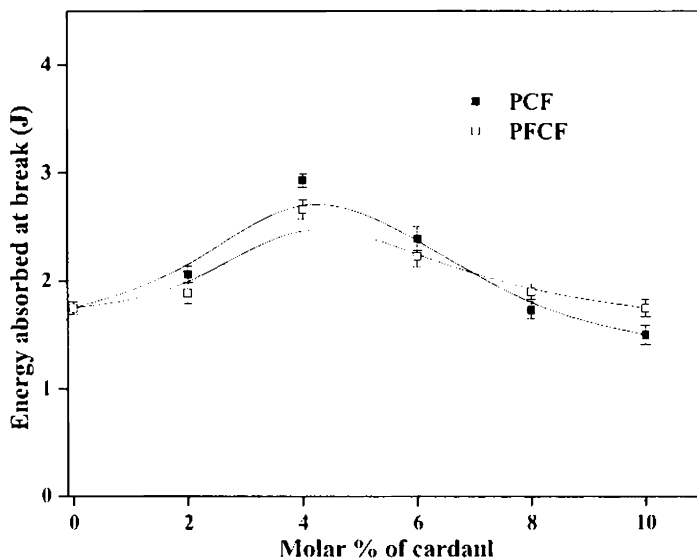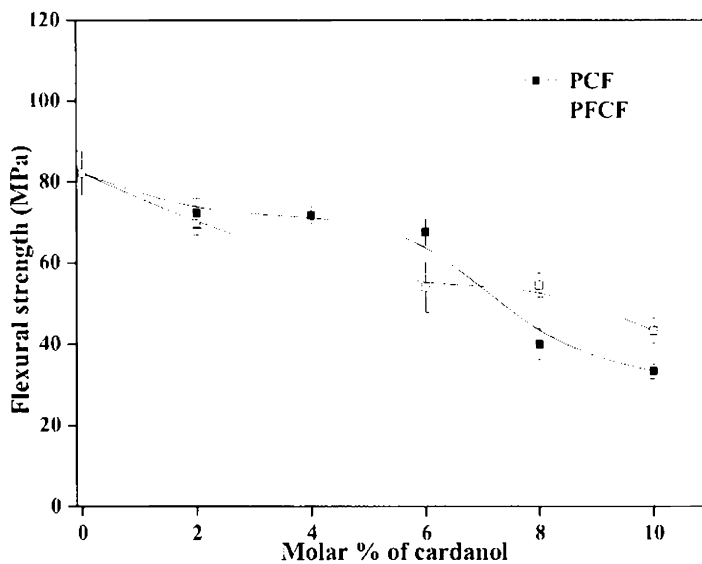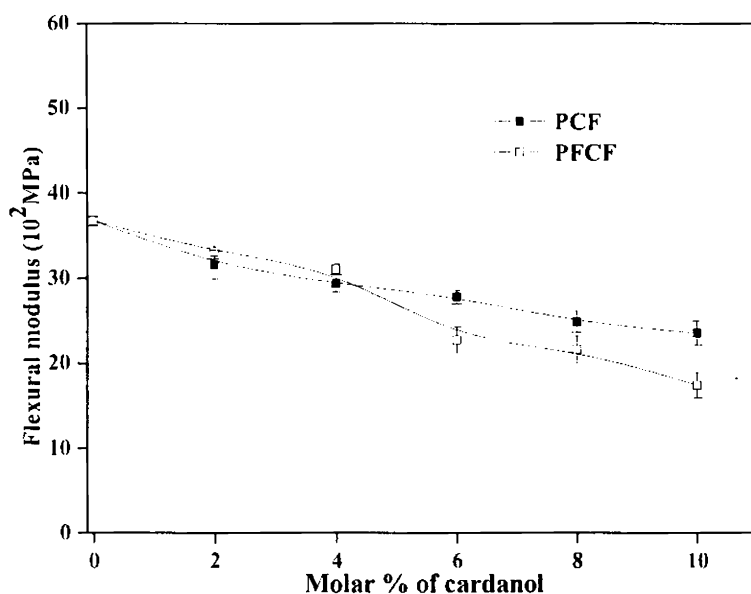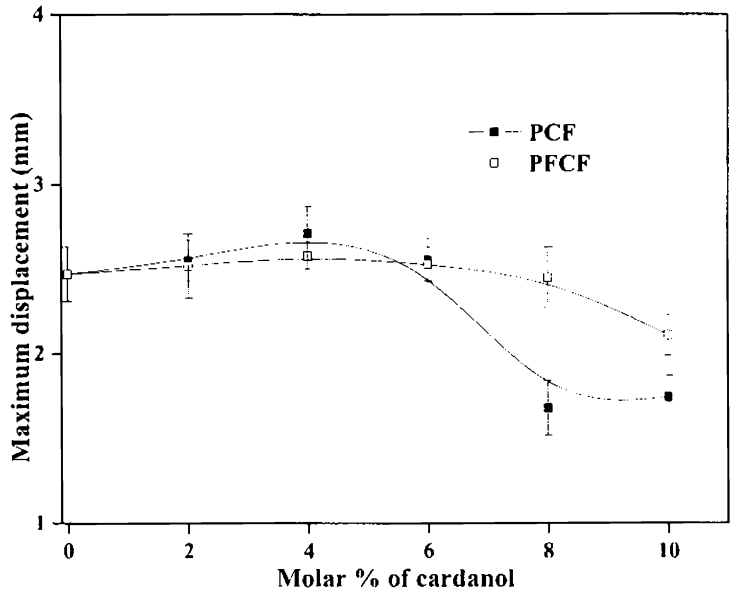**Fig. 3.8** Variation of flexural modulus with cardanol content

Fig. 3.9 Variation of maximum displacement with cardanol cont‹

The Variation of energy absorbed in flexural mode of fracture is Fig. 3.10. In both cases, the energy absorption is increased only nomina molar % of cardanol. Above this it shows a decreasing tendency.
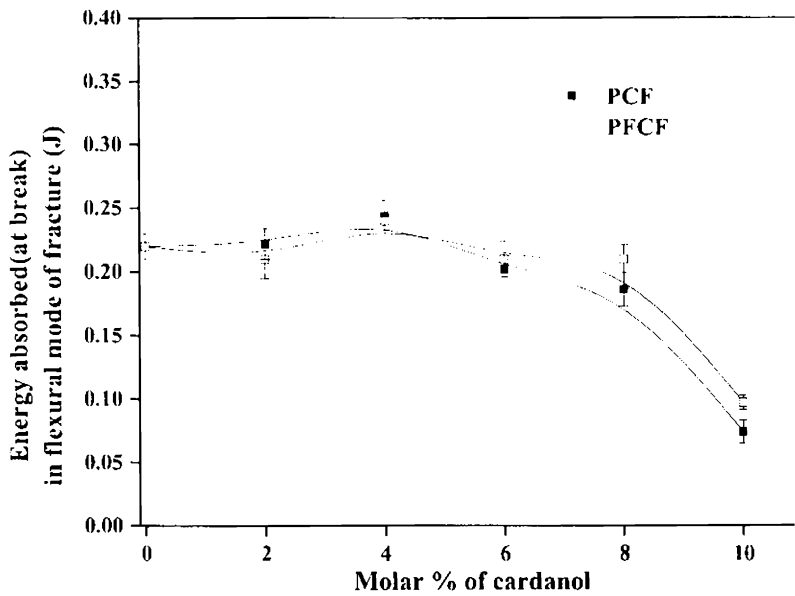
Fig. 3.10 Variation of energy absorbed in flexural mode of fractu cardanol content

However, the replacement of phenol by cardanol up to ~ 8 molar percentage does not affect both the maximum displacement and energy absorption values.

Fig. 3.11 indicates the variation of impact strength of PCF and PFCF resins with cardanol content. The impact strength of both PCF and PFCF resins are higher than the neat resin up to 7-8 mole percent of cardanol. At higher cardanol contents it decreases. The improvement in the impact strength may be due to lower crosslink densities and the flexibility imparted by the long hydrocarbon chains in the cardanol units. On comparing the impact strength of PCF and PFCF resol resins the latter shows better impact properties. As can be seen from the SEM pictures, microscopically the two constituent resins of PFCF resin exist in different phases. This heterogeneity may be the reason for the better impact strength of PFCF resin in addition to the plasticizing effect of the side chain of cardanol units.
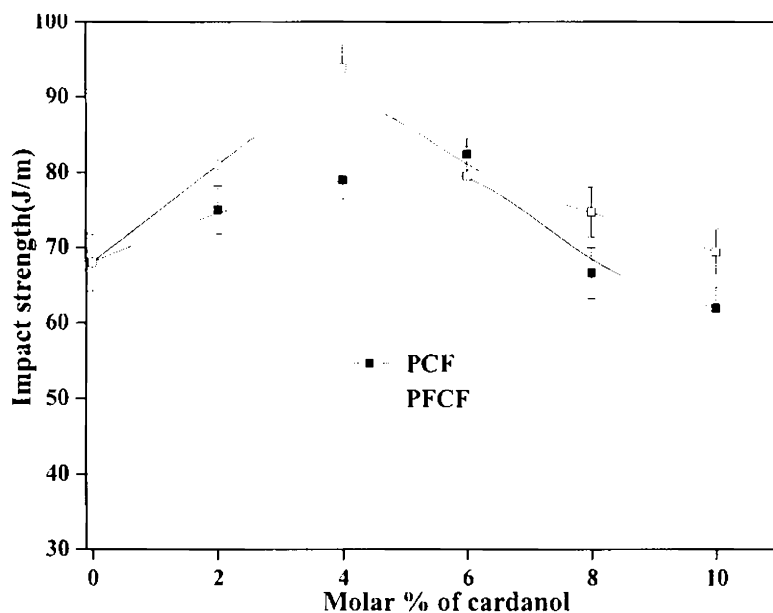
Fig. 3.11 Variation of impact strength with cardanol content
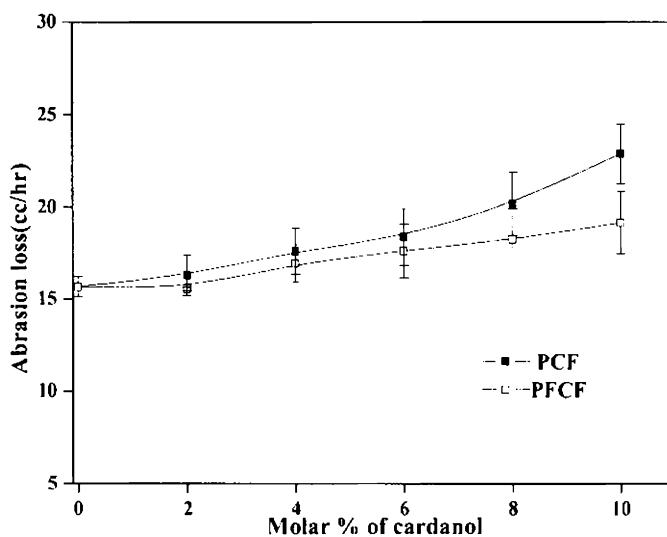
Fig. 3.12 Variation of abrasion loss with cardanol content

Fig. 3.12 shows the variation of abrasion loss with cardanol content. It is clear from the graph that the abrasion loss increases with the increase in the cardanol content. Compared to PCF resin, PFCF shows better abrasion resistance. The CF resin phase separates during the curing process and occupies the microvoids formed by the curing of PF resins and gets separately cured therein. As a result, the density of PFCF resin is higher compared to the PCF resin and hence it exhibits higher abrasion resistance.
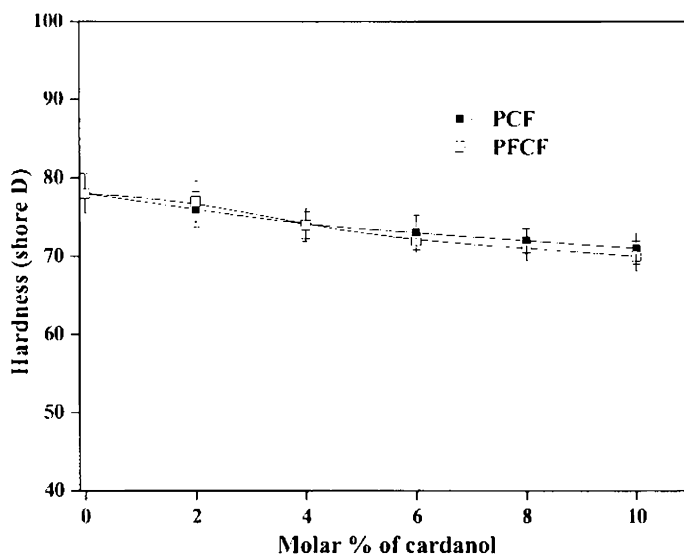
Fig. 3.13 Variation of hardness with cardanol content

The variation of hardness with cardanol content is shown is Fig. 3.13. For both PCF and PFCF resol resins a general lowering of hardness can be seen. The large bulky group in the cardanol imparts flexibility and softness to the cured resin due to poor molecular packing.
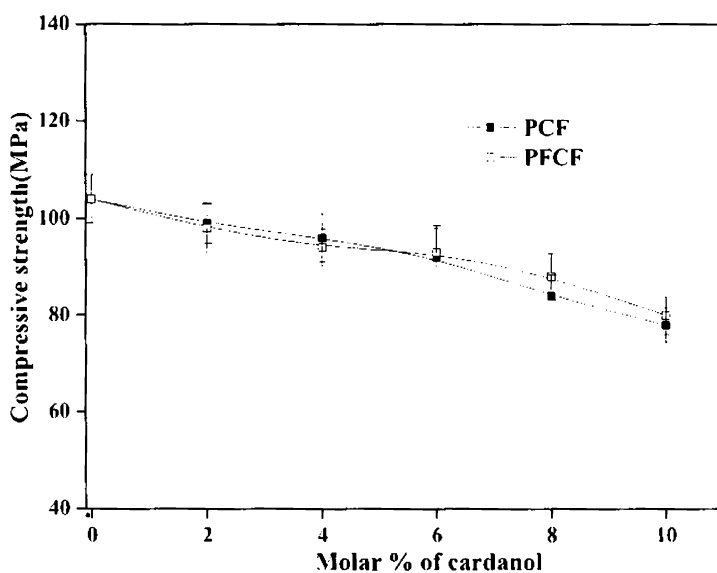
Fig. 3.14 Variation of compressive strength with cardanol content

There is a general decrease in the compressive strength of the PCF and PFCF resins with increase in cardanol content as shown in Fig. 3.14. Compressive strength of both PCF and PFCF resins decreases gradually with increase in cardanol content. The plasticizing effect of cardanol as well as a lower level of packing due to the side groups may have resulted in the reduction of compressive strength of both resins.

3.3.3 Morphological studies

Scanning electron micrographs of neat resin, PCF4 and PFCF4 are shown in Figs. 3.15 (a) to (c).

All the micrographs contain microvoids in the cured resin. Even though all the resins were cured slowly and with care, formation of microvoids could not be avoided. The formation of microvoids is an inherent problem of PF resins even

when it contains added diluents to reduce the viscosity and facilitate easy escape of the condensation byproducts[13][13].

(a)   (b)

(c)
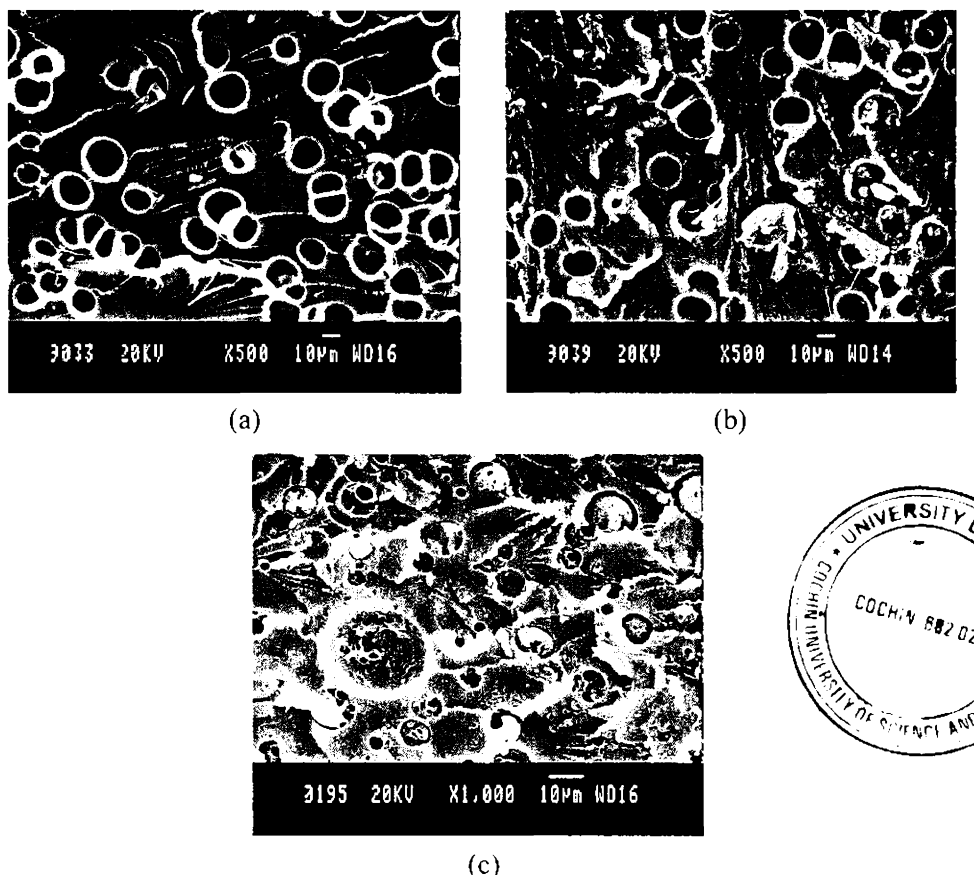
Fig. 3.15 Scanning electron micrograph of fractured surfaces of (a) PF (b) PCF4 and (c) PFCF4

Referring to Micrograph (a) the fracture path for neat resin is narrow and ends at microvoids indicating rapid crack propagation along the axis of crack growth. The fracture surface is also very smooth. Micrograph of PCF4 (b) shows a profusion of cracks far broader and thefractured surface is rougher indicating greater energy absorption. Referring to PFCF4 (c), the fractured surface is more rough and cracks are still broader. Another interesting feature of Micrograph (c) is that it contains filled microvoids. This may be due to the difference in the cure rate of PF resin and CF resin. PF resin cures at a faster rate than the CF resin. This causes the separation of CF resin

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along with the condensation byproducts like water which proceed to fill the microvoids. The filling of the microvoids and broader crack areas lead to greater energy absorption than that recorded by PCF and neat resins. This is also reflected in improvement of the impact strength of PFCF resin over the other two.

3.3.4 Thermal studies
i)   TGA

The thermograms of neat resin, PCF4, PCF6, PFCF4 and PFCF6 are shown in Fig. 3.16. The results of thermal studies are summarized in Table 3.2.

The temperature for 10% and 20% degradation is higher for phenolic resins containing cardanol. The initial loss is mainly due to the loss of volatiles, mainly water, from the cured resin. The reduction in the amount of volatiles in the cardanol-containing phenolic resins may be due to the repulsion between the polar volatiles and non polar side chain units which leads to easy escape of volatiles during curing. But the temperature at maximum rate of degradation is shifted to a lower temperature range. This is because of easier degradation of the hydrocarbon chain in the cardanol unit. The hydrocarbon chain degrades normally at around 420-430°C. The residue also reduces with increase in the cardanol content. On comparing the thermal stability of PCF and PFCF resins,
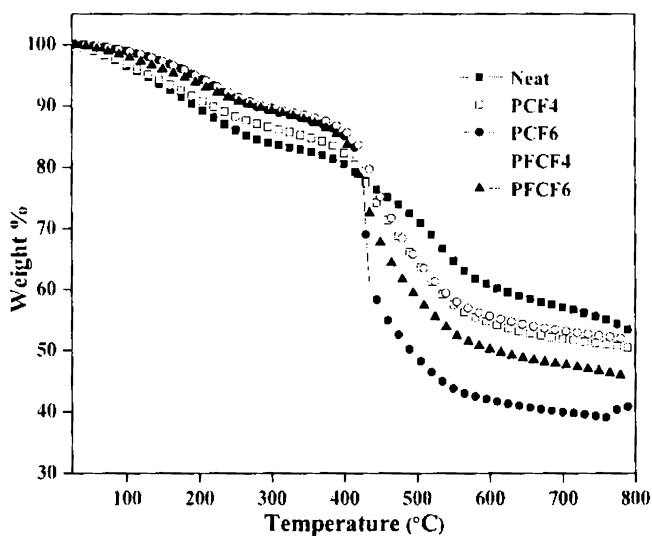
Fig. 3.15 Thermograms of different phenolic resins

Table 3.2 Thermal decomposition characteristics of cured phenolic resins

Sample	Temperature at different stages of degradation (°C)					Temp. at max. degradation (°C)	Residue (%)
	10%	20%	30%	40%	50%		
PF	194	406	512	614	>800	531	53
PCF4	218	417	467	529	>800	433	50
PFCF4	288	434	472	535	>800	437	52
PCF6	273	429	430	435	491	430	41
PFCF6	272	416	442	491	605	424	46

PFCF resin shows better thermal stability. PCF4 and PFCF4 resins show the same thermal resistance at advanced stages. This is evident from the fact that 50% degradation temperatures for PF, PFCF4 and PCF4 resins are all in excess of 800C. Figs. 3.17 shows the kinetic plots (Coats-Redfern plots) of PF, PCF4, PFCF4, PCF6 and PFCF6 degradation. The calculated values of activation energy, E along with correlation coefficient and pre-exponential factor (Arrhenius constant, A) are given in Table 3.3.
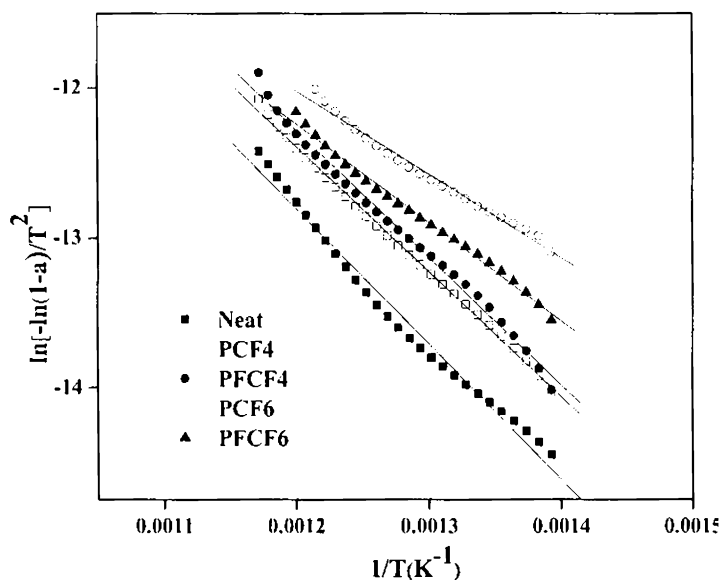
Fig. 3.17 Coats-Redfern plots for phenolic resins

The activation energy of the phenolic resin decreases as the cardanol content in the resin increases. Arrhenius constant also follows the same trend. Both the E value and A factor are comparably higher for PFCF resin. This indicates better thermal stability for the blend of PF and CF resins. Cardanol can lead to a decrease in thermal stability due to the presence of the long hydrocarbon chain which is more susceptible to thermal attack. However, the better thermal stability of the PFCF resin over PCF resin may be due to the stabilization of the radical formed by the thermal cleavage of the side chain of the cardanol unit by the phenolic resol resin which is a separate entity in the PFCF resin.

Table 3.3 Activation parameters for the thermal degradation of cured resols

Sample	E(KJ/mol)	A(X10^2)	Correlation coefficient
PF	79.3	1.2134	0.9820
PCF4	70.6	0.5060	0.9814
PFCF4	70.8	0.5661	0.9802
PCF6	46.9	0.0226	0.9847
PFCF6	57.6	0.0557	0.9824

ii)   DMA

Fig. 3.18 shows the variation of storage modulus (E′) of neat resin, PCF4 and PFCF4 with temperature. The initial storage modulus of the neat PF sample is higher than the other two. PFCF4 has the least storage modulus among the three. The decrease in the initial storage modulus of cardanol modified PF resin is due to the flexibility imparted by the cardanol units.
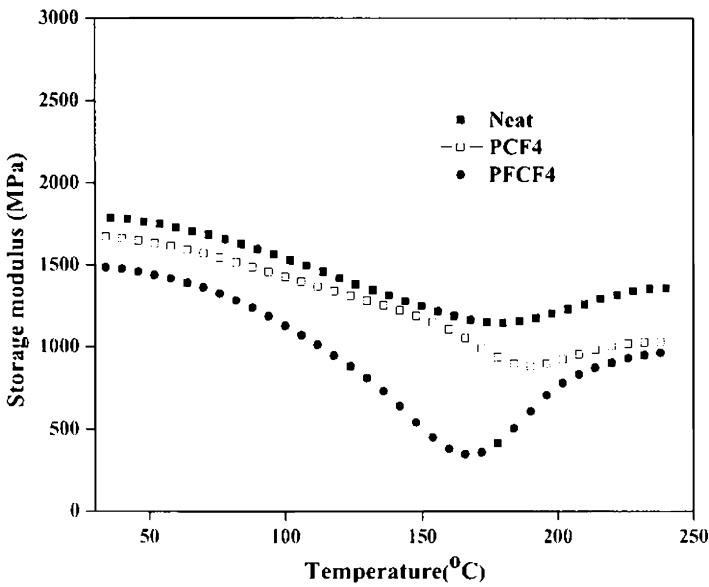
Fig. 3.18 Storage modulus (E') with temperature
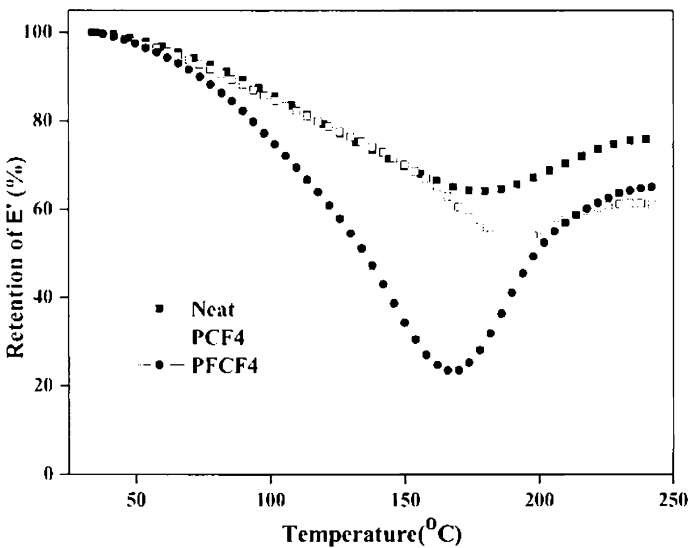
Fig. 3.19 % Retention of E' with temperature

Fig. 3.19 depicts the % retention of E' with temperature. The retention of E' is greater for the neat resin. But for the samples PCF4 and PFCF4 the E' value decreased by 10-15%. The storage modulus of PFCF4 decreased sharply with the increase in temperature up to ~170°C and then increased. This may be due to residual crosslinking of PFCF4, which can result from the difference in the cure

rates of PF and CF resins. Interestingly the % retention of E′ at higher temperatures is higher for PFCF4 than PCF4. This supports the higher thermal stability of the former compared to the later which is confirmed by thermal studies.
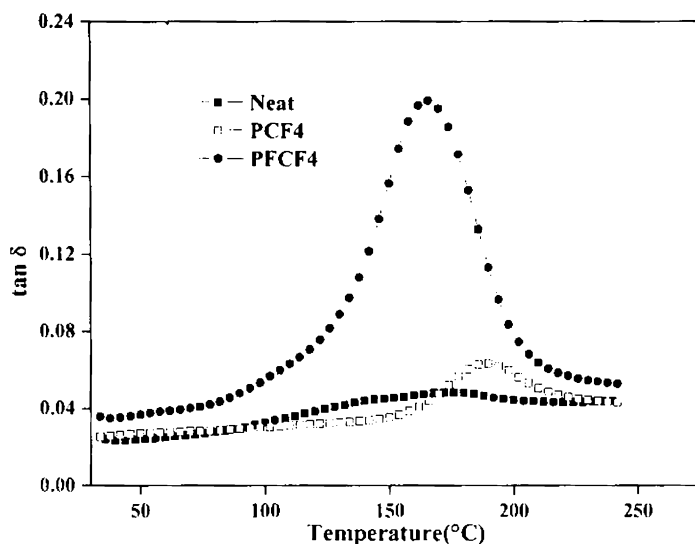
Fig. 3.20 tan δ with temperature

Fig. 3.20 indicates the variation of tan δ with temperature. The tan δ values are very low for both the neat resin and PCF4. This may be due to the homogencity and also high crosslink density of these resins. But the tan δ values of PFCF4 are very high. This can be attributed to residual crosslinking and also lower crosslink density of the sample.

3.4 Conclusions

Phenol cardanol formaldehyde was synthesised by two different methods. The gel time increased whereas the specific gravity of uncured resin followed a reverse trend on incorporating cardanol units into the PF resin. The mechanical properties of both PCF and PFCF resins are comparable. But PFCF resins showed better impact strength and abrasion loss compared to PCF resins. The SEM micrographs of the tensile fractured samples of PCF and PFCF resins exhibit different surface morphologies. This is partly responsible for the better impact strength and abrasion loss of PFCF resins.

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Thermal properties of the cardanol containing PF resins are poor compared to the neat resin due to the presence of the side chain in cardanol. However, the blends of PF and CF resins show better thermal stability than PCF resin. DMA analysis confirms better flexibility for cardanol containing PF resins, which is indicated by the lower storage modulus values for these resins. The % retention of storage modulus with temperature decreased for all samples, but the neat resin retains its rigidity to a greater extent compared to cardanol modified samples. The higher retention of E' for PFCF resin at higher temperature compared to PCF resin shows better thermal stability of the former.

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MODIFICATION OF PHENOLIC RESOL RESIN USING UNSATURATED POLYSTER

4.1 Introduction

As the curing reaction of phenolic resol resin advances, the resin viscosity rises and the escape of the condensation products becomes more difficult. The entrapment of the condensation products in the cured resin leads to microvoids, which adversely affect the properties of the cured resin. These problems associated with the curing of phenolics were largely solved by Baekeland, who developed molding methods employing heat and pressure to get products with less porosity [1]. Another method to reduce the microvoids is by adding diluents such as glycols [2,3]. The addition of diluents yields dual advantages. Firstly, it reduces the viscosity of the resin which helps the escape of condensation products and secondly, the glycols disperse the condensed water into fine droplets of dimensions less than that of the wave length of visible light [4]. It has also been reported that acid curing agents like toluenesulfonic acid not only accelerate the curing reaction but also reduce the microvoids [5].

Glycols and some dicarboxylic acids are effective in enhancing the mechanical properties of phenolic resin [3,6]. The quinone methide moieties present in phenolic resin prepolymers are capable of forming a ring structure with double bonds [7]. Unsaturated polyester (UP) is a thermoset polymer that can provide the combined advantages of diols, dicarboxylic acids and double bonds. Thus low molecular weight UP holds promise to both reduce the microvoids and improve the properties of resol phenolic resin, in general. With this possibility in mind, UP is used as a modifier in this work. Initially, the commercial PF resol resin was modified by UP with varying maleic anhydride/phthalic anhydride (MA/PA) ratios. Having identified the best MA/PA ratios, UP with varying chain lengths (acid values) and optimal MA/PA values were synthesized. These resins were then blended with phenolic resols in various proportions to obtain modified phenolics. The modified samples were tested for evaluating the improvement in properties by comparison with the virgin material. The structural changes were analysed by

FTIR. TGA and DMA were employed to study the thermal properties of the modified resin and the fracture behavior and the void size were analysed by SEM.

4.2 Experimental
4.2.1 Materials

1,2 Propylene glycol (B.P.=188^{0}C, d^{20}=1.04), maleic anhydride (M.W.=98.06, 98.5% assay), phthalic anhydride (M.W.=148.12, 99% assay), xylene (B.P.=137-142^{0}C, 95% assay), triphenyl phosphate and glacial acetic acid used were laboratory reagent (LR) grade supplied by E. Merck India Ltd, Mumbai. Commercial resol resin in alkaline medium was obtained from M/S.Polyformalin (P) Limited, Thripunithura, Kerala, India. The physical properties of the PF resin are given in Table 4.1

Table 4.1 Physical properties of the commercial PF resol resin

Appearance	Deep brown colour
Viscosity	~ 2000 cps
Water tolerance	~ 1:3
Solid content	~ 50
F:P ratio	~ 1.85

The resol resin was neutralized with glacial acetic acid until the pH reached a value of ~7.0. It was then kept overnight for phase separation and the water layer was decanted off. The resin was subsequently dried for 12 hours using a vacuum oven to completely remove the water.

4.2.2 Synthesis of unsaturated polyester (UP)

The optimal procedure for synthesis of UP is to initially react PA with the total stoichiometric amount of PG (for PA and MA) and subsequently react the product with MA [8]. This procedure has been adopted for the synthesis. UPs with four different maleic anhydride to phthalic anhydride (MA/PA) ratios (90/10,

70/30, 50/50 & 30/70) designated as UP1, UP2, UP3 & UP4 respectively were synthesized (acid value ~26mg KOH/g). Propylene glycol and phthalic anhydride were taken in the molar ratio 1.1:0.30 in a 1 liter three-necked RB flask equipped with a mechanical stirrer, N_2 inlet and a reflux condenser. A small amount of excess PG was included to allow for evaporation losses. The reaction was conducted under an inert blanket of N_2. 0.05% of triphenyl phosphate was added to prevent decolourisation. About 10 ml xylene was used to remove water of condensation azeotropically. The reaction mixture was heated at 210°C for 2 hours. At this temperature MA is isomerised to less strained and more planar trans fumaric acid [9]. The predetermined amount of maleic anhydride was then added. The acid value was monitored every hour. When the acid value became 40, vacuum was applied to bring it below 30 by removing the water of condensation. UP with different acid values were obtained by withdrawing samples at different stages.

4.2.3 The acid value and number average molecular weight ($\overline{M_n}$)

Acid value determination is the most common method for estimating the extent of reaction and finding the number average molecular weight indirectly (ASTM D 2849). 100 cc of 50/50 methanol/benzene solvent was made mildly alkaline to phenolphthalein indicator by the addition of 0.2 N KOH solution. About 2g of polyester resin was then added to the flask containing the solvent. The resin was allowed to dissolve. The solution was then titrated against 0.2 N KOH solution until a pink colour (permanent for 5 minutes) was obtained. The volume of 0.2 N KOH was noted. The number average molecular weight ($\overline{M_n}$) was calculated as 56000/acid value. The acid value and $\overline{M_n}$ of the UP is shown in Table 4.2

$$\text{Acid value} = \frac{\text{Vol. of KOH} \times \text{Normality of KOH}}{\text{Weight of the sample}} \times 56.1$$

Table 4.2 Acid value and $\overline{M}_n$ of the synthesised UP

MA/PA ratio	Acid value (mg KOH/g)	$\overline{M}_n$	Designation of UP	Designation of blends
90/10	~ 26	2154	UP1	RUP1
70/30	~ 27	2074	UP2	RUP2
	~ 93	602	UP2a	RUP2a
	~ 70	800	UP2b	RUP2b
	~ 60	933	UP2c	RUP2c
	~ 50	1120	UP2d	RUP2d
50/50	~ 25	2240	UP3	RUP3
30/70	~ 26	2154	UP4	RUP4

4.2.4 Sample preparation

Dried phenolic resol resin (R) was mixed with varying proportions of UP dissolved in methyl ethyl ketone using a mechanical stirrer for 20 minutes. The solvent was then removed by applying vacuum for about 45 minutes. The modified resins were designated as RUP1, RUP2, RUP3 and RUP4 corresponding to a different MA/PA ratio. Since UP2 corresponding to an MA/PA ratio of 70:30 was observed to give the best overall mechanical properties when blended with phenolic resin, subsequent studies using polyesters to UP2 only. RUP2a to d represent various blends containing UP2 of different acid values, namely: 93, 70, 60 and 50.

4.2.5 Specific gravity

For specific gravity measurement, cylinder shaped specimens were cast according to the temperature schedule earlier mentioned (Section 2.2.3). Specific gravity at 25°C was determined by following Archimedes' principle using water.

4.2.6 Thermogravimetric analysis (TGA)

Approximately 10mg of each of the cured samples were kept at 100°C for 30 minutes in N_2 atmosphere to find out the amount of volatiles (particularly water) in the cured sample. A TA instrument, TGA Q 50 Analyzer was used for this study.

4.2.7 Void size characterisation and distribution [10-12]

The voids in the cured sample are assumed to be uniformly distributed in the bulk. Magnified micrographs can be used to calculate the morphological parameters. The distribution of the void parameters was determined by measuring the diameters on the magnified SEM micrographs.

These are calculated using the equations (1) – (6)

$$\text{Number-average diameter,}\ \overline{D_n} = \frac{\sum N_i D_i}{\sum N_i} \quad\text{.............................(1)}$$

$$\text{Weight-average diameter,}\ \overline{D_w} = \frac{\sum N_i D_i^2}{\sum N_i D_i} \quad\text{.............................(2)}$$

$$\text{Surface area -average diameter,}\ \overline{D_a} = \sqrt{\frac{\sum N_i D_i^2}{\sum N_i}} \quad\text{...............(3)}$$

$$\text{Volume-average diameter,}\ \overline{D_v} = \sqrt[3]{\frac{\sum N_i D_i^3}{\sum N_i}} \quad\text{.......................(4)}$$

where N_i is the number of particles having a diameter D_i.

The poly dispersity index (PDI), which is a direct measure of size distribution of the voids, is calculated as

$$PDI = \frac{\overline{D_w}}{\overline{D_n}} \quad\text{...(5)}$$

The volume fraction of void (V_D) may be calculated as:

$$V_D = \frac{\pi}{4}\left(\frac{\sum N_i D_i^2}{A_T}\right) \quad\text{...(6)}$$

where A_T is the area of micrographs under analysis. Equation (6) assumes that the volume fraction is an isotropic property; hence values measured in the micrograph plane are the same as those in the real volume.

4.3   Results and discussion

4.3.1 Properties of PF modified by UP with different MA/PA ratios

i)   Mechanical

Fig. 4.1 shows the variation of tensile strength of UP modified PF. In all the cases tensile strength increases with increase in the UP content. About 30% improvement in the tensile strength is shown by the modified resins. It shows a maximum at ~ 7.5% of UP. The tensile strength is maximum for UP2 modified phenolic. UP with higher PA content exhibits lower tensile strength compared to other UPs. The improvement in the tensile strength by the UP2 may be attributed to the decrease in the void content. The decrease in the tensile strength with the decrease in the MA content may be due to reduction in the reaction involving the double bond of the MA unit and quinone methide structure of the phenolic resol resin.

Fig. 4.2 indicates the variation of the % elongation of the modified samples which shows a general increasing tendency on addition of UP. ~70% improvement in the elongation is shown by the sample RUP2. Unlike tensile strength, an appreciable difference in the % elongation is exhibited on changing the MA/PA ratio in the modifier UP. Polyester chains distributed in the phenolic matrix can at least partially be in a coiled or entangled form.
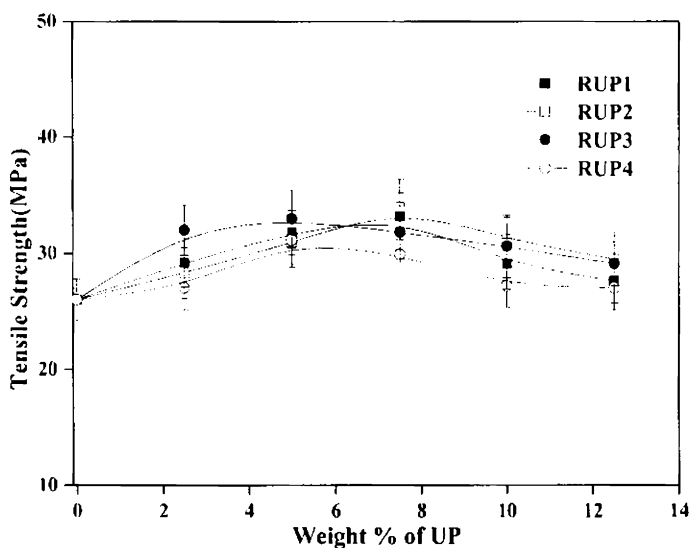

Fig. 4.1 Variation of tensile strength with UP content for modified resins
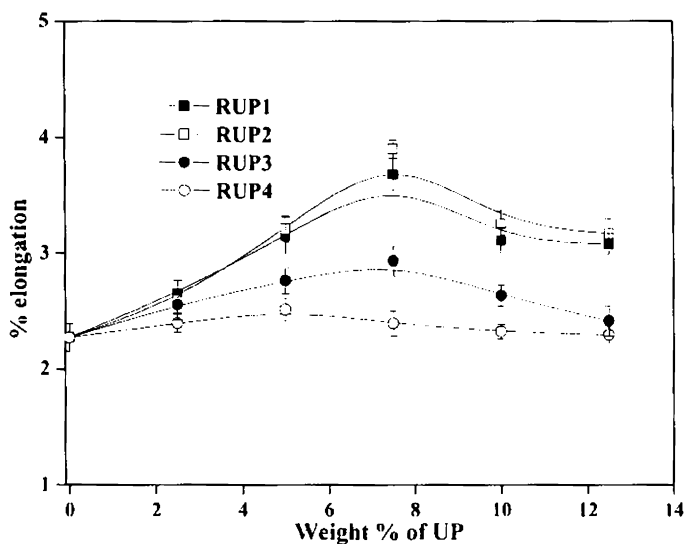
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Fig. 4.2 Variation of % elongation with UP content for modified resins

Even when chemical interaction takes place between the resol resin and UP, the segments of the polyester may still undergo stretching under loading. As the MA content goes up there is a steady increase in the elongation at break. This may be due to a greater elongation of the chains under tensile loads when more and more sites of unsaturation are present. But as the UP content goes further up possibilities arise for increased crosslinking between MA group and/or reaction between the quinone methide structure of resols. This may be the reason for the flattening of the curves at higher % of UP. The % elongation decreases with increase in the PA content in the UP. Both UP1 and UP2 show an identical pattern in increase in the % elongation. The higher % elongation of modified PF resin with UP1 and UP2 may be due to a greater flexibility of the MA part in these UPs.

Fig. 4.3 represents the effect of % UP on modulus for modified resins with various MA/PA ratios. It can be seen that the modulus of the modified resins slightly increases with increase in PA content. Since the MA part is more flexible than the PA part, the modulus values also change according to their relative ratios.

114
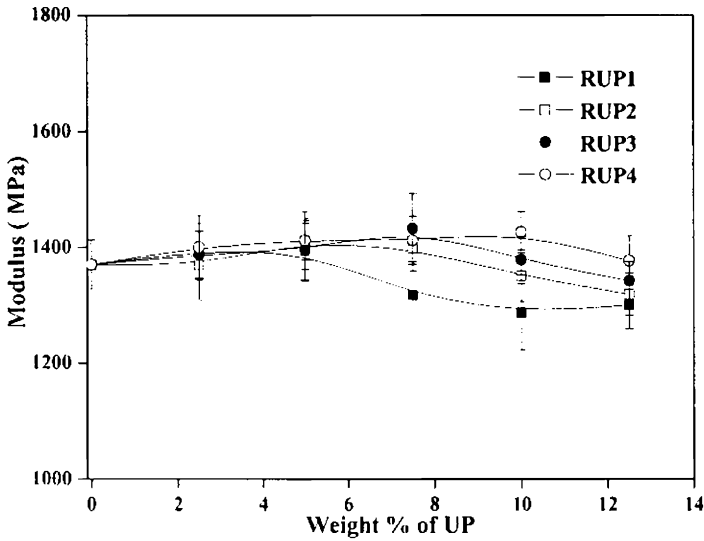
Fig. 4.3 Variation of tensile modulus with UP content for modified resins

Fig. 4.4 depicts the variation of the energy absorbed during tensile fracture for modified resins. It can be seen that energy absorption has increased in all cases, but it is the least for the modified sample containing the highest amount of PA in UP. An appreciable increase in the energy absorption is exhibited by PF resins modified by UP1 and UP2. About 7.5-10% of UP has shown maximum property in these cases.
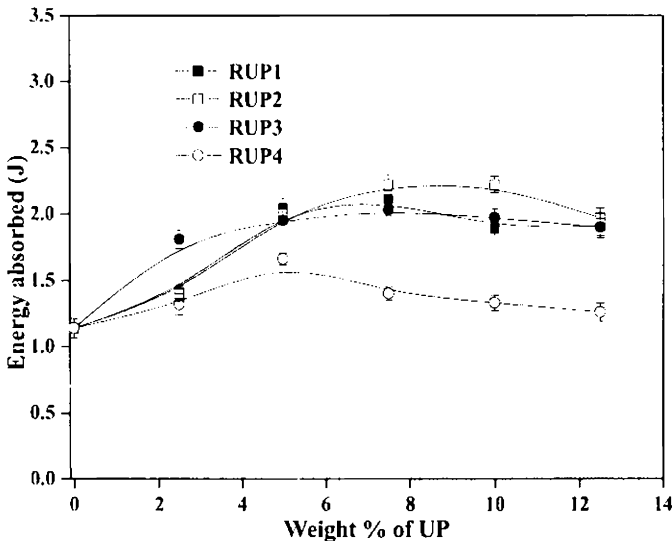
Fig. 4.4 Variation of the energy absorbed during tensile fracture with UP content

115
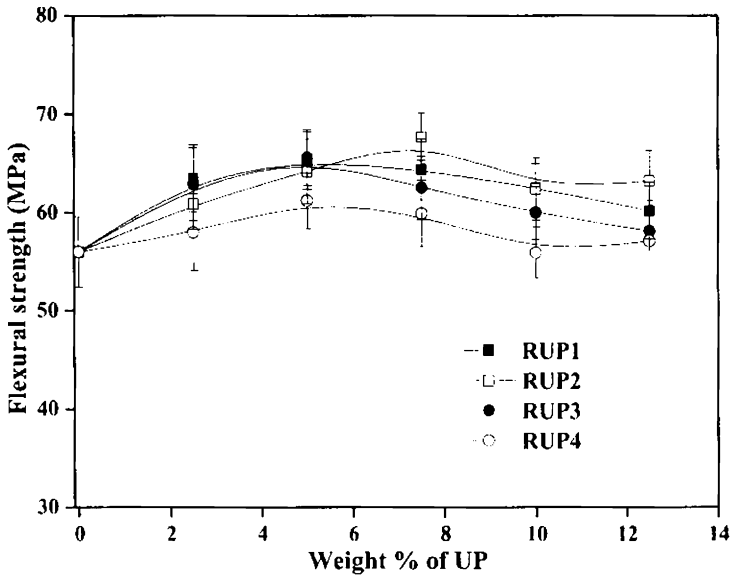
Fig. 4.5 Variation of the flexural strength with UP content for modified resins

The variation of flexural strength of UP modified resin is shown in Fig. 4.5. All the modified resins show an increase in the flexural strength. In general resins with higher MA content show marginally better flexural strength.
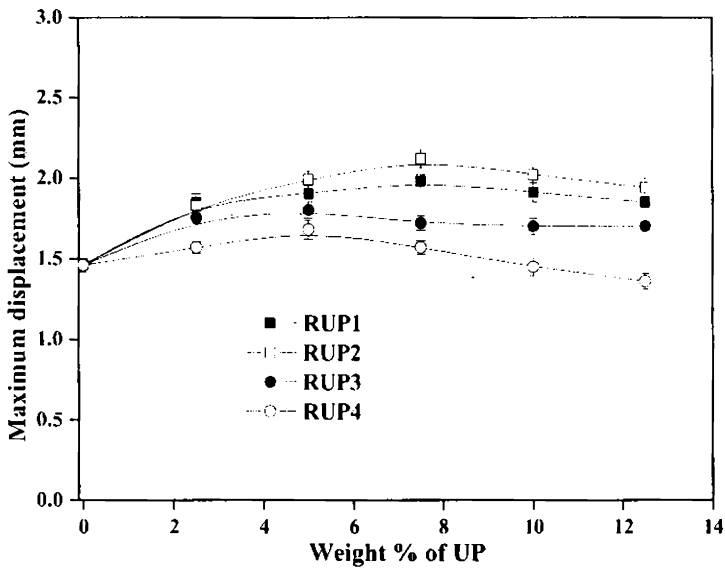
Fig. 4.6 Variation of the maximum displacement with UP content

Maximum displacement in the flexural mode of deformation increases gradually as the UP content increases up to 5-7.5% as shown in Fig. 4.6. Above 7.5% the values are almost constant. The increase in the displacement value indicates that PF resin gets flexibility on modification with UP. But the enhancement is only marginal when the PA content in the UP is increased.
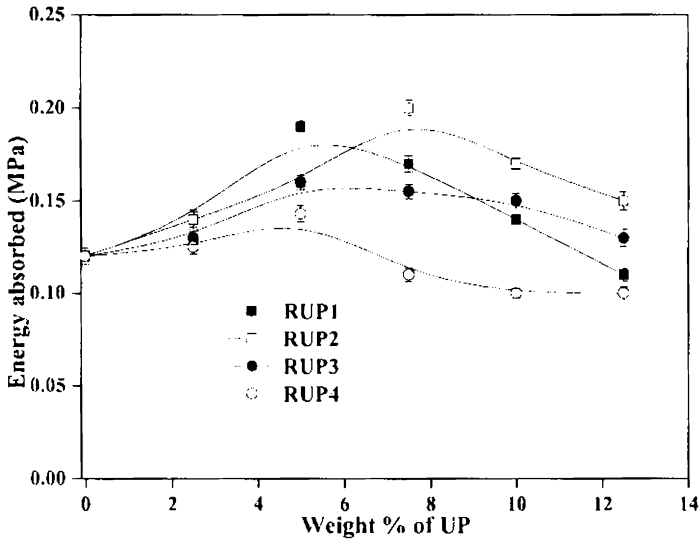

Fig. 4.7 Variation of the energy absorbed during flexural fracture with UP content

Variation of the energy absorbed during flexural mode of fracture is shown in the Fig. 4.7. Here also the use of 5-7.5% of UP leads to maximum energy absorption. Maximum energy absorption is shown by the PF resin modified with UP2. All the samples show the same trend. The energy absorption gradually increases on addition of UP and at higher weight ratios of UP it shows a decreasing tendency.

Fig. 4.8 depicts the variation of the flexural modulus with the amount of UP for modified resins. The modulus values remain almost constant for all the samples.
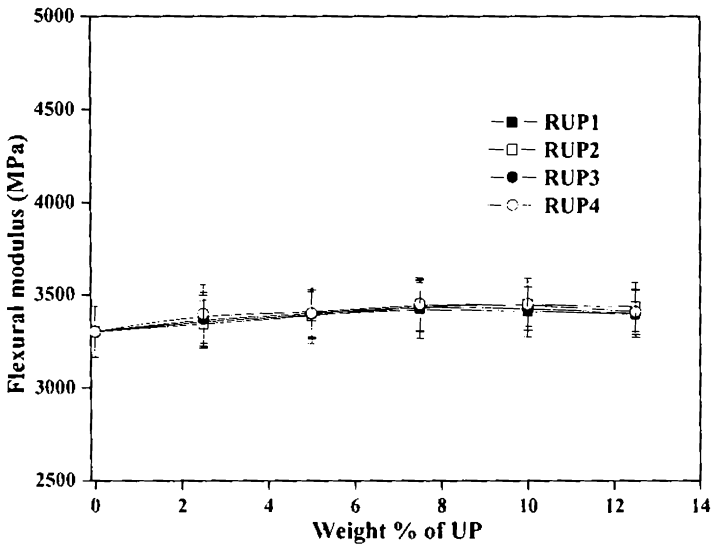
Fig. 4.8 Variation of the flexural modulus with UP content for different modified resins

Impact strength of PF resin improves tremendously on modification as shown in Fig. 4.9. All the samples show identical pattern of variation of impact strength. In all modified samples the impact strength shows a maximum at 7.5% of UP immaterial of the MA/PA ratio. The flexibility imparted to the PF resin on modification and also the reduction in the microvoids may be the possible reason for the improvement in the brittleness of the PF resin.
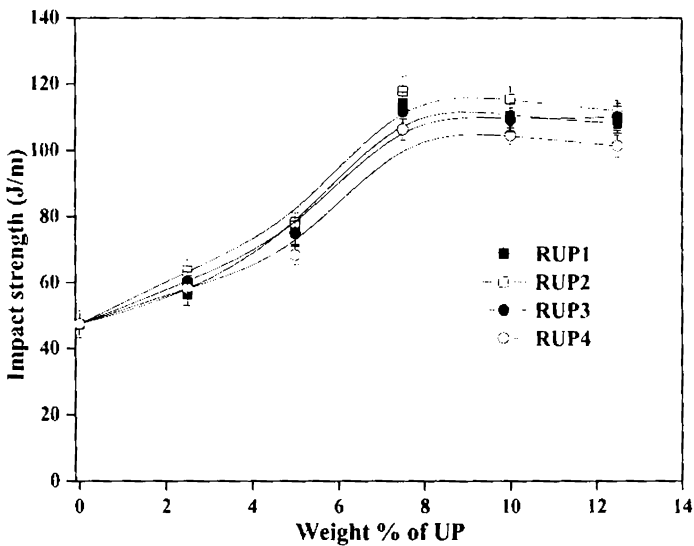
Fig. 4.9 Effect of UP content on impact strength for modified resins
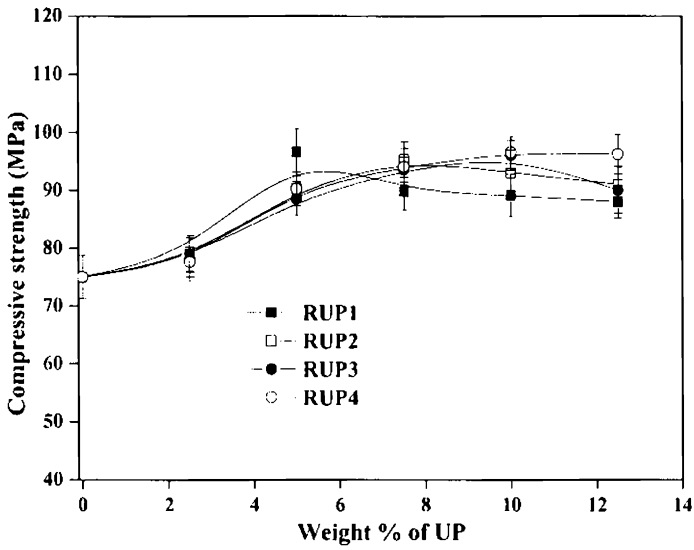
Fig. 4.10 Variation of the compressive strength with UP content

The variation of the compressive strength with UP content is shown in the Fig. 4.10. The compressive strength of the PF samples improves on blending with UP. But contrary to the pattern in other properties compressive strength is seen to be maximum for the sample modified by UP4. A similar trend was also noticed in tensile modulus values. A higher proportion of PA in UP can be expected to impart rigidity. This is borne out by the increase in the compressive strength at higher PA ratios.
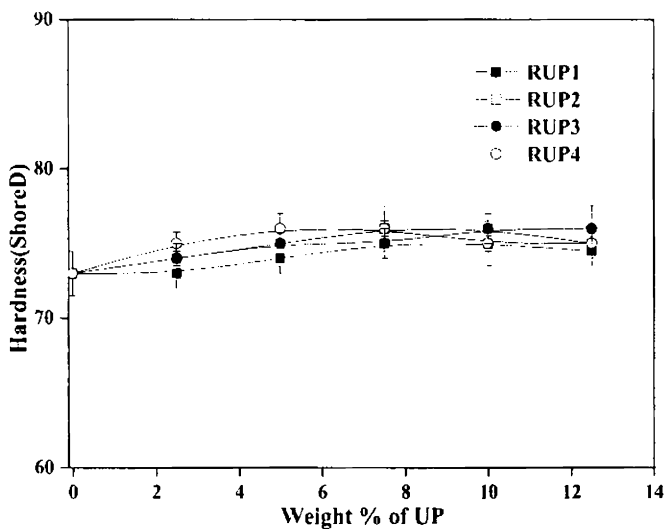
Fig. 4.11 Variation of the hardness with UP content for modified resins

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The variation of surface hardness for modified resins is depicted in Fig. 4.11. The hardness of the samples increases nominally with increase in the amount of UP in the resin. The higher hardness of the modified samples with UP3 and UP4 may be due the rigidity imparted by the PA part in the UP.
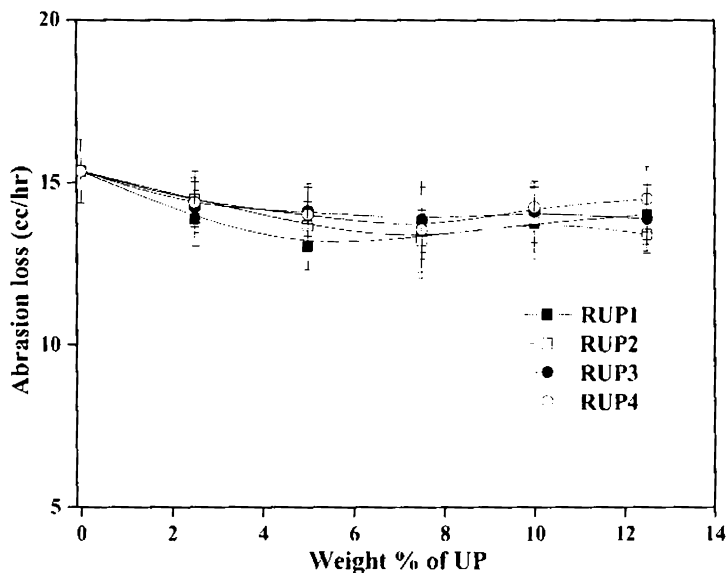
Fig. 4.12 Variation of abrasion loss with UP content for modified resins

A general decrease in the abrasion loss can be seen with incorporation of UP to PF resin (Fig. 4.12). The reduction in abrasion loss is only moderate. But sample UP2 is found to be superior in this respect. The abrasion loss increases above 7.5 weight % of UP in the PF resin. The decrease in the microvoids may be the prime reason for the reduction in the abrasion loss.

ii)   Other properties

Fig. 4.13 shows the variation of specific gravity of cured resol resins modified by UP with different MA/PA ratios. For all MA/PA ratios the specific gravity of the cured resin is seen to increase with increase in the UP content.

The increase in the specific gravity values indicates that the microvoids gradually disappear as the UP content in the phenolic resin increases. The flattening towards the higher concentrations of UP content indicates that practically

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all microvoids have been eliminated at this stage. The curves also show that a higher amount of MA in UP has only a marginal influence on the specific gravity of the cured sample.
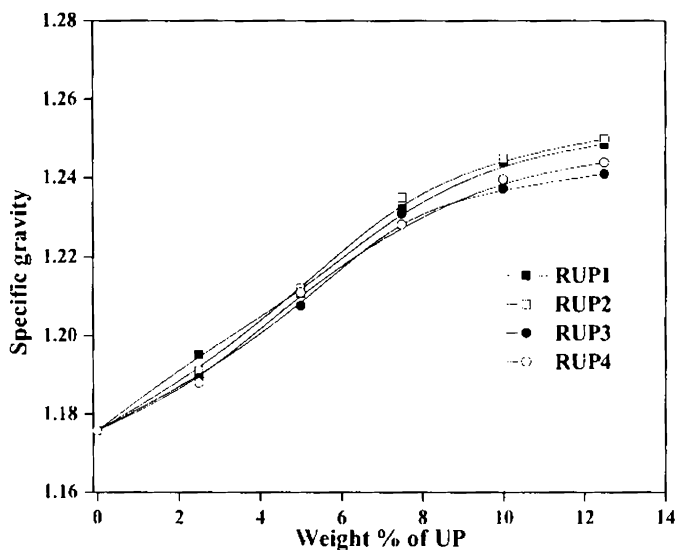
Fig. 4.13 Variation of specific gravity with UP content for modified resins

The amount of soluble matter present in the various cured resins on Soxhlet extraction using acetone is shown in Fig. 4.14. The amount of acetone soluble matter drastically decreases with the addition of UP, irrespective of the MA/PA ratio. Even a small amount of UP (~2.5%) reduces the soluble matter in the cured resin by as much as 30%. The decrease in the acetone soluble content points to the fact that monomers or oligomers are present to a lesser extent in the modified resin. The added UP has apparently been incorporated, chemically, into the phenolic resin. Moreover, condensation by-products like water are present to a lesser extent in the modified resin.

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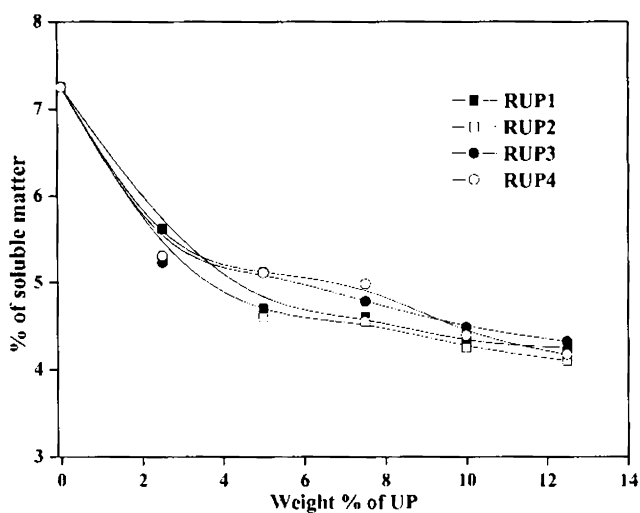
Fig. 4.14 Variation of soluble matter content with UP content for modified resins

A similar trend is also noticed in the TGA results. For this, all the modified cured samples with 7.5% of UP were kept at 100°C for 30 minutes. The variation of weight loss during isothermal TGA programme is shown in Fig. 4.15. The thermogram clearly indicates that the amount of condensation by-products is highest in the neat cured phenolic resin. There is also a significant decrease in the weight loss for modified resins containing higher amounts of MA in the modifier UP. These results also support the Soxhlet extraction data.
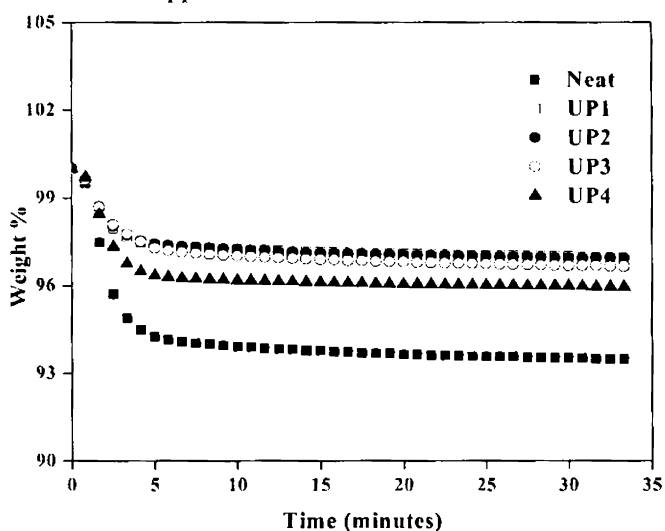
Fig. 4.15 Isothermal TGA curve of cured resol modified with UP of varying MA/PA ratio

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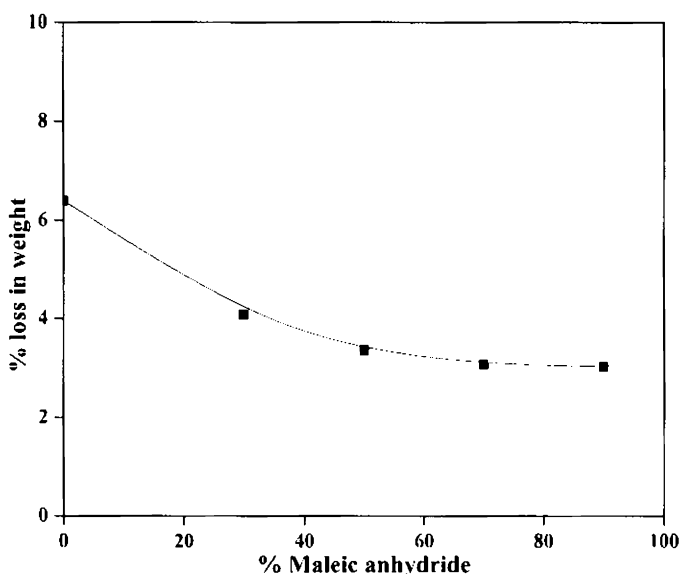
Fig. 4.16 Variation of weight loss during isothermal TGA as a function of % MA in the UP

Fig.4.16 represents the loss in weight as a function of MA content for a constant UP content of 7.5% after isothermal study. The weight loss is less for samples with high MA content; but beyond 70% MA, the variation of weight loss is not substantial. An MA/PA ratio of 70/30 appears to be optimal. On the basis of this finding and also the results from the mechanical property evaluation, all samples for subsequent studies were made using a UP of MA/PA ratio = 70/30 (UP2).

4.3.1.1 Properties of modified PF using UP2 with varying acid values

The dependence of modified resol properties on acid value was investigated by employing UP of varying acid values. These are UP2-93 (UP2a), UP2-70 (UP2b), UP2-60 (UP2c) and UP2-50 (UP2d), the number after hyphen denoting the acid value of the particular UP under consideration. The corresponding modified resol resins are RUP2a, RUP2b, RUP2c and RUP2d respectively.

i)   Other properties

Fig. 4.17 represents the variation of specific gravity of the modified resol resin with the amount of UP2, each curve representing a different acid value. As in

the previous study, there is a clear dependence on the amount of UP ʼ assuming a sigmoid shape. From the curves in Fig. 4.17, the lc gravities are exhibited by samples RUP2a and RUP2, corresponding of 93 and 26 respectively. Intermediate acid values are seen to 1 specific gravity for the modified resin.
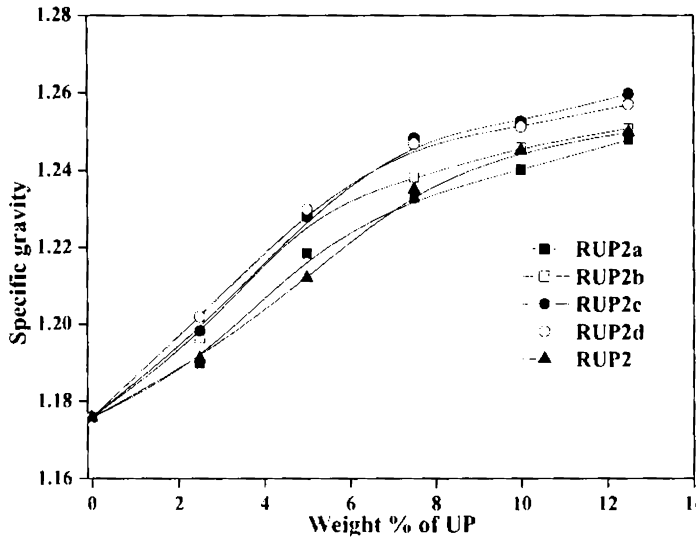
Fig. 4.17 Variation of specific gravity for UP2 modified re
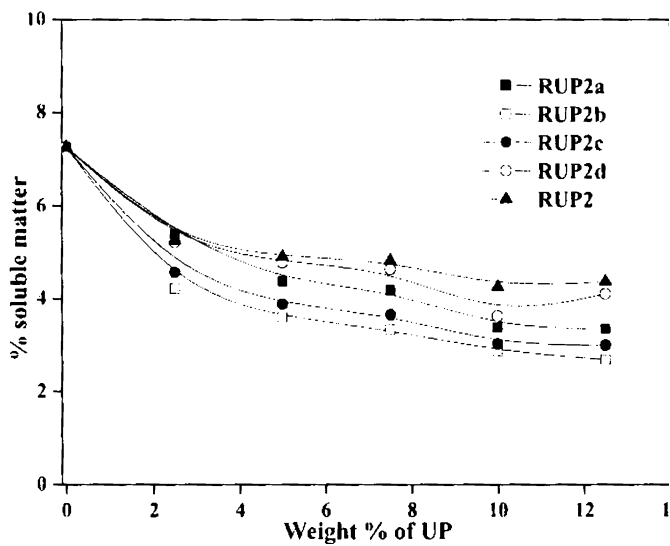
Fig. 4.18 Variation of soluble matter for UP2 modified re:

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The variation of soluble content on Soxhlet extraction is shown in Fig.4.18. The amount of soluble content decreases initially with increase in the UP content, irrespective of the acid value of the UP. The soluble content is minimal for cured resin modified with UP of intermediate acid value i.e. RUP2b and RUP2c. This supports the observation from specific gravity measurements.
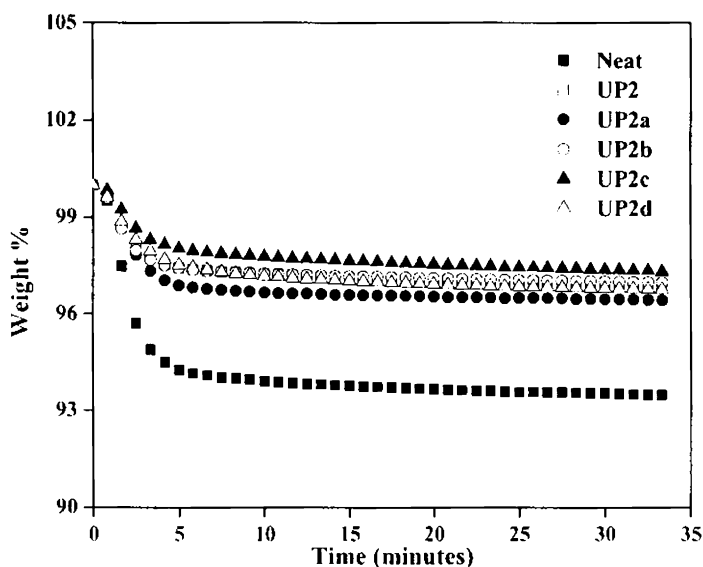
Fig. 4.19 Isothermal TGA curve of cured UP2 modified resols

The isothermal TGA analysis of cured resol resin with 7.5% of UP2 having different acid values is given in Fig. 4.19. A plot of % loss in weight against acid value is shown in Fig. 4.20. The dependence of weight loss during isothermal TGA on the acid value is evident. For higher and lower acid values of UP2, the amount of volatiles are higher compared to the intermediate acid values. This is consistent with the observations in Fig. 4.17. Thus UP of intermediate acid value is more efficient in controlling water and other volatile by-products during the curing of resol phenolic resin.

Fig. 4.21 represents the isothermal TGA of modified PF resin containing different amounts of UP2c which gave the best overall results. The neat resin contains a higher amount of volatiles (presumably moisture) compared with the modified resins. The addition of UP has a dramatic effect.
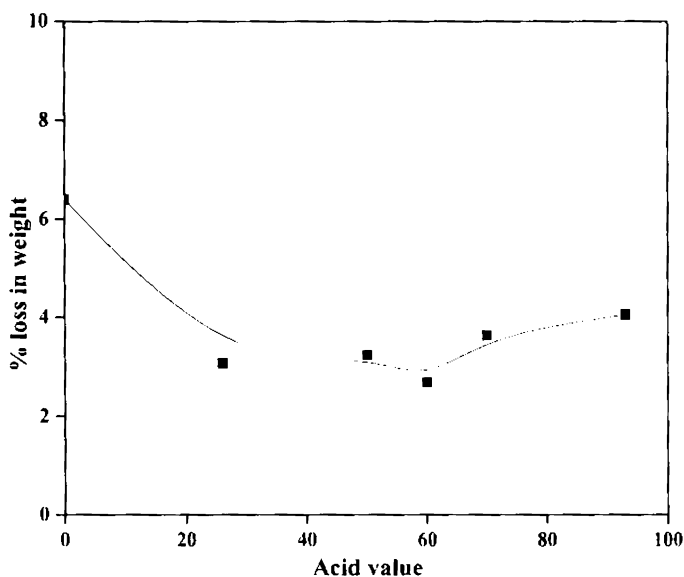
Fig. 4.20 Variation of loss in weight on iso-thermal TGA with acid value of UP2 modified phenolic resin

The thermograms of cured phenolic resin containing 7.5% UP2c and above are almost identical. This indicates that 7.5% of UP is sufficient for modifying the phenolic resin.
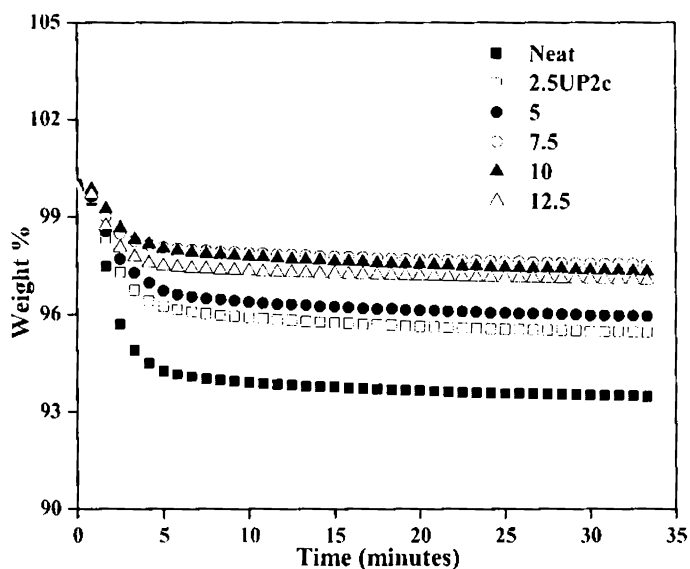
Fig. 4.21 Isothermal TGA curve of modified phenolic resin with varying amount of UP2c

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The loss in weight during the above isothermal TGA is illustrated in Fig. 4.22. The reduction in the weight loss is seen to level off at 7.5% of UP2c.
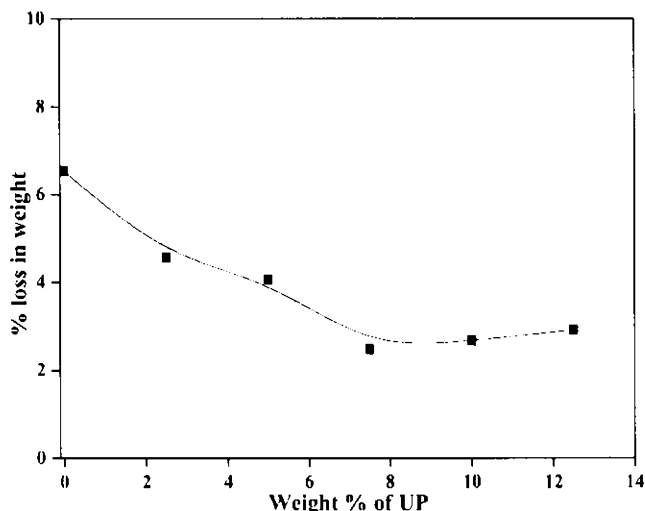
Fig. 4.22 Variation of weight loss during isothermal TGA of cured resin containing varying amount of UP2c

ii) Mechanical properties

Fig. 4.23 represents the variation of tensile strength of modified resin with acid value of UP2. Tensile strength of all the samples is higher than that of the neat resin. The extent of improvement of tensile strength varies only in a narrow range for various modifications. RUP2c shows the maximum tensile strength.
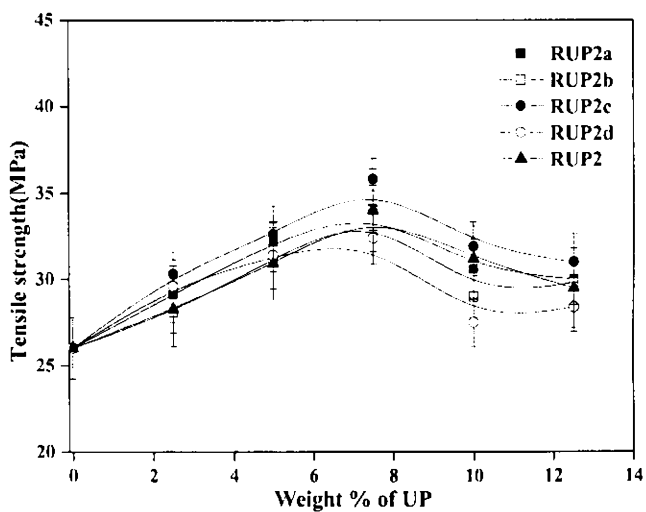
Fig. 4.23 Variation of tensile strength with UP2 content

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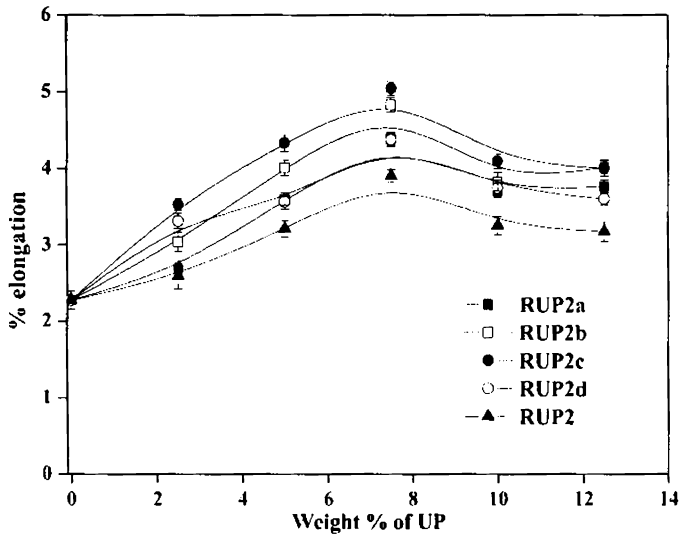
Fig. 4.24 Variation of % elongation for modified resols with UP2 content

The effect of acid value of UP2 on % elongation is depicted in Fig. 4.24. A considerable variation of the % elongation is noticed on changing the acid value of UP2. Maximum increase in the % elongation is shown by the sample modified by UP2c. The trend shows that UP2 with intermediate acid values exhibit higher elongation compare to UPs with high and low acid values. Several factors like reduction in the microvoids and plasticizing effect might have contributed to the increase in the % elongation.
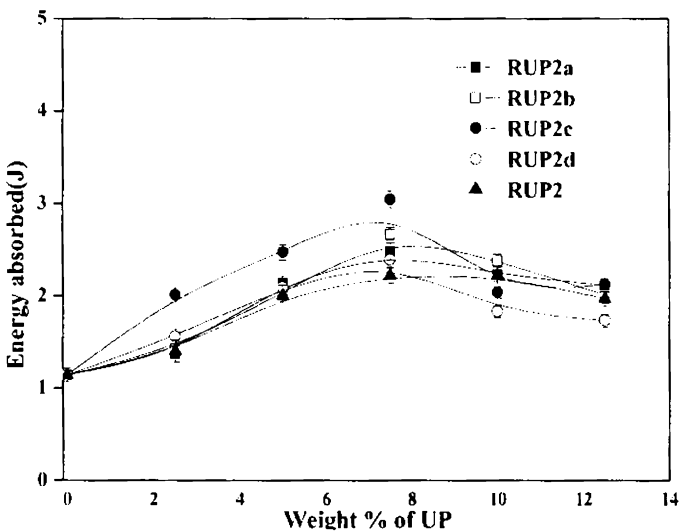
Fig. 4.25 Variation of the energy at break on tensile mode of fracture with UP2 content

A similar variation of the energy absorption is also noticed on (Fig. 4.25). This is a good indication of improved toughness of the PF resin on UP modification. Here also the maximum energy absorption is shown by the modifier UP2c with addition of 7.5 weight %. Further addition of UP causes a small decrease in the energy absorption.

Figs. 4.26 and 4.27 represent the variation of flexural strength and impact strength respectively with acid value of UP2. The sample modified with UP2c shows the highest value of flexural strength and impact strength. The impact strength of RUP2c is approximately 3 times that of the neat resin. Higher % of UP does not reduce the void formation further. At this stage the amount of water present in the system is almost negligible.
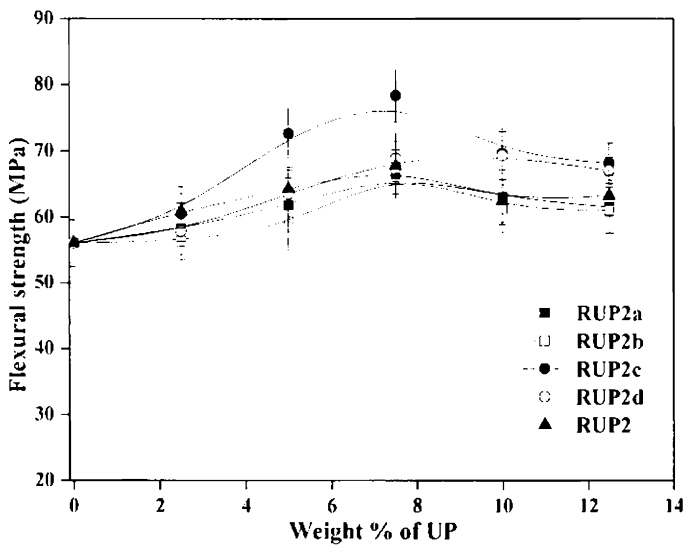
Fig. 4.26 Variation of flexural strength with UP2 content for modified resols
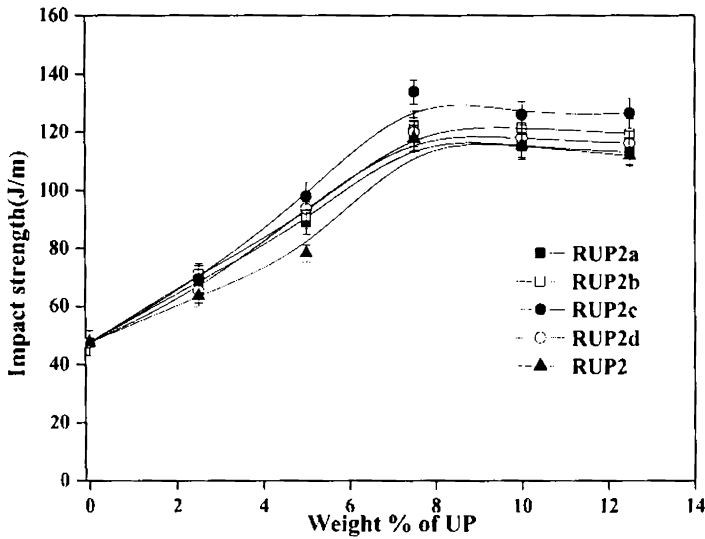
Fig. 4.27 Variation of impact strength for modified resols with acid value of UP2

Other mechanical properties of the modified PF resin on addition of 7.5% of modifiers are shown in Table 4.3. In general the graphs follow the pattern observed in the earlier section and hence are not reproduced here. All the properties have been considerably altered by UP modification.

Table 4.3 Mechanical Properties of phenolic resin modified with 7.5 weight % of UP2

Properties	Neat	RUP2a	RUP2b	RUP2c	RUP2d	RUP2
			Samples			
Tensile modulus (MPa)	1370±43	1309±39	1253±37	1138±42	1224±29	1398±39
Maximum Disp. (mm)	1.46±0.005	2.2±0.076	2.68±0.079	3.07±.076	2.59±0.079	2.12±0.06
Flexural energy (J)	0.12±0.005	0.23±0.007	0.25±0.08	0.29±0.006	0.26±0.008	0.2±0.005
Comp. strength (MPa)	75±4.8	96±4.5	103±4.3	105±4.2	99±3.95	95.3±3.1
Hardness (Shore D)	73±1.5	77±1.0	76±1.0	76.5±1.5	77±0.75	76±0.5
Abrasion loss (cc/hr)	15.3±0.98	13.8±1.0	14.18±0.92	13.94±1.0	13.69±0.82	13.2±0.95

4.3.2 Chemical interaction -theoretical possibilities

The following physical and chemical consequences are noticeable on modification.

1. UP resin is chemically incorporated into the phenolic network structure. This is very clearly established by the Soxhlet extraction studies.

2. The incorporation of the UP imparts flexibility to the cured phenolic resin as evidenced by mechanical property evaluation.

3. The modification of phenolic resin by UP reduces the formation and/or trapping of the condensation products as indicated by the isothermal TGA and specific gravity studies.

The role played by UP in modifying the phenolic resol resin at the structural level is somewhat complex. The actual constitution of the crosslinked structure calls for more investigations. The intractable nature of the cured resin makes it difficult to resolve the chemistry of the cured structure. However, a number of possibilities exist for chemical interaction between the phenolic matrix and the modifying UP resin. The actual scenario may involve one (or a combination) of the following possibilities.

1. The chemical anchoring of the UP to phenolic resol resin is possible through the quinone methide structure of phenolic resin. The double bonds present in the UP combine with the quinone methide moiety of phenolic resol resin to form a cyclic ether-like structure. The FTIR spectra (in the region of interest) of the neat resin and resin modified with 7.5% of UP2c are shown in Figs.4.28 and 4.29. The broadening at $\sim 1230 cm^{-1}$ and the appearance of a shoulder peak at $\sim 1050\ cm^{-1}$ are indications of the formation of cyclic ether linkages. The merging of peaks at $\sim 1610 cm^{-1}$ and $1550 cm^{-1}$ and decrease in the intensity of the peak at $\sim 1507 cm^{-1}$ due to the aromatic -C=C- bond stretching might have resulted from structural changes in the aromatic ring. 'Diels Alder'

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type addition of –C=C– into the o-quinone structure of phenolic resin during the cure process (Scheme1) may be responsible for this. The small peak at ~920cm^{-1} due to the ring deformation of phenolic ring becomes broad in the modified resin. This also indicates that the phenolic ring has undergone some structural changes.
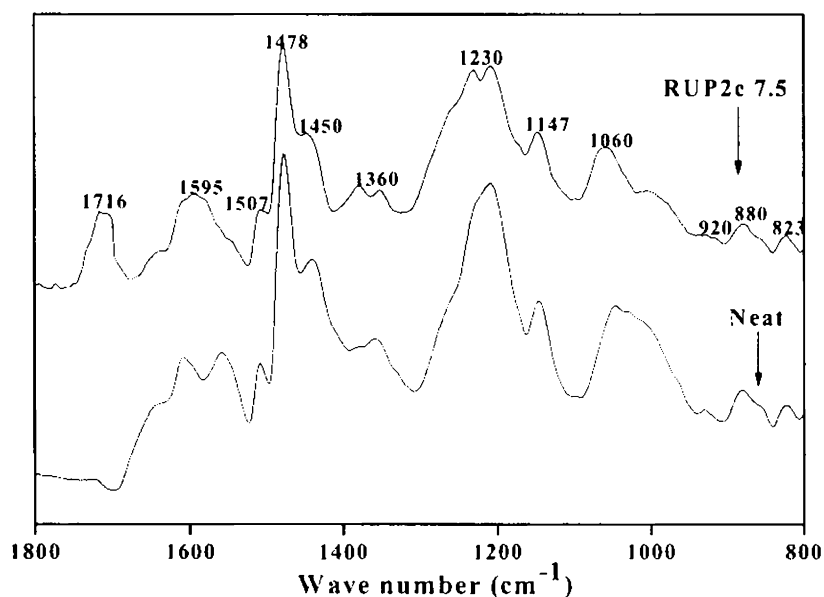
Fig. 4.28 FTIR spectra in the region 1800-800 cm^{-1}
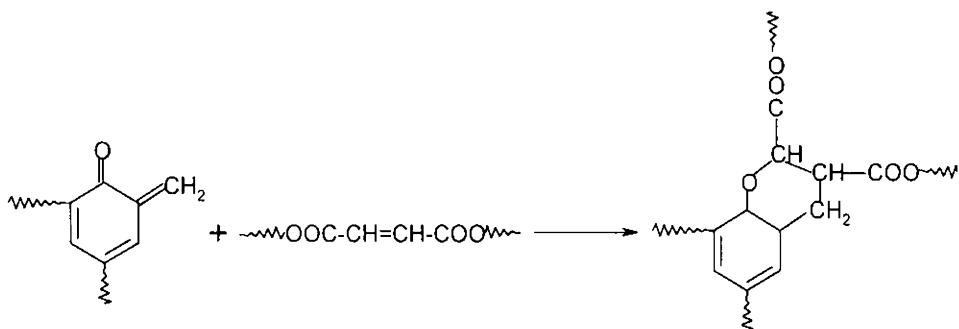
Scheme 1. Formation of cyclic ether linkages in the cured resin.

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The peak at ~1716 cm^{-1} is due the C=O stretching frequency in the ester linkage. This indicates that the UP is chemically incorporated into the phenolic resin. The reduction in the intensity of -OH stretching frequency at ~3300cm^{-1} (Fig. 4.29) with the addition of UP suggests an appreciable reduction in the water content of the cured resol resin.
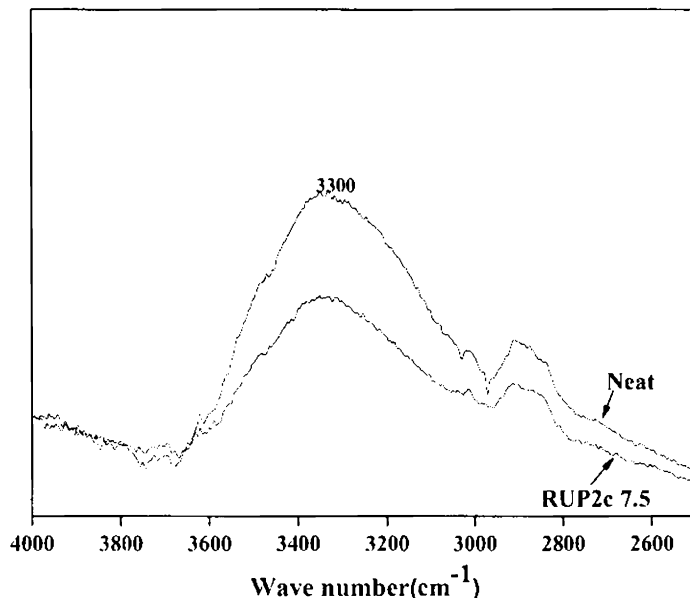
Fig. 4.29 FTIR spectra region 4000-2600 cm^{-1}

2. The –COOH end groups of the UP can combine with methylol groups of phenolic prepolymers to form ester linkages (Scheme 2). The formation of ester linkages by the reaction of UP with the resol resin prevents the generation of dimethylene ether linkages (-CH$_2$-O-CH$_2$-). This may further reduce the number of methylene bridges and the liberation of formaldehyde.
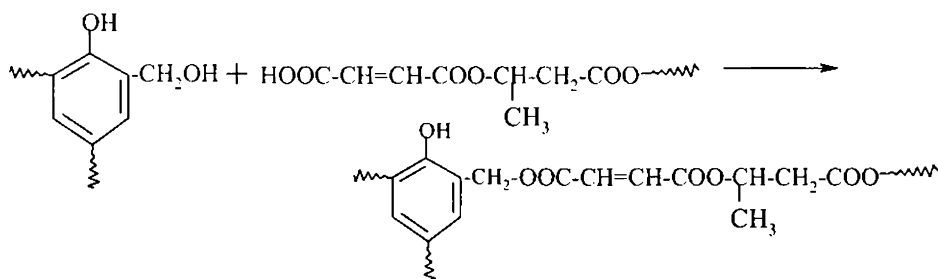
Scheme 2. Formation of ester linkages in the cured resin

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3. There is the possibility of the molecules of water of condensation hydrolyzing the ester linkages in UP under the curing conditions. This may lead to splitting of the ester groups and formation of still lower chain lengths. UPs with high acid value will have shorter chain lengths and a higher number of acid end groups. The total number of ester groups in the UP decreases with increase in the acid value. The decrease in the number of ester linkages and the resultant shorter chain lengths may cause less than complete utilization of the water of condensation and the trapping of the same inside the cured resin. The low acid value UP contains longer chain lengths and a higher number of ester groups which may cause excessive hydrolysis. This may, in turn, lead to recombination of the products and formation of water. But this may happen only to a limited extent under the existing conditions. For the intermediate acid values (when this effect is maximum), the UP may be of a "critical chain length" that satisfies the conditions conducive to the formation of a minimum number of voids.

The modifying action may also result from a wholly physical reason. The UP chains may have a plasticizing effect on the phenolic resin leading to a fall in viscosity of the system. This might make the physical escape of volatile matter from the resin easier. On top of the chemical interaction this can give a greater modifying action.

4.3.3 Morphological studies

The SEM micrographs of the tensile fracture surfaces of the neat and UP2 modified samples are shown in Fig. 4.30. The size characterisation of the voids ($\overline{D_n}$, $\overline{D_w}$, $\overline{D_a}$ and $\overline{D_v}$) and PDI values in the modified samples are presented in Table 4.4.

(a)

(b)

(c)

(d)

(e)
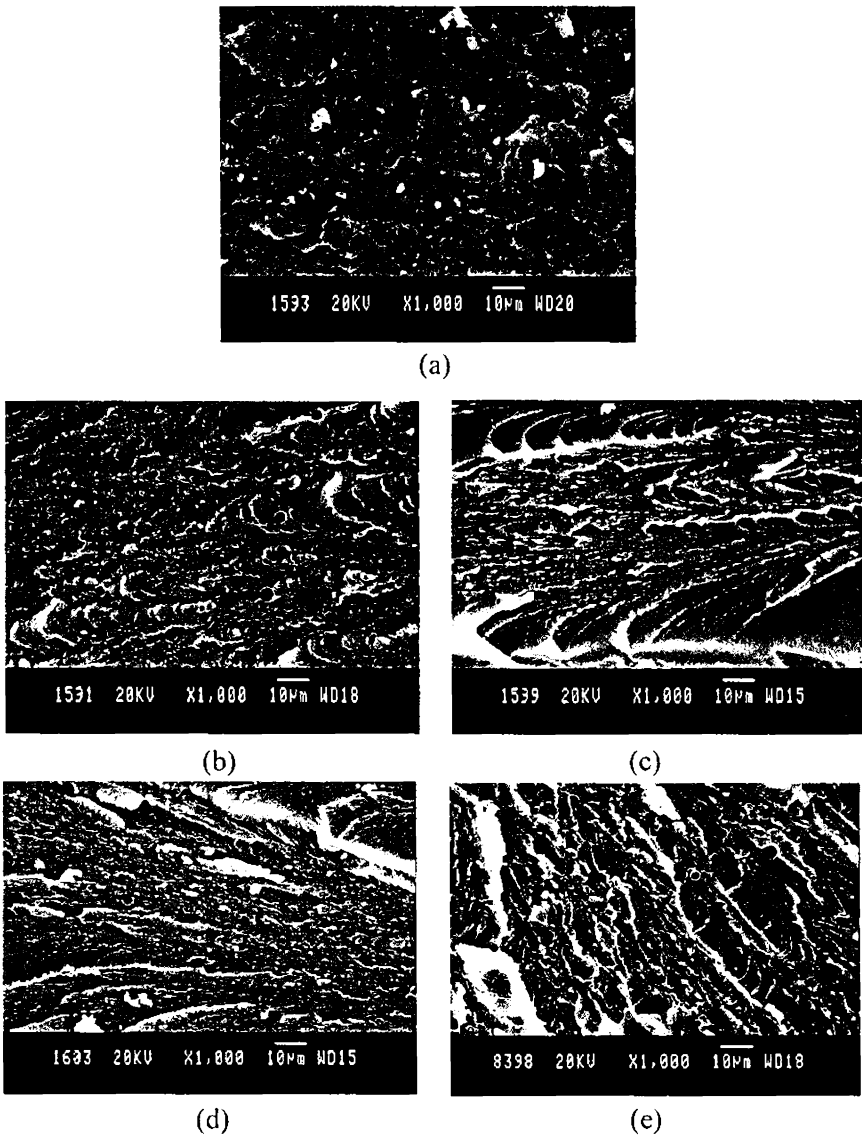
Fig. 4.30 SEM micrographs of modified phenolics with 7.5% UP2
(a) RUP2a **(b)** RUP2b **(c)** RUP2c **(d)** RUP2d and **(e)** RUP2

In samples modified with high and low acid value UP resins voids are of ~1 μm size. The size of the voids does not vary largely. The PDI values indicate that the void size is almost uniform. The samples modified with UP2c and UP2d do not contain any voids and show the best properties. The micrographs of the samples RUP2a and RUP2b show a jagged and cratered surface indicating rapid crack propagation. But Figs. 4.30 (c)-(e) contain the least number of voids and

have a different surface morphology. The volume fraction of the voids is also less as the acid value of the UP2 is decreased.

Table 4.4 Size characterisation of voids and its distribution in the samples modified with 7.5% of UP2 having different acid values

Samples	$\overline{D_n}$ (µm)	$\overline{D_w}$ (µm)	$\overline{D_a}$ (µm)	$\overline{D_v}$ (µm)	PDI	V_D
RUP2a	1.04	1.15	1.1	1.14	1.11	0.12
RUP2b	1.01	1.18	1.09	1.21	1.16	0.0028
RUP2c	-	-	-	-	-	-
RUP2d	-	-	-	-	-	-
RUP2	1.02	1.17	1.09	1.16	1.14	0.045

Fig. 4.31 represents the fractographs of RUP2c with varying amounts of UP2c. The size characterisation of the voids and their distribution in the modified samples are presented in Table 4.5.

The neat resin contains microvoids of number average diameter ~ 11.95µm. The weight average, surface area average and volume average void diameters of neat resin are also higher compared to the modified samples. The volume fraction of the voids in the neat resin is approximately 20% of the total volume. But with the addition of 2.5% UP2c the void size is reduced to ~8.43µm ($\overline{D_n}$) and the volume fraction of the voids is also reduced by 25%.

The addition of 5% UP2 further reduces the micro void size to 4.61µm and the volume fraction of the voids is reduced approximately to half of its original value. A further addition of 2.5% of UP2c succeeded in preventing the formation of microvoids completely.
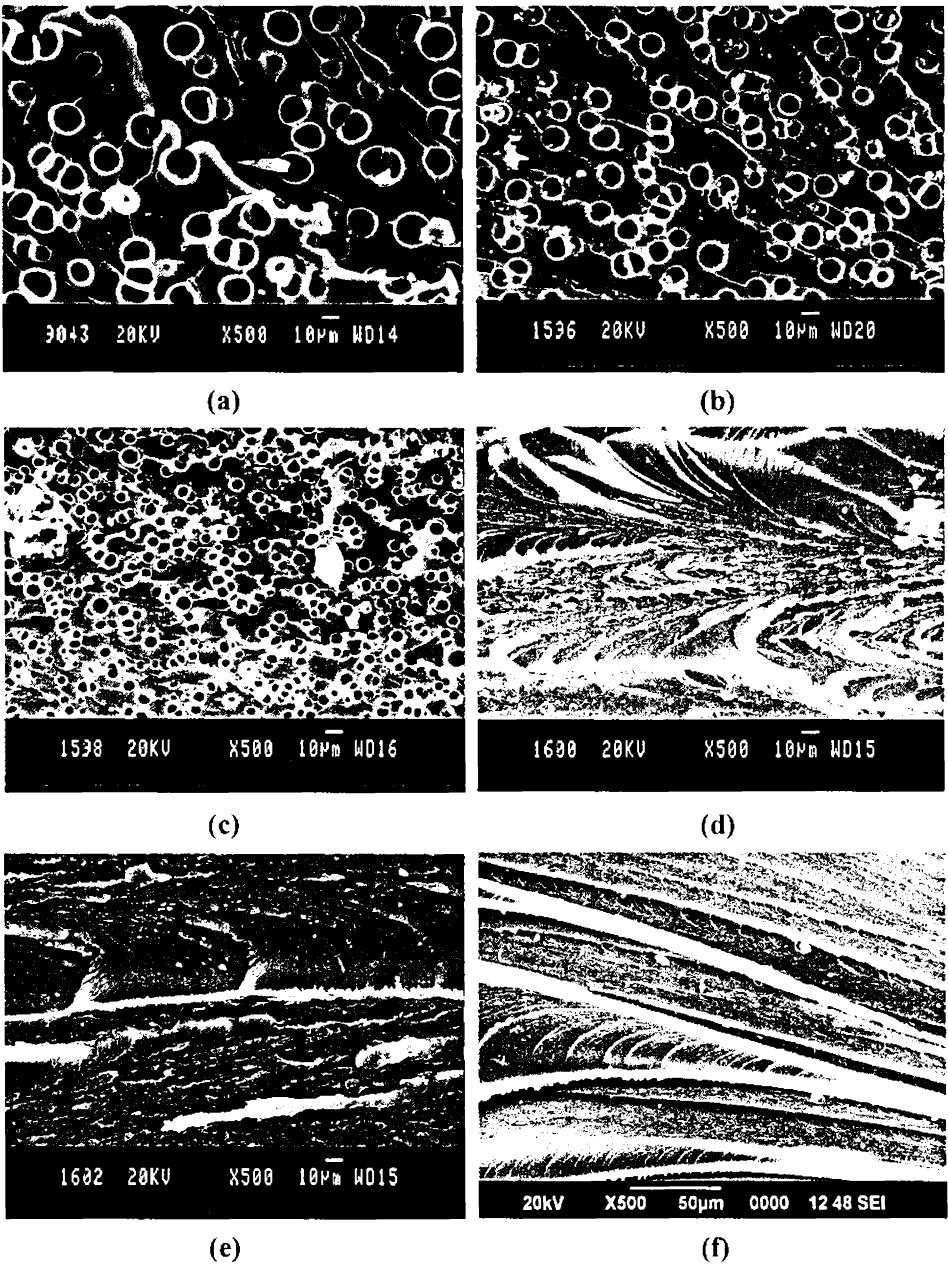
Fig. 4.31 SEM micrographs of modified phenolics with varying amounts of UP2c (a) 2.5% (b) 5.0% (c) 7.5% (d) 10% and (e) 12.5%

The surface morphology of the neat resin shows that failure follows a crazing mechanism as indicated by the crack lines in between microvoids. In the

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modified sample with 7.5% of UP2c, i.e. RUP2c 7.5, the morphology is entirely different. The fracture surface of this sample is rough and ridge patterns could be seen on the fracture surface. The roughness of the fracture surface is due to two reasons. First it is an indication of crack path deflection i.e. the crack deviates from its original plane. There are apparent steps and changes of level of the crack. These appear as feather markings, caused by the crack forking due to the excess of energy associated with the relatively fast crack growth. The multiplanar nature of the surface and repeated forking are ways of absorbing excess energy in a very brittle material during the fast crack propagation phase that follows the crack initiation [13]. Secondly, the roughness indicates the ductile nature of the crack. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure and hence increased toughness. At higher % of UP2, the samples follow the same toughening mechanism as shown in Figs 4.31 (e) and (f).

Table 4.5 Size characterisation of voids and their distribution in RUP2c modified with varying amounts of UP2c

Samples	$\overline{D_n}$ (µm)	$\overline{D_w}$ (µm)	$\overline{D_a}$ (µm)	$\overline{D_v}$ (µm)	PDI	V_D
Neat	11.95	13.16	12.54	13.75	1.11	0.2000
RUP2c2.5	8.43	9.56	8.98	9.44	1.13	0.1536
RUP2c5.0	4.61	4.96	4.78	4.93	1.07	0.1142
RUP2c7.5	-	-	-	-	-	-
RUP2c10	-	-	-	-	-	-
RUP2c12.5	-	-	-	-	-	-

4.3.4 Thermal studies

i)   DMA

Fig. 4.32 shows the variation of storage modulus with temperature of the phenolic resin modified with 7.5% UP2 with varying acid values. The initial storage modulus values are different for the modified samples. RUP2a, RUP2c and RUP2 exhibit slightly higher initial storage moduli than the neat resin whereas

RU2b and RU2d show slightly lower initial storage modulus values. A clear influence of the chain length of UP on the storage modulus of the modified resins can be seen above 100°C. The E' values decreased with increase in chain length or in other words E' decreased with the decrease in the acid value.

Almost all the modified samples possess the same storage modulus at 250°C and it is well below the storage modulus of the neat resin. The slight increase in the storage modulus at high temperature is due to residual curing. But for the neat and modified samples the extent of increase is almost the same. This indicates that the curing of the phenolic resol resin is not affected by the the presence of UP and also the modified samples have undergone the same degree of curing as that of the neat resin.
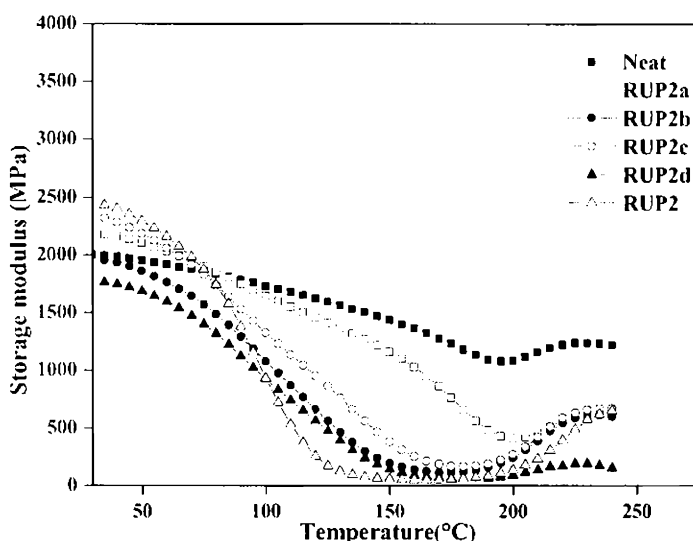
Fig. 4.32 Storage modulus versus temperature

The % retention of storage modulus with temperature is depicted in Fig. 4.33. Retention of modulus is maximum for the neat sample. For modified samples % retention is almost the same and is approximately 30%. A maximum shift in the graph is observed by the sample modified with UP2 of acid value ~26 and it is minimum for the sample modified with UP2 of acid value ~93. The increase in the chain length may be responsible for higher flexibility. Another reason for the

decrease in the modulus value as the chain length increases may be due to the decrease in the crosslink density of the cured resin.
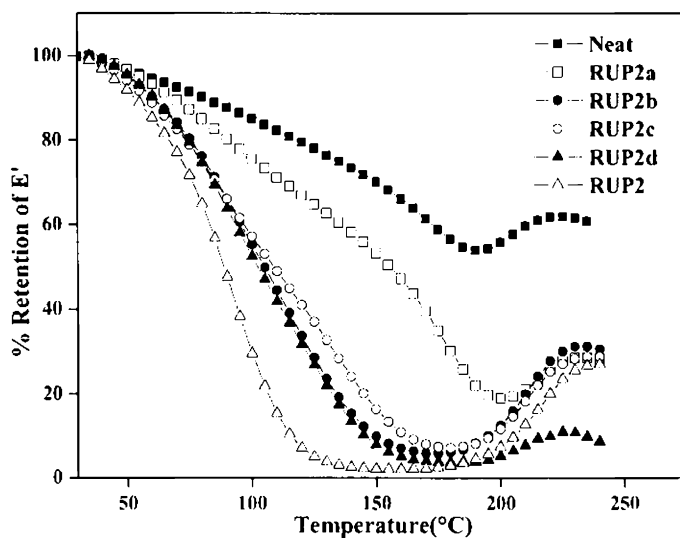
Fig. 4.33 Retention of E' with temperature
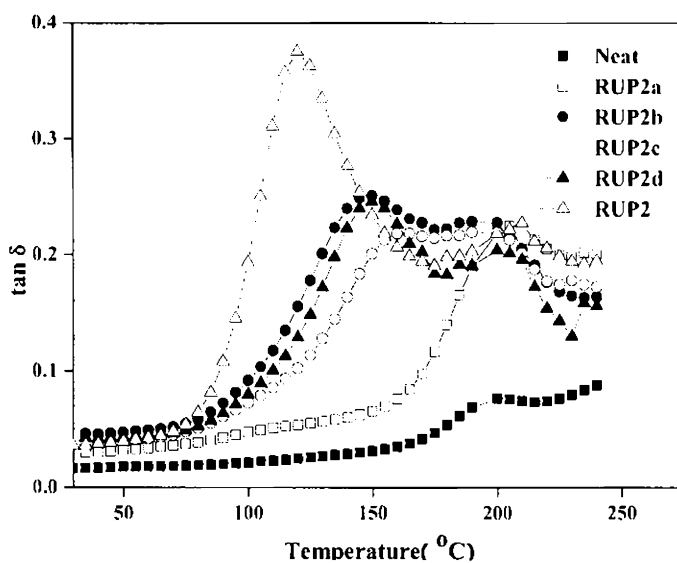
Fig. 4.34 Variation of tanδ with temperature

Fig. 4.34 shows the variation of tan δ with temperature of modified samples with 7.5% of UP2 of varying acid values. For all the modified samples tanδ values are higher than that of the neat sample. This is an indication of the decrease in

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crosslink density [14]. The increase in the tanδ value also suggests that the damping property is higher for the modified samples.

Table 4.6 shows T_g values from storage modulus graphs and the corresponding tanδ values of the neat and modified phenolic resins. The temperature corresponding to the maximum of the tanδ is designated as T_g- tanδ. This is an indication of glass transition temperature. The neat resin and the modified sample RUP2a show only one T_g-tanδ. All the other modified samples possess two peaks. In sample RUP2c the two peaks almost merge into each other.

Table 4.6 T_g and tanδ values of the modified sample

Sample	T_g (°C)	T_g-tanδ (°C)	tanδ
Neat	167.1	201.0	0.078
RUP2a	163.8	205.0	0.225
RUP2b	97.0	147.8	0.251
		191.0	0.220
RUP2c	98.3	161.0	0.219
		195.5	0.222
RUP2d	93.0	149.5	0.246
		199.2	0.202
RUP2	83.4	98.9	0.430
		200.4	0.231

This indicates that the sample consists of one single phase. Moreover, the acid value (chain length) of the UP resin has an important role in modifying the phenolic resin.

Fig. 4.35 shows the variation of the E' values with temperature, of samples modified with 5%, 7.5% and 10% of UP2c. All the samples have slightly different initial E' values. But above 90°C the neat sample has the highest E' and the E' values of the modified samples decrease as the % of the UP2c in the resin increases. But above 180°C the modulus values of the samples follow the same trend.
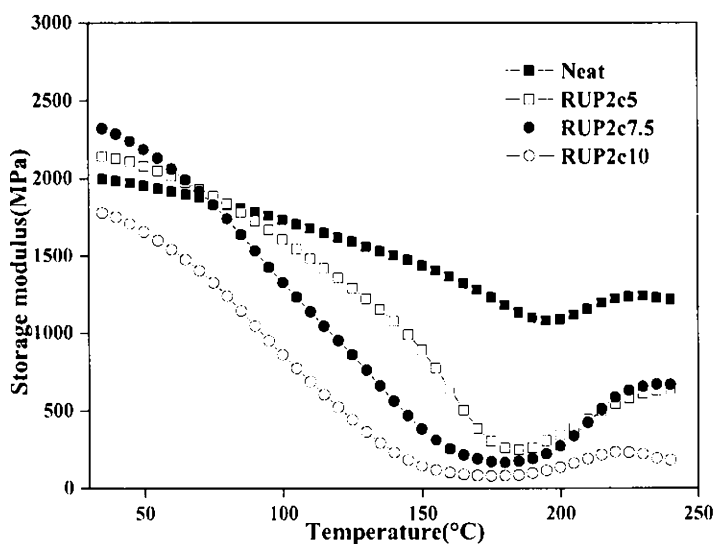
Fig. 4.35 Storage modulus versus temperature
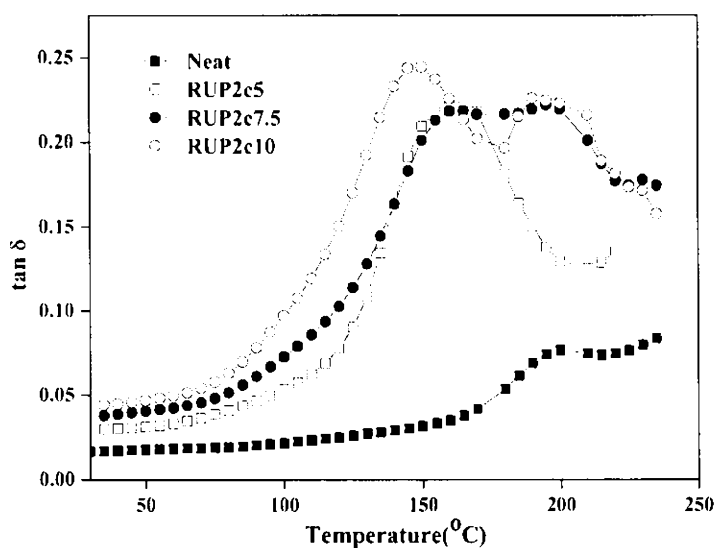
Fig. 4.36 tanδ versus temperature

Variation of tanδ with temperature is shown in the Fig. 4.36. The initial tanδ values increase with increase in the amount of UP2c in the resin. The neat sample showed a peak at ~201°C and the sample modified with 5% UP2c has a peak at ~160°C. This indicates that the modified sample has achieved very good flexibility on modification. The sample modified with 7.5% UP2c has a peak at ~160°C and also at ~201°C with the same tanδ values. But the sample modified with 10% UP2c

possesses two distinct peaks one at ~140°C and the other at 201°C. This may be due to heterogeneity resulting either from a phase separation of the UP at higher concentrations or structural heterogeneity. Phase separation is not likely because no evidence for this can be noticed in SEM pictures presented already (Section 4.3.3). This suggests that at this concentration of UP there is almost complete structural integration of UP into phenolic matrix. Hence an amount of 7.5% UP is enough to modify phenolic resin for better mechanical properties.

ii)   TGA

Fig. 4.37 shows the thermograms of the neat resin and resin modified by 7.5% of the UP2 with varying acid values.

The thermogram shows that for all the modified samples the rate of degradation above 400°C is higher. The important results are given in Table 4.7.
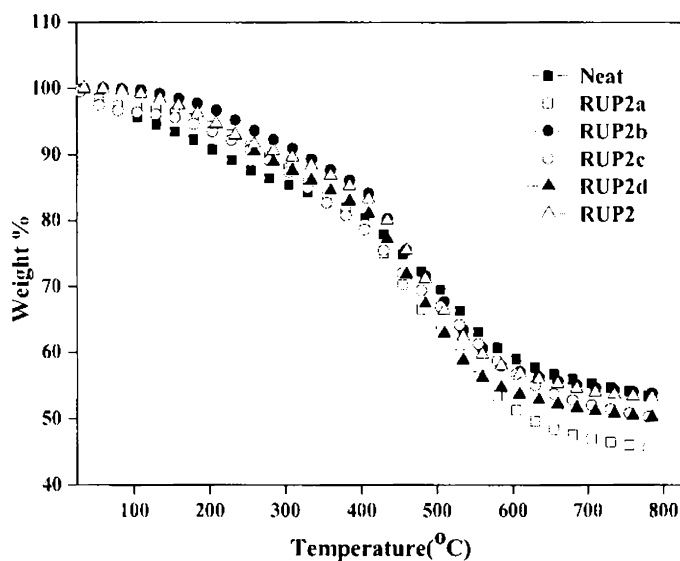
Fig. 4.37 Thermogram of the neat and modified resin

The initial weight loss in the modified samples is comparatively less than that in the neat resin. But above 30% the degradation values indicate that the thermal stability of the sample decreases on modification. The temperature of maximum degradation is also drastically decreased on modification. The poor

thermal stability of the ester linkages is the reason for the marginal decrease in the thermal properties of the modified resol resin. The final residue at 800°C is similar to that for the modified resins.

Table 4.7 Thermal analysis of the neat and samples modified by 7.5% of UP2 with varying acid values.

Sample	Temperature at different stages of decomposition (°C)					Temp. of maxm. degradation (°C)	Residue (%)
	10%	20%	30%	40%	50%		
Neat	218	410	501	589	>800	533	53
RUP2a	275	399	456	528	623	434	45
RUP2b	324	437	495	564	>800	437	53
RUP2c	267	389	474	567	800	432	50
RUP2d	266	419	470	526	800	444	50
RUP2	301	435	491	556	>800	451	53

iii) Thermal degradation kinetics

The kinetics of the thermal degradation reaction was followed using TGA. Fig. 4.38 represents the Coats-Redfern plots for the neat and modified resins.
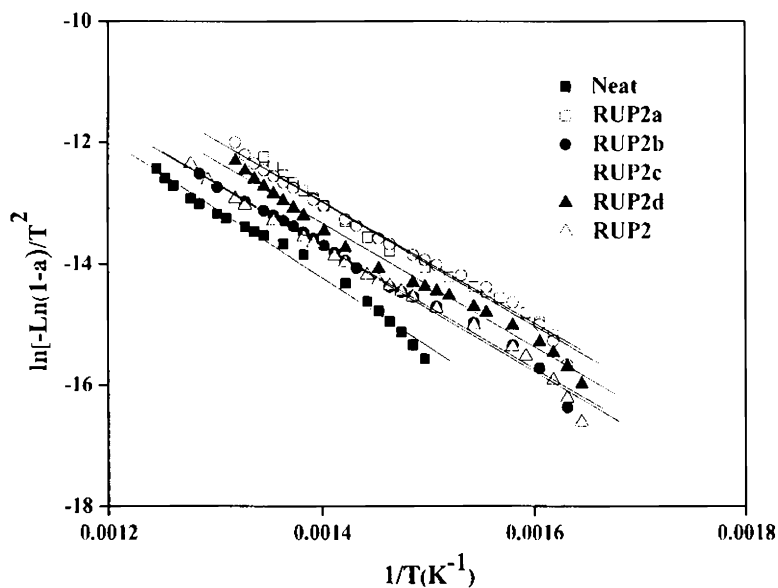
Fig. 4.38 Coats-Redfern plots for the modified phenolic resins

The activation parameters for the thermal degradation of modified resols are shown in the Table 4.8. The activation energy and the Arrhenius constant decrease on modification with UP

Table 4.8 Activation parameters for the thermal degradation of modified resols

Sample	E(KJ/mol)	A(X10^4)	Correlation coefficient
Neat	94.6	2.2456	0.9940
RUP2a	83.5	1.0900	0.9948
RUP2b	84.9	0.6900	0.9953
RUP2c	84.9	1.3748	0.9943
RUP2d	85.0	0.9834	0.9951
RUP2	85.9	0.7889	0.9947

The decrease in the activation energy with UP modification of PF resin indicates that the thermal stability is decreased compared to the unmodified resin.

4.4 Conclusion

Phenolic resol resin can be gainfully modified with low molecular weight unsaturated polyester. Higher MA contents in the UP exert only a marginal influence on the quality of phenolic resol resin. The UP with MA/PA ratio 70:30 gives the best comparative overall performance. The decrease in the acetone soluble matter on Soxhlet extraction along with structural changes noticed in the FTIR spectra of the modified resin indicate chemical anchoring of UP to the resol resin. Modification by UP of acid value ~60 resulted in a minimum number of voids, as shown in the SEM micrograph of fractured surfaces. The higher specific gravity, lower soluble content on extraction and lower volatile matter, as revealed by the isothermal TGA measurements of the cured resin modified by UP with acid value ~60, support the SEM evidence. The optimal quantity of UP required for the modification is ~7.5%. Tensile and impact strength values of modified samples also indicate the positive results of modifying resols with unsaturated polyester.

DMA studies indicate that there is a general lowering of T_g for the modified sample. This leads to increased flexibility.

TGA studies show that the modification of phenolic resol resin by unsaturated polyester leads to a nominal decrease in the thermal stability. The activation energy of the phenolic resols is found to decrease on modification.

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Chapter 5

MODIFICATION OF PHENOLIC RESOL RESIN USING EPOXIES

5.1 Introduction

The use of phenol formaldehyde resin as a curing agent for epoxy resins is well established [1,2]. The epoxy groups can react with groups having replaceable hydrogen atoms. Hence they can combine with the active groups in the the resol resin and impart better properties.

A number of studies investigating the reactions between phenolics and epoxies and their application have been reported. The earliest and the most significant work in this field was done by Schechter and Wynstra [3-5].

In this part of the work, the influence of epoxidised novolacs on the properties of phenolic resol resin has been studied. Epoxidised novolac, a two-step resin, is made by reacting epichlorohydrin with phenol formaldehyde condensates. These are linear, thermoplastic B-stage phenolic resins. Epoxidised novolacs have high strength, excellent dielectric properties and improved oxidative resistance [6].

The reaction between the phenolic hydroxyl groups of novolac oligomers and the epoxide may be catalysed by a wide variety of catalysts including acids, bases, triaryl or trialkyl nucleophiles of Group Va compounds and quaternary ammonium complexes [7,8]. Typically, tertiary amine or phosphine catalysts are employed, with triphenyl phosphine being most commonly used. The proposed mechanism for the triphenyl phosphine-catalysed phenol-epoxy reaction is shown in Scheme 1 [9]. In the first step, the triphenyl phosphine catalyst ring-opens the epoxide ring and produces zwitterions. A rapid proton transfer follows this from the hydroxyl group of the phenol to the zwitterions. The third step of the mechanism shows two reaction pathways available for the phenoxide molecule. Phenoxide may react with the electrophilic carbon next to the phosphorus of the secondary alcohol, regenerating triphenyl phosphine (PPh$_3$), or it may react with another epoxide ring and abstract a proton from a phenol molecule, thus regenerating the nucleophilic phenoxide.

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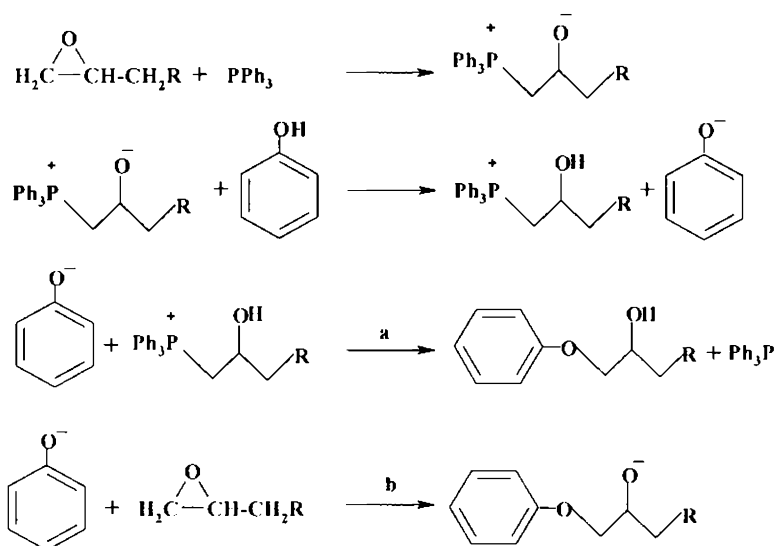
Scheme 1. Mechanism for a PPh₃-catalysed epoxy-phenol reaction

Since epoxidised novolacs contain at least two epoxy groups it can combine with two resol prepolymer molecules either through the methylol groups or through phenolic –OH groups. It leads to the combination of resol prepolymer chains through epoxy groups and also a simultaneous crosslinking reaction through the methylol groups in the resol resin. As a result of this, both the quantity of byproducts released during curing and also the crosslink density can be reduced without affecting the structural integrity of the cured resol. Hence phenolic resol resins with better properties can be expected from this modification.

In this part of the study, various epoxy novolacs based on simple phenol, p-cresol and o-cresol with varying phenol to formaldehyde ratios were synthesised and subsequently epoxidised using epichlorohydrin. These epoxy novolacs were used as modifiers. Commercial epoxy resin, commercial epoxidised phenolic novolac and epoxidised cardanol have also been used for the study.

5.2 Experimental
5.2.1 Materials

Phenol (MW=94.11, M.P.39.5-41°C), p-cresol (MW=108.14, BP=202°C, 98% assay), o-cresol (MW=108.14, BP=190°C, 98% assay), formaldehyde (37-

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41% w/v, d^{20}=1.08), sodium hydroxide (MW= 40, 97% assay) and oxalic acid (MW=126.07, 99.8% assay) were L.R. grade supplied by Loba Chemie, Mumbai, India. Epichlorohydrin (L.R., MW=92.53, 98% assay BP=114-118^{0}C) was supplied by Research Laboratory, Mumbai, India. Benzene (MW= 78. 98% assay) and triphenyl phosphine (MP=78-82^{0}C, MW=262.3, 98% assay) were obtained from E. Merck India, Mumbai. Commercial grade Epoxy Resin 103 was supplied by M/S Sharon Engineering Enterprises, Cochin. EPN 1138 (Araldite, wpe = 178) was obtained from M/s Vantico Performance Polymers Pvt. Ltd, Mumbai.

5.2.2 Synthesis of epoxy modifiers
a)   Novolac resins

Initially, novolacs were prepared by reacting phenol with formaldehyde in the molar ratio 1:0.7 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 mixture was neutralised with sodium hydroxide, filtered, washed with water and vacuum dried. The novolac resin formed contains 4-6 benzene rings per molecule [10]. The same procedure was used to synthesise novolac resins from p-cresol, o-cresol and cardanol. Further, different novolac resins containing phenol and formaldehyde in varying molar ratios such as 1:0.5 and 1:0.9 were also prepared by the same procedure.

b)   Epoxidised phenolic novolacs (EPN) [11]

1 mole of the novolac resin (1:0.7) 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 a 30 % aqueous solution was added dropwise. The rate of addition was maintained such that the reaction mixture remained 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 resins were similarly prepared from p-cresol novolac (EPCN) and o-cresol novolac

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(EOCN) by the same procedure. Novolac resins containing phenol and formaldehyde in varying molar ratios such as 1:0.5 and 1:0.9 were also subjected to epoxidation to form EPNs of different compositions. These epoxy novolacs were designated as EPN5, EPN7 and EPN9 respectively. Epoxidised p-cresol novolacs were designated as EPCN5, EPCN7 and EPCN9 whereas epoxidised ortho-cresol novolacs were designated as EOCN5, EOCN7 and EOCN9. The weight per epoxide values of the various epoxy novolacs were determined (Section 5.2.3).

c)   **Epoxidised cardanol (EC) [12]**

Cardanol (1mole) was dissolved in a mixture of an excess of epichlorohydrin (2 moles) and 20 cc water in a one litre three necked flask. The flask was equipped with a mechanical stirrer, thermometer and a Liebig's condenser. The mixture was heated gently over a water bath till the epichlorohydrin began to boil. Heating was stopped and caustic soda (1 mole) was added in portions of two pellets down the condenser. The reaction was allowed to subside before a new portion of alkali was added. When all the caustic soda pellets were added, the reaction mixture was refluxed for nine hours. 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.

5.2.3 Determination of epoxide equivalent (weight per epoxide)

The epoxy content of liquid resins is frequently expressed as weight per epoxide (wpe) or epoxide equivalent which is defined as the weight of the resin containing one gram equivalent of epoxide. The epoxy content can also be expressed as equivalents/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). In this study, weight per epoxide values of the synthesised and commercial epoxy resin

samples were determined by the pyridinium chloride method as per ASTM D 1652-73 using the same principle.

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 unreacted acid present in it was estimated by back titration with standard NaOH solution (0.1N) using phenolphthalein indicator. A blank titration 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.

Various epoxies used in the study are given in Table 5.1 with abbreviation of each epoxy resin.

Table 5.1 List of epoxies used as modifiers and their abbreviations

Type epoxy	Abbreviation	wep
Epoxidised phenolic novolac	EPN5	210
	EPN7	186
	EPN9	171
Epoxidised p-cresol novolac	EPCN5	221
	EPCN7	193
	EPCN9	217
Epoxidised o-cresol novolac	EOCN5	281
	EOCN7	247
	EOCN9	245
Commercial epoxy resin	Epoxy(C)	188
Commercial epoxidised phenolic novolac	EPN(C)	178
Epoxidised cardanol	EC	465

5.3 Sample preparation

Dried phenolic resol resin was mixed with varying proportions of epoxies dissolved in methyl ethyl ketone using a mechanical stirrer for 20 minutes. 0.5% of PPh$_3$ on resol basis was also added. The solvent was then removed by applying vacuum for about 45 minutes.

5.4 Results and discussion

5.4.1 Epoxide equivalents

The wpe (epoxy equivalents) values for EPN5, EPN7 and EPN9 were found to be 210 (4.76eq/Kg), 186(5.376eq/Kg), and 171(5.85eq/Kg) respectively. EPN9 which contains phenol and formaldehyde in the ratio 1:0.9 was found to have greater epoxide content than the other two epoxy novolacs.

The wpe (epoxy equivalents) for EPCN5, EPCN7 and EPCN9 were found to be 221(4.52eq/Kg), 193(5.18eq/Kg), and 217(4.61eq/Kg) respectively. The wpe values for EOCN5, EOCN7 and EOCN9 were found to be 281(3.56eq/Kg), 247(4.05eq/Kg), and 245(4.08eq/Kg) respectively.

The epoxidised cardanol was found to have a wpe value of 465 (2.15eq/Kg). This very low value indicates that it contains unreacted cardanol. This can be due to several reasons like the monofunctionality of the cardanol and its low reactivity [11]. The commercial epoxy resins (Epoxy (C)) and commercial EPN (EPN (C) gave wpe values 187.7 (5.33 eq/Kg) and 178 (5.62 eq/Kg) respectively.

5.4.2 Spectroscopic data[13]
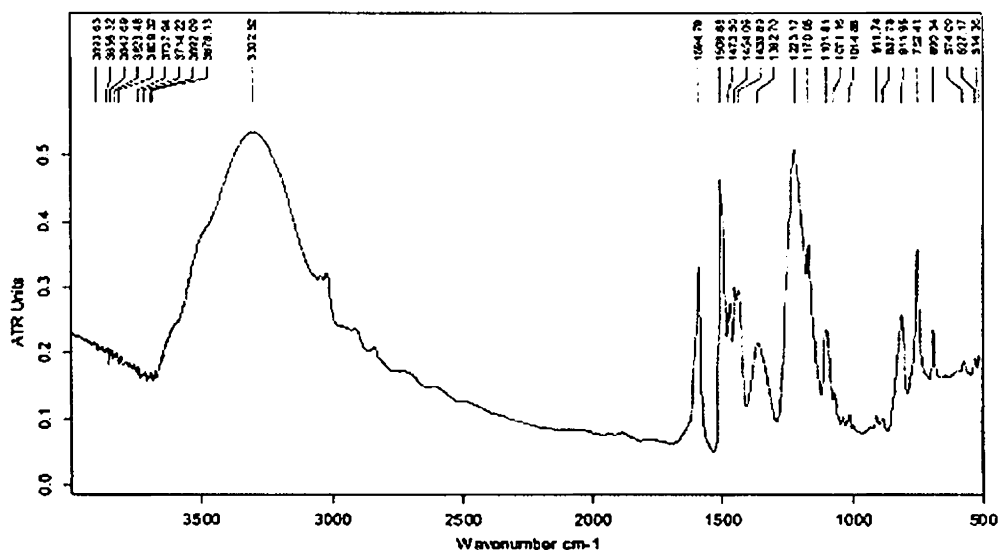
Fig. 5.1 FTIR spectrum of PF (novolac)
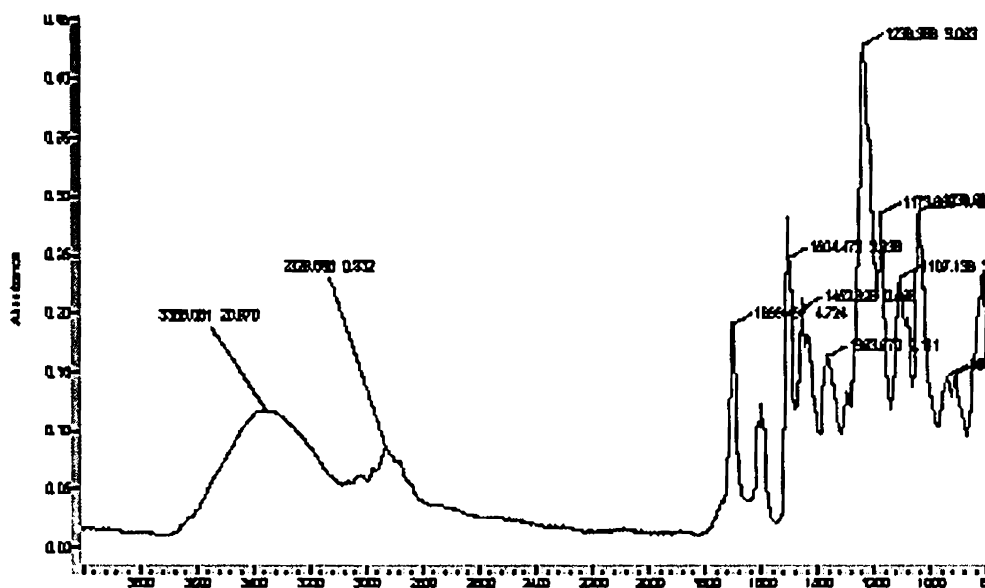
Fig. 5.2 FTIR spectrum of EPN

Fig. 5.1 shows the FTIR spectrum for phenol-formaldehyde novolac (1:0.9) resin and epoxidised novolac resin (EPN9). Characteristic absorptions were found around 3300cm^{-1}(hydroxyl group, broad band), 3100cm^{-1}(aromatic C-H str. weak), 1594cm^{-1} and 1500cm^{-1} (phenyl ring) and 1475cm^{-1}(CH$_2$ bending). The two strong bands around 1230cm^{-1}and 1010 cm^{-1} are characteristic of C-O stretching in phenol and alcohol groups respectively.

The FTIR spectrum of synthesised epoxidised novolac resin (EPN9) is given in Fig. 5.2. The strong band at 1236.9cm^{-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}, 840cm^{-1} and 760cm^{-1} are also typical of epoxides.

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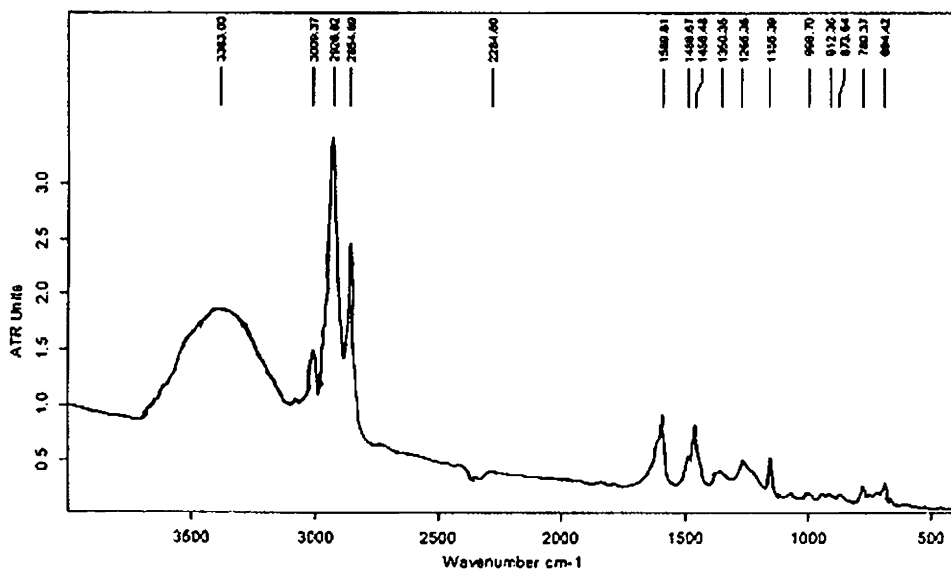
Fig. 5.3 FTIR spectrum of cardanol

Figs. 5.3 & 5.4 show the FTIR spectra of cardanol and the synthesised epoxidised cardanol resin (EC). The bands at 2924.37cm^{-1} (C-H stretching of epoxide), 1265.28cm^{-1}(symmetrical C-O str.) and 915.9cm^{-1} are characteristic of the epoxy group. The intensity of the broad band at 3343cm^{-1} in Fig. 5.3 due to the phenolic hydroxyl group has decreased considerably in Fig. 5.4 indicating the involvement of that group in epoxidation.
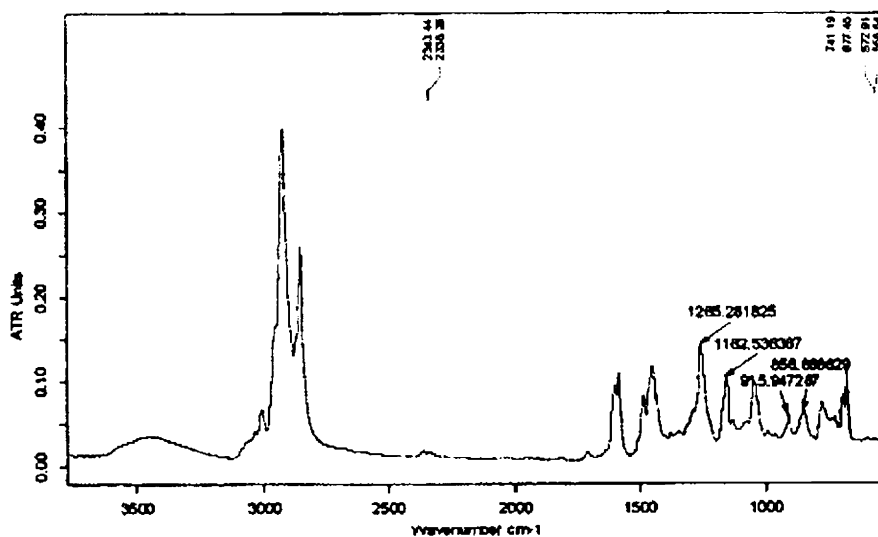
Fig. 5.4 FTIR spectrum of epoxy cardanol (EC)

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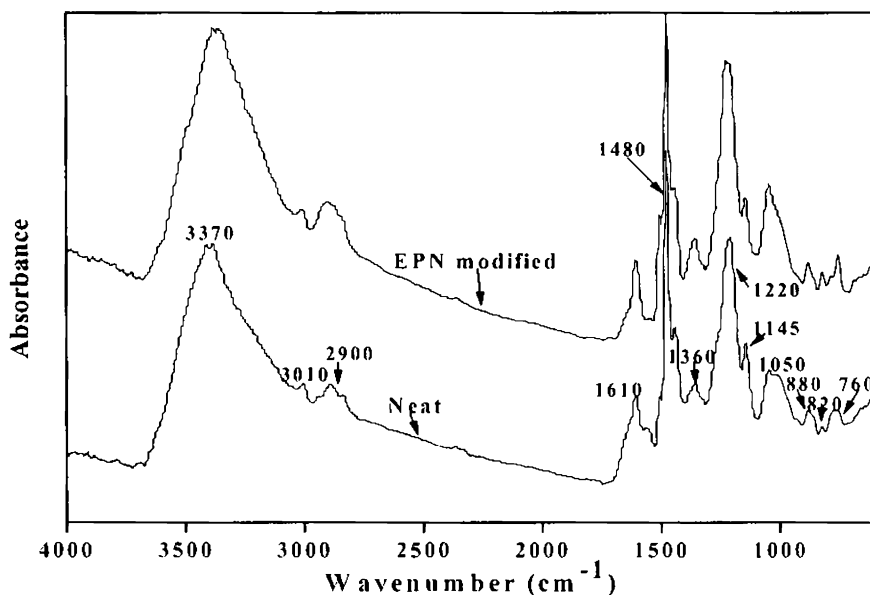
Fig. 5.5 FTIR spectrum of cured neat and EPN9 modified resin

The FTIR spectra of cured neat and EPN9 modified resol resin are given in Fig. 5.5. The spectra of both the resins are similar. The increase in the peak intensities at ~2900cm⁻¹ and 1360cm⁻¹ is mainly due to the increase in the – CH₂– groups as a result of blending with EPN, which originally contained – CH₂– groups. The increase in the peak intensities at ~1050cm⁻¹ and ~1220cm⁻¹ is due to the stretching vibrations of the C-O bond of the secondary alcoholic group, formed by the reaction of epoxy group in the EPN with the –OH groups of the resol. The peak due to the epoxy ring at ~915cm⁻¹ is not observed in the modified resin indicative of the ring opening of the epoxy group during crosslinking.

5.4.3 Modification of PF resin by epoxidised phenolic novolacs (EPN)
a)   Mechanical properties

The effect of addition of various EPNs on the tensile properties is shown in Figs. 5.6-5.9.
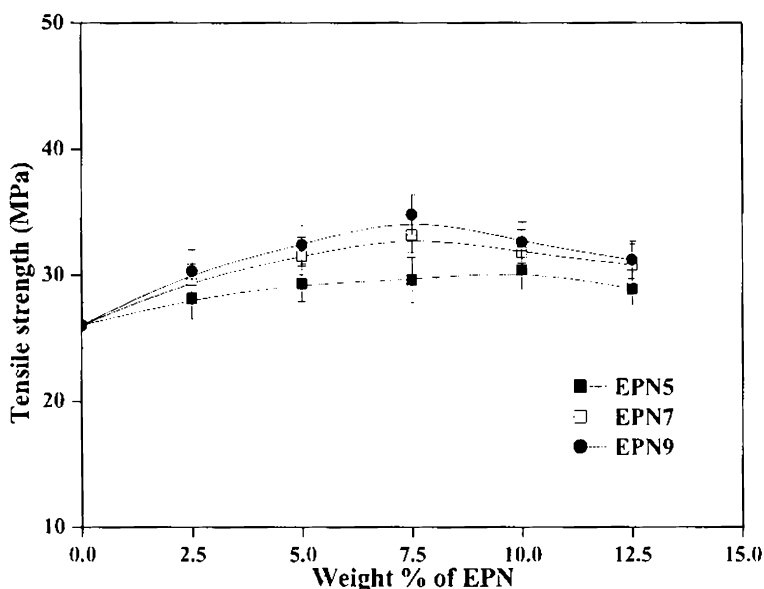
Fig. 5.6 Tensile strength of modified resin versus EPN concentration

In Fig. 5.6 tensile strength obtained by adding EPN9 is comparatively higher than those obtained by adding other EPNs. Tensile strength reaches a maximum at 10% for EPN5 and 7.5% for EPN7 and EPN9. Beyond this stage, addition of more EPN results in lower tensile strengths. But all the EPN modified resins show better tensile strength than the neat resin at all percentages. The improvement in the tensile strength on EPN modification may be partly due to the cross linking of resol through the epoxy functionality. This can reduce the release of water and formaldehyde during curing. But at higher percentages, EPN might have undergone a self crosslinking reaction instead of combining with PF resin. In the presence of PPh3, it generates O⁻ ions which can initiate the curing reactions of epoxies at higher EPN concentrations. This results in phase separation and a weak interphase. Thus the load bearing capacity starts to decrease. The higher tensile strength of EPN9 modified resin may be possibly due to its high epoxy content compared to the others.
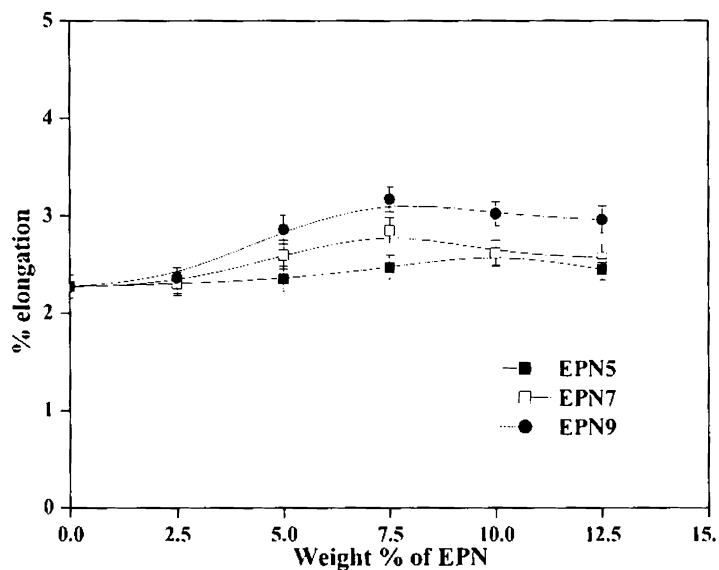
Fig. 5.7 Elongation at break of modified resin versus EPN concentration

The effect of EPN addition on the elongation at break is shown in Fig. 5.7. Compared to the unmodified resin the modified resins show some increase in elongation. The addition of EPN9 produces the greatest increase in elongation at about 7.5-10% of EPN concentration. The other two EPNs also show the same trend. The chain flexibility of EPN may be responsible for this observation.
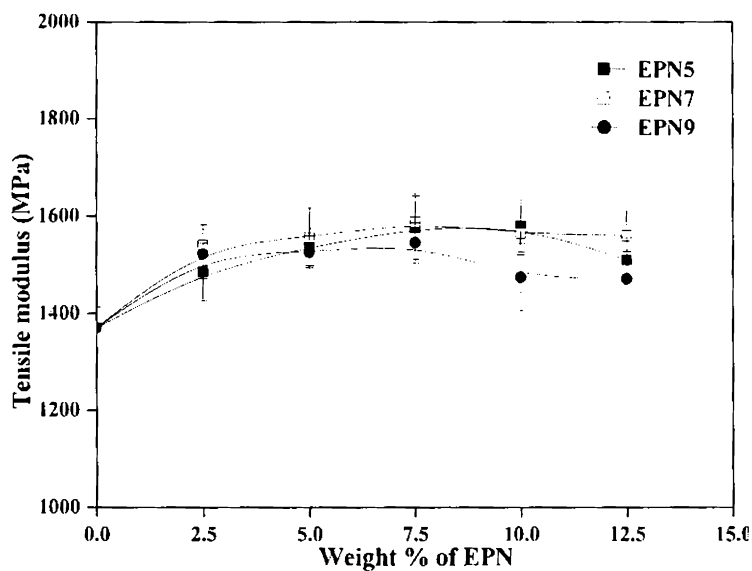
Fig. 5.8 Tensile modulus of modified resin versus EPN concentration

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Fig. 5.8 shows the effect of EPNs on tensile modulus. Modulus values are slightly higher than the base resin values at all concentrations. In presence of EPNs, reactions between phenolic –OH groups are also possible (Scheme 1). This might result in a slight increase in the modulus values. Decrease in the number of microvoids can also contribute to an increase in the modulus.
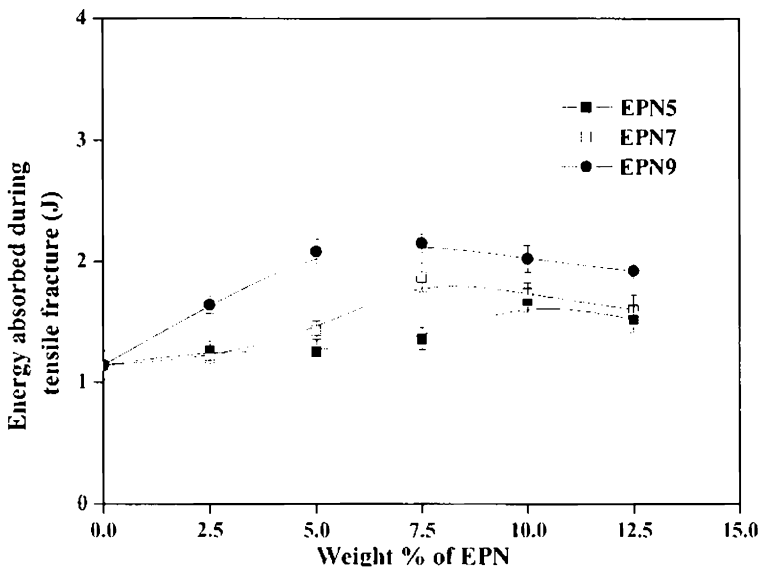
Fig. 5.9 Energy absorbed during tensile fracture versus EPN concentration

The variation of energy absorption values during tensile fracture with EPN content is shown in Fig. 5.9. The energy absorption values of the modified samples are higher than the unmodified sample. About 90% increase in energy absorption is observed by EPN modification. The enhanced energy absorption can be attributed to a greater level of flexibility and increased chances for spatial rearrangements.
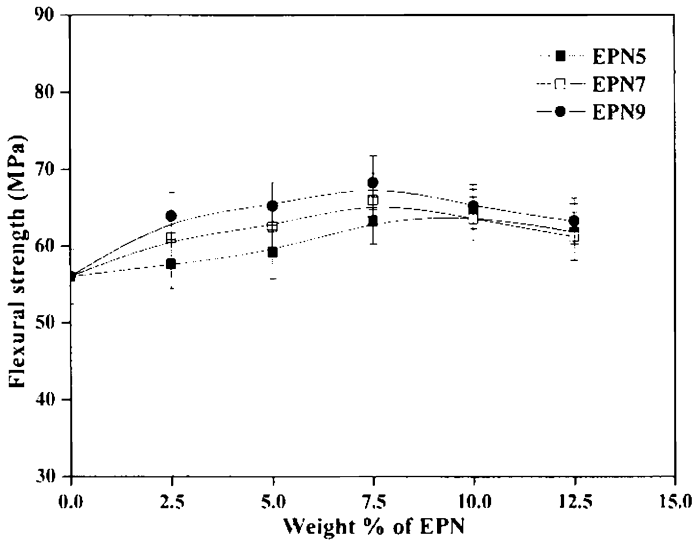
Fig. 5.10 Flexural strength of the modified resin versus EPN concentration

Fig. 5.10 shows the variation of flexural strength with EPN concentration. The flexural strength of the modified samples is comparatively higher than that of the neat resin. Here also the EPN9 modified resin shows maximum improvement, at a concentration of 7.5% (~22% increase). But at higher percentages the flexural strength became similar for all the modified samples. The improvement in the flexural strength may be due to fewer microvoids and multifunctional nature of EPN.
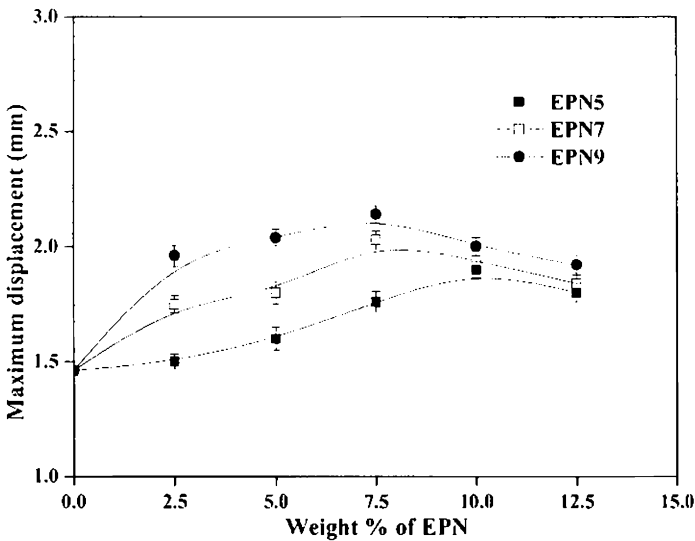
Fig. 5.11 Maximum displacement versus EPN concentration

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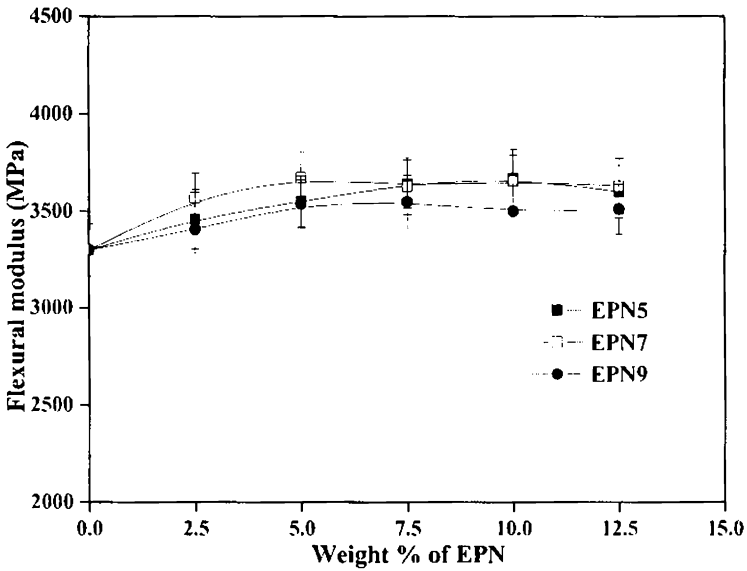
Fig. 5.12 Flexural modulus of the modified resin versus EPN concentration

The variation of the maximum displacement in flexure with EPN concentration is shown in Fig. 5.11. All the modified resins show increase in the maximum displacement irrespective of the type of EPN used. However, EPN9 shows a higher degree of displacement than the others.
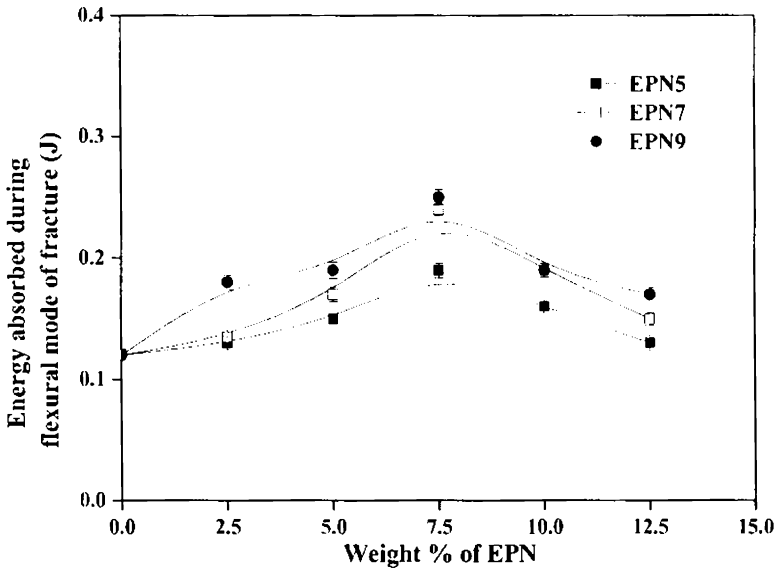
Fig. 5.13 Energy absorbed during flexural mode of fracture versus EPN concentration

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The increase in the maximum displacement values is an indication of flexibility gained by the EPN modification. This can be explained as a result of the lengthier crosslinks generated on reaction of EPN with phenolics. A slight increase in the flexural modulus on modification can be seen in Fig. 5.12. All the modified samples exhibit a maximum at 5% remaining unchanged above 5% irrespective of the modifier. The small increase in the modulus values may be due to the decrease in the microvoid density in the modified samples.

Fig. 5.13 indicates the variation of the energy absorbed during flexural testing with EPN content in the modified resin. The energy absorption by modified samples is higher than the unmodified sample. Here also the EPN9 modified samples exhibit better energy absorption.

The variation of impact strength with EPN concentration is shown in Fig. 5.14. In this respect also EPN9 shows maximum improvement (~110%), at a concentration of 10%. This can also be explained in terms of a higher degree of molecular flexibility and greater capacity for spatial molecular rearrangement.
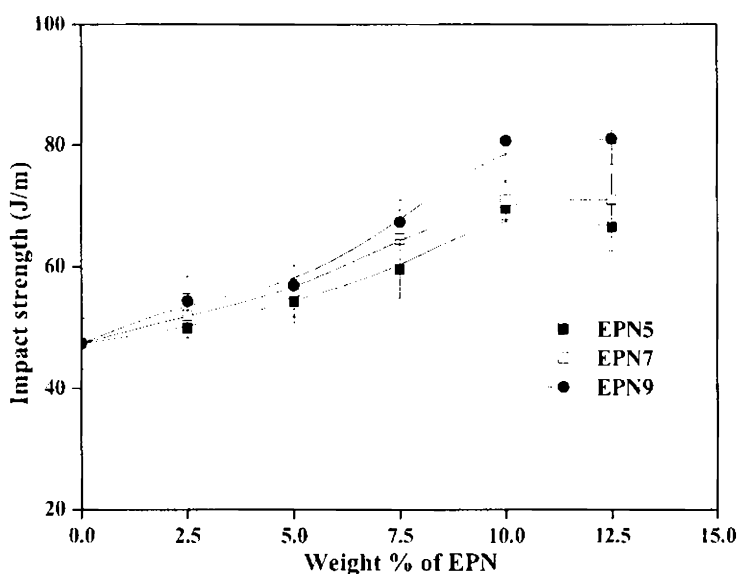
Fig. 5.14 Impact strength of modified resin versus EPN concentration
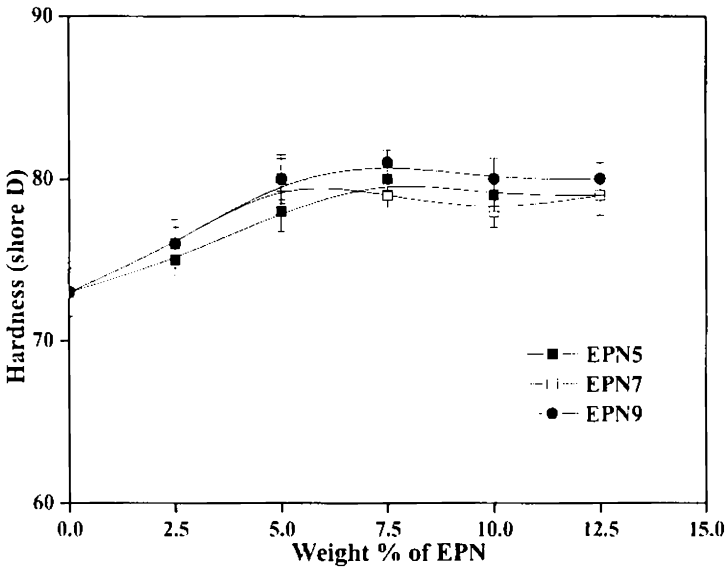
Fig. 5.15 Surface hardness of modified resin versus EPN concentration

Fig. 5.15 indicates an initial increase in the surface hardness which remains constant at higher concentrations of EPN. The increase in the surface hardness is presumably due to the decrease in the population of the microvoids which in turn increases the density of the modified samples.
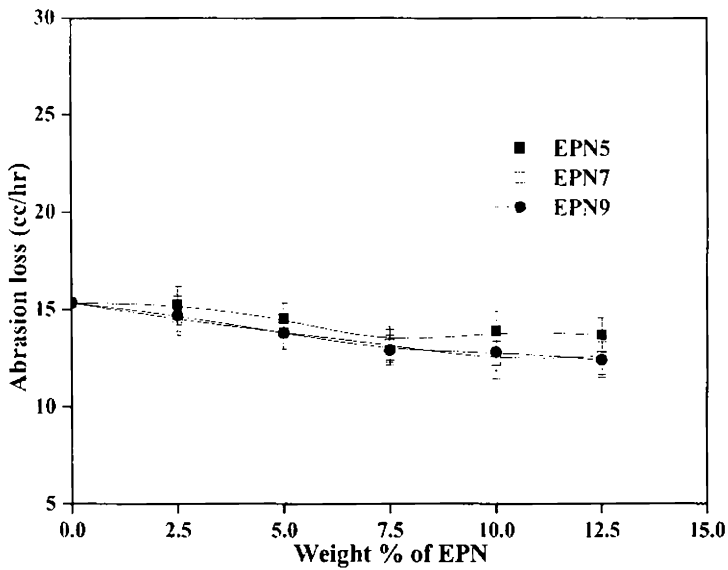
Fig. 5.16 Abrasion loss versus EPN concentration

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There is a slight decrease in the abrasion loss with increase in EPN concentration (Fig. 5.16). The decrease in the abrasion loss is not considerable and the reason for the modest change is the ability of the EPNs to reduce the void volume.
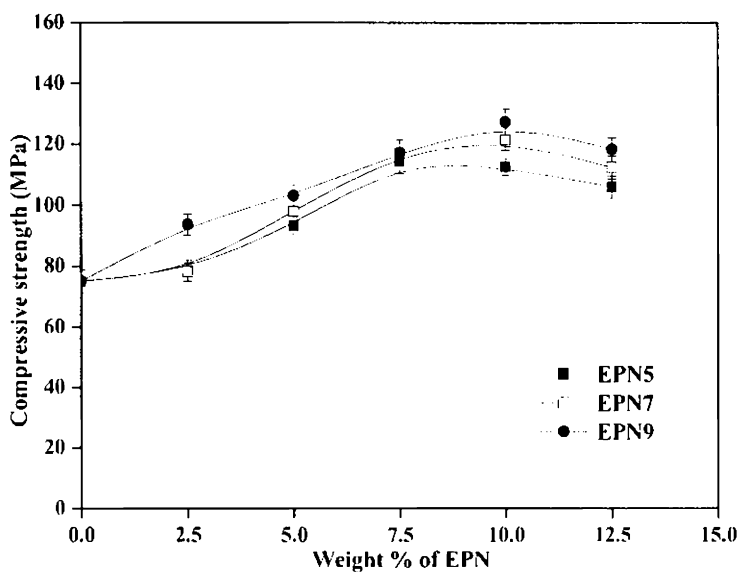
Fig. 5.17 Compressive strength EPN concentration

The variation of the compressive strength of the modified resin with the EPN content is shown in Fig. 5.17. Compressive strength of the modified samples is higher than that of the neat resin. It shows a maximum at 10% of the modifier concentration. The resin modified with EPN9 shows superiority over the other two. The increase in the compressive strength may be due to the decrease in the number of tvoids.

b)   Soxhlet extraction

The % soluble content change in the neat and modified resins with EPN content is shown in Fig. 5.18. % soluble matter in the resin decreases initially but at higher concentrations of EPN (say, above 7.5%) the soluble content remains almost constant. The decrease in the soluble matter indicates that the EPN is incorporated into the matrix either by chemical bonds or by interpenetration.
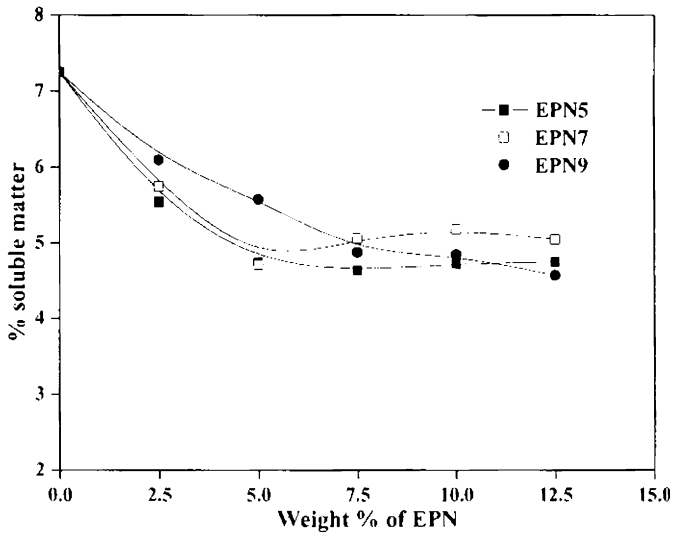
Fig. 5.18 % soluble matter in the modified resin versus EPN concentration

c) Morphological studies

Scanning electron micrographs of the fractured surfaces of the unmodified and modified PF resins are shown in Fig. 5.19.
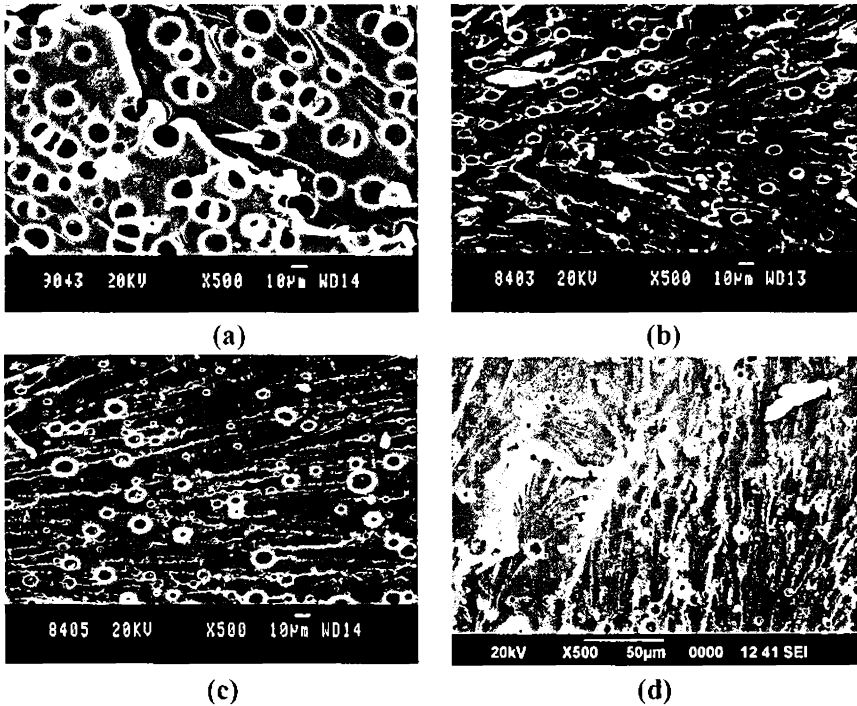
Fig. 5.19 Scanning electron micrographs of fractured surfaces **(a)** Neat PF **(b)** PF/EPN5 **(c)** PF/EPN7 **(d)** PF/EPN9

All the samples contain microvoids. But it can be seen that the void size as well as the crazes in the fractured surfaces are different for the neat sample and modified samples.

The size characterization of the voids ($\overline{D_n}$, $\overline{D_w}$, $\overline{D_a}$ and $\overline{D_v}$) and PDI values of the neat and modified samples are presented in Table 5.2.

Table 5.2 Size characterisation of voids in the neat and EPN modified samples

Samples	$\overline{D_n}$ (μm)	$\overline{D_w}$ (μm)	$\overline{D_a}$ (μm)	$\overline{D_v}$ (μm)	PDI	V_D
Neat	11.95	13.16	12.54	13.75	1.11	0.2000
PF/EPN5	5.74	6.78	6.24	4.02	1.18	0.0502
PF/EPN7	4.27	5.48	4.83	5.37	1.28	0.0371
PF/EPN9	3.52	4.74	4.08	4.71	1.345	0.0178

The void size in the neat resin is very high compared to the EPN modified resins. The void size in the modified resin is minimum for PF/EPN9 and maximum for PF/EPN5. But the PDI value indicates that the void size remains in the same range in the neat sample whereas the void size variation is high in the modified sample, particularly PF/EPN9. It can also be seen that the void volume also reduces tremendously on modification. This establishes that EPNs are capable to reduce the microvoids in the PF resin.

Fig. 5.20 shows how the voids are distributed on modification. In the neat sample the majority of the voids are in the range 10-15 μm. It also contains microvoids of size up to 20 μm. In PF/EPN5 most voids possess dimensions in the range 5-7 μm. It also contains microvoids in the very small range as well as in the higher range upto 10 μm, but their number is less. In PF/EPN7, the micro void size range is further shifted to the left and their range is in between 3.5-5 μm. Microvoids of higher sizes are also present in the modified sample. The void size in PF/EPN9 is mostly concentrated in the range 1-4 μm. Here also a few bigger size microvoids are present.
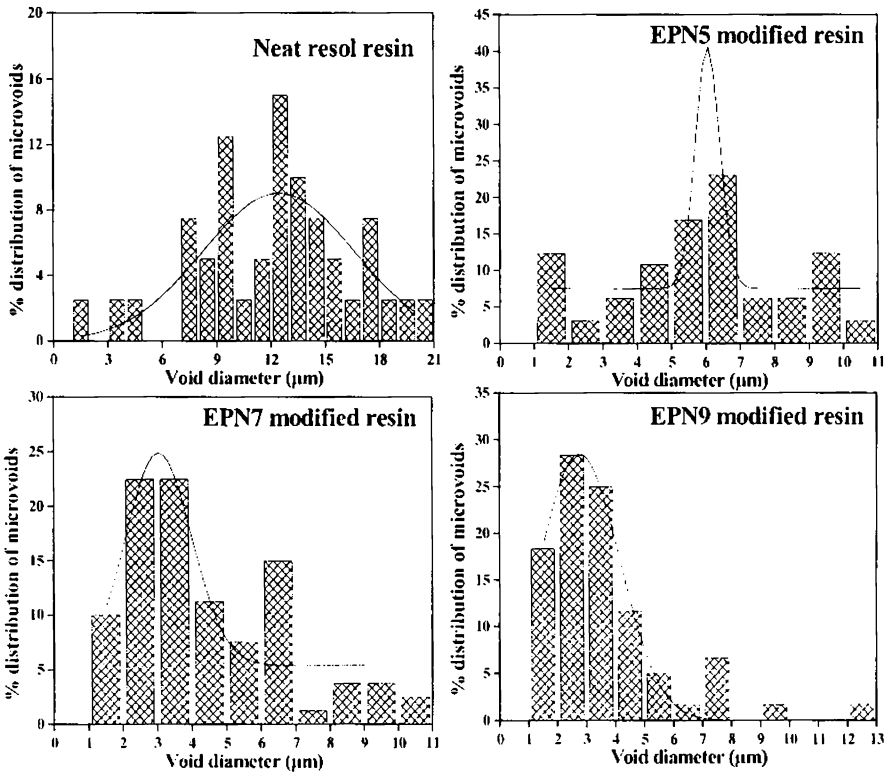
Fig. 5.20 Microvoid distribution diagram of the neat and EPN modified samples.

The distribution pattern shows that EPN9 is most effective in reducing the microvoids in the cured PF resin. The reduction in voids by the addition of epoxy compounds can be explained in the light of the chemical reaction between epoxies and phenolics (Section 5.1). This reaction does not lead to volatile condensation by products and results in reducing the microvoid population.

As can be seen from the SEM pictures, the surface morphology has changed on modification. The fracture pattern of EPN5 modified resin is shown in (b). This is a low deformation fracture. Separate ductile deformed films and fibrils are seen. The micrograph of EPN7 modified resin (c) shows ductile deformed films and thicker boundaries. Referring to EPN9 modified resin (d), the fracture paths have a feathery texture with large breadth. Excessive whitening is also observed. These

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points to improved toughness and load bearing characteristics of the modified samples. Hence the improvement in mechanical properties of the modified resin is not solely due to reduction in the microvoid size and number but also due to the toughening effect.

d)   Thermal studies

i)   DMA

Fig. 5.21 shows the variation of the storage modulus (E′) with temperature of neat and modified resins. The initial E′ value of all modified samples are higher than that of the neat resin. The modulus values of the samples decrease with increase in temperature. This may be due to the increased segmental mobility at higher temperatures. At ~200°C the modulus values of the neat and modified samples reach a plateau and henceforth show a slight increasing tendency.
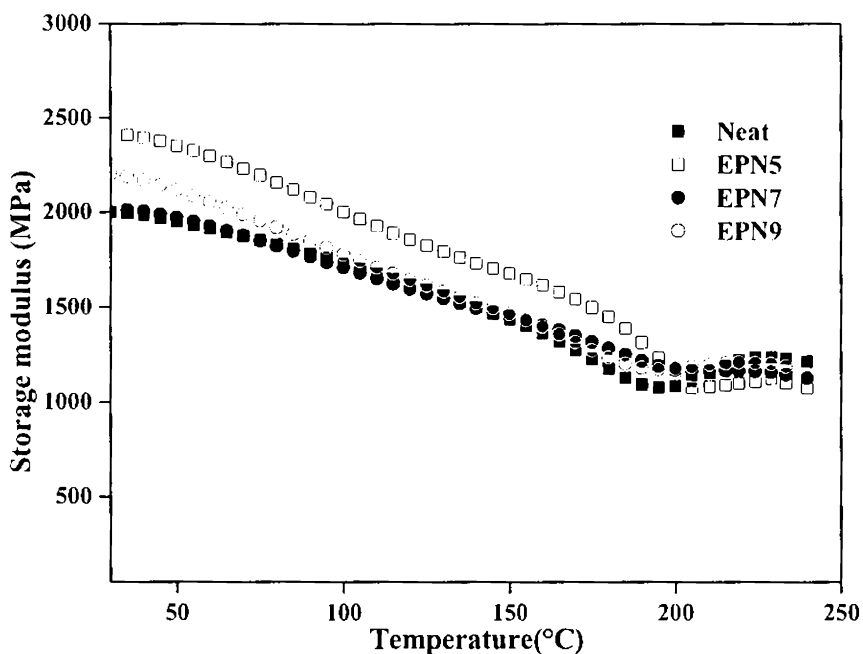
Fig. 5.21 Storage modulus versus temperature
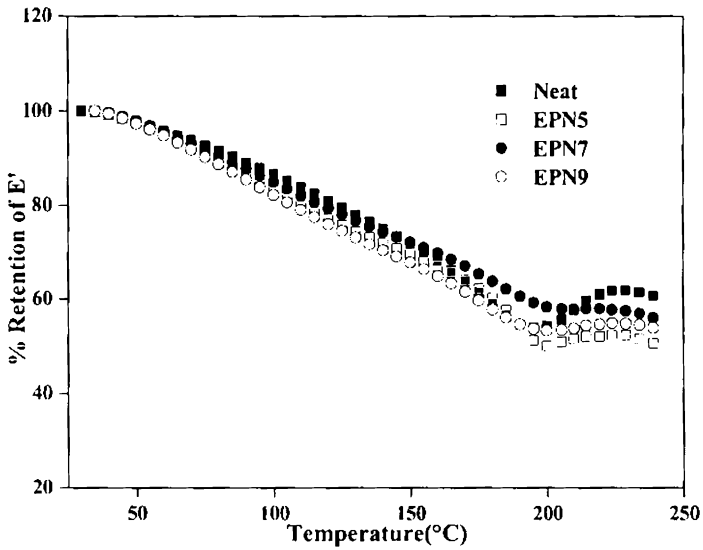
Fig. 5.22 % Retention of E' versus temperature

Fig. 5.22 indicates the variation of the % retention of E' of the both neat and modified resins with temperature. The % retention of E' of all resin samples undergoes a steady decrease in E' until ~190°C. After this only the neat resin shows any increasing tendency. This may be due to further crosslinking in the neat resin. But for the modified samples the % retention of E' remains constant even at higher temperatures. This indicates that the modification of by EPN leads to an increase in the degree of curing compared to the neat resin.
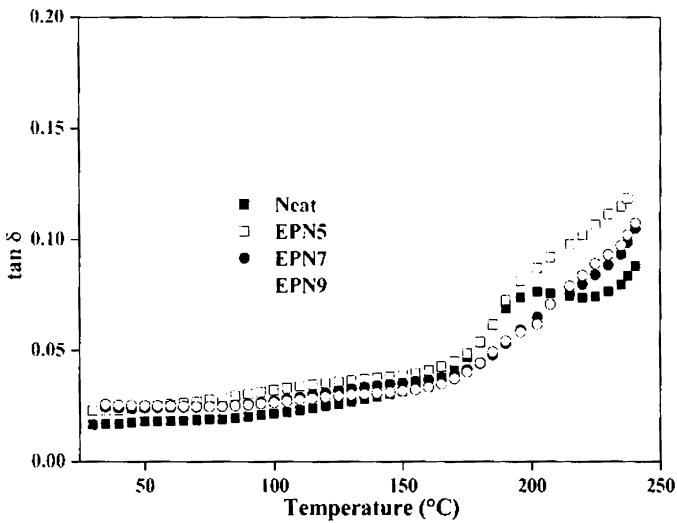
Fig. 5.23 tan δ versus temperature

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Table 5.3 T_g, T_g-tanδ and tanδ values of the modified samples

Sample	T_g (°C)	T_g-tanδ (°C)	tanδ values at different temperatures			
			100°C	150°C	200°C)	250°C
Neat	167	201	0.025	0.040	0.076	0.088
EPN5	170	-	0.031	0.038	0.087	0.118
EPN7	179	-	0.027	0.035	0.065	0.113
EPN9	171	-	0.026	0.032	0.062	0.107

The variation of the tanδ values of the neat and modified resins with temperature is shown in Fig. 5.23. tanδ values of modified samples are higher than that of the neat resin except for a limited range. This indicates a decrease in the crosslink density on modification. Broadening of tanδ plots and increase of tanδ values are possible indication of lowering of crosslink density. This is also an indication of better damping properties of the modified samples.

The T_g (from storage modulus vs temperature plot), T_g- tanδ and tanδ values at different temperatures are shown in Table 5.3. The T_gs of the modified samples are higher than that of the neat resin. This may due the the multifunctional nature of EPN. The tanδ peak is observed only for the neat resin and the modified resins do not show this peak in the temperature range analysed.

ii)   TGA

Fig. 5.24 represents the thermogram of the neat resin and resins modified by EPNs. The thermogram shows that modified resins have marginally better thermal properties on the basis of loss in weight of the samples with rise in temperature.
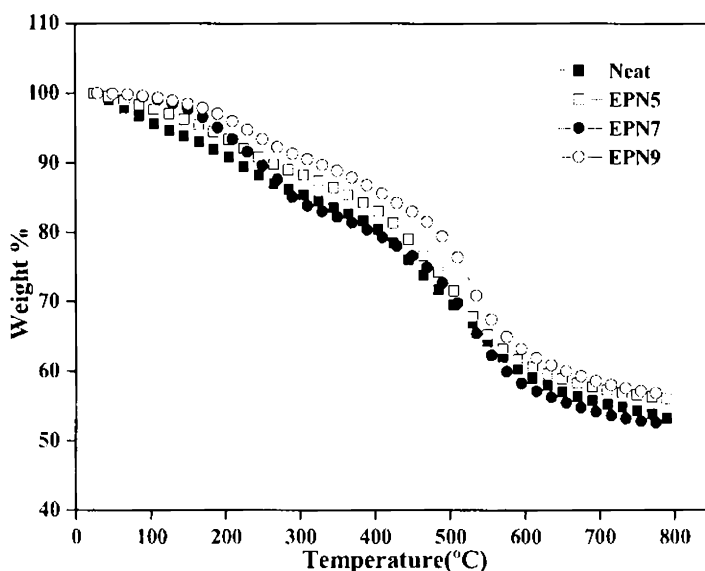
Fig. 5.24 Thermogram of the neat and modified resins

Table 5.4 Thermal analysis of the neat and EPN modified samples

Sample	Temperature at different stages of decomposition (°C)					Temp. at max. degradation (°C)	Residue (%)
	10%	**20%**	**30%**	**40%**	**50%**		
Neat	218	410	501	589	>800	533	53
EPN5	260	437	516	622	>800	516	56
EPN7	246	396	508	573	>800	528	52
EPN9	322	483	542	658	>800	524	57

Table 5.4 shows the thermal analysis data of the neat resin and the modified resins. The temperature at different stages of decomposition increases on modification with EPN. The temperature of maximum degradation falls slightly decreased on modification while the final %residue has increased in most cases.

Thermal degradation kinetics

The kinetics of the thermal degradation reaction was followed using TGA. Fig. 5.25 represents the Coats-Redfern plots for the neat and modified resins. Kinetic parameters from the plots are given in Table 5.5.

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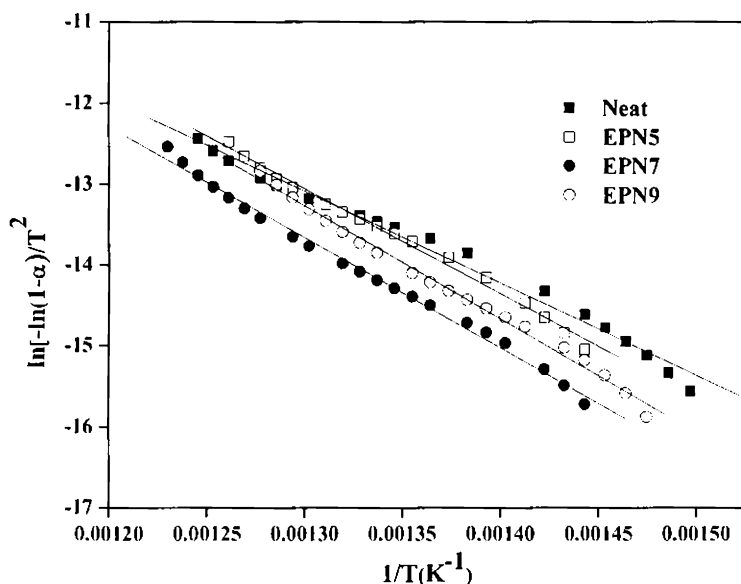
Fig. 5.25 Coats-Redfern plot for the neat and EPN modified resins

Table 5.5 Kinetic parameters of the thermal degradation of modified resols

Samples	E(KJ/mol)	A(X10^4)	Correlation coefficient
Neat	94.6	2.24	0.9940
EPN5	108	2.44	0.9928
EPN7	114	3.18	0.9942
EPN9	116	7.24	0.9938

The activation energy values of the modified samples are higher than that of the neat sample. The Arrhenius constant, A, is higher for the modified samples. This indicates higher thermal stability for the EPN modified samples compared to the neat sample.

5.4.4 Modification of PF resin by epoxidised para cresol novolacs (EPCN)

a) Mechanical properties

Referring to Fig. 5.26 tensile values obtained on blending with EPCN are higher than that of the unmodified resin. Tensile strength reaches a maximum at ~10-wt%; but further addition of EPCN does not improve the tensile strength. The

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improvement in tensile strength over that of the base resin is mainly due to the decrease in the microvoids in the modified resin.
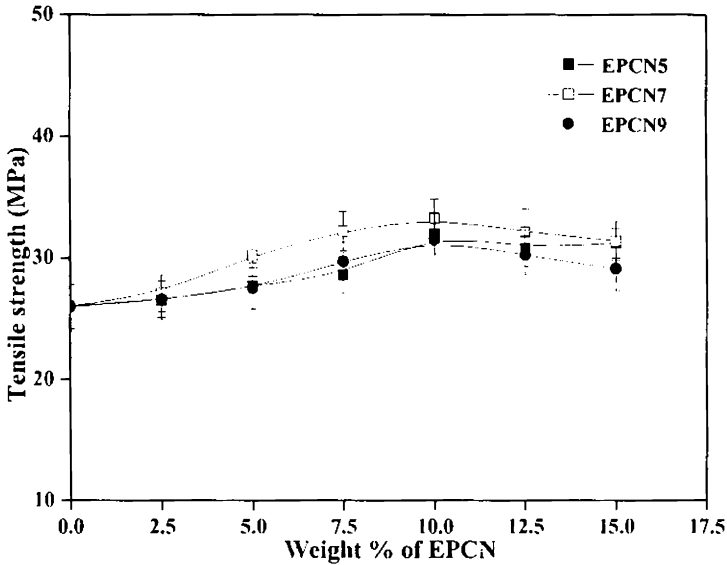
Fig. 5.26 Tensile strength of modified resin versus EPCN concentration

At higher percentages the EPCN may undergo self crosslinking and also many epoxy chains may go uncrosslinked. This causes a weakening of the matrix. Maximum improvement in tensile strength is exhibited by EPCN7. This may presumably be due to the greater amount of epoxy functionality in EPCN7

The effect of addition of EPCNs on elongation at break is given in Fig. 5.27. Compared to unmodified resin the blends show substantial increase in elongation. EPCN modified samples show maximum elongation at 10-12.5 wt.% of EPCNs. This is primarily due to the linear nature of EPCN, in which all the para cresol units are connected by $-CH_2-$ group at ortho positions. The plasticizing effect is higher when EPCNs are introduced into the phenolic matrix.

Flexural strength values of the EPCN modified samples are comparatively higher than that of the unmodified resin (Fig. 5.28). Among the EPCNs, EPCN7 shows the maximum flexural strength. The better flexural strength of modified resins may be attributed to the capacity of the EPCNs to control microvoids by the

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chemical interaction possible between the phenolic –OH of the resol epoxy groups of the EPCNs.
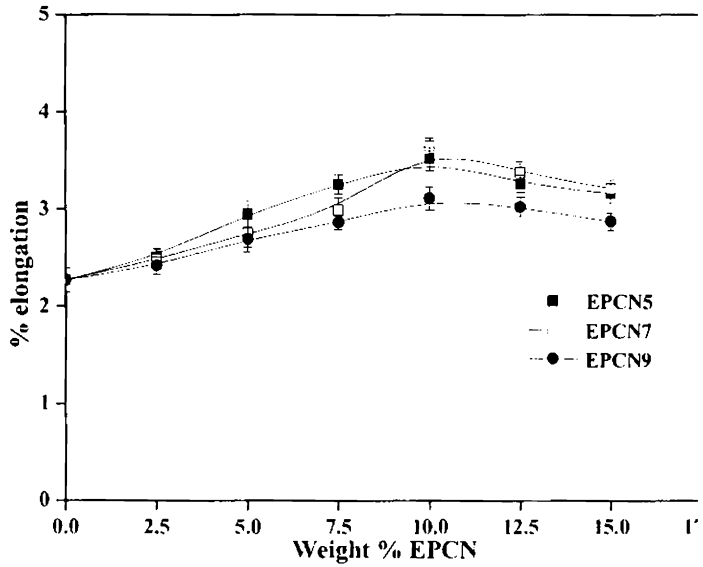
Fig. 5.27 % Elongation of modified resin versus EPCN concen
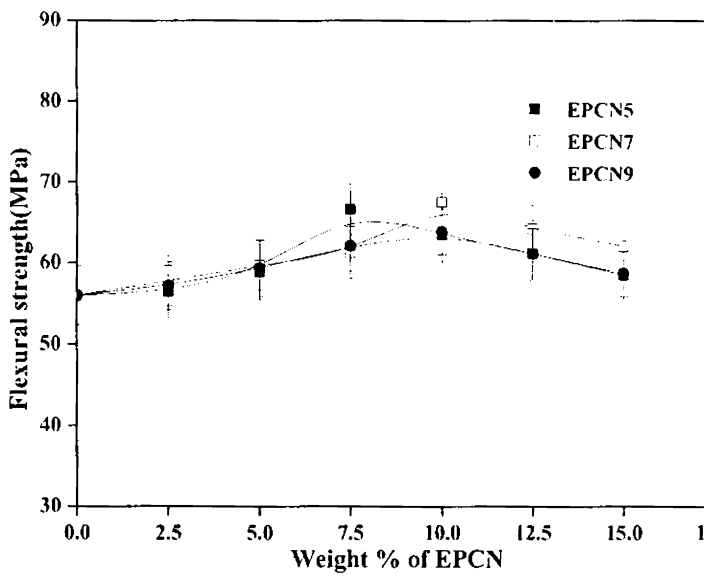
Fig. 5.28 Flexural strength of modified resin versus EPCN conce

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Fig. 5.29 shows the variation of maximum displacement with EPCN content on modification. The maximum displacement values are significantly higher compared to that of the neat resin. The maximum value of displacement is shown by EPCN7 modified sample at ~10 wt. %.
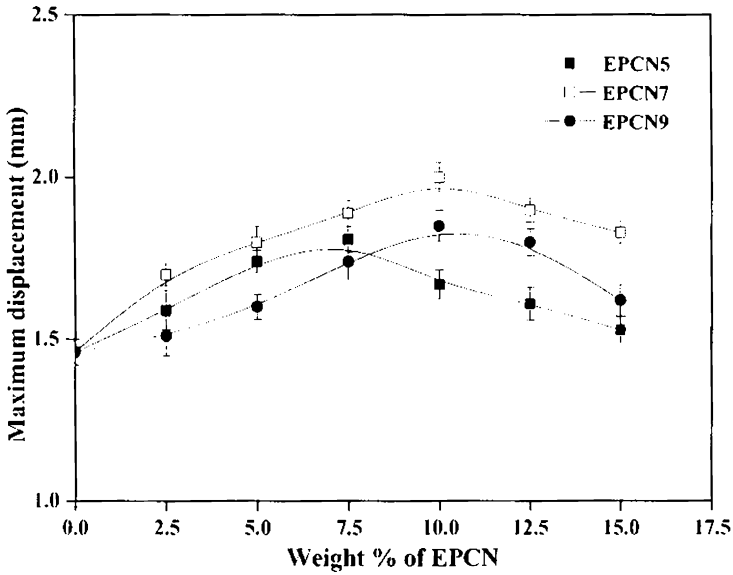
Fig. 5.29 Maximum displacement of modified resin versus EPCN concentration
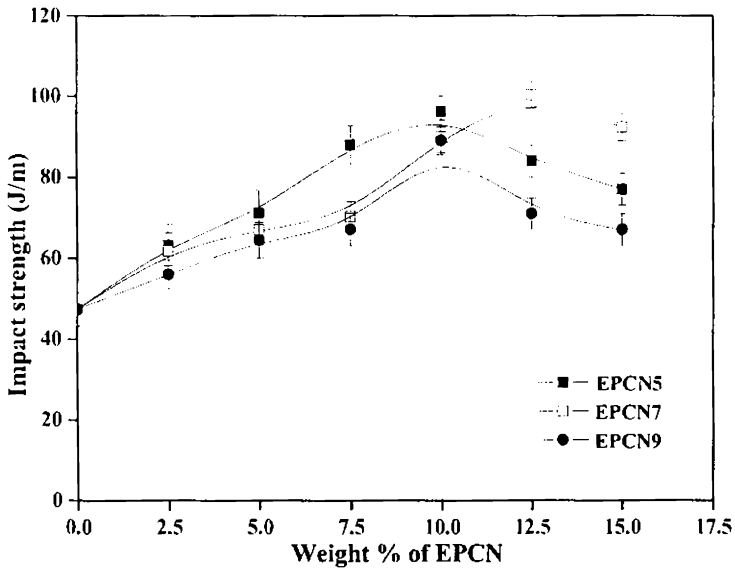
Fig. 5.30 Impact strength of modified resin versus EPCN concentration

The flexibility may be the result of the linear EPCN chains attached between resol prepolymer chains, which act as chain extenters. This also results in a loose packing of the chains. Impact strength of the modified samples is higher in comparison with the base resin (Fig. 5.30). In this respect also EPCN7 shows maximum improvement again, at a concentration of 12.5%.
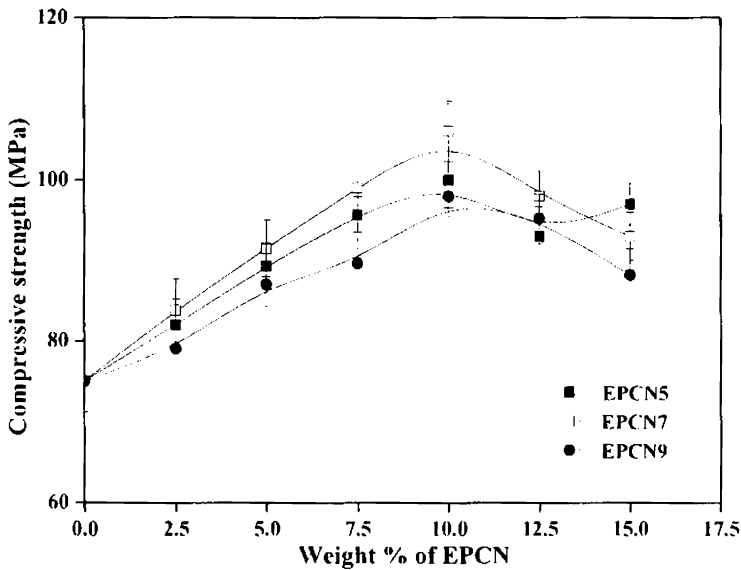
Fig. 5.31 Compressive strength of modified resin versus EPCN concentration

Fig. 5.31 exhibits the variation of the compressive strength of the modified resins with EPCN content. At all percentages the compressive strength is higher compared to the base resin. About 30-40% increase in the compressive strength is observed by EPCN modification. The improved compressive strength may be due to the reduction in the void density. The capacity to improve the compressive strength on modification depends on the functionality of the EPCN to some extent. EPCN7 is seen to be the best in this respect.

There is a decrease in the abrasion loss with EPCN modification (Fig. 5.32). But at higher concentrations the curves flatten out. The abrasion values are similar in magnitude for all the cases. The slight decrease in the abrasion loss is mainly due the decrease in the void volume.

Fig. 5.32 Abrasion loss of modified resin versus EPCN concentration

Table 5.6 Other mechanical properties of modified resins

Properties	Neat	PF-EPCN5				PF-EPCN7				PF-EPCN9			
Wt. % EPCN		5	7.5	10	12.5	5	7.5	10	12.5	5	7.5	10	12.5
Tensile modulus (MPa)	1370±43	1341±61	1384±52	1398±61	1379±38	1357±35	1378±71	1422±54	1422±44	1370±52	1376±61	1410±49	1400±50
Energy absorbed (tensile) (J)	1.14±0.075	1.54±o.62	1.8±0.065	2.26±0.07	2.02±0.06	1.57±0.066	1.87±0.05	2.39±.07	2.12±0.048	1.52±0.06	1.86±0.055	2.02±0.07	1.91±0.06
Flexural modulus (MPa)	3300±150	3450±125	3506±125	3435±134	3395±172	3348±158	3446±126	3600±159	3578±142	3430±138	3560±157	3510±152	3480±136
Energy absorbed (flexural) (J)	0.12±0.0045	0.16±0.0038	0.18±0.0052	0.19±0.0046	0.16±0.0049	0.15±0.0044	0.17±0.0052	0.21±0.0047	0.18±0.0035	0.14±0.0058	0.16±0.0041	0.17±0.0061	0.15±0.0048
Hardness (Shore D)	73±1.5	76.5±1.25	77.5±1.5	78±1.75	78.5±1.0	76.5±1.25	77.5±1.5	79±1.25	79±1.0	76.5±1.5	77.5±1.5	78.5±1.25	78±1.0

Table 5.6 shows other mechanical properties of the neat and modified resins. Both the tensile and flexural modulus values of the modified resins show increase compared to the neat resin. The energy absorption in both tensile and flexural mode of fracture increases with the addition of EPCN. This indicates their toughening character. The hardness also slightly increases with the incorporation of EPCN to the phenolic matrix. EPCN7 modified samples show comparatively better properties than the other two. The improvement in the properties by the EPCN modification is presumably due to the plasticizing effect of the EPCN chains, chain extension effect and decrease in void density.

b)   Soxhlet extraction

As can be seen from the Fig. 5.33 the % soluble matter decreases with EPCN concentration. But at higher concentration of EPCNs the soluble content remains almost constant. The decrease in the soluble content indicates that the EPCNs are chemically anchored to the phenolic matrix and they reduce the amount of leachable material in the cured sample. It is also likely that formation of the by-products of the condensation process is decreased and/or the escape of the condensation by-products is facilitated by the EPCN modification.
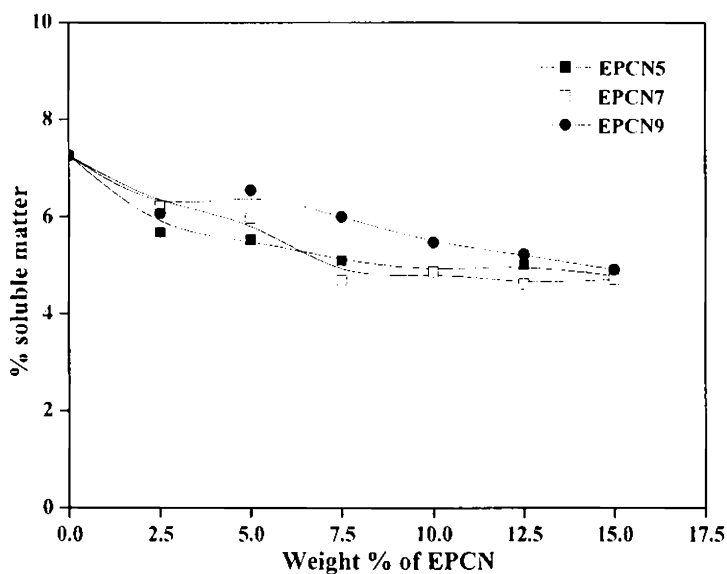
Fig. 5.33 % soluble matter of modified resin versus EPCN concentration

c) Morphological studies

Scanning electron micrographs of the fractured surfaces of the unmodified and EPCN modified PF resins are shown in Fig. 5.34. The size characterisation of the voids is presented in Table 5.7.

It can be seen from the Table 5.7 that the size of the microvoids considerably decreases on blending with EPCN. The microvoid size is minimum for EPCN7 modified sample. EPCN5 modified sample is better than the EPCN9 modified sample. In general, the volume occupied by microvoids is significantly decreased on blending resol resin with EPCN. In terms of void density EPCN7 gives the best performance.

(a)

(b)

(c)

(d)
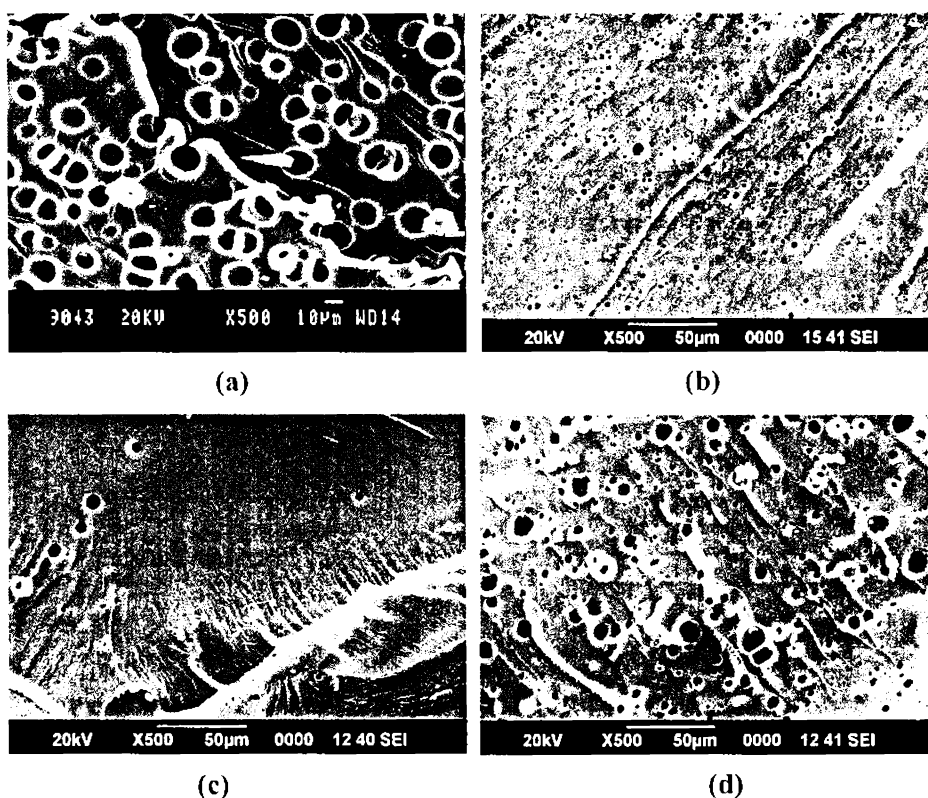
Fig. 5.34 Scanning electron micrographs of fractured surfaces **(a)** neat PF **(b)** PF/EPCN5 **(c)** PF/EPCN7 **(d)** PF/EPCN9

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Table 5.7 Size characterisation of voids in the neat and EPCN modified samples

Samples	$\overline{D_n}$ (µm)	$\overline{D_w}$ (µm)	$\overline{D_a}$ (µm)	$\overline{D_v}$ (µm)	PDI	V_D
Neat	11.95	13.16	12.54	13.75	1.11	0.2000
EPCN5	2.5	2.84	2.67	2.82	1.14	0.045
EPCN7	1.76	2.83	2.23	2.89	1.61	0.0093
EPCN9	3.57	5.05	4.25	4.96	1.41	0.056

The size distribution of microvoids is graphically represented in Fig. 5.35. It is very clear from the graph that the peak shifted to the left on modification. In the neat sample the majority of the voids are in the range 10-15 µm. In both PF/EPCN 5 and PF/EPCN9 the majority have sizes in between 2 and 4 µm. But in PF/EPCN9, the distribution is somewhat broader compared to PF/EPCN5. It can also be seen that the PF/EPCN9 contains voids with larger dimensions. The PF/EPCN7 contains only less number of microvoids and the void density also minimum for this sample.
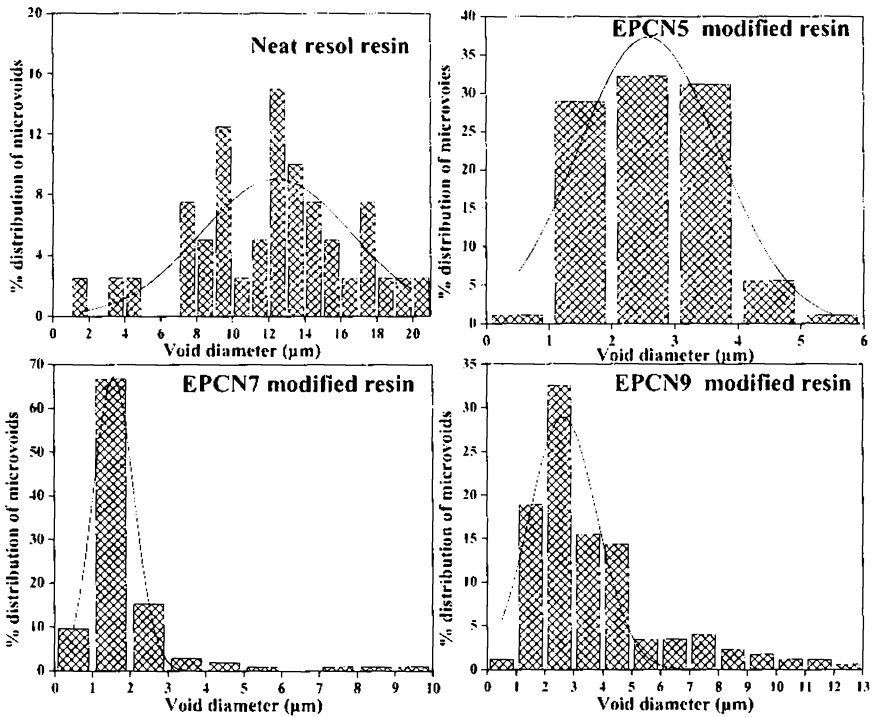
Fig. 5.35 Microvoid distribution diagram of the neat and EPCN modified samples

The morphology of the fractured surfaces of the neat and the modified samples shows significant differences. The smooth surface of fracture of the neat resin is changed to a rough texture on modification. The layered structures in the fractured surface indicate better energy absorption capacity compared to the unmodified samples. The fractured surface of the PF/EPCN7 has a wavy nature with valleys and peaks. These indicate improved toughness and load bearing characteristics.

d)   Thermal studies

i)   DMA

Fig. 5.36 shows the variation of storage modulus with temperature. All the modified samples possess higher storage modulus than the neat resin. This may be attributable to the decrease in the number of microvoids.
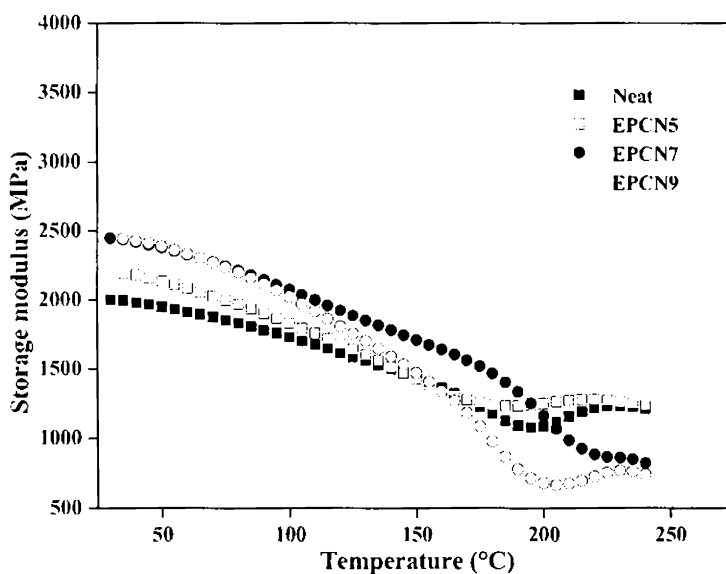
Fig. 5.36 Storage modulus versus temperature
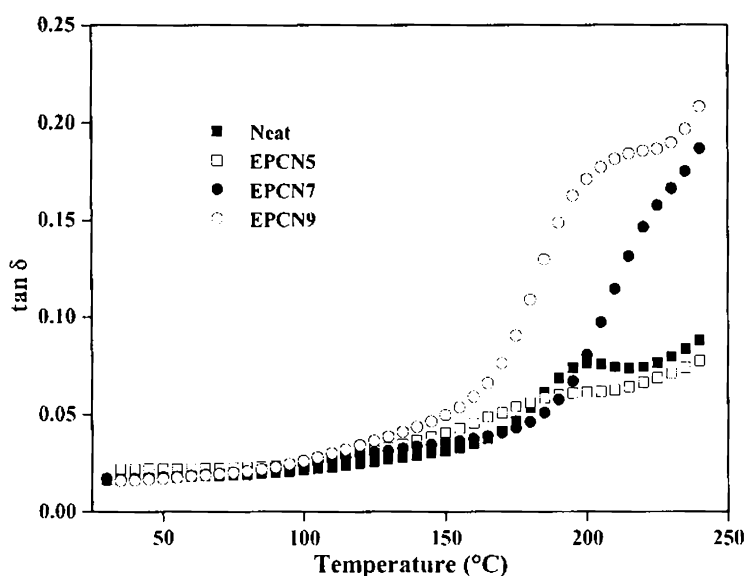
Fig. 5.37 tan δ versus temperature

Fig. 5.37 shows the variation of tanδ with temperature. The tanδ values are higher for the modified samples compared to the neat sample. This indicates that the modified samples have got lower crosslink density and also good damping property.

Table 5.8 T_g, T_g-tanδ and tanδ values of the EPCN modified samples

Sample	T_g (°C)	T_g-tanδ (°C)	tanδ value at different temperatures			
			100°C	150°C	200°C	250°C
Neat	167	201	0.021	0.031	0.076	0.087
EPCN5	143	-	0.025	0.041	0.060	0.078
EPCN7	195	-	0.024	0.035	0.080	0.187
EPCN9	174	212	0.026	0.050	0.170	0.208

T_g values and tanδ values are shown in Table 5.8. A general increase in T_g can be seen for the modified samples which points to a higher stiffness compared to the base resin. The tanδ values are almost similar at low temperature but at higher temperatures they vary widely. The higher values of tanδ indicate better damping property.

ii) TGA
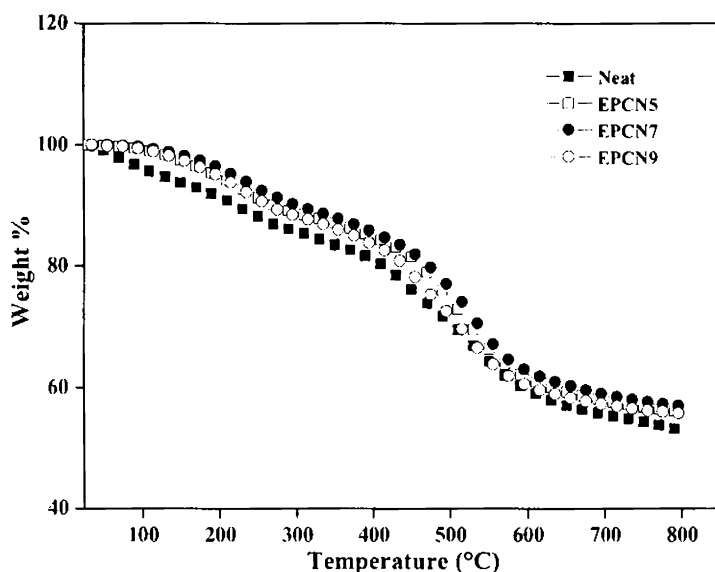
Fig. 5.38 Thermogram of the neat and EPCN modified resins

The thermogram of the neat and the modified resins are shown in Fig. 5.38. It shows that both the neat and the modified samples follow the same mechanism of thermal degradation. The thermal analysis data are shown in Table 5.9.

Table 5.9 Thermal analysis of the neat and EPCN modified samples

Sample	Temperature at different stages of decomposition (°C)					Temp. at maxm. degradation (°C)	Residue (%)
	10%	20%	30%	40%	50%		
Neat	218	410	501	589	>800	533	53
EPCN5	272	463	528	631	>800	528	56
EPCN7	301	473	538	661	>800	535	57
EPCN9	264	442	512	606	>800	523	56

The thermal data shows the higher thermal stability of the EPCN modified samples. The temperature at any stage of the decomposition is higher than that of the neat resin. But the temperature of maximum degradation is slightly decreased on modification. The modified samples also yield higher amounts of residues.

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Thermal degradation kinetics

The kinetics of the thermal degradation reaction was followed using TGA. Kinetic parameters are given in Table 5.10.

Table 5.10 Kinetic parameters of the thermal degradation of modified resols

Samples	E(KJ/mol)	A(X10^4)	Correlation coefficient
Neat	95	2.24	0.9940
EPCN5	111	3.00	0.9970
EPCN7	107	1.31	0.9942
EPCN9	106	1.96	0.9943

The activation energy increases on modification with EPCN. The Arrhenius constant, A, of the modified samples is comparatively lower than that of the unmodified sample. This may be due to the presence of the side chain $-CH_3$, which is susceptible to thermal decomposition.

5.4.5 Modification of PF resin by epoxidised o-cresol novolacs (EOCN)

i)   Mechanical properties

Figs.5.39& 5.40 indicate the variation of the tensile strength and elongation at break respectively with EOCN content.
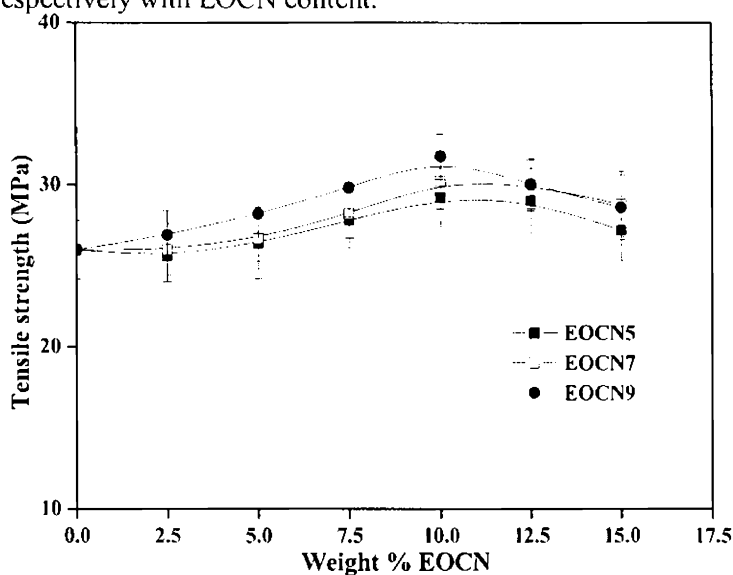
Fig. 5.39 Tensile strength of modified resin versus EOCN concentration
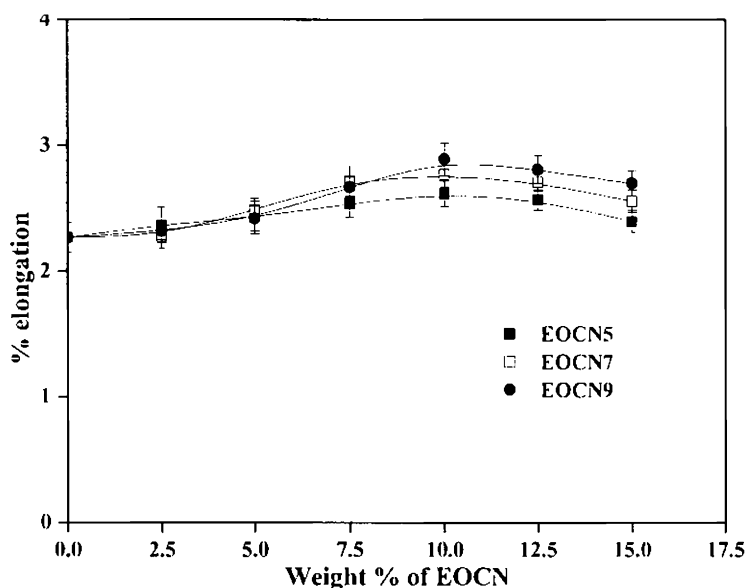
Fig. 5.40 % Elongation of modified resin versus EOCN concentration

The tensile strength and elongation at break values show moderate increases on modification. Both values reach a maximum at about 10-12.5 wt.% of EOCN. But the extent of increase is less compared to EPN and EPCN modified samples. This may be due to the lower epoxy content in the EOCN modifiers and also the presence of the methyl group at the ortho position which can retard the reaction between the epoxy group and –OH groups in the resols (section 5.4.1)

The variation of flexural strength and maximum displacement with EOCN content is shown in Figs. 5.41 & 5.42. The addition of EOCN produces a marginal increase in flexural strength and the maximum displacement occurs at ~ 12.5%. But only a small variation of the properties of the modified samples is observed. The improvement in the properties can be attributed to the reduction in the microvoids and also to the plasticizing effect of the EOCN chains.
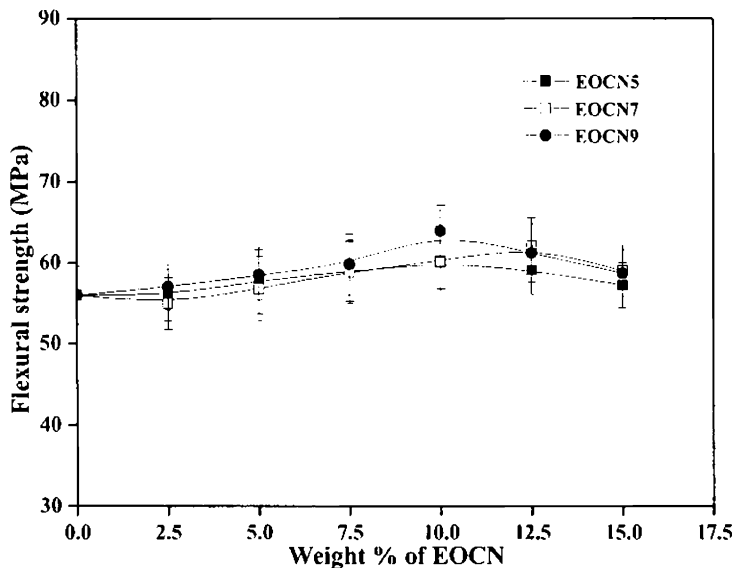
Fig. 5.41 Flexural strength versus EOCN concentration
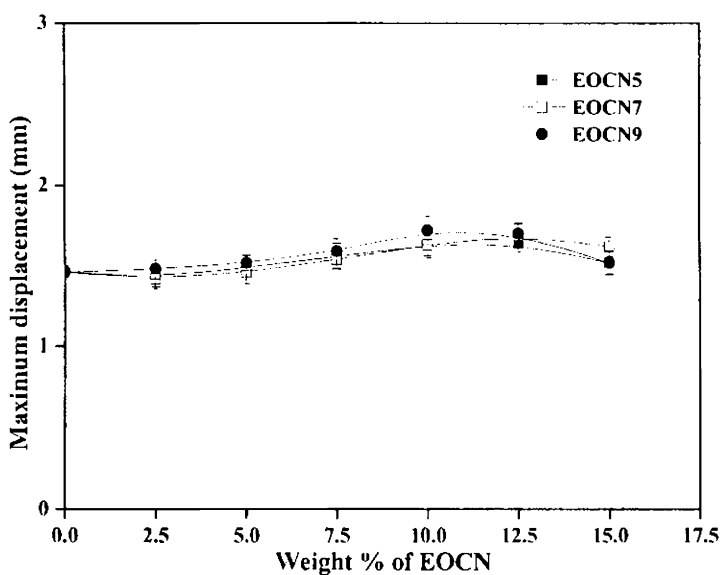
Fig. 5.42 Maximum displacement versus EOCN concentration

The variation of the impact strength of the EOCN modified resin with EOCN content is shown in Fig. 5.43. All the modified resins show increased impact strength compared to the neat resin. The effect is maximum for EOCN9 modified resin at ~ 10-12.5% of EOCN concentration.

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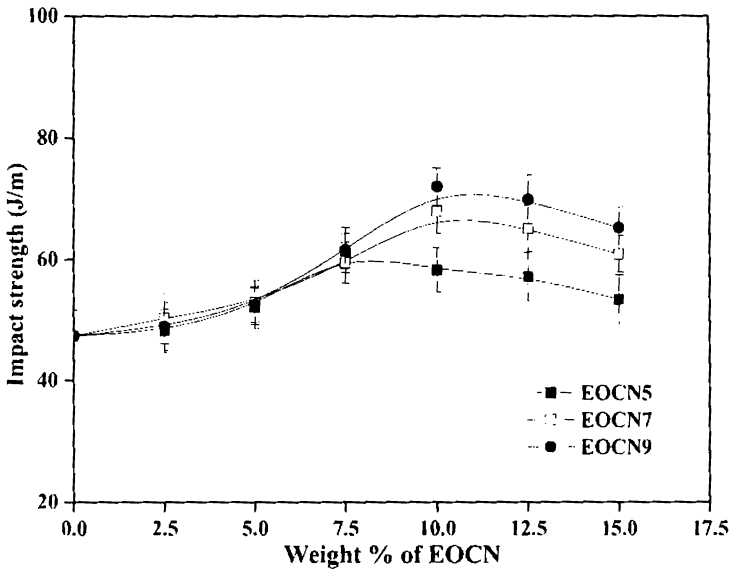
Fig. 5.43 Impact strength of modified resin versus EOCN concentration

The variation of impact strength is almost the same for all the samples until about 7.5% of EOCN. In the case of EOCN9, the impact strength shows notable improvement. The lower void volumes may be responsible for this.
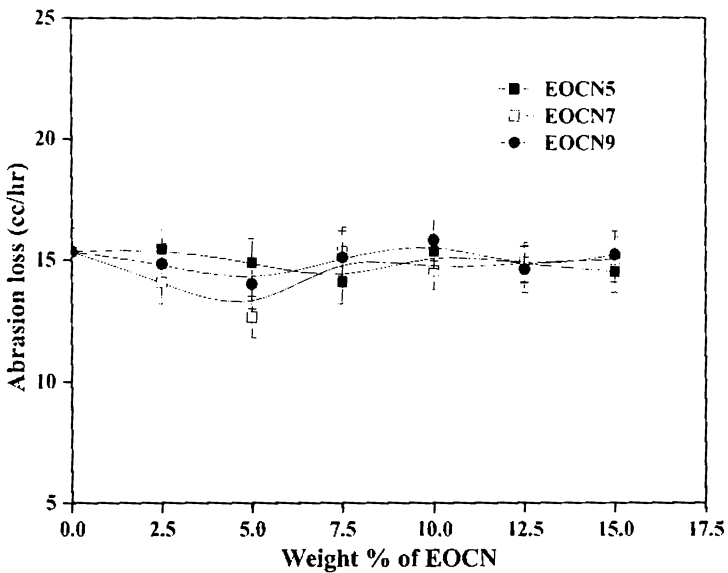
Fig. 5.44 Abrasion loss of modified resin versus EOCN concentration

There is only a very small variation of abrasion loss values (Fig. 5.44). The variations in the other mechanical properties with EOCN content are presented in Table 5.11.

Table 5.11 Other mechanical properties of the neat and modified resins

Properties	Neat	PF-EOCN5				PF-EOCN7				PF-EOCN9			
Wt. % EOCN		5	7.5	10	12.5	5	7.5	10	12.5	5	7.5	10	12.5
Tensile modulus (MPa)	1370±43	1467±81	1420±43	1431±69	1466±58	1460±62	1433±57	1442±75	1433±66	1410±71	1393±68	1453±58	1440±44
Energy absorbed (J)	1.14±0.075	1.39±0.07	1.39±0.09	1.47±0.075	1.42±0.055	1.43±0.08	1.48±0.07	1.62±0.065	1.55±0.055	1.42±0.08	1.49±0.07	1.75±0.075	1.68±0.06
Flexural modulus (MPa)	3300±150	3428±150	3472±165	3416±135	3342±136	3452±134	3398±142	3470±152	3426±141	3410±142	3440±171	3480±162	3375±112
Energy absorbed Flexural mode (J)	0.12±0.0045	0.13±0.0055	0.145±0.004	0.165±0.003	0.16±0.0046	0.12±0.0034	0.135±0.006	0.16±0.004	0.175±0.006	0.13±0.0038	0.165±0.006	0.185±0.005	0.17±0.0048
Hardness (Shore D)	73.0±1.5	75.5±2.0	76.0±1.5	76.5±0.5	75.5±1.0	73.5±1.0	74.0±0.75	75.0±1.5	76.0±1.5	75.0±1.25	76.5±0.5	77.0±0.75	76.5±1.0
Compressive Strength (MPa)	75.0±3.8	81.4±4.0	84.1±3.2	89.7±2.8	91.3±3.1	80.3±4.0	84.2±2.8	88.5±3.5	90.0±3.1	82.0±3.1	86.8±2.6	90.2±3.8	93.6±3.6

The modulus values of the modified samples are slightly higher than that of the neat resin. The stiffness of the modified resin mainly arises from the decrease in the void density. EOCN modified samples show less energy absorption compared to EPN and EPCN modified samples. But they are still better than the neat resin.

The hardness and compressive strength of the resin are increased on blending with EOCN. The increase may be due to the decrease in the void content which in turn increases the density of the material. Among the EOCNs, EOCN9 with the highest epoxy content exhibits the best mechanical properties.

b)   Soxhlet extraction
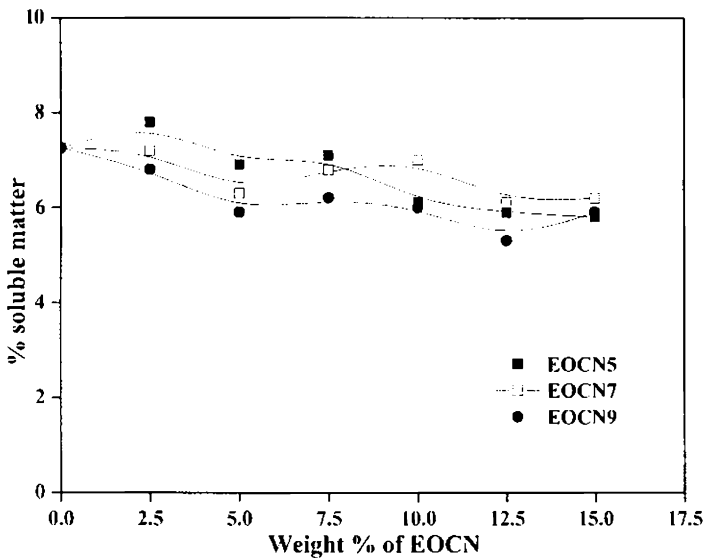
Fig. 5.45 % soluble matter in modified resin versus EOCN concentration

The variation of the amount of soluble matter with EOCN concentration is shown in Fig. 5.45. It can be seen that the soluble matter in the modified resin decreases only to a smaller extent than the other two modifier resins viz, EPNs and EPCN. The presence of a methyl group at ortho position in o-cresol may retard the reaction between the –OH groups and epoxy functionality. Also the lower epoxy content in EOCN indicates the possibility of unreacted o-cresol novolac in the cured resin, which leaches out on extraction. This indicates that it is bound to a lesser extent to the phenolic resin than the other modifiers.

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c) Morphological studies

The scanning electron micrographs of fracture surfaces of unmodified and modified PF are shown in Fig. 5.46. Referring to Micrograph (a) the fracture surface contains a large number of microvoids and the fracture follows a crazing mechanism indicated by the crack lines in between microvoids. Micrograph of EOCN5 modified resin (b) shows that the size of the voids has decreased compared to the neat resin. But the fracture paths are narrow and thin indicating a brittle fracture. Referring to (c), the fractured paths are broader and the texture shows a few ridges. It also contains microvoids, but a large number of voids have disappeared. This leads to better energy absorption compared to Case (b). The fractured surface of (d) contains broader and thicker fractured paths and also uneven contour. The microvoids are also comparatively less in number though a reduction in size is not visible.
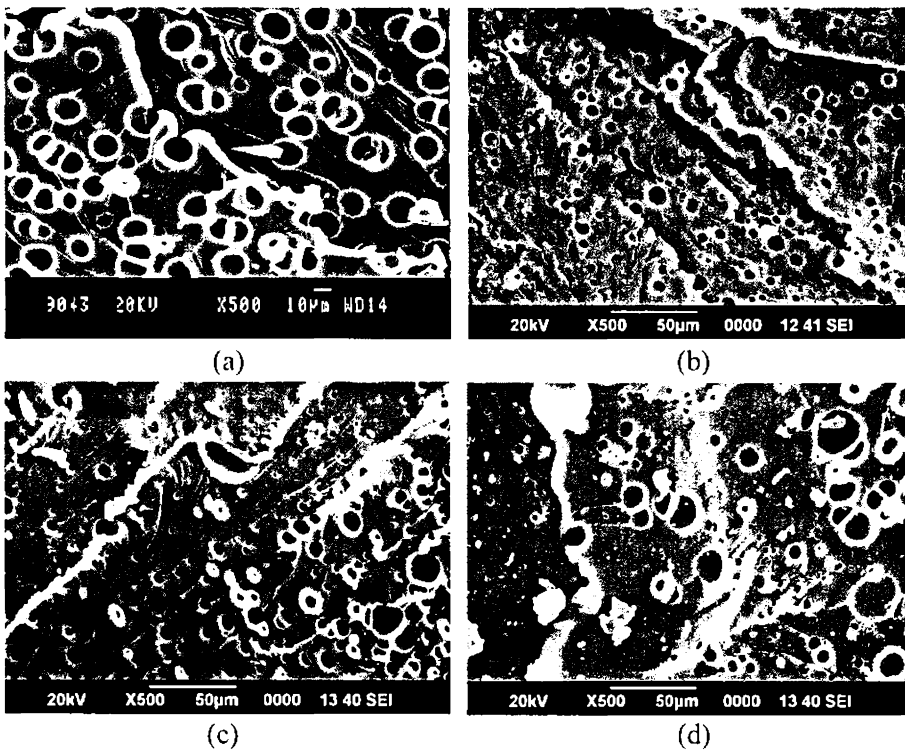
Fig. 5.46 Scanning electron micrographs of fractured surfaces (a) neat PF (b) PF/EOCN5 (c) PF/EOCN7 (d) PF/EOCN9

The void parameters and the distribution of the voids are shown in Table 5.12 and in Fig. 5.47 respectively.

Table 5.12 Size characterisation of voids in the neat and EOCN modified samples

Samples	$\overline{D_n}$ (µm)	$\overline{D_w}$ (µm)	$\overline{D_a}$ (µm)	$\overline{D_v}$ (µm)	PDI	V_D
Neat	11.95	13.16	12.54	13.75	1.11	0.2000
EOCN5	5.08	6.04	5.54	5.94	1.19	0.0770
EOCN7	4.24	6.28	5.16	6.18	1.48	0.0767
EOCN9	5.5	9.38	7.22	8.90	1.69	0.0744
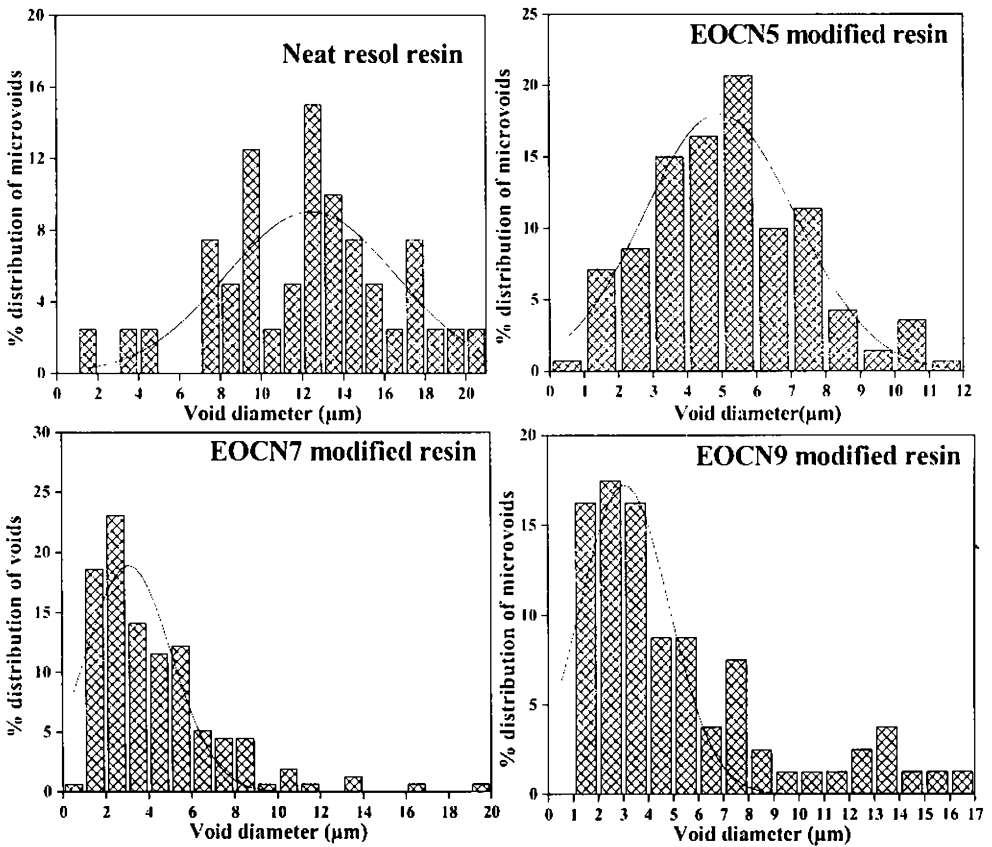
Fig. 5.47 Microvoid distribution diagram of the neat and EOCN modified samples

The void parameters are higher for the EOCN9 modified sample among the modified samples. But the properties of the sample are discernibly better for the EOCN9 modified sample. This may be due to the low volume fraction of void (V_D) of the sample. The void distribution curve shows that both the EOCN7 and EOCN9 modified samples contain a large number of voids of very small size, but the EOCN5 modified sample contains microvoids of similar but larger size (~5-6 μm). This leads to somewhat inferior properties compared to the other two EOCN modified samples.

d)   Thermal properties

i)   DMA

The variation of the storage modulus of the EOCN modified samples with temperature is shown in Fig. 5.48.
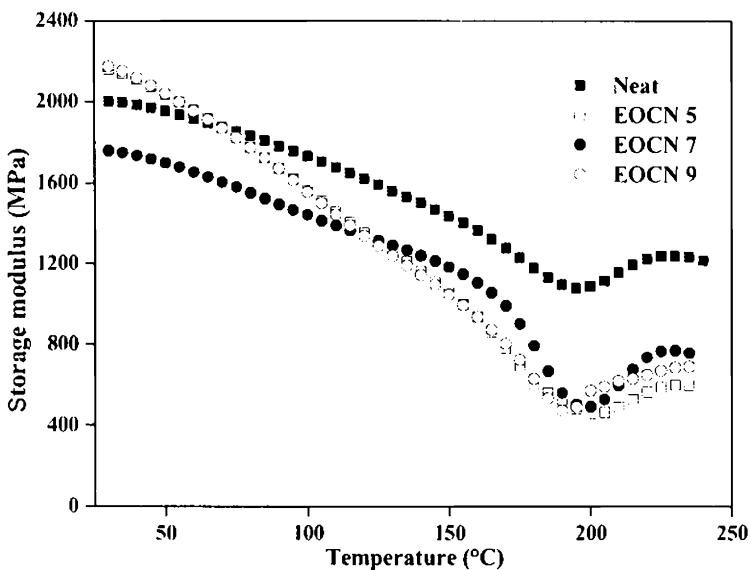
Fig. 5.48 Storage modulus of modified sample versus temperature

The initial E' values of EOCN5 and EOCN9 modified samples are higher than that of the unmodified resin. But ~ above 70°C the storage modulus values of all the modified samples are less than that of the neat resin. The dip in the plots occurs at the same temperature for both neat and modified samples. The depth of the dip in the plots is same for the neat and the modified samples. This

indicates that the modified samples undergo further crosslinking as that of the neat sample.
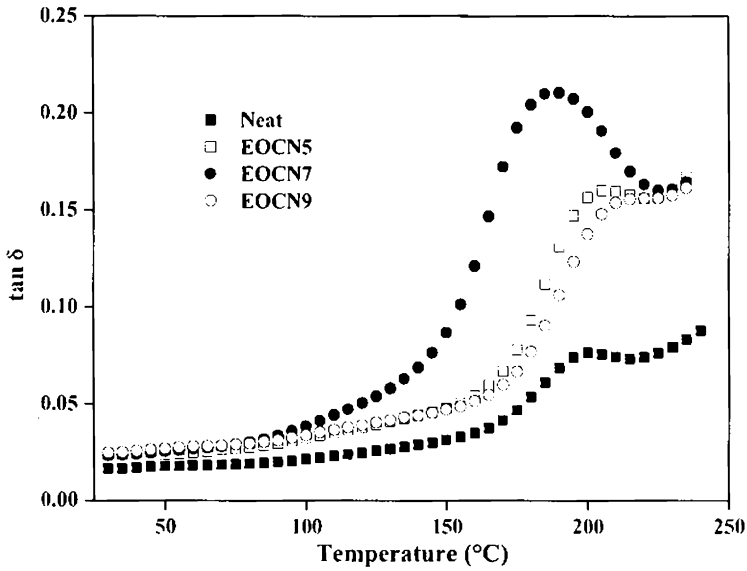
Fig. 5.49 tanδ of modified sample with temperature

Table 5.13 T_g, T_g-tanδ and tanδ values of the EOCN modified samples

Sample	T_g (°C)	T_g-tanδ (°C)	tanδ value at different temperatures			
			100°C	150°C	200°C	250°C
Neat	167	201	0.025	0.04	0.06	0.07
EOCN5	169	202	0.031	0.046	0.147	0.167
EOCN7	168	185	0.033	0.042	0.187	0.164
EOCN9	172	205	0.032	0.046	0.123	0.161

Table 5.13 shows the T_g, T_g-tanδ and tanδ values of the modified resols from Fig. 5.49. All the modified samples have similar T_g values as that of the neat resin. The T_g-tanδ also remains same. But the higher tanδ values of the modified samples indicate improved damping property.

ii) TGA

Fig. 5.50 exhibits the thermograms of the modified samples. It shows that both the neat and the modified samples follow similar mechanism of thermal degradation.
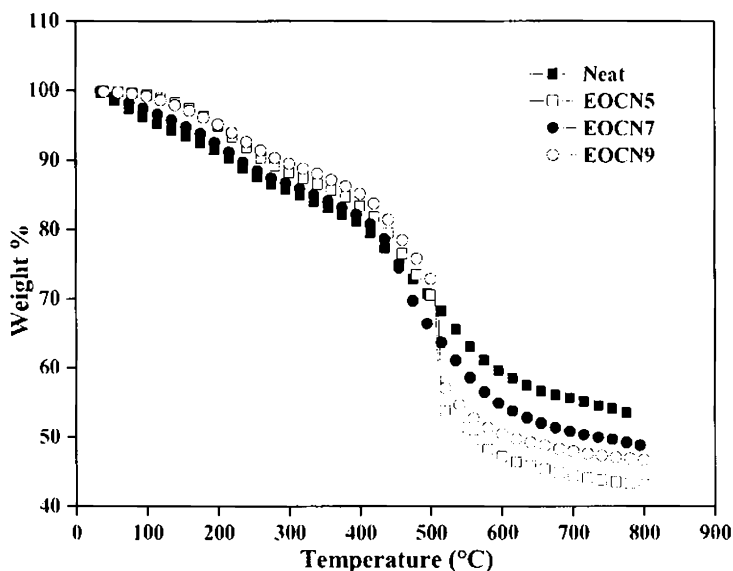
Fig. 5.50 Thermogram of the neat and EOCN modified resins

But the modified samples undergo an acceleration in thermal decomposition at ~ 500 °C. This may be due to the free unepoxidised o-cresol novolacs and unreacted EOCNs present in the modified sample.

Table 5.14 Thermal analysis of the neat and EOCN modified samples

Sample	Temperature at different stages of decomposition (°C)					Temp. of maxm. degradation (°C)	Residue (%)
	10%	20%	30%	40%	50%		
Neat	218	410	501	589	>800	533	53
EOCN5	267	463	527	541	765	505	50
EOCN7	282	435	517	600	>800	521	51
EOCN9	243	441	511	586	>800	512	53

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The thermal analysis data are shown in Table 5.14. The temperature of maximum decomposition has decreased for all the modified samples. The amount of residue is similar for the neat and modified samples.

Thermal degradation kinetics

Table 5.15 Kinetic parameters of the thermal degradation of modified resols

Samples	E(KJ/mol)	A(X10^4)	Correlation coefficient
Neat	95	2.24	0.9940
EOCN5	93	0.09	0.9902
EOCN7	99	0.53	0.9966
EOCN9	98	1.20	0.9963

The kinetics of the thermal degradation reaction was followed using TGA. Kinetic parameters from are given in Table 5.15. The activation energies of the neat and modified samples are almost similar. But the Arrhenius constant decreased considerably. This is mainly because of the –CH$_3$ side chain as the hydrocarbon side chains are more susceptible to thermal degradation. The thermal stability of the EOCN modified samples is considerably less than that of the EPN and EPCN modified samples.

5.4.6 Modification of PF resin by commercial epoxy resin, commercial EPN and epoxidised cardanol

a)   Mechanical properties

Referring to Fig. 5.51 tensile strength values obtained by adding EPN(C) are somewhat higher than that of the neat resin. Here the better performance of EPN (C) modified resin is mainly due to its structural compatibility. Both EC and Epoxy (C) cause steady reduction of tensile strength.
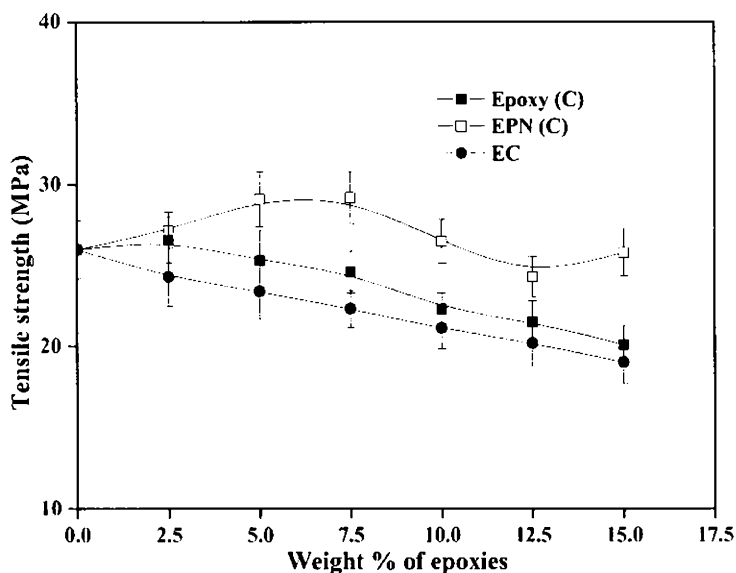
Fig. 5.51 Tensile strength of modified resin versus epoxy concentration

The variation of flexural strength of the cured resin with epoxy content is shown in Fig. 5.52. Both Epoxy (C) and EPN (C) show similar variation of the flexural strength. The moderate increase in the strength may be attributed to the decrease in the number of voids. The EC modified samples do not show any appreciable change in flexural strength.
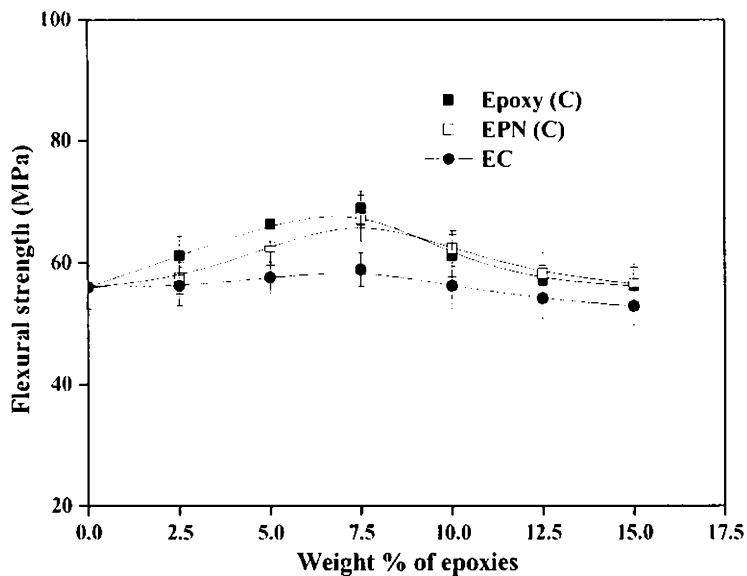
Fig. 5.52 Flexural strength of modified resin versus epoxy concentration
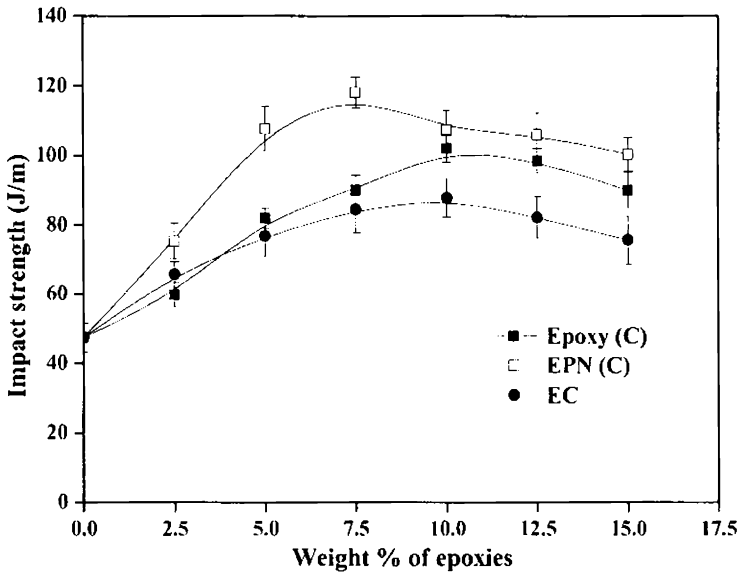
Fig. 5.53 Impact strength of modified resin versus epoxy concentration

Fig. 5.53 shows the variation of impact strength with epoxy content. The effect is maximum for EPN (C) at 7.5 wt.%. The impact strength of EC modified samples is poor compared to the other epoxies. This may be mainly due to their inefficiency in controlling the microvoids compared to the other two.
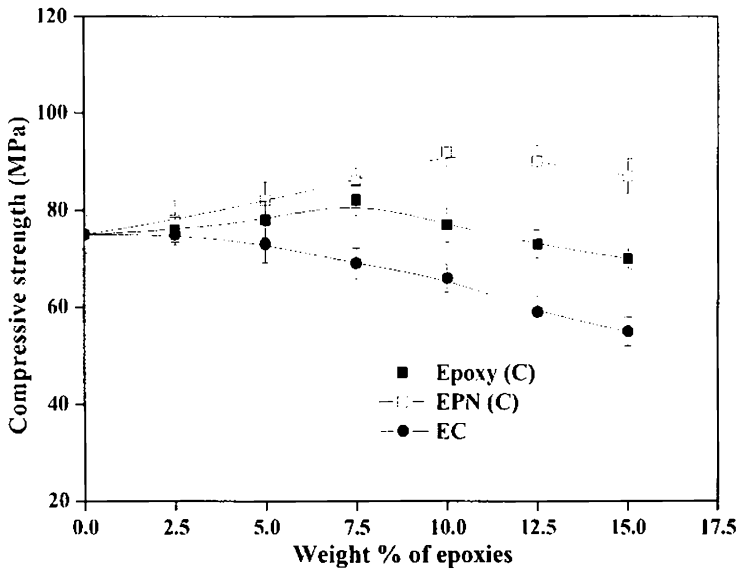
Fig. 5.54 Compressive strength of modified resin versus epoxy concentration

The variation of compressive strength of the modified samples is shown in Fig. 5.54. An appreciable improvement in compressive strength is shown only by EPN (C) modified samples. This may be due to the decrease in the void volume. The Epoxy (C) modified samples show a slight increase in the compressive strength values, but at higher concentrations it disappears. This may be due to incompatibility at higher concentrations. The EC modified samples exhibit a downward trend in compressive strength values.

Fig. 5.55 shows the variation of abrasion loss on modification. The EPN (C) modified samples show the least abrasion loss where as the EC modified one exhibits a steady increase. The poor abrasion resistance of PF/EC may be due to the low crosslink density, larger microvoid content and monofunctionality.
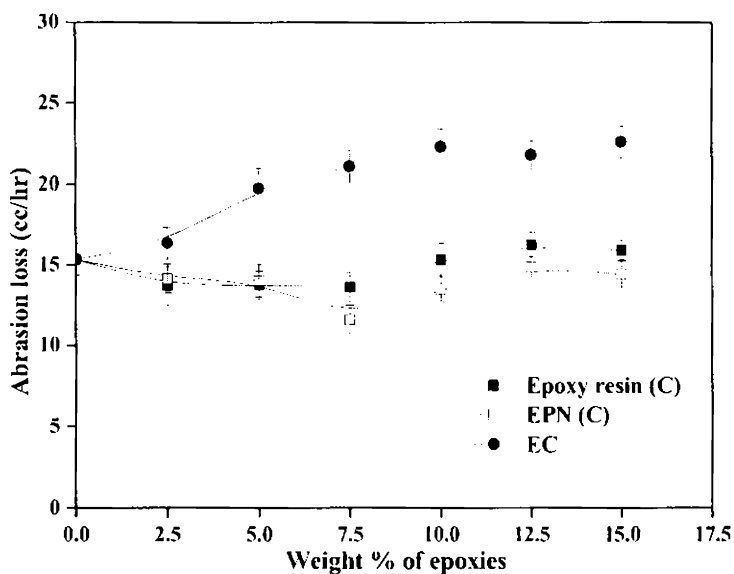
Fig. 5.55 Abrasion loss of modified resin versus epoxy concentration

b)   Soxhlet extraction

The amount of soluble matter on Soxhlet extraction of the modified samples is shown in Fig. 5.56.

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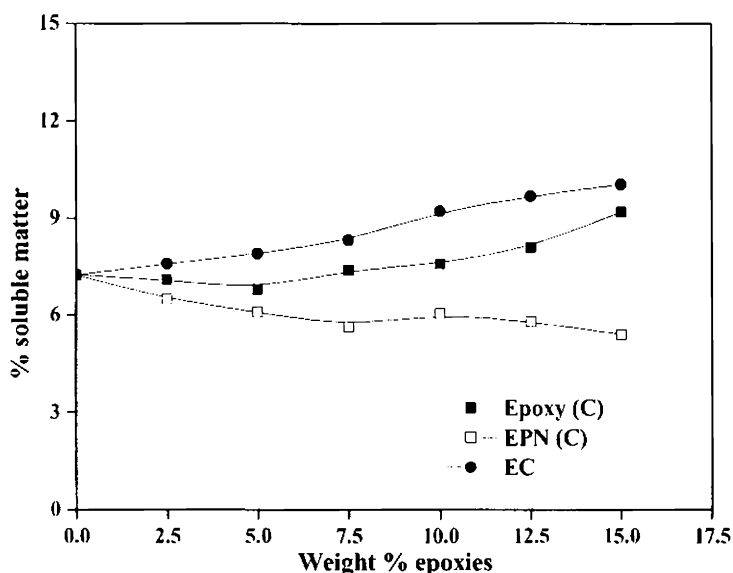
Fig. 5.56 % soluble matter versus epoxy concentration

The presence of soluble matter is less compared to the neat sample only in the EPN (C) modified resin. Both PF/Epoxy (C) and PF/EC samples contain higher amounts of soluble matter especially at higher concentrations of epoxies. In PF/Epoxy (C), the incompatibility at higher concentrations leads to leaching out during extraction. The diluents and other additives in the commercial epoxy may be responsible for this. But in the case of PF/EC samples, the EC might contain unreacted cardanol molecules.

c)   **Morphological studies**

Scanning electron micrographs of the fractured surfaces of the unmodified and modified PF resins are shown in Fig. 5.57. The size characterisation of the voids is presented in Table 5.16. Referring to the Micrograph (a) the fracture surface contains a large number of microvoids and it follows a crazing mechanism as indicated by the crack lines in between microvoids. The micrograph of PF/Epoxy resin (b) contains microvoids with small size, but their number is very high. EPN(C) modified resin fracture surface is shown in Micrograph (c). It contains fracture paths with feathery texture. They are also discontinuous. These

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are indications of improved toughness and load bearing characteristics. The fractured surface also contains lengthy fault lines.
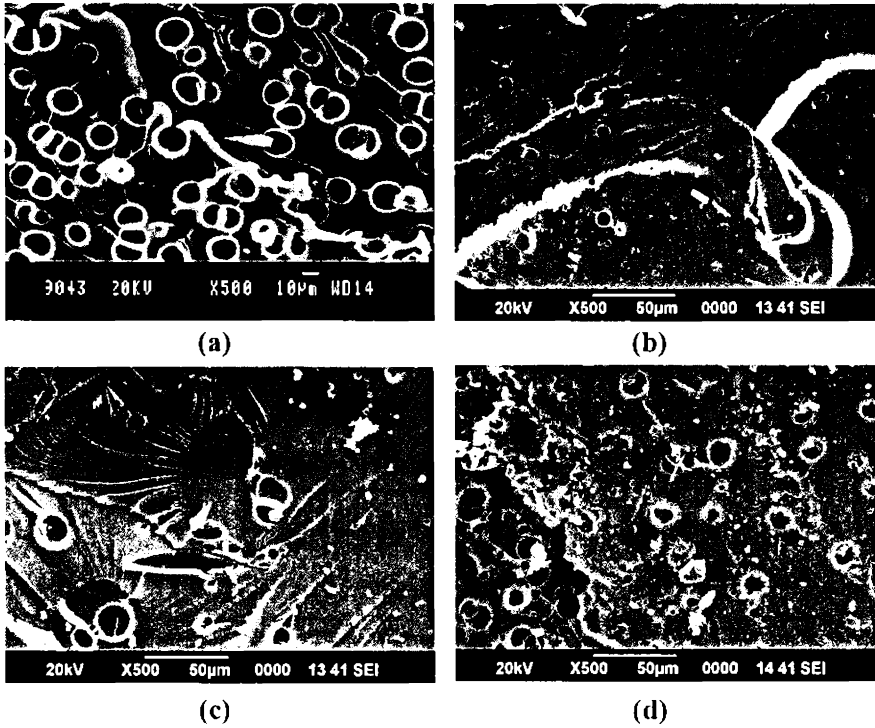
Fig. 5.57 Scanning electron micrographs of fractured surfaces (a) neat PF (b) PF/Epoxy (C) (c) PF/EPN (C) (d) PF/EC

This may be due to the presence of impurities or diluents in the commercial EPN. This can adversely affect the properties of the modified resin. The microvoids in PF/EC, as indicated by (d), is less in number compared to the neat resin. But the fracture surface shows a brittle nature.

Table 5.16 Size characterisation of voids in the neat and modified samples

Samples	$\overline{D_n}$ (µm)	$\overline{D_w}$ (µm)	$\overline{D_a}$ (µm)	$\overline{D_v}$ (µm)	PDI	V_D
Neat	11.95	13.16	12.54	13.75	1.11	0.2000
Epoxy(C)	2.39	3.04	2.70	2.99	1.27	0.0814
EPN (C)	6.45	11.01	8.43	9.905	1.71	0.0330
EC	7.59	10.4	8.88	9.89	1.37	0.0770

The size of the voids is larger in the neat sample. The void size is minimum in Epoxy resin(C) modified sample. But the total void volume is high compared to other modified samples. The EC modified sample contains relatively larger microvoids.

The size distribution of microvoids in the modified samples is graphically represented in Fig. 5.58.
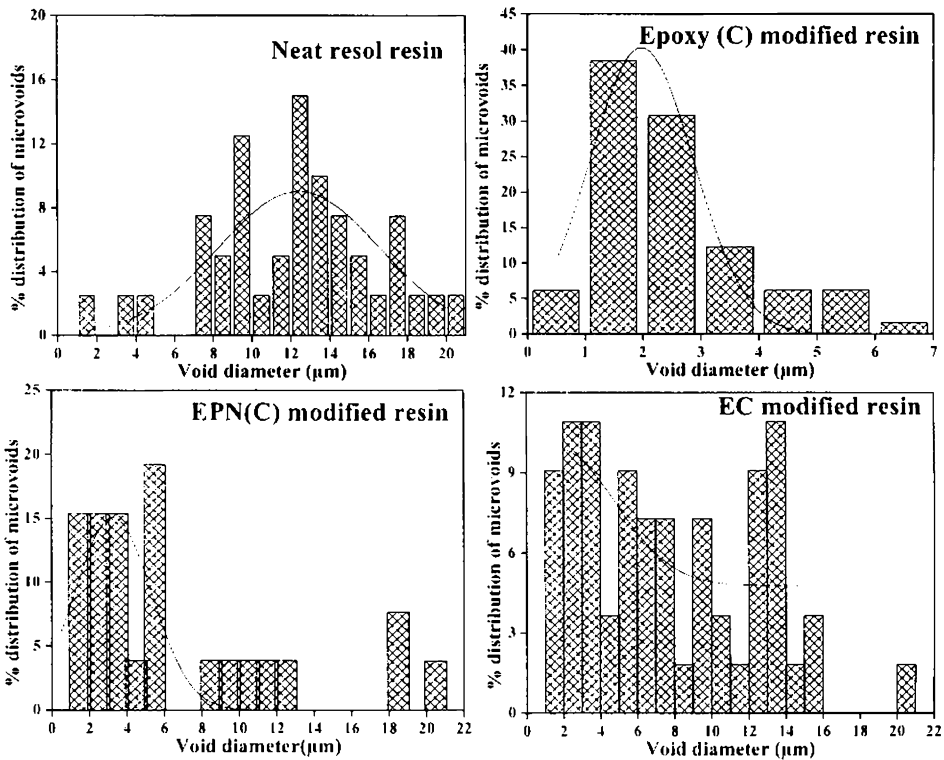
Fig. 5.58 Microvoid distribution diagram of the neat and modified samples

The distribution of the microvoids shifts towards left of the plot. In PF/EPN(C), most of the microvoids have ~ 4 μm size and a few have bigger sizes. In spite of this it possesses better properties. This indicates that the improved properties are not only due to microvoid reduction but also due to toughening. The EC/PF resin contains microvoids of big and small sizes in equal quantities. This is reflected in the properties also.

d) Thermal properties

i) DMA

Fig. 5.59 shows the variation of E' with temperature for neat and modified samples. The initial modulus of the samples is almost the same as that of the neat resin except for PF/EPN (C). As the temperature is increased the modulus values of all the modified samples show a steep fall.
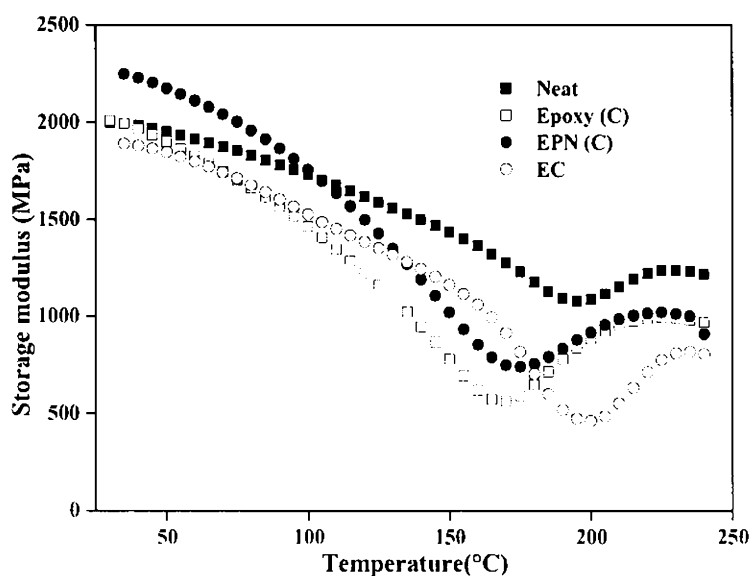
Fig. 5.59 Storage modulus versus temperature

The dip in the E' plots is almost similar for the neat and PF/EPN(C) resins. This indicates that they have undergone the same degree of crosslinking. But the other two modified samples undergo further crosslinking at a greater extent compared to the neat and EPN (C) modified samples.

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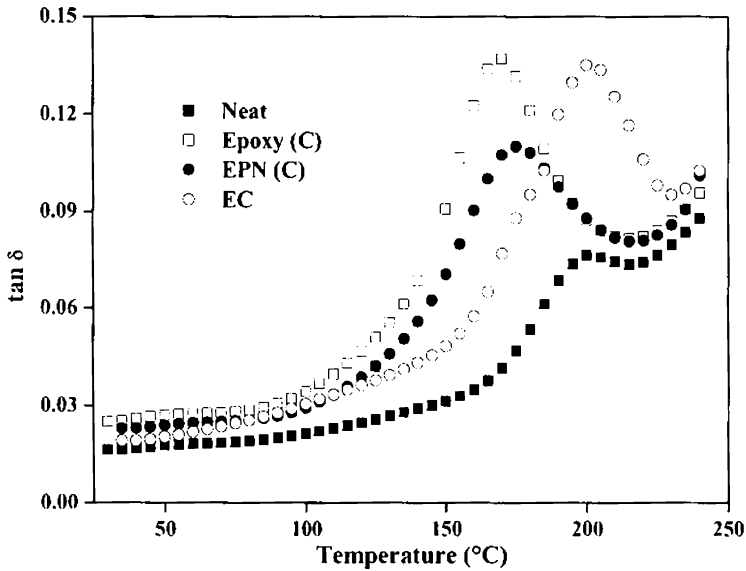
Fig. 5.60 tanδ versus temperature

The variation of tanδ of the modified samples with temperature is shown in Fig. 5.60. All the samples possess higher tanδ values than the neat resin.

Table 5.17 T_g, T_g-tanδ and tanδ values of the modified samples

Sample	T_g (°C)	T_g-tanδ (°C)	tanδ value at different temperatures			
			100°C	150°C	200°C	250°C
Neat	167	201	0.025	0.040	0.060	0.070
Epoxy resin C)	145	170	0.035	0.090	0.087	0.096
EPN (C)	150	174	0.029	0.070	0.088	0.100
EC	157	201	0.030	0.048	0.135	0.102

Table 5.17 shows the T_g, T_g-tanδ and tanδ values of the modified resols. The T_g values of the modified samples are less than that of the neat sample. The T_g-tanδ values also decrease on modification showing the flexibility of the modified samples. The tanδ values are slightly higher than that of the neat sample indicating lower crosslink density and also better damping property.

ii) TGA

Thermal degradation analysis values of the modified samples are shown in the Table 5.18. The temperature of maximum degradation have apparently decreased indicating reduced thermal stability of these samples especially for Epoxy (C) and EC modified samples. The final residue remains almost the same in all the samples.

Table 5.18 Thermal analysis of the neat and modified samples

Sample	Temperature at different stages of decomposition (°C)					Temp. at maxm. degradation (°C)	Residue (%)
	10%	**20%**	**30%**	**40%**	**50%**		
Neat	218	410	501	589	>800	533	53
Epoxy (C)	248	417	483	580	765	457	55
EPN (C)	291	431	502	578	>800	514	54
EC	277	434	496	571	>800	441	54

Table 5.19 presents the kinetic parameters of thermal degradation of the neat and modified samples. It can be seen that the activation energy of the modified samples has decreased compared to the neat sample. The Arrhenius constant has also lessened considerably, except in the case of PF/EPN(C). This indicates a decrease in the thermal stability of the other two modified resins.

Table 5.19 Kinetic parameters of the thermal degradation of modified resols

Sample	E(KJ/mol)	A(X10⁴)	Correlation coefficient
Neat	95	2.240	0.9940
Epoxy (C)	89	0.012	0.9958
EPN (C)	110	5.20	0.9960
EC	91	0.15	0.9955

Table 5.20 shows the summary of the mechanical properties of modified resols. The % improvement in each property is shown with the concentration of epoxy resin.

Table 5.20 The overall improvement in mechanical properties of the modified resols

Properties	% Improvement/ composition (wt %)											
	EPN			EPCN			EOCN			Other epoxies		
	EPN5	EPN7	EPN9	EPCN5	EPCN7	EPCN9	EOCN5	EOCN7	EOCN9	Epoxy (C)	EPN(C)	EC
Tensile strength (MPa)	17/10	28/7.5	34/7.5	18/12.5	28/10	21/10	12/12.5	16/10	22/10	-14/10	12/7.5	-19/10
Elongation on at break (%)	15/10	26/7.5	40/7.5	55/10	61/10	37/10	15/10	22/10	27/10	19/7.5	45/75	43/7.5
Flexural strength (MPa)	14/10	18/7.5	22/7.5	19/7.5	21/10	14/10	7/10	11/12.5	14/10	23/7.5	20/7.5	5/7.5
Maximum displacem ent (mm)	30/10	39/7.5	47/7.5	24/7.5	37/10	28/10	12/12.5	16/12.5	18/10	27/7.5	41/7.5	37/7.5
Impact strength (J/m)	47/10	50/10	71/12.5	103/10	112/12.5	88/10	30/7.5	43/10	52/10	115/10	126/10	84/10
Compressive Strength (MPa)	50/10	62/10	70/10	25/10	41/10	31/10	22/12.5	20/12.5	25/12.5	9/7.5	23/10	-12/10

5.5 Conclusion

Epoxidised novolacs can be used to modify resol resins. The mechanical properties of the modified resins are in general better compared to the unmodified resol resin. The efficacy of the modifier depends on the P/F ratio of the novolac resin and also on the epoxy content of the modifier.

Among the epoxidised novolacs, the EPN synthesised in the laboratory imparts the best tensile and compressive strength whereas EPCN gives the greatest improvement in flexibility and impact properties. In all cases epoxidised novolacs with lower P/F ratio show better properties. Modification by EC shows inferior properties because of its monomeric nature. Epoxy (C) and EPN (C) show improved impact strength which is similar in magnitude to that of EPN and EPCN modified samples.

The morphology of the fractured surface of the modified samples indicates that the modification leads to a maximum decrease in the micro void dimensions and void density in the case of EPN and EPCN.

The increased tanδ values of the modified samples from DMA indicate some lowering of the crosslink density, which leads to somewhat better energy absorption by the modified samples.

Thermal stability of the modified samples is comparatively better than that of the neat sample as indicated by the activation energies of the modified samples. The Epoxy (C) and EC modified samples show inferior thermal properties compared to the neat samples.

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Chapter **6**

MODIFIED PHENOLIC RESOLS WITH FIBER REINFORCEMENT

6.1   Introduction

Fiber reinforced polymer composites are finding increasing use in many applications such as high-strength, lightweight structures and components in transport, building and maritime industries. Phenolic resins and glass/phenolic composites are inherently fire-retardant and have superior flammability properties to polyester, vinyl ester and epoxy resins and composites [1-3]. In addition to this, phenolics generate only low levels of toxic combustion products and smoke when they do burn. But their mechanical properties and durability are unsatisfactory for use in complex structural designs. These properties need to be improved to be on par with glass/polyester, glass/vinyl ester or glass/epoxy composites. Phenolics have good bondability to natural fibers due to chemical interaction between the cellulose in the natural fibers and the reactive groups in the phenolic resin [4]. The modification of phenolic resin may influence the bondability to glass as well as natural fibers.

The effect of matrix modification on the mechanical properties of glass and cotton-reinforced composites is discussed in this chapter. Glass reinforced and cotton reinforced laminates made of modified resins as well as unmodified resin were prepared using woven roving glass mat and cotton cloth. Mechanical properties such as tensile strength, flexural strength, impact strength, dynamic mechanical properties and water absorption characteristics were compared. The fracture behaviour was studied by SEM.

6.2   Experimental

6.2.1 Materials

Woven roving mat (WRM- Binani-IS:11272/BS:3749, 610g/m^2) was supplied by M/s Sharon Engineeering Enterprises, Cochin. Cotton cloth was supplied by Ambika Mills, Coimbatore (100 grams per square meter and 40 yarns per square inch).

6.2.2 Preparation and testing of glass and cotton reinforced laminates

The dried resins were mixed with methanol (30%) prior to application on glass and cotton mats. After each treatment, the excess resin was repeatedly

pressed out of the mats with a rubber roller to ensure good penetration. 13 plies of glass mat and 14 plies of cotton mat cut to size were used to make laminates. The resin-impregnated laminate was kept at room temperature for two days and subsequently in an air oven at 70°C for one hour. It was then placed in between two polished steel plates at 150°C and pressed for 30 minutes at a pressure of 180kg/cm². The molded sheets were ~ 2mm thickness.

Glass and cotton reinforced laminates were also prepared using reactive blends of PF/UP and PF/EPN. These reactive blends were prepared by taking optimum concentrations (7.5% wt.% of UP and 10 wt.% of epoxidised novolacs and epoxies, Sections 4.3.2B & 5.3.4)

i)   Void content

The theoretical density of the composites was calculated according to the following ASTM equation (ASTM 2734-94)

$$T_d = \frac{100}{\left[\dfrac{R}{D} + \dfrac{r}{d} \right]} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6.1)$$

where T_d is the theoretical density. R and r represent resin and fiber wt.% respectively. D and d denote densities of resin and fiber respectively.
The void content is calculated using the equation

$$V = \frac{100(T_d - M_d)}{T_d} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6.2)$$

where T_d is the theoretical composite density, M_d measured composite density and V the void content in volume percentage.

ii)   Mechanical

Specimens used for testing were cut from the reinforced laminates using a diamond tipped cutting wheel. The tensile and flexural properties (ASTM D 638 and D 790 respectively) were tested on a Shimadzu Autograph (AG-1 50 kN)

Universal Testing Machine. Impact tests were conducted on a Resil Impact Analyser (Junior) according to ASTM D 256.

iii)   Water sorption studies

Moisture penetration into composite materials occurs by three different mechanisms [5]. The main process consists of diffusion of water molecules into the microgaps between polymer chains. The other common mechanisms are capillary transport into the gaps and flaws at the interfaces between fibers and polymer because of incomplete wetting and also impregnation and transport by microcracks in the matrix formed during the fabricating process [6,7]. Moisture absorption may induce irreversible changes in polymers and composites such as chemical degradation, cracking and debonding. These damages to the material will also change the weight gain behaviour of the material correspondingly [8].

Crosslinked thermoset matrix has practically no sorption. The water penetration and diffusion are mainly through the fiber-matrix interfacial region and cross sectional portions of the fiber at the ends by capillary mechanism. This mechanism involves flow of water molecules between the matrix and fibers [9]. Hence extent of fiber-matrix adhesion is an important factor in determining the sorption behavior of the composite.

For water sorption experiments square samples of 10mmX10mm size were cut from the composite sheets. Corners of the samples were chamfered to avoid non-uniform water diffusion. The thickness of the samples was measured. They were subsequently immersed in distilled water. Increase in weight of the samples was noted at predetermined time intervals. This process was continued till equilibrium was reached. The mole percent uptake of water at time t by 100g of the composite, Q_t, was plotted against time. The Q_t values were calculated using the equation[10].

$$Q_t = \frac{M_{(w)} / M_{r(w)}}{M_{i(s)}} \times 100 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (6.3)$$

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where $M_{(w)}$ is the mass of water at time t, $M_{r(w)}$ the relative molecular mass of water, ie. 18, $M_{i(s)}$ is the initial mass of the sample. When equilibrium was reached, Q_∞ was taken as the mole % uptake at infinite time. Sorption curves were obtained by plotting mole % uptake against square root of time. The effective diffusivity, D of the composite-solvent system was calculated from the initial portion of the sorption curves using the equation [11]:

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \quad \text{...(6.4)}$$

where θ is the slope of the initial linear portion of the sorption curves of Q_t vs $t^{1/2}$, and h the initial sample thickness.

Another parameter called sorption coefficient was calculated from the equilibrium swelling using the relation,

$$S = \frac{M_\infty}{M_0} \quad \text{..(6.5)}$$

where M_0 is the mass of the initial polymer sample, M_∞ is the mass of the solvent taken up at equilibrium swelling. The permeability coefficient P, which implies the net effect of sorption and diffusion, is given by the relation [12].

$$P = DS \quad \text{...(6.6)}$$

6.3 Results and Discussion
6.3.1 Hardness, density and void content

The composition, hardness and density of the composites are given in Tables 6.1 and 6.2. The samples contain 51-55 volume % of glass fibers and 42-48 volume % of cotton. The density of the glass reinforced composites of UP modified PF resins is greater than that of the unmodified reinforced composite. The hardness values also follow the same trend.

Table 6.1 Hardness, density and void content values of glass/PF/UP & cotton/PF/UP composites

	Composite	Glass/Cotton vol. %	Hardness (Shore D)	Density Experimental (g/cc)	Density Theoretical (g/cc)	Void content Theoretical (vol.%)
Glass/PF	Glass/PF	51.7	78	1.8468	1.9069	3.15
	Glass/PF/UP1	53.0	87	1.9149	1.9553	2.07
	Glass/PF/UP2	53.1	86.5	1.9263	1.9597	1.70
	Glass/PF/UP3	53.9	87	1.9561	1.9886	1.52
	Glass/PF/UP4	54.2	87.5	1.9669	1.9992	1.63
	Glass/PF/UP2a	51.5	88	1.8548	1.8988	2.32
	Glass/PF/UP2b	51.6	88.5	1.8593	1.9052	2.40
	Glass/PF/UP2c	54.8	88.5	1.9953	2.0236	1.40
	Glass/PF/UP2d	51.4	78	1.8537	1.8975	2.30
Cotton/PF	Cotton/PF	45.4	75	1.3320	1.3644	2.37
	Cotton/PF/ UP1	42.6	75	1.3100	1.3563	3.41
	Cotton/PF/ UP2	42.5	75	1.3231	1.3563	2.45
	Cotton/PF/ UP3	42.9	75.5	1.3201	1.3575	2.76
	Cotton/PF/ UP4	42.2	75.5	1.3207	1.3556	2.60
	Cotton/PF/ UP2a	42.2	76	1.3475	1.3555	0.60
	Cotton/PF/ UP2b	45.7	75	1.3549	1.3777	1.65
	Cotton/PF/ UP2c	42.8	75	1.3286	1.3570	2.10
	Cotton/PF/ UP2d	42.6	76	1.3450	1.3565	0.85

Table 6.2 Hardness, density and void content values of Glass/PF/epoxy & Cotton/PF/epoxy composites

	Composite	Glass/Cotton (vol. %)	Hardness (Shore D)	Density Experimental (g/cc)	Density Theoretical (g/cc)	Void content Theoretical (vol.%)
Glass/PF	Glass/PF	51.7	78.0	1.8468	1.9069	3.15
	Glass/PF/EPN5	53.1	77.5	1.8754	1.9549	4.07
	Glass/PF/EPN7	51.5	77.0	1.8522	1.8936	2.20
	Glass/PF/EPN9	53.0	78.5	1.8916	1.9482	2.90
	Glass/PF/EPCN5	52.2	79.5	1.9169	1.9268	0.50
	Glass/PF/EPCN7	52.0	78.5	1.8673	1.9105	2.26
	Glass/PF/EPCN9	53.0	77.5	1.8858	1.9514	3.36
	Glass/PF/EOCN5	51.0	76.0	1.8029	1.8811	4.16
	Glass/PF/EOCN7	54.0	77.0	1.9333	1.9929	2.99
	Glass/PF/EOCN9	54.4	75.0	1.9269	2.0065	3.98
	Glass/PF/Epoxy resin (C)	51.1	76	1.7999	1.8846	4.49
	Glass/PF/ECN (C)	51.6	78	1.8216	1.9040	4.33
	Glass/PF/EC	52.0	76	1.8089	1.9181	5.69
Cotton/PF	Cotton/PF	45.4	75	1.3320	1.3644	2.37
	Cotton/PF/EPN5	46.8	73	1.3766	1.3673	0
	Cotton/PF/EPN7	44.0	75.5	1.3752	1.3598	0
	Cotton/PF/EPN9	47.8	74.5	1.3505	1.3695	1.39
	Cotton/PF/EPCN5	47.8	75	1.3613	1.3695	0.60
	Cotton/PF/EPCN7	44.2	76	1.3586	1.3604	0.13
	Cotton/PF/EPCN9	45.0	74.5	1.3590	1.3622	0.23
	Cotton/PF/EOCN5	48.0	73.5	1.3360	1.3714	2.58
	Cotton/PF/EOCN7	48.0	75.5	1.3494	1.3708	1.56
	Cotton/PF/EOCN9	42.9	75.5	1.3221	1.3572	2.58
	Cotton/PF/Epoxyresin(C)	42.5	75.5	1.3308	1.3562	1.87
	Cotton/PF/EPN(C)	44.2	75	1.3223	1.3604	2.8
	Cotton/PF/EC	44.6	76	1.3450	1.3625	1.28

The void volume of the composites containing UP modified phenolics has decreased considerably compared to epoxy modified phenolic composites. The decrease in the void volume increases the density of the composite which can cause an increase in the hardness as well. The void content affects the mechanical properties of the composite. A nearly linear relationship exists between composite void content and mechanical properties of the composites [13].

The density of the cotton fiber reinforced UP modified resin composites shows a general decrease. The variation of the void content does not follow any discernible trend. Hardness of these composites almost remains the same. The epoxidised novolac modified resin composites exhibit an increase in the density and decrease in the void volume; but the hardness remains the same.

6.3.2 Mechanical properties

Fig. 6.1 indicates the tensile strength of laminates with UP modified phenolic resins as the matrix. The glass-reinforced modified resins show increased tensile strength compared to that of unmodified reinforced resins. The improvement in the tensile strength may be attributed to the decrease in the void content and also due to improved bondability with glass fiber.
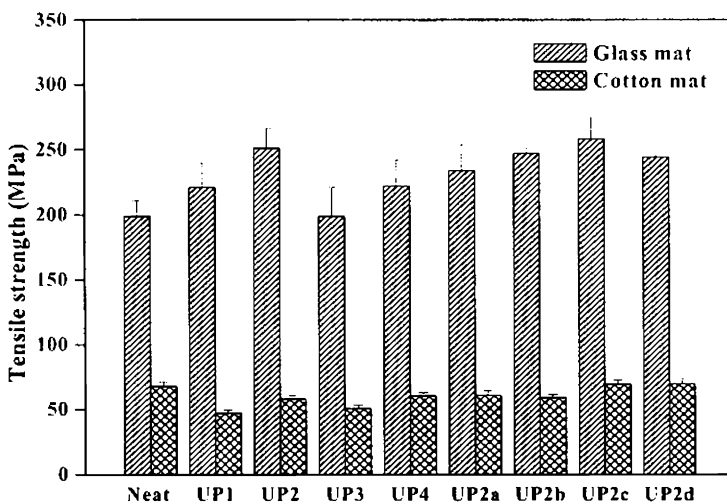

Fig. 6.1 Tensile strength of glass and cotton reinforced composites using UP modified resins

The tensile strength of the cotton-reinforced laminates of UP modified phenolics has slightly decreased in comparison with the unmodified laminate. This has happened even in cases where the void content in the modified composites is less than that in the unmodified resins. This indicates that the presence of UP leads to reduction in chemical interaction between the resin and the cellulose of the cotton fibers.
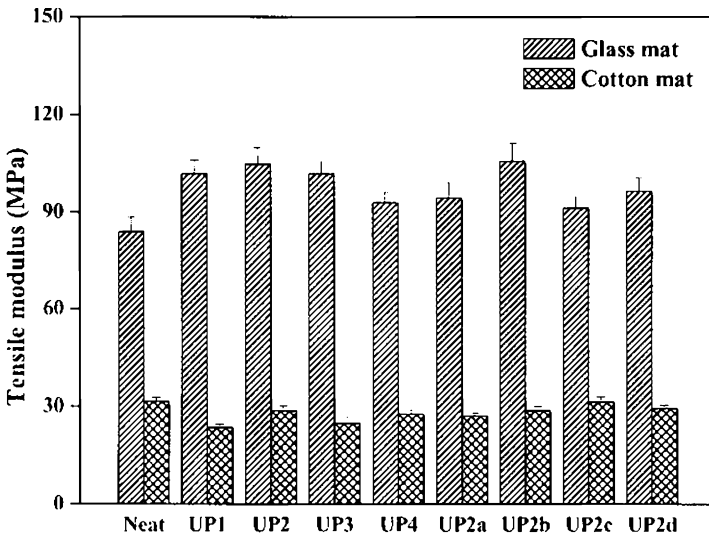
Fig. 6.2 Tensile modulus of glass and cotton reinforced composites using UP modified resins

The tensile moduli of the glass- and cotton-reinforced neat and UP modified composites are shown in Fig. 6.2. The tensile modulus is understandably higher for glass-reinforced samples compared to cotton-reinforced samples. A general increase in the tensile modulus is seen for the glass-reinforced resin composites on modification. The increase may be attributed largely to the decrease in the microvoids in the modified resin composites. This can also be a result of the overall improvement in the properties of the resin which can give better and stronger interfaces. The tensile modulus values of the cotton-reinforced modified resin show only minor variation from the unmodified sample. The influence of the modification might have been suppressed in this case due to wetting/bonding problems earlier suggested.

Fig. 6.3 % elongation of glass and cotton reinforced UP modified resin composites

Fig. 6.3 indicates the % elongation of the modified resin composites. The percentage elongation-at-break is determined by the fibers. Hence the influence of the resin is only marginal. There is no discernible trend in the variation of elongation-at-break on modification.

Fig. 6.4 exhibits the flexural strength of the glass- and cotton-reinforced modified resins. The flexural strength of the glass-reinforced modified resin composites is comparatively higher than that of the neat composite whereas for the cotton-reinforced modified resin composites the values are lower than that of the unmodified resin. The nature of the matrix and the interface play an important role in determining flexural properties. The improved resin properties and better wetting have resulted in higher flexural strength for modified glass-reinfored composites. But less effective bonding/wetting has probably nullified the advantage of improved resin properties in the case of cotton-reinforced composites.
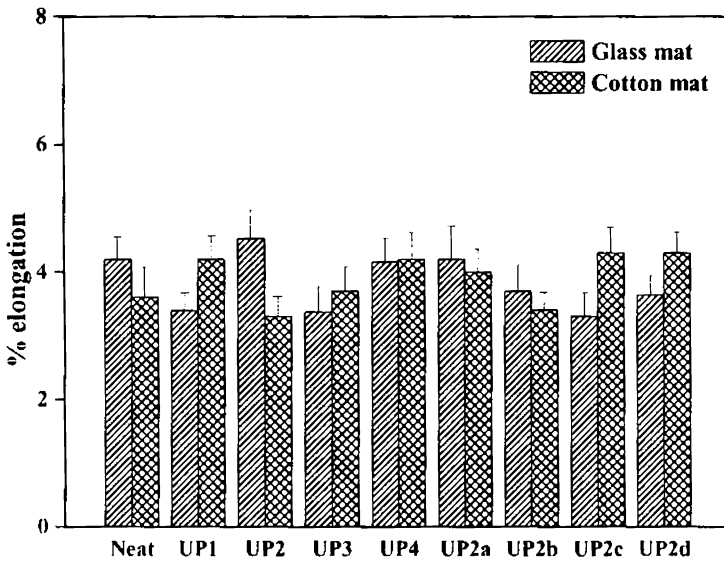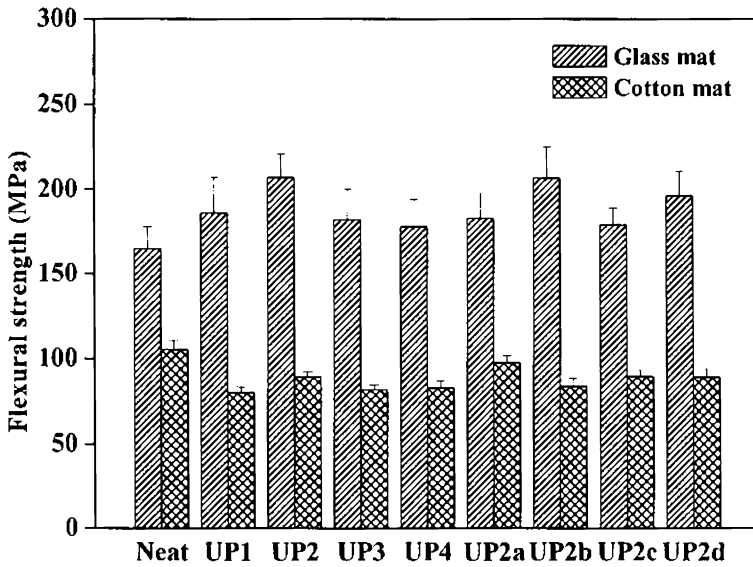
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Fig. 6.4 Flexural strength of glass and cotton reinforced UP modified resin composites
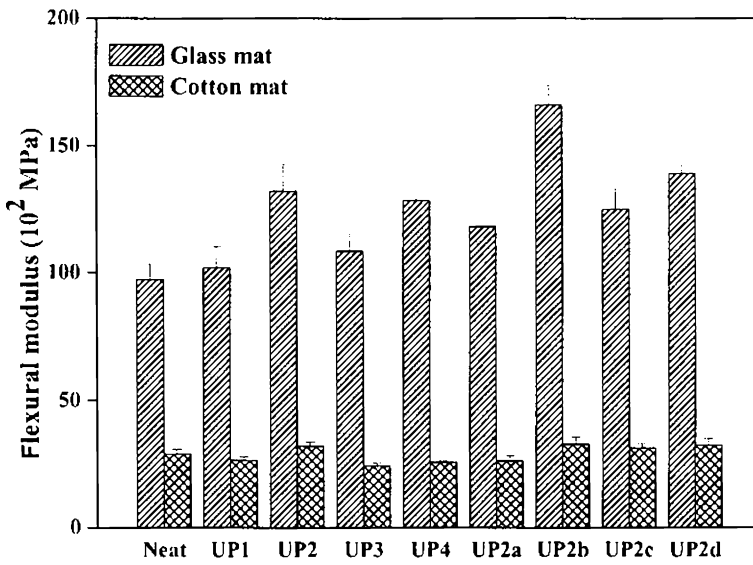

Fig. 6.5 Flexural modulus of glass and cotton reinforced UP modified resin composites

Fig. 6.5 represents the variation of flexural modulus of the modified resin composites. The increase in the modulus values for the glass reinforced modified

resins compared to the unmodified resin is mainly due to the greater interaction between the glass fibers and the modified resins. This leads to a greater stiffness against flexure in the composite.

The modulus values of the cotton reinforced modified resins remain unchanged. The replacement of the phenolic resin by UP leads to a weakening of the inter phase between the matrix and fiber. Here again, the cotton-reinforced samples have failed to achieve any improvement on resin modification.
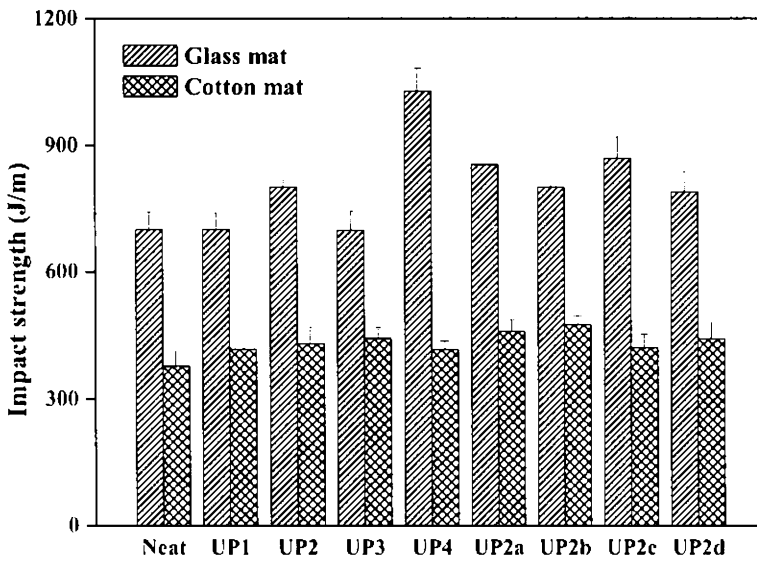
Fig. 6.6 Impact strength of glass and cotton reinforced UP modified resin composites

The impact strength of the modified composites is shown in Fig. 6.6. The impact strength of the glass-reinforced UP modified resin composites shows improvement on matrix modification. The cotton-reinforced UP modified resin composites also show an increase, though less impressive.

6.3.3 Scanning electron microscopy

Figs. 6.7 and 6.8 show the SEM pictures of the impact fractured surfaces of both glass and cotton reinforced composites of UP modified PF resins. The glass reinforced composite of neat resin indicates poor adhesion between resin and the

fibers as indicated by the pullout of the fibers (Fig. 6.7a). Figs. 6.7(b) & (c) represent the SEM micrographs of glass reinforced UP2 and UP2c modified resin composites respectively. The fibers in the UP2 modified composite adhere to the resin more firmly and grooves resulting from fiber pullout can be noticed. The fracture surface topology of UP2c modified resin composite shows a uniform cross-section of the composite and also delamination. This explains the increase in the impact strength of the glass reinforced UP modified composites.

(a)

(b)

(c)

Fig. 6.7 SEM pictures of impact fractured surface of glass reinforced (a) neat (b) UP2 (c) UP2c modified resin composites

In cotton-reinforced neat resin composites a strong interaction between the resin and the fibers can be seen (Fig. 6.8(a)). This is partly due to better chemical compatibility between the fibers and resin. The other reason is the uneven surface of the fibers. The use of UP2 modified resin in place of the neat resin has resulted in reduced fiber resin adhesion as indicated by bunches of fibers not yet wet by the resin (Fig. 6.8(b)). In cotton-reinforced UP2c modified

resin, the fibers are pulled out of the resin matrix as indicated by the holes and also fibers projecting out of the fractured surface. The poor interfacial bond between the fiber and the matrix leads to a lower tensile strength but some improved toughness for the composites [14-17].
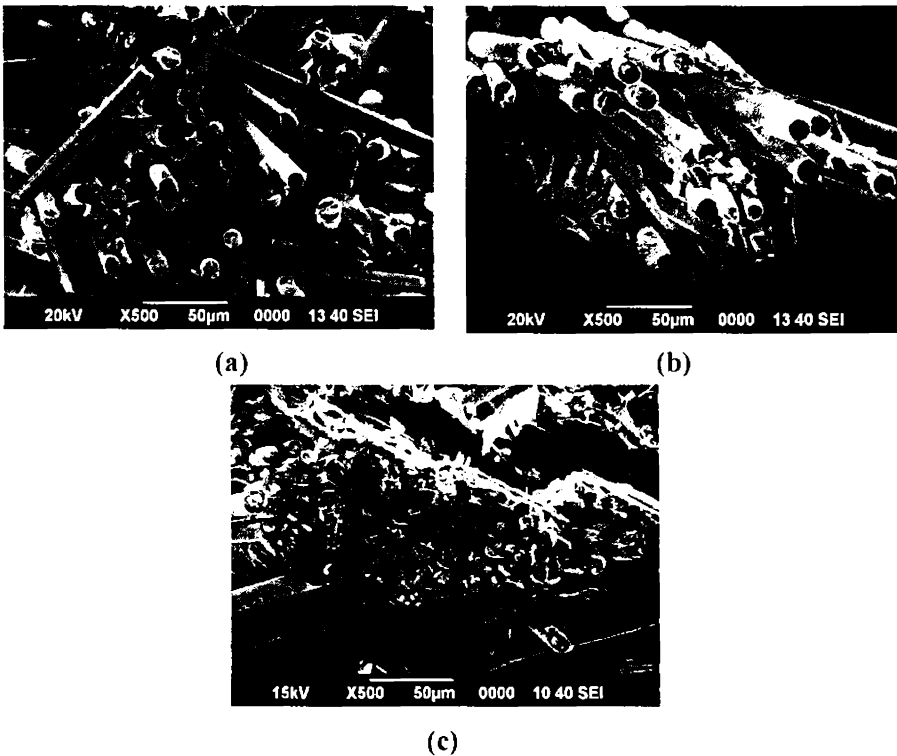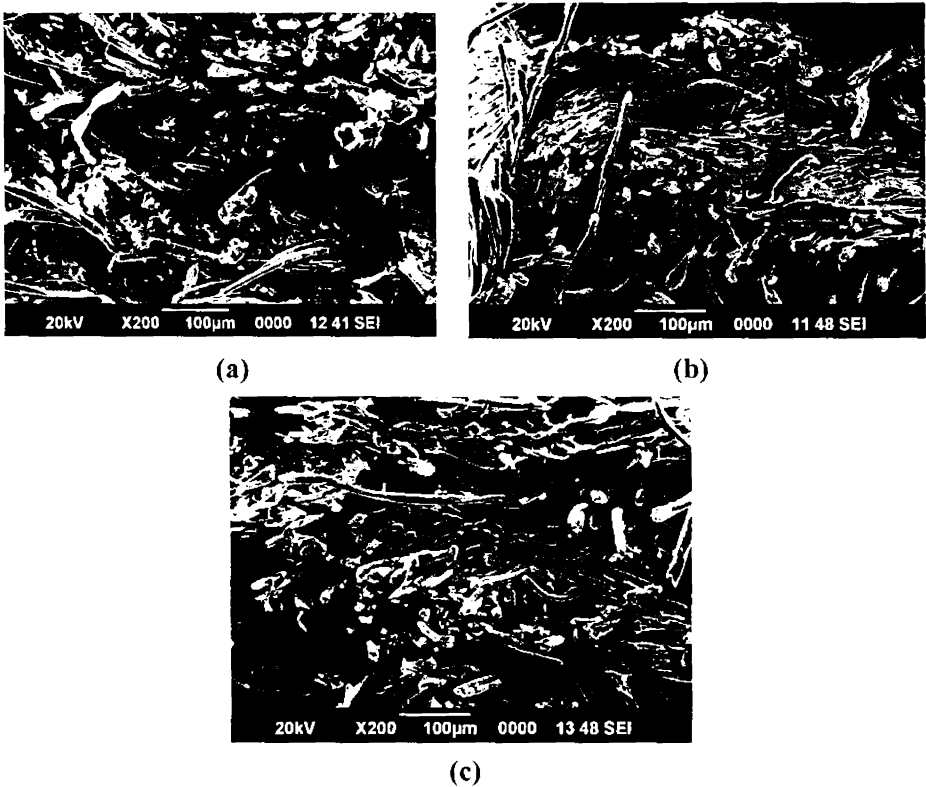

Fig. 6.8 SEM pictures of impact fractured surface of cotton reinforced (a) neat (b) UP2 (c) UP2c modified resin composites

ii) Glass and cotton reinforced laminates of epoxy modified resins

Fig. 6.9 indicates the tensile strength of glass and cotton reinforced unmodified as well as epoxy modified resin composites. Most of the epoxidised novolac modified resin glass composites show better tensile strength than the unmodified composites. But the tensile strengths of Epoxy (C) and EC modified resin composites show a decrease. In the case of EC the properties of the blend falls short of that of the base resin due to the monomeric nature of EC resin. This

can lead to a weak interface between the resin and the fiber. The improvement in the tensile strength of different epoxidised novolac modified composites is due to superior interfacial adhesion between fiber and matrix resulting from the presence of the epoxy group. But the cotton reinforced epoxy composites show only a nominal increase in the tensile strength. The epoxy modification of the matrix may lead to a decrease in the bondability of the resols with cellulose. Hence the slight increase in the tensile strength in this case may be due to the decrease in the void content.
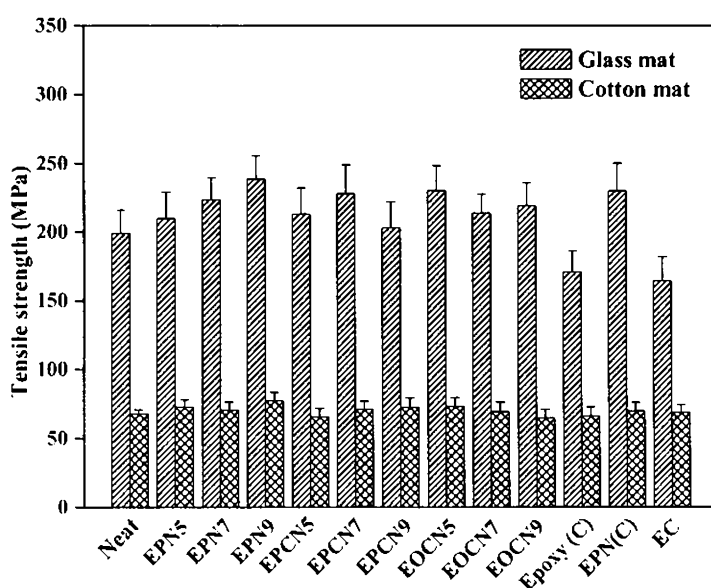
Fig. 6.9 Tensile strength of glass and cotton reinforced composites using epoxy modified resins

The tensile modulus of the cotton reinforced composites remains almost the same as that of the unmodified composite whereas the modulus of the glass reinforced composites shows an increasing tendency (Fig. 6.10). The EC containing resin shows a decrease in the modulus value.
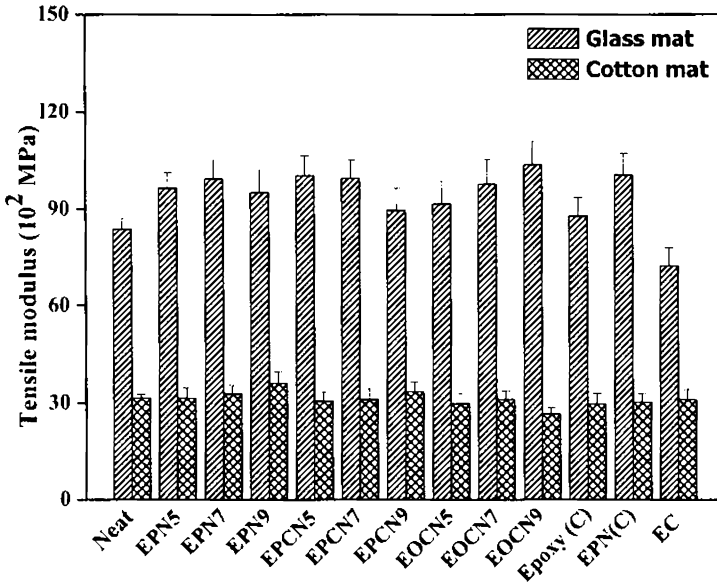
Fig. 6.10 Tensile modulus of glass and cotton reinforced composites using epoxy modified resins
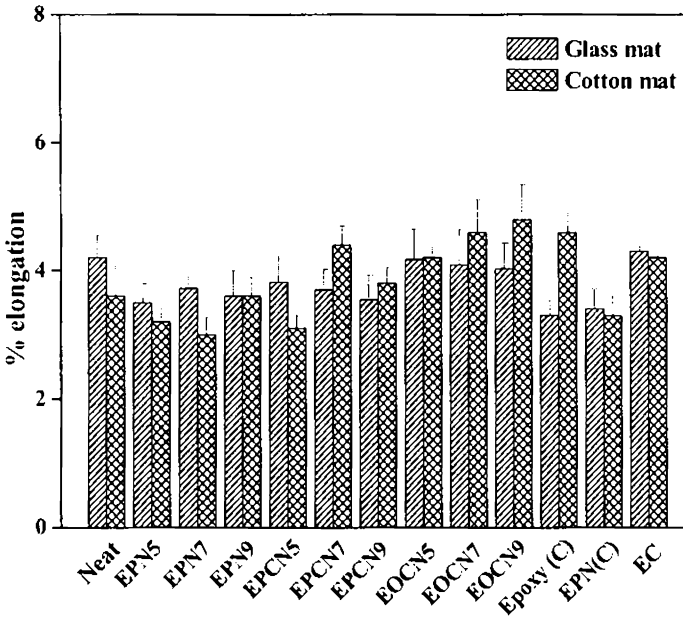
Fig. 6.11 % elongtion of glass and cotton reinforced epoxy modified resin composites

Fig. 6.11 shows the % elongation of the modified composites. These composites also show a trend similar to that shown by UP modified resin composites.
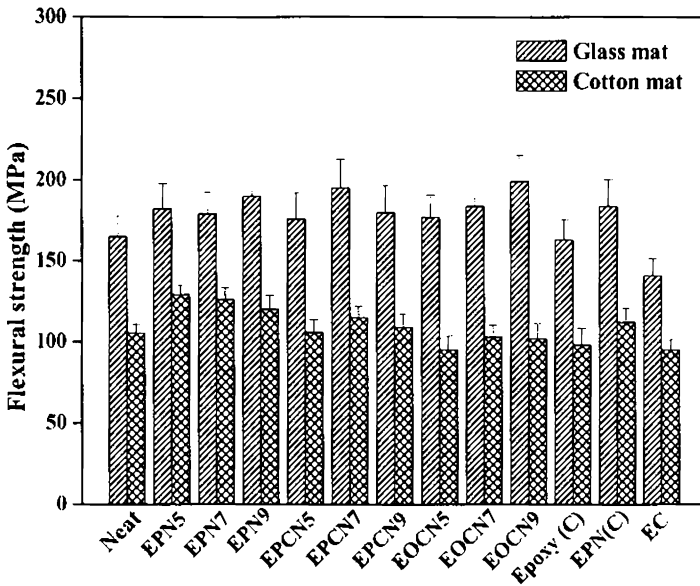
Fig. 6.12 Flexural strength of glass and cotton reinforced epoxy modified resin composites
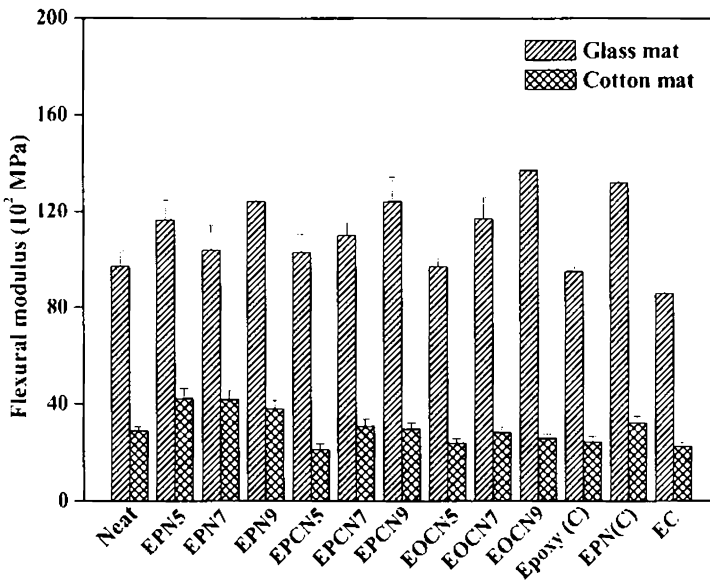
Fig. 6.13 Flexural modulus of glass and cotton reinforced epoxy modified resin composites

Figs. 6.12 and 6.13 exhibit the flexural strength and flexural modulus of glass and cotton reinforced epoxy modified resin composites. The flexural strength and modulus of the glass reinforced composites are nominally higher compared to the unmodified composites. But the cotton reinforced composites show a somewhat

different trend. EPN modified resin based composites possess comparatively better strength and modulus than the unmodified composite. This suggests that the higher values are related to the void content in the composites.

Figure 6.14 indicates a general increase in the impact strength of the glass reinforced epoxy modified resins. Almost all of the glass-reinforced epoxy modified PF resins exhibit an increase in the impact strength. This may be due to the increase in the strength of the fiber- matrix interface. This trend is not so evident in the case of cotton-reinforced composites. Here the increase in impact strength is marginal and is not shown by all samples.
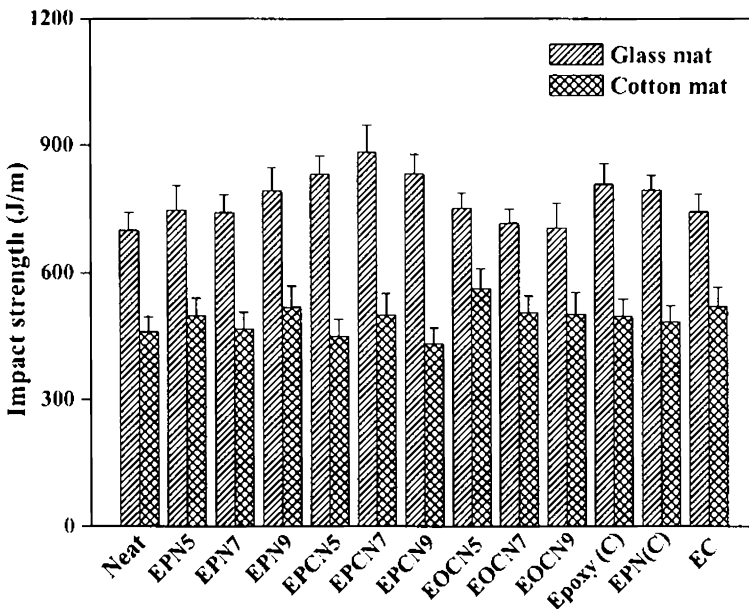
Fig. 6.14 Impact strength of glass and cotton reinforced epoxy modified resin Composites

Fig. 6.15 represents the SEM pictures of the impact fractured surface of glass reinforced composites of epoxy modified PF resins. Fig. 6.15(a) represents the fractured surface of the neat composite. The glass reinforced composite of neat resin shows comparatively poor adhesion between resin and the fibers as indicated by the pullout of the fibers. The other SEM pictures, Fig. 6.15(b) to (e) (Modifiers EPN9, EPCN7, EOCN9 and EPN(c) respectively) of modified composites show

comparatively better adhesion of fibers to the matrix. But delamination and debonding take place even when adhesion has improved. Delamination and debonding can increase energy absorption and impact strength.

(a)

(b)

(c)

(d)

(e)
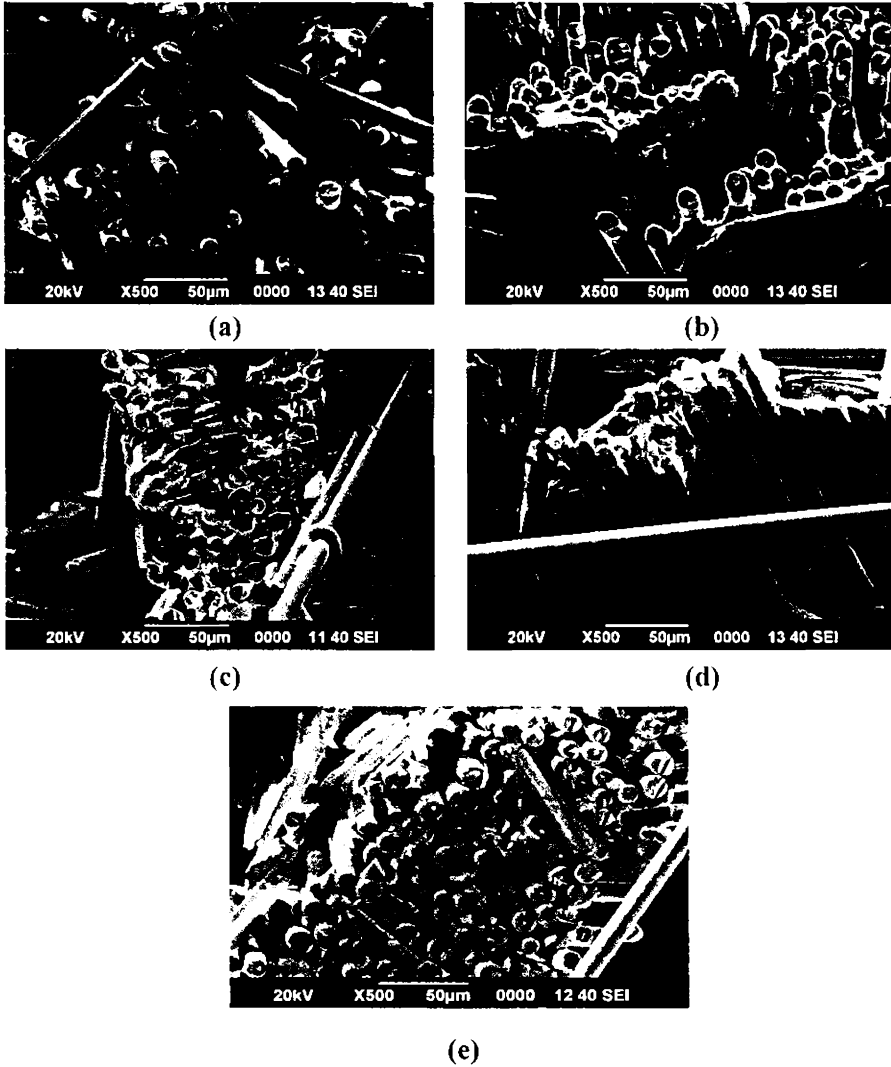
Fig. 6.15 SEM pictures of impact fractured surface of glass reinforced (a) neat (b) EPN9 (c) EPCN 7 (d) EOCN9 and (e) EPN (C) modified resins composite

The impact strength of the cotton-reinforced modified resins is nominally higher compared to the neat composite. The plausible reason for the small increase in impact strength may be weaker bonds between the fiber and matrix which tend

to debond under impact. Fig. 6.16 shows the morphology of the impact fractured surface of the cotton reinforced composites of neat and epoxy modified PF resins. Fig. 6.16(a) shows the fractured surface of the neat resin which has a uniform surface, indicating a brittle fracture. The SEM pictures 6.16(a) – (d) represent the fractured surfaces of the modified composites (Modifiers – EPN9, EPCN7, EOCN9 and EPN(c) respectively). The uneven fracture surface and also fiber pullout are responsible for the improved impact toughness of the composite.
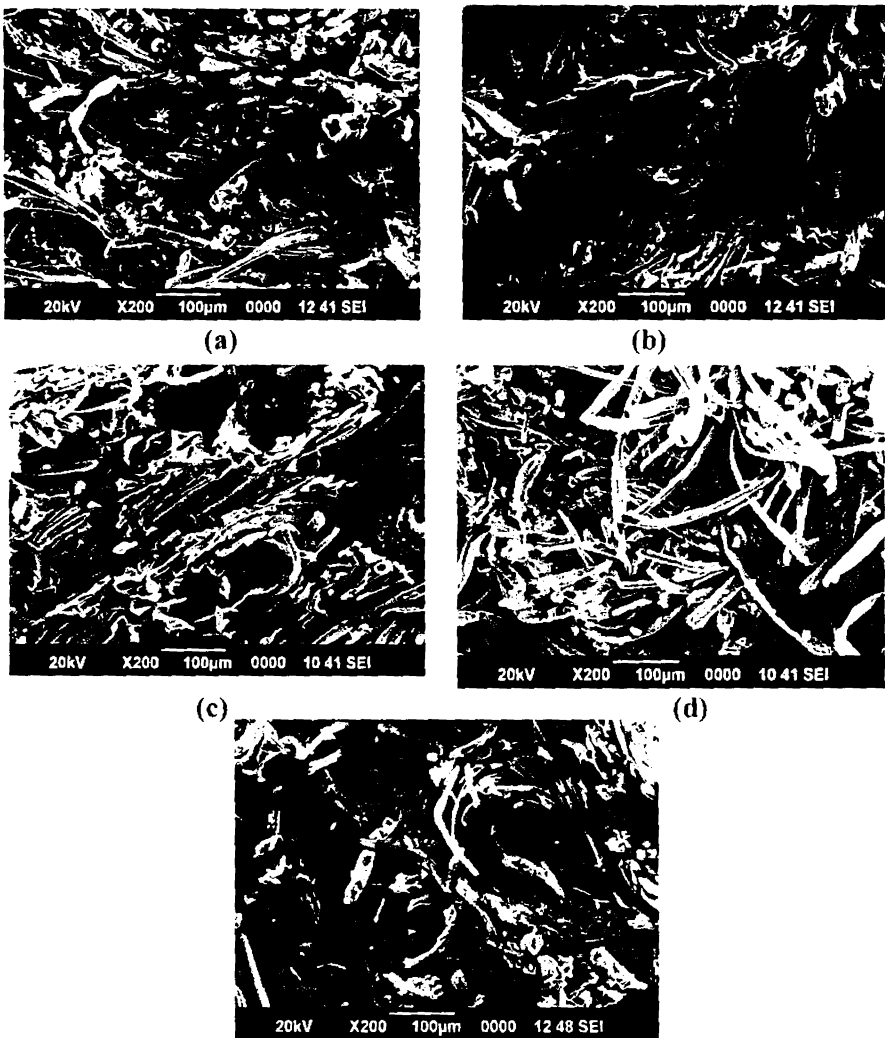
Fig. 6.16 SEM pictures of impact fractured surface of cotton reinforced (a) neat (b) EPN9 (c) EPCN 7 (d) EOCN9 and (e) EPN (C) modified resins composites

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iii)   Theoretical modeling

A large number of theoretical models based on the "Rule of Mixtures" have been developed to predict the tensile strength (TS) and Young's modulus (YM) of composites as a function of fiber volume fraction [18,19]. The most widely applied models to predict TS and YM of composites are Parallel and Series models [20,21]which assume a state of uniform strain and a state of uniform stress in the individual components, respectively. The Parallel model represents the upper bound and the Series model represents the lower bound for the TS and YM. These models assume a perfect interface [22]. Another commonly used model is the Modified Rule of Mixtures (Modified ROM) [23]. This model is based on the assumption that the ultimate strength of a composite is affected not only by the fiber and matrix fractions but also the microgeometry of the composite components.

Parallel model:

According to this model, the tensile strength T_c is given by the following equations.

$$T_c = T_f V_f + T_m V_m \quad\text{..(6.7)}$$

where T_c, T_f and T_m are tensile strength of the composite, fiber and matrix respectively.

For the case of a biaxially oriented reinforcement the actual glass fiber content applicable is only 50% of the total fiber content [24]. Hence a factor β (fiber efficiency factor) is also introduced into Equation 6.7.

$$T_c = 3T_f V_f + T_m V_m \quad\text{...(6.8)}$$

Modified rule of mixtures:

$$\sigma_{cu} = \sigma_m \left(1 - V_f\right) + \sigma_{fu} V_f \quad\text{..(6.9)}$$

where σ_{cu} is the ultimate strength of the composites, σ_m is the matrix strength at the failure strain of the fiber, σ_{fu} is the ultimate strength of the fiber, V_f is the fiber volume fraction and V_{fe} is the effective fiber volume fraction. The effective volume fraction is given in terms of the fiber volume and the ratio of real contribution as given below.

$$V_{fe} = V_f \beta \, (1\text{-}P) \quad\dotfill\text{(6.10)}$$

where P is the degradation parameter for the effective fiber volume fraction which varies in the range 0 to 1. P can be calculated from the microgeometry of the composite components and depends only on the fiber volume fraction and the processing technique. The following equation is obtained from the rule of mixtures with the modification

$$\frac{-\sigma_u}{\sigma_{fu}} = V_f \beta P \quad\dotfill\text{(6.11)}$$

where $\Delta \sigma_u$ is the difference between the experimentally measured strength and strength predicted by the rule of mixtures.

Since same types fibers and almost equal volume fractions of these were taken for making composite, it is assumed that the degradation parameter P remains the same for the entire composite. Therefore the increase or decrease in the strength of the composite is related to fiber-matrix interaction. Hence a parameter X is also included in Equation 6.10.

$$V_{fe} = V_f \beta \, (1\text{-}P)X \quad\dotfill\text{(6.12)}$$

This enables us to calculate the X value of each modified composite, taking the X value of the neat composite as 1.

Figs. 6.17 to 6.20 give a comparison of the experimental and theoretical tensile strengths of glass and cotton reinforced neat and modified PF resin composites.

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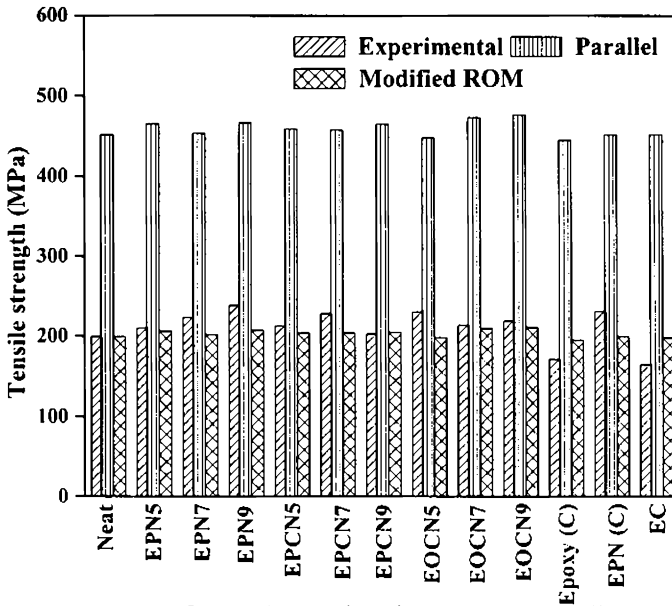
Fig. 6.17 Variation of experimental and theoretical tensile strength values of glass reinforced epoxy modified resin composites

Fig. 6.17 shows the variation of the experimental and theoretical tensile strength of glass reinforced epoxy modified resin composites. Parallel model shows large deviations from the experimental values of the modified composites.

Fig. 6.18 Variation of experimental and theoretical tensile strength values of cotton reinforced epoxy modified PF resin.

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This is mainly because of the poor interfacial adhesion between the phenolic resin and glass fiber. In most cases the tensile strength calculated from the modified ROM is less than that of the neat resin.

The comparison of the experimental and theoretical tensile strength of cotton reinforced neat and modified resin composites is shown in Fig. 6.18. 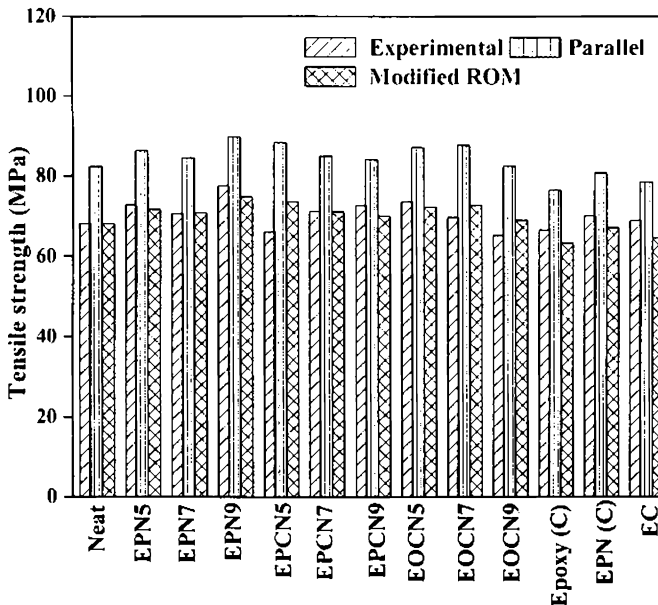Here the deviation from the parallel model is considerably reduced compared to the glass reinforced composites. The lower extent of deviation of the cotton reinforced composites is mainly due to the greater interaction between the phenolic resin and the cotton fibers. The tensile strengths from the modified ROM show a random variation. The V_{fe} and X values from the modified ROM are shown in Table 6.3. The epoxy modification of the resin leads to an increase in the X values of the glass reinforced composites in most cases. This is an indication of improved fiber-matrix adhesion. For the cotton reinforced composites the X values are similar to the neat composite in most cases. It indicates that the cotton fiber matrix interaction in not improved by epoxy modification of the resin.

Table 6.3 The V_{fe} and X values of glass and cotton reinforced epoxy modified resin composites

Composite	V_{fe}	X	Composite	V_{fe}	X
Glass/PF (neat)	0.109	1.00	Cotton/PF (neat)	0.179	1.00
Glass/PF/EPN5	0.115	1.02	Cotton/PF/EPN5	0.189	1.02
Glass/PF/EPN7	0.122	1.12	Cotton/PF/EPN7	0.173	0.99
Glass/PF/EPN9	0.131	1.16	Cotton/PF/EPN9	0.198	1.05
Glass/PF/EPCN5	0.116	1.05	Cotton/PF/EPCN5	0.164	0.87
Glass/PF/EPCN7	0.125	1.13	Cotton/PF/EPCN7	0.175	1.00
Glass/PF/EPCN9	0.111	0.99	Cotton/PF/EPCN9	0.187	1.05
Glass/PF/EOCN5	0.127	1.18	Cotton/PF/EOCN5	0.194	1.02
Glass/PF/EOCN7	0.118	1.03	Cotton/PF/EOCN7	0.180	0.95
Glass/PF/EOCN9	0.120	1.04	Cotton/PF/EOCN9	0.157	0.92
Glass/PF/Epoxy (C)	0.094	0.87	Cotton/PF/Epoxy (C)	0.179	1.07
Glass/PF/EPN (C)	0.128	1.17	Cotton/PF/EPN (C)	0.184	1.06
Glass/PF/EC	0.091	0.82	Cotton/PF/EC	0.191	1.08

Fig. 6.19 indicates the experimental and theoretical tensile strengths of the glass reinforced UP modified resins composites. The lower value for the tensile strength calculated from the modified ROM shows improved interfacial adhesion between the matrix and the fiber.

A comparison of the experimental and the theoretical tensile strengths of the cotton reinforced composites is shown in the Fig. 6.20. In these composites the deviation from the parallel model is larger for the modified composites than the neat composite. A decreased adhesion between the matrix and resin is responsible for this. The tensile strength values from the modified ROM are comparatively higher than the experimental values. X values from modified ROM of these composites are shown in Table 6.4.
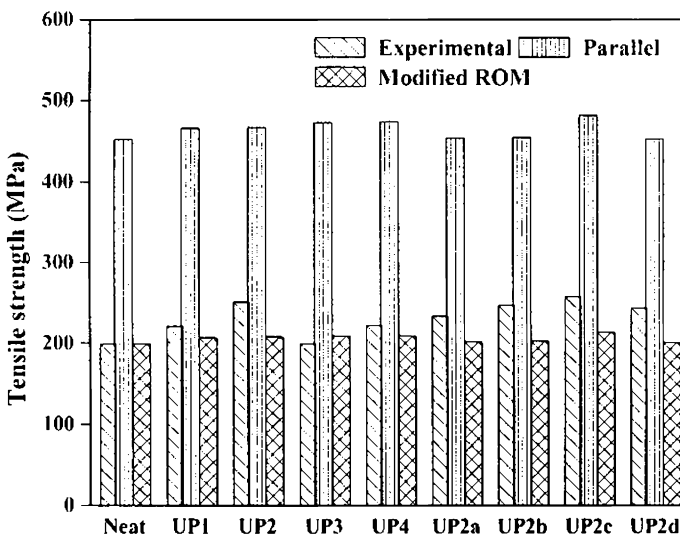
Fig. 6.19 Experimental and theoretical tensile strength values of glass reinforced UP modified PF resin

The X values of the glass reinforced UP modified composites are higher than that of the neat composite. This indicates an improved interfacial adhesion between the modified matrix and glass fiber. But the cotton reinforced composites show an

opposite trend. This is an indication of the weakening of the interface between the matrix and cotton fiber.
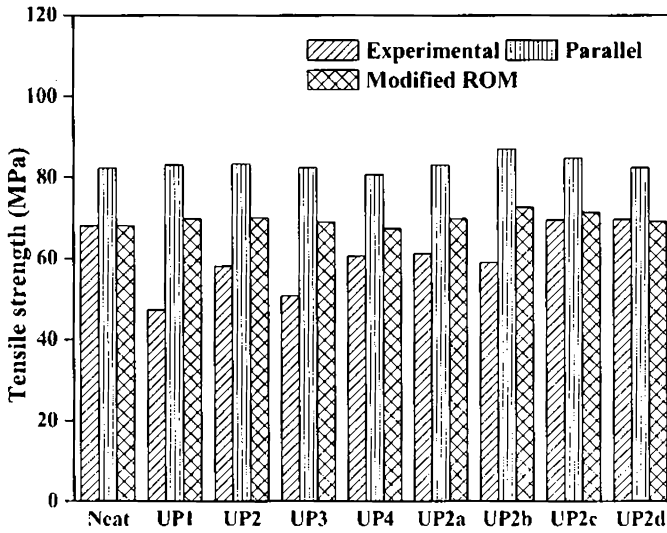
Fig. 6.20 Experimental and theoretical tensile strength values of cotton reinforced UP modified resin composites

Table 6.4 The V_{fe} and X values of glass and cotton reinforced UP modified resin composites

Composite	V_{fe}	X	Composite	V_{fe}	X
Glass/PF (neat)	0.109	1.00	Cotton/PF (neat)	0.179	1.00
Glass/PF/UP1	0.121	1.07	Cotton/PF/UP1	0.094	0.56
Glass/PF/UP2	0.138	1.23	Cotton/PF/UP2	0.129	0.76
Glass/PF/UP3	0.108	0.95	Cotton/PF/UP3	0.109	0.64
Glass/PF/UP4	0.123	1.07	Cotton/PF/UP4	0.144	0.86
Glass/PF/UP2a	0.128	1.17	Cotton/PF/UP2a	0.138	0.82
Glass/PF/UP2b	0.136	1.24	Cotton/PF/UP2b	0.135	0.75
Glass/PF/UP2c	0.142	1.22	Cotton/PF/UP2c	0.163	0.96
Glass/PF/UP2d	0.134	1.23	Cotton/PF/UP2d	0.170	1.01

6.3.4 Dynamic mechanical properties of reinforced composites

The variation of the storage modulus with temperature of some of selected glass reinforced composites is shown in the Fig. 6.21. It can be seen that the modulus values for the modified composites are considerably higher than the unmodified composite. The modulus values remain almost constant with temperature. This indicates the improved thermal stability of glass reinforced samples. The increase in the modulus values is an indication of the improved interfacial adhesion between the fiber and the matrix. It is maximum in the UP modified composites. Fig. 6.22 shows the change in the storage modulus with temperature of selected cotton reinforced composites. The initial modulus is similar for the unmodified and modified composites. The modulus values decrease steadily with increase in the temperature. The decrease in the modulus values are higher for UP modified resin composites compared to the other composites. This indicates a weak interface between the cotton fiber and the matrix on UP modification.
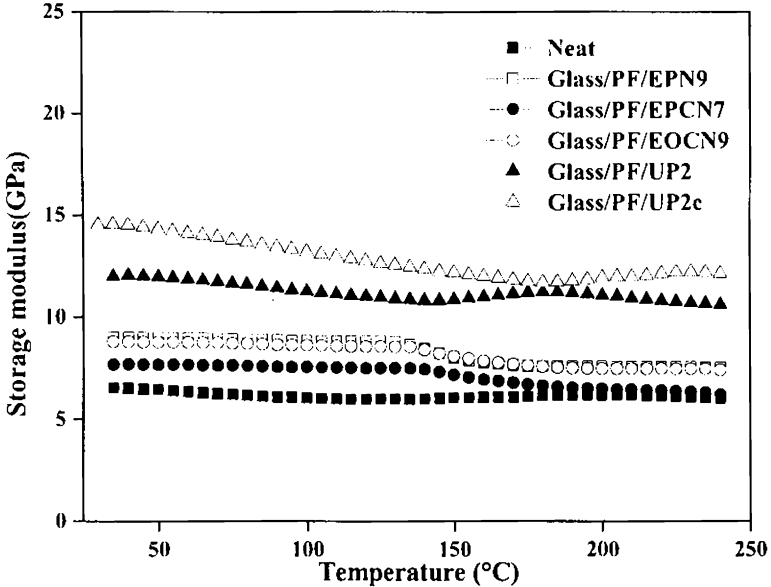
Fig. 6.21 Effect of matrix modification on the storage modulus of the glass fiber reinforced composites

Fig. 6.22 Effect of matrix modification on the storage modulus of the cotton fiber reinforced composites

Fig. 6.23 represents the variation of tanδ with temperature of different composites. The initial tanδ values of the modified composites are lower than that of the unmodified composites.
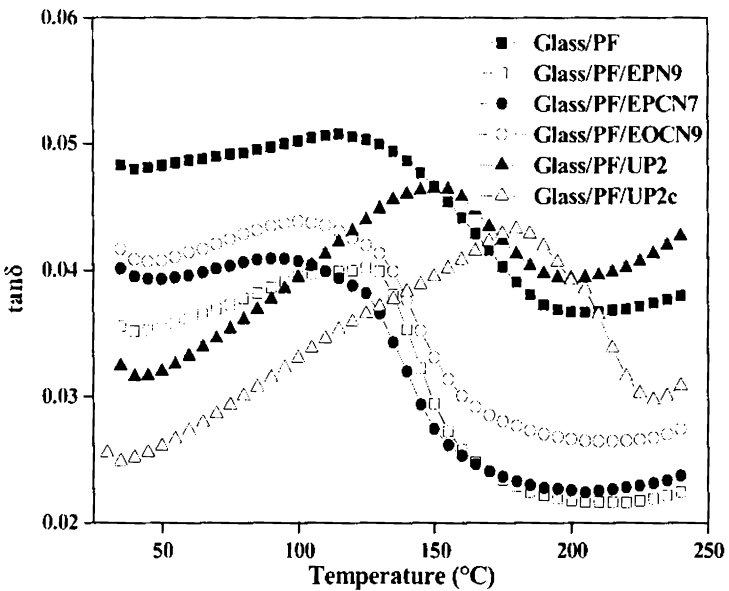
Fig. 6.23 Effect of matrix modification on the tanδ of the glass fiber reinforced composites

This indicates an increase in the fiber matrix adhesion. tanδ is a damping term, which can also be related to the impact resistance of the material [25]. Since the damping peak occurs in the region of glass transition where the material changes from rigid to a more rubbery state, it is associated with the segmental mobility of the chains, which are initially in the frozen state.

The higher the peak tanδ value, the greater is the degree of molecular mobility. The nature of the tanδ variation with temperature is almost the same for the unmodified composite and epoxidised novolac modified resin composites. This may be due to the structural similarity of the matrix and the modifier. But UP modified composites show greater increase in tan δ with increasing temperature. This is an indication of improved damping property of these composites. Near the T_g of the matrix, the molecular chains of the matrix have high mobility and hence the damping of the composite is primarily due to the matrix. The UP chains in the modified resin provide enough room for chain mobility. Hence the high damping property of the UP modified resol resins is reflected in the composites also. The T_g of the unmodified and epoxidised novolac modified resin composites are similar but it is higher for the UP modified resin composites.

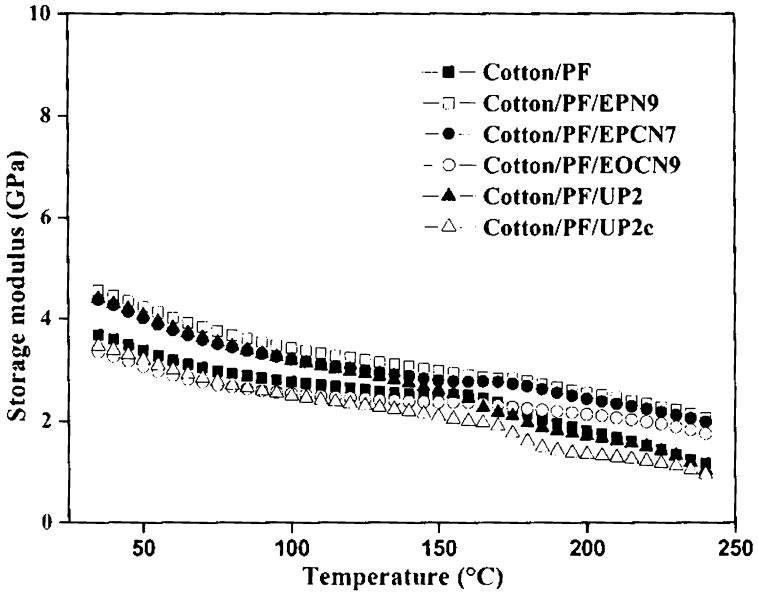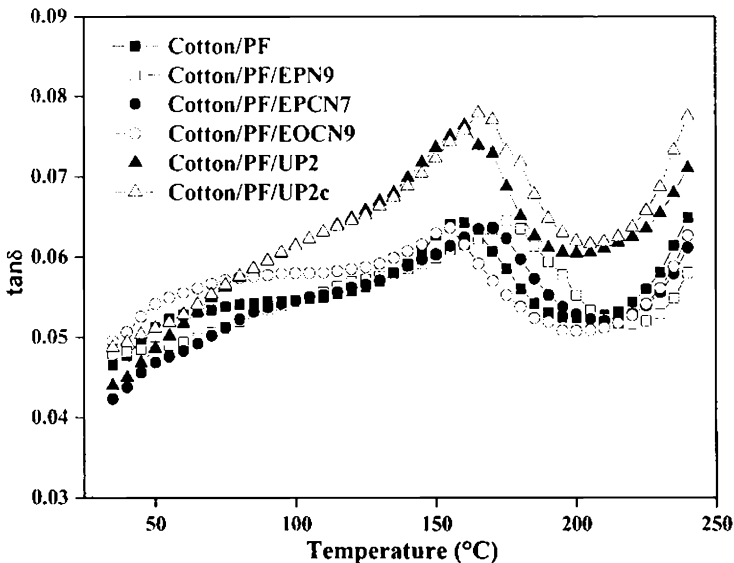**Fig. 6.24** Effect of matrix modification on the tanδ of the cotton fiber reinforced composites

Fig. 6.24 shows the variation of the tan δ values with temperature. The T_g of both the unmodified and modified composites have not changed with the modification of the resin. Here again, the UP modified resin composites show higher tan δ values than the unmodified and epoxidised novolac modified resin. The glass and cotton reinforced UP modified resin composites exhibit better damping than the other modified composites.

6.3.5 Water absorption studies of the modified resin composites

The water sorption curves of the selected glass and cotton reinforced composites are shown in Figs. 6.25 and 6.26 respectively. It can be seen that the glass reinforced composites using modified resins show substantially reduced uptake of water.
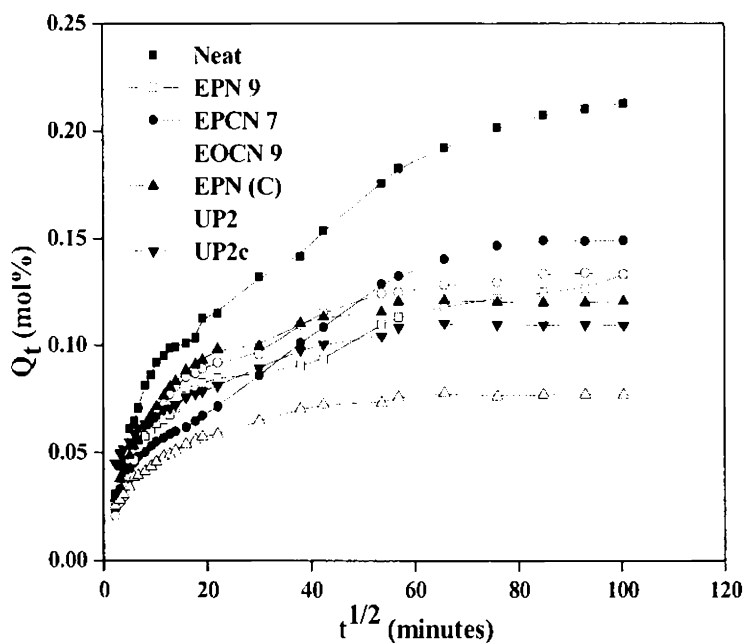
Fig. 6.25 Sorption curves showing the mol % uptake of glass reinforced modified resin composites

The uptake of water in the case of UP modified resin composites is remarkably lower than that of the neat resin. In this case, the water absorption as percentage increase in weight is only about one third that of the reinforced neat

resin. This can be due to a combination of reasons like structural features of the UP modified phenolic resin, improved adhesion between glass fiber and the resin etc.

The uptake of water by EPN based composites is less than that of the epoxidised cresol novolac based composites. The highest uptake is shown by the unmodified composite.
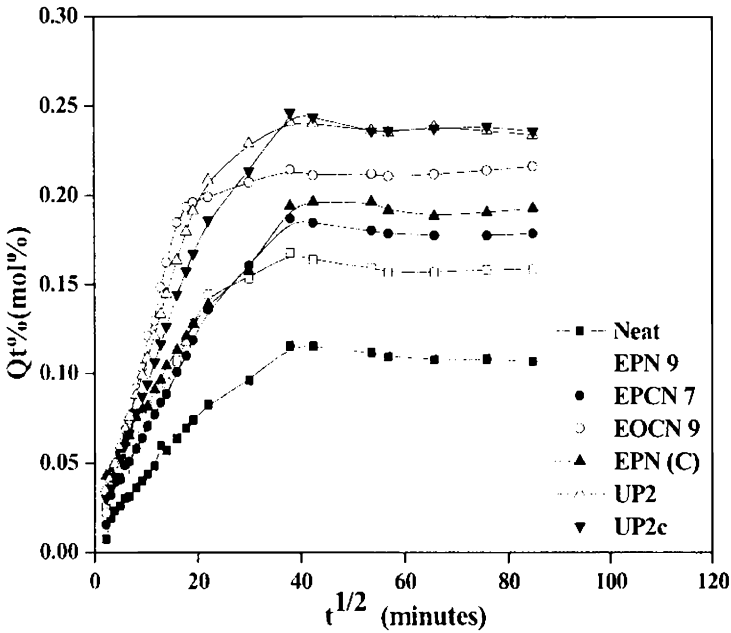
Fig. 6.26 Sorption curves showing the mol % uptake of cotton reinforced modified resin composites

But the cotton reinforced composites show a totally different trend. The water uptake is increased on using the modified resin as the matrix for the composite. The water uptake is maximum for the UP modified resin composites and least for the unmodified composite. The epoxy novolac modified resin composites show intermediate water absoption. This behavior may be the result of lowered interfacial adhesion between cotton and modified resins. The reduction in water uptake is hence a function of the structural characteristics of each modifier resin. In this respect UP resin is found to give rise to the least amount of adhesion and hence the highest amount of water uptake.

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Kinetics of water sorption

The kinetics of water sorption in permeable fiber/polymer composites is usually assumed to be a concentration independent diffusion process. In order to study the mechanism of water sorption, parameters n, k, diffusion coefficient (D), sorption coefficient (S) and permeability coefficient (P) of water sorption in different composites were analysed using the following empirical relationship [26].

$$ \log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6.13), $$

where Q_t is the mole percent water uptake at time t, Q_∞ is the mole percent water uptake at equilibrium. 'k' is a constant characteristic of the sample which indicates the interaction between the sample and water and 'n' is an indication of the mechanism of sorption.

For a Fickian mode of diffusion, the value of 'n' is equal to 0.5. This occurs when the segmental mobility of the polymer chains is faster than the rate of diffusion of permeant molecules. This happens in the case of diffusion into polymers, which are above their glass transition temperature up to about 50% of the equilibrium penetrant uptake. When 'n'=1, the penetrant diffusion rates are much faster than polymer relaxation process, which is usual in rigid polymers with glass transition temperature well above the room temperature. When the 'n' value is in between 0.5 and 1, the diffusion is said to be anomalous. This is the case when permeant mobility and polymer segmental relaxation rates are almost equal. The values of 'n' and 'k' were determined in this study by linear regression analysis.

Table 6.5 shows the kinetic parameters and transport coefficients of water sorption studies in glass and cotton reinforced modified resin composites.

For the glass reinforced composites 'n' is much less than 0.5. This may be due to the highly crosslinked structure of PF resins and relatively hydrophobic nature of the glass fiber. Hybrid oil palm fiber with glass reinforced PF resin shows identical behavior and is assumed to follow non-Fickian behaviour [27]. For the

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cotton reinforced composites the 'n' value is close to 0.5. This suggests that the mode of diffusion is close to the Fickian model. This may due to the hydrophilic nature of the cotton fibers. The amount of water absorption increases linearly with the square root of time and then gradually approaches the equilibrium plateau. This means that water sorption is diffusion controlled and the same mechanism has been reported for reinforced epoxies [28].

The k value shows a general increase with resin modification in both glass and cotton fiber reinforced composites. The value of k depends on the structural characteristics of the polymer in addition to its interaction with the solvent [29]. The value of D, the diffusion coefficient, decreases with modification and depends on the type of modification of the resin in glass reinforced composites.

Table 6.5 Values of n, k, diffusion coefficient, sorption coefficient and permeability coefficient of glass and cotton reinforced modified resin composites at room temperature

Composite	n	$k(\times 10^{-2} g/g$ $min^n)$	$D(\times 10^{-8}$ $cm^2 S^{-1})$	$S(\times 10^{-2}$ $g\ g^{-1})$	$P(\times 10^{-9}$ $cm^2 S^{-1})$
Glass/PF	0.37	8.58	17.60	3.37	5.93
Glass/PF/EPN9	0.33	12.29	11.50	2.28	2.62
Glass/PF/EPCN7	0.33	10.18	14.60	2.27	3.31
Glass/PF/EOCN9	0.43	7.59	23.20	2.33	5.41
Glass/PF/EPN(C)	0.28	15.90	14.80	2.18	3.22
Glass/PF/UP2	0.21	23.32	7.40	1.36	1.01
Glass/PF/UP2c	0.13	33.61	4.08	1.95	0.80
Cotton/PF	0.52	4.20	14.50	1.94	2.81
Cotton/PF/EPN9	0.38	7.99	17.40	2.83	4.92
Cotton/PF/EPCN7	0.50	4.81	11.30	3.20	3.62
Cotton/PF/EOCN9	0.52	5.14	24.20	3.79	9.18
Cotton/PF/EPN(C)	0.27	13.47	8.10	3.39	2.75
Cotton/PF/UP2	0.41	7.06	14.80	4.26	6.30
Cotton/PF/UP2c	0.41	6.00	22.40	4.28	9.59

The value of D is least for UP modification. But the cotton reinforced modified resin composites in general show a reverse trend. The decrease in the diffusion coefficient for glass reinforced modified resin composites indicates that the fiber-matrix interaction is improved while with cotton it is decreased with modification. Both the S and P values show a similar trend and this also supports the above observation.

6.4 Conclusion

Matrix modification is found to alter the mechanical properties of PF-glass composites favourably. But this is not uniformly true of cotton–reinforced composites. The capacity of the modifiers, to improve the mechanical properties, is poor when it is reinforced with cotton fibers. This may be due to a variety of factors like fiber modifier interaction and the inadequacies of the fabrication process which can lead to wide variations in void content.

Both the UP and epoxidised novolac modifiers improved the properties of the glass reinforced composites. Only commercial epoxy and epoxidised cardanol show inferior properties. The SEM, DMA and water sorption studies show that the modifiers increase the glass fiber-matrix adhesion and improve the strength of the fiber-matrix interface. An attempt has been made to correlate the tensile strength of some of the composites with fiber volume fraction using theoretical models. The modelling studies also confirm the improvement of interfacial adhesion in glass reinforced composites.

Water absorption studies of glass reinforced UP modified resins show that the strength of the interface between glass and the resin has improved to a greater extent upon UP modification compared to epoxy modification.

The mechanical properties of the cotton reinforced composites are not improved to an appreciable level. It can be seen from the SEM, DMA and water sorption studies that the interfacial adhesion between the cotton fiber and resin is decreased on incorporating the modifier to the matrix resin.

The studies show that UP modified phenolic has better interaction with the glass fibers while with cotton fibers it is decreased. With the cotton fibers, unmodified resin exhibits better adhesion. In both cases the epoxy modifier shows an intermediate level of interaction.

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Chapter $\boxed{7}$

SUMMARY AND CONCLUSION

7.1 Introduction

This concluding chapter provides a glimpse of the summary and conclusions of the work carried out on the modification of phenol formaldehyde resol resin. It is found that a small amount of modifier can greatly reduce microvoids and improve the impact resistance and other properties of phenolics. The improvement is accomplished without significant deterioration of the thermo mechanical properties of the resin.

7.2 Summary

The focus of this study is on developing new modified systems for resol phenolic resin via chemical modifications. The contents of the various chapters of the thesis are presented below.

A literature survey on the modification of phenolic resin, a brief discussion on various thermoset resins, curing of phenolic resins, an account of the mechanical properties and modification methods of phenolic resin and fiber reinforced phenolics are included in Chapter 1.

Preparation of different phenol formaldehyde resol resins and optimisation of the stoichiometry are presented in Chapter 2. The resins are characterised by FTIR spectroscopy. The mechanical and thermal properties of the cured resins are studied by UTM, TGA and DMA to optimise the stoichiometry.

Cardanol based phenolic resol resins are prepared by reacting a mixture of phenol and cardanol with formaldehyde (PCF) and also by blending phenol formaldehyde and cardanol formaldehyde resol resins together (PFCF). Their mechanical and thermal properties are evaluated to understand the comparative performance of these cardanol based resols. The morphology of the fractured surfaces is monitored by scanning electron microscopy (SEM). The results of these studies are given in Chapter 3.

Experimental details of modifying commercial resol resin by reactive blending with unsaturated polyester (UP) are given in Chapter 4. Firstly,

unsaturated polyesters based on maleic anhydride (MA) and phthalic anhydride (PA) with varying ratios are prepared and blended with resol resin in different proportions. The optimisation of MA/PA ratio in the UP is done on the basis of the specific gravity, total soluble contents and mechanical performance. The influence of the acid value is also subsequently monitored. The mechanical, thermal and morphological studies on these modified resins are discussed in detail in this chapter. The void content in the resin is also evaluated from SEM micrographs.

A comparative account of the modification of resol resin by epoxies is discussed in Chapter 5. Various epoxidised novolacs, viz., epoxidised phenolic novolac (EPN), epoxidised para-cresol novolac, epoxidised ortho cresol novolacs and epoxidised cardanol are used for the study. Commercial grades of epoxy resin and epoxidised phenolic novolac are also employed for the modification. The mechanical, thermal and dynamic properties of the modified samples are evaluated and compared to find out the effectiveness of these epoxies. The microvoid distribution patterns in the modified and neat resins are also recorded and compared.

The effect of matrix modification on the mechanical properties of glass-reinforced composites is presented in Chapter 6. Reinforced laminates made of both virgin resin and modified resin are prepared using glass woven roving mat (WRM) and cotton cloth. The hardness, void content and density of the composites are measured. The mechanical, dynamic mechanical and water sorption studies on the modified composites are done to ascertain their ability to improve the properties of phenolic laminates.

7.3 Conclusion

The following conclusions have been reached based on the results of the studies.

- An increase in the formaldehyde content of resol resin leads to higher amounts of $-CH_2-O-CH_2-$ linkages.

- The extent of hydrogen bonding in the resin reaches a maximum at an F:P ratio of 1.75:1. The resin has optimal mechanical properties at this stage.

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- The cured resin shows maximum thermal stability when the F:P ratio is in the range 1.5:1 to 1.75:1.

- When phenol/cardanol/formaldehyde resols are prepared by two methods (PCF and PFCF), PFCF resins show better impact strength and abrasion resistance.

- The inclusion of cardanol leads to longer gel times for the resin.

- The inclusion of cardanol also leads to poorer thermal stability. In this respect PFCF shows better results.

- Modification of PF resol resin by UP results in considerable decrease in the number of microvoids in the cured resin.

- The presence of UP leads to higher tensile and impact strengths.

- The best overall results are obtained when UP with MA/PA ratio of 70:30 at a concentration of about 7.5% is employed for modification.

- An acid value of about 60 in the UP is found to give rise to a minimum number of microvoids and consequently the best properties.

- The inclusion of UP leads to a marginal lowering of T_g and thermal stability.

- The effectiveness of epoxy novolacs in general in modifying PF resins is dependent on the P/F ratio of the novolac resin and the epoxy content.

- Among the epoxidised novolacs studied EPN synthesised in the laboratory imparts the best tensile and compressive properties whereas EPCN gives greatest improvement in the flexibility and impact properties.

- A reduction in microvoid population results on modification using epoxies.

- Epoxidised novolacs with low P/F ratios show maximum effectiveness as modifier.

- There is an improvement in thermal stability on addition of most epoxy modifiers.

- Among all modifier resins studied UP gives the best overall results

- Both UP and epoxidised novolac modifiers improve the mechanical and water resistance properties of glass reinforced composites.

- Modifiers in general increase the glass matrix adhesion.

- Mechanical properties of the cotton reinforced composites do not show any improvement on modification of the resin.

7.4 Future outlook

There is ample scope for carrying out extensive investigations on the modification of phenolic resins. Some specific areas are outlined below:

- Large scale manufacture of modified resins has to be investigated and problems relating to regular production have to be solved.

- The improvement in properties of glass-reinforced composites employing modified resins has to be comprehensively investigated.

- Commercial significance of using modified resins has to be further studied. Field trials can conducted and performance reports can be procured from actual users.

- Being the best modifier, the mechanism of modification by UP has to be studied in detail. The possibility to try out various thermally stable UPs as modifiers has to be explored.

- Individual roles played by toughening phenomena and microvoid reduction in improving the properties of phenolic resols have to be investigated.

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ABBREVIATIONS AND SYMBOLS

ASTM	American Society of Testing and Materials
ABS	Acrylonitrile-Butadiene-Styrene
b	Width of specimen tested
BMC	Bulk molding compounds
BP	Boiling point
CF	Cardanol-formaldehyde resol
CNBENP	Carboxylic nitrile butadiene elastomeric nanoparticles
CNSL	Cashew nut shell liquid
cps	Centipoise
CTBN	Carboxyl terminated butadiene-acrylonitrile rubber
d^{20}	Density at 20^0C
d	Depth of specimen
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DMC	Dough moulding compounds
DSC	Differential scanning calorimetry
$\overline{D_a}$	Surface area -average diameter
$\overline{D_n}$	Number-average diameter
$\overline{D_v}$	Volume-average diameter
$\overline{D_w}$	Weight-average diameter
E'	Storage modulus
E''	Loss modulus
E_a	Activation energy
EB	Elongation-at-break
E_B	Modulus of elasticity in bending
EC	Epoxy cardanol
ENP	Elastomeric nanoparticles
EOCN	Epoxy ortho cresol novolac
EPN	Epoxidised phenolic novolac
EPCN	Epoxy para cresol novolac
F:P	Formaldehyde: Phenol
FRP	Fiber reinforced plastics
FTIR	Fourier Transform infrared
GP	General purpose

GPC	Gel permeation chromatography
GRP	Glass Reinforced Polymers
h	Hours
HMP	Hydroxymethylated phenol
HMTA	Hexamethylenetetramine
HTPB	Hydroxyl terminated polybutadiene
Hz	Hertz
ILSS	Inter laminar shear stress
L	Support span
L.R.	Laboratory reagent
MA	Maleic anhydride
MF	Melamine- formaldehyde
min	Minutes
mol	Mole
m	Slope of the tangent to the initial straight line portion of the load-deflection curve
$\overline{M}_n$	Number average molecular weight
MEK	Methyl ethyl ketone
MP	Melting point
MPa	Mega Pascal
MPFR	Modified phenol formaldehyde resin
MW	Molecualr weight
MWNT	Multy wall nano tube
N	Normality
NBR	Acrylonitrile-butadiene rubber (nitrile rubber)
nm	Nanometre
NMR	Nuclear magnetic resonance
P	Load at any point on the load -elongation curve
PA	Phthalic anhydride
P_B	Breaking load
PDI	Polydispersity index
PCF	Phenol cardanol formaldehyde
PF	Phenol formaldehyde
PFCF	Phenol formaldehyde Cardanol Formaldehyde
PMF	Maleimide-functional phenolic
PMMA	Polymethyl methacrylate
PTSA	Para toluene sulphonic acid
PU	Polyurethane
rpm	Revolutions per minute

ROM	Rule of Mixtuers
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
T_d	Theoretical density
TDI	Toluene diisocyanate (TDI)
TGA	Thermogravimetric analysis
T_g	Glass transition temperature
TSC	Total solid content
UF	Urea-formaldehyde
UP	Unsaturated polyester
UTM	Universal Testing Machine
VARI	Vacuum assisted resin injection
V_D	Volume fraction of void
V_f	Volume fraction
V_{fe}	Effective volume fraction
wpe	Weight per epoxy
WRM	Woven roving mat

PUBLICATIONS AND PRESENTATIONS

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[3] Cardanol-based Resol Phenolics – a Comparative Study P.S. Parameswaran, B.T. Abraham and E.T. Thachil *Progress in Rubber lastics and Recycling Technology* (In press).

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