NOVEL ADHESIVE SYSTEMS BASED ON NEOPRENE-PHENOLIC BLENDS

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by

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CERTIFICATE

This is to certify that the thesis entitled **"Novel adhesive systems based on neoprene-phenolic blends"** which is being submitted by Ms. Lity Alen Varghese 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 her 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 "**Novel adhesive systems based on neoprene-phenolic blends**" is based on the original research work carried out by me under the guidance and supervision of **Dr. Eby Thomas Thachil**, Reader, Department of Polymer Science And Rubber Technology, Cochin University of Science and Technology, Cochin-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.*

Cochin-22 LITY ALEN VARGHESE
29th December 2006

PREFACE

Bonding has become an indispensable technique for joining two or more substrates with each other. As a means of joining materials, the adhesives are occupying by and large, a conspicuous plateau in the modern industrial world by virtue of their versatility in diverse fields of applications. The use of adhesive offers considerable advantages when compared to other conventional joining methods. Good adhesion is vital to a number of important areas like adhesive bonding, lamination, painting, coating and composite production. The diversity of substrates and the continuous introduction of new processes and materials have ensured the field of adhesives technology as a swiftly expanding manufacturing endeavour.

The adhesives may be either synthetic or natural in origin. The present work aims at developing high performance adhesives based on neoprene-phenolic blends. The rapid development of bond strength of films from solution, tack or auto- adhesion and resistance of the cured bond line to heat, oxidation, water, solvents, oils, acids and alkalis are advantages that have led to the extensive use of neoprene in adhesives. Phenolic resins have good high temperature resistance and chemical resistance. Cardanol, the main ingredient of cashew nut shell liquid (CNSL), is a meta-substituted phenol. Some of the positive aspects of cardanol based resins are their anti-microbial, anti-termite, low cost, flexibility, water resistance etc. The application of cardanol based resins as a full or partial replacement for synthetic resins is of immense interest in these days of diminishing petroleum reserves.

The thesis consists of five chapters. An introduction and literature survey is given in the first chapter. The optimisation of basic components of the adhesive, the effect of varying of phenol/cardanol ratio and the influence of phenol/ formaldehyde ratio on adhesive performance is covered in the second chapter. The effect of replacing phenolic resins with epoxidized phenolic resins is outlined in chapter three. The ability of the adhesive joints to withstand severe environmental conditions and the effect of the adhesives for bonding different substrates are described in chapter four. The major findings of this study along with scope for

future research are summarised in the last chapter. List of abbreviations and symbols are given at the end of the thesis and references at the end of each chapter.

The successful completion of the present research endeavour was made possible by the generous, enthusiastic and inspiring guidance of my supervising teacher Dr. Eby Thomas Thachil, who always kept an eye on the progress of my work and was available when I needed his advises. His emphasis on perfection and aptness helped me to complete the thesis in the present form. With great pleasure, I express my sincere gratitude for the unparallel guidance and competent advice received. I am extremely grateful to Dr.Thomas Kurian, Head of the Department and Dr.K.E. George and Dr. Rani Joseph former Heads of the Department for providing all facilities during my research work. I am thankful to Dr. Philip Kurian for the valuable suggestions and fruitful discussions during the course of my work. With pleasure, I thank all faculty members especially Dr.Sunil K Narayanankutty, Ms. Jayalatha and all non-teaching staff of the Department for the whole-hearted co-operation and support throughout the course of this work. I am also indebted to Dr.G.Madhu, Head and all faculty members of Division of Safety and Fire Engineering for all the support and co-operation.

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Above all, I thank the Lord Almighty for showering his abundant grace on me throughout the course of my work. 'The Lord gives wisdom and from His mouth come knowledge and understanding' said the Wise Solomon in his book 'The Proverbs' in the Bible. The inspiration and knowledge received from the Lord for the completion of this thesis is beyond words to describe and let all Glory and Honour be unto Him.

Lity Alen Varghese

CONTENTS

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

ABSTRACT

The aim of the investigation is to develop new high performance adhesive systems based on neoprene-phenolic blends. Initially the effect of addition of all possible ingredients like fillers, adhesion promoters, curing agents and their optimum compositions to neoprene solution is investigated. The phenolic resin used is a copolymer of phenol-cardanol-formaldehyde prepared in the laboratory. The optimum ratio between phenol and cardanol that gives the maximum bond strength in metal-metal, rubber-rubber and rubber-metal specimens has been identified. Further the ratio between total phenols and formaldehyde is also optimised. The above adhesive system is further modified by the addition of epoxidized phenolic novolacs. For this purpose, phenolic novolac resins are prepared in different stoichiometric ratios and are subsequently epoxidized. The effectiveness of the adhesive for bonding different metal and rubber substrates is another part of the study. To study the ageing behaviour, different bonded specimens are exposed to high temperature, hot water and salt water and adhesive properties have been evaluated. The synthesized resins have been characterized by FTIR, ^{1}HNMR spectroscopy. The molecular weights of the resins have been obtained by GPC. Thermogravimetric analysis and differential scanning calorimetry are used to study the thermal properties. The fractured surface analysis is studied by scanning electron microscopy. The study has brought to light the influence of phenol/formaldehyde stoichiometric ratio, addition of cardanol (a renewable resource), adhesion promoters and suitability of the adhesive for different substrates and the age resistance of adhesive joints among other things.

Chapter 1

Introduction and literature survey

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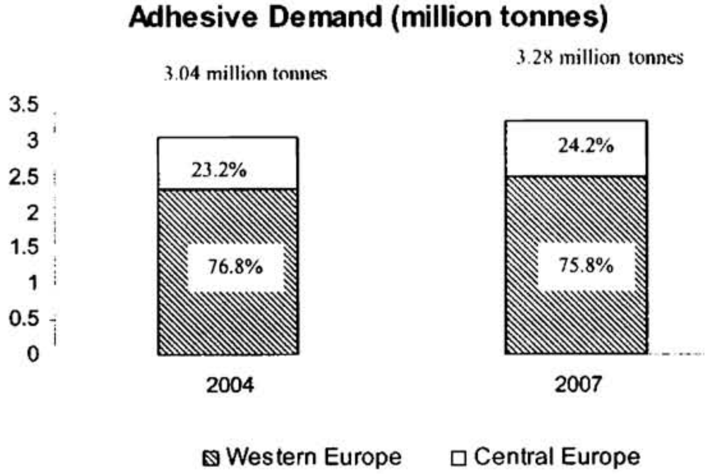
1. ADHESIVE BONDING

Adhesive bonding employs adhesives to establish a union between two substrates. An adhesive is a substance capable of bonding at least two surfaces together in a strong and permanent manner [1]. According to ASTM D-907, adhesion is 'the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both'. The use of adhesive extends back to the biblical times. Bitumen was supposedly the mortar for the Tower of Babel; beeswax and pine tar were used in caulking Roman vessels that dominated the Mediterranean Sea [2]. Plant gums and mucilage have been known and in use since very early times, reference being made to them in the Bible; they seem to have been of commercial value for several thousand years, especially in India, Asia, Africa, Australia and China [3]. Beeswax, rosin, rubber, shellac, sulphur, tar and vegetable gums were some of the materials used by early human beings as adhesives. In the early 1900s, synthetic polymeric adhesives began to displace many of these naturally occurring products owing to their stronger adhesion, greater formulation possibilities and superior resistance to operating environments. By early 20th century phenol-formaldehyde resins came on the scene. Phenol-formaldehyde resins became the first synthetic resin to be used as adhesive and later on epoxy resins were introduced [4].

Significant growth again occurred in the 1940s and 1950s with the development of structural adhesives and sealants for the military aircraft industry [5]. Because of the exceptional strength-to-weight ratio of adhesive bonded joints, the development of modern adhesives and sealants is closely related to the history of aircraft and aerospace industries.

The science of adhesion is now well accepted, and the basic rules and methods for achieving high performance joints have been well established. The industry has a strong foundation of formulations and processes. The avenues for application of adhesives are also growing fast. They include construction, packaging, furniture, automotive, appliance, textile, aircraft and many others. The statistics of the European adhesives market for the year 2004-2007 as reported by FEICA

(Association of European Adhesives Manufacturers) is shown in Fig.1.1. Of the total adhesive demand of 3.04 million tonnes in 2004, Western Europe showed a demand of 76.8% as compared to central Europe with 23.2%. The statistics predict a total demand of 3.28 million tonnes by 2007 with an annual growth rate of 2.6% per annum.



Data obtained from FEICA (Association of European Adhesives Manufacturers)

Fig 1.1 European adhesive demand (2004-2007)

1.1 COMMON JOINING METHODS

A variety of joining methods can be used to assemble parts to form an assembled joint. These methods include adhesive bonding, welding, brazing, soldering and mechanical fastening. All fastening and joining systems fall into one of the three general categories.

- Periodic- the attachment of two members by occasionally placing through-hole fasteners or other individual mechanisms.
- Linear- a continuous or occasional edge attachment, such as welding.
- Area- an attachment achieved by full-face contact and union between the two mating surfaces.

Table 1.1 Comparison of joining processes [6]

	Welding	Brazing and soldering	Mechanical fastening	Adhesive bonding
Permanence	Permanent joints	Usually permanent	Threaded fasteners permit disassembly	Permanent joints
Stress distribution	Local stress points in structures	Fairly good stress distribution	Points of high stress at fasteners	Good uniform load distribution over joint area
Appearance	Joint appearance usually acceptable	Good appearance of joints	Surface discontinuities sometimes unacceptable	No surface marking. Joint almost invisible
Materials joined	Generally limited to similar material groups	Some capability of joining dissimilar metals	Most forms and combinations of materials can be fastened	Ideal for joining most dissimilar materials
Temperature resistance	Very high temperature resistance	Temperature resistance limited by filler metal	High temperature resistance	Poor resistance to elevated temperatures
Mechanical resistance	Special provision often necessary to enhance fatigue resistance	Fairly good resistance to vibration	Special provision for fatigue and resistance to loosening at joints	Excellent fatigue properties. Electrical resistance reduces corrosion

In identifying the appropriate joining method for a particular application, a number of factors must be considered (Table1.1). There generally is no single method of fastening that is obviously the best choice. Some fastening methods can quickly be eliminated from consideration, such as the welding of ceramic substrates or the use of an organic adhesive that has to withstand extremely high service temperatures. Adhesives are usually the proper choice when the substrates are physically dissimilar or metallurgically incompatible materials, thermoset plastics, ceramics, elastomers, thin materials or very small parts. Adhesive bonding is also appropriate when there are large areas to join, or when improvement in manufacturing productivity is required. Welding is usually done at high temperatures and mechanical fastening destroys the lightness and aesthetics of the final product.

1.2 ADVANTAGES AND LIMITATIONS OF ADHESIVE BONDING

The science of adhesive bonding has advanced to a degree where adhesives must be considered an attractive and practical alternative to mechanical fastening in many cases. Adhesive bonding presents several distinct advantages over conventional mechanical methods of fastening. Following are some major advantages of using an adhesive bond.

1.2.1 Mechanical advantages [1]

Dissimilar metals usually have different coefficients of thermal expansion or thermal conductivities making them difficult to weld. Some metals have unstable oxides, while light metals such as aluminium, magnesium and titanium are weakened or distorted by the heat of welding. Adhesives provide a low temperature, high strength joint with many of these substrates thereby avoiding many of the problems commonly encountered with other methods of joining. Many polymeric adhesives are viscoelastic and act like tough, relatively flexible materials with the ability to expand and contract. This allows the bonding of materials having greatly different coefficients of thermal expansion or elastic moduli. Toughness also provides resistance to thermal cycling and crack propagation. The stress distribution characteristics and inherent toughness of adhesives also provide bonds with superior fatigue resistance. They damp vibration and absorb shock.

In adhesive bonding, the stress will be uniformly distributed from one member to another, thus eliminating localized stress concentrations that can occur with other fastening systems. When using mechanical fasteners, substrates may need to be thicker or otherwise strengthened to handle the concentrated stress, which increases the weight and cost of the final assembly. Consequently, adhesives often allow structures to be built with lower cost and less weight.

1.2.2 Design advantages

Adhesives offer a better strength-to-weight ratio than other methods of mechanical fastening. Unlike rivets or bolts, adhesives produce smooth contours that are aerodynamically and aesthetically beneficial. Adhesives can join any combination of solid materials regardless of shape, thickness or mismatch in physical properties such as coefficient of thermal expansion or elastic modulus.

1.2.3 Production advantages

Adhesive bonding is, at times, faster and less expensive than conventional fastening methods. As the size of the area to be joined increases, the time and labour saved by using adhesives instead of mechanical fasteners progressively increase because the entire joint can be bonded in one operation. They minimize or prevent galvanic corrosion between dissimilar metals.

Adhesives have the following disadvantages too.

1.2.4 Mechanical limitations

The most serious limitation on the use of polymeric adhesives is their time-dependent degradation in strength in degrading environments such as moisture, high temperatures or chemicals. For example, organic adhesives perform well between –50 and 175°C, but only a few adhesives can withstand operating temperatures outside that range. The rate of strength degradation may be accelerated by continuous stress or elevated temperatures. With most structural adhesives, strength is more directional than with mechanical fasteners. Residual stresses inside the joint can also present serious problems. Adhesives are generally formulated to cure in thin sections. Certain epoxy adhesives, when applied in bulk, could over-heat due to their own crosslinking reaction and, infact, burn or degrade when cured in thick sections.

1.2.5 Design limitations

Many rigid adhesives do not work well when external stresses act to peel or cleave the substrates from one another. These stresses can be reduced or eliminated by careful joint design. It is also very difficult to predict the useful life of a bonded adhesive joint. An effective method to do this is to test prototypes under environmental conditions that will accelerate the stress on the bond.

1.2.6 Production limitations

All adhesives require clean surfaces to obtain the best results. Depending on the type and condition of the substrate and the bond strength desired, surface preparations ranging from a simple solvent wipe to chemical etching are necessary. If the adhesive has multiple components, the parts must be carefully weighed and mixed. The curing operation often requires heat and pressure. Long setting time makes jigs and fixtures necessary for assembly. Rigid process controls are also necessary as the adhesive properties are dependent on curing parameters and surface preparation. The inspection of finished joints for quality control is very difficult.

1.2.7 Other limitations

Adhesives are sometimes composed of material that may present personnel hazards, including flammability and dermatitis. The storage life of the adhesive may be unrealistically short and some adhesives require refrigerated storage. Once bonded, samples cannot easily be disassembled. If misalignment occurs and the adhesive cures, usually the part must be scrapped.

1.3 CLASSIFICATION OF ADHESIVES ON VARIOUS GROUNDS

Adhesives are classified by many methods. Perhaps, the broadest classification scheme is to categorise an adhesive as being manufactured from materials that are either synthetic or naturally occurring. Synthetic adhesives are manufactured from man-made materials mainly polymers. Natural adhesives are manufactured from naturally occurring materials such as animal or agricultural by-products. The common methods of classifying adhesives are [1] based on their

- Function
- Chemical composition
- Method of curing
- Physical form
- End use

1.3.1 Function

The functional classification defines adhesives as being either structural or non-structural. Structural adhesives are materials of high strength and permanence. Their primary function is to hold structures together and be capable of resisting high loads without deformation. They are generally presumed to survive the life of the application while non-structural adhesives creep under moderate load and are often degraded by long-term environmental exposure. Non-structural adhesives are sometimes referred to as holding adhesives. They are at times used with other types of mechanical fasteners. In these applications, the adhesive bond is considered a secondary fastener.

1.3.2 Chemical composition

Based on chemical composition adhesives are classified as being thermosetting, thermoplastic, elastomeric or alloys (hybrids) of these.

Thermosetting adhesive systems cure by an irreversible chemical reaction at room or elevated temperatures. This chemical reaction is often referred to as crosslinking. The crosslinking that occurs during the curing reaction is brought about by the linking of two linear polymers, resulting in a three dimensional rigidized chemical structure. Crosslinking usually occurs by chemical reaction. These adhesives generally degrade and weaken upon heating at high enough temperatures because of oxidation or molecular chain scission. Epoxy, phenolic and urethane adhesives are examples of common adhesives of the thermoset family.

Thermoplastics are solid polymers that soften or melt when heated. Since thermoplastic adhesives do not cure into a crosslinked structure, they can be melted with application of heat and then applied to a substrate. Once applied to the substrate, the parts are joined and the adhesive hardens by cooling. Hot-melt adhesives, commonly used in packaging are examples of thermoplastic material applied in a molten state. Adhesion develops as the melt solidifies during cooling. Thermoplastics can also be dissolved in solvent to produce a flowable solution and then rehardened on evaporation of the solvent. They have a more limited operating temperature range than thermosetting types. As these materials are not crosslinked they tend to creep under load at lower temperatures. These adhesives do not have, in general, resistance to solvents or chemicals as do the thermosetting adhesives.

Elastomeric adhesives are based on synthetic or naturally occurring elastomeric polymers having great toughness and elongation. These adhesives are made from polymeric resins that are capable of high degrees of extension and compression. They return rapidly to their initial dimensions and shape after the load is removed. As a result, elastomeric adhesives have energy absorbing characteristics and offer high strength in joint designs having non-uniform loading. As elastomeric adhesives are viscoelastic materials, they are characterized by a high degree of elongation, low modulus and high toughness. This provides adhesives with high peel strength and a high degree of flexibility to bond to substrates with different expansion coefficients.

Hybrid adhesives are made by combining thermosetting, thermoplastic or elastomeric resins into a single adhesive formulation. Generally high temperature, rigid resins are combined with flexible, tough elastomers or thermoplastics to provide improved peel strength and energy absorption. Nitrile-phenolic, epoxy-polysulphide and neoprene-phenolics are examples of these adhesives. These adhesives show improved resilience and toughness due to the elastomeric ingredients in the formulation. But the elastomeric component present lowers the glass transition temperature and degrades the elevated temperature and chemical resistance of the more rigid resin.

1.3.3 Method of curing

Adhesive curing can be done by chemical reaction [7], by loss of solvent, by loss of water or by cooling from a melt.

a. Chemical reaction

Most thermosetting adhesives crosslink and cure by primary chemical reactions. In order to cure these adhesive systems, a curing agent or catalyst is required. The curing reaction then proceeds at room or at elevated temperatures depending on the nature of the reaction.

i. Multiple part adhesive system

Multiple component systems consist of two or more components that must be kept separate until just before the bonding operation. These components must be metered in the proper ratio, mixed and then dispersed. Epoxies, polyurethanes, acrylics, phenolics and silicones are common adhesive systems that are available in multiple parts.

ii. Single component systems

Most single component adhesive systems incorporate a latent curing agent or hardener in the formulation along with other fillers and additives. This hardener is activated with heat and then on continued heating reacts with the base resin to produce a thermosetting molecular structure. Single component adhesive families that cure by heat include epoxy, polyimide, polybenzimidizole, phenolic and phenolic hybrids.

iii. Moisture curing adhesives

These adhesive systems use the humidity in the ambient air to react with the base resin in the adhesive formulation. The moisture diffuses into the adhesive and reacts with the molecules to form a solid structure. Polyurethanes and silicones are common single component adhesives that cure by reacting with environmental moisture. These are available as pastes and liquids [8, 9].

iv. UV / light curing adhesives

UV and light cure adhesives use photoinitiators to activate the free radical curing mechanism. The free radicals formed by the photoinitiators are able to crosslink with other components in the adhesive formulation. That part of the adhesive film not directly exposed to light will not cure. Hence the substrates to be bonded are generally limited to those that are transparent. Aerobic acrylic adhesives are generally used in UV curing applications.

v. *Adhesives catalysed by the substrate*

Some single component adhesives cure by a chemical reaction mechanism that uses the active metal ions (eg., iron and copper) on the substrate as a catalyst. These types of adhesive systems are called anaerobic adhesives. Once placed between substrates, the air is eliminated and the adhesive reaction is catalysed by the metal ions on the substrate surface. On curing, these adhesives will have high strength and good resistance to moisture, solvents and elevated temperatures. Anaerobic adhesives cure very fast depending on the substrate. They are formulated mostly with methacrylate monomers.

b. Solvent or water loss

Solvent solutions and water based latexes and dispersions harden by the evaporation of their carrier material-either solvent or water. The carrier material's function is to lower the viscosity of the adhesive so that it can be easily applied to the substrate. There are primarily four types of adhesives that harden by loss of solvent or water.

i. Contact adhesives

Contact adhesives are applied to both substrates by spray or roll coating. After the solvent evaporation, the adhesive rapidly bonds or knits to itself with the application of contact pressure. Contact adhesives generally have relatively high shear and peel strengths but generally have less 'green strength' or immediate tack than pressure sensitive adhesives and cannot be applied to only one substrate.

ii. Pressure sensitive adhesives

Pressure sensitive adhesives are usually based on elastomer (natural, butyl, nitrile and styrene butadiene thermoplastic), acrylate or silicone resins. They are applied much like contact adhesives and instantly provide a degree of tackiness. Unlike contact adhesives, their tackiness is permanent and there is no optimal time range when the substrates must be joined. They build a stronger bond over time.

iii. Reactivatable adhesives

These systems can be applied to a substrate via solvent coating and then dried to a non-tacky state. The coated substrate is then usually stored or it proceeds to the next step in the manufacturing operation. When it is time to bond the coated substrates to another substrate, the coated piece is exposed to solvent. This partially liquefies the adhesive and it becomes tacky so that the substrates can be mated under contact pressure. These adhesives are normally highly formulated thermoplastic resins.

iv. Resinous solvent adhesives

The adhesive is a resinous material dissolved in the solvent. It is applied to porous substrates that are then joined. The solvent evaporates leaving the resin to mechanically lock the substrates together.

c. Hardening from melt

These are generally thermoplastic adhesives that soften on heating and melt when heated and harden on subsequent cooling. The hot melt system must achieve a relatively low viscosity when in the molten state to achieve wetting. Once the hot melt adhesive is applied in the molten condition, the substrates must be joined immediately. Alternatively the adhesive can be applied and the adhesive coated substrate placed in storage for later activation. At a later date, the coated substrates are reheated and joined under slight pressure. Materials that are primarily used as hot melt adhesives include ethylene and vinyl acetate copolymers, polyvinyl acetates, polyamides and polyesters.

1.3.4 Physical form

The most common forms of adhesives are one part solventless (liquid or paste), multiple part solventless (liquid or paste), one part solution (liquid) and solid (powder, tape, film etc.)

a. Pastes and liquids

The difference between paste and liquid adhesive lies mainly in viscosity and method of application. Liquid adhesives are free flowing and can be applied in thin films. They tend to flow, spread and sag during cure, especially at elevated temperatures when their viscosity is even further reduced. Paste adhesives are heavily bodied, often thixotropic systems that must be applied with spreading equipment such a trowel or caulking gun.

i. One part solventless

They are supplied in a ready-to-apply condition. Most of these systems are heat curing or cure by reaction of moisture in the air. Some systems can cure by ultraviolet, anaerobic or some other catalytic reaction mechanism. Most one part thermosetting adhesives contain a latent hardener that activates and cures the adhesive at elevated temperatures. Usually, one part systems have a limited shelf life and refrigerated storage may be required.

ii. Two part solventless

Two part solventless adhesive systems usually require proportioning and mixing immediately prior to use. Most can cure at low temperatures or in shorter times at elevated temperatures. Once mixed, two part adhesives have a limited working life.

As the mixture cures, the viscosity increases to the extent that it can no longer be applied.

b. Solvent based adhesives

Solvent based adhesives use organic solvent to reduce viscosity for easier application. Solvent adhesives are applied by spraying, dipping, or brushing.

c. Solid forms

The main advantages of the solid form adhesives are that metering and mixing is not required. They can be applied uniformly to a substrate with little or no waste. The common forms of solid adhesives are tape or film and powder forms.

1.3.5 End use

Based on end use adhesives are classified into metal adhesives, wood adhesives, vinyl adhesives etc which refer to the substance to which they will bond. Similarly, acid resistant adhesives, heat resistant adhesives and weatherable adhesives indicate the environments for which they are best suited. Adhesives are also classified by the method of application like sprayable, brushable, extrudable etc.

1.4 ADHESIVE FORMULATION [7]

The majority of adhesives used today are composed of mixtures of several complex materials that may be organic, inorganic or hybrid. The components of the adhesive are usually determined by the need to satisfy the end-properties required, the application and processing requirements and the overall cost. But one or more polymeric binders will always be part of the formulation. The various components of an adhesive formulation include the following substances.

1.4.1 Base or binder

This is the primary and often the largest component of an adhesive and it provides the main characteristics such as wettability, curing properties, strength and environmental resistance. Epoxy resins, phenolic resins, epoxy-phenolics, nitrile-phenolics, neoprene – phenolics etc serve as binders

1.4.2 Catalysts and hardeners

They are the substances added to an adhesive to promote the curing reaction. They cause curing by chemically combining with the base resin or by catalyzing the crosslinking reaction. Reactive polyamides, primary polyamines like diethylenetriamine and triethylenetetramine, aromatic amines like m-phenylenediamine and diaminodiphenyl sulfone etc are the commonly used hardeners for epoxy binder systems. Acids, sulphur compounds and peroxides also serve as catalysts.

1.4.3 Accelerators, inhibitors and retarders

These are critical components that control the curing rate, storage life and working life of the adhesive. An accelerator speeds up the curing reaction while an inhibitor arrests the reaction. Thiocarbanilide, mixtures of litharge or sulphur, NA-22 are examples of accelerators used in neoprene based systems. A retarder slows down the reaction and prolongs the working life of the adhesive. N-propyl gallate is an example of a retarder.

1.4.4 Solvents

Solvents are needed to disperse the adhesive to a consistency that is more easily applied such as brush or spray. They also reduce the viscosity of the base resin so that addition of other components and uniform mixing may be more easily achieved. Generally, organic solvents are used with synthetic resins and elastomers. Toluene, acetone, methyl ethyl ketone, water etc serve as solvents. The choice of solvent depends on the nature of synthetic resins and elastomers used.

1.4.5 Diluents

Diluents are added to reduce the concentration of base resin or binder. They are used to lower the viscosity and modify the processing conditions of adhesives. Diluents do not evaporate like solvents, but they become part of the final adhesive. Coal and pine tar are the commonly used nonreactive diluents.

1.4.6 Extenders

They are substances usually with some adhesive property added to reduce the concentration of other adhesive components and the cost of the overall formulation. Common extenders used are flours and soluble lignins.

1.4.7 Fillers

They are non-adhesive materials, usually in particulate form which improve the working properties, permanence, strength or other qualities. Fillers are also added to reduce the material costs. Common fillers are wood flour, silica, alumina, carbon black, titanium oxide, silica etc.

1.4.8 Plasticizers

Plasticizers are incorporated in a formulation to provide the adhesive bond with flexibility. They generally affect the viscoelastic properties of the base resin, whereas diluents simply reduce the viscosity of the system. They lower the modulus of the adhesive system. Certain resinous materials which act as plasticizers also serve as tackifiers. Aliphatic and aromatic hydrocarbons, terpenes and rosin esters are the commonly used tackifiers in adhesive formulations.

1.4.9 Stabilizers

Stabilizers are added to increase resistance to adverse service conditions such as light, heat, radiation etc. Titanium dioxide is usually added to improve the storage life of the adhesives. Naphthylamine, substituted phenols etc. also improve the ageing resistance of adhesives.

1.4.10 Wetting agents

They promote interfacial contact between adhesive and adherends by improving the wetting and spreading qualities of the adhesive. Sodium lauryl ether sulphate, sodium alkylaryl ether sulphate etc are used as wetting agents.

1.5 DISPENSING METHODS [10]

Dispensing is the process whereby the adhesive is applied to the surface being bonded. Commonly used methods are the following.

1.5.1 Brushing and trowelling

This is one of the widely used processes for applying the adhesive on the adherends. The adhesive is applied using tools such as brushes, trowels or spatulas. The choice of tool is determined by the consistency of the adhesive and the area to be coated. The bond quality depends on levels of coverage, extent of coverage, surface wetting, placement of adhesive and open/drying times. These dispensing operations neither require capital investment nor highly skilled operators.

1.5.2 Roller transfer

This method is also referred to as wheel or disc coating. In this method, the adhesive, stored in a reservoir, is transferred to a roller (either directly through immersion in the reservoir or by 'pumping' onto the roller) and then (either directly or indirectly via another roller) to the adherend. This process is suitable for assembly line/ conveyor belt production in applications where large areas are to be coated/ bonded.

1.5.3 Spray application

Spray application is suitable for covering large areas with adhesive. Some of the spraying methods are conventional air spray, hydraulic cold airless spray, hot spray and hot airless spray.

1.5.4 Pin transfer

This is one of the fastest methods of applying patterns of adhesive to surfaces (eg. printed circuit boards). A dedicated tool with an array of pins, designed to match the adhesive dot pattern on the substrate, is dipped into a tray of adhesive, wetting the pins in predictable amounts. The pins are then touched to the substrate and adhesive transfers to the board. This method is considered to be difficult for small components. The adhesive viscosity is also very important as a degree of fluidity is needed to wet the pins and for transference to the board but 'non-drip' properties are required to hold the adhesive in place between dipping and transfer.

1.5.5 Stencil printing

Stencil printing is a viable and cost-effective method of applying adhesives. A stencil patterned with apertures corresponding to the desired placement of adhesive is placed on the surface to be bonded. The adhesive is applied to the top of the stencil using a roller to force the adhesive into the openings, making contact with the surface below. The size and shape of the resulting dots can be controlled through the geometry of the stencil apertures (principally stencil thickness and aperture diameter) and rheology of the adhesive. The storing and cleaning of the stencil after a production run can be time consuming. Also new stencils will be required each time the dispense pattern is changed.

1.5.6 Nozzle dispensing methods

a. Squeeze bottle

It is used to dispense fluid adhesives. Adhesive flows when the bottle is inverted or pressure is applied to the bottle. It is difficult to precisely control the volume of the adhesive dispensed.

b. Sealant gun

It is a simple means of dispensing pastes from standard catridges. The catridge is secured in the gun; squeezing or triggering the handle depresses a plunger at the base of the adhesive catridge that forces the paste out through the catridge nozzle.

c. Pressure pump

Here the adhesive is contained in a pressurized syringe and the flow is controlled using air pulsed through a nozzle valve to dispense the desired amount of adhesive.

d. Auger pump

In this method a pump with a rotating screw thread is used to displace the adhesive in a reservoir.

e. Piston pump

It is a positive displacement method of adhesive application. The movement of piston in a closed chamber precisely determines the volume of adhesive dispensed. In most dispensing applications the pump is set to a fixed displacement to give a specified shot size.

f. Jet dispensing

This is a method of applying adhesive using a spring loaded pin to force adhesive through the nozzle in a cyclic manner rapidly. Air pressure raises the pin above the reservoir and when the air pressure is removed the spring drives the pin down to force adhesive through the nozzle.

1.6 ADHESION AND THEORIES OF ADHESION

Adhesion is the state in which two surfaces are held together by interfacial forces of attraction, resulting from the interactions of molecules, atoms and ions on the two surfaces [11]. The science of adhesion is a multifaceted subject requiring an understanding of interatomic forces, chemical composition and physical properties of materials, and the forces to which the final structure will be subjected [12]. The forces range in magnitude from the strong chemical bonds formed when two atoms share electrons or when electric charges attract each other to comparatively weak attractive forces, known as van der Waal's interactions occurring whenever two surfaces are placed in intimate contact [13-17]. Adhesion science can be studied in two ways: from the chemistry and physics of surfaces and interfaces and from the fracture mechanics of adhesive joints [18]. Popular theories on adhesion are given below.

1.6.1 Mechanical theory

The surface of a solid material is never truly smooth but consists of a maze of peaks and valleys. McBain and Hopkin proposed the mechanical interlocking theory in 1925 [19]. According to this theory, the adhesive must penetrate the cavities on the surface, displace the trapped air at the interface, and lock on mechanically to the substrate. The mechanism of adhesion can be described as a 'hook and eye' approach. Mechanical anchoring of the adhesive appears to be the prime factor in bonding many porous substrates like wood, paper, textiles etc. Adhesives also frequently bond will to nonporous abraded surfaces than to natural surfaces. One of the most consistent examples illustrating the contribution of mechanical anchoring was given by Boroff and Wake [20]. Their work on the adhesion between the textile cords and the rubber casing, proved that the only significant factor in such joints was the penetration of the fibre ends into the rubber. Wake [21] proposed that the effects of both mechanical interlocking and thermodynamic interfacial interactions could be taken into account as multiplying factors for estimating the joint strength G:

$$G = (\text{constant}) \times (\text{mechanical keying component}) \times (\text{interfacial interactions component})$$

According to the above equation, a high level of adhesion should be achieved by improving both the surface morphology and physicochemical surface properties of substrate and adhesive. But in most cases, the enhancement of adhesion by mechanical keying can be attributed simply to the increase in interfacial area due to surface roughness.

The major criticism of the mechanical theory is the attainment of good adhesion between smooth surfaces. The works of Tabor *et al* [22, 23] who studied the adhesion between two perfectly smooth mica surfaces and Johnson *et al* [24] who examined the adhesion to optically smooth rubber surfaces, clearly demonstrate that adhesion may be attained with smooth surfaces. In certain cases mechanical interlocking may contribute to already existing intrinsic adhesion mechanisms. In any case, the substrate has to be specifically pretreated to obtain the appropriate topography for this to occur and this appears to happen in only a few instances. The frequently observed increases in measured joint strengths with increasing rugosity are most usually attributed to other factors such as removal of weak surface layers, improved interfacial contact and the enhancement of energy dissipative mechanisms in the adhesive [25].

1.6.2 Diffusion theory

This theory states that the intrinsic adhesion of polymers to themselves (autohesion) and to other polymers, is due to the mutual diffusion of polymer molecules across the interface [26-28]. This is primarily applicable when both the adhesive and adherend are polymeric, having compatible long-chain molecules capable of movement. The adhesive and the adherend must be chemically compatible in terms of diffusion and miscibility. This theory can be applied in only a limited number of cases, as situations in which the adherend and adhesives are soluble in one another are relatively rare. Vasenin [29] has developed a model for diffusion from the first law of Fick which relates the amount of material, 'w', diffusing in a given x-direction across a plane of unit area normal to the concentration gradient, $\frac{\partial c}{\partial x}$, and the time, t, by

$$\partial \mathrm{w} = -\mathrm{D_f}\, \partial t \frac{\partial c}{\partial x}$$

D_f = Diffusion coefficient

However, this can only be applied to steady-state diffusion where the concentrations at points within the system do not vary with time. This is clearly not the case for the penetration of a segment of polymer chain into the surface regions of a polymeric substrate. For many diffusion processes in polymers, a linear increase of the penetration depth (x) with the square root of the contact time (t) is found to hold as per the equation.

$$x^2 = 2\, D_f\, t$$

This is not only valid for the diffusion of liquids in polymers, but also for the interdiffusion of rubbers [30].

The interdiffusion of polymer chains across a polymer / polymer interface requires the polymers to be mutually soluble and the macromolecules or chain segments to have sufficient mobility. These conditions are usually met in the autohesion of elastomers and in the solvent welding of compatible, amorphous plastics. In both these examples interdiffusion does appear to contribute significantly to the intrinsic adhesion. However, where the solubility parameters are not similar, or one polymer is highly crosslinked, crystalline or below its glass transition temperature, interdiffusion is unlikely to be the mechanism of adhesion.

1.6.3 Electronic theory

The electrostatic theory states that electrostatic forces in the form of an electrical double layer are formed at the adhesive-adherend interface. Therefore, the adhesive-substrate junction can be imagined as a capacitor. During interfacial failure of this system, separation of the two plates of the capacitor leads to an increasing potential difference until a discharge occurs. Consequently, this electrostatic force contributes significantly to the intrinsic adhesion [31-33]. According to Deryaguin's approach [33], the adhesion depends on the magnitude of the potential barrier at the substrate-adhesive interface. Although this potential barrier does exist in many cases [34, 35], no clear correlation between electronic interfacial parameters and work of adhesion is usually found. Several groups of workers [36-39] have investigated the improvement in the adhesion of thin metal films recorded when the insulator substrate is subjected to a low-pressure glow discharge prior to coating. Stoddart *et al* [37] found no net surface electric discharge on the substrate but found that the electron emission was altered, indicating that the surface electronic states of the substrates have been changed. Thus, in certain specialized interfaces the influence of an electrostatic double layer has been clearly demonstrated. However, for typical adhesive/ substrate interfaces, any electrical double layer generated does not contribute significantly to the intrinsic adhesion.

1.6.4 Adsorption theory

The adsorption theory states that adhesion results from molecular contact between two materials and the surface forces developed. Materials adhere because of interatomic and intermolecular forces established between the atoms and molecules on the surfaces of the adhesive and substrate. The common forces are van der Waal's attractions referred to as secondary bonds or hydrogen bonding. In addition, chemical bonds may sometimes be formed across the interface. This is termed chemisorption and involves ionic, covalent or metallic interfacial bonds that are referred to as primary bonds. Donor-acceptor interactions may occur across an interface and these are typically intermediate in strength between secondary and primary bonds [25].

1.7 SURFACE AND INTERFACIAL PROPERTIES

To get good adhesion, the primer and the adhesive should be able to spread over the entire solid surface and it should displace air and other contaminants present on the surface. Such an adhesive, if liquid, must exhibit a zero or near zero contact angle and should have a low viscosity. The adhesive should be brought together with the substrate at a rate that should assist the displacement of any trapped air. For molecules to get attracted, the distance between them should not be more than 0.3nm [40].

The process of establishing continuous contact between an adhesive and the adherend is known as 'wetting'. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface. Poor wetting results when the adhesive bridges over the valleys formed by these crevices. Wetting is favoured when the substrate surface tension, γ_{SV}, or its critical surface energy γ_C, is high, and the surface tension of the wetting liquid, γ_{LV}, is low.

For good wetting: $\gamma_{\text{adhesive}} << \gamma_{C\text{ substrate}}$

For poor wetting: $\gamma_{\text{adhesive}} >> \gamma_{C\text{ substrate}}$

The thermodynamic work of adhesion, W_A, required to separate a unit area of a solid and a liquid phase forming an interface across which secondary forces are acting may be related to the surface and interfacial free energies by the Dupré equation [41]. The reversible work of adhesion is first expressed by Dupré and is given as

W_A = (Sum of the surface free energies of the solid and liquid phases- the interfacial free energy)

i.e. $W_A = \gamma_S + \gamma_{LV} - \gamma_{SL}$

The amount of work for holding an adhesive to a substrate or maintaining the cohesive integrity of a solid can be measured as the work necessary to separate two surfaces beyond the range of forces holding them together. The degree to which a liquid wets a solid is measured by the contact angle [42].

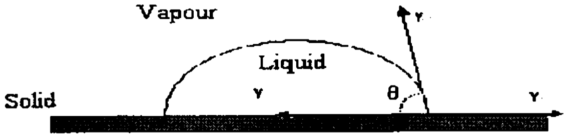


Fig 1.2 Wetting of a solid substrate by a liquid phase

The Young equation [43, 44] relates the surface tension to contact angle, θ. It may be written as:

$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$

where γ_{SV} - Solid-vapour interfacial tension

γ_{SL} - Solid-liquid interfacial tension

γ_{LV} - Liquid-vapour interfacial tension

The γ_{SV} is not the true surface energy of the solid. The true surface energy (γ_S) is related to the γ_{SV} through the relationship:

$\gamma_{SV} = \gamma_S - \pi_e$

where π_e is the equilibrium spreading pressure. It is a measure of the energy released through adsorption of the vapour onto the surface of the solid, thus lowering the surface energy.

When $\theta > 0^\circ$ the liquid is nonspreading, but when $\theta = 0^\circ$ the liquid wets the solid completely and spontaneously spreads freely over the surface. Thus for spontaneous wetting to occur,

$$\gamma_{SV} \geq \gamma_{SL} + \gamma_{LV}$$

$$\gamma_S \geq \gamma_{SL} + \gamma_{LV} + \pi_e$$

Let S the equilibrium-spreading coefficient may be represented by

$$S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$$

$$S = \gamma_S - \gamma_{SL} - \gamma_{LV} - \pi_e$$

Hence, a liquid will spread spontaneously and completely wet a solid surface when $S \geq 0$.

1.8 SURFACE PREPARATION

Since adhesives must function by surface attachment, the nature and condition of the substrate surface are critical to the success of any bonding operation. The main aims of surface pre-treatment are one or more of the following [45]:

a) To remove or prevent the formation of any weak surface boundary layer on the substrate.

b) To maximize the degree of intimate molecular contact attained between the adhesive and the substrate during the bonding operation.

c) To ensure that the level of intrinsic adhesion forces established across the interface(s) are sufficient for obtaining both the initial joint strength and subsequent service life that are required. In the case of low-energy polymeric surfaces surface treatments aim at increasing the surface free energy of the substrate. It may also be necessary to introduce chemical groups into the surface regions which can form acid-base or stronger primary bonds with the adhesive.

d) To generate a specific surface topography on the substrate.

e) To assist in the hardening of the adhesive

f) To protect the surface of the substrate so that weak boundary layers do not develop prior to bonding.

Surface treatments can be either passive or active [1]. Passive processes do not actively alter the chemical nature of the surface. They only clean the substrate and remove weak boundary layers in the form of contamination without altering the surface chemistry. Active surface treatments alter the surface chemistry.

1.8.1 Solvent cleaning

This is the process of removing soil and organic contaminants from a substrate surface with an organic solvent. Solvent cleaning is widely used and should precede any chemical or abrasive surface preparation. Solvents such as toluene, acetone, methyl ethyl ketone (MEK), methyl alcohol, isopropanol, and trichloroethylene are used [46-49].

1.8.2 Chemical cleaning

These methods are popular on polymeric surfaces where solvent cleaning may degrade the part. This is commonly used in combination with other surface treatments. Commonly used cleaning agents are caustics, silicates, amines, phosphates, acids, chelates etc.

1.8.3 Passive mechanical treatment

Mechanical methods for surface preparation include abrasive blasting, wire brushing and abrasion with sandpaper, emery cloth or metal wool. These methods are most effective for removing heavy, loose particles such as dirt, scale, tarnish and oxide layers. Solid particles left on the surfaces can be removed by blasts of clean, dry air and solvent wiping. Each substrate reacts favourably with a specific range of abrasive sizes. In many applications joint strength generally increases with the degree of surface roughness [50, 51]. However, excessively rough surfaces also increase the probability that voids will be left at the interfaces, causing stress risers that may be detrimental to the joint in service. Cryogenic and hydrodynamic blasting have been used as an abrasive-free surface treatment prior to adhesive bonding. The cryogenic process uses pelletized carbon dioxide at -100°F as a fluidised abrasive cleaning agent for surface preparation and removal of corrosion and old coatings [52]. High pressure water blast has been used for prebond surface treatments to eliminate hazardous materials. The combination of high pressure water abrasion with subsequent application of an adhesive primer has been found to provide high strength and durable aluminium bonds [53, 54]. Polymer blasting media have also been used for removal of paint, coatings and other contaminants for a variety of different applications [55]. The abrasive medium consists of hard plastic material.

1.8.4 Active physical surface treatments

a. Corona discharge

This is a popular method of dry surface preparation for polymer films. The purpose of the treatment is to make the surface more receptive to coatings [56, 57]. The electric equipment consists of a high frequency generator, a stationary electrode electrically connected to the generator and a dielectrically covered treater roll that serves as the grounded electrode. The material to be processed is carried over this roller for continuous processing. A suitable voltage that produces a corona discharge by ionising the air in the gap between the electrodes is developed. The ionised particles in the air gap bombard and penetrate into the molecular structure of the substrate. Free electrons and ions impact the substrate to break the molecular bonds on the surface of most polymeric substrates. This creates free radicals that react rapidly with oxygen to form polar chemical groups on the substrate surface and increase the surface energy.

b. Flame treatment

It consists of exposing a surface to a gas flame for less than several seconds. The treatment burns off contaminants and oxidizes the surface of the polymer. The flame treatment is believed to provide a polar surface that is conducive to adhesion. This method is used to promote good adhesion between thermoplastic substrates (e.g. polypropylene, polyethylene, polyolefins and nylon) and adhesives, paints and inks [56].

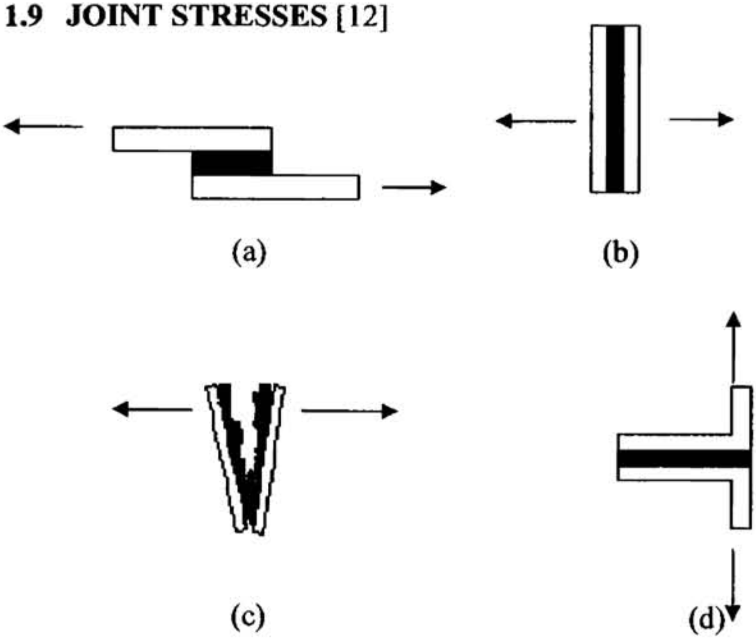
c. Plasma treatment

In plasma treatment, a low pressure inert gas is activated by an electrodeless radio-frequency discharge or microwave excitation to produce metastable excited species that react with the polymeric surface. It produces changes only to the depth of several molecular layers. It has proved effective in preparing the surfaces of metallic and polymeric materials for bonding [58, 59]. Plasma treatment has been successfully applied to titanium alloys, producing a surface oxide layer of uniform thickness and composition.

1.8.5 Active chemical surface treatments

Chemical treatments alter the physical and chemical properties of the surface to produce one that is highly receptive to adhesion. The chemicals used are acidic or alkaline in nature. Common chemical treatments include the use of sulphuric acid-sodium dichromate, phenol, sodium naphthalene, ferric chloride-nitric acid and nitric acid- hydrofluoric acid solutions.

1.9 JOINT STRESSES [12]



(a) (b)

(c) (d)

Fig 1.3 Types of stress to which an adhesive joint be subjected

a) lap shear b) tensile loading c) cleavage d) peel

The strength of an adhesive in the absence of external or environmental factors is determined by the mechanical properties of the materials comprising the joint, the extent of interfacial contact and residual stresses within the joint. There are four basic types of stresses that are important when considering adhesive joints. These are shear, tension, cleavage and peel (Fig.1.3).

1.9.1 Shear

Shear stress results when forces acting in the plane of the adhesive try to separate the adherends. A shear loading imposes an even stress across the whole bonded area. The centre of the lap joint contributes little to joint strength. Shear stresses are measured as force per bonded area. The shear strength of metal-to-metal adhesives is determined by ASTM D1002. The maximum permissible length of overlap between metal strips may be computed from the following relationship.

$L = F_{ty} t/r$

where L = length of overlap (mm)

F_{ty} = yield point of metal (N/mm^2)

t = thickness of metal (mm)

r = 150% of the estimated average shear strength in adhesive bond (N/mm^2)

The formula may also be used with some non-metallic adherends where the yield point of the material will permit its use. Bond strength of lap shear specimens are directly proportional to the width of the specimen, but as the length of overlap increases, the unit strength decreases due to stress concentrations at the overlapping edges. In lap shear specimens an optimum film thickness exists. Bond strengths will decrease when films are very thin or thick. For maximum bond strengths the optimum will vary with adhesives of different moduli. The thickness varies from about 2mils for high modulus materials to 6mils for low modulus materials. Shear strength of adhesives can be determined also by compression loading rather than tensile loading. An adhesive will show higher bond strengths for compression shear specimens than for tensile lap shear specimens. The high bond strength is ascribed to better stress distribution [60].

1.9.2 Tension

Tensile stress develops when forces acting perpendicular to the plane of the joint are distributed uniformly over the entire bonded area. In tension, the adhesive develops high stress regions at the outer edge and those edges then support a disproportionate amount of the load. The first crack that occurs at the weakest area of one of the highly stressed edges will propagate swiftly and lead to failure of the joint. Proper design requires that the joint has parallel substrate surfaces and axial loads. The adherends must also have sufficient rigidity so that the stress is distributed evenly over the entire bonded area. Tensile stress is expressed as force per unit bonded area.

1.9.3 Cleavage

Cleavage is defined as the stress occurring when forces at one end of a rigid bonded assembly act to separate the adherends. It is done as per ASTM D 1062. Joints loaded in cleavage offer lower strength than joints loaded in shear. Cleavage forces are measured as force per linear length of bond. Specimens are ordinarily made of metal, but other rigid materials can be employed as well. With low modulus adhesives, a lap length of 25mm is sufficient. The stress distribution in a cleavage test is complex and the forces required both to initiate and continue separation are considerably influenced by the dimensions of the specimen, the mechanical properties of the adherends as well as the strength and elastic characteristics of the adhesive.

1.9.4 Peel

Peel stress is similar to cleavage, but applies to a joint where one or both of the adherends are flexible. Peel strength is the weakest property of a joint. Peel or cleavage stress should be avoided where possible, since the stress is confined to a very thin line at the edge of the bond. Brittle adhesives are particularly weak in peel as the stiffness of the adhesive does not allow distribution of stress over an area much larger than the thickness of the bond line. Flexible adhesives, on the other hand, distribute the peeling stress over a wider bond area and show greater resistance to peeling forces.

1.10 FRACTURE MECHANICS OF ADHESIVE JOINTS

Adhesive joints usually fail by the initiation and propagation of flaws. The main aim of the various fracture mechanics theories is to analyse mathematically the loads at which the flaws propagate and describe the manner in which they grow. The source of naturally occurring flaws may be voids, cracks, dirt particles, additive particles, inhomogeneities in the adhesive, etc. which may be initially present at a critical size or develop during the fracture test. Fracture mechanics is found to be useful in characterizing the toughness of adhesives, identifying the mechanisms of failure and estimating the service life of 'damaged' structures – the damage being in the form of cracks, air-filled voids, debonds etc. [25].

The energy criterion arising from Griffith's [61] and Orowan's [62] work supposes that fracture occurs when sufficient energy is released by growth of the crack to supply energy requirements of the new fracture surfaces. The energy released comes from the stored elastic or potential energy of the loading system and can be calculated for any type of test piece. Therefore, this approach provides a measure of the energy required for extending a crack over unit area and this is termed the fracture energy or critical strain energy release rate and is denoted as G_c.

For bonded structures exhibiting bulk linear-elastic behaviour,

$$Gc = \frac{F_c^2}{2b}\frac{\partial C}{\partial a}$$

where F_c is the load at the onset of crack propagation

C, the compliance of the structure

a, crack length

b, specimen thickness

This equation is the foundation of many calculations of G_c, since if C is determined as a function of a, then $\frac{\partial C}{\partial a}$ may be found [63].

Irwin [64] found that the stress field around a sharp crack in a linear-elastic material could be uniquely defined by a parameter named the stress intensity factor, K, and stated that fracture occurs when the value of K exceeds some critical value K_c. The basic aim of fracture mechanics is to identify fracture criteria such as G_c and K_c.

1.11 EFFECT OF JOINT GEOMETRY

Gent and Kinloch [65] have shown that the adhesive fracture energy is independent of the type of specimen in the case of rubber based adhesives. Similar works have been reported for structural adhesives also [66]. They have shown that adhesive fracture energy and fracture toughness for joints where the adhesive was brittle are independent of the test geometry and equivalent to that of the fracture energy and fracture toughness of the bulk adhesive [67].

1.11.1 Flexible peel joints

Very few results are reported on the effects of joint geometry upon the measured peel strength or energy, P and the calculated adhesive fracture energy, G_C [68-71]. Available studies have investigated the effects of the thickness of the adhesive layer, thickness of the flexible substrate and peel angle. In the case of adhesive thickness, h_a, it is argued that the boundary cleavage stress, σ_p, actually represents the mean stress throughout the adhesive in the region of the debonding peel front and not the much larger stress which acts at the actual line of separation. Thus, the degree of stress concentration at the line of separation will depend upon the thickness of the adhesive layer so that a larger mean stress will be necessary to bring about the same detachment stress in a thin layer as in a thick one. Both the stress anlaysis approach and the fracture mechanics approach predict that the peel force, P, should be independent of the thickness of the adhesive layer. But it is commonly observed [70, 72-76] the peel strength, P, and the calculated value of G_c, increase as the thickness, h_a, of the adhesive layer increases. This behaviour is more pronounced when the adhesive thickness, h_a, is low but the value of P or G_c eventually reaches a plateau value for relatively thick adhesive layers.

The effect of the thickness of the flexible, peeling substrate is mentioned in the works of Gent and Hamed [68-70]. They suggested that for sufficiently long peeling strip the bending energy stays constant as peeling proceeds. Thus, if the strip is perfectly elastic, no energy is dissipated within the substrate. However, if the level of adhesion is sufficiently high, or if the peeling strip is sufficiently thin, bending stresses may cause irreversible deformations of the substrate in the course of peeling and the peel energy, P, will be augmented by the work expended in plastic deformation of the substrate.

Both fracture mechanics and stress analysis show that peel energy, P, is inversely proportional to (1- Cosα), where α is the peel angle. Thus, the value of P should be a maximum when $\alpha \rightarrow 0$, and a minimum at $\alpha = 180^o$, but the adhesive fracture energy should be a constant.

1.11.2 Structural adhesive joints

The thickness of the adhesive layer does not usually affect the measured value of the adhesive fracture energy for relatively brittle adhesives but for tougher adhesives the thickness may significantly affect the measured value of G_c of the joint. For a toughened adhesive, typically toughened by the inclusion of a second rubbery phase, the relation between adhesive fracture energy and thickness of the adhesive is complex with G_c passing through a maximum value, G_{cm}, at a certain thickness, h_{am} [77].

Kinloch and Shaw [77] have investigated the effect of joint width on adhesive fracture energy. They found that for tough adhesives, the relationships between G_c and adhesive layer thickness, h_a, were a function of joint width, b. The effect of joint width on the adhesive fracture energy of tough adhesives appears to be due to the effect of the substrates changing the stress field around the crack tip and enhancing the extent of plasticity and energy dissipation ahead of the crack.

1.12 RENEWABLE RESOURCES FOR ADHESIVES

Human beings have apparently had a propensity for gluing things together since the dawn of recorded history and probably more. Starch, blood, and collagen extracts from animal bones or hides were the principal early sources. Somewhat later, milk protein and fish skin extracts were discovered. But, vegetable proteins appear not to have been utilized as adhesives until recent times [78]. Tree pitch and petroleum bitumen were known and exploited as weatherproof coatings and caulks but not as adhesives, due to their plastic-flow behaviour [79].

1.12.1 Protein glues

a. Soybean adhesives

Soybeans are legumes, the seeds of a low-growing field vine. The soybean meal intended for adhesive use is processed at temperatures below 70°C to preserve the alkaline solubility of the proteins [80]. The meal must be ground to an extremely fine flour and is treated with either a strong alkali such as sodium hydroxide or trisodium phosphate or a weak alkaline substance like hydrated lime or ammonia [81, 82] to improve its dispersion in water. The high alkali soybean glue is commonly used as wood adhesive [83] and low alkali formulation is widely used as briquetting binder for wood, charcoal and other absorbent particles. It is particularly suitable for paper and soft board laminating, where a colourless glue line and minimum swelling of the glue film on high-humidity exposure are required [84].

b. Blood glues

Glue of this type is made from serum albumen, a blood component obtainable either from fresh animal blood or dried soluble powder to which water has been added. Addition of alkali to albumen-water mixtures improves adhesive properties. Unlike vegetable proteins, high solubility blood proteins can be dispersed and rendered strongly adhesive by more moderate alkaline agents such as hydrated lime or ammonia [85]. A considerable quantity of glue products from blood is used in the plywood industry.

c. Animal glues

Animal glues are derived by the hydrolysis of the protein constituent collagen of animal hides and bones. When treated with acids, alkalies or hot water, the normally insoluble collagen slowly becomes soluble. If the original protein is pure and the conversion process mild, the high-molecular weight product is called gelatine and may be used for food or photographic products. The lower-molecular weight material produced by more vigorous processing is normally less pure and darker in colour and is termed as animal glue [86]. Traditionally, animal glue has been used in wood joining, book bindery, sandpaper manufacture, heavy gummed tapes and similar applications. In spite of its advantage of high initial tack, much animal glue has been modified or replaced by synthetic adhesives.

d. Casein glues

This product is made by dissolving casein, a protein obtained from milk, in an aqueous alkaline medium. The strength and type of alkali influences product behaviour. In wood bonding, casein glues are generally superior to true animal glues in moisture resistance and heat exposure [79]. Casein protein is an important adhesive for furniture and paint pigments and the preferred sizing agent for the canvas of Renaissance paintings [87, 88].

1.12.2 Carbohydrate adhesives

a. Cellulose adhesives

The two most common sources for cellulose are cotton linters and wood pulp.. Since cellulose does not dissolve in most common solvents, it is not useful as an adhesive. Instead, cellulose is converted to various derivatives that can be readily dissolved into aqueous or organic solvents. The common derivatives derived from cellulose are cellulose nitrate, cellulose acetate, cellulose acetate butyrate (CAB), methyl cellulose, ethyl cellulose, carboxymethyl cellulose (CMC) and hydroxyethyl cellulose. The cellulose nitrates are used in plastics, lacquers, coatings and adhesives. Though cellulose acetate is the most important ester derived from cellulose, its use in adhesives is limited. CAB is soluble in a greater range of organic solvents and can be applied either as a hot-melt adhesive or in solvent solution. Methyl cellulose is used for paper coating and sizing to impart grease resistance, in ceramics as binder and as a non-staining paste for wallpaper. The resistance of ethyl cellulose to chemical degradation has led to its use in films, lacquers, and in adhesives. In adhesives, ethyl cellulose may be either applied in a solvent or as a hot melt.

b. Starch adhesives

Starch is a naturally occurring polymer of glucose. The majority of starch derived adhesives are used in the paper and textile industries as binders and sizing materials. They are used in corrugated boards, laminates, bag manufacture, carton sealing, tapes, stamps, labels, envelopes etc.

c. Natural gums

Gums are hydrophobic or hydrophilic polysaccharides derived from plants or microorganisms. Natural gums include plant exudates (gum Arabic, gum ghatti, gum karaya, gum tragacanth), seed gums (guar gum, locust bean gum, tamarind), plant extracts (arabinogalactan from larch; agar, algin and funoran from seaweed), and the extracellular microbial polysaccharides (xanthan gum, dextran). Adhesive uses from natural gums include pressure-sensitive tape, denture adhesives, pharmaceutical tablet binders, household products and label pastes [89].

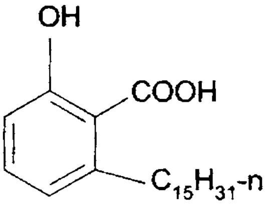
1.12.3 Cardanol based adhesives

Cashew nut shell liquid (CNSL) is a by-product of the cashew industry. CNSL occurs as a greenish-yellow viscous liquid in the soft honeycomb of the shell of the cashew nut. The liquid has a reddish-brown colour, due to charring as well as chemical changes occurring during frying. Industrial grade CNSL is reddish-brown in colour. The earliest work published concerning the composition of cashew nut oil was by Staedeler [90]. Many researchers investigated its extraction, [91-94] chemistry and composition [95-103]. CNSL contains mainly four components- cardanol, cardol, anacardic acid and 6-methyl cardol [104-106]. Figs. 1.4 and 1.5 shows the chemical structures of these compounds. Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during the roasting process which converts anacardic acid to cardanol or 2-pentadeca dienyl phenol. The components of CNSL are themselves mixtures of four constituents differing in side-chain unsaturation, namely saturated, monoene, diene, and triene. Symes and Dawson [107] and Cornelius [108] identified the components or cardanol as 3-penta-anisole, 3-(8′-pentadecenyl) anisole, 1-methoxy-3-(8′, 11′-pentadecadienyl) benzene, and 1-methoxy-3-(8′, 11′, 14′-pentadecatrienyl) benzene. Table 1.2 shows typical composition of natural and technical CNSL.

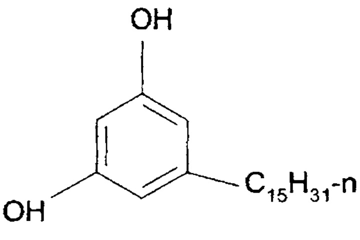
Table1.2 Phenolic composition of natural and technical CNSL (values are in wt%) [106]

Component	Natural CNSL	Technical CNSL
Cardanol	1.2	62.86
Cardol	11.31	11.25
2-Methyl cardol	2.04	2.08
Polymer	20.3	23.8
Anacardic acid	64.93	-

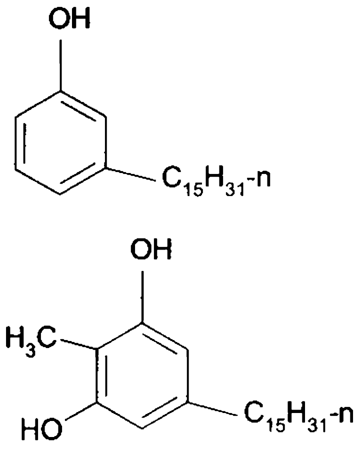
ANACARDIC ACID



CARDOL



CARDANOL



2-METHYL CARDOL

n = 0, 2, 4, 6

Fig 1.4 Components of CNSL

$C_{15}H_{31-n}$ =

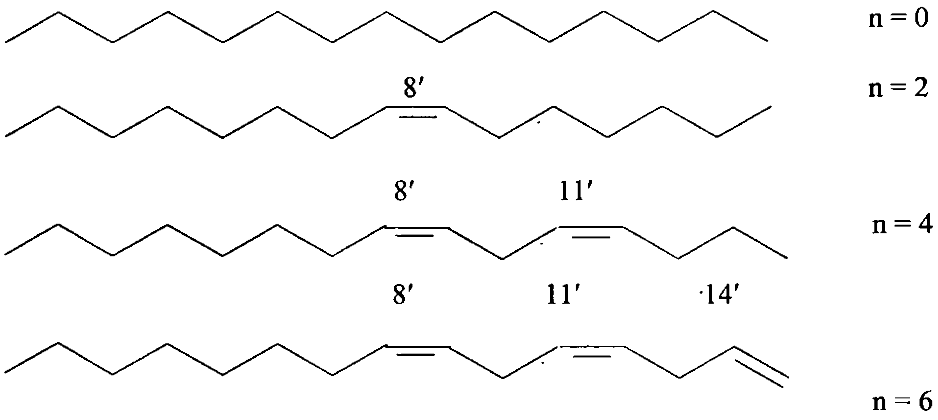


Fig 1.5 Components of the side chain

Applications of CNSL

i. Brake linings and clutch facings [109, 110]

Numerous patents exist on the technique of producing friction materials starting from CNSL. Clutch facings with low hygroscopy have been developed from CNSL. Friction compositions without any volatile products, and possessing improved fading resistance, good resistance to noise, wear resistance, improved reliability, heat resistance, high resistance to hygroscopy, corrosion resistance, and rust resistance have also been reported. Phenol-cardanol-aldehyde resins have been used as binders for extrudable brake linings. About 90% of CNSL put on the market is used to make resins for clutches and disc brakes [111].

ii. Surface coatings

The chemically stable nature of CNSL, the solubility of the resin in various solvents, the inherent hydrophobicity and chemical resistance, the film-forming nature, and a high degree of unsaturation make CNSL polymers highly suitable for surface coating applications. The formulation and manufacture of various classes of paints based on CNSL have been described by Ramanujam [112]. Water- based CNSL-HCHO paint prepared by treating CNSL with HCHO and crosslinking with maleic anhydride and neutralization with ammonia has been reported [113]. Anti-corrosive paint formulations designed for ship bottoms also have been widely reported [114, 115]. Phosphated CNSL-HCHO reaction products give coatings with improved heat resistance, flexibility, and adhesion. Surface coatings with epoxy groups have been prepared by the reaction of epichlorohydrin with CNSL-phenol-formaldehyde resins [116]. Esters of acrylic acid with cardanol are useful for the manufacture of varnishes which are resistant to water and dilute Na_2CO_3 solutions [117]. It is also reported that lacquers can be made from CNSL [118].

iii. Adhesives

The high polarity, inherent tackiness of phenolic materials, and the ease with which liquid to solid conversion can be accomplished, make CNSL a desirable starting material for adhesive formulations. The preparation of adhesives by condensation of xylol, HCHO, and CNSL using various catalysts and hardeners has been reported [119, 120]. PCNSL shows a five-fold increase in adhesive properties from those of conventional CNSL-HCHO resin [121]. CNSL based resins have been used as adhesives for plywood [122]. Red onion skin extract and HCHO resins modified with CNSL have been used in the formulation of wood adhesives with better water resistance and shear strength [123]. Adhesives are also prepared from casein and CNSL [124].

iv. Rubber compounding

The incorporation of CNSL has been found to improve the properties of rubber products. It aids processing and enhances the vulcanizate properties [99]. The effect of cardanol on the processing, mechanical and ageing properties of elastomers has been studied [125].

v. Other applications

Pillai *et al.* have shown that high-performance speciality polymers can be produced from cardanol by a variety of methods [126]. CNSL is also used as an antibacterial agent [127]. CNSL is used an antioxidant for food and cosmetics. CNSL is treated with As_2O_3 or boric acid to improve its toxicity towards termites [128]. Cation exchange resins can be prepared by the reaction of CNSL with H_2SO_4 and anionic exchange resins by the reaction with tetraethylene pentamine [129]. Fish nets can be coated with CNSL to prolong their lives. CNSL is also used as a hypergolic rocket fuel [130].

1.13 NEOPRENE ADHESIVES

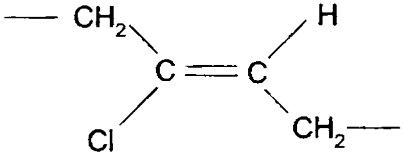
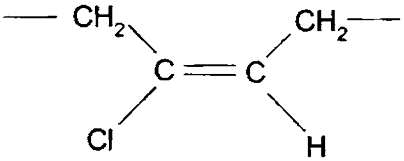
Neoprene or polychloroprene is the basis for one of the largest and most important groups of rubber adhesives. At present 27 grades of neoprenes are produced in solid form and 16 in latex form. Most of them are used as adhesives. The rapid development of bond strength of films from solution, combined with tack or auto-adhesion as well as resistance of the cured glue line to heat have led to widespread use of neoprene adhesives in the shoe, furniture, automotive and construction industries.

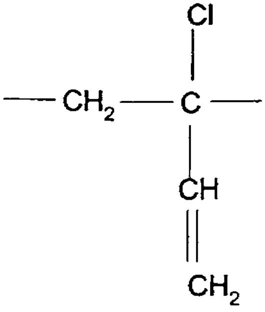
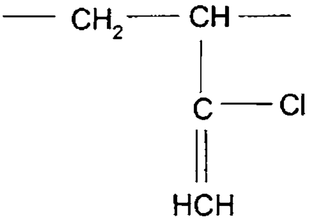
Neoprene was the first synthetic elastomer developed possessing many of the properties of natural rubber. Dr. Nieuwland of Notre Dam synthesized divinyl acetylene from acetylene with $CuCl_2$ as catalyst in the early 1920's. In the late 1920's, Carothers and co-workers found that by varying the conditions of polymerization, monovinylacetylene could be readily prepared, with divinylacetylene present only as an impurity. It was further found that the vinylacetylene could be reacted with hydrochloric acid to form chloroprene or 2-chlorobutadiene, which could be polymerized to yield a rubber-like polymer [131]. It was first known as "Duprene", but later designated as "neoprene" by DuPont in 1936.

1.13.1 Grades of neoprene

The polymer structure of commercial neoprene is determined by the manner in which the chloroprene monomer, 2-chloro-1,3-butadiene, reacts with the growing polymer chain. Upon polymerization, the chloroprene moiety may take any of four isomeric forms, as shown in Table 1.3. The proportion of these configurations determines the amount of crystallization (trans-1,4) and reactivity towards vulcanization (1,2 addition).

Table 1.3 Molecular structure of neoprene

Type of addition	Formula	Properties
Trans-1,4		Increases crystallization
Cis-1,4		Decreases crystallization

1,2		Active sites for vulcanization (decreases crystallization)
3,4		Decreases crystallization

a. Neoprene AC

Neoprene AC was developed in 1947. It has high viscosity, stability and resistance to discolouration. It is characterized by rapid cohesive strength development, good heat resistance and application properties, and when properly formulated yield non-phasing cements. Neoprene AC is less prone to acid evolution primarily because of the presence of Thiuram E. Neoprene AC is a fast crystallizing polychloroprene and contains about 90% trans-1,4.

b. Neoprene AD

Neoprene AD was developed in 1958. It is considerably more stable than Neoprene AC. It is lighter in colour in both chip and solution, more resistant to discolouration from contamination by trace metals such as iron, copper, etc., cures faster with NA-22 (ethylene thiourea) but slower with metal oxide, and is less resistant to discolouration from UV light than Neoprene AC. Its solution maintains stable viscosities over longer periods.

c. Neoprene W

It is a general purpose elastomer having good tack, lower cohesive strength. It is a non-crystallizing polychloroprene and contains 85% trans-1,4 segments.

d. Neoprene AF

It was developed in 1963. This is a carboxyl-containing polychloropene and is characterized by faster cohesive strength development at room temperature, higher strength at elevated temperatures, increased resistance to phasing, but poorer in stability compared to the rapidly crystallizing types Neoprenes AC or AD. Unlike other room temperature curing adhesives, AF can be compounded to provide a solution stable for months.

e. Neoprene AG

It was developed in 1967. This is a gel polymer designed to provide improved application properties. The unique characteristic of Neoprene AG is that dispersions in solvent exhibit thixotropy permitting the formulation of high solids, high viscosity mastics that are easily applied by trowelling or extruding but resist slump or flow after application. The adhesives are buttery, not stringy. Low viscosity (lower solids) formulations based on Neoprene AG have better spray characteristics (no cob-webbing) than other neoprenes.

f. Neoprene AH

It was developed in 1975. This is an acrylic copolymer of chloroprene, which can be peptized in aliphatic solvents to form stable colloidal dispersions. This enables one to formulate high solids systems exhibiting the application advantages of a latex system with the bond strength development of solution adhesives. Its dispersion adhesive formulations can be designed to develop hot bond strength equivalent to types AC and AD, but at the expense of tack time.

g. Neoprene HC

It was developed in 1962. It is the most rapidly crystallizing type and hence suitable for cold setting, heat-sealable adhesives. But it has also been withdrawn recently.

h. Fluid Neoprenes, FB and FC

This permits the formulation of 100% solids Neoprene mastics and caulks. It was developed in 1961.

i. Neoprene AJ

It was developed in 1966. This is a highly reactive peptizable polymer that can be used as a base for pressure-sensitive and one-way adhesive systems requiring high peel strength, high creep and flame resistance. But it has been withdrawn recently.

j. Neoprene GNA

Neoprene GNA is a sulphur modified polychloroprene stabilized with a thiuram disulphide and a staining antioxidant. It should not be used in applications where resistance to staining or discolouration of finishes is necessary. Neoprene GNA breaks down or softens under the mechanical shear imposed during mixing to produce smooth processing compounds.

k. Neoprene TW

Neoprene TW is a non-staining general purpose polychloroprene. It do not decrease in molecular weight during mixing and processing and cannot be chemically peptized. Neoprene TW is an excellent polymer base for extruded products, providing high extrusion speed, low die swell, excellent definition and very good collapse resistance. In calendered goods, it produces smooth sheeting with low shrinkage.

1.13.2 Method of application

Neoprene adhesive are conventionally applied by spraying, curtain coating, roller coating, brushing or extrusion. The basic physical characteristics required of neoprene adhesives for these application techniques are summarized below:

a. Spraying

Spraying is the most important commercial technique employed. It permits rapid lay down of adhesive and minimizes drying time. A low Mooney, low nerve neoprene is preferred for spraying. Milling improves spray characteristics as it further reduces nerve. Viscosity should be below 250cps with rubber solids 10-15%. The solvent blend should contain predominantly fast evaporating solvents.

b. Curtain coating

In the curtain coating process, a bath with an aperture in the base allows a continuous curtain of the adhesive to fall into the gap between two conveyors. The substrate to be coated is passed along the conveyor at a controlled speed and hence receives the coating on its upper surface. Fig 1.6 shows the set up for curtain coating. This type of coating enables uniform thickness but is only suitable for flat surfaces. It is also highly viscosity dependent. A low Mooney, low nerve neoprene is preferred. Milling improves curtain coating characteristics as it further reduces nerve. Viscosity should be 200-300cps utilizing relatively slow evaporating solvents.

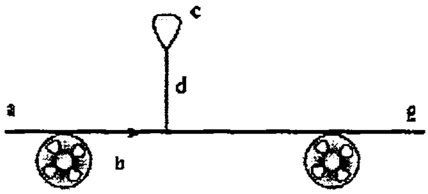


Fig 1.6 Curtain coating set up

c. Roller coating

Roll coating is the process of applying a coating to a flat substrate by passing it between rollers. Roll coating is also limited to flatwork and is extremely viscosity dependent. But it has high production rates. Milling is recommended to reduce stringiness. Viscosity is best between 500-1000cps using relatively slow evaporating solvents.

d. Brushing

Brushing is one of the easiest methods of application. This can be employed to coat complex substrates. But to get uniform coating skilled labourers are required. Brushing can be employed when viscosity is around 1000cps.

e. Extrusion

In the extrusion process, the coating is squeezed out by gravity or under pressure through a slot and onto the substrate. The line speed is frequently much faster than the speed of the extrusion. This enables coatings to be considerably thinner than the width of the slot. High gel, low viscosity thixotropic neoprene is best. Solvent blend should contain predominantly fast evaporating solvents.

1.13.3 Applications

Neoprene is similar in physical properties to natural rubber, but is stronger and has better ageing and high temperature properties. Neoprene bonds are useful in the range of -70 to 180°F. Mechanically, neoprene bonds absorb vibration and display good shear and peel strengths. Cured neoprene films are more rigid than thermoplastic adhesives, but not as rigid as epoxy or phenolic adhesives. Neoprenes have good resistance to water, salt spray, commonly encountered chemicals, and biodeterioration. Hence, they are often used in building construction for decorative plastic laminates, wood working, plywood and hardboard panelling to wall, etc. For structural applications, neoprene elastomers are blended with synthetic resins, often phenolic resins, to promote mechanical strength and heat stability.

1.14 PHENOLIC ADHESIVES

Phenolic resins are the reaction products of phenols and/or substituted phenols with formaldehyde. Processing techniques for today's phenolic resins were discovered by Leo Bakeland in the early 1900s [132, 133]. However, the first patent covering phenolic resins was granted to A. Smith in 1899 [134]. Adolf Baeyer in 1872, first reacted phenol and acetaldehyde in the presence of an acid catalyst to yield a resinous mass [135]. But, nothing was done with this resinous material. Ter Meer [136], A. Claus and E. Trainer [137] continued the experiments. Claus and Trainer obtained a resinous material from two moles of phenol and one mole of formaldehyde and hydrochloric acid [137]. After the non-converted phenol was distilled off, a soluble resin was obtained with a melting point of 100°C. However, they also could not think of any application for this material. Between 1907 and 1909 Baekeland conducted small-scale experiments with a few industrial companies and as a result, patented numerous applications for phenolic resins till 1909. He found that moulding compounds can be made of pulverized, fusible phenolic resins made in alkaline environment and fillers, and moulded to a shaped product of high toughness, strength and chemical resistance [138]. Phenolic resins are excellent binders for abrasive materials [139]. Ammonia-catalyzed solid resins in organic solvents can be used for valuable varnishes [140] and coatings for food containers [141]. He also found that temperature and steam-resistant lining materials can be made of phenol resin impregnated asbestos fibres, paper or cloth [142] and these resins are useful for coating wood, yielding a hard and abrasion resistant surface of high gloss or can be applied as adhesive for veneer facing [143]. The production of paper laminates and laminated paper tubes made of liquid or dissolved resins [144], the manufacture of noiselessly running cog-wheels [145], phenolic resin putties and glues to bond various materials and impregnating resin coils and similar electrical devices [146, 147] were also suggested by Baekeland at that early stage.

A large variety of resins are possible depending on (1) the choice of phenols (2) the phenol: formaldehyde ratio (3) the type and amount of catalyst used, and (4) the time and temperature of reaction. The phenols of commercial importance are phenol (C_6H_5OH), cresols ($C_6H_4(CH_3)OH$), xylenols ($C_6H_3(CH_3)_2OH$), p-amyl phenol, p-phenyl phenol, p-tertiary butyl phenol and cardanol derived from cashew nut shell liquid(CNSL).

The phenol: formaldehyde molar ratio along with choice of catalyst used, determines whether the polymer will be phenol terminated or methylol ($-CH_2OH$) terminated. If phenol terminated the resin is referred to as a novolac or a two step resin. Such a resin is not heat reactive until a second ingredient is added that supplies the additional formaldehyde needed to effect cure. The most widely used curing agent is hexamethylenetetramine or 'hexa'. If methylol terminated the resin is referred to as a resol or one step resin. This type is heat reactive and except when based on a difunctional phenol, a phenol in which one of the ortho and para sites are blocked e.g., p-tertiary butyl phenol, will cure to a thermoset structure upon application of heat.

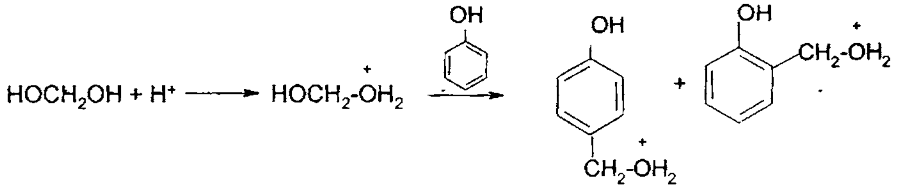
Those resins based on para substituted phenols can be either one-step or two-step type. But they are not capable of crosslinking to a thermoset state. These resins are employed as tackifiers in contact, pressure sensitive and hot melt adhesives. The thermosetting nonsubstituted phenolic resins are employed as structural adhesives, for laminating, and for bonding applications like bonded and coated abrasives, friction materials, fibre bonding, foundry sand and wood bonding.

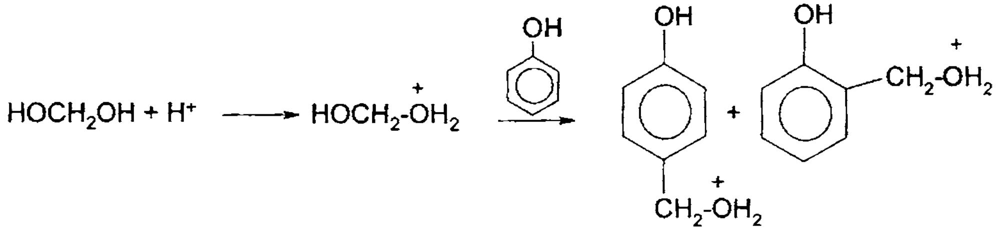
1.14.1 Chemistry and synthesis [148]

Phenolic resins are prepared by the reaction of a phenol or substituted phenol with an aldehyde, especially formaldehyde, in the presence of an acidic or basic catalyst.

a. Novolac resins

They are prepared by reacting phenol with formaldehyde under acidic conditions. The formaldehyde to phenol molar ratios are between 0.5 and 0.8. The phenolic novolacs are thermoplastic resins with molecular weights of 500- 5000 and a glass transition temperature T_g of 45-70°C. In aqueous solution formaldehyde exists as methylene glycol and is converted to the corresponding hydrated carbonium ion which adds to the ortho and para positions of phenol with the elimination of water.





In the next step the hydrated benzylic carbonium ion reacts with free ortho and para positions on the phenols to form methylene-linked bisphenols. Continued reaction leads to the formation of novolac polymers with a molecular weight of up to 5000. Acid-catalyzed resins contain 50-75% 2,4' linkages. At typical molecular weights of 500-1000, novolac molecules are essentially linear because of the much lower reactivity of doubly reacted phenolic units. In higher molecular weight polymers, the low concentration of end groups and unreacted phenol causes branching. The properties of an acid catalyzed phenolic resin are shown in Table 1.4. The typical acid catalyst used for novolac resins is sulfuric acid, sulphonic acid, oxalic acid or occasionally phosphoric acid.

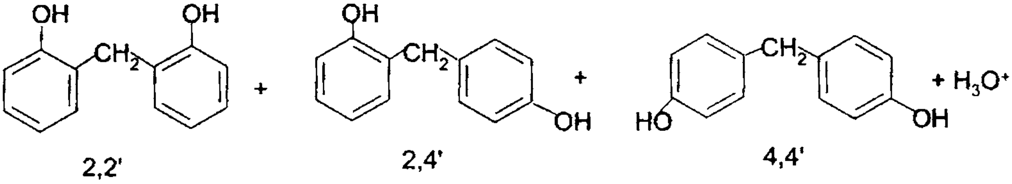


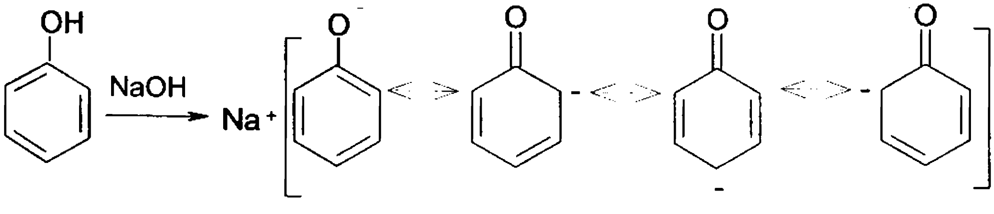
Table 1.4 Novolac resin properties [149]

Property	Acid catalyst
Formaldehyde-phenol molar ratio	0.75
nmr analysis	
2,2', %	6
2,4', %	73
4,4', %	21
gpc analysis	
phenol, %	4
M_n	900
M_w	7300
Water, %	1.1
T_g, °C	65
Gel time, s	75

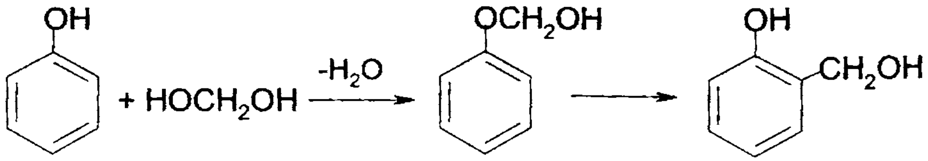
b. Resole resins

Resole-type phenolic resins are prepared with a molar ratio of formaldehyde to phenol of 1.2: 1 to 3.0: 1. For substituted phenols, the ratio is usually 1.2: 1 to 1.8: 1. Common alkaline catalysts are NaOH, $Ca(OH)_2$, and $Ba(OH)_2$. Resoles may be solids or liquids, water-soluble or insoluble, alkaline or neutral, slowly curing or highly reactive.

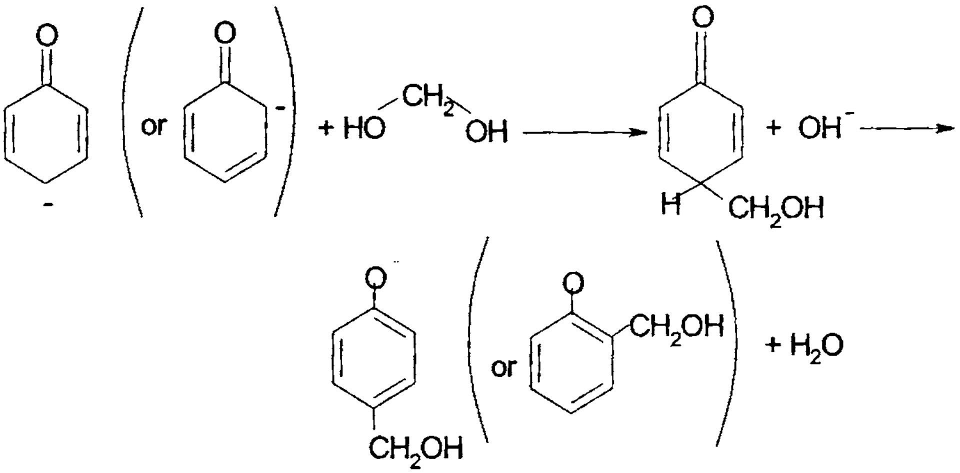
In the first step the phenolate anion is formed with delocalization of the negative charge to the ortho and para positions.



The mechanism of the formaldehyde addition to the phenolate is still not completely understood. A proposed mechanism involves the contribution of phenol hemiformals [150].



Rate studies show that base-catalyzed reactions are second order and depend on the phenolate and methylene glycol concentrations. The most likely path involves a nucleophilic displacement by the phenoxide on the methylene glycol, with the hydroxyl as the leaving group. In alkaline media the methylolated quinone intermediate is readily converted to the phenoxide by hydrogen-ion abstraction [151]. The ratio of ortho to para substitution depends on the nature of the cation and the pH. Para substitution is favoured by K^+ and Na^+ ions and higher pH, whereas ortho substitution is favoured at lower pH and by divalent cations, such as Ba^{2+}, Ca^{2+} and Mg^{2+} [152, 153].



Although monomeric methylolated phenols are used in certain applications, higher molecular weight resins are usually desirable. Molecular weight is increased by further condensation of the methylol groups. Dibenzyl ether and diphenylmethylene can be formed. The formation of diphenylmethylene bridges is favoured above 150°C and under strongly alkaline conditions. Dibenzyl ether formation is favoured at lower temperatures and near neutral pH. The properties of a resole resin are given in Table 1.5.

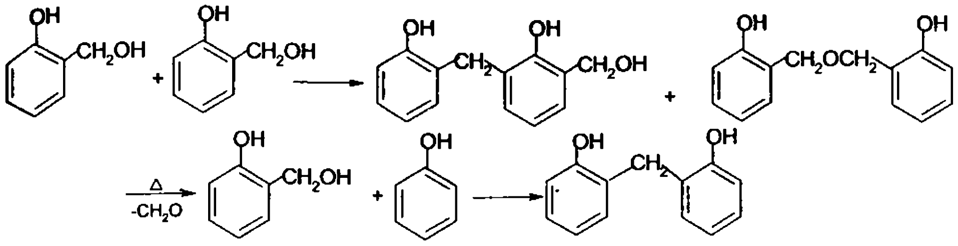


Table 1.5 Properties of resole resins [149]

Property	NaOH catalyst
Formaldehyde-phenol ratio	2.0
Water solubility, %	100
GPC analysis	
Phenol%	6
M_n	280
M_w	500
T_g, °C	35
Gel time, s	65

1.14.2 Applications of phenolic resins in adhesives

Phenolic resins exhibit adhesive functions in all kinds of applications [148]. Their adhesion to most materials is very good due to the marked polarity of the phenolic structures. Polyvinylacetal- phenolic resin blends are frequently used for structural metal bonding. Resoles are also used for plywood glues which may be cured using alkaline catalysts at 135°C. These glues have good resistance to aging, moisture and bacteria [154]. In many applications phenolic resin acts as binder. Examples of this are found in brake linings, grinding wheels and flexible abrasives. Phenolic resin composites are used in aircraft industry for their high temperature resistance, high strength and low smoke generation. Phenolic resins are used as socket putties for light bulbs, radio valves, and the like because of their high temperature resistance and strong adhesion. Casting type resins which are used for the production of decorative articles, bowling balls etc. are prepared using formaldehyde in excess (P/F ratio 1: 2-3) with sodium hydroxide or alkaline earth oxides as catalyst [155].

1.15 SCOPE AND OBJECTIVES OF THE WORK

The present work aims at developing novel adhesives based on neoprene-phenolic blends for high performance applications. The performance of the adhesives on different substrates and environments will be subsequently investigated. Also to be explored is the use of cardanol a renewable resource as a starting material for adhesive formulations.

The specific objectives of the work can be summarised as follows

1. To optimize the basic composition of a neoprene-phenolic adhesive formulation consisting of elastomer, filler, resin, adhesion promoters, curatives etc.
2. To study the utilization of cardanol, a naturally occurring phenol for adhesive formulation.
3. To synthesize phenol cardanol formaldehyde resin and to identify a) the optimum ratio between phenol and cardanol that gives the best adhesive performance and b) the optimum stoichiometric ratio between total phenol and formaldehyde that gives the maximum bond strength.
4. To investigate the use of epoxidized phenolic novolacs in adhesive applications.
5. To study the ability of the adhesive joints to withstand different environmental conditions.

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Chapter 2

Development of neoprene phenolic adhesives

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2.1 INTRODUCTION

Neoprene phenolic adhesives

Rubber based adhesives offer the greatest variety of properties for any generic class of adhesives. They may contain a wide variety of component materials such as elastomers, resins, tackifiers, fillers, plasticizers and softeners, antioxidants, curing agents, etc. Neoprene or polychloroprene rubber (CR) based adhesives enjoy a pre-eminent position as elastomeric binders at the expense of materials like natural rubber (NR) and styrene butadiene rubber (SBR) [1], which are less effective but cheaper. Of the different grades available, CR- AC and CR- AD are more popular for use in adhesives. They are characterized by rapid cohesive strength development and good heat resistance. But these fast crystallizing types of neoprenes have poor tack retention. Neoprene W which is a non-crystallizing type is often added to type AC and AD to increase their tack.

Neoprene-phenolic alloys are used to bond a variety of substrates. Because of high resistance to creep and most service environments, neoprene-phenolic joints can withstand prolonged stress. They also have excellent fatigue and impact strength. However, compared to other modified phenolic adhesives they have moderate shear strength.

Fillers like carbon black, silica, clay, calcium silicate, etc are added to reduce the cost, increase the specific gravity and raise the viscosity of adhesive formulations [2]. Tackifiers enhance the adhesion of non-polar elastomers by improving wettability, increasing polarity and altering the viscoelastic properties of the adhesive mass. Commonly employed tackifiers are polyterpene resins, rosins, rosin esters, coumarone–indene resins, petroleum hydrocarbon resins, etc [3]. Adhesion promoters which have the ability to migrate to the interface and improve the adhesion are also included in the formulations. Numerous adhesion promoters like cobalt / nickel salts [4-6], resorcinol formaldehyde resins, and melamine resins [7, 8], titanates, allyl phosphite/ phosphate esters, maleic anhydride modified polybutadiene [9, 10], organofunctional silanes [11, 12] etc. have been suggested.

Silane adhesion promoters increase the initial bond strength and also stabilize the surface to increase the permanence of the joint in moist ageing environments [13, 14]. They are also capable of increasing the environmental resistance of aluminium [15], titanium [16] and stainless steel joints [17]. Silane coupling agents can be either applied to the substrate or blended into the adhesive. Outstanding improvement of metal-metal bonding has been reported when silane coupling agents were integrally mixed with urethane and epoxy adhesives [18].

2.2 ADHESIVE PROPERTIES OF NEOPRENE AND THE EFFECT OF VARIOUS ADDITIVES

2.2.1 EXPERIMENTAL

a. Materials

Styrene Butadiene Rubber (SBR 1502) was obtained from Japan Synthetic Rubber Co. Ltd. Tokyo. It had a Mooney viscosity [ML(1+4) at 100°C] of 45. Chloroprene Rubber (CR) – AD grade was supplied by E. I. DuPont, Akron, Ohio. It had a Mooney Viscosity [ML(1+4) at 100°C] of 45. Chloroprene Rubber (CR)- W type ([ML(1+4) at 100°C] of 45) was supplied by E. I. DuPont, Akron, Ohio. Epoxidized natural rubber (ENR-50) was supplied by Rubber Research Institute of India, Kottayam, India.

Phenol (M.W- 94.11, Specific gravity- 1.071, MP- 41°C), toluene (M.W- 92.14, 99%assay) and methyl ethyl ketone were obtained from E. Merck India, Mumbai. Formaldehyde (37-41% w/v, d^{20}=1.08), sodium hydroxide (M.W- 40, 97.5% assay) and oxalic acid (M.W-126.07, 99.8% assay) were LR grade supplied by S.D.Fine Chemicals, Mumbai, India. Pentalyn H (pentaerythritol ester of partially hydrogenated wood rosin) was supplied by Hercules Inc. Rosin and Terpene Specialities, Brunswick, GA, USA. Cashew Nut Shell Liquid (CNSL) was obtained from Vijayalaksmi Cashew Exports, Kollam, India.

Zinc oxide was supplied by M/s Meta Zinc Ltd., Mumbai. It had the following specifications: Specific gravity – 5.5, Zinc oxide content- 98%, Acidity- 0.4% (max), Heat loss (2 h at 100°C)- 0.5% (max).

Stearic acid was supplied by Godrej Soap (Pvt) Ltd., Mumbai, India and had the following specifications: Melting point- 50-69°C, Acid number- 185-210, Iodine number- 9.5 (max), Specific gravity- 0.85±.01, Ash- 0.1% (max).

Carbon black (HAF N330) was obtained from Phillips Carbon Black Ltd., Kochi, India. It had the following specifications: Iodine number- 82, DBP adsorption- 102±5ml/100g, Mean particle diameter- 32nm. Acetylene black was obtained from Senka Carbon Pvt. Ltd., Tamil Nadu, India.

Precipitated silica was supplied by Sameera Chemicals, Kottayam, India. It had the following specifications: Specific gravity- 1.98, Heat loss (2h at 100°C) - 4.7% (max), Ignition loss (2 h at 100°C)- 3.6%, N_2 surface area- 155-195mm^2/g, pH- 5.6-6.8, Residue 45m sieve- 3%, SiO_2- 93%.

Aromatic oil was supplied by Hindustan Petroleum Corporation Ltd. It had the following specifications: Specific gravity- 0.95-0.98, Aniline point- 38°C, Viscosity Gravity Constant (VGC) - 0.907.

Sulphur was supplied by Standard Chemical Company Private Ltd., Chennai and had the following specifications: Specific gravity- 2.05, Acidity- 0.01% (max), Ash- 0.10% (max), Solubility in CS_2- 98% (max).

Dibenzothiazyl disulfide (MBTS) having the specification - Specific gravity- 1.34 and Melting point- 165°C- was supplied by Bayer India Ltd., Mumbai. Tetra Methyl Thiuram Disulphide (TMTD) was supplied by NOCIL, Mumbai, India. It had the following specification: Specific gravity- 1.4, Melting point- 136°C.

Vulcanox HS (polymerized 2,2,4 trimethyl 1,2-dihydroquinoline) was obtained from Bayer India Ltd., Mumbai and had a specific gravity of 1.1. Vulcanox 4020 (N(1,3-dimethyl butyl)N'-phenyl-p-phenylenediamine) was obtained from Bayer India Ltd., Mumbai. It had a specific gravity of 1.1.

3- aminopropyltriethoxysilane was supplied by Sigma Aldrich, Bangalore, India.

The aluminium substrate used in this study was extruded aluminium alloy AA 6060-T6. It was supplied by Hindalco Industries Ltd., Mumbai, India.

b. Substrate preparation

i. SBR substrate

The rubber compounding for the preparation of elastomeric substrates was done on a laboratory size (15 x 30 cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D3186 [19]. The mill opening was set at 0.2mm and the elastomer was passed once through the nip without banding. Then the rubber was banded on the front roll with the mill opening at 1.4mm. The temperature of the rolls was maintained at 70±5°C. After the band became smooth, the nip gap was set to 1.9mm. The compounding ingredients were added as per ASTM D3186 in the following order: activators, fillers, processing aids, accelerators and curing agents. After complete mixing the compound was homogenised by passing six times through a tight nip of 0.8mm and finally sheeted out at a nip gap of 6mm by passing through the rolls four times, folding it back on itself each time. The compound was subsequently moulded in an electrically heated hydraulic press employing a pressure of 200kg/cm^2 and a temperature of 150^{0}C to form strips of 100 x 25 x 2 mm size.

The time of cure was in accordance with the results of cure studies initially performed on a Rubber Process Analyser (RPA 2000, supplied by Alpha Technologies, USA). This instrument has two directly heated biconical dies that are opposed each other and are designed to achieve a constant shear gradient over the entire sample chamber. The lower die is oscillated and the torque transducer on the upper die senses the force being transmitted through the rubber. This arrangement allows a fast thermal response as well as a constant shear gradient over the entire chamber area.

The formulation for the compounding of SBR substrates is given in Table 2.2.1.

Table 2.2.1 SBR substrate compounding recipe

Ingredient	phr*
SBR 1502	100
Zinc Oxide	5
Stearic acid	1
HAF	50
Aromatic oil	10
Vulcanox HS	1
Vulcanox 4020	1
MBTS	0.5
TMTD	0.5
Sulphur	1

* per hundred rubber

ii. Aluminium substrate

Aluminium strips used were of size 100 x 25 mm machined from 0.8 mm thick sheets to serve as metal substrates for peel studies. For lap shear strength studies strips of size 100 x 25 mm were machined from sheets of 1.6 mm thickness.

iii. Surface preparation

Mechanical cleaning (surface roughening) was done on both metal and rubber substrates with a No. 100 emery paper. For metal strips, after mechanical cleaning solvent degreasing was done by trichloroethylene. The roughened rubber strips were further cleaned by rubbing with a soft cloth.

c. Tests for adhesive joints

i. Peel tests

Peel tests involve stripping away a flexible adherend from another adherend that may be flexible or rigid. The specimen is usually peeled at an angle of 90 or 180 degrees. The most common types of peel tests are the T-peel, 180^0 peel, the floating roller peel and the climbing-drum methods. Peel values are recorded in

Newton per millimetre (N/mm) of width of the bonded specimen. The most popular of all peel tests is the T-peel test and it is carried out as per ASTM D 1876 [20]. This test is used when both adherends are flexible. A variation of the T-peel test is a 180 degree stripping test and it is carried out as per ASTM D 903 [21]. This method is commonly used when one adherend is flexible enough to permit a 180° turn near the point of loading. A peel test specimen is given in Fig 2.2.1

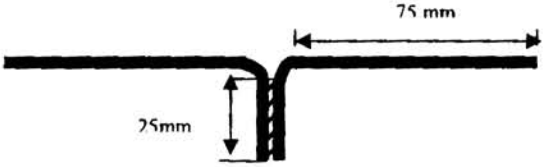

Fig 2.2.1 90° Tpeel test specimen

ii. Lap shear test

The lap shear test measures the strength of the adhesive in shear. It is done as per ASTM D 1002 [22]. This is the most commonly used shear test for structural adhesives. Testing is carried out by pulling the two ends of the overlap in tension causing the adhesive to be stressed in shear. This test is called the tensile-shear test. The dimension of a typical lap shear specimen is given in Fig 2.2.2. It is expressed in force per unit bonded area.

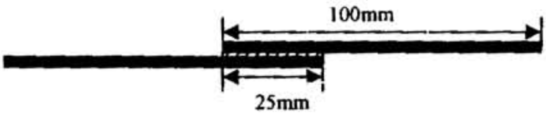

Fig 2.2.2 Lap shear test specimen

The peel and shear strength tests were performed on a Shimadzu Universal Testing Machine (10kN) with a grip separation rate of 50mm/min.

d. Rubber content

Preliminary studies were conducted to evaluate the adhesive properties of CR (chloroprene rubber) solution. CR-AD solutions were prepared in toluene in different concentrations of 5, 10, 15, 20, 25 and 30% by wt. For this CR-AD chips were milled on a two-roll mill (15 x 30 cm) at close nip for 7 minutes. The masticated rubber was dissolved in toluene. A single coating of the rubber solution was given on each substrate. After allowing 30minutes for air drying, the substrates were joined and the assembly heated for 5 minutes at 150^0C.

In the second part of the study CR-AD and CR-W blends were used for making the adhesive solution. The ratio of CR-AD / CR-W was varied as 100/0, 90/10, 80/20, 60/40, 40/60, 20/80 and 0/100.

e. Fillers

Moderate loadings of fillers, particularly high structure carbon black, result in an increase in bond strength [23]. Initially, studies were conducted using CR-AD solutions containing a) carbon black- HAF (N330) (high structure black) and b) acetylene black (AB) (very high structure black) as fillers. From the preliminary study on rubber-rubber bonding, it was concluded that acetylene black was superior to HAF. Hence, in subsequent studies, acetylene black was compounded with CR-AD/W blend in various concentrations of 2, 4, 6, 8 and 10phr. The resulting rubber solutions were tested for adhesive properties.

Precipitated silica was employed as filler in the next set of experiments. For this, silica in proportions of 2, 4, 6, 8 and 10phr were compounded with CR-AD/W blend and the resulting adhesives were tested.

f. Phenolic resin

Cardanol was separated from commercial CNSL by distillation under reduced pressure (1mm Hg). The pale yellow fraction collected at 206-208^0C is cardanol [24]. The refractive index of the cardanol was measured using an Abbe Refractometer at a wavelength of 589nm. The viscosity was measured using Brookfield Viscometer Model RVF.

Phenol-cardanol-formaldehyde (PCF) resin was synthesized by reacting mixtures of phenol and cardanol with formaldehyde. A resole type resin was preferred as it is heat reactive. Phenol and cardanol were taken in the ratio of 60/40 (by weight) in a three necked round bottom flask equipped with a water condenser. To this formaldehyde was added and the mixture was refluxed for 1hour at 95°C with 6ml of 33% NaOH as catalyst. The reaction was stopped when the reaction mixture became viscous and hydrophobic. Phenolic resin was prepared with a molal stoichiometric ratio of 1:1.7 between total phenols and formaldehyde. The resole type resin obtained was neutralized with oxalic acid and washed with hot water to remove unreacted phenol and then vacuum dried.

The resin concentration was varied from 10 to 60 phr for rubber-to-rubber bonding. For metal-to-metal bonding the resin concentration was varied from 40 to 120phr. The resin was added to the CR-AD/W blend adhesive solution containing optimum level of filler.

g. Adhesion promoter

To study the effect of adhesion promoter on metal-to-metal bonding an aminosilane (3-aminopropyltriethoxysilane) in varying concentrations (1.0, 1.5, 2.0, 2.5, 3.0 phr) was added. The silane was added to the adhesive solution containing optimum level of resin.

h. Crosslinking agents

To study the effect of crosslinking agents on adhesive strength, a combination of zinc and magnesium oxides was added to the rubber during milling. The recommended quantities are 4phr MgO and 5phr ZnO [25]. In this study varying proportions of MgO and ZnO viz., 4&5, 3.75&3.0, 2&2.5 and 1&1.25 phr were compounded with CR-AD/W blend. The heat reactive phenolic resin forms a complex with part of the MgO in the rubber compound during the adhesive curing process. The remaining MgO serves as an acceptor for HCl formed during thermal or UV degradation of the CR when the adhesive is in use [26].

i. Sulphur

To study the effect of sulphur on adhesive strength, sulphur was added in varying proportions from 0.5 to 2 phr. The amount of sulphur is very important because too much sulphur will lead to a highly crosslinked layer with poor adhesive properties.

j. Zinc phosphate

Zinc phosphating [27] is a surface treatment employed on metal surfaces to improve adhesion. To study the effect of zinc phosphate on adhesive strength, it was added to CR AD/W blend in varying proportions of 0.5, 1, 1.5, 2 and 2.5phr during milling while preparing adhesive for Al-Al specimens.

k. Epoxidized natural rubber (ENR)

ENR is a rubber with improved heat stability [28]. To study the effect of ENR on adhesive strength, blends of CR AD and ENR were prepared. The ratio of CR AD/ENR was varied as 100/0, 90/10, 80/20, 70/30 and 60/40 wt%.

The different ingredients of the adhesive formulation and their proportions investigated in the study are tabulated in Table 2.2.2.

Table 2.2.2 Ingredients of the adhesive formulation

Adhesive component	**Range**
CR-AD	5-30 wt%
CR- AD/W	100/0, 80/20, 60/40, 40/60, 20/80, 0/100 wt%
Acetylene black	2-10 phr
Silica	2-10 phr
PCF resin	10-120 phr
Silane	1-3 phr
ZnO/ MgO	1.25/1.0- 5.0/4.0 phr
Sulphur	0.5 -2phr
Zinc phosphate	0.5- 2.5phr
CR-AD/ENR	100/0, 90/10, 80/20, 70/30, 60/40 wt%

l. Morphological studies- Scanning electron microscopy [29]

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology and microstructure [30]. Scanning electron microscope (Cambridge Instruments S 360 Stereoscanner- Version V02-01, England) was used to investigate the morphology of the failed adhesives 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 surfaces of failed peel specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an E-101 ion-sputtering unit for gold coating of the sample to make it conducting. The gold-coated sample was subjected to SEM.

2.2.2 RESULTS AND DISCUSSION

a. Effect of rubber content

Fig. 2.2.3 shows the variation of peel strength with CR-AD content. It is found that at about 20% rubber content, peel strength value is the highest for rubber-to-rubber bonding. Peel failure occurred in a cohesive manner (within the adhesive). As rubber concentration increases, nonuniform wetting of the surface results. Beyond 10%, it is also possible that the thickness of the rubber film does not permit higher peel strength values [31]. In the case of Al-Al bonding, peel strength shows very little dependence on rubber concentration and the values are uniformly low.

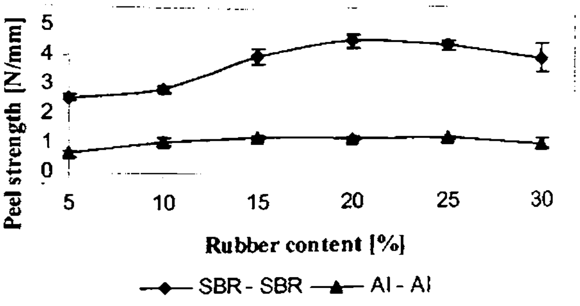

Fig 2.2.3 Effect of rubber (CR-AD) content on peel strength

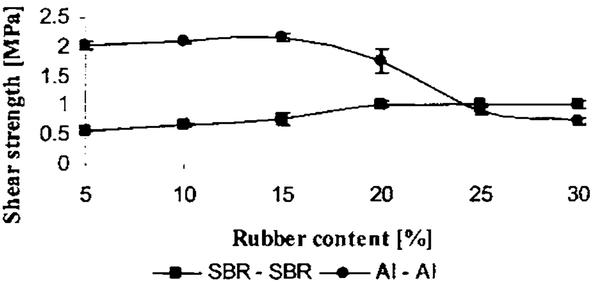

Fig 2.2.4 Effect of rubber (CR-AD) content on shear strength

Fig. 2.2.4 shows that in the case of metal-to-metal bonding, the maximum shear strength occurs at 15% CR-AD rubber. Shear strength values shown by rubber-to-rubber specimens were high enough to cause fracture of the substrate for all concentrations above 20%.

From Figs. 2.2.5 and 2.2.6 it is seen that a blend of 90% CR-AD and 10% CR-W gives superior values in the case of metal-to-metal bonding. CR-W is predominantly amorphous in nature. So traditionally some amount of CR-W is blended with CR-AD in adhesive formulations. From the graph it is clear that about 10% CR-W can be incorporated in all cases without substantial loss of peel and shear properties. Beyond 10% of CR-W there is a sudden drop in the shear strength of Al-Al bonds presumably due to the fall in crystallinity.

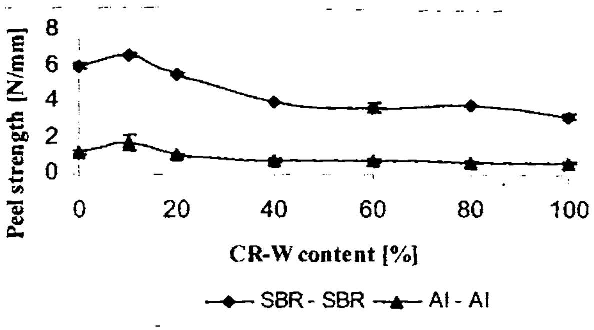

Fig 2.2.5 Effect of CR-W on peel strength

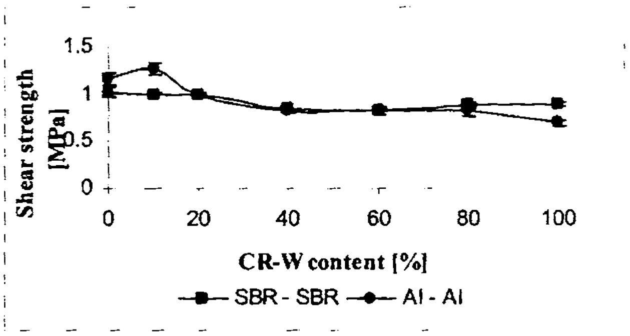

Fig. 2.2.6 Effect of CR-W on shear strength

b. Effect of fillers

Figure 2.2.7 shows that the effect of reinforcing the adhesive with acetylene black (AB) is negligible on peel strength in the case of metal-to-metal bonding. But there is a clear superiority for reinforced formulations in the range of 6 to 8 phr for rubber-to-rubber bonding. Since carbon black is recognized as a reinforcing filler for rubbers, the improvement in cohesive strength resulting from the presence of carbon black might be responsible for better peel strength in rubber- to -rubber bonding. Acetylene black is a high structure black, and its aggregates are composed of many primary particles. These fine primary particles tend to tie up more rubber per unit weight of carbon thereby enhancing the cohesive forces in rubber-based adhesives [32]. But as the filler percentage increases beyond a certain level, molecular flexibility decreases. Increased levels of fillers tend to make it more difficult for the molecules to move towards or away from each other. Shear strengths of rubber-to-rubber bonds are high enough to cause substrate fracture at all percentages of AB (Fig. 2.2.8). There is only a marginal improvement in shear strength in metal-to-metal bonding on addition of acetylene black. High abrasion furnace (HAF) also improves the bond strength of rubber-rubber bonds; but not to the level of AB.

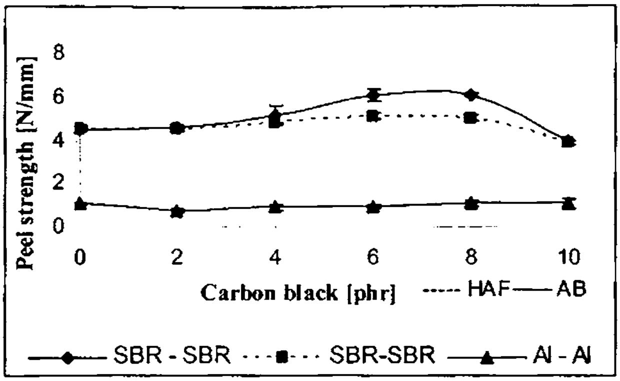

Fig. 2.2.7 Effect of carbon black on peel strength

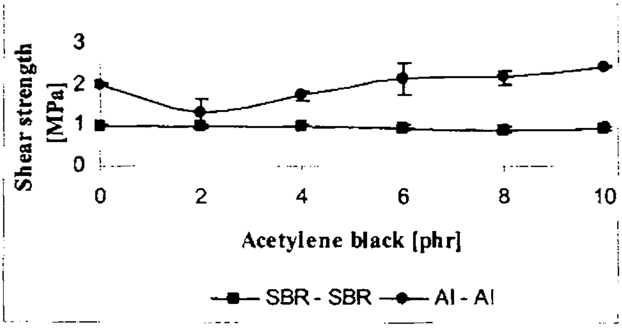

Fig 2.2.8 Effect of carbon black on shear strength

Fig. 2.2.9 shows that the addition of silica has only marginally affected the peel strength of rubber-to-rubber and metal-to-metal specimens. Also Fig. 2.2.10 shows that shear strength is also only marginally affected although, data for metal-to-metal specimens shows substantial scatter especially at lower silica contents. Silica is known to disperse poorly in rubber solutions. This could be the underlying reason for the negligible improvement in adhesive properties on addition of silica.

As in the case of acetylene black, all rubber-to-rubber shear specimens containing silica undergo fracture of the rubber substrate.

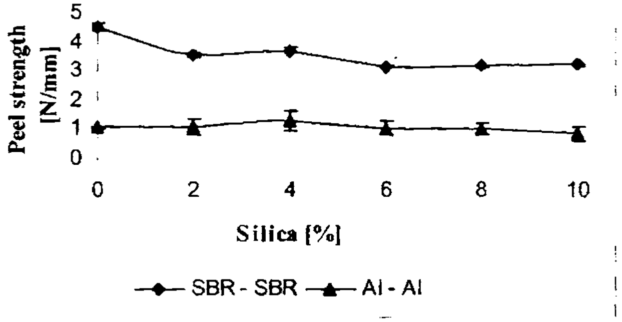

Fig 2.2.9 Effect of silica on peel strength

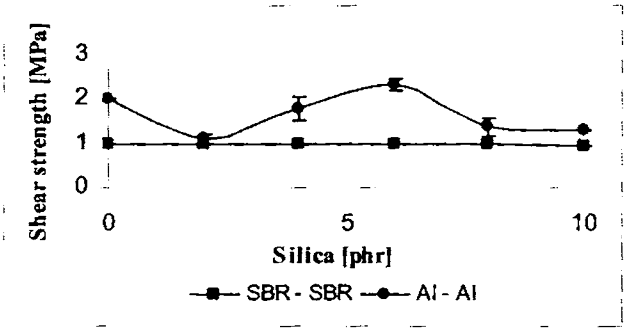

Fig 2.2.10 Effect of silica on shear strength

c. Effect of phenolic resin and tackifiers

Fig. 2.2.11 shows the effect of adding the synthesized phenol-formaldehyde resin on peel strength of rubber-to-rubber specimens. There is a slow but steady rise in peel strength values up to 30phr resin. But as the resin content increases beyond 30phr, the flexibility of the system decreases, resulting in a reduction of peel strength. Fig. 2.2.12 shows that both peel and shear strengths of metal-to-metal specimens increase progressively on addition of resin. As in the case of rubber-to-rubber specimens, peel strength goes through a maximum. But shear strength reaches a plateau and is unaffected by further addition of resin. In general, the addition of resin beyond a level reduces the flexibility and consequently, the peel strength. But the shear strength reaches a maximum and on addition of more resin the values do not improve.

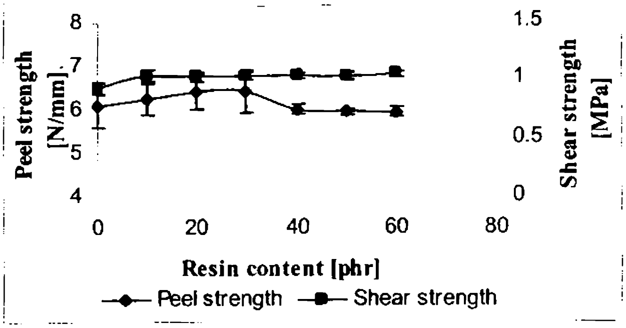

Fig. 2.2.11 Effect of PCF resin on SBR-SBR bonding

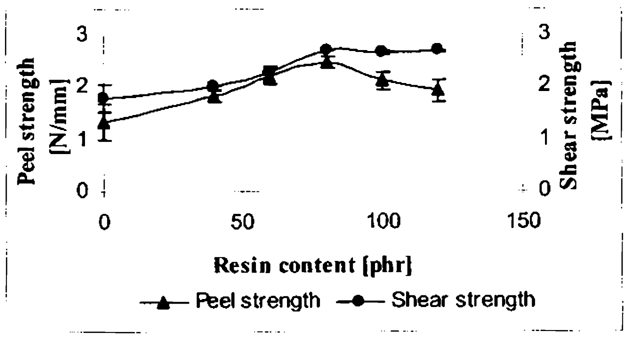

Fig. 2.2.12 Effect of PCF resin content on Al- Al bonding

The effects of tackifier Pentalyn H on peel and shear strength values are shown in Figs. 2.2.13 and 2.2.14 respectively. The tackifier is not seen to affect substantially the peel and shear strength values for both metal-to-metal bonding and rubber-to-rubber specimens.

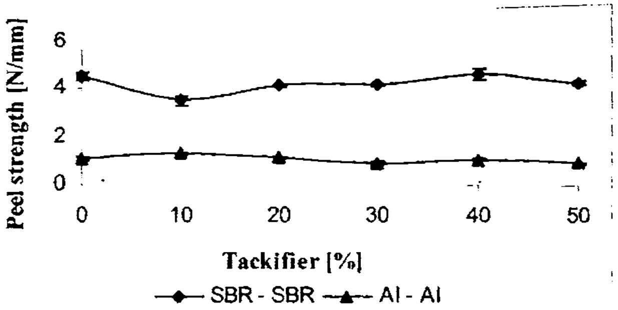

Fig. 2.2.13 Effect of tackifier on peel strength

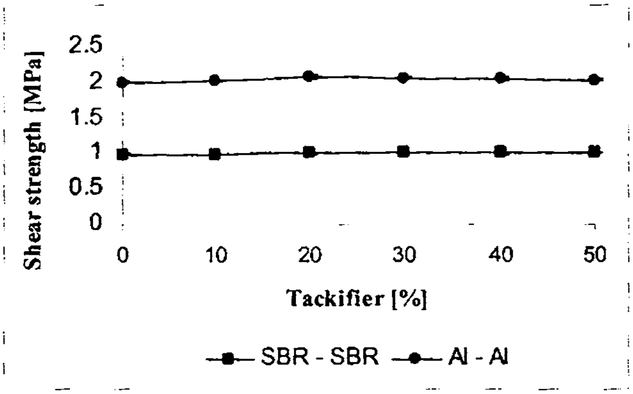

Fig. 2.2.14 Effect of tackifier on shear strength

d. Effect of adhesion promoter

Silane adhesion promoters are employed for improving the bond between a polymeric material and a nonpolymeric material like metal or glass. Fig. 2.2.15 shows the effect of the silane coupling agent used as promoter for bonding to metal substrates. The addition of silane improves both peel and shear strengths considerably in the case of metal-to-metal bonding. Silanes can form strongly adsorbed polysiloxane films on metal surfaces. The polysiloxane structure has an open porous structure and the liquid adhesive can penetrate into it and then harden to form an interpenetrating interphase region. Another reason for the increase in bond strength on addition of silane may be the reaction of the functional group in the silane (amino group) with the resin [33].

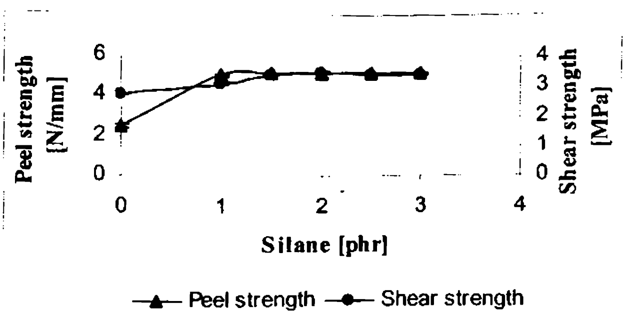

Fig 2.2.15 Effect of adhesion promoter on Al-Al bonding

e. Effect of crosslinking agents

Fig. 2.2.16 confirms the fact that increasing degrees of crosslinking lead to a fall in peel strength for both types of substrates due to reduction in flexibility of the films. Fig. 2.2.17 shows that addition of low percentages of crosslinking agents does not significantly affect the shear strength of metal-to-metal specimens. But as the concentration of crosslinking agents increases beyond a certain level, shear strength decreases. This may be due to the fact that cohesive properties of crosslinked adhesives depend on the molecular weight between the crosslinks, M_c. When the crosslinking increases, M_c decreases and shear strength decreases [34].

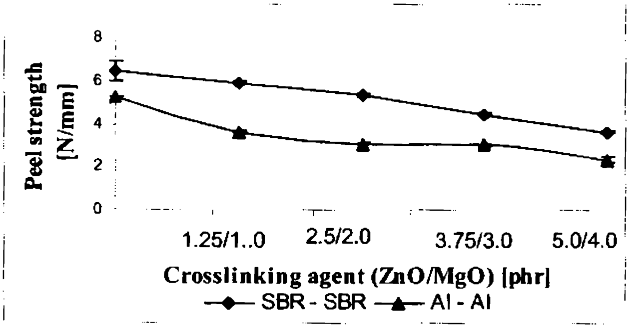

Fig. 2.2.16 Effect of crosslinking agents on peel strength

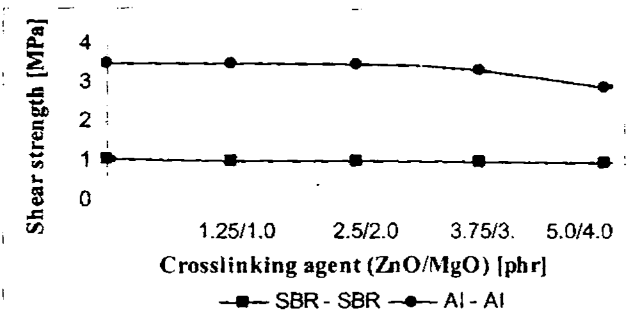

Fig. 2.2.17 Effect of crosslinking agents on shear strength

f. Effect of sulphur

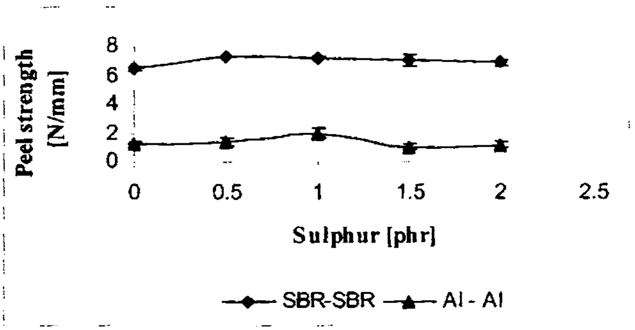

Fig. 2.2.18 Effect of sulphur on peel strength

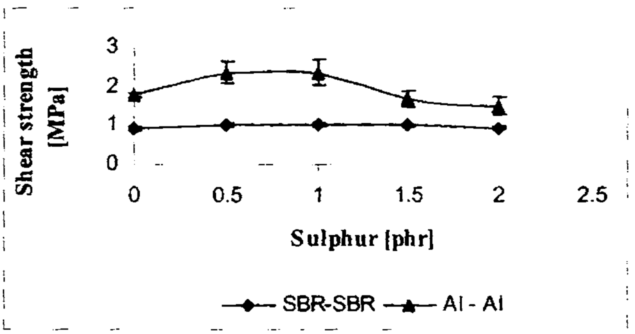

Fig. 2.2.19 Effect of sulphur on shear strength

Effect of sulphur on peel strength and shear strength of Al-Al and SBR-SBR bonds is shown in Figs. 2.2.18 and 2.2.19. It can be seen that the peel and shear strength values increase by a small amount on addition of sulphur. Sulphur can migrate from the adhesive to the rubber and result in the formation of interfacial bonds between the adhesive layer and the substrate [35].

g. Effect of zinc phosphate

From Fig.2.2.20 it can be seen that both peel strength and shear strength slightly increase with the addition of zinc phosphate. This effect is observed beyond a concentration of 1phr. It is generally noted that phosphate etching improves the initial joint strength of aluminium bonds [36] and the presence of this substance may be the reason for the slight improvement in bond strength. Too high a concentration on the other hand nullifies this effect, presumably by introducing crosslinks.

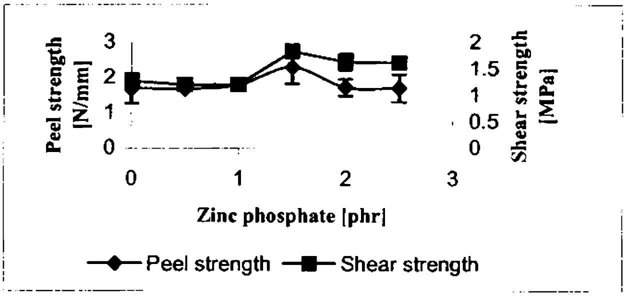

Fig 2.2.20 Effect of zinc phosphate on Al-Al bonding

h. Effect of ENR

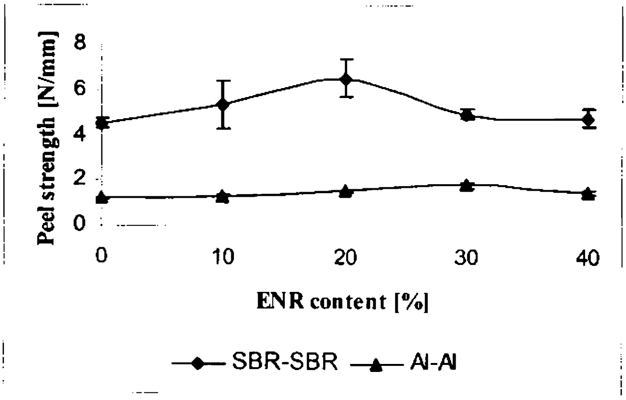

Fig. 2.2.21 Effect of ENR on peel strength

Figs. 2.2.21 and 2.2.22 show the effect of using a blend of CR AD and ENR on peel and shear strength respectively of metal-metal and rubber-rubber bonding. It can be seen that peel strength of SBR-SBR bonds slowly increases with ENR content upto 20wt%. For Al-Al bonds the highest peel strength was obtained for a blend consisting of 70parts CR AD and 30parts ENR by weight. The better bond strength may be due to the presence of the polar epoxy group which has helped to flexibilize the system. The shear strengths on the other hand is largely unaffected.

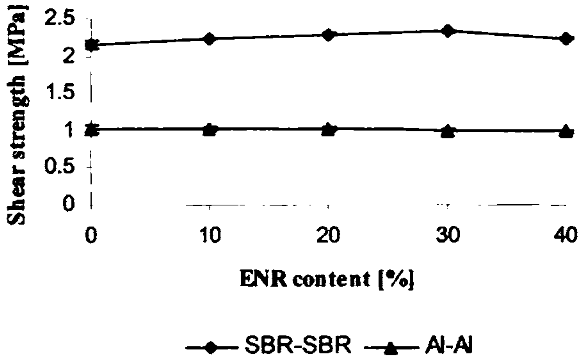

Fig. 2.2.22 Effect of ENR on shear strength

i. SEM analysis

Figs. 2.2.23 and 2.2.24 show the SEM pictures of the fracture surfaces of the peel specimens of SBR and Al respectively. Comparing the two figures, Fig. 2.2.24 shows a more brittle failure. This may be due to the lower rubber content in the adhesive used for metal-metal bonding.

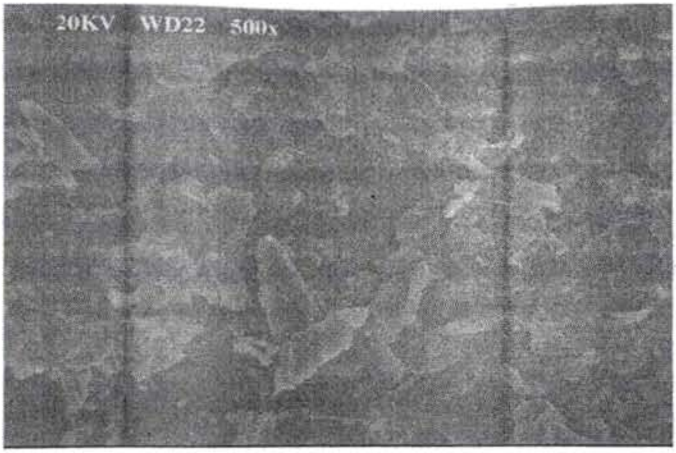

Fig. 2.2.23 SEM photograph of SBR substrate

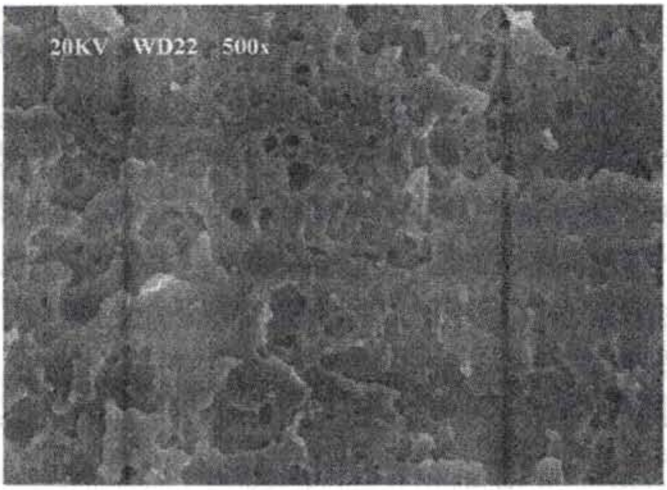

Fig 2.2.24 SEM photograph of Al specimens

2.2.3 CONCLUSION

A concentration of 15 – 20wt% CR solution in toluene gives the best performance for both rubber-rubber and metal-metal specimens. In the case of metal-metal specimens, addition of acetylene black has very little effect on the adhesive performance. Addition of silica is not found to improve the adhesive properties substantially with the exception of shear strength of Al-Al bonds. 3-aminopropyltriethoxysilane (>1phr) is found to improve the peel strength and shear strength of Al-Al specimens. A marginal improvement in SBR-SBR and Al-Al bonding is obtained by using a 90/ 10 blend of CR-AD/W compared to pure CR-

AD. Addition of acetylene black (6phr) improves this further in SBR-SBR bonding. The tackifier Pentalyn H does not improve the adhesive performance. Addition of curatives to polychloroprene rubber reduces the peel strength in both metal-to-metal and rubber-to-rubber bonding. Addition of zinc phosphate and sulphur has some effect on the peel and shear strengths. Replacing part of the CR-AD with ENR improves only the peel strength for both metal – metal and rubber – rubber bonding.

Cardanol can be a useful renewable resource for formulating adhesives. The copolymer, phenol -cardanol -formaldehyde when added to the rubber solution containing fillers, is found to give better peel and shear strengths.

2.3 OPTIMISATION OF PHENOL /CARDANOL RATIO

While it has been established that cardanol could be a useful starting material for adhesives the relative proportions of phenol and cardanol to be used for the resin synthesis have to be identified [37]. Further, the total resin content for each ratio of phenol/cardanol that gives optimum results for bonding aluminium to aluminium (Al-Al), aluminium to SBR (Al-SBR) and SBR to SBR (SBR-SBR) has to be established. In this study, the metal-to-metal adhesive formulation is used as a primer and the rubber-rubber formulation as the adhesive for Al-SBR bonding.

a. Phenol formaldehyde resins

Phenolic resins are versatile polymers and are widely employed in industries for the manufacture of adhesives and paints, owing to their low cost, dimensional stability and exceptional heat and fire resistance. These excellent properties are attributed to the highly crosslinked aromatic structure and resonance-intensifying hydroxyl groups [38-45].The brittle nature, however, significantly limits their usage. Hence the improvement of the toughness of phenolic resin is an important prerequisite for more demanding applications. The properties of phenolic resins can be improved by blending them with other polymeric materials such as polyamide [46], poly (ethylene glycol) [47], poly (ethylene oxide) [48], poly (vinyl alcohol) [49], poly (dimethylsiloxane adipamide) [50], poly (adipic ester) [51], poly (hydroxyl ether of bisphenol A) [52], poly (ethylene-co-vinyl acetate) [53] and nitrile rubber [54]. Nitrile-phenolics developed in the early 1950s [55] by blending nitrile rubber with thermosetting phenolic resins are used in the aerospace industry for structural bonding of metals and are still making a name for the excellent bond durability under severe environments [56, 57]. Phenolic resins have shown considerable growth in aerospace industry applications due to their versatile properties [58].

b. Cardanol based resins

Cardanol, a meta-substituted phenol, is the main ingredient of CNSL, obtained from the nut of the tree *Anacardium occidentale L.* Earlier studies have shown that cardanol and its polymers have interesting structural features for chemical modification and polymerisation into speciality polymers [59-67]. In the twentieth century, high technology has fostered active participation of phenolic resins based on CNSL in "high-tech" areas ranging from electronics, computers, communications, aerospace, biomaterials, biotechnology and advanced composites [68-75]. The use of CNSL as a starting material for synthetic resins is of immense interest in these days of diminishing petroleum reserves. Some of the important aspects of cardanol based resins are their low cost, flexibility, water resistance, anti-microbial and anti-termite characteristics and low fade characteristics. Besides, the monomeric compounds derived from these natural plant products can be crosslinked to produce environmentally friendly resin matrices that are cost effective and renewable [76].

Cardanol is valuable for the production of thermoset resins [77]. Resole and novolac –type of CNSL-based resins may be prepared by varying the cardanol: formaldehyde mole ratio. Fig 2.3.1 shows a possible structure for cross-linked cardanol-formaldehyde resin, where R stands for the side chain [78].

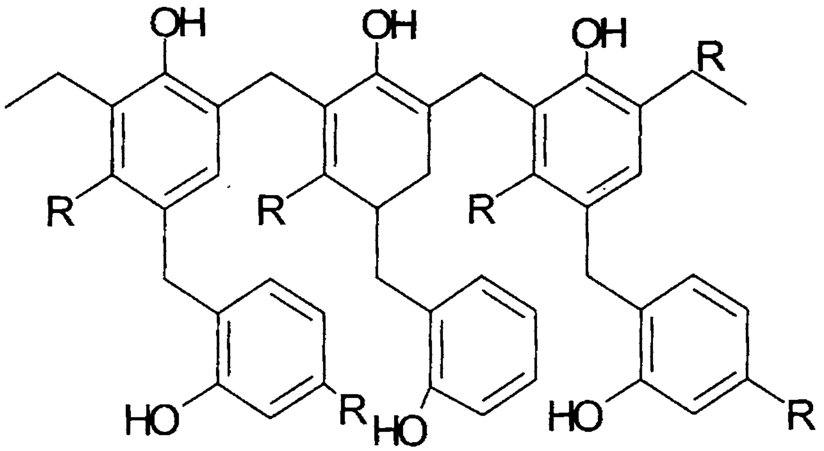

Fig 2.3.1 Probable cardanol-formaldehyde structure

2.3.1 EXPERIMENTAL

a. Resin preparation

Different phenolic resins with varying phenol/cardanol ratio, viz. 20/80, 40/60, 60/40, 80/20 and 100/0 wt% were synthesized. Using these resins individual studies were carried out for testing SBR-to- SBR, Al-to-Al and Al-to-SBR bonds.

The resins were prepared with a stoichiometric ratio of 1:1.7 between total phenols and formaldehyde in an alkaline medium. The resole type resin thus obtained was neutralized and dried.

The resin was added to neoprene solution in toluene containing other ingredients (Table 3.1.1). The neoprene consisted of blends of CR AD and CR W. Such blends are found to give better performance compared to pure grades [79]. The adhesive was then applied on substrates and an interval of 30 minutes was given for drying the film. The substrates were subsequently joined and the adhesive cured at 150^{0}C for 30 minutes.

b. Testing of liquid resin

The quality of the resins was tested by determining the specific gravity, viscosity, gel time and solids content

i. Specific gravity

The specific gravity of the resin was determined according to ASTM D 792 [80] using a specific gravity bottle.

ii. Gel time

About 2g of the sample is filled into a test tube and dipped into a water bath at 100°C. The increase in viscosity is monitored with a glass rod used roughly like a reciprocating piston. As soon as the gel point is reached, the glass rod gets trapped in the resin. This period of time is recorded as the gel time. The test is done as per DIN 16945 [82].

iii. Solids content

About 2-3 g of the resin was taken in a porcelain cup and heated to 150°C in a hot air oven to constant weight. The cup is cooled in a desiccator and weighed [83].

c. Gel permeation chromatography (GPC)

This method, also called size exclusion chromatography, makes use of a chromatographic column filled with a gel or porous solid beads having a pore size similar to that of the polymer molecules [84]. A dilute solution of the polymer is introduced into a solvent stream flowing through the column. Smaller molecules of the polymer will enter the beads while the larger ones will pass on. Thus the larger molecules have a shorter retention time than the smaller molecules. The chromatogram is a plot of retention time (or volume) against the amount of eluted molecules. The prepared PCF resins were subjected to GPC analysis with a view to estimate the molecular weight of the resins. The analysis was carried out using Waters GPC equipped with a Waters 510 (SEC) pump, Waters 410 differential refractometer (at 40 °C, wavelength = 930 nm) and Waters WISP 712 autoinjector with injection volume of 50 μL (SEC). Tetrahydrofuran (THF, Biosolve, stabilized with BHT) was used as the eluent at a flow rate of 1.0 mL/min. SEC calibration was done using polystyrene (PS) standards (Polymer Laboratories). Data acquisition and processing (SEC) were performed using the Waters Millennium 32 (v3.2) software.

d. Thermal studies [85]

i. Thermogravimetric analysis (TGA)

For certain applications, the serviceability of the polymer at different temperatures is of interest. Thermal analysis reveals the stability of the polymer sample to degradation by heat. The thermogravimetric (TG) analysis was carried out using TA Instruments Model TQ 50 TG Analyzer. The sample was taken in a platinum pan and was heated from 30°C to 800°C at a heating rate of 20°C/min in nitrogen atmosphere. Sample weights were between 5 and 10 mg.

ii. Differential scanning calorimetry (DSC)

DSC gives a measure of the difference in the rates of heat absorption by a sample with respect to an inert reference (maintained at the same temperature) as the temperature is raised at a constant rate. It is used to investigate thermal transitions, including phase changes, crystallization, melting, or glass-rubber transitions, of a material as a function of temperature. Heat flow, i.e. heat absorption (endothermic) or heat emission (exothermic), is measured, per unit time, for the sample and the result is compared with that of a thermally inert reference. TA Instruments DSC Q 100 equipped with a RCS cooling system was used to study thermal transitions in the samples at a heating rate of 10°C/min in a nitrogen purged environment. The sample weight was between 4 and 6 mg. The sample was taken in a hermetic aluminium pan and sealed.

e. Spectroscopic studies

Fourier transform infra red (FTIR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indicative of the bond strengths and structural geometry in the molecule.

FTIR spectra of the samples were taken in Bruker Tensor 27 FTIR Spectrometer. NMR spectroscopy is also used for the characterization of the synthesized resins. ^{1}HNMR spectra (400 MHz) were recorded on a Varian Mercury Vx 400 spectrometer using $CDCl_3$ as the solvent.

f. Viscosity

The viscosity of the adhesive formulation was measured at room temperature using a Brookfield Viscometer Model RVF as per ASTM D 2393 [81]. The appropriate spindle was allowed to rotate in the resin for 30 seconds and the dial reading was taken. The procedure was repeated for constant dial reading. The reading was then converted into centipoises using the conversion table.

g. Adhesive strength

i. SBR - SBR bonding

For preparing the adhesive the rubber was initially masticated on a two-roll mill along with acetylene black and sulphur. It was then dissolved in toluene to get a 20 wt% solution. The resin was dissolved in methyl ethyl ketone separately and the solution blended with the rubber solution. The resin concentration was varied from 10 to 50 phr for each resin prepared with a different phenol/cardanol ratio. The resulting adhesive formulations were tested for peel strength between SBR-SBR specimens. The shear strength of SBR-SBR bonds was high enough to cause fracture of the substrate irrespective of the type of resin and concentration and is not reproduced here.

ii. Al - Al bonding

The neoprene rubber was masticated on a two-roll mill to reduce crystallinity and improve solubility. Other ingredients as listed in Table 2.3.1 were incorporated during mastication and the compounded rubber was dissolved in toluene so as to get a 15 wt% solution. The resin concentration was varied from 40 to 100phr. The peel and shear strength tests were performed on a Shimadzu Universal Testing Machine (50kN) with a grip separation rate of 50mm/min.

iii. SBR - Al bonding

SBR-Al bonding studies were carried out using an adhesive-primer combination. Different phenolic resins (100/0, 80/20, 60/40, 40/60 and 20/80) were employed for formulating the adhesive as well as the primer. For this, the resin content in the primer was fixed as 80phr and the resin content on the adhesive side was varied from 10 to 50 phr in steps of 10. Later, for fine-tuning, the resin content in the adhesive was kept at 40phr (the optimum value from the previous study) and the resin content in the primer was varied from 40 to 100 phr in steps of 20.

Table 2.3.1 Ingredients of the adhesive formulation, phr

Ingredients	Al-to-Al bonding	SBR-to-SBR bonding
Neoprene AD	90	90
Neoprene W	10	10
Silica	4	-
Acetylene black	-	6
Sulphur	1	0.5
Zinc phosphate	1.5	-
Silane	2	-
Phenolic resin	40-100	10-50
Total solid content (%)	15-17	20-22

2.3.2 RESULTS AND DISCUSSION

a. Resin properties

Figs. 2.3.2 to 2.3.4 show the effect of replacement of phenol by cardanol on the properties of the resins. From the Fig.2.3.2 it can be seen that the gel time increases with the cardanol content. This is attributed to the low reactivity of cardanol based resins. The solids content gradually decreases with the cardanol content probably due to the low reactivity of cardanol resulting in unreacted raw materials. This may also be due to small amounts of volatile matter present in cardanol. Fig.2.3.4 shows a fall in specific gravity as the cardanol content increases. The non polar nature of the long hydrocarbon chain and its bulkiness may lead to poor intermolecular packing and hence low specific gravities.

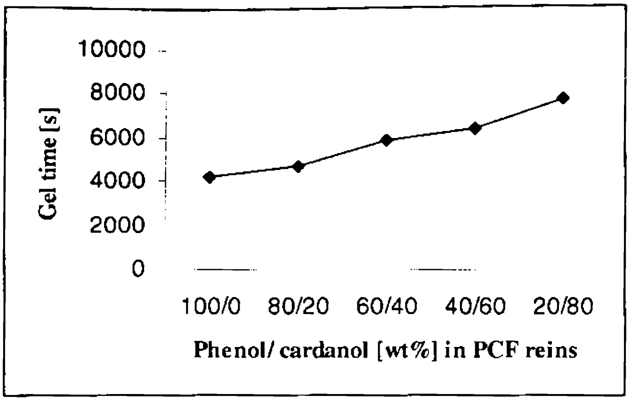

Fig. 2.3.2 Variation of gel time at 100°C with cardanol content

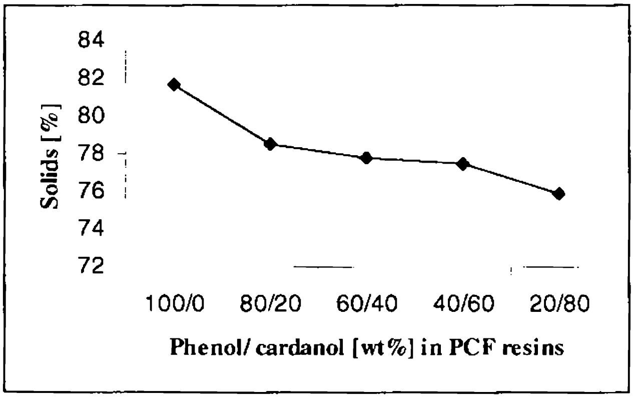

Fig.2.3.3 Variation of solid content with cardanol content

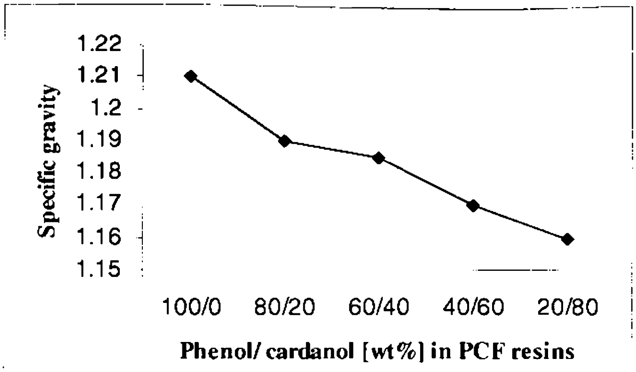

Fig. 2.3.4 Variation of specific gravity with cardanol content

b. Thermal studies

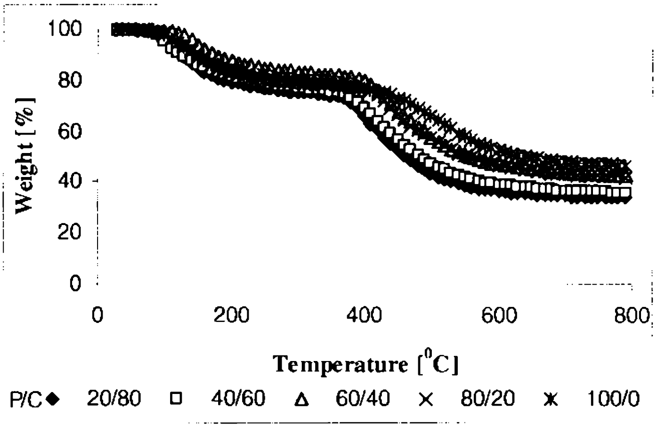

Fig 2.3.5 TGA traces of the synthesized phenolic resins

Fig. 2.3.5 shows the TGA plot of the resins prepared with different compositions. From the figure it can be seen that higher phenolic content shows increased thermal stability. As the cardanol content increases, the thermal stability decreases slowly. This is in agreement with the findings reported by O'Connor and Blum [86]. The difference in thermal stability is attributed to the structural features of cardanol. The degradation of the side chain in the cardanol may take place at an early stage.

Table 2.3.2 Thermal properties of cardanol based resole resins

Phenol: Cardanol (wt%)	T_{50} (°C)	Peak degradation temperature (°C)	Residue wt (%)
100:0	644	475	46.8
80:20	553	435	42.5
60:40	556	433	42.8
40:60	483	411	36.0
20:80	463	400	33.9

Table 2.3.2 gives the peak degradation temperature, temperature at 50% degradation and residue at 800°C. All the properties gradually decrease as the cardanol content in the resin increases.

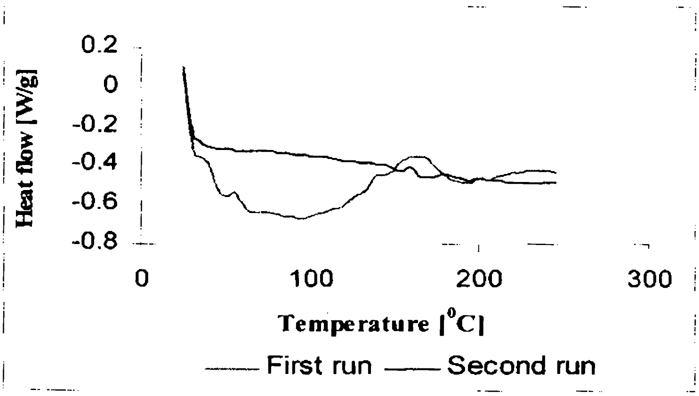

Fig 2.3.6 DSC plot of 60/40 resin

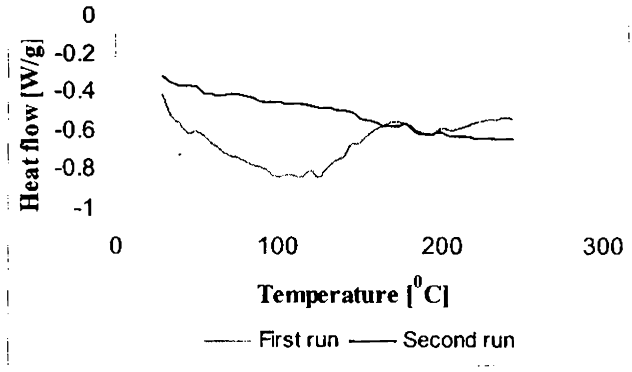

Fig 2.3.7 DSC plot of 80/20 resin

DSC analysis was performed on PCF 60/40 and 80/20 resins. Figs 2.3.6 and 2.3.7 show the DSC thermogram of the above resins subjected to two consecutive runs. The glass transition temperature is obtained at about 50-55°C. A broad endotherm is seen between 70 and 130°C indicating the presence of water molecules and the by-products of the CNSL-formaldehyde condensation reaction [87]. An exothermic peak is obtained at 160°C, which indicates the curing temperature of PCF resins. The second run shows no exothermic or endothermic peaks indicating that the resin has fully cured.

c. GPC

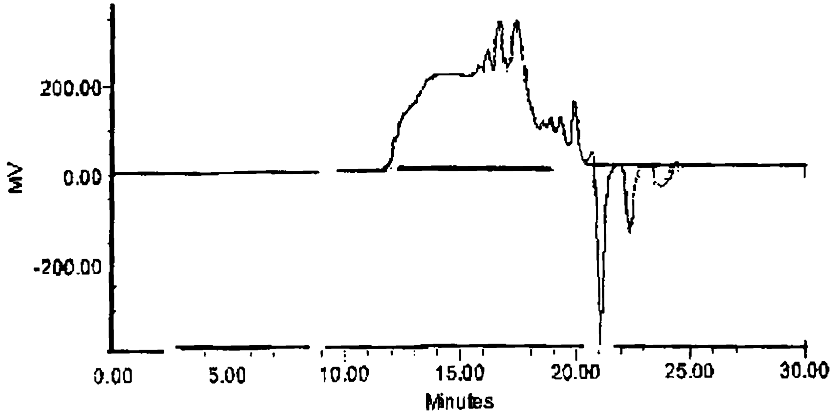

Fig 2.3.8 GPC plot of 60/40 PCF resin

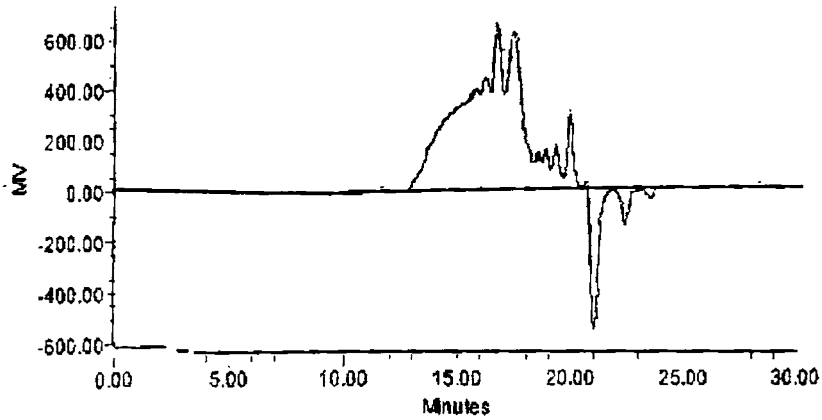

Fig. 2.3.9 GPC plot of 80/20 PCF resin

Table 2.3.3 GPC data of the PCF resins

Resin	Mn	Mw	Mz	Mw/Mn	Mz/Mw
60/40	1968	2216	2493	1.126	1.125
80/20	1582	1786	2063	1.129	1.156

Figs 2.3.8 and 2.3.9 show GPC plots of the two resins studied. The GPC results are tabulated in the Table 2.3.3. From the table it can be seen that the 60/40 ratio has a higher molecular weight compared to 80/20 resin. As 60/40 resin has higher cardanol content compared to 80/20 resin, the higher molecular weight is due to the higher molecular weight of cardanol compared to phenol.

d. Spectroscopic analysis

Figs.2.3.10 shows the FTIR spectrum of cardanol Characteristic absorptions were found around 3346cm^{-1} (hydroxyl group), 2936cm^{-1} (C-H stretching) and 1456 cm^{1} (CH$_2$ stretching).

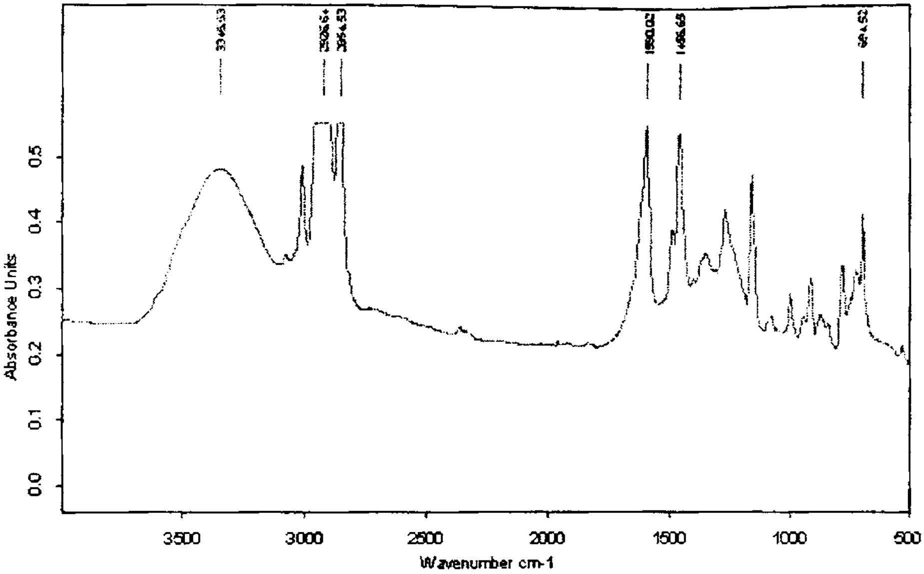

Fig. 2.3.10 FTIR spectrum of cardanol

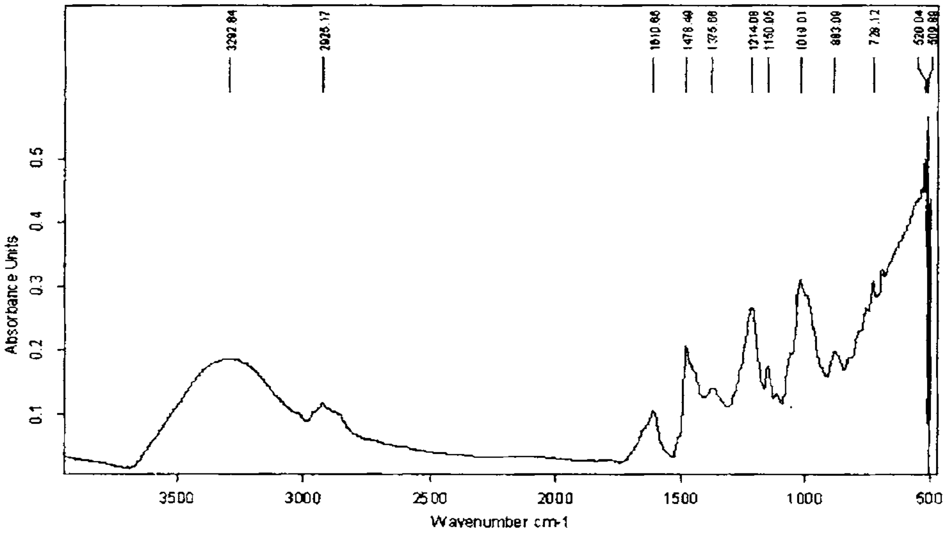

Fig. 2.3.11 FTIR spectrum of PCF resole resin

Fig. 2.3.11 and 2.3.12 give the FTIR spectrum of and PCF and phenol-formaldehyde (PF) (1:1.1.7) resins respectively. Characteristic absorptions were found around 3290cm^{-1} (hydroxyl group, broad band), 2925cm^{-1}(aromatic C-H stretching weak), 1509 cm^{-1} (phenyl ring) and 1479 cm^{-1}(CH_2 bending). The two strong bands around 1213 $cm^{-1}$and 1019 cm^{-1} are characteristic of C-O stretching in phenol and methylol groups respectively. The bands around 885cm^{-1} and 822cm^{-1} are characteristic of ortho-para substitution. The band around 754cm^{-1} is characteristic of ortho- ortho substitution.

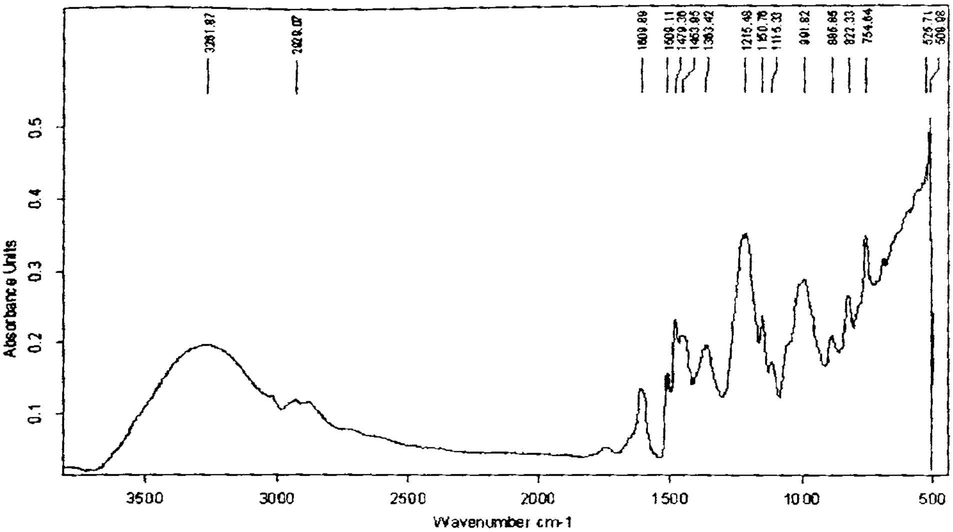

Fig. 2.3.12 FTIR spectrum of PF resole resin

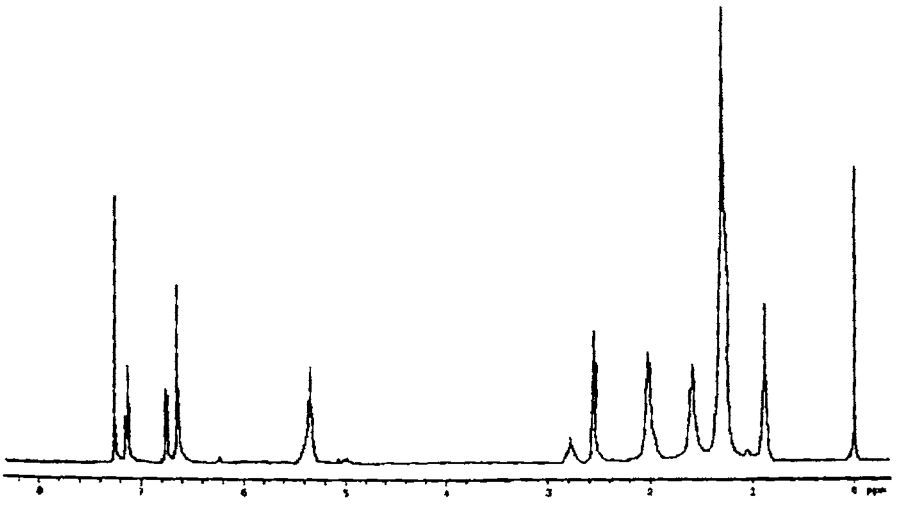

Fig. 2.3.13 ^{1}HNMR spectrum of cardanol

Fig. 2.3.13 and 2.3.14 show the ^{1}HNMR spectra of cardanol and PCF resin respectively. The spectra displayed peaks of aromatic protons (δ 7.2), $-CH{=}CH-$ protons (δ 5.35), $-CH_2-Ar$ protons (δ 2.55), $-CH_2-CH{=}CH-$protons (δ 2.01), $-CH_2-CH_2-Ar$ protons (δ 1.59) and $-CH_3$ protons (δ 0.88). The strong peak at δ 1.3 is attributed to the long side chain of methylene groups in the cardanol.

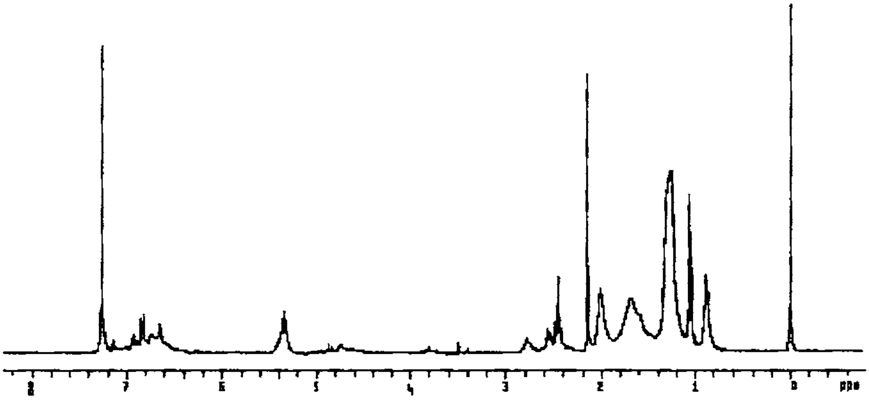

Fig. 2.3.14 ^{1}HNMR spectrum of PCF resin

e. Viscosity

The viscosity of the Formulation 1 used for metal-metal bonding was found to be 100-150cps and that of Formulation 2 used for rubber-rubber bonding 500-600cps.

f. Adhesive strength

Fig. 2.3.15 shows the variation of peel strength of Al-to-Al bonds with resin content when different resins are used. The highest peel strength is observed for the resin containing 60% phenol and 40% cardanol. For this case, 80phr resin shows a marginal superiority although the peel strength is not very sensitive to resin content in the range above 40phr. Moreover, judging from the fracture surface and bond quality over the area, around 80phr of resin gives a satisfactory performance.

It is interesting to note that a 60/40 mixture of phenol/cardanol is superior to the pure phenol based resin in performance. The resin based on pure cardanol was found to have very poor adhesive properties and has not been included in this study. Resins containing high percentages of cardanol (say, phenol/cardanol ratio of 20/80) also show markedly inferior properties.

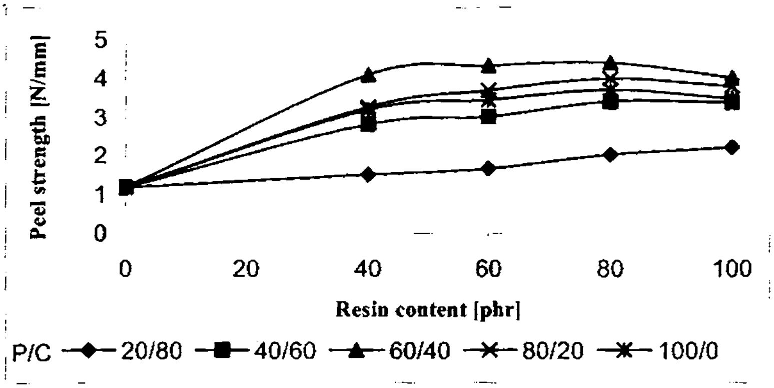

Fig. 2.3.15 Variation of peel strength of Al-Al bonds

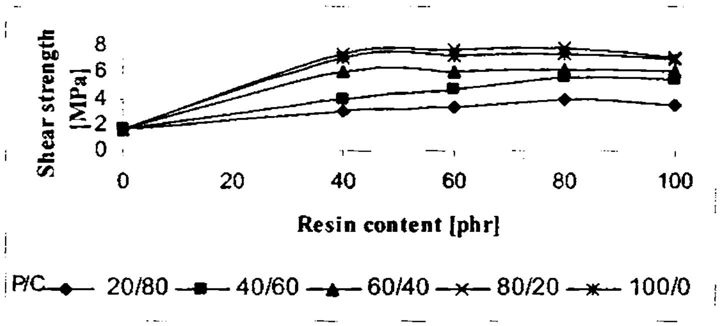

Fig 2.3.16 Variation of shear strength of Al-Al bonds

Fig. 2.3.16 illustrates the change in shear strength with phenol/ cardanol ratio and total resin content for Al- Al bonds. The 80/20-phenol/cardanol mixture gives the best results. Shear strength is high but not very sensitive to resin content in the 40-80phr range. Here again, the copolymer of phenol and cardanol shows superior performance compared to resins based on either of the pure components. While the values attained for pure phenol are also high its copolymerisation with cardanol leads to still higher shear strength values. This can be attributed to the chemical structure of cardanol, which has a long chain ,substitution at the meta position of the benzene ring. The long side chain can improve adhesive properties by entanglement. Too much cardanol on the other hand may lead to unreacted material.

Fig. 2.3.17 shows the variation of peel strength of SBR-to-SBR bonds with resin content. The resin containing 40% cardanol gives the best values. Peel strength is poor for formulations containing more than 40% cardanol. The peel strength falls gradually in the range above 30phr of resin for this case. The decrease in peel strength beyond 30phr resin is due to the lowering of flexibility of the system on resin addition. The performance of the resin based on pure phenol is also good though marginally inferior to the 60/40 composition.

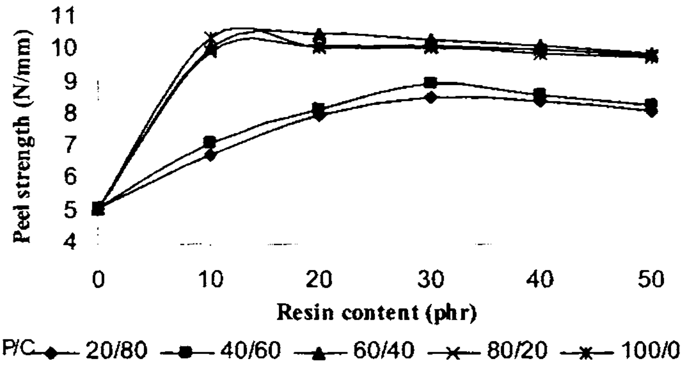

Fig 2.3.17 Variation of peel strength of SBR-SBR bonds

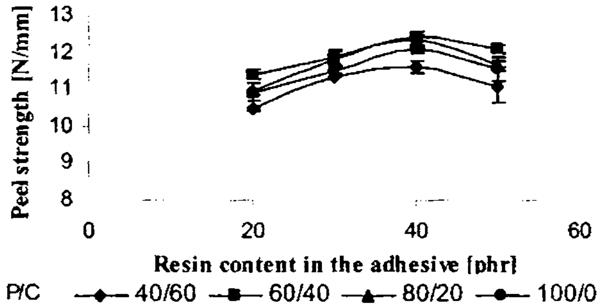

Fig.2.3.18 Variation of peel strength of SBR-Al bonds

Fig. 2.3.18 shows the variation of peel strength with resin content in the case of SBR-to-Al bonding. The resin content in the primer was kept at 80phr and the adhesive resin content varied. The highest peel strength was obtained when a copolymer containing 40% cardanol was used and the resin content kept at 40phr. For all the resins studied, the primer-adhesive combination showed the best performance at about 40phr resin in the adhesive formulation.

Fig. 2.3.19 shows the effect of varying the resin content in the primer on peel strength keeping the adhesive resin content constant at 40phr. The graph clearly indicates that 80phr is an optimum value for the primer resin content. Beyond this value the primer film gets too thick and inflexible leading to inferior peel strength values.

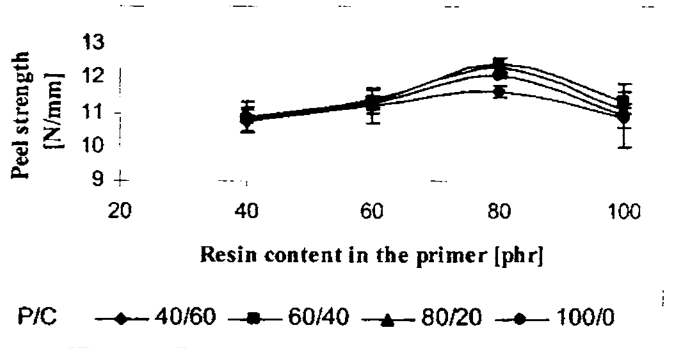

Fig.2.3.19Variation of peel strength of SBR-Al bonds

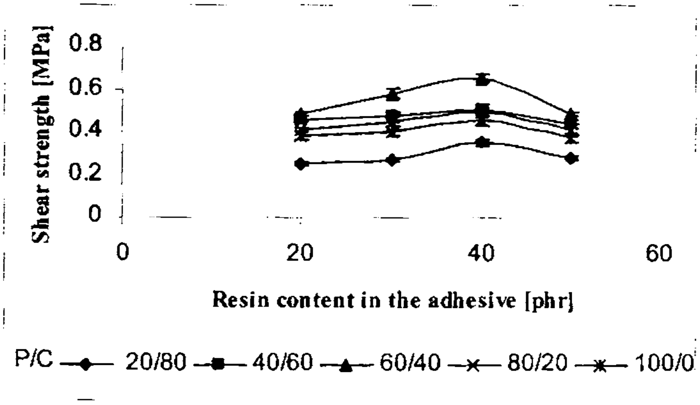

Fig. 2.3.20 Variation of shear strength of SBR- Al bonds

Figs. 2.3.20 and 2.3.21 show the variation of shear strength with resin content in the primer and the adhesive respectively on bonding SBR to Al. As in the case of peel strength this study resulted in identifying the optimum values for primer and adhesive resin contents. Shear strength shows less sensitivity to variation in resin content of both formulations compared to peel strength. Shear strength study also confirms that 40phr resin in the adhesive and 80phr in the primer give the best results. The superiority of the 40% cardanol resin is also demonstrated.

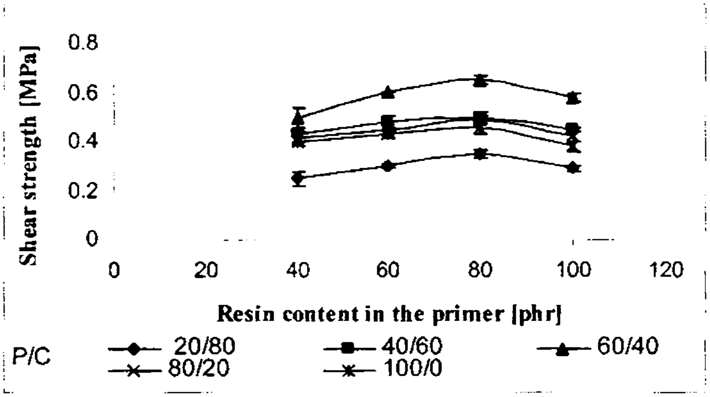

Fig. 2.3.21 Variation of shear strength of SBR- Al bonds

2.3.3 CONCLUSION

Blends of cardanol and phenol are better raw materials for resin preparation and subsequent adhesive formulation compared to either of pure phenol or cardanol. Such partial replacement of phenol with cardanol is useful from the viewpoint of conservation as well as utilization of a cheap renewable resource.

In the case of aluminium-to-aluminium bonding, about 80phr of 60/40 phenol/cardanol formaldehyde resin gives the best peel strength and 80phr of 80/20 resin gives the best shear strength. For SBR-to-SBR bonds a 60/40 phenol/cardanol formaldehyde resin yields the best peel strength values. For Al-SBR bonding, the optimal concentration in the primer side is 80phr and on the adhesive side, 40phr of a copolymer resin containing 40% cardanol and 60% phenol.

2.4 EFFECT OF PHENOL / FORMALDEHYDE RATIO ON ADHESIVE STRENGTH

The ingredient ratios and parameters of the resin formulation are frequently adjusted empirically to tailor phenolic resin properties to specific production requirements such as the resin reactivity, formaldehyde emissions, dimensional stability and so forth. The ultimate performance of a fully cured PF resin largely depends on its synthesizing parameters, including formaldehyde/ phenol (F/P) molar ratio, sodium hydroxide/ phenol (NaOH/P) molar ratio, viscosity, reactivity, and so on [88]. The F/P ratio and NaOH/P molar ratios affect the cure shrinkage [89] and surface tension of PF resol resins [90]. Both ratios also affect the rigidity of the cured resins, showing that high F/P and NaOH/P ratios give high relative rigidity.

In this section, peel and shear properties of a) aluminium to aluminium (Al-Al), b) SBR to SBR (SBR-SBR) and c) aluminium to SBR (Al-SBR) bonds are evaluated under conditions of varying total phenol/ formaldehyde (P/F) ratio. Further, the total resin content for each phenol/cardanol ratio that gives optimum results is also established. While Al-Al and SBR-SBR specimens were bonded with a single component adhesive formulation, a primer/adhesive combination was employed for Al-SBR bonds. The adhesive formulation developed for metal-to-metal bonding has been used as the primer and the one for rubber-to-rubber bonding as the adhesive.

2.4.1 EXPERIMENTAL

a. Resin preparation

Phenol-cardanol-formaldehyde (PCF) resin was synthesized by reacting a mixture of phenol and cardanol with an aqueous solution of formaldehyde (formalin) at 90^0C for about one hour under alkaline conditions as described earlier. Different copolymers with varying stoichiometric ratios between total phenols and formaldehyde (1:1.5, 1:1.7, 1:2, 1:2.3 & 1:2.5) were prepared. For each stoichiometric ratio two different phenolic resins with varying phenol / cardanol ratio viz. 60 / 40 (PCF-I) and 80 / 20 (PCF-II) % by wt were synthesized.

b. Resin characterization

The gel time of the synthesized resins were determined as mentioned earlier [Section 2.3.1.b].

c. Thermal studies

The thermogravimetric analysis of the different resins prepared in different stoichiometric ratios were done as mentioned in Section 2.3.1.d.

d. Adhesive strength

The adhesives for SBR-SBR, Al-Al and SBR-Al were prepared as mentioned in Section 2.3.1.g. Different phenolic resins in various stoichiometric ratios of 1:1.5, 1:1.7, 1:2, 1:2.3 & 1:2.5 were prepared and employed for formulating the adhesives.

2.4.2 RESULTS AND DISCUSSION

a. Gel time

Gel time studies on the synthesized PCF resins indicate that shorter gel times are achieved as more and more formaldehyde is employed for the synthesis. This is because of higher methylol content and a greater possibility of condensation between methylol groups [88]. A high formaldehyde resin, in general, leads to a short gel time and often a short shelf life. From comparison of the two curves in Fig. 2.4.1 the presence of cardanol is found to marginally increase the gel time, although at high formaldehyde ratios the difference is not very noticeable.

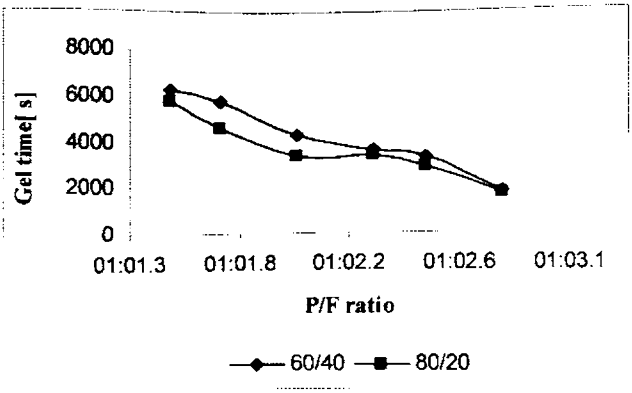

Fig. 2.4.1 Gel time at 100°C of synthesized PCF resins

b. Thermal analysis

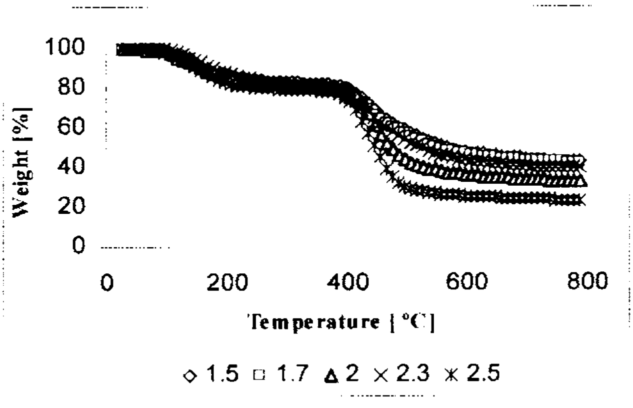

Fig. 2.4.2 TGA plot of the PCF resins

Fig.2.4.2 shows the TGA plot of the PCF II resin prepared in different stoichiometric ratios. From the figure it can be seen that the char residue gradually decreases when the stoichiometric ratio increases. When the F/P ratio is high, the methylol groups may interact with one another and form dimethylene ether links with the liberation of water [91]. The dimethylene ether links may release one of the bound formaldehydes via disproportion to yield methylene bridge. This may be the reason for the decrease in the residue content at higher stoichiometric ratios. The peak degradation temperature, temperature at which 50% degradation occurs and residual weight are tabulated in Table 2.4.1

Table 2.4.1 Thermal properties of cardanol resole resins prepared in different stoichiometric ratios

P/C: F ratio	$T_{50\%}$ (°C)	Peak degradation temperature (°C)	Residue wt (%)
1:1.5	569	435	42.9
1:1.7	553	435	42.2
1:2.0	471	440	33.9
1:2.3	458	450	25.4
1:2.5	451	447	23.1

c. Adhesive strength

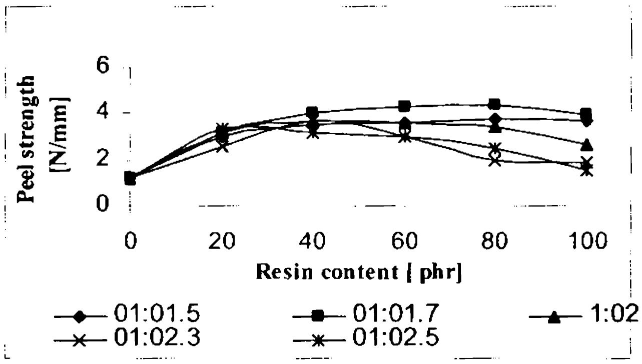

Fig 2.4.3 Peel strength of Al-Al bonds

Fig. 2.4.3 is a plot of peel strength obtained for Al-Al bonds employing phenolic resins of varying P/F ratios. A P/F ratio of 1/1.7 is found to give the best peel strength. Optimum resin content for this case is about 80phr although peel strength is not very sensitive to P/F ratio in the range of 40- 100phr. Lower amounts of formaldehyde signify higher condensate molecular weights and a lower extent of crosslinking. The difference in performance between resins with varying P:F ratios is not significant at lower resin contents, say 20 and 40phr. As the formaldehyde content goes up peel strength falls drastically at higher resin contents.

Referring to Fig 2.4.4, shear strength of Al- Al bonds are also maximum for a P: F ratio of 1: 1.7. A high methylol content, facilitated by high formaldehyde ratios, is not conducive to shear strengths of Al- Al bonds especially at resin contents less than 80phr. At a high resin concentration of 80phr all the resins are almost equivalent in performance.

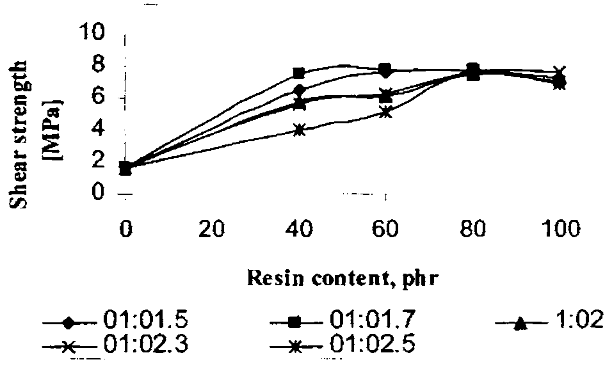

Fig 2.4.4 Shear strength of Al-Al bonds

Fig 2.4.5 shows the peel strength of SBR- SBR specimens. The resin with P:F ratio of 1: 1.7 yields a high peel strength irrespective of the resin content. But surprisingly, the best peel strength is shown by the resin with a P: F ratio of 1: 2.3 at a low concentration of 10phr. For high F/P ratios, high resin contents tend to lower the peel strength. The performance of the resin with 1:2.3 stoichiometry, points to the complex relationship between phenolic resin chemistry and performance of the final adhesive formulation.

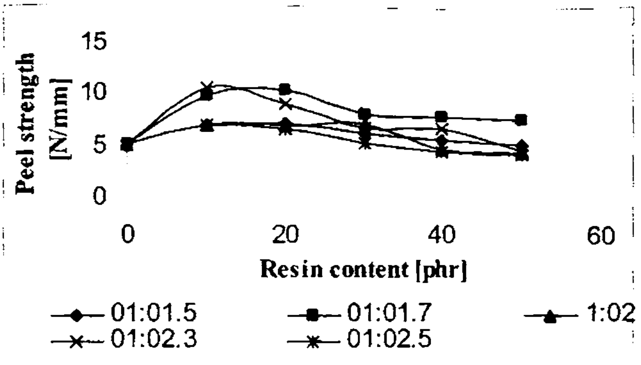

Fig 2.4.5 Peel strength of SBR-SBR bonds

Fig 2.4.6 wherein shear strength of SBR- SBR specimens are plotted indicates that all the P:F ratios studied lead to comparably high values. All the tests end in fracture of the substrates. The resin with P: F ratio of 1: 1.7 retains its superiority especially at lower resin contents. For a resin with a particular P:F ratio, the dependence of shear strength on resin content is marginal.

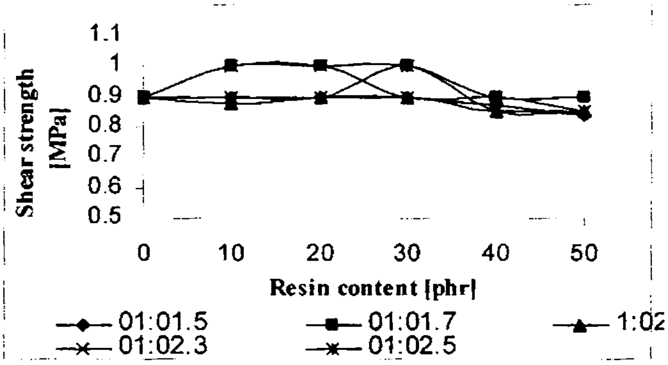

Fig 2.4.6 Shear strength of SBR-SBR bonds

Fig 2.4.7 shows the variation of peel strength of Al- SBR bonds with P/F ratio. The resin with P/F ratio of 1/1.5 shows a marginal superiority. The peel strength of SBR-Al bonds is affected significantly by the P/F ratio. But the dependence on resin content is less noticeable although most formulations show some kind of optimum at about 30phr resin. Strengthening/ stiffening of the adhesive film by the resin in this case do not improve the bonding action beyond a point.

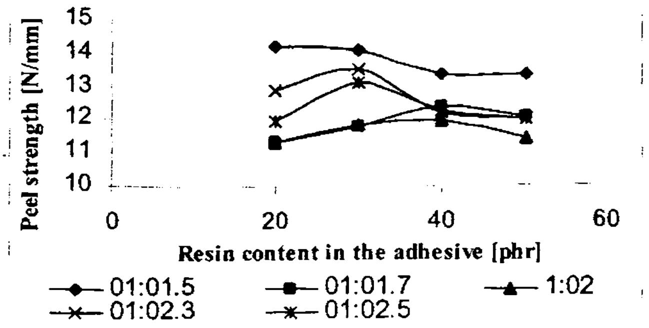

Fig 2.4.7 Peel strength of SBR-Al bonds

Fig 2.4.8 shows that low formaldehyde content leads to high shear strength in SBR-Al bonds. The maximum shear strength is obtained at 30-40phr. The resin content and P/F ratio affect the shear strength significantly. Too high a resin content leads to lowering of the shear strength by increasing the average degree of crosslinking. The same principle applies to high formaldehyde content also.

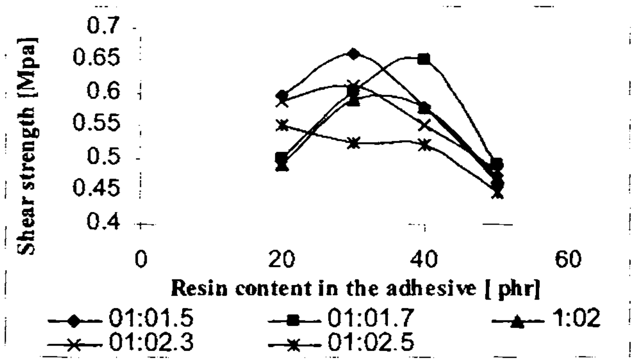

Fig 2.4.8 Shear strength of SBR-Al bonds

2.4.3 CONCLUSION

The method of preparation of the resin reflected by the P:F ratio is seen to influence the peel properties more. While Al-Al bonding requires higher levels of resin addition of the order of 80phr, SBR-SBR specimens require the least amount of resin (10-30 phr). Al- SBR specimens perform best when the resin content of the adhesive is in the range of 20 - 40phr. The char residue of the PCF resins slightly decreases when the F/P ratio increases from 1.5 to 2.5 and points to somewhat inferior thermal resistance. In all the cases except rubber-metal peel strength, 1:1.7 resin shows a slight superiority over other ratios. In the case of peel strength of SBR-Al bonds, 1:1.5 resin based formulation gives the highest bond strength.

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Chapter 3

Adhesives based on phenolic-epoxy blends

3.1 INTRODUCTION

The term epoxy refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms already united in some other way. The simplest epoxy is a three membered ring, to which the term α-epoxy or 1,2-epoxy is applied. Ethylene oxide is an example of this type (Fig 3.1). The term oxirane, a trivial name for ethylene oxide is also used in referring to the epoxy group. This group may lie within the body of the molecule but is usually terminal. The three membered epoxy ring is highly strained and is reactive to many substances, particularly proton donors.

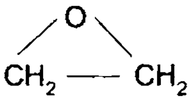

Fig 3.1 Ethylene oxide

Epoxy resins dominate the field of structural adhesives due to their excellent mechanical and chemical properties and good temperature resistance [1]. Epoxies offer very high shear strengths and can be modified to meet a wide variety of bonding needs. Generally, epoxy bonds are rigid; they fill gaps well with little shrinkage. But fully cured epoxies have the limitation of high brittleness [2]. Hence the main challenge of epoxy adhesive formulators is to improve the flexibility of the adhesive system. This can be done by attaching chemical groups to the epoxy structure or by adding flexibilizing resins or elastomers to the formulation to create a hybrid epoxy adhesive system. The blending of phenolic resins with epoxies improves the adhesion strength. Resistance to weathering, oil, solvents, moisture and oxidation are also very good for these blends [3]. Usually the phenolics used are the resole type and often the epoxy is a minor component [4]. The phenolic: epoxy ratio is adjusted to be stoichiometrically equivalent in order to give a cross-linked material with moderate flexibility and excellent resistance to chemicals, heat and moisture. Phenolic resins with low molecular weights can also act as curing agents for epoxy resins. These resins can react with epoxy resins via the hydroxyl groups of the phenolic resin and the epoxide ring structures [5].

3.1.1 Types of epoxy resin [6]

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

a. Phenoxy resins

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

b. Multifunctional epoxy resins

i. Aromatic glycidyl ether resins

Epoxidized phenol novolac resins (EPN) and cresol novolac resins (ECN) are made by glycidylation of phenol/cresol- formaldehyde condensates (novolacs) obtained from acid catalysed condensation of phenol/cresol and formaldehyde. This gives random ortho and para methylene bridges (Fig.3.2). Epoxidation of novolacs with an excess of epichlorohydrin minimizes the reaction of phenolic hydroxyl groups with glycidylated phenol groups and prevents branching. A wide variety of novolac resins based on a range of phenols including cresols, ethyl phenols, t-butyl phenols, resorcinol, hydroquinone and catechol may be used to prepare epoxy novolac resins. An increase in the molecular weight of the novolac increases the functionality of the resin. EPN resins range from a high viscosity liquid to a solid. The epoxy functionality is between 2.2 and 3.8. ECN resins derived from o-cresol novolacs have even higher functionalities (2.5 to 6).

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

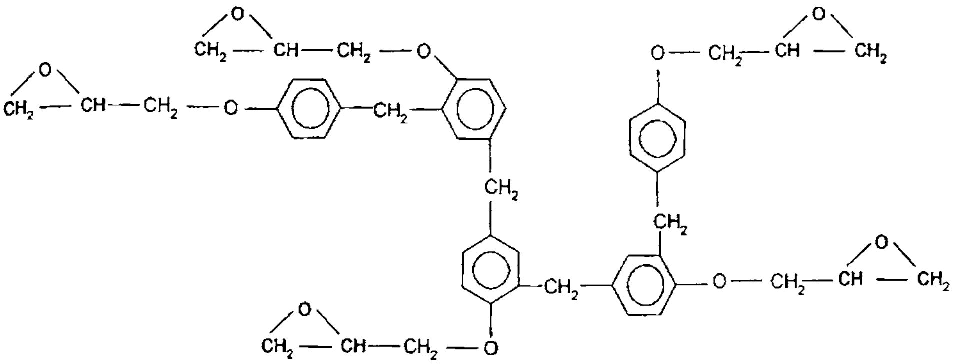

Fig 3.2 Typical structure of EPN

The major applications of epoxy novolac resins have been in heat resistant structural laminates, electrical laminates; chemical resistant filament wound pipes and high temperature adhesives. Epoxy phenol novolacs cured by hyper branched (3-hydroxy phenyl) phosphate exhibit improved thermal properties [7]. EPNs can be modified by different methods of which the one using polysiloxane is found to give a tough resin with enhanced thermal resistance [8].

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

ii. *Aromatic glycidyl amine resins*

Among the multifunctional epoxies with aromatic amine backbone, only a few have gained commercial importance. The triglycidyl derivative of p-amino phenol is formed by glycidilation of p-aminophenol with a large excess of epichlorohydrin under controlled conditions. The resin has low viscosity, 2500-5000 mPa.s at 25^{0}C and weight per epoxy value (wpe) 105-115. The trifunctional resin can be cured at

70^0C and it possesses excellent elevated temperature properties. Tetraglycidyl methylene dianiline (MDA) resins are used as binders in graphite reinforced composites. They have viscosity in the range 5000-25000 mPa.s at 50^0C and wpe values in the range 117-133. Commercially these are available as Araldite MY 720. Glycidylation of cyanuric acid with epichlorohydrin gives triglycidyl isocyanurate marketed as PT 810 (Ciba Geigy). This crystalline compound (wpe 108) acts as a cross-linking agent for carboxylated polyesters. In addition, many glycidyl esters such as diglycidyl ester of hexahydrophthalic acid are also commercially available. They have low viscosities of the order of 500 mPa.s.

c. Non-glycidyl ether epoxides

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

Among acyclic aliphatic resins, three types of resins can be identified; epoxidised diene polymers, epoxidised oils and polyglycol diepoxides. Epoxidation of unsaturated fatty acids and their glycerol esters is effected by peracids. Epoxidised soybean and linseed oils have been available for many years as stabilisers for polyvinyl chloride. Cationic polymerisation of a bio-based epoxy, epoxidised castor oil initiated by N-benzyl pyrazinium and quinoxalinium hexafluroantimonates (BPH and BQH respectively) as catalyst has been reported recently [9].

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

3.1.2 Applications for epoxy adhesives

a. For bonding dissimilar materials

Epoxy adhesives are used in a number of special applications for attaching metals to plastics, generally polyester and phenolic laminates to aluminium or steel. There are a number of aerospace applications in which the epoxy adhesives are employed for bonding dissimilar materials, perhaps typical of which is bonding solar cells in satellites and copper to phenolic in printed circuit boards. In addition to these applications, the epoxy adhesives are used rather widely, but in very small amounts, for mounting gems [10] and for museum restoration work [11].

b. As primers

The epoxy may be used as primers to promote adhesion of a subsequently applied top coating or to provide improved resistance to corrosion. Typical of these applications is the use of an epoxy system over old alkyd paint before application of an alkyd recoat [12]. Such epoxy primers are also used as intercoats to permit the bonding of new concrete to old.

c. As chemically resistant adhesives and sealants

Because of the chemical resistance of the epoxies, they are often used in fairly severe chemical environments. Typical examples of the use of epoxy adhesives in chemical environments are for caulking seams and sealing rivets on chemical storage tanks [13], for bonding paint brush bristles [14], as sealants for pipes handling corrosive fluids- particularly effective with caustics, as shear keys for prestressed concrete bridges [15], and for miscellaneous maintenance and repair applications, such as sealing leaking oil-filled transformers.

d. For bonding plastics

Epoxy resins bond well to thermosetting plastics, except for the silicones, and to most thermoplastic materials except polyolefins, fluorinated compounds, and some plasticized vinyls. Specialized adhesives are used for attaching bondable polytetrafluoroethylene gaskets and for bonding nylon-phenolic ablative coatings to missile nose cones.

e. For bonding glass

Epoxy adhesives provide extremely good bonds to glass, making them particularly suitable for the fabrication of glass laminates. In addition, they are used to bond sheet glass for the construction of stained-glass windows [16].

f. For bonding metal

Epoxy adhesives are employed for a variety of metal bonding applications. They have been used to bond pipe railings to eliminate visible fastening devices and to avoid the high cost of cleanup of welded joints [17]. Epoxy adhesives have proved particularly suitable for the bonding of metallic honeycomb structures. Epoxy bonded aircraft honeycomb parts are used in doors, fuselage side panels, elevators, rudders, trim tabs, trailing edges, wing tips, rotor blades, and in wings themselves [18].

3.2 EXPERIMENTAL

3.2.1 Materials

The novolac epoxy resin (EPN 1138) having epoxy functionality 3.6 and epoxy value 5.4eq/kg (wpe = 178) was obtained from Hindustan Ciba Geigy, Mumbai, India. Epichlorohydrin (LR., M.W- 92.53, 98% assay BP- 114-118^{0}C) was supplied by Research Lab, Mumbai, India. Benzene (M.W- 78, 98%assay), triphenyl phosphine(MP=78-82^{0}C, M.W- 262.3, 98%assay) and caustic soda (M.W- 40, 97.5% assay) were obtained from E. Merck India, Mumbai. P-tertiary butyl phenolic resin (grade DAP 1001) was supplied by Dujodwala Chemicals, Mumbai. The epoxy resin used was a hot set epoxy.

3.2.2 Preparation of epoxidized phenolic novolac (EPN)

1 mole of the novolac resin was dissolved in 6 moles of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 4 hours while 1 mole of sodium hydroxide in the form of 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. Novolac resins prepared by reacting phenol and formaldehyde in varying molar ratios such as 1:0.7, 1.08 and 1:0.9 were subjected to epoxidation by the above procedure to form EPNs of different compositions. These epoxy novolacs were designated as EPN-A, EPN-B and EPN-C respectively. The wpe values of the various epoxy novolacs were determined [Section 3.2.4]. The epoxide functionality in the resin was confirmed by FTIR spectroscopy.

3.2.3 Spectroscopic analysis

The FTIR and ^{1}HNMR analysis of the EPN prepared were done as mentioned in Section 2.3.1.e.

3.2.4 Epoxide equivalent (Weight per epoxide)

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

A common method of analysis of epoxide content of liquid resins involves the opening of the epoxy ring by hydrogen halides (hydrohalogenation) [19]. 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.

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

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

3.2.5 Preparation of PCF resin

PCF resin was synthesized by reacting phenol and cardanol with formaldehyde at 90-95°C for about one hour. Two different phenolic resins with varying phenol / cardanol ratio (wt%), viz. 60 / 40 (PCF-I) and 80 / 20 (PCF-II), were synthesized. The resins were prepared with a stoichiometric ratio of 1:1.7 between total phenols and formaldehyde in an alkaline medium. The resole type resin obtained was neutralized and dried. In the adhesive formulation, part of the PCF resin was replaced by the epoxidized resins.

3.2.6 Surface preparation

Aluminium strips of size 100x 25 mm were machined from 0.8 mm thick sheets to serve as metal substrates for peel studies on metal-to-metal bonds. Strips of 100x25x1.8mm were used for testing shear strength. Mechanical cleaning (surface roughening) was done with a No. 100 emery paper. Solvent degreasing with trichloroethylene followed mechanical cleaning.

The mixing and homogenization of SBR and other compounding ingredients for the substrates were done on a laboratory size (15x 30cm) two-roll mill as per ASTM D3186 prior to compression moulding in a hydraulic press. The compound was moulded into 150mm x 150mm x 2mm sheets employing a pressure of 200kg/cm^2 and a temperature 150^{0}C. The time of cure was in accordance with the results of cure studies initially done on a Rubber Process Analyser (RPA 2000, supplied by Alpha Technologies, USA). The moulding was cut into strips of 100mm x 25mm x 2 mm size to serve as substrates. Surface roughening of rubber substrates was done with a No. 100 emery paper.

3.2.7 Adhesive preparation

a. Metal to metal bonding

Neoprene rubber for the adhesive formulation was masticated on a two roll mill along with other ingredients and dissolved in toluene so as to get a 15wt% solution. The formulations are given in Table 3.1. From the previous study [Section 2.3.2.f] it was found that the optimum resin concentration for Al - Al bonding was 80phr. Keeping the total resin content at 80phr, a part of the phenolic resin (PCF or PTBP) was progressively replaced with EPN. The resulting adhesive solution was applied on each substrate on an area of 25 x 25 mm so as to get an approximate coating thickness of 0.1mm. Different phenolic / EPN ratios, viz. 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 were employed. PCF-I resin was employed for peel tests and PCF-II, for shear tests. This is in accordance with findings of an earlier study [Section 2.3.2.f] where 60/40(PCF-I) and 80/20(PCF-II) resins were compared for peel and shear performance.

The adhesive formulations studied had the following designation.

Case A- Neoprene-phenolic-EPN adhesive where the phenolic resin is a copolymer of cardanol, phenol and formaldehyde. Depending on the percentage of cardanol in the phenol/cardanol (P/C) mixture, there are two cases namely PCF-I and PCF-II.

PCF-I refers to a P/C ratio of 60/40 by wt

PCF-II refers to a P/C ratio of 80/20 by wt

Case B- An adhesive formulation consisting of neoprene, EPN and p-tertiary butyl phenol formaldehyde (PTBP) resin.

On applying the adhesive, the substrates were kept aside to aid the evaporation of solvent. They were subsequently bonded together and the adhesive cured for 30 minutes at 150°C and a pressure of 12.5kg/cm^2.

Table 3.1 Adhesive formulation

Ingredients	Al-to-Al bonding (Formulation-1)	SBR-to-SBR bonding (Formulation-2)
Neoprene AD	90	90
Neoprene W	10	10
Silica	4phr*	-
Acetylene black	-	6phr
Sulfur	1phr	0.5phr
Zinc phosphate	1.5phr	-
Silane	2phr	-
Triphenyl phosphine	1% of resin	1% of resin
Case A) Phenolic resin/EPN	100/0 - 0/100phr	100/0 - 50/50phr
Case B) PTBP resin/EPN	100/0 - 0/100phr	100/0 - 50/50phr
Solid content %	15-17	20-22

* phr here refers to parts per hundred rubber by weight.

b. Rubber to rubber bonding

A 20wt% solution of neoprene rubber in toluene along with other ingredients was prepared. The total resin concentration in the adhesive was fixed at 30phr [Section 2.3.2.f]. Various proportions of Case A (PCF-I / EPN) and Case B (PTBP / EPN) were employed. The amount of EPN was varied from 0 to 50 phr in steps of 10. The resulting adhesive solution was applied on each rubber substrate. After drying for about 30minutes the substrates were joined and curing was done at 150°C

3.2.8 Adhesive performance

Peel strength and lap shear strength of rubber to rubber and metal to metal specimens were determined as per ASTM D 903 and ASTM D 1002 respectively.

These tests were performed on a Shimadzu Universal Testing Machine (UTM) (50KN) with a grip separation rate of 50mm/min at 30°C.

3.2.9 Thermal analysis

Thermogravimetric analysis was carried out using TA Instruments Model TQ 50 TGA, at a heating rate of 20°C in nitrogen atmosphere.

3.2.10 Morphological studies

The fracture surface morphology was investigated by environmental scanning electronic microscopy (ESEM, Philips XL30 FEG operated at 1-10 kV).

3.3 RESULTS AND DISCUSSION

3.3.1 Spectroscopic data [20]

The FTIR spectrum of commercial epoxy resin is given in Fig.3.3. The C-H stretching in epoxies is at 2960 -2990 cm^{-1}. Symmetrical stretching or ring breathing frequency is observed at 1245 cm^{-1} and this is characteristic of the epoxy ring. The band at 915 cm^{-1} (asymmetric ring stretching in which C-C stretches during contraction of C-bond), 840 cm^{-1} and 750cm^{-1} are typical of the epoxy group [20].

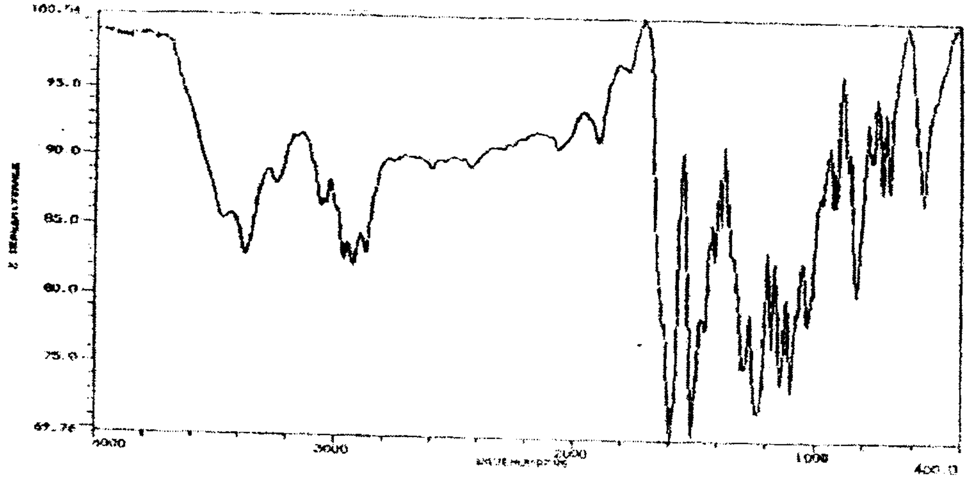

Fig. 3.3 FTIR spectrum of epoxy resin

Fig 3.4 gives the FTIR spectrum of phenolic novolac resin (1:0.8). Characteristic absorptions were found around 3300 cm^{-1}(hydroxyl group, broad band), 3000cm^{-1} (aromatic C-H stretching weak), 1500 cm^{-1} (phenyl ring) and 1475 cm^{-1} (CH_2 bending). The two strong bands around 1220 cm^{-1}and 1101 cm^{-1} are characteristic of C-O stretching in phenol and alcohol groups respectively.

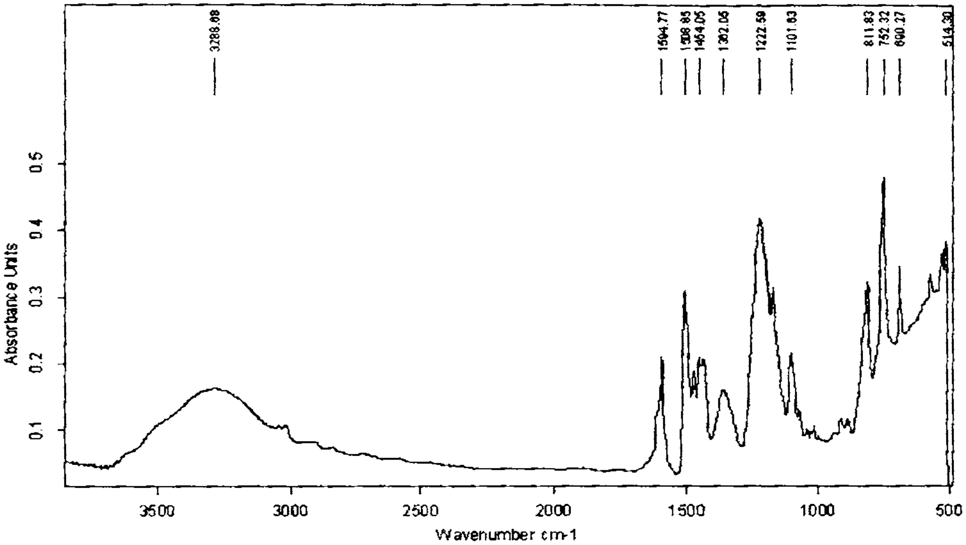

Fig 3.4 FTIR spectrum phenolic novolac resin

The FTIR spectrum of the synthesised epoxidised novolac resin (EPN-B) is given in Figure 3.5. The strong band at 1238 cm^{-1} denotes symmetrical C-O stretching (ring breathing frequency) in epoxides. The C-H stretching in epoxides occurs at 2924.85cm^{-1}. Further, the bands at 910cm^{-1}, 810 cm^{-1} and 753 cm^{-1} are also typical of epoxides. Also the intensity of the broad band at 3288 cm $^{-1}$ in Fig. 3.4 due to phenolic hydroxyl group has decreased considerably in Fig.3.5 indicating the involvement of that group in epoxidation.

The ^{1}HNMR spectrum of EPN-B is given in Fig. 3.6. The δ values are shown in the figure itself.

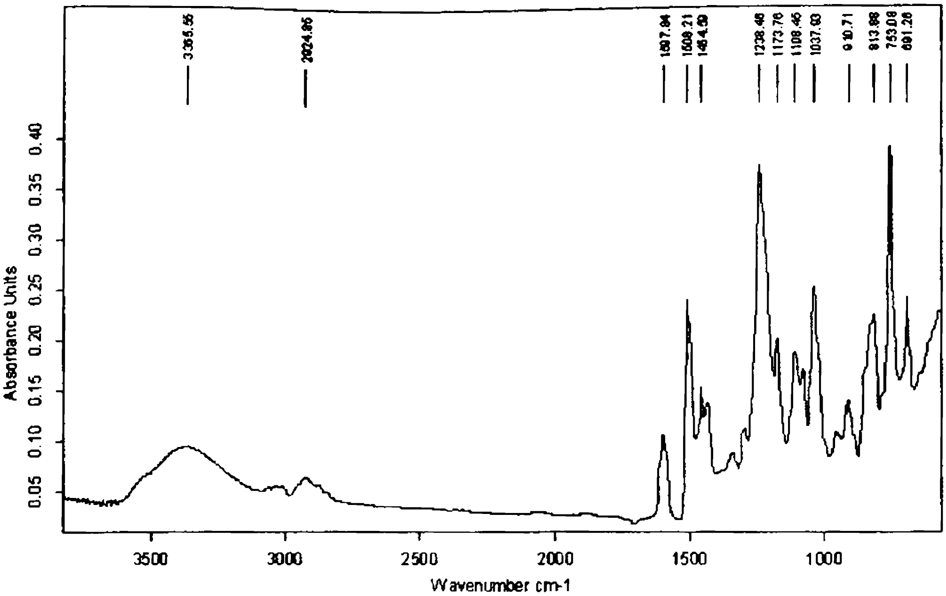

Fig. 3.5 FTIR spectrum of EPN

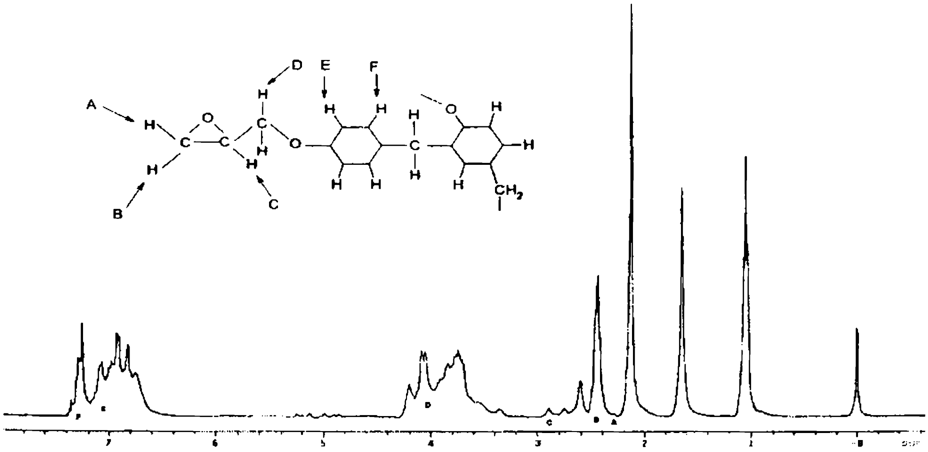

Fig 3.6 ^{1}HNMR spectrum of EPN

3.3.2 Epoxide equivalents

The epoxide equivalents of the epoxy novolac (EPNs) resins prepared from novolacs of different phenol-formaldehyde ratios were determined. The wpe (epoxy equivalents) for EPN-A, EPN-B and EPN-C were found to be 175 (5.714eq/Kg), 169.5 (5.91eq/Kg) and 202 (4.95eq/Kg) respectively. EPN-2 which contains phenol and formaldehyde in the ratio 1:0.8 was found to have greater epoxide content than the other epoxy novolacs.

3.3.3 Shear and peel properties

Fig.3.7 illustrates the change in peel strength with the addition of EPN for Al-Al bonds. The highest peel strength is obtained on addition of 60 parts EPN into the system for both Case A (PCF-I) and Case B. Case A (PCF-I) gives somewhat better values than Case B. The addition of epoxidized resins improves the polarity of the system. EPN molecules are large in size because of their polyphenolic nature. Their presence can also contribute to higher energy absorption and hence better peel properties. A higher degree of crosslinking can also result from the multifunctional nature of EPN. This can lead to improvement in shear strength. But as the amount of EPN goes beyond 60 phr, the system becomes more and more brittle due to excessive crosslinking and the peel strength decreases. The effect of addition of EPN on shear strength of Al-Al bonds is shown in Fig.3.8. In this case, it is found that the addition of about 60phr EPN gives the best performance for the Case A (PCF-II) resin system. But with PTBP resin system (Case B) the addition of about 80phr EPN gives the maximum value. The instantaneous adhesion or tack is generally higher for PCF based resins. This can be the underlying reason for the slightly superior performance of these resins in both shear and peel modes.

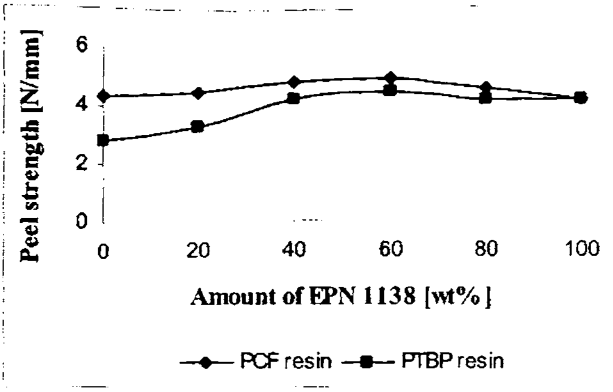

Fig.3.7 Variation of peel strength of Al-Al bonds with EPN

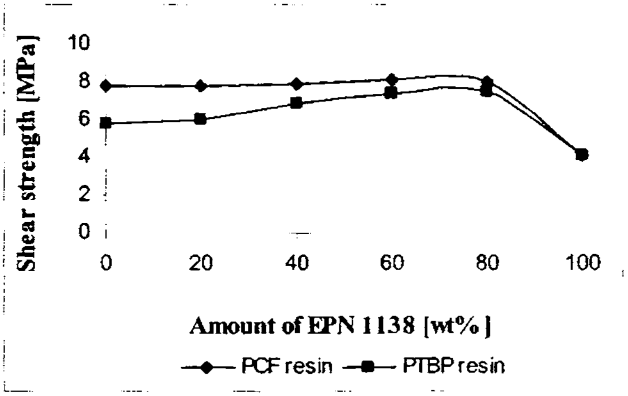

Fig.3.8 Variation of shear strength of Al-Al bonds with EPN

Fig. 3.9 shows the effect of varying EPN content on the peel strength of SBR-SBR substrates. Both Case A and Case B resin systems show the same pattern of behaviour. The highest peel strength is observed for formulations containing a minimum of 30 parts EPN for Case A and 10 parts for Case B though the PTBP resin does not show much sensitivity in the 20-40wt% range. Fig.3.10 shows the effect of incorporation of EPN on the shear strength. In all the cases substrate failure occurred by snapping of the rubber. The highest values are indicated for formulations containing 30 parts EPN. It is generally agreed that cardanol based resin leads to an adhesive film of greater flexibility. Hence better peel properties can be expected in this case especially in the case of rubber-rubber bonding. This is borne out by the performance of both resins indicated in Fig. 3.9.

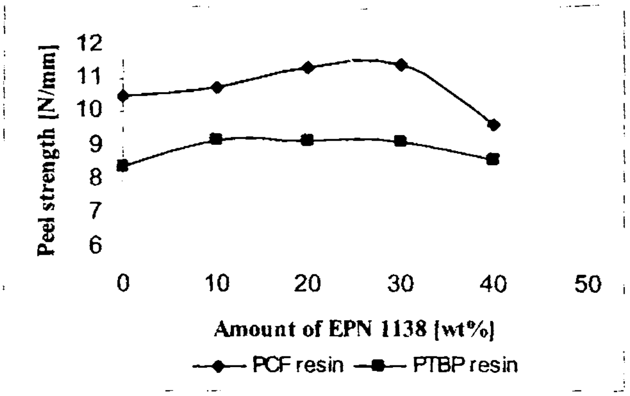

Fig.3.9 Variation of peel strength of SBR-SBR bonds with EPN

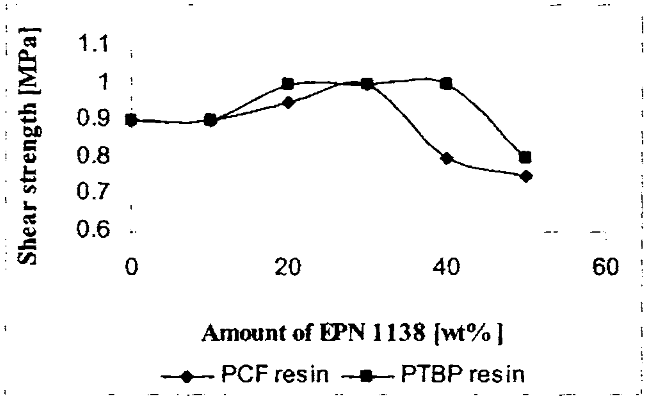

Fig.3.10 Variation of shear strength of SBR-SBR bonds with EPN

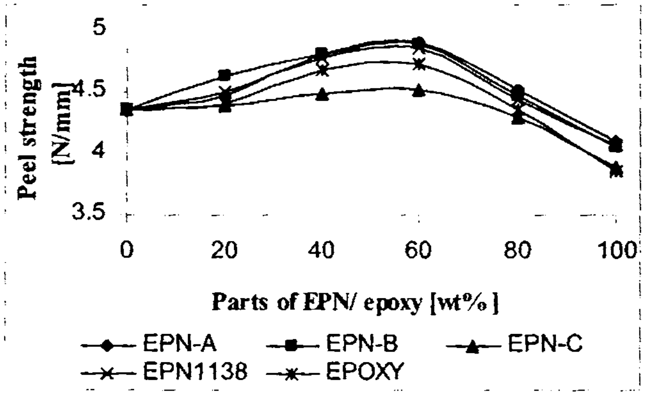

Fig. 3.11 Variation of peel strength of Al-Al bonds with EPN/ Epoxy

Figs 3.11 and 3.12 show the variation of peel strength and shear strength of Al-Al bonds on using EPNs prepared in different stoichiometric ratios. From the Fig.3.11 it can be seen that EPNs A, B, 1138 and Epoxy are showing the same peel behaviour. But EPN C shows slightly lower peel values. In EPN C, the methylol content is high and hence the molecular weight of the resins formed may also be high due to greater crosslinking which leads to lower peel strength. The formulation containing epoxy resin has a higher degree of crosslinking due to the presence of the hardener. This may explain slightly lower peel values especially at higher epoxy contents.

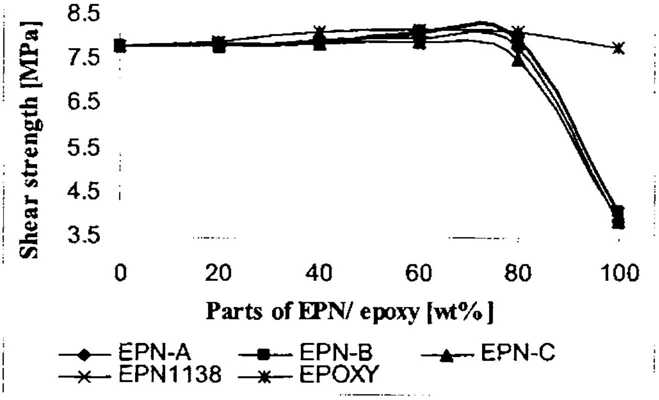

Fig. 3.12 Variation of shear strength of Al-Al bonds with EPN/ Epoxy

Fig.3.12 shows the effect of varying epoxy/ EPN content on shear strength of Al-Al bonds. All the resin systems show similar behaviour upto 80%. At 100% EPN content, the shear values drop drastically. This may be due to the fact that, the EPN does not crosslink to an adequate level. The higher value of epoxy at concentrations greater than 80% are due to the higher degree of crosslinking facilitated by the hardener.

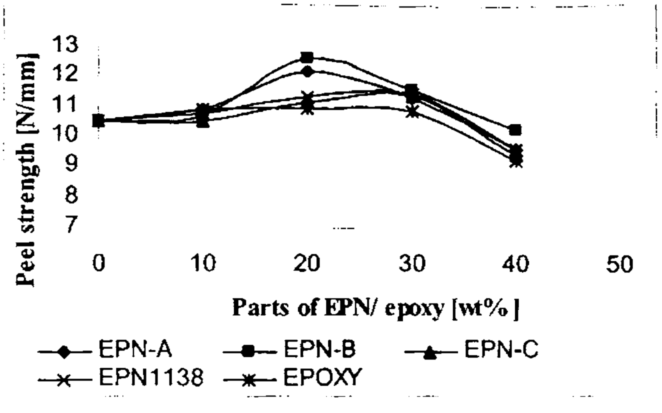

Fig. 3.13 Variation of peel strength of SBR-SBR bonds with EPN/ Epoxy

Referring to Fig. 3.13, EPN-B gives better peel values in the case of SBR-SBR bonding. The excessive crosslinking in epoxy resin may be the reason for the lower peel strength in SBR-SBR bonds. The behaviour in general follows the pattern of peel properties in metal-metal bonding (Fig. 3.11).

3.3.4 Thermal studies

Thermal stability of the novolac, EPN and the adhesive system were studied in nitrogen atmosphere by thermogravimetric analysis. Fig. 3.14 shows the TGA plot of phenolic novolac resin (1:0.8) and EPN B. From the figure it can be seen that the epoxy resins have slightly better thermal stability compared to phenolic novolac resins. The thermogravimetric (TG) as well as the differential thermogravimetric (DTG) plots were obtained for a) unmodified neoprene, b) phenolic resin modified neoprene and c) the optimum EPN- phenolic modified adhesive system for both Cases A and B and for both Formulations 1 and 2 (Figs. 3.15-3.18). The weight loss at around 100°C is due to the loss of water. The next two steps of mass loss in TG trace and the peaks observed in DTG in all the three cases indicate a two-step thermal degradation process. The peak degradation temperature slightly decreases on addition of epoxidized phenolic resin. This may be due to the presence of epoxide group. But the residual weights are almost equal to that of the phenolic resin.

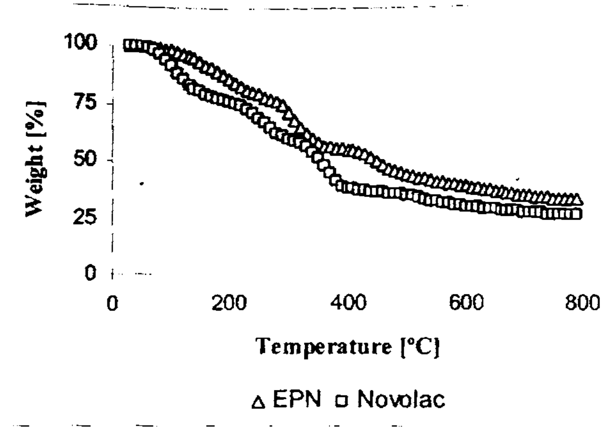

Fig. 3.14 TGA plot of novolac and EPN resins

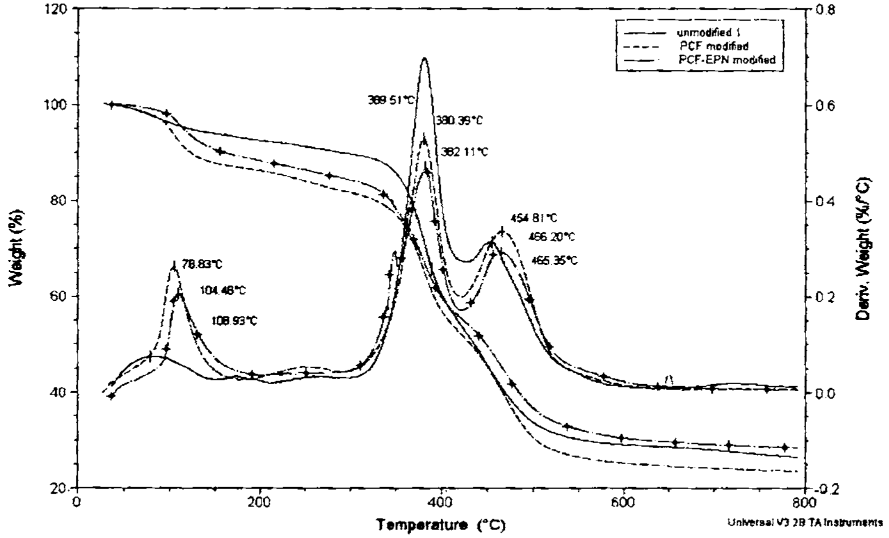

Fig. 3.15 TGA and DTG traces of a) unmodified neoprene (Formulation 1) b) optimum PCF modified and c) optimum PCF-EPN modified adhesive

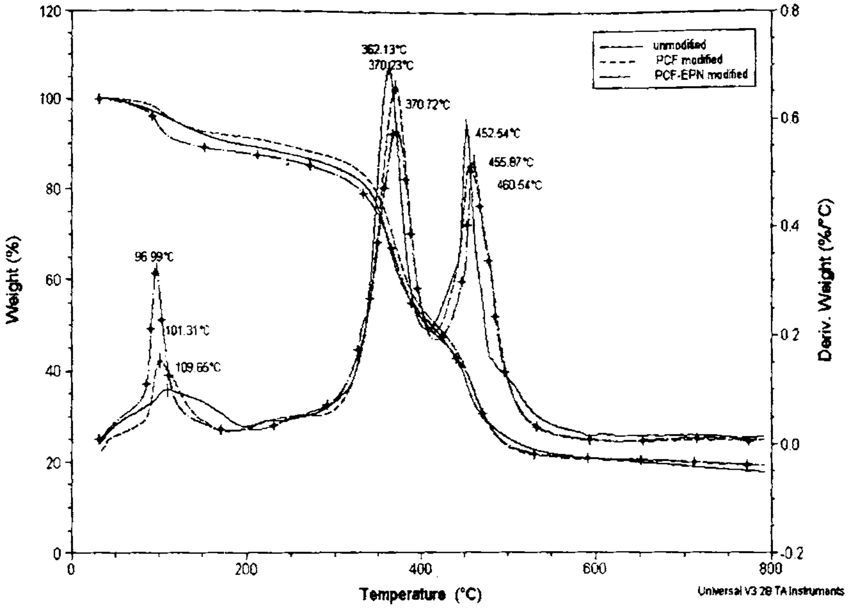

Fig. 3.16 TGA and DTG traces of a) unmodified neoprene (Formulation 2) b) optimum PCF modified and c) optimum PCF-EPN modified adhesive

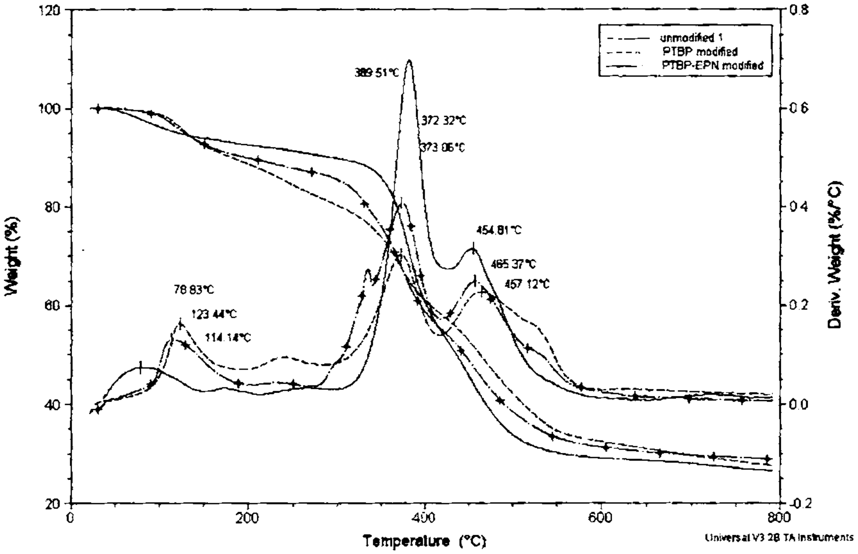

Fig. 3.17 TGA and DTG traces of a) unmodified neoprene (Formulation 1) b) PTBP resin modified neoprene and c) the optimum EPN- PTBP modified adhesive

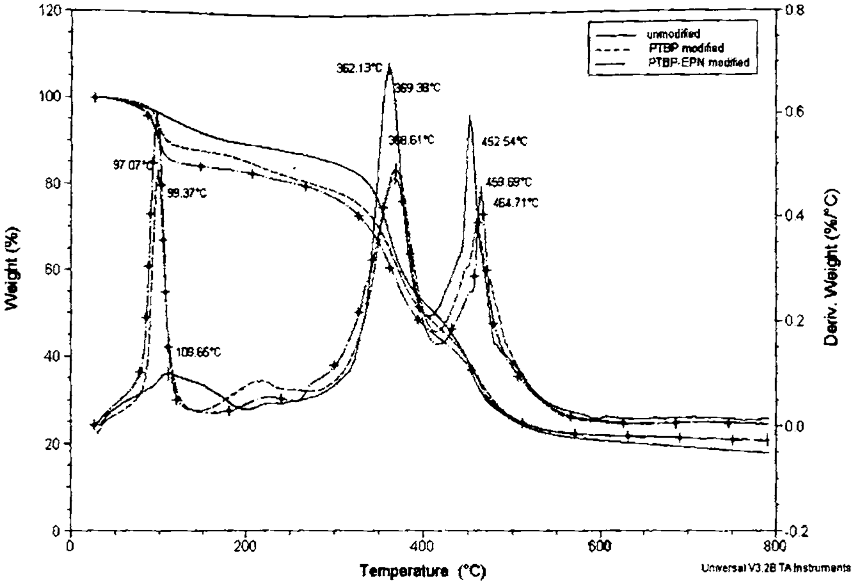

Fig. 3.18 TGA and DTG traces of a) unmodified neoprene (Formulation 2) b) PTBP resin modified neoprene and c) the optimum EPN- PTBP modified adhesive

Table 3.2 Thermal properties of Formulations 1 and 2

Component		**$T_{50\%}$ (^{0}C)**	**Residue wt (%)**
Formulation 1	Unmodified	436	26
	PCF modified	432	24
	PCF-EPN modified	449	29
	PTBP modified	463	28
	PTBP-EPN modified	446	29
Formulation 2	Unmodified	412	18
	PCF modified	418	19
	PCF-EPN modified	407	19
	PTBP modified	399	21
	PTBP-EPN modified	388	21

3.3.5 Morphological studies

Fracture surfaces of the failed adhesive bonds were subjected to scanning electron microscopy (SEM) to observe morphological features. Figs.3.19-26 show fracture surfaces after peel test.

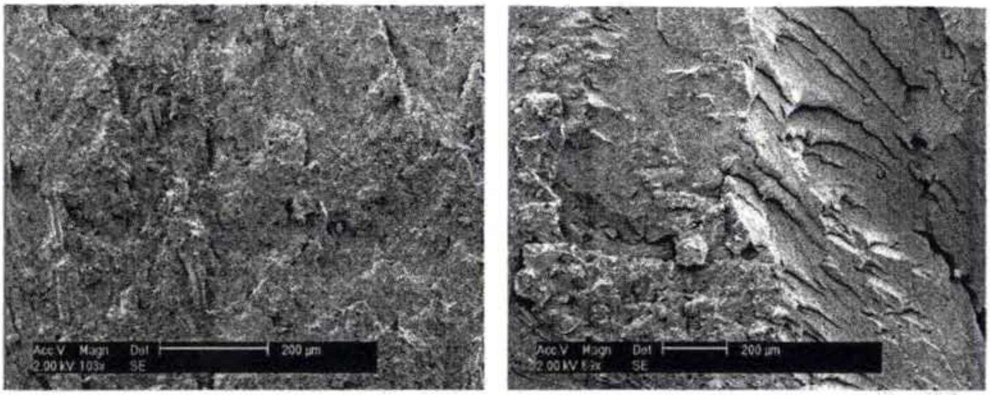

Fig. 3.19 **Fig. 3.20**

SEM of SBR substrate bonded with neoprene - PCF blends (3.19) neoprene - PCF –EPN blends (3.20)

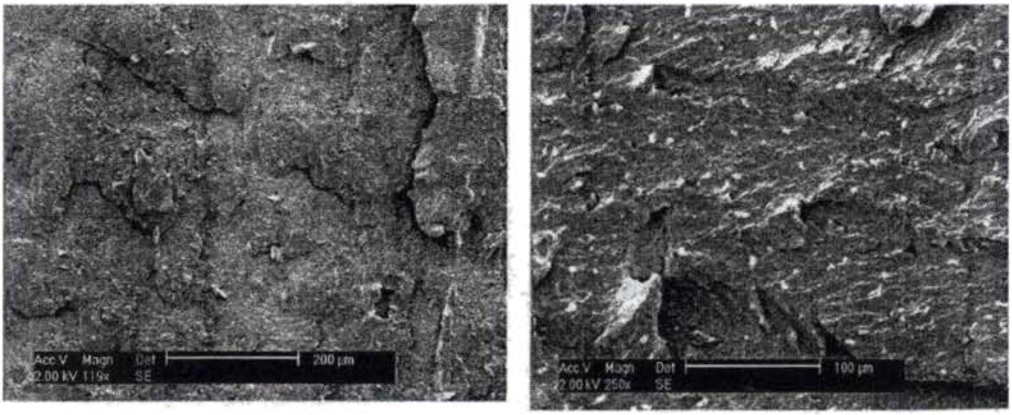

Fig 3.21 **Fig.3.22**

SEM of SBR substrate bonded with neoprene - PTBP blends (3.21) neoprene - PTBP –EPN blends (3.22)

Fig. 3.19 is a view of the fractured surface of a SBR substrate when an adhesive consisting of only neoprene and PCF-I is employed. Fig.3.20 shows the fracture pattern when the formulation contains 30phr EPN. The striations on the surface caused by layer-by-layer failure in Fig.3.19 as well as more prominent valleys and peaks indicate a more emphatic cohesive failure of the substrate. Similarly Figs. 3.21 and 3.22 of the fractured SBR surfaces indicate the effect of addition of EPN to neoprene-PTBP blends. A deepening of the crevices is seen in Fig. 3.22. Here again the positive effect of adding EPN is indicated.

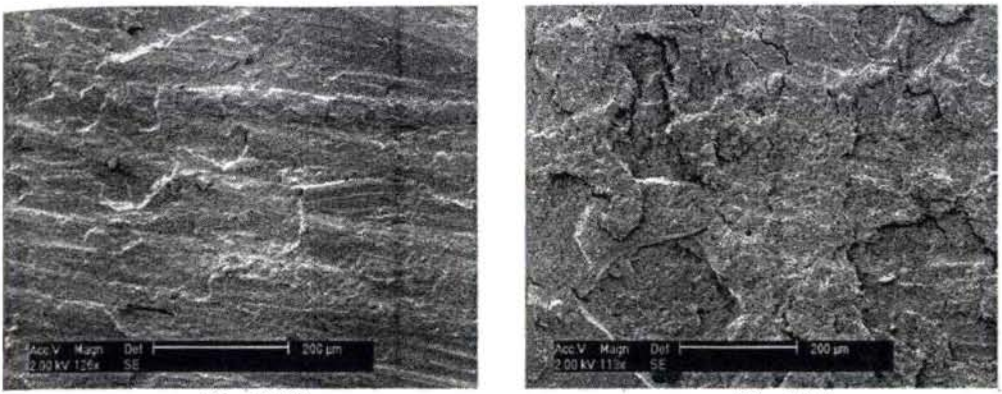

Fig. 3.23 **Fig.3.24**

SEM of Al substrate bonded with neoprene - PCF blends (3.23) neoprene - PCF – EPN blends (3.24)

Figs 3.23 and 3.24 show the effect of addition of EPN to PCF-I / neoprene mixtures used for Al-Al bonding. As Fig.3.24 indicates, the addition of EPN (60phr) alters the fracture pattern. In Fig.3.23 the fracture surface is akin to that of a normal thermoset failure whereas Fig. 3.24 shows higher energy absorption by the creation of deeper cavities and larger fracture areas.

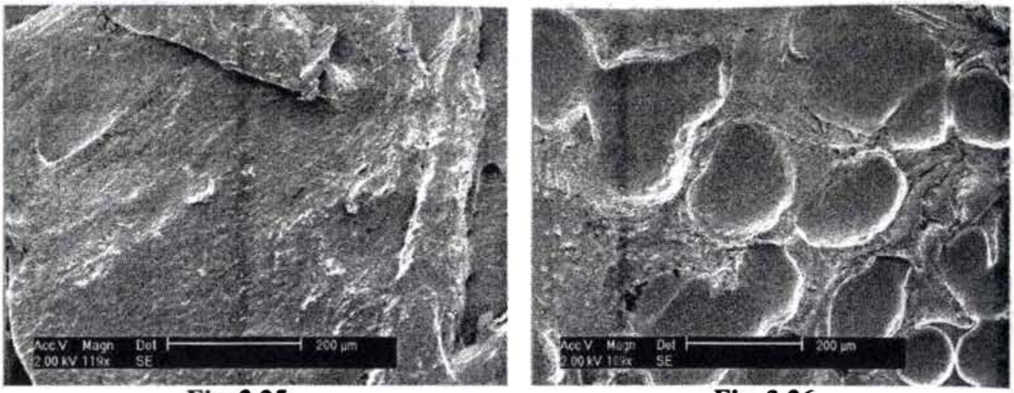

Fig. 3.25 Fig. 3.26

SEM of Al substrate bonded with neoprene - PTBP blends (3.25) neoprene - PTBP –EPN blends (3.26)

Figs 3.25 and 3.26 compare the effect of addition of EPN into PTBP / neoprene mixtures for Al-Al bonding. Fig.3.25 is the case of 60phr EPN. In comparison with Fig.3.26, the fracture surface shows extensive cavitation on addition of EPN.

3.4. CONCLUSION

Cardanol, a renewable substance, in combination with phenol can be an effective starting material for adhesive formulations for Al-Al and SBR-SBR substrates. Cardanol based formulations are superior to t-butyl phenolic resin based formulations for Al-Al bonding. In both these cases, replacement of 30phr of phenolic resin with EPN gives the best peel and shear strength values for SBR-SBR bonds. For Al-Al bonding, peel properties are maximum for both cardanol based and p-tertiary butyl based resin formulations when 60phr of the phenolic resin is replaced by EPN. But for shear strength, 80phr of EPN is optimum for the p-tertiary butyl phenol based resin formulation as against 60phr for the cardanol based formulation. The addition of EPN to phenolic / neoprene adhesive formulations has led to some or considerable improvement in peel and shear properties of both Al-Al and SBR-SBR bonds.

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Chapter 4

Evaluation of adhesive performance

PART 1

4.1 ADHESIVE BONDING OF DIFFERENT SUBSTRATES

- 4.1.1 INTRODUCTION
- 4.1.2 EXPERIMENTAL
  - a. Materials
  - b. Preparation of PCF resin
  - c. Metal-metal bonding
  - d. Rubber-rubber bonding
- 4.1.3 RESULTS AND DISCUSSION
- 4.1.4 CONCLUSION

PART 2

4.2 AGEING STUDIES ON ADHESIVE BONDS

- 4.2.1 INTRODUCTION
- 4.2.2 EXPERIMENTAL
  - a. Metal-metal bonding
  - b. Rubber-rubber bonding
  - c. Rubber-metal bonding
  - d. Ageing studies
  - e. Storage life of the adhesive
- 4.2.3 RESULTS AND DISCUSSION
  - a. Ageing under ambient conditions
  - b. Ageing in hot air oven
  - c. Ageing in hot water
  - d. Ageing in salt water

PART 1

4.1 ADHESIVE BONDING OF DIFFERENT SUBSTRATES

4.1.1 INTRODUCTION

Advantages of adhesive bonding include the ability to join dissimilar materials, the ability to join thin sheets efficiently and increase in design flexibility. Of the many adhesive types, structural adhesives are extensively used in the aerospace industry to join metals such as aluminium, titanium and their respective alloys. These adhesives are often based on low molar-mass phenolic or epoxy resins, which polymerise or cure to give highly crosslinked adhesives. Cardanol based resins are desirable starting materials for adhesive formulations due to their renewable nature, high polarity and inherent tackiness.

All metals have a relatively high surface energy and are generally considered easy to bond. A base metal is highly reactive in most cases and forms various oxides, sulphides and hydrates when exposed to the atmosphere. Hence during metal-to-metal bonding, it is important to consider not only the bulk metal but also the ability to bond to its hydrated oxide. In the case of aluminium, the oxide is extremely stable and serves as a protective coating. Aluminium is an ideal substrate for adhesives. It has high energy and is very resistant to most environments [1]. It is also a material with good formability and high strength to weight ratio. Hence, adhesive - bonded aluminium joints are commonly used in the aircraft and automotive industries.

The use of organic structural adhesives for the industrial production of steel joints is first referred to in the paper by Preiswerk and Zeerleder [2]. After the introduction of phenolic resins for adhesive - bonded aluminium joints de Bruyne and others [3, 4] pointed out the usefulness of epoxide resins as structural adhesives for practically all technical materials, including steel. It was further realised that steel joints could also be produced by using adhesives based on phenolic, polyester and acrylic resins. Titanium is widely used in aerospace applications that require high strength-to-weight ratio at elevated temperatures [1]. It also shows good fracture toughness and creep resistance.

In the case of elastomeric substrates two different types of bonding are possible. In one type, already vulcanized elastomers are bonded using adhesives. This is termed as 'post-vulcanized bonding'. In the second type an adhesive bond is created during the vulcanization of the elastomer. This is termed as 'vulcanized bonding'. When bonding to post-vulcanized elastomers, one is working with an elastomeric substrate that is completely cured and formed [1, 5].

In this part of the work, the effectiveness of a blend of neoprene and phenol-cardanol-formaldehyde (PCF) resin adhesive system for bonding the following substrates is investigated. a) Aluminium (Al), stainless steel (SS), titanium (Ti) and galvanized iron (GI) as metal substrates and b) SBR (Styrene butadiene rubber), NR (Natural rubber), NBR (Acrylonitrile butadiene rubber), CR (chloroprene rubber) and EPDM (ethylene propylene diene monomer) as elastomer substrates. The metal substrates selected are three common materials employed for structural applications. The elastomers are five most common rubbers employed in industries. The optimum resin content that gives the maximum bond strength in each case is also identified.

4.1.2. EXPERIMENTAL

a. Materials

The chloroprene (neoprene) rubbers AD and W were obtained from DuPont, Akron, Ohio. Styrene butadiene rubber (SBR 1502) was obtained from Japan Synthetic Rubber Co. Ltd., Tokyo. ISNR-5 (Indian Standard Natural Rubber) was supplied by the Rubber Research Institute of India, Kottayam, India. Acrylonitrile butadiene rubber (N 553 with 33% acrylonitrile content) was obtained from Apar Polymers Ltd, Mumbai, India. EPDM was supplied by DuPont, USA. CNSL (Cashew nut shell liquid) was procured from Vijayalakshmi Cashew Exports, Kollam, India. Carbon black (HAF) was obtained from Phillips Carbon Black Ltd., Cochin, India and it had the following specifications- Dibutylphthalate (DBP) adsorption - 102± 5ml/ 100g and iodine number- 82. Precipitated silica used in this study was GSL-150 grade procured from Sameera Chemicals, Kottayam, India. 3-Aminopropyltriethoxysilane was obtained from Sigma Aldrich, Bangalore, India.

The aluminium substrate used in this study was extruded aluminium alloy AA 6060-T6 and had a thickness of 1.6mm. It was supplied by Hindalco Industries Ltd, Mumbai, India. The composition of this alloy by weight is 0.46% Mg, 0.4% Si, 0.18% Fe, 0.021% Mn, 0.002% Cu, 0.015% Zn, 0.01% Ti and rest Al. Stainless steel used was of the type A403 and grade WP304 of thickness 1mm. It has a composition of 0.08% (max) C, 2% Mn, 0.045% (max) P, 0.03% (max) S, 1% Si, 18-20% Cr, 8-11% Ni and rest Fe. It was supplied by Tata Iron and Steel Company Ltd., Jamshedpur, India. Titanium alloy used was T1-6Al-4V of 1mm thickness. Galvanized iron used was of general purpose and had a thickness of 1.8mm.

b. Preparation of copolymer (PCF) resin

PCF resin was synthesized by reacting a mixture of phenol and cardanol with formaldehyde at 90-95°C for about one hour. The resins were prepared with a stoichiometric ratio of 1:1.7 between total phenols and formaldehyde in an alkaline medium. The resole type resin obtained was neutralized using oxalic acid and dried. Two different phenolic resins with varying phenol / cardanol ratio (wt%), viz. 60 / 40 (PCF-I) and 80 / 20 (PCF-II), were synthesized.

c. Metal to metal bonding

i. Substrate preparation

Metal strips of size 100x 25 mm were machined from plain sheets to serve as metal substrates for lap shear strength studies on metal-to-metal bonds. Mechanical cleaning (surface roughening) was done with a No. 100 emery paper. Solvent degreasing with trichloroethylene followed mechanical cleaning.

ii. Adhesive preparation

Neoprene rubber for the adhesive formulation was masticated on a two-roll mill along with other ingredients and was dissolved in toluene so as to obtain a 15 wt%

solution. The PCF resin was dissolved in methyl ethyl ketone separately and subsequently blended with the rubber solution. The formulations are given in Table 4.1.1 For metal-to-metal bonding only PCF-II was used in the adhesive system because earlier studies [Section 2.3.2.f] has proved the effectiveness of this resin for this purpose. The resin (PCF-II) concentration was varied from 40 to 100phr in steps of 20phr. A set of experiments was also carried out using the basic adhesive formulation, i.e. without the resin.

Table 4.1.1 Adhesive formulation

Ingredient	Al-to-Al bonding (Formulation-1)	SBR-to-SBR bonding (Formulation-2)
Neoprene AD	90	90
Neoprene W	10	10
Silica	4phr	-
Acetylene black	-	6phr
Sulphur	1phr	0.5phr
Zinc phosphate	1.5phr	-
Silane	2phr	-
PCF resin	40-100 phr	0-50 phr
Solid content wt%	15-17	20-22

After applying the adhesive, the substrates were kept aside for half an hour to evaporate the solvent. The adhesive was applied to a thickness of 0.1mm. It was applied on both substrates. The substrates were then subsequently bonded together and the adhesive cured for 30 minutes at 150°C by employing a pressure of 12.5 kg/cm^2.

d. Rubber to rubber bonding

i. Substrate preparation

1. SBR substrate

SBR is a copolymer of styrene (i.e. vinyl benzene) and butadiene. It is considered as a general purpose rubber as it can be used for many applications and especially in tyre compounds. With the exception of some grades, the styrene content is 23.5% by wt. Based on the polymerisation reaction temperature it is classified into cold SBR (4°C) or hot SBR (50°C) grades. The 1500 series is a cold polymerised non-pigmented type rubber. The structure of SBR can be represented as

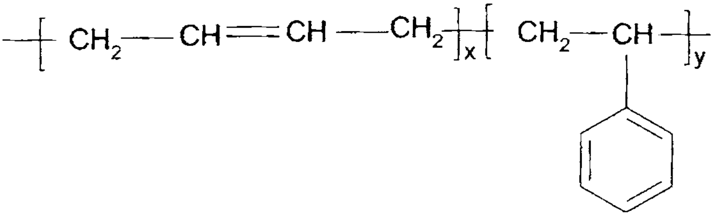


Table 4.1.2 SBR substrate compounding recipe

Ingredient	phr
SBR 1502	100
Zinc Oxide	5
Stearic acid	1
HAF	50
Aromatic oil	10
Vulcanox HS	1
Vulcanox 4020	1
MBTS	0.5
TMTD	0.5
Sulphur	1

The rubber compounding for the preparation of elastomeric substrates was done on a laboratory size (15 x 30 cm) two-roll mill at a friction ratio of 1:1.25 as per ASTM D3186. It was done as mentioned in Section 2.2.1.b. The compounding recipe for SBR substrate is given in Table 4.1.2. Typical cure curve obtained is shown in Fig. 4.1.1. A cure time of 11.9 minutes is obtained. Optimum cure time is the time required for a torque value of $[(T_{max} - T_{min}) \times 0.9 + T_{min}]$, where T_{max} is the maximum torque and T_{min} is the minimum torque.

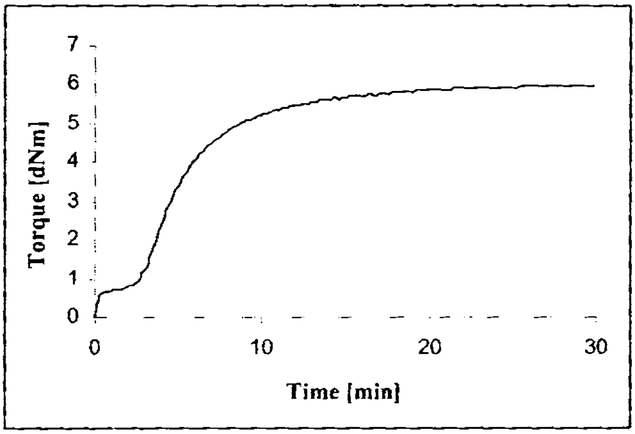
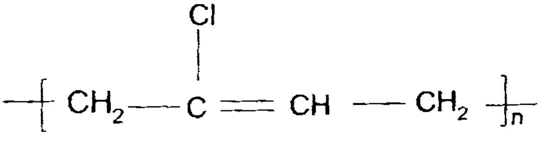


Fig. 4.1.1 Cure graph of SBR substrate

2. *CR substrate*

Chloroprene rubbers are manufactured by polymerising 2-chloro-1,3-butadiene in the presence of catalysts, emulsifying agents, modifiers and protective agents. The polymer chain is built up through addition of monomer units, of which approximately 98% add in the 1,4positions. Pure gum vulcanizates of CR show high levels of tensile strength. They show high resistance to oxidative ageing and flex cracking CR has inherent flame resistance because of the presence of chlorine molecule and products made from it are normally self extinguishing. The structure of CR is represented as



$$-\!\left[CH_2 - \overset{\overset{\displaystyle Cl}{|}}{C} = CH - CH_2 \right]_n\!-$$

Table 4.1.3 CR substrate compounding recipe

Ingredient	phr
CR-W	100
ZnO	4
MgO	5
HAF	40
Aromatic oil	6
NA22	0.5

During compounding, CR is first masticated on a two roll mill. To protect against scorching, MgO is added first followed by HAF and aromatic oil. ZnO and NA 22 are added last. It is then homogenized and sheeted out and kept 22 hours for maturation. After maturation the cure time is determined. The compounding formulation is given in Table 4.1.3. The cure curve is shown in Fig.4.1.2. A typical marching curve is obtained. The cure time is obtained as 20.5 minutes.

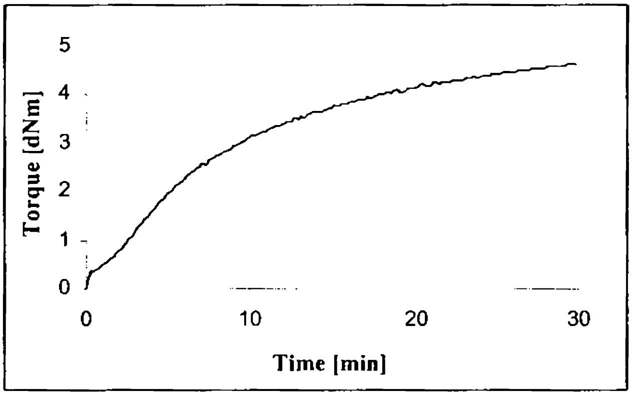
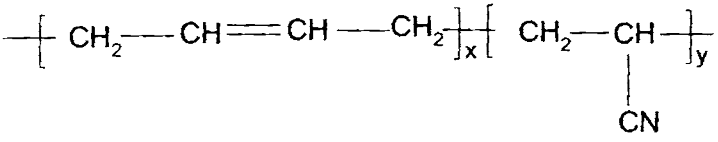


Fig. 4.1.2 Cure graph of CR substrate

3. NBR substrate

Nitrile rubbers are manufactured by emulsion copolymerisation of butadiene rubber with acrylonitrile. It is characterized by excellent oil resistance, solvent resistance and fuel resistance. The physical properties of nitrile rubbers are good when the rubbers are compounded with carbon black. It possesses better heat resistance than CR but prone to ozone cracking. The structure can be represented as



$$\left[CH_2-CH=CH-CH_2 \right]_x \left[CH_2-\underset{\displaystyle CN}{\underset{|}{CH}} \right]_y$$

The compounding of NBR is similar that of SBR. But as sulphur is less soluble in nitrile rubber, it is added first to get a good dispersion. This is followed by the other ingredients in the following order- ZnO, stearic acid, HAF, DOP, antioxidants and accelerators. The compounding recipe is given in Table 4.1.4. After homogenization it is sheeted out and matured. Later the cure time is determined. The cure time is 5.1 minutes. The curve graph is given in Fig 4.1.3.

Table 4.1.4 NBR substrate compounding recipe

Ingredient	**phr**
ZnO	5
Stearic acid	2
HAF	45
DOP	10
Vulcanox 4020	1.5
MBTS	1
TMTD	0.5
Sulphur	1.5

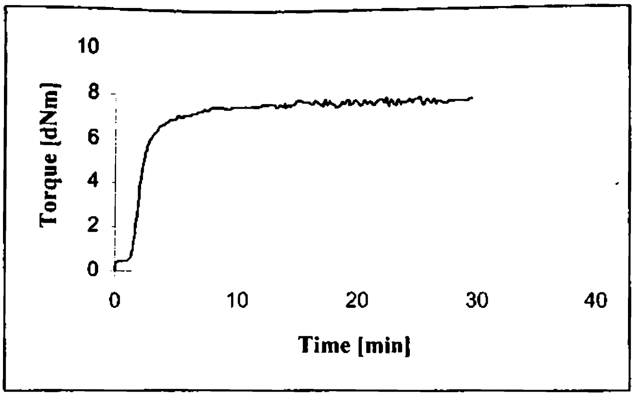
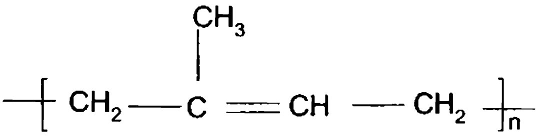


Fig. 4.1.3 Cure graph of NBR substrate

4. NR substrate

NR is the most widely used elastomer. The rubber hydrocarbon component of NR consists of over 99.9% of linear cis-1,4-polyisoprene. The raw NR has good strength and building tack. It also shows excellent extrudability and calenderability. The structure of NR is represented as



$$\left[CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]_n$$

NR was compounded in the same way as SBR. The compounding recipe is given in Table 4.1.5. The cure curve is shown in Fig. 4.1.4. The cure graph shows a reversion after 15 minutes. The cure time obtained is 6.61 minutes.

Table 4.1.5 NR substrate compounding recipe

Ingredient	phr
NR	100
ZnO	5
Stearic acid	2
HAF	40
Aromatic oil	3
Vulcanox HS	1
Vulcanox 4020	0.5
CBS	0.6
TMTD	0.3
Sulphur	2

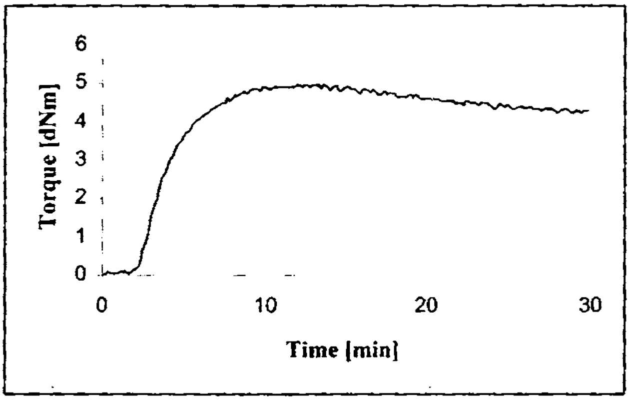


Fig. 4.1.4 Cure graph of NR substrate

5. EPDM substrate

The monomers ethylene and propylene are copolymerised with Zeigler-Natta type catalysts. The properties of the copolymers depend on the relative proportion of the two monomer units in the chain, the average molecular weight, the molecular distribution and the relative content of propylene in the head and tail positions. In addition to these olefins, the EPDM contains a non-conjugated diene as the third monomer. The third monomer in the EPDM used was dicyclopentadiene (DCPD).

The structure can be represented as shown below. EPDM vulcanizates show excellent resistance to oxygen and ozone.

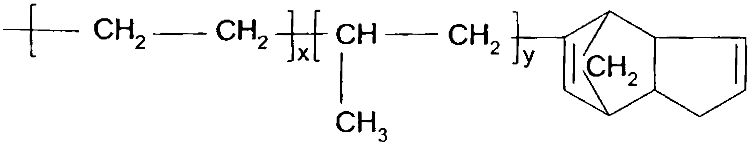


Table 4.1.6 EPDM substrate compounding recipe

Ingredient	phr
EPDM	100
ZnO	4
Stearic acid	1.5
HAF	50
Paraffinic oil	10
Vulcanox 4020	1
MBTS	1
TMTD	0.5
ZDC	0.5
Sulphur	1

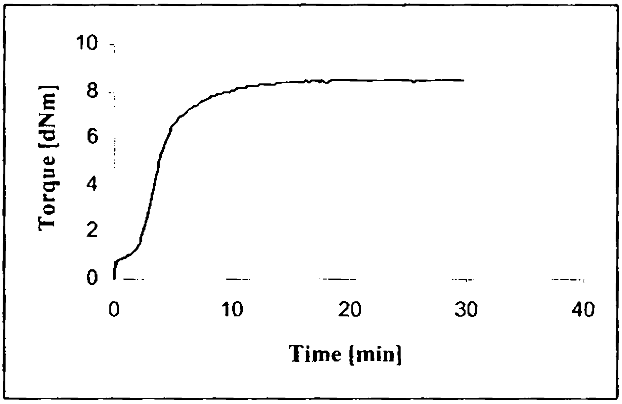


Fig 4.1.5 Cure graph of EPDM substrate

The compounding formulation of EPDM substrates is given Table 4.1.6. The typical cure curve obtained is given in Fig. 4.1.5. The cure time is found to be 10.22 minutes.

ii. Adhesive preparation

A 20wt% solution of neoprene rubber in toluene along with other ingredients – carbon black and sulphur (Table 4.1.1) was prepared. Only PCF-I was used in the blend in view of earlier observations [Section2.3.2.f] regarding the suitability of this resin for rubber-to-rubber bonding. The total resin (PCF-I) concentration in the adhesive was varied from 0 to 50phr in steps of 10phr.

The adhesive solution was applied to an approximate thickness of 0.1mm on both rubber substrates. After drying for about 30minutes the substrates were joined and curing was done at 150°C for 30 minutes applying a pressure of 12.5kg/cm^2.

4.1.3 RESULTS AND DISCUSSION

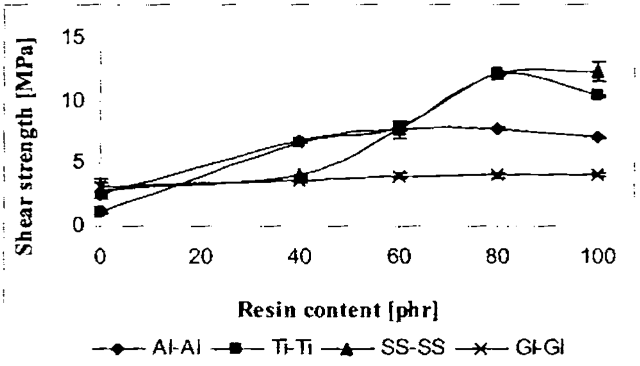


Figure 4.1.6 Effect of varying resin content on shear strength in metal-metal bonding

Fig. 4.1.6 shows the effect of varying the resin content on metal-to-metal shear strength. In most cases the shear strength value increases with resin content. As the resin content increases, the modulus of the adhesive increases. Furthermore, phenolic resin molecules have many OH groups and hence show good affinity towards metal surfaces [6], and this results in strong metal-metal bonds. The effect of resin addition is not very noticeable in the case of GI-GI. In the case of GI, the outermost film of zinc or its oxide may be involved in chemical interaction with the neoprene rubber in the adhesive. Zinc oxide is the crosslinking agent for neoprene rubber (Table 4.1.3). This may explain the lack of improvement in lap shear strength on addition of resin in this case. In the case of aluminium and titanium the maximum shear strength is observed on addition of 80phr resin. In the case of SS-SS bonding, the shear strength increases with resin content and reaches a maximum at 100phr resin. This can be attributed to the higher modulus of steel. It is reported that chromium based adhesion promoters are used as primers to increase the strength and durability of adhesive joints [7]. Hence the presence of chromium in stainless steel might have contributed to the higher bond strength of SS-SS joints.

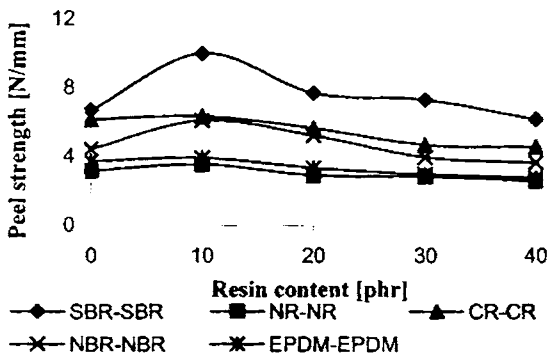


Figure 4.1.7 Effect of varying resin content on peel strength in rubber-rubber bonding

Fig 4.1.7 shows the variation of peel strength with resin content in rubber-to-rubber bonding. In this case also the peel strength increases with resin content initially, reaches a maximum and then decreases. The maximum peel strength was obtained at 10phr resin. As the resin content increases the flexibility of the adhesive film decreases, which leads to inferior peel strength values. It was also found that SBR-SBR bonds gave the highest peel strength. SBR has a lower Young's modulus compared to other rubbers. It is possible that the mismatch of moduli is the least in the case of SBR and the adhesive.

Fig 4.1.8 shows the effect of resin content on shear strength of rubber-to-rubber bonds. Though the highest shear strength was obtained with SBR-SBR specimens, bond failure with fracture of the substrates occurred in all the cases. It was found that in the case of SBR and NBR the shear strength value increases with resin content up to 30phr and then decreases. This may be due to their similarity in reactivity and unsaturation arising from the diene structure. CR has a high level of crystallinity and NR shows stress-induced crystallization. Addition of resin beyond a certain level may hinder the tendency to crystallization and hence the incorporation of more resin leads a detrimental effect on shear strength.

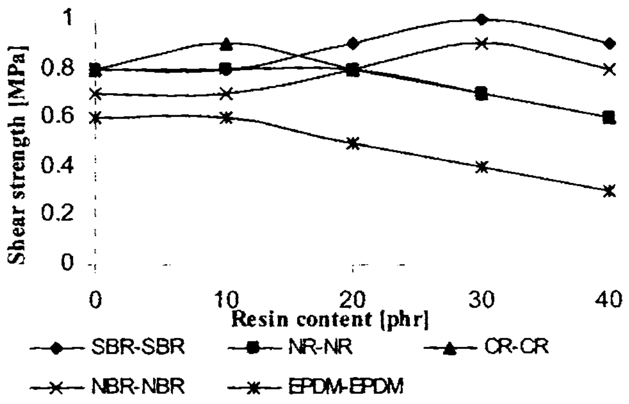


Figure 4.1.8 Effect of varying resin content on shear strength in rubber-rubber bonding

Though theoretically possible, EPDM rubbers cannot be cured by resin in practical use [8]. Hence the addition of higher amount of resin for bonding EPDM substrates will not have a positive effect in the absence of a chemical interaction. Among the different elastomers, SBR shows the highest bondability and EPDM the lowest. This can be attributed to the highest and lowest bondability index values of SBR and EPDM, respectively [1]. The polar-nonpolar incompatibility may also lead to the inferior bond strengths in the case of EPDM and NR. Table 4.1.7 shows some mechanical properties of the rubber substrates used for bonding.

Table 4.1.7 Mechanical properties of rubber vulcanizates

Elastomer →	SBR	CR	NBR	NR	EPDM
Tensile strength (MPa)	15	15.2	18.6	20.6	23.3
Modulus (MPa)	4.01	4.01	5.97	7.55	5.47
Elongation (%)	793	793	735	633	895
Hardness (Shore A)	60	60	65	62	68

4.1.4 CONCLUSION

A copolymer of phenol-cardanol-formaldehyde along with neoprene rubber constitutes an effective adhesive system for bonding different rubber-to-rubber, metal-to-metal and rubber-to-metal combinations. In the case of metal-to-metal bonding, SS-SS shows the highest shear strength values of the order of 12MPa. For rubber–to-rubber bonding, SBR-SBR bonds yield the best peel and shear strength values.

PART 2

4.2 AGEING STUDIES ON ADHESIVE BONDS

4.2.1 INTRODUCTION

For an adhesive to be useful, it should not only withstand the mechanical forces that are acting on it, but must also resist the elements to which it is exposed during service. Thus, one of the most important characteristics of an adhesive joint is its endurance to the operating environment. This endurance is also known as joint permanence or durability. The permanence of the adhesive joints depends on environmental elements like high and low temperatures, moisture or relative humidity, chemical fluids and outdoor weathering.

All polymeric materials are degraded to some extent by exposure to elevated temperatures. To withstand elevated temperature exposure, an adhesive must have high melting or softening point and resistance to oxidation. Exposure to high temperatures results in chain scission leading to decreased molecular weight of the bulk polymer. This results in both reduced cohesive strength and brittleness. Many of the base resins used in high temperature adhesive formulations are rigidly crosslinked or are made –up of a molecular backbone referred to as a 'ladder structure'. The ladder structure provides high bond dissociation energy and acts as an energy sink to its environment [1]. The rigidity of the molecular chain decreases the possibility of chain scission by preventing thermally agitated vibration of the chemical bonds.

Water is the substance that causes the greatest problems to the environmental stability of adhesive joints. Water may enter and alter a joint by one or a combination of the following processes [9]. It may enter the joint by diffusion through the adhesive, by transport along the interface, by capillary action through cracks and crazes in the adhesive or by diffusion through the adherend if it is permeable. The water admittes can alter the properties of the adhesive in a reversible (plasticization of the adhesive) or in an irreversible (causing hydrolysis, cracking or crazing) manner. It can also attack the adhesive/adherend interface either by displacing the adhesive or by hydrating the metal or metal oxide surface of the adherend.

For most bonded metal joints, corrosive environments are a more serious problem than the influence of moisture. Of the different corrosive environments, salt can have a severe effect on joint strength durability. It was found that exposure to a 5% salt spray for three months had a more severe effect on aluminium joints than exposure to a semi-tropical environment for three years [10]. On exposure to sea water, corrosion of the metal interface occurs resulting in a weak boundary layer.

In this section, the results of ageing studies conducted on Al-Al, Al-SBR and SBR- SBR bonds are presented. The adhesive employed was an optimal composition developed during studies reported in Chapters 2 & 3. The ageing process was mostly done in a heated air oven at 100°C for 24 hours. In addition, ageing in different environments like hot water and salt water is also investigated.

4.2.2 EXPERIMENTAL

a. Metal to metal bonding

Aluminium substrates for both peel and shear studies were prepared by mechanical cleaning followed by solvent degreasing. The following cases were studied.

i. Neoprene based formulation containing 80phr phenol cardanol formaldehyde (PCF) resin. For peel studies a 60/40 P/C resin and for shear studies a 80/20 P/C resin of 1:1.7 stoichiometric ratio between total phenols and formaldehyde were used.

ii. Neoprene based formulation containing the optimum blend of PCF and EPN resins (40 & 60 parts respectively), keeping the total resin content at 80phr.

iii. Neoprene based formulation containing a commercially available phenolic resin viz. para-tertiary butyl phenolic resin (PTBP).

iv. Neoprene based formulation containing a blend of PTBP and EPN resins (40 & 60 parts respectively) keeping the total resin content at 80phr.

Table 4.2.1 The formulation of adhesive used for Al-Al bonding

Ingredients	**Al-to-Al bonding (Formulation 1)**
Neoprene AD	90
Neoprene W	10
Silica	4phr
Acetylene black	-
Sulphur	1phr
Zinc phosphate	1.5phr
Silane	2phr
i. PCF resin	80phr
ii. PCF/EPN resin	40/60 by wt
iii. PTBP resin	80phr
iv. PTBP/EPN resin	40/60 by wt
Solid content %	15-17

For the next part of the study an adhesive formulation containing Neoprene AD (70parts by wt.) and epoxidized natural rubber (ENR) (30 parts by wt.) along with 80phr PCF / PTBP resin was used. Only peel strength of Al-Al bonds was evaluated under different ageing conditions.

b. Rubber to rubber bonding

SBR substrates of dimension 100 x 25 x 2 mm were prepared to serve as rubber substrates. The following systems were studied:

i. Neoprene based formulation containing 20phr phenol cardanol formaldehyde (PCF) resin. For peel studies and shear studies a 60/40 P/C resin of 1:1.7 stoichiometric ratio between total phenols and formaldehyde was employed.

ii. Neoprene based formulation containing the optimum blend of PCF and EPN resins (70 /30 parts respectively), keeping the total resin content at 20phr.

iii. Neoprene based formulation containing a commercially available phenolic resin viz. para-tertiary butyl phenolic resin (PTBP).

iv. Neoprene based formulation containing a blend of PTBP and EPN resins (70 /30 parts respectively), keeping the total resin content at 20phr.

For the second part of the study, an adhesive formulation containing Neoprene W (80 parts by wt) and ENR (20 parts by wt) along with 20phr PCF/ PTBP resin was used. Only peel strength of SBR-SBR was evaluated under different ageing conditions.

Table 4.2.2 Formulation of adhesive used for SBR-SBR bonding

Ingredients	**SBR-to-SBR bonding (Formulation 2)**
Neoprene AD	90
Neoprene W	10
Silica	-
Acetylene black	6phr
Sulphur	0.5phr
Zinc phosphate	-
Silane	-
i. PCF resin	20phr
ii. PCF/EPN resin	80/20 by wt
iii. PTBP resin	20phr
iv. PTBP/EPN resin	80/20 by wt
Solid content %	20-22

c. Rubber to metal bonding

In rubber to metal bonding, SBR served as the metal substrate and aluminium as the metal substrate. A primer- adhesive combination was used for the bonding. The adhesive formulated earlier for Al –Al bonding served as the primer for SBR-Al bonding and the formulation for SBR-SBR bonding served as the adhesive. Both peel and shear studies were carried out on rubber-metal joints.

d. Ageing studies

The following ageing studies were conducted on the specimens.

i. Ageing under ambient conditions for 3 months. The samples were tested after 3 months exposure to outside atmosphere
ii. Air-oven ageing at 100°C for 24 hours
iii. Hot water ageing by immersing the samples in boiling water for 24 hours

iv. Salt water ageing by immersing the samples in collected sea water for 3 months. The samples were periodically tested.

e. Storage life of the adhesive

The test is based on ASTM D 1337. The adhesives selected for this study were a) the optimum SBR-SBR formulation and b) the primer or the optimised formulation for Al-Al bonding. These consisted of neoprene and PCF blends developed in Chapter 2. Samples were bonded using the same adhesive after passage of definite intervals of time and tested. Peel tests were performed for metal-metal, rubber-rubber and rubber-metal joints. The total period of time covered was 19-20 days.

4.2.3 RESULTS AND DISCUSSION

a. Ageing under ambient conditions

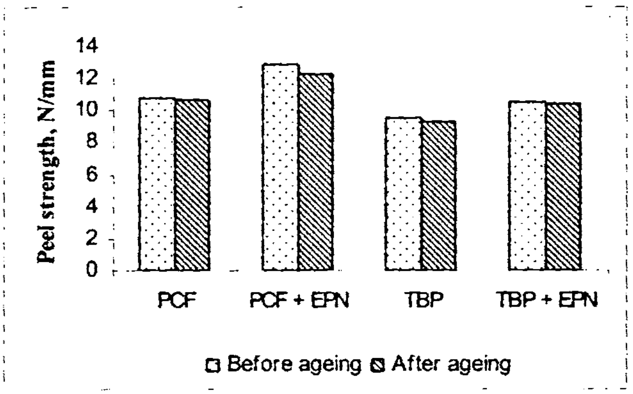


Fig 4.2.1 SBR-SBR peel specimens bonded using different adhesives and aged under ambient conditions

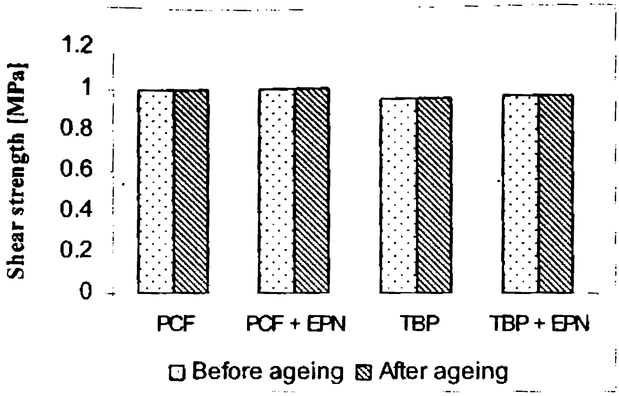


Fig 4.2.2 SBR-SBR shear specimens bonded using different adhesives and aged under ambient conditions

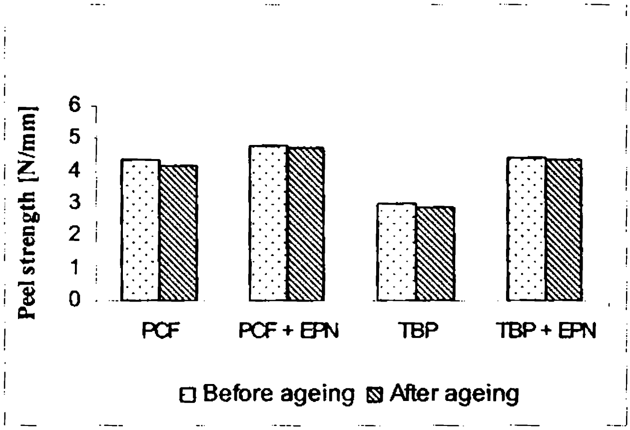


Fig 4.2.3 Al-Al peel specimens bonded using different adhesives and aged under ambient conditions

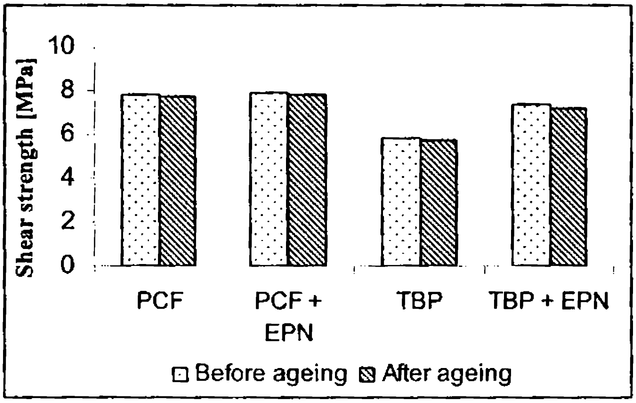


Fig 4.2.4 Al-Al shear specimens bonded using different adhesives and aged under ambient conditions

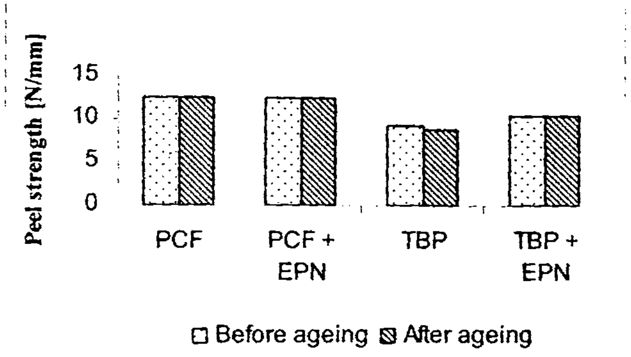


Fig 4.2.5 SBR-Al peel specimens bonded using different adhesives and aged under ambient conditions

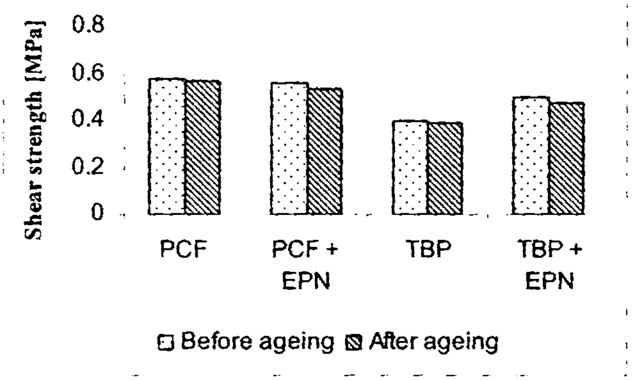


Fig 4.2.6 SBR-Al shear specimens bonded using different adhesives and aged under ambient conditions

Table 4.2.3 Properties after ageing under ambient conditions for 3 months

Ageing condition	Resin system used	SBR- SBR		Al - Al		SBR- Al	
		% fall in peel strength	% fall in shear strength	% fall in peel strength	% fall in shear strength	% fall in peel strength	% fall in shear strength
Ambient conditions-3months	PCF	1.02	Shear strength not affected	3.90	0.77	0.24	1.72
	PCF + EPN	2.2		1.88	0.63	0.16	3.57
	TBP	2.15		5.00	1.54	4.0	2.50
	TBP + EPN	5.38		1.58	1.90	0.76	4.00

Figs 4.2.1- 4.2.6 and Table 4.2.3 show the loss in adhesive property of SBR-SBR, Al-Al and SBR-Al bonds when aged under ambient conditions i.e. at relative humidity of 85% and at room temperature for 3 months. It can be seen that in rubber-rubber bonding, the PCF based system shows the highest strength retention after ageing, though the highest bond strengths are obtained for those systems containing EPNs. From the figures it can be concluded that the bond strength of the adhesive joints does not deteriorate when aged under ambient conditions.

b. Ageing in hot air oven

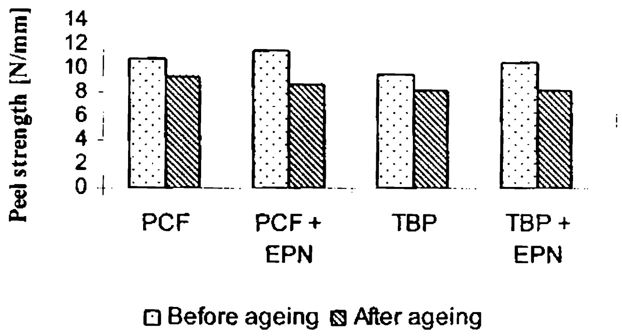


Fig 4.2.7 SBR-SBR peel specimens bonded using different adhesives and oven aged at 100°C

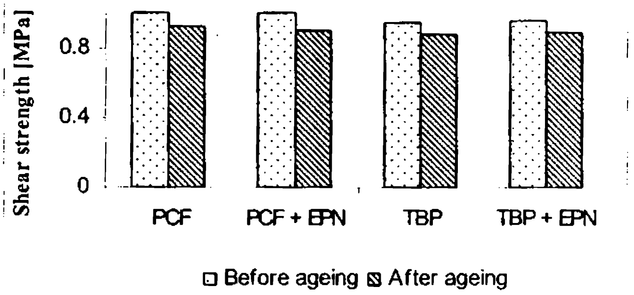


Fig 4.2.8 SBR-SBR shear specimens bonded using different adhesives and oven aged at 100°C

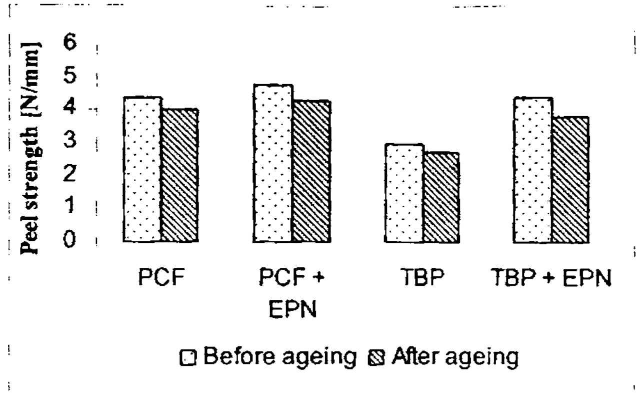


Fig 4.2.9 Al-Al peel specimens bonded using different adhesives and oven aged at 100°C

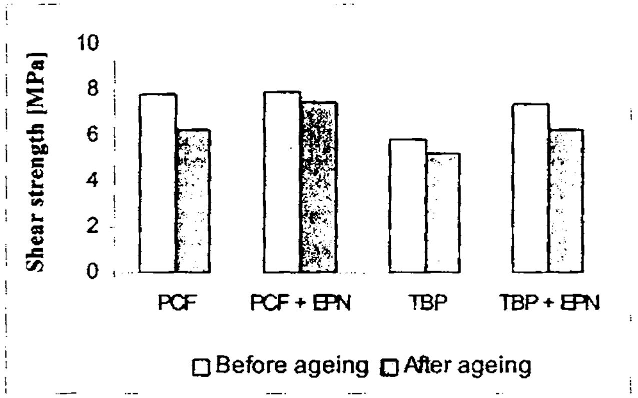


Fig 4.2.10 Al-Al shear specimens bonded using different adhesives and oven aged at 100°C

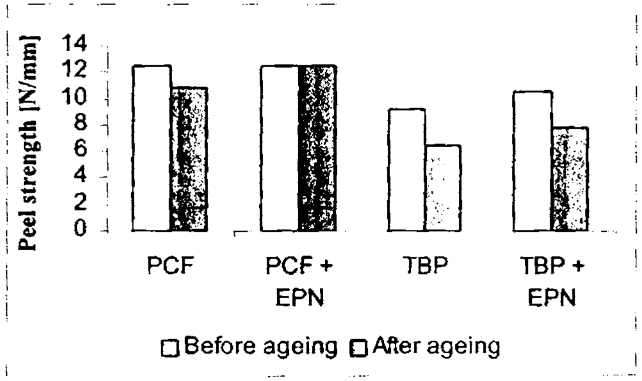


Fig 4.2.11 SBR-Al peel specimens bonded using different adhesives and oven aged at 100°C

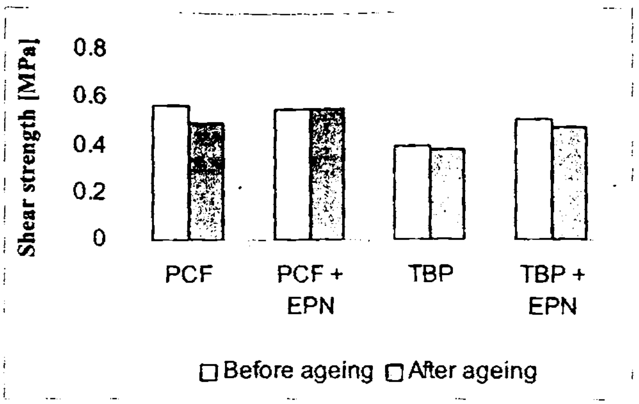


Fig 4.2.12 SBR-Al shear specimens bonded using different adhesives and oven aged at 100°C

Table 4.2.4 Properties after ageing at 100°C for 24 hours

Ageing condition	Resin used	SBR -SBR		Al - Al		SBR - Al	
		% fall in peel strength	% fall in shear strength	% fall in peel strength	% fall in shear strength	% fall in peel strength	% fall in shear strength
Air oven ageing at 100°C for 24 hours	PCF	13.4	Shear strength mostly not affected	8.0	8.1	12.3	13.8
	PCF + EPN	24.8		9.4	5.2	6.4	3.57
	TBP	13.5		8.3	30.8	30.8	5.0
	TBP + EPN	21.4		12.9	25.1	25.1	6.0

Figs.4.2.7 – 4.2.12 and Table 4.2.4 show the behaviour of SBR-SBR, Al-Al and SBR-Al bonds on exposure to hot air at 100°C. In the case of SBR-SBR peel strength, there is a drastic reduction in magnitude for the resin system containing PCF and EPN resins. The presence of higher functionality in EPN resins results in a higher degree of crosslinking. During ageing at elevated temperature, additional crosslinks may occur resulting in a highly crosslinked network. This may also result in modulus mismatch between the adhesive film and the substrate in rubber-rubber bonding leading to adhesive failure at low loads.

c. Ageing in hot water

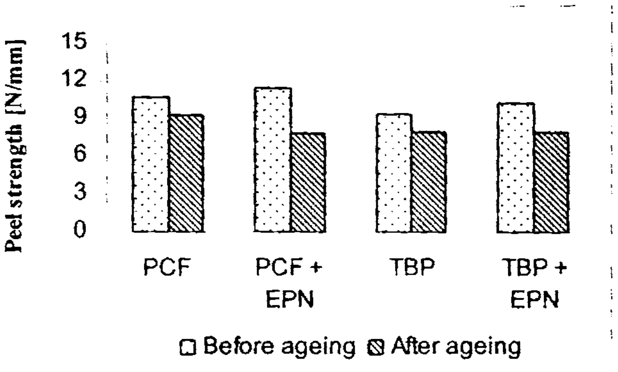


Fig 4.2.13 SBR-SBR peel specimens bonded using different adhesives and aged at 100°C water

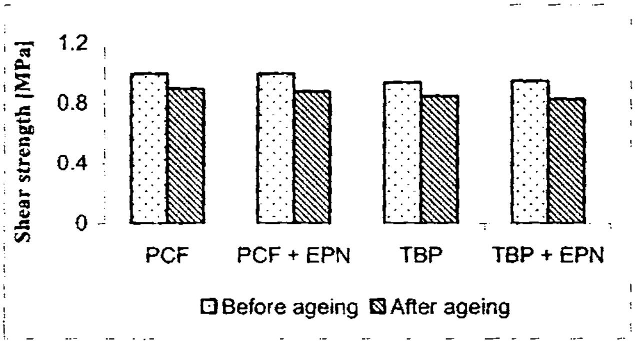


Fig 4.2.14 SBR-SBR shear specimens bonded using different adhesives and aged at 100°C water

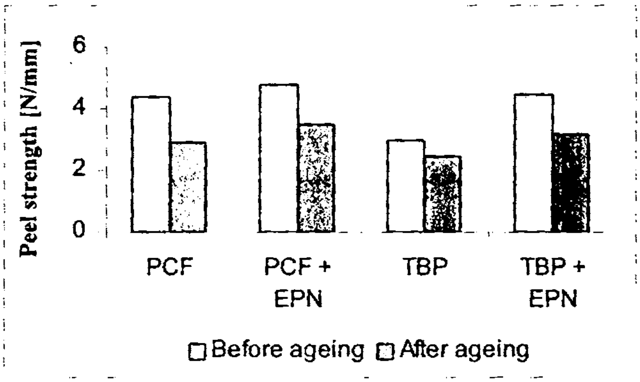


Fig 4.2.15 Al-Al peel specimens bonded using different adhesives and aged at 100°C water

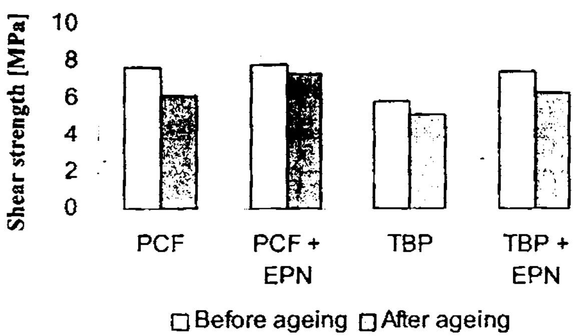


Fig 4.2.16 Al-Al shear specimens bonded using different adhesives and aged at 100°C water

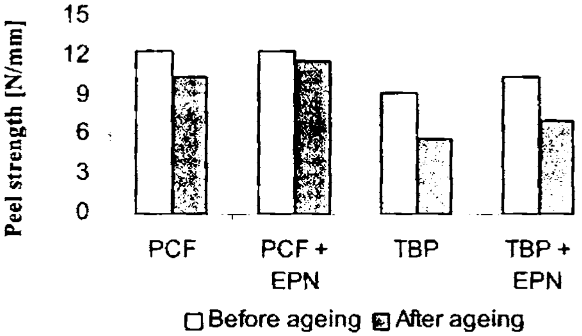


Fig 4.2.17 SBR-Al shear peel specimens bonded using different adhesives and aged at 100°C water

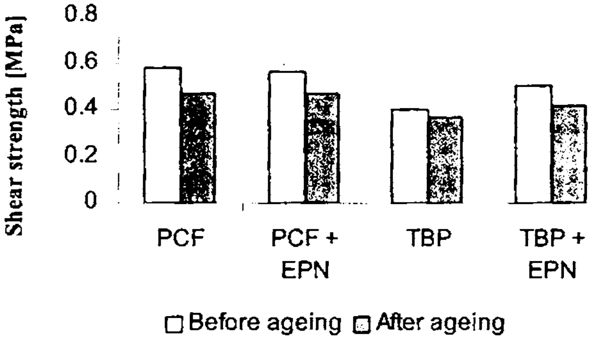


Fig 4.2.18 SBR-Al shear specimens bonded using different adhesives and aged at 100°C water

Table 4.2.3 Properties after ageing in hot water for 24 hours

Ageing condition	Resin used	SBR -SBR		Al - Al		SBR - Al	
		% fall in peel strength	% fall in shear strength	% fall in peel strength	% fall in shear strength	% fall in peel strength	% fall in shear strength
Hot water-100°C for 24hours	PCF	14.4	Shear strength not affected	10.32	20.3	16.2	19.0
	PCF + EPN	31.2		15.6	7.2	6.5	16.1
	TBP	14.9		19.0	16.4	37.1	7.5
	TBP + EPN	22.9		14.2	15.9	32.3	16

Figs.4.2.13 -4.2.18 and Table 4.2.5 show the effect of SBR-SBR, Al-Al and SBR-Al bonds on exposure to hot water at 100°C for 24 hours. It can be seen that fall in adhesive properties is slightly higher on exposure to hot water. Water is the substance that gives the greatest problems in terms of environmental stability for many adhesive joints. Water is a problem because it is very polar and permeates most polymers. Moisture may enter by wicking along the adhesive –adherend interface or by wicking along the interfaces caused by reinforcing fibres and the resin. The presence of moisture can degrade the adhesive properties at the interface. The temperature may also enhance the degradation.

d. Ageing in salt water

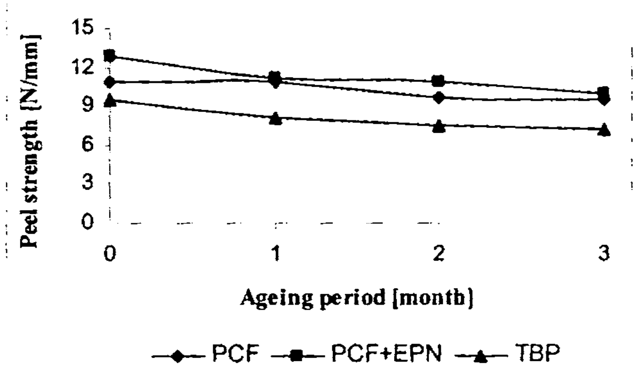


Fig 4.2.19 SBR-SBR peel specimens bonded using different adhesives and aged in salt water

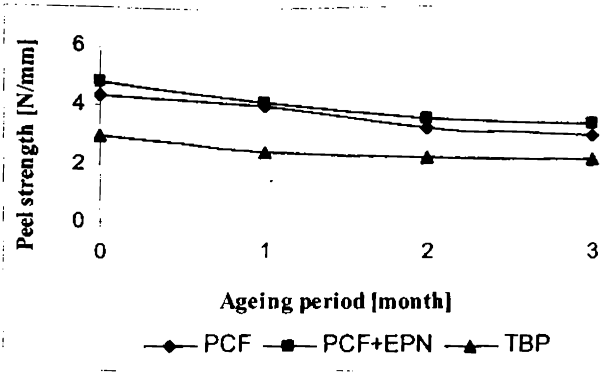


Fig 4.2.20 Al-Al peel specimens bonded using different adhesives and aged in salt water

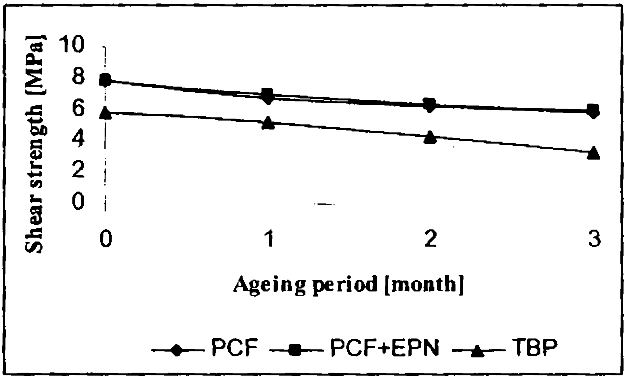


Fig 4.2.21Al-Al shear specimens bonded using different adhesives and aged in salt water

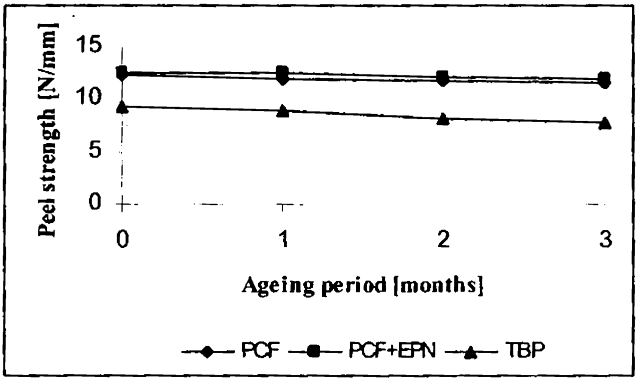


Fig 4.2.22 SBR-Al peel specimens bonded using different adhesives and aged in salt water

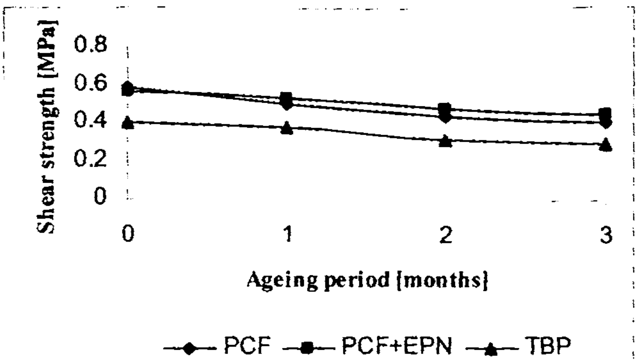


Fig 4.2.23 SBR-Al shear specimens bonded using different adhesives and aged in salt water

Table 4.2.6 Properties after ageing in salt water for 3 months

Ageing condition	**Resin system used**	**SBR-SBR**	**Al-Al**		**SBR - Al**	
		% fall in peel strength	**% fall in peel strength**	**% fall in shear strength**	**% fall in peel strength**	**% fall in shear strength**
Salt water for 3 months	PCF	11.6	34.6	24.8	7.5	29.3
	PCF + EPN	13.9	33.1	24.2	3.6	19.6
	TBP	24.0	31.7	43.5	16.2	25.0

Figs.4.2.19 - 4.2.23 and Table 4.2.6 show the effect of salt water ageing on SBR-SBR, Al-Al and SBR-Al bonds. The presence of salt can have a very severe effect on joint strength durability. Deterioration in joint strength is normally much more rapid with salt solution than with water. This supports the view that corrosive attack along the bondline is involved in the presence of salt whereas attack by water first involves diffusion through the adhesive [11].

e. Ageing of CR/ENR based adhesives

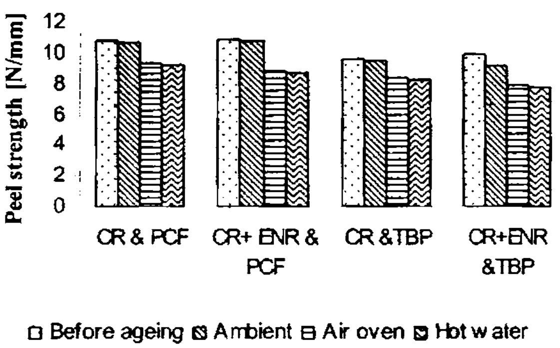


Fig 4.2.24 SBR-SBR peel specimens bonded using CR/ENR based adhesives and aged under ambient condition, hot air and hot water

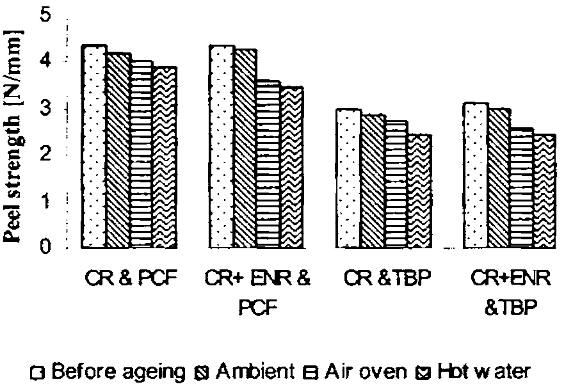


Fig 4.2.25 Al-Al peel specimens bonded using CR/ENR based adhesives and aged under ambient condition, hot air and hot water

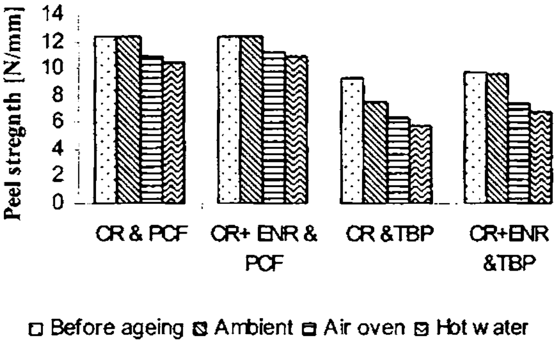


Fig 4.2.26 SBR-Al peel specimens bonded using CR/ENR based adhesives and aged under ambient condition, hot air and hot water

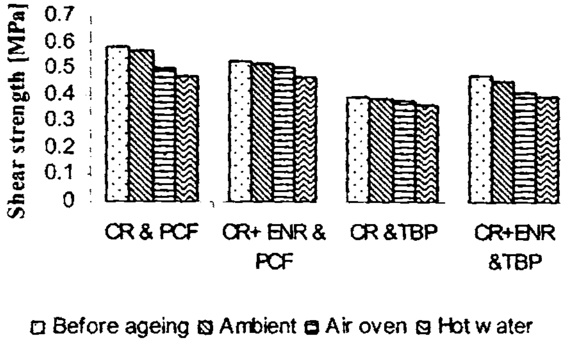


Fig 4.2.27 SBR-SBR shear specimens bonded using CR/ENR based adhesives and aged under ambient conditions, hot air and hot water

Table 4.2.7 Properties after ageing for adhesives with and without ENR

Elastomer and resin used	Ageing details	SBR- SBR	Al- Al	SBR- Al	
		% fall in peel strength	% fall in peel strength	% fall in peel strength	% fall in shear strength
CR & PCF	Ambient – 3 months	1.0	3.9	0.2	1.7
	Hot air 70°C	13.4	8.0	12.3	13.8
	Hot water 70°C	14.4	10.3	16.2	18.9
CR + ENR & PCF	Ambient – 3 months	1.1	2.5	0.3	1.9
	Hot air 70°C	19.6	17.8	9.9	3.8
	Hot water 70°C	21.0	21.0	12.8	11.3
CR & TBP	Ambient – 3 months	2.1	5	4.0	2.5
	Hot air 70°C	13.5	8.3	30.8	5
	Hot water 70°C	14.9	19.0	37.1	7.5
CR + ENR & TBP	Ambient – 3 months	7.2	5.10	2.6	4.2
	Hot air 70°C	20.6	18.5	25.3	14.6
	Hot water 70°C	21.6	22.3	30.5	16.7

Figs.4.2.24- 4.2.27 and Table 4.2.7 show the ageing properties on using CR-AD and ENR as elastomers. From the figures and table it can be seen that drastic reduction in adhesive strength occurs when exposed to hot water at 100°C. The water entering an adhesive joint may alter the properties of the adhesives in a reversible manner: i.e. they may produce plasticization effect on the bonded area. The temperature may enhance the diffusion phenomenon. It is reported that silanes used as adhesion promoters form polysiloxane coatings on the metal surface [12]. Though they may lead to more durable interfaces, they also greatly assist the entry of water into adhesive joints. It is also noted that the addition of ENR improves the ageing properties to a small extent.

f. Storage life of the adhesive

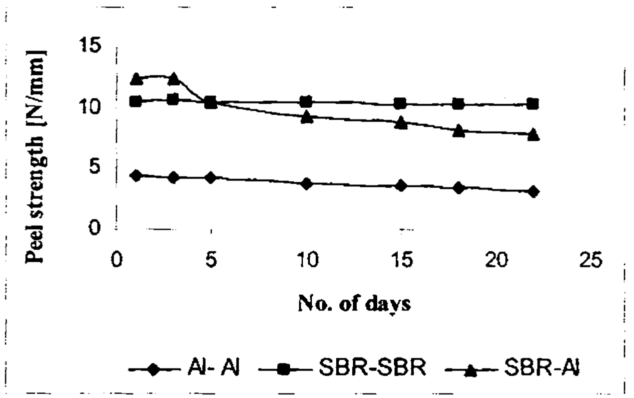


Fig 4.2.28 Variation of peel strength with time

Fig. 4.2.28 shows the dependence of peel strength of the adhesive joints on the storage life of the adhesive. From the graph we can see that the peel strength of SBR-SBR bonds is unaltered with time. This shows that the adhesive used for joining rubber-rubber substrates is stable over a period of time. But in the case of SBR- Al bonds the mode of failure changes from cohesive to a mixed mode and later to adhesive after a week. This may be due to the hydrolysis and polymerization reactions of the silane with the phenolic resins and moisture.

4.2.4 CONCLUSION

From the ageing studies performed, it is found that the bonded specimens do not lose adhesive strength when aged under ambient conditions. But when the specimens are exposed to elevated temperatures they are showing a reduction of adhesive properties. This effect is enhanced when the samples are kept in water at 100°C. The addition of EPN and ENR improves the initial joint strength. Specimens bonded with formulations containing EPN are showing slightly higher resistance when aged in salt water. From the storage life studies it is found that the formulation developed for rubber-rubber bonding is quite stable while the formulation developed for metal-metal bonding is losing adhesive strength with time. From the ageing studies it is amply proved that the cardanol based resins has clear superiority over the commercially available para tertiary butyl phenolic resin.

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Chapter 5

Summary and conclusion

5.1 INTRODUCTION

This chapter gives a glimpse of the summary and conclusions of the work carried out. The study reveals the effectiveness of neoprene phenolic adhesives for bonding different substrates and the role of various ingredients with special reference to polymeric resins. It also investigates the possibility of using cardanol as a starting material for the adhesive formulation.

5.2 SUMMARY

The focus of the study is to develop new adhesive systems based on neoprene and phenolic blends for rubber-rubber, metal-metal and rubber-metal bonding applications. The contents of the various chapters in this thesis are summarized below.

In Chapter 1, adhesive bonding, an overview of different types of adhesives, adhesive application methods, adhesive formulation, theories of adhesion, different surface preparation methods, joint stress and joint geometry are discussed. Renewable resources for adhesives and a discussion of neoprene and phenolic adhesives are also included.

The optimisation of the basic components of the adhesive formulation like fillers, adhesion promoters, curing agents, solvents etc., the synthesis of phenol cardanol formaldehyde (PCF) resins, the optimisation of the ratio between phenol and cardanol on the basis of adhesive performance and the optimisation of the stoichiometric ratio between total phenol and formaldehyde are included in Chapter 2. The adhesive performance is evaluated by conducting peel and lap shear strength tests on metal-metal, rubber-rubber and rubber-metal bonds. The synthesized resins are characterised by spectroscopic methods (FTIR and ^{1}H NMR). The thermal properties are studied using TGA and DSC techniques. The synthesised resins are also subjected to GPC.

A detailed account of the effect of replacing the phenolic resins with epoxy resins is given in Chapter 3. Novolac type phenolic resins are prepared in different stoichiometric ratios and are subsequently epoxidized. These epoxy phenol novolacs (EPN) are used along with PCF resin. Thermal properties are monitored using TGA. The synthesised EPNs are characterized by FTIR and ^{1}HNMR. The adhesive performance is evaluated by estimating peel and shear strengths. The fractured surfaces of adhesive bonded substrates are examined using SEM. A parallel study is also conducted using a blend of commercially available p-tertiary butyl phenolic resin and EPN.

In the first part of Chapter 4, the effectiveness of the adhesive formulations for joining different rubber and metal substrates is discussed. Various rubbers, viz. natural rubber (NR), styrene butadiene rubber (SBR), chloroprene rubber (CR), acrylonitrile butadiene rubber (NBR) and ethylene propylene diene monomer (EPDM) are employed as substrates. The rubbers are compounded and strip specimens are moulded. The metals used in bonding studies are aluminium, stainless steel, titanium and galvanized iron. In the second part of Chapter 4, the effect of ageing on adhesive properties of rubber-rubber, metal-metal and rubber-metal substrates are evaluated. The bonded joints are subjected to ageing under ambient conditions, air oven ageing, hot water ageing and salt water ageing. The storage life of the adhesive is also evaluated.

5.3 CONCLUSIONS

The conclusions from the investigation can be stated as follows.

Neoprene solution and additives

- On the basis of SBR-SBR and Al-Al bonding, a 90/10 CR AD/W of 15-20wt% solution in toluene gives the best adhesive strength.
- Addition of 6phr acetylene black to the adhesive formulation improves SBR-SBR bonding while the incorporation of 4phr silica improves the Al-Al bonding.
- Addition of curatives of polychloroprene rubber reduces the peel strength for both Al -Al and SBR-SBR bonding.
- Sulphur, silane and zinc phosphate are effective adhesion promoters.

- Addition of epoxidized natural rubber to chloroprene improves the bond strength.

Cardanol and phenol based resins

- Mixtures of cardanol and phenol are better raw materials for resin preparation and subsequent adhesive formulation compared to either of pure phenol or cardanol.
- In the case of Al-Al bonding, about 80phr of 60/40 phenol/cardanol formaldehyde resin gives the best peel strength and 80phr of 80/20 resin gives the best shear strength.
- For SBR-SBR bonds, a 60/40 phenol/cardanol formaldehyde resin yields the best peel strength values.
- For Al-SBR bonding, the optimal concentration in the primer side is 80phr and on the adhesive side, 40phr of a copolymer resin containing 40% cardanol and 60% phenol.
- A ratio of 1:1.7 between total phenol and formaldehyde is the best suitable for SBR-SBR and Al-Al bonds.
- A ratio of 1:1.5 between total phenol and cardanol is ideal for peel strength of SBR-Al bonds.
- A ratio of 1:1.7 between total phenol and cardanol is optimal for shear strength of SBR-Al bonds.

EPN formulations

- Replacing part of the substituted phenolic resin with epoxidized phenolic resins yields higher adhesive strength in both Al-Al and SBR-SBR bonding.
- Among the EPNs, EPN prepared with a stoichiometric ratio of 1:0.8 between phenol and formaldehyde gives the best bond strength values.

Adhesion on different substrates

- Stainless steel-stainless steel bonds give better shear strength compared to titanium-titanium, aluminium-aluminium and galvanized iron-galvanized iron samples for the optimal adhesive formulation based on neoprene-PCF blends.
- In rubber-rubber bonding, SBR-SBR samples give the highest peel and shear strength values.

Ageing studies

- The bond strength of these adhesive joints does not substantially decrease with time (3 months) under ambient conditions.
- EPN based systems show better retention of properties for Al-Al and SBR-Al bonds when aged under ambient conditions.
- Formulations containing neoprene and PCF/EPN blends show initial high peel and shear strengths compared to those containing only neoprene and PCF. But resistance to high temperatures and hot water is lower for EPN containing formulations.
- Formulations containing ENR similarly show high initial strength but show substantial fall in properties when exposed to high temperature or hot water.
- Compared to SBR-SBR and SBR-Al bonds, Al-Al bonds show considerable reduction in properties on exposure to sea water for 3 months. In this respect peel strength shows greater deterioration compared to shear strength.

5.4 FUTURE OUTLOOK

The mechanism of adhesion is influenced by many parameters. The present work covered a few of them. Some other areas where investigation can be done are suggested below.

- The role of surface treatment of substrates on adhesive performance has to be investigated further.
- The present study was mainly using vulcanized rubber as substrate in rubber-metal bonding. The adhesive performance on unvulcanized rubber-metal bonding is an area where further study can be made.
- Study to improve the ageing resistance of adhesive joints under different environmental conditions to be further pursued.

List of abbreviations

Al	Aluminium
ASTM	American Society for Testing and Materials
BP	Boiling point
CBS	N-cyclohexyl-2-benzothiazylsulfenamide
CNSL	Cashew Nut Shell Liquid
CR	Chloroprene rubber
CS_2	Carbon di sulphide
DBP	Dibutyl phthalate
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetic analysis
ENR	Epoxidized natural rubber
EPN	Epoxidized phenolic novolac
EPDM	Ethylene propylene diene monomer
F	Formaldehyde
FTIR	Fourier transform infra red
GI	Galvanized iron
GPC	Gel permeation chromatography
HAF	High Abrasion Furnace Black
HCl	Hydrochloric acid
LR	Laboratory reagent
MBTS	Dibenzothiazyl disulfide
MgO	Magnesium oxide
$\overline{Mn}$	Number average molecular weight
$\overline{Mw}$	Weight average molecular weight
$\overline{Mz}$	Z average molecular weight

MP	Melting point
M.W	Molecular weight
N_2	Nitrogen
NA 22	Ethylene thiourea
NaOH	Sodium hydroxide
NBR	Acrylonitrile butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
P	Phenol
PCF	Phenol cardanol formaldehyde
PTBP	para tertiary butyl phenol
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope
SS	Stainless steel
TGA	Thermogravimetric analysis
Ti	Titanium
TMTD	Tetramethyl thiuram disulphide
UV	Ultraviolet
VGC	Viscosity Gravity Constant
Vulcanox HS	polymerized 2,2,4 trimethyl 1,2-dihydroquinoline
Vulcanox 4020	N(1,3-dimethyl butyl)N'-phenyl-p-phenylenediamine
wt	Weight
w/v	Weight by volume
wpe	Weight per epoxy value
ZDC	Zinc Dithiocarbamate
ZnO	Zinc oxide

cm	Centimetre
cps	Centipoise
g	Gram
h	Hour
kg	Kilogram
kN	Kilo newton
m	Metre
min	Minute
ml	Millilitre
ML(1+4) at 100°C	Mooney viscosity number. L indicates the large rotor, 1 is the time in minutes that the specimen is preheated, 4 is the time in minutes after starting the motor at which the reading is taken and 100°C is the temperature of the test
mm	Millimetre
MPa	Mega Pascal
N	Newton
nm	Nanometre
phr	Per hundred rubber

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